Design and fabrication of micro-coils for NMR micro probes

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NANYANG TECHNOLOGICAL UNIVERSITY

Design and Fabrication of Micro-coils for NMR
Micro Probes

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Abstract

The miniaturization of probes for Magnetic Resonance (MR) analytical methods -Nuclear Magnetic Resonance (NMR), Magnetic Resonance Imaging (MRI), or relaxometry- has been the latest trend which allows portability and analysis of the chemical composition of minute (in the range of nL to μL) volumes of sample. MR analyses typically require that such a probe is used in an external setup with a very strong constant magnetic field with no temporal variation and external detector circuits. A critical aspect for the success of such an experiment is to ensure a high **signal-to-noise ratio (SNR)**. However, the resulting value of the SNR delivered by a miniature probe has a complicated dependence on both the external measurement setup, chemical composition of the sample and the probe design. For probe designers, there are no clear guidelines to suggest how a given probe will behave under any external measurement setup or chemical composition of the sample under test, or how to approach a probe design so as to optimize design parameters for a good performance in terms of SNR in an MR analysis, e.g. an NMR experiment.

In this thesis, we first begin with formulating a clear guideline on how to design such a micro-probe from an electronic engineering perspective. We considered that a single planar micro-coil will act as both oscillating magnetic field generator and MR signal detector. In this case we have used an innovative micro-coil design that is very different from the classical planar design since the micro-coil conductors are ‘buried’ in trenches realized in the silicon substrate. This eliminates all drawbacks of previously reported realizations due to the following intrinsic advantages:

- Vertical conductor orientation for a more compact integration, reduced resistance in a smaller space and increased central MF focusing. The resulting

reduced micro-coil resistance ensures lower thermal noise and proper output signal coupling during SNR signal reception;

- Entrenching the turns in the Si substrate results in 2 crucial advantages:
 - Excellent heat dissipation, hence large currents can be used to maximize the generated **magnetic field strength (MFS)**
 - Excellent surface planarity, enabling subsequent co-integration of other components on the same chip, including microfluidics and/or sample holders on top of the micro-coil
- The usage of Cu-filled trenches (instead of Al thin film) decreases the overall resistance, again allowing to inject high currents;
- Possibility to add a magnetic pillar and/or a magnetic backplate for drastically increased MFS focusing in the center and boosted inductance (and hence quality factor Q).

Detailed electromagnetic simulations of various versions of micro-coil structures together with sample holders revealed the effects of different parameters that may affect the SNR. This analysis led us to the introduction/definition of an original and novel parameter: the performance parameter, **P**, whose maximization (by changing a micro-probe's design) optimizes the resultant SNR in any external setup. Several micro-coils of large and small dimensions (depending on the size of the overall surface area covered by the respective micro-coils) as well as of different aspect ratios of the conductor have been simulated in detail and the performance factor P was calculated in each case.

Next, receiver micro-coils were fabricated first in a silicon wafer through electro-deposition of copper inside **High Aspect Ratio (HAR)** trenches realized in the silicon substrate using **Deep Reactive Ion Etch (DRIE)**. However, the presence of post-DRIE scallops on the lateral walls of the trenches posed a severe problem for the continuous deposition of the Cu seed layer in the subsequent step. Hence, an inventive trench wall planarization process has been developed that significantly reduced (with 80%) the roughness of trench walls, enabling the subsequent seed layer deposition without any problems.

The reason for choosing HAR DRIE trenches in silicon to define the micro-coils was to make sure the resistance of the micro-coils is low and at the same time also to provide a smaller surface area occupied by the micro-coil. This ensures lower thermal noise and proper output signal coupling during signal reception. The copper electroplating process into HAR Si trenches had to be optimized using an orthogonal **Design of Experiments (DoE)**. These experiments determined the best deposition parameters required for void-free copper **ElectroChemical Deposition (ECD)** deposition inside the Si trenches. Different optimizations had to be carried out for copper filling of high aspect ratio trenches (7 μm wide and 20 μm deep). Post electroplating, the excess Cu overburden was removed using a novel copper wet etching technique in a solution of sodium persulphate. This wet etching process was also optimized through orthogonal DoE and then employed in order to remove copper everywhere except inside the trenches. The etching procedure proved to be extremely fast compared to conventional **Chemical Mechanical Polishing (CMP)** of Cu. Moreover, the difficulty that is typically faced by fluids in accessing high aspect ratio trenches proved to be advantageous for this wet etching technique since the etch rate of the Cu inside the Si trenches is much reduced compared to the normal vertical etch rate. Therefore, the deposited Cu inside the trenches was not etched, rather only the Cu overburden was successfully etched off keeping the micro-coil structure intact. Next these micro-coils were annealed in a hydrogen environment to reduce the resistance. The resistances were obtained through I-V probing and the values measured before and after hydrogen annealing were compared. Low resistance micro-coils for receiver coils were hence obtained.

The **magnetic field (MF)** generating micro-coils designed after the full **P** factor analysis were next fabricated. These were wider micro-coils, with a 1 : 1 aspect ratio (AR), for which the inherent problem of blind via filling through ECD of copper became more challenging. Hence, the Cu electroplating procedure was now changed and optimized through progressive, time-dependent DC electroplating and optimizing the ratio of additives to ensure the void free copper filling inside trenches through inhibiting the ECD of copper in the side walls and at trench corners. This process, however resulted in a very thick Cu overburden on the top which was very difficult to remove through wet etching only. Also, since these

micro-coils were much wider than the previous micro-coils with $AR = 3 : 1$, the probability of the liquid Cu etchant to go inside the trenches was much higher. Therefore, both wet etching and CMP were employed in order to remove the Cu overburden. Subsequent DoE optimization of the CMP process revealed that the chemical reaction of the slurry with the Cu was of utmost importance and mechanical removal played only a secondary role in Cu removal. A high rotational speed of the polishing pad inhibited the removal rate as it spilled more slurry chemicals due to high centrifugal force and lessened the amount of slurry on the pad in contact with the wafer during CMP. It was also noted that the copper removal rate was extremely thickness-dependent and, hence, time-dependent. This reduced the Cu removal rate as time progressed even at a constant high pressure and rotational polishing pad speed. Once the excess copper removal was successful, connection pads were defined through Al deposition and dry etching. The electric resistance and the MF generated by these coils were measured, compared with the simulated design values, and their interdependence was studied.

Alternative methods to increase the SNR of NMR micro-probes have also been explored, such as realizing planar micro-coils using carbon nanotubes (CNTs) in Si. However, CNTs have large electrical conductivity only along their length, but very poor lateral conductivity. Since the latter is necessary when CNTs are used instead of Cu in micro-coils, adjacent CNT bundles were graphitized to achieve lower resistance. Electrical measurements showed that these graphitized CNT micro-coils exhibited very high Q values despite a relatively high resistance. The most probable explanation is the presence of iron nano-particles inside the CNT structures, and whose ferromagnetic properties determine a high inductance, and, hence, a high Q value. Hence, these coils can be used in future to develop micro-coils responsible for generating stronger magnetic field required for NMR.

We also investigated a micro-probe design with provision for cryo-cooling of the micro-coils. This ensures low thermal noise by lowering the resistance at the cryogenic temperature. The challenge for this design was to keep any living biological sample under test is at a viable temperature for a considerable amount of time while the micro-coil is cryo-cooled. Therefore, a good thermal insulation is required for the sample. The trade off between a good magnetic coupling and optimum thermal insulation was achieved by designing a structure employing heat

exchange at micro-scale. Extensive thermal **Finite Element Analysis (FEA)** simulations have been carried out to ensure optimum design dimensions. The corresponding fabrication process is also proposed for future implementation.

The major contributions of the thesis are:

- Developing a parameter 'P', which will serve as a guide to a micro-probe designer when designing a probe with high SNR, without considering the external measurement conditions such as the DC magnetic field, proton density of the chemical under test. This P factor has been compared with the SNR for a micro-probe design already reported in the literature. We extrapolated the SNR value of this reported micro-probe from the 'P' factor we calculated using our method. The extrapolated SNR value was compared to reported experimental SNR value to gain confidence in our 'P' factor design approach.
- We have reported fabrication of Cu micro-coils through Cu-electroplating, embedded in DRIE trenches of Si substrate. The major problem faced while realizing such a coil was scalloping of DRIE-ed trench walls of Si. These scalloped walls caused discontinuous deposition of Cu seed layers inhibiting uniform electroplating. The scalloping was reduced by 80.5% compared to others and the technique used by us had a very low thermal budget compared to other similar post-DRIE smoothening techniques reported in the literature.
- For the first time we have reported in detail, fabrication of Si embedded Cu micro-coils inside high aspect ratio (HAR) Si trenches. Compared to the existing literature, where HAR micro-coils are fabricated mostly using a strict bottom up Cu ECD technique that requires additional fabrication steps, our micro-coils has been fabricated inside HAR blind Silicon trenches. In such a trench, it was shown that a very balanced vertical and horizontal Cu deposition technique is required to achieve void free trench filling. Furthermore, we have developed a novel wet etching technique using Sodium Persulphate that is used to successfully remove the Cu overburden left after ECD of Cu. This wet etching technique is faster and cheaper when compared to existing CMP process for Cu removal. Also, this wet etch method does not require any

special set up or complex chemical blend to achieve successful Cu etching. Furthermore, being embedded in Si we were able to reduce the resistance of these coils by a factor of 3 using annealing under hydrogen environment. Comparison with existing literature shows our micro-coils fabricated using the above process flow has lesser and simpler fabrication steps as well as have a lower electrical resistance.

- Next, we have shown fabrication of micro-coils designed using the 'P' factor approach; these micro-coils have an aspect ratio of 1 : 1. Though these coils have a lower AR compared to previous HAR coils the fabrication requires progressive electroplating technique to have void free trench filling. The Cu overburden however increases with the increased time associated with this electroplating technique and hence this increased overburden had to be reduced by a novel combination of Cu wet etched method developed previously and CMP. Lastly, we measure the magnetic field which is similar to the simulated value obtained during design of the micro-coils using 'P' factor approach.
- For future work, we have proposed a novel micro-coil structure obtained through graphitization of the CNT that allows lateral conduction of current in the plane of the micro-coil. The advantage of these coils compared to that of conventional Cu is that we can easily fabricate HAR micro-coils since CNTs are easier to grow compared to Cu electroplating. Moreover, initial inductance measurement showed higher inductance values compared to existing Cu micro-coils, the most probable reason of which might be presence of ferrous nano-clusters from the iron catalyst used as catalyst for CNT growth. Apart from this CNT-graphitic micro-coil, we have also introduced a design for NMR micro-probe having provision for cryogenic cooling. Compared to already reported structure, our design has much smaller dimensions (in μm range) and achieves successful thermal insulation between the biological sample & the cryo-cooled micro-coil while not compromising on the magnetic coupling.

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Abbreviations

3D	3 Dimensional
ALD	Atomic Layer Deposition
APC	Automatic Pressure Control
APTMS	(Amino-Propyl)-TriMethoxy-Silane
AR	Aspect Ratio
BPSG	Boro-Phospho-Silicate Glass
CAR	Conductor Aspect Ratio
CMP	Chemical Mechanical Polishing
CNTs	Carbon Nano Tubes
CNT-GHM	CNT-Graphitic Heterostructure Material
CST	Computer Simulation Technology
DMAB	Di-Methyl-Amino-Benzaldehyde
DoE	Design of Experiments
DRIE	Deep Reactive Ion Etch
ECD	Electro Chemical Deposition
EDTA	Ethylene-Diamine-Tetraacetic Acid
EDX	Energy-dispersive X-ray
FIB	Focussed Ion Beam
HAR	High Aspect Ratio
IPA	Iso Propyl Alcohol
LF	Low Frequency
LN	Liquid Nitrogen
LOC	Lab On Chip
MF	Magnetic Field

MFS	Magnetic Field Strength
MR	Magnetic Resonance
NR	Not Reported
NMR	Nuclear Magnetic Resonance
PDMS	Poly-Di-Methyl-Siloxane
PECVD	Plasma Enhanced Chemical Vapour Deposition
PR	Photo Resist
PSG	Phospho-Silicate Glass
PSI	Pound-force per Square Inch
PVD	Physical Vapour Deposition
RF	Radio Frequency
RPM	Revolutions Per Minute
SCCM	Standard Cubic Centimeters per Minute
SEM	Scanning Electron Microscope
SLM	Standard Litre per Minute
SNR	Signal to Noise Ratio
TEOS	Tetra-Ethyl OrthoSilicate
TPV	Through Polymer Via
TSV	Through Silicon Via

Chapter 1

Introduction

1.1 Background and motivation

Nuclear Magnetic Resonance (NMR) spectroscopy is an analytical technique that determines the physical and chemical properties of molecules based on the magnetic properties of their atoms' nuclei. NMR is a very useful investigation tool which can provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules. Edward Mills Purcell and Felix Bloch shared the 1952 Nobel Prize in Physics for the discovery of NMR [1].

In a nucleus with an odd number of nuclides, a magnetic moment will be present. Consequently, each such nucleus acts just like a tiny bar magnet. In absence of an external Magnetic Field (MF), these nuclei arrange themselves randomly and, hence, due to this random statistical distribution the net magnetization of a sample is zero. When a strong external MF is applied, these nuclei will end up oriented in one of two possible configurations, viz:

a) Parallel to the applied field which is most favorable configuration since it has the lowest energy, and b) In anti-parallel orientation with the applied field, which is the orientation with higher energy.

Consider a strong DC MF B_0 applied along the z axis, so that the net magnetization vector M_0 of the sample is also oriented along the z axis (which is known as longitudinal magnetization). In this case, the nucleus of each atom of the sample

Figure 1.1: Orientation of nuclei under strong DC magnetic field to produce longitudinal magnetization

precesses at a definite frequency called the Larmor frequency, given by

$$f_o = \frac{\gamma \cdot B_o}{2\pi} \quad (1.1)$$

where γ is the gyro-magnetic ratio of the sample. For example, the value of $\frac{\gamma}{2\pi}$, for hydrogen (H^1) and deuterium (H^2) are 42.576 and 6.536 MHz/T, respectively. Hence, for a DC. MFs of 1 T the Larmor frequencies of H^1 and of H^2 will be 42.576 MHz and 6.536 MHz, respectively. However, the precessions of all nuclei are out of phase with respect to one another, as we can see in the Fig. 1.1. In order to detect the frequency f_o , an oscillating MF of angular frequency ω_r is applied along the direction orthogonal to the direction of M_0 . In a rotating reference frame, the apparent relative frequency is now given by eqn. 1.2.

$$\Omega = \omega_0 - \omega_r \quad (1.2)$$

hence the B_0 field now reduces to an apparent value as shown in the eqn. 1.3

$$\Delta B = \frac{\Omega}{\gamma} \quad (1.3)$$

Figure 1.2: Application of a time varying signal causes some of the nuclei in the lower energy state to shift to higher energy state resulting in diminishing of longitudinal magnetization

When the time-varying pulse is applied, some of the nuclei will absorb its energy and will be excited to a higher energy state as a result of which the longitudinal magnetization now starts diminishing by ΔB , as shown in Fig. 1.2. If we now look at the vector diagram in the rotating frame, we can see that ΔB is oriented along the z axis, while the oscillating field B_1 is along the x axis (or y axis). Therefore, the resultant MFS vector B_{eff} will be oriented at an angle θ with the z axis, as shown below in Fig. 1.3. B_{eff} & θ are given by eqn. 1.4:

Figure 1.3: Vector diagram of NMR system with application of B_1

Figure 1.4: Equal distribution of nuclei in lower and higher energy state causing longitudinal field to be zero

$$B_{eff} = \sqrt{(\Delta B)^2 + (B_1)^2} \quad (1.4)$$

A specific case of interest is that of the so-called 90° excitation, when the applied the oscillating pulse results in $\omega_r = \omega_0$, $\Delta B = 0$, $B_{eff} = B_1$ and $\theta = \pi/2$.

Hence, when the oscillating frequency is equal to the Larmor frequency the longitudinal magnetization of each nucleus is rotated with $\pi/2$, resulting in an overall longitudinal magnetization equal with zero as there are equal amounts of nuclei in higher and lower energy states, as shown in Fig. 1.4. Additionally, besides reducing the longitudinal magnetization, an external oscillating input also forces all the nuclei to revolve synchronously, in phase, by pushing all the nuclei to one side, as shown in Fig. 1.5. For a 90° pulse all the nuclei are in phase and a net transverse magnetization field now appears rotating at Larmor frequency around the z axis, as shown in the next Fig. 1.6. This transverse magnetization can be detected by a coil acting as an antenna.

Next, when the external oscillating pulse is turned off, two phenomena will occur:

- Recovery of the longitudinal magnetization, known as spin-lattice relaxation. This takes place by dissipating the previously absorbed energy into the material with a time constant T_1 .

Figure 1.5: External oscillating field causes all the nuclei to spin in phase

Figure 1.6: For an oscillating field with same frequency as the Larmor causes all the nuclei to be in-phase and forms a net transverse magnetization field - such an external magnetic field is called 90° pulse

- De-phasing of the nuclei, known as spin-spin relaxation, which takes place with a time constant T_2 .

Figure 1.7: De-phasing of the nuclei after removal of oscillating B_1 field

These two phenomena are illustrated in Figs 1.7 & 1.8. All the images in Figs. 1.1, 1.2 & 1.4 to 1.8 have been adapted from online YouTube Video sources [2] under the standard YouTube license.

However, conventional NMR instruments are bulky, very expensive and require to be operated by highly qualified staff. Moreover, the NMR analysis is usually time-consuming. The huge equipments are necessary because conventional NMR/MRI generally requires an extremely strong magnetic field (in order to provide a very large SNR, as will be seen later), generated by huge magnets (generally occupying an entire room) that are cryogenically cooled. The recent need of fast and cheap analysis of very small samples in point-of-care(POC) lab-on-chip (LOC) microsystems also imposed the miniaturization of the NMR systems for investigation of samples in the nano/pico-litre volume. This would enable the detection of counterfeit drugs, adulterated water or even traces of explosive materials.

A miniaturized NMR probe, or NMR micro-probe, in its simple form consists of at least one coil (or a coil-like) conductive structure and a sample holder in close proximity (as close as possible) to the conductive coil. The coil which generates the oscillating MF B_1 and its interaction with the sample generates the MR signal which can be picked up either by the same coil or another one. In some high-end

Figure 1.8: The recovery time for longitudinal magnetization after oscillating B_1 field is removed

applications, an array of several pick-up coils can be used instead of a single one. Hence, in the simplest NMR micro-probe, the same coil may act both as generator/transmitter (TX) and detector/receiver (RX) of the MR signal.

As will be seen in the next chapter, most of the reported micro-probe structures consist of micro-coils realized on various substrates. One way to quantify the efficiency of the MR experiments carried out using these micro-probes is by using the SNR value provided by the micro-probe in an MR experiment. Unfortunately, each experimental setup has widely different parameter settings which makes it difficult to assess the performance of the micro-probe alone by using the SNR. Moreover, there is no proper literature available on how to design a micro-probe that will ensure good SNR in any measurement setup. Most of the literature focuses on the optimization of the generic Q value, e.g. by reducing the electrical resistance of the micro-coil. However, this is not sufficient for the design of an efficient NMR probe where the successful coupling of the oscillating MF B_1 into the sample plays an important role in determining the probe performance in terms of SNR. The literature review also revealed that the HAR structures were not considered for NMR micro-probes. Additionally, while HAR Through Silicon Vias

(TSVs) or Through Polymer vias (TPVs) have been studied rigorously, no such detailed work exists for buried micro-coils realized in HAR trenches. The fabrication challenges and potential solutions for metal deposition in standard TSVs or TPVs that are isolated cylindrical vias do not necessarily extend to HAR trenches etched in the substrate and of considerable length. Our group has reported previously achieving HAR micro-coils, but the fabrication process details were not reported since the micro-coils were realized using proprietary recipes from third party developers. Thus, there is no information in literature that details the fabrication challenges and solutions for realizing HAR micro-coils in a silicon substrate.

Hence, the objective of this Thesis are:

- Introduction of a novel approach to design NMR micro-probes which will ensure good SNR in any experimental setup.
- Propose several different micro-probe structure designs that will be studied in order to optimize their SNR.
- Using HAR micro-coils realized in the silicon substrate and presenting the challenges faced, followed by the solution proposed, to fabricate such structures
- Propose an innovative technique for further improvement of SNR, viz. introduction of CNT-graphitic heterostructure to realize high Q coils for micro-probes and/or cryogenic cooling of micro-probe structure while still maintaining proper magnetic coupling between the coil and the sample.

1.2 Thesis outline & major contributions

Chapter 1: Introduction

The objectives and motivation of the Thesis are detailed in this chapter. It also describes the outline of the Thesis, and then briefly highlights the main contributions brought by this Thesis.

Chapter 2: Literature Review

This chapter summarizes thoroughly the micro-NMR probes that have been reported previously. Also, since a major part of this work involved fabrication of

planar micro-coils, an intensive literature review of fabrication of different types of micro-coils has also been presented in this chapter. Besides these various reports, a review of the literature focusing on improvement of SNR of NMR micro-probes using cryocooling techniques as well as CNT growth and CNT heterostructure has also been carried out.

Chapter 3: Definition of a Novel Performance Factor P

This chapter proposes a novel approach to design miniaturized micro-scale NMR probes for which the sample noise is not significant owing to the sample's small volume (nL - μL). This chapter focuses on the theoretical study of various factors affecting SNR of such a micro-probe. Most importantly, this chapter defines a micro-probe performance factor P that enables one to optimize its SNR performance, independently of the external setup and of the proton density of the measured sample. Literature data provide no design guidelines and/or indicate how to optimize the performance. At the same time, the SNR values reported in literature are largely dependent on the external measurement setup and chemical composition of the sample. Furthermore, the probe characterization and/or design is mainly done based on the optimization of the Q of the micro-coils. This is neither efficient nor sufficient, since in an MR micro-probe the efficiency (SNR) also depends on the interaction/coupling between the oscillating MF and the sample. This Thesis addresses this important issue and details the analysis and calculation of the main components of P , namely the filling factor η and the inhomogeneity factor K . Hence, through the approach outlined here a designer can design a micro-probe ensuring high SNR in any setup. In the next chapter, this approach is used to design the micro-coils structures which will be realized later.

Chapter 4: P Factor Based Design of NMR Micro-probes

This chapter evaluates the P factor for the subsequent detailed study of different micro-probes. The literature review revealed that planar micro-probes are mostly implemented using planar spiral micro-coils. However, our probe designs are not restricted only to planar spiral micro-coils but other planar structures are also considered. Using the previously defined P factor, the SNR performance of various structures is compared and then the best optimal design is chosen.

Chapter 5: Fabrication of High Aspect Ratio (HAR) Planar Micro-coils Embedded in Silicon

First the fabrication of the HAR micro-coil previously reported by our group is briefly described. The motivation was to fabricate coils with low resistance which would ensure a low thermal noise and hence a better SNR. HAR conductors were used to make the micro-coils in order to ensure low resistance through a larger conductive cross-sectional area and less chip area to maximize the number of devices on a single wafer. The previously reported HAR coils achieved by our group did not present the fabrication process and its challenges, particularly those related to copper electroplating since it was carried out by a third party with their proprietary recipe. Also, although literature focuses on copper Electro chemical deposition (ECD) into Through Silicon Vias (TSVs) or Through Polymer vias (TPVs), no such information is available for ECD of copper for micro-coil structures used in this work, namely into HAR trenches of micro-coils embedded in a Si substrate which are extensively long compared to TSVs. Such structures were adopted to realize the micro-coils used in this work due to significant advantages which they can offer:

- **a)** As mentioned previously, by using a conductor that is vertically oriented instead of horizontally, the micro-coil resistance can be reduced by increasing the conductive cross-sectional area but with much less increase in the total surface area occupied by the device;
- **b)** Embedding the micro-coil in the Si substrate enables excellent heat dissipation, making it possible that at least hundreds of mA can be easily injected in the coil to maximize the generated magnetic field, provided that a suitable external heat sink is also mounted. This is in stark contrast with many traditional realizations which employ glass substrates, e.g. for biomedical applications, for which such heat dissipation capability is significantly reduced due to the intrinsic smaller heat conductivity of the glass and/or polymers;
- **c)** Having the conductors entrenched inside the Si substrate results in an almost ideal planarity of the surface, enabling easy co-integration of components (e.g. passives for the matching circuit and/or signal processing IC)

in the same substrate next to the micro-coil, as well as easy subsequent integration/post-processing of other devices (e.g. other components and/or microfluidics) above the micro-coil.

Although 3D micro-coils have been realized using TSVs, they have a major disadvantage: both backside and front side photolithography are required to define the interconnections among TSVs necessary to realize the them. In contrast, our micro-coil is defined in one lithographic step and hence is less complex and easier to fabricate.

Chapter 5 also presents the Cu ECD procedure along with other fabrication details, together with solutions for the different challenges that arose with ECD of Cu in HAR trenches. Specifically, the greatest challenge was achieving void-free filling with Cu of HAR trenches with an aspect ratio (AR) of 3 : 1. This is because the lateral deposition of Cu on the sidewalls of the trenches makes this process entirely different from Cu electroplating of isolated vias in which the Cu deposition/filling occurs exclusively vertically (from bottom to top).

An orthogonal design of experiment (DoE) for copper electroplating in our HAR trenches of $AR = 3 : 1$ has been performed for the first time to deduce the influence of different parameters of the Cu ECD process. More specifically, here only external parameters were varied, without changing the electrolyte composition which generally involves cumbersome chemical analysis and periodical replenishment of additives in a proper ratio to achieve electroplating. In most of the electroplated process such as TSVs, chemical mechanical polishing (CMP) is used to remove the excess copper overburden and planarize the surface. However, CMP is an extremely slow process. Here we introduce a novel solution of wet etching of copper using sodium persulphate which is extremely fast and has been used to remove the Cu overburden. Such wet etching has been reported for the first time here and again an orthogonal DoE has been performed to optimize this Cu wet etching recipe. Once the micro-coils are realized they have been annealed in an environment of hydrogen and argon to achieve the dual purpose of reduction of copper oxides (which have high resistivity) and to increase the grain size (which impacts the electrical resistivity of the material). This treatment has successfully reduced the resistance of our micro-coils greatly, and our measured results are then

compared with those reported in literature.

Chapter 6: Fabrication of Micro-coils for Magnetic Field Generation in NMR Micro-probes

This chapter gives a detailed description of the fabrication process of the micro-coils proposed in chapter 4. Unlike the ECD procedure with pre-mixed electrolyte used for the previous batch of HAR micro-coils, here we optimize the volume of additives to be added followed by ECD of Cu into 1 : 1 aspect ratio trenches. Additionally, a time varying DC electroplating recipe has also been developed and used in order to ensure void free filling. Just as ECD of Cu in HAR TSVs or TPVs, Cu electroplating in blind via trenches is equally challenging, although for very different reasons. The main hurdle is given by the fact that much wider trenches (of low AR) have now to be filled up. In this chapter it is shown that although the lateral Cu deposition is still unavoidable, it can be controlled in order to prevent void formation at later ECD steps near the trench mouth.

Next, instead of the Cu removal through wet etching presented in the previous chapter, in this case a combination of wet etching and CMP was used to remove the excess copper. Such a combination was required since the copper thickness was quite large compared to that resulted for the previous micro-coils since the trench depths were now larger and the deposition times were longer. Consequently, although trenches with lower aspect ratios were used here, the volume of copper required to be deposited in order to fill up these trenches was quite larger compared to the previous case and the void-free filling took a longer time.

Again, a customized CMP recipe has also been developed from scratch to optimize the copper removal for our structures. Finally, after the micro-coils were realized measurements of their resistance and generated magnetic field were carried out. The measured dependence of the generated MFS on the micro-coils' resistances showed that the higher resistance associated with voids present in the Cu filled trenches caused poor magnetic fields.

Chapter 7: Future Work for SNR Improvement

Two possible methods of improving the SNR are proposed. The first entails using a CNT-graphitic heterostructure -instead of the typical Cu- which supports lateral current conduction (unlike CNT) to define the micro-coil. The advantage of such a structure is that it exhibits very high measured values for the quality factor

Q, due to presence of iron particles that had been used initially as the catalyst for the initial CNT growth.

Secondly, we propose an entirely original micro-structure which supports cryogenic cooling of the micro-coils in an NMR probe. The great challenge of such a cooling technique applied for a micro-probe is to achieve a compromise between sample placement for efficient cooling while at the same time ensuring different strength of the magnetic field it interacts with. The problem was solved with a structure which utilizes the heat exchange principle at micro-scale.

Chapter 8: Conclusions

This chapter summarizes the most important outcomes. Following this, the chapter suggests the use of the designed & fabricated micro-coils in the proposed micro-probe structures for improved SNR.

Chapter 2

Literature Review

2.1 NMR probes and the difficulties in comparing their SNR performance

Nuclear Magnetic Resonance (NMR) analyses at micro-scale, such as NMR spectroscopy, are very useful tools used to determine the composition of very minute volumes of samples. Micro-NMR systems reported previously have been realized with several types of coils, such as Helmholtz [3–5], solenoidal [6–8], planar [9–14] or even micro-strip lines [15]. These systems operate at different Larmor frequencies with values varying in a wide range, from 63.88 MHz for the protons when the externally applied DC magnetic field (MF) has the magnetic field strength (MFS, i.e. magnetic flux density) $B_0 = 1.5 \text{ T}$ [16], to as high as 500 MHz when $B_0 = 11 \text{ T}$ [10].

The first generic expression for the signal-to-noise ratio (SNR) for an NMR experiment was formulated almost 40 years ago by D. Hoult *et al.* [17]:

$$SNR = \frac{K\eta(\frac{B_1}{i})\omega_0 M_0 V_s}{\text{Sample Noise} + \text{Thermal noise from coil}} \quad (2.1)$$

where K is the inhomogeneity factor of the MF generated by the coil, η is the filling factor which indicates the extent of coupling of the magnetic energy generated by the coil with the sample, B_1 is the time-varying MFS which lies in the plane

perpendicular to the direction of B_0 , i is the current generating the RF MF of strength B_1 , ω_0 is the Larmor frequency, M_0 is the strength of the magnetization vector which depends on B_0 and the sample under investigation, and V_s is the sample volume. Further details on the terms of equation 3.1 by [17] will be given in chapter 3. The equation indicates the parameters involved in the calculation or optimization of SNR, but it may need to be modified (or some of its components recalculated) depending on the specifics of the used system. Most importantly, it will show that the final value of the SNR is strongly dependent not only the performance of the coil/probe, but also on the characteristics of the measurement setup. This chapter will justify this claim and will also summarize the various types of MF generating/pick-up structures.

All the previously published papers about micro-probes can be divided into 3 categories, depending on the MF-generating micro-structures: solenoidal coils, microstrip lines and planar micro-coils.

In the case of 3-dimensional (3D) coils of relatively large dimensions, such as Helmholtz and solenoidal coils, samples of large sizes and/or volumes [3] are generally used which makes both the sample noise and coil noise significant. One such example is a solenoidal coil with inner radius of $37.5 \mu m$ and 5 turns for which an SNR of 13.6 was reported [6]. Another miniaturized 3D solenoid-like coil, fabricated by Badilita et al. [7], exhibited a high Q value of 46 at 400 MHz and has been successfully used for MRI.

Microstrip lines have also been used for MRI microscopy as an alternative to coils: a micro-strip line generated the RF magnetic field and a separate coil was used to pick up the sample signal with a SNR between 4.5 to 5.2 for microstrip lines of widths ranging from $500 \mu m$ to $2000 \mu m$ [15].

Among the planar micro-coils used for NMR experiments [9–13], the highest average SNR per acquisition of 60 was achieved with a circular spiral micro-coil made of Cu, having an outer radius of $1000 \mu m$, 4 turns and a sample volume of 470 nL located $50 \mu m$ above the coil center. Other reported planar architectures include stacked multiple planar micro-coils. One such realization comprised 4 square spiral micro-coils made of Au, having 5 turns each, stacked on a $4 \times 4 mm^2$ area, and fabricated on a $5 \mu m$ thick polyimide substrate. The assembly exhibited a Q of 24.3, resistance of 9.5Ω and an SNR of 7 at 17.1 MHz when used with a

natural rubber sample [14].

Table 2.1: Previous reports on NMR microprobes with different coil geometries, operating parameters and volume of samples used

Ref.	Coil type	Sample type & placement	Sample volume V_s	Larmor frequency f_0 MHz	DC magnetic field B_0 (T)	Q-Factor at the Larmor frequency	SNR
Hayes et al. ¹⁶	Planar circular coil with diameter of 8, 10 & 14 cm	Phantom containing distilled water doped with NaCl and CuSO ₄ placed on the top of the coil from center	231 mL	63.88	1.5	274, 298 & 245 for 3 diameter variants	SNR plot given in arbitrary units with respect to depth of phantom
Peck et al. ⁶	Solenoidal Cu coil with 37.5 μ m radius & 5 turns where the copper wire diameter is varied from 16 - 30 gauge	5 mM CuSO ₄ solution placed inside a glass capillary tube around which the solenoid was wrapped	0.3 nL	200	4.7	36.3	13.6 normalised to a single acquisition
Stocker et al. ³¹	Planar square gold (3 μ m thick) coil with 3.5 turns & inner radius of 30 μ m on GaAs substrate	Water Sample placed inside fused capillary placed 50 μ m above coil surface	0.1 nL	250	5.9	1.3	25 per acquisition
Dechow et al. ¹⁰	Planar circular Au (3 μ m thick) coil with 4 Turns & inner radius of 25 μ m on GaAs substrate	Silicone oil placed on the backside of the substrate below microcoil	60 nL	500	11	Not reported	Not reported
Renaud et al. ¹¹	Planar rectangular Cu microcoil (38 μ m thick) with 4 turns & area of 1000 μ m $\times$ 500 μ m on a n-type Si substrate with SiO ₂ as isolation	De-ionized water and butter samples & the microcoil was immersed in sample	330 μ L	85.13	2	10	95 with 4 averages and water sample
Continued on next page							

Ref.	Coil type	Sample type & placement	Sample volume V_s	Larmor frequency f_0 MHz	DC magnetic field B_0 (T)	Q-Factor at the Larmor frequency	SNR
Massin et al. ⁴⁰	Circular Cu (12 μm thick) microcoil with 4 turns & inner radius of 250 μm	Ethylbenzene placed inside a capillary tube above the microcoil	160 nL	300	7	24	20
Massin et al. ⁹	Planar circular microcoil of 4 turns with radius of 250 μm , 500 μm & 1 mm on a glass substrate	Sucrose in D_2O placed 50 μm from coil surface	30 nL, 120 nL & 470 nL	300	7	17, 18 & 19 for different coil radius	Average value of 60 for a volume of 470 nL
Goloshevsky et al. ⁴	Copper Helmholtz Coil on glass substrate having an average diameter of 3.5 mm each spiral half where the microcoil lines have a width of 120 μm and thickness of 15 μm	Water, methanol & 1-propanol placed inside a tubing between the halves of the coil	2.45 μL	25	0.6	6.6	233.5 peak value for water; 108 peak value for methanol & peak value of 58 for 1-propanol
Ehrman et al. ¹²	Planar circular Cu coil with a radius of 500 μm on glass substrate	CHO DG44 cells in deuterated phosphor buffered saline medium placed above the microcoil surface	25 nL	Not reported	Not reported	Not reported	Time domain NMR spectrum given
Xiaonna et al. ¹³	Planar circular Cu coil on glass substrate with 4 turn & 200 μm radius	Sucrose suggested as a future work	Not reported	85.3	2	21	Not reported
Badilita et al. ⁷	Solenoidal microcoil made from insulated Au wire of diameter 25 μm wound around SU8 with 5 turns & radius of 700 μm	Water doped with CuSO_4 kept inside the SU8 sample-holder around which the gold wire is wound using automatic wire bonder	0.31 μL	400	9.4	46	Mean value of 520 per voxel

Table 2.1 summarizes the key features and measured performance parameters for the most of the relevant NMR micro-probes reported in the literature. It can be seen from the data in Table 2.1 that it is very difficult to compare directly the performance of all these various types of coils, and especially to understand which are the key parameters influencing their SNR (particularly for a new researcher) given the great diversity of micro-coils and large number of papers reporting such devices, of which only some may indicate the obtained SNR.

Two very good reviews by A.G. Webb [18,19] discuss the different problems associated with various micro-coil types used for NMR. Solenoids produce a uniform magnetic flux density concentrated in the core of the coil; however, the dimensions of the solenoidal micro-coils (which actually are minicoils given their large dimensions, typically in the order of mm , when realized with a round wire) are typically limited either by the limitations of the NMR equipment or by the fabrication process for on-chip realizations. Additionally, solenoidal coils also feature a susceptibility mismatch between air, coil and the sample when the sample under study is placed within the core of the solenoid. To solve this latter problem, susceptibility matching fluids may need to be used.

In contrast, planar spiral micro-coils enable a greater miniaturization and may be more easily fabricated, even buried in the substrate for good surface planarization, excellent heat dissipation and easy subsequent processing of other devices onto the surface [20,21]. However, they provide a very inhomogeneous magnetic field across the surface. Nevertheless, in spiral micro-coils the magnetic flux can be focused to a high density in a small central region and this gives the freedom to place the sample in a volume that coincides with the core/center of the micro-coil.

One way to increase the SNR is by reducing the thermal noise of the micro-coils. The first measure in this direction is to reduce the coil electrical resistance R as much as possible. This can be achieved, on one hand, by using conductors of cross-sectional area as large as possibly allowed by the layout or by other design constraints, and on the other hand by using high conductivity materials, such as copper or even gold. However, increasing the cross-sectional area of the micro-coil conductors will also increase the surface area occupied by the coil, which, in turn, will affect the homogeneity of the MF. Furthermore, the usage of Au may provide only a marginal improvement and is also more expensive.

Secondly, a much more significant increase in SNR could be achieved if the coil temperature can be drastically reduced, and this is the reason why all large NMR/MRI systems employ cryogenic cooling for their probes and preamplifiers. Unfortunately, this method has had until now a very limited application for microprobes. One such recently reported realization is that of a planar micro-coil of 3 turns with each turn being 0.25 mm wide and separated by a gap of 0.5 mm embedded in a PMMA substrate. The micro-coil was cooled cryogenically using liquid nitrogen (LN) pumped through a microfluidic channel 1 mm deep and 2 mm wide that had been fabricated out of PDMS just beneath the copper coil [22]. The cryocooling of this structure improved the SNR by a factor of 1.5. However, in order to ensure that the cells in the examined sample were kept alive at a viable temperature, the sample was kept at a large distance (1.6 mm) from the micro-coil surface. Despite the large separation between the sample and the micro-coil (which reduces drastically the magnitude of B_1), the SNR was improved from 110 (peak value) for the non-cryogenically cooled structure to around 160 when a sample of 0.1% $CuSO_4$ solution was tested in a NMR machine with a B_0 of 4.7 T at 200 MHz. However, the effect of cryocooling on SNR of NMR coils with micro dimensions has not been thoroughly examined.

Additionally, until now there has been very little, if any, discussion regarding the variation and quantification of the magnetic flux density homogeneity within the sample. Moreover, the filling factor η –an essential component of equation [17]– does not appear to have been calculated explicitly in any previously published paper nor has it been shown how it depends on the sample volume or on its placement with respect to the micro-coil. Previously, a simplified parameter, the product of η and coil quality factor Q , was suggested by Darrasse *et al.* [23] to analyze the coil performance with respect to the sample placement. However, although the value of Q indicates the magnetic performance of a coil, it is related to the **total** MF generated **everywhere** around the coil, while in the case of MR analysis we are interested only in the field inside the sample (whose volume is strictly determined by several factors). Hence, the $\eta \cdot Q$ product may not be a useful parameter to evaluate a micro-probe's performance.

2.2 Micro-fabricated coils

2.2.1 Fundamental differences between micro-coils realized in blind trenches vs. those in TSVs

An area where the current aggressive down-scaling trend has been less successful is the miniaturization of inductive components, i.e. spiral mini- and micro-coils. The key reason is that the size of a planar mini- or micro-coil is typically dictated by the desired inductance, which in turn determines the outer diameter and number of turns. Mohan *et al.* describe many expressions of inductances for planar inductors of different shapes and sizes [24]. All of them show that the inductance increases with the number of turns N which also increases the surface area and hence also the parasitic capacitance. The most popular micro-coil structures which can be realized using micro-fabrication are the 3D and the planar micro-coils, respectively. A 3D micro-coil consists of Through Silicon Via (TSVs) or Through Polymer Vias (TPVs) [25] filled with Cu joined diagonally by planar metallized strips connecting the adjacent TSV (or TPVs) on both the front and the backside of the substrate replicate in a different way a conventional solenoid. Therefore, complex and double photolithographic steps are required with double alignment on both the front side and back side of the wafer, which increases the number of fabrication steps and, hence, the process complexity.

The other variety of micro-coils are the planar ones, defined on the surface of the substrate or embedded inside substrate trenches. In almost all cases, the planar coil's conductor has a rectangular cross-section which is placed horizontally, i.e. with the long side of the rectangle representing the width of the conductor resting onto the substrate, and the short side of the rectangle representing the thickness of the conductor. The ratio of the conductor thickness to its width is called the Aspect Ratio (AR). Using conductors of high aspect ratio (HAR), defined as $AR > 1$ results in two advantages; firstly, HAR increases the conductor cross sectional area that reduces the coil resistance - essential for signal detecting to reduce thermal noise. Second, this reduces the area occupied by the coil on the substrate and hence helps in miniaturization.

Traditional micro-coils reported in literature were achieved on top of (not em-

Table 2.2: Comparison of various on-chip planar micro-coils realized through Cu electrodeposition inside trenches of various substrates (N.R. = Not reported).

Reference	Coil type	AR value	Resistance (Ω)	Q factor
Kim et al. [33]	Double rectangular spiral inductor with 10 turns covered with a NiFe film inside Silicon substrate	10:92	2.88	15.9 (5 MHz)
Ramadan et al [34]	Circular spiral of 35 turns Cu coil inside Silicon substrate	10:3	20.25	N.R.
Pan et al. [35]	Rectangular spiral Cu coil inside low resistivity Si substrate	5:6	N.R.	60 (30-40 MHz)
Wang et al. [36]	Rectangular spiral coil achieved using TSV by bottom to top growth Cu electroplating	1:1	0.023	N.R.
Jiang et al. [37]	Circular spiral coil achieved using TSV by bottom to top growth Cu electroplating	16	0.037	85 (1.6 GHz)
M. Tang et al. [38]	3-7 turn circular spiral coil embedded in thick SiO_2 layer	5:4	N.R.	43.1 (6.9 GHz)
Lee et al. [39]	10 turns spiral copper coil inside polyimide mold on a glass substrate	1:5	2	N.R.
Massin et al. [40]	3 turns circular, spiral, Cu coils inside SU8 molds on a glass substrate	3:10	0.7	23.5 (300 MHz)
Li et al. [41]	Single turn rectangular Cu coil electroplated inside PR mold on a Silicon Dioxide layer above Si substrate	1:10	N.R	5.06 (1 GHz)
Walker et al. [42]	Rectangular spiral Cu coils electroplated within parylene mold with NiFe core above and below the Cu coil	3:5	N.R.	14.5 (10 MHz)
Schroeder et al. [43]	Circular multilayer spiral Cu coil, electroplated inside SU8 molds	N.R.	N.R.	N.R.

bedded in) the Si substrate with thin sputtered metal layers [26–29] while similar planar coils were also realized on the surface of GaAs substrates by [10, 30, 31] as well as on glass substrates by [32].

Table 2.2 summarizes the most relevant planar micro-coils realized through copper electroplating inside trenches of different substrates. It can be seen from Table 2.2 that micro-coils embedded in a silicon substrate have been reported by [33–37] and they employ Cu electroplating to achieve thick copper depositions in the Si substrate. Similarly, planar micro-coils embedded inside other polymer based materials such as SU8 [40, 43], parylene [42], polyimide [39] and even inside trenches defined by photoresist [41] have also been reported. Even a micro-oil

embedded inside thick silicon dioxide has been reported [38].

However, achieving a planar micro-coil inside the Si substrate has advantages of its own, such as better heat dissipation compared to polymer-based materials. Our previous research group's reports [21, 34, 44] show that currents up to 250 mA could be used without any problems, and other unreported tests we did, showed that we could easily inject currents up to 500 mA, and for an extremely short time we even tried 1 A. A Si substrate also gives a highly planar top surface which allows realizing polymer-based microfluidics or other structures fabricated by subsequent post-processing. But the greatest advantage of realizing micro-coils in Si is that it is IC-compatible process [36]. It can start with silicon wafers with ICs already built by commercial IC foundry. Therefore, it is possible that fully-integrated CMOS based circuitry can be fabricated by an IC foundry before fabricating the coils or other MEMS structures above the IC through subsequent post-processing. Such a CMOS-MEMS process capable of fabricating DRIE Si trenches for integrated inertial sensors [45, 46]. This advantage of CMOS compatibility made possible through using only Si as the substrate for micro-coils has also been re-iterated [35]. Therefore, Si substrate has been our choice for fabricating the embedded micro-coils reported in this thesis.

Previous work in our group proposed and demonstrated a vertical orientation for the planar micro-coil's conductor that was embedded in silicon (i.e. the conductor rests on its short side and, hence, is characterized by an $AR > 1$) [47]. This vertical orientation provides new advantageous features that make such micro-coil structures more attractive than the traditional planar ones realized on top of a substrate. Firstly, reducing a conductor dimension (width in our case) produces higher field gradients next to and along that dimension. We have shown that the peak field gradient value for a conductor $2\ \mu\text{m}$ wide and $10\ \mu\text{m}$ thick, is 4.2 times larger than that of a conductor $10\ \mu\text{m}$ wide and $2\ \mu\text{m}$ thick [47]. It is also imperative to increase the conductor thickness while proportionally reducing its width in order to maintain a constant conductor cross-sectional area. As a result, a larger central magnetic field strength (MFS) B and magnetic gradient ∇B are generated by the micro-coil yet still minimizing the overall footprint of the micro-coil as it has been described in Section 3.1 by Ramadan *et. al.* [44].

The micro-coils reported in this thesis are obtained through ECD of Cu in-

side HAR Si blind vias obtained by DRIE. Tingrui *et. al.* [35] also reported such micro-coils, but with $AR < 1$ and no detailed analysis of Cu ECD inside these low aspect ratio Si blind vias is given. Our group [34] also reported previously HAR micro-coils embedded in Si but gave no details of the blind trench filling process with Cu due to proprietary concerns. Other reported planar micro-coils embedded in HAR Si trenches [36, 37] are radically different from those presented in this thesis. The micro-coils achieved by them are fabricated using Cu electroplating inside Si substrate with through-silicon trenches. In their case, the seed layer was present only at the bottom of the trenches, achieved by pasting a separate wafer with seed layer on the surface (often called the seed layer or the ‘contact wafer’) at the backside of the substrate wafer with Si trenches resulting in a dedicated bottom to top Cu electrodeposition. This is unlike our micro-coils where the trenches in Si are not through but are blind trenches and the seed layer is present both at the bottom and the sidewalls of the trenches. It has been shown that the Cu deposition from electroplating in such a bottom-up approach inside TSVs clearly occurs only vertically, from the bottom ‘contact wafer’ attached at the backside of the ‘device wafer’, to the top of the TSV, along the entire thickness (height) of the TSVs [48].

In contrast, our micro-coils did not employ any type of through silicon etched trenches but HAR trenches etched in Si that differ greatly from through-Si trenches or vias in these respects:

- They are much shallower (only 25 μm deep at most);
- They are so-called blind trenches, i.e. do not go through the entire wafer;
- Finally, and most importantly, in our blind trenches the seed layer is continuous and present both at the bottom and on the sidewalls of the trenches.

Consequently, the bottom-to-top electroplating approach used for the TSVs or through Si trenches are much easier/less challenging and no longer applicable in the case of our HAR, blind, and very long trenches in which the ECD of Cu occurs both laterally, from the sidewalls, and from the bottom to the top of the trench. Yung *et al.* also analyzed this difference between Cu electroplating in open, i.e. through-silicon trenches, and that in blind silicon trenches [49], while Pradeep *et.*

al. have also mentioned this difference between bottom up electroplating in TSVs and in trenches with seed layer on all the trench sidewalls [48]. Additionally, the fabrication procedure of micro-coils using TSVs is radically different as it does not allow any subsequent backside processing of the Si substrate wafer, such as backside bulk wet etching of Si substrate and followed by deposition of magnetic materials as reported previously by our group [34]. The features and challenges of electroplating copper in damascene processing for typical multilayer interconnections in ICs, or the different types of copper corrosion in micro-structures filled with Cu have been characterized [50–52]. For TSVs, the underlying Cu electroplating mechanism, issues and challenges have also been detailed earlier [53–57]. However, due to the great differences between TSVs and our trenches mentioned earlier, the solutions proposed in these reports for these challenges might not necessarily extend to Cu ECD inside long HAR blind vias of Si to realize planar micro-coils like those realized in this work and reported in the following chapters. The next sub-sections will detail the key physical and fabrication steps and related challenges of micro-coils realized in blind trenches, whose solving for the realization of our devices will be detailed in the subsequent Chapters of this Thesis.

2.2.2 Scalloped DRIE trench walls

Deep Reactive Ion Etching (DRIE) is the most popular dry etching technique used to produce nearly vertical trenches in Si. This popularity is due to DRIE’s intrinsic capabilities of etching at large depths and/or high aspect ratios, compatibility with using simple photoresist (PR) masks and of producing vertical sidewalls on silicon substrates of any crystalline orientation. One of the typical DRIE process is the so-called Bosch process, which consists of alternate polymer deposition-dry etching steps [58,59]. However, scalloping is a well-known phenomenon that arises from DRIE of silicon substrates using the Bosch process [60] and is undesirable in many cases due to the negative influence it may have on subsequent process steps, e.g. filling up these trenches with metal by electroplating. The effect of scalloping on trenches filled with copper has been rigorously studied in a recent report [61], which details the effect of scallops of different sizes on resistance, capacitance and electromigration-induced stress in copper-filled through-silicon-vias (TSVs). Two

basic approaches can be used to control, or at least to minimize, this undesired scalloping: modifying the DRIE etch process parameters, or carrying out additional post-etching processing of the etched trenches/features.

A good review paper [62] describes the advantages of DRIE over wet etch procedures, and also highlights how the scalloped lateral walls of DRIE-realized trenches hinder the subsequent deposition of seed layers and ultimately may cause electrical discontinuity and hence failure of the electrodeposition of metals inside such DRIE trenches. It also suggests how this scalloping can be reduced by modifying the DRIE recipe. Other researchers have also explored similar solutions based on modifying the initial Bosch DRIE process. For instance, Kuo *et al.* [63] pointed out that the inefficient removal of the passivation layer during the etching step of the Bosch sequence is the main reason for the resulting surface roughness of the lateral walls in DRIE structures and which can be reduced using a higher coil power to increase the flux density of etchant ions, by reducing the switching time between the etching - passivation steps [64] or by increasing the pressure of the etchant gas to decrease the anisotropy as well as the roughness for high aspect ratio microstructures [65]. Pike *et al.* [66] showed that scallops appeared when the width of DRIE trenches is increased beyond 100 μm . This finding was confirmed by another study [67] which showed that the surface roughness was reduced below 25 nm when the aspect ratio (AR) increased to values larger than 150:1 by reducing the width of the trench openings at only 250 nm.

A very recent literature review details the effect of DRIE process parameters on the roughness of the etched trench's sidewalls, and even suggests an optimal recipe that would provide minimum sidewall damage [68]. Two other papers compare the results obtained using different DRIE BOSCH process variations. Hermersdorf *et al.* [69] compare the trenches etched using either a radio frequency (RF) or a low frequency (LF) - biased substrate, and show that the latter produced trenches with less scalloping and width variation. Similarly, Guo *et al.* report that by adding O_2 to SF_6 and C_4F_8 , the etched structures have less scalloping and more vertical sidewalls. However, the addition of O_2 lowers the roughness at the cost of selectivity [70].

It may be argued that this direct approach, of optimizing the DRIE recipes, is the most effective and more practically relevant as it attempts to address the very

root of the problem (the DRIE process itself causing the scalloping). However, in many cases this approach is not feasible, either because the DRIE machine is not available to the user who designed the chip and wants to fabricate it (like in our case), or - even if the DRIE machine is available and within reach- the modification of the DRIE process recipe(s) is not desired or possible as it/they may have already been optimized and is/are being used for other more important production purposes. Therefore, a post-processing approach, although requiring additional effort and processing steps, is in many cases the only possible alternative. Instead of, or besides tweaking the DRIE process parameters, post-DRIE methods can also be used to remove, or at least minimize, the scalloping of the lateral trench walls resulting after the DRIE process. Three categories of post-DRIE methods are found in literature.

The first category of such post-DRIE processing techniques employs anisotropic wet etching of Si in order to alleviate the scalloping by faster etching away the sharp corners of the scalloped profiles, e.g. using either KOH and isopropyl alcohol (IPA) [62], or a KOH aqueous solution [71]. In the latter case, the average roughness of the sidewalls has been reduced from an initial value of 300 nm to 50 nm. The best results were obtained after an etching time of 25 min for trenches 300 μm wide and 1.4 mm deep. A similar report [72] shows that a post-DRIE treatment using a similar aqueous solution of KOH also enhanced the surface smoothness. The improvement in this case, however, was not measured directly but in terms of finesse as the DRIE patterned structures were used for optical resonators. This smoothening process resulted in a 21.8% improvement in effective finesse for the optical resonator fabricated using DRIE.

Isotropic Si wet etching was also used to smoothen scalloped silicon walls, e.g. by dipping the structures in a mixture of $\text{HF} + \text{HNO}_3$ resulting in a peak-to-valley roughness reduction from about 1 μm to 150 nm. To cover up the residual roughness produced by the $\text{HF} + \text{HNO}_3$ treatment itself, a thermal oxide was grown for 72 hours at 1200°C to reduce the average roughness to a value of 20 nm [73]. However, although isotropic wet etching is cheap and simple, its etch rate is rather high and difficult to control accurately. This generally leads to high silicon consumption and distorts the shapes of the initial DRIE-patterned micro structure, e.g. widening of deep trenches, hence changing their aspect ratio and

shape. Additionally, the subsequent oxidation used in [73] was carried out at a very high temperature and for a very long time, both of which are not compatible with low thermal budget processing and may be unrealistic or very difficult to implement as post-processing steps in the framework of an actual CMOS fabrication process. Finally, when a deep trench had been etched anisotropically using DRIE, the applicability of using anisotropic wet etching for equal removal of scallops on all lateral walls, irrespective of their crystalline orientation, may not be feasible.

A second category of post-DRIE smoothening techniques employs oxidation of the DRIE trenches followed by removal of the oxide. This technique is based on the fact that the silicon consumption during oxidation is higher at the tip of sharp ends, such as the DRIE scallop tips, compared to other areas [74]. Juan *et al.* seem to be the first researchers who used this technique and documented the effect of the oxidation temperature as well as compared the effects of wet and dry oxidation for roughness reduction. It was found that oxide growth below 965°C is not very helpful for roughness reduction. For further roughness reduction, boron diffusion was also used at 1175°C followed by selective wet etching using EDP at 110°C [75]. However, the trenches used in Juan's work for sidewall smoothening were not DRIE trenches but rather etched using Cl_2 plasma from an ECR source. Hence, one cannot directly compare the effectiveness of this method with smoothening scalloped DRIE walls.

The same alternate oxidation and oxide etch process was used to reduce the sidewall roughness by 50% of a tunable optical filter. However, no details of the roughness reduction process were given; only a short mention of this step as part of the larger fabrication process [76].

The work of Le *et al.* also belongs to this second category. However in this case, Le *et al.* combined 3 techniques (viz. careful design, optimizing DRIE parameters and 3 cycles of alternate oxidation of the trenches followed by oxide removal) to reduce the sidewall peak to valley roughness up to 50% [77]. In contrast, our work here uses only alternate cycles of oxidation and oxide removal and results in an increased roughness reduction.

The third category includes other miscellaneous roughness reduction techniques. One such solution planarized the scalloped profile by depositing a 2 μm thick PSG layer in DRIE trenches 5 μm wide and 15 μm deep, resulting in a re-

duction of the RMS roughness value from 22 nm to 8 nm [78]. Alternatively, post-DRIE focused ion beam (FIB) milling has effectively reduced the sidewall roughness from 28.1 nm to 1.6 nm and the peak-to-valley roughness from 153 nm to 5.7 nm [50]. Another approach employed simple annealing in pure hydrogen at 1100°C and 10 torr for 10 min to reduce the roughness of scalloped DRIE walls from 26 nm to 0.26 nm [79]. A similar technique provided the best results by annealing at 1300°C for 30 min. resulting in a reduction of the average roughness from 200 nm to 50 nm [80].

However, all these processes in the 3rd category have serious drawbacks. For example the deposition of phosphosilicate glass (PSG) or borophosphosilicate glass (BPSG) thin films using Low-Pressure Chemical Vapor Deposition (LPCVD) or Plasma-Enhanced Chemical Vapor Deposition (PECVD) [78] leads to significant overhanging (especially for PECVD layers) near the trench opening. Usage of the Focus Ion Beam (FIB) milling process requires access to such a special tool, and -more importantly- it is essentially a very time-consuming serial access technique (i.e. which needs to 'repair' each trench one by one), hence it clearly cannot be used for mass-production processing. Finally, the thermal annealing procedure leads to rounding off of the corners of Si micro-structures due to Si atoms migration, hence only micro-structures whose dimensions are larger than the annealed corner radius can be smoothened with this technique or else the structure's shape becomes more circular. Moreover, in order to provide enough energy for the Si atoms migration to be effective, the annealing methods require high temperatures and/or long time to be effective, thus once again precluding their usage for devices which require a low thermal budget processing.

2.2.3 Metal deposition

General considerations

Although physical vapour deposition techniques, such as sputtering and thermal evaporation, are popular for depositing thin metal films and are environment friendly [81], they have several serious disadvantages when compared to electroplating and electroless deposition of metals. For our micro-coils' conductors, a very good conductive material should be used, hence copper and gold are some

obvious choices. Dini gives a detailed review of deposition of Cu as well as gold through different processes [82] while Brande & Vinand compared sputtering and electroplating of Cu and concluded that sputtering leads to layer by layer deposition while in case of electroplating an initial island growth model is followed [83]. This difference is mainly due to the different physical and chemical mechanisms that take place during condensation of the deposited copper. Gungulee studied the grain sizes of copper deposited through CVD and electrodeposition [84, 85]. The electroplated copper has smaller thickness independent grain sizes and microstructural defects which lead to higher resistivity compared to the bulk material. Annealing of the electroplated copper hence reduced the resistivity down to the bulk values. Walsh *et. al* gives a detailed comparison of copper deposition using sputtering, thermal evaporation, electroless deposition and electroplating, which concluded that the thickest layer (25 μm) was obtained with electroplating, indicating clearly that this method provided the highest metal deposition rate [86]. However, the smallest grain size was also obtained for the electroplated copper, making it the most vulnerable to chemical reactions and, hence, to the attack of chemical etchants, followed by the electrolessly deposited material. Furthermore, both the electroplated and electroless Cu had more $< 100 >$ planes than sputtered and evaporated variants and, hence, were less resistant to oxidation [82]. It was also reported that sputtered copper films exhibited a very large inbuilt tensile stress which made them have a much higher tendency of peeling off [87, 88]. In conclusion, it was suggested that electroplated and probably electroless copper might be the best candidates for depositing the thick layers required for the fabrication of the micro-coils.

Another alternative to Cu is Au. Despite its larger resistivity (compared to that of Cu), unlike Cu it is chemically inert and has excellent biocompatibility, hence it is preferred in cases where *in vivo* insertion of the micro-coil or microprobe is required. An initial review [82] suggested that electroplating of gold produces larger grain sizes compared to its physical vapour deposition (PVD) variant, the opposite of what was noticed for Cu deposited using the same methods, as mentioned above.

The next subsection, reviews the electroplating and electroless deposition of Cu and Au and will highlight which was ultimately the best option for the fabrication

of our micro-coils.

Electroplating and electroless deposition of Cu and Au

Electroplating and electroless plating have been long used to deposit the thick metal layers necessary for the realization of micro-coils. Copper is the most commonly used metal for such purposes. The key features of Cu electroplating and of its resulting films will be briefly reviewed here and compared with those for the Cu films deposited using electroless plating. L. Hamelin *et al.* investigated in detail the material properties of electroplated Cu [89]. For the beginning, the deposition rate of two different bath compositions, Cabas & Electrobrite, were compared. The deposition rate values were in the range 0.6 to 1 $\mu\text{m}/\text{min}$, i.e. 36 to 60 $\mu\text{m}/\text{hr}$ for a current density of about 1 A/dm^2 . The resistivity of the electroplated copper was also measured for 60 days to observe its variation in time. It was seen that the resistivity immediately after electroplating was higher than that of the bulk material (1.7 $\mu\Omega\cdot\text{cm}$). However, the resistivity decreased significantly with time regardless of the current density that had been used in the plating process. After 30 days at room temperature, the samples reached a quasi-bulk material resistivity (1.8 $\mu\text{m}\cdot\text{cm}$). It was suspected that the microstructure of the plated layer underwent recrystallization with time. The mechanical resistance of the plated Cu was also analyzed; it was seen that a large deformation was exhibited after the annealing process. The thinning process also contributed to further deformation to 350 μm , which possibly generated deviation from the expected performance in the application. Other reports also describe in detail the fundamentals of copper electroplating, giving important information such as the type of electrolyte to be used, the required setup and seed layers to be considered for the process [90–94].

Another existing procedure is electroless deposition. Electroless plating is an autocatalytic process in which the metal is deposited on an object as a result of a redox reaction. An electroless plating solution typically consists of:

- *Metallic salt*: to supply the source of metal ions for plating
- *Reducing agent*: to reduce metal ions to atoms
- *Complexant*: to form complexes with metal ions, to keep ions dissolved in

the solution and plating on the activated surface

- *Accelerator*: to accelerate the plating rate
- *Stabilizer*: to adhere to suspending particles in the solution, preventing metal ions plating on the particles that would result in a reduction of the plating rate
- *Buffer*: to regulate the pH of the solution and keep stable throughout the entire plating process

Copper ions for electroless plating must be bound into a complex. Suitable copper ion ligands are polyhydroxy compounds (polyhydroxy alcohols, hydroxyacid anions) and compounds having a tertiary amine group and hydroxyl groups (hydroxyamines, EDTA, etc.). EDTA and tetraoxypropylethyl ethylenediamine are mostly used in practice [95].

In general, the layer fabricated by electroless plating is more uniform than that deposited by electroplating. However, the plating rate is lower than that by electroplating. The comparison of electroless plating and electroplating is shown in Table 2.3. In 2005, Rajendra K. Aithal *et al.* proposed a way to perform electro-

Table 2.3: Comparison between electro-less plating and electroplating

Process parameter	Electro-less plating	Electroplating
<i>Deposition rate</i>	3 – 8 μ /hr	30 – 60 μ /hr
<i>Uniformity</i>	High	Low
<i>Adhesion</i>	Seed layer to enhance adhesion	Conductive seed layer
<i>Stability</i>	Can be unstable, easily peeled off	Stable
<i>Processing temperature</i>	High (35°C – 70°C)	Generally room temperature
<i>Power supply</i>	No	Required
<i>Pattern</i>	No specific design rule	Continuous pattern required

less copper deposition directly onto silicon [96]. To prevent copper from diffusing into the silicon substrate and improve the adhesion, the substrate was first sputter deposited with a 50 nm Ti layer. The substrate was then immersed in an acidic colloidal solution of 2.5 g of tin chloride ($SnCl_2 \cdot xH_2O$) and 0.05 g of palladium chloride ($PdCl_2$) and 15 ml of hydrochloric acid (HCl) in 30 ml of DI water for 1 – 3 min. To remove excess tin from the activated surface and expose the catalytic Pd, the substrate was then immersed in a solution consisting of 1 : 1 H_2O and HCl for 1 – 2 min. The reaction is shown as follows:

The copper sulfate (0.01 M $CuSO_4 \cdot 5H_2O$) served as the metallic salt, while the complexant was provided by 0.025 M of ethylenediaminetetraacetic acid (EDTA), 2 – 3 ml/l formaldehyde (HCHO) was the reducing agent, and sodium hydroxide (NaOH) was the pH regulator. Small amounts of 2,2-dipyridyl and Triton X-100 were added to ensure complete wetting of the substrate surface and enhance film uniformity. The hydrogen gas was expelled by bathing with nitrogen. The temperature and pH were varied between 40–60°C and 12–13, respectively. After the plating process, the sample was post-annealed in nitrogen at 300°C to remove defects and reduce the resistivity. Subsequently, the thickness of the electrolessly plated Cu layer was measured as a function of the concentration of the metallic salt and reducing agent. The corresponding deposition rate results between 20 – 100 nm/10 min., i.e. 0.12 – 0.6 μ/hr . Copper ions for electroless plating must be bound into a complex.

Table 2.4 shows several compositions of copper electroless plating solutions. It can be seen that all these solutions have relatively similar compositions, but their additive types and concentrations are quite different. Highly ductile Cu coatings can be obtained if the electroless deposition is carried out at higher temperature (> 40°C) and at a relatively low copper deposition rate [95,96].

Conventional gold electroless plating utilizes a stable gold cyanide complex with borohydride or (Dimethylamino)benzaldehyde (DMAB) as the reducers. The

Table 2.4: Composition of a few copper electroless plating solutions [95, 96]

Component	Solution A	Solution B	Solution C	Solution D
<i>Metallic salt</i> $CuSO_4 \cdot H_2O$	0.01 M	7 g/l	15 g/l	15 g/l
<i>Reducing agent</i> $HCHO$	2 - 3 ml/l	25 g/l	20 g/l	20 g/l
<i>Complexant</i>	EDTA (0.025M)	K-Na Tartrate (25 g/l)	Na_2EDTA (30 g/l)	Na_2EDTA (45 g/l)
<i>Accelerator</i>	Triton X - 100 (0.1ml/l) 2,2 - dipyridyl (0.3 g/l)	$NiCl_2 \cdot 6H_2O$ (2 g/l)	Sodium diethyldithiocarbamate, $K_4Fe(CN)_6$	2,2 - dipyridyl, polyethylene glycol
<i>Buffer</i> $NaOH$	Concentration unknown	4.5 g/l	10 g/l	10 g/l
<i>pH</i>	12 - 13	12.2 - 12.5	12.7	12.6
<i>Temperature</i>	$40^\circ C - 60^\circ C$	$20^\circ C$	$20^\circ C$	$70^\circ C$
<i>Deposition rate</i>	0.12 - 0.6 μ /hr	0.4 - 0.5 μ /hr	2 μ /hr	3 μ /hr

reaction is [97]

However, as is well known, cyanide compounds have an extremely high toxicity (hence they give rise to challenging problems related to both safety for the working place and environmental issues regarding the disposal of the residues and consumed chemicals), and the cyanide ions are known to attack the interface between the photoresist and the substrate [97, 98]. In 2008, Jiandong Hu *et al.* proposed another way to deposit Au by electroless plating onto a glass surface, using the Au(III) chloride complex as the metallic source [99]. BK7 glass slides were used as substrates for this deposition. They were immersed first in a 10% solution of (3-aminopropyl)-trimethoxy-silane (APTMS) in methanol (adhesive promoting agent) for 16 hr and then dried using a stream of nitrogen gas. Secondly, the surface was coated with colloidal gold nanoparticles as catalytic sites for the subsequent Au electroless reduction reaction obtained by immersing the nanoparticle-coated substrate in $HAuCl_4 \times 4H_2O$ with KBH_4 as the reducing agent. Finally, the substrate coated with gold nanoparticles was immersed in an aqueous solution containing 10 ml of 0.01% $HAuCl_4$ and 500 μL of 30% H_2O_2 . The thickness of the gold film measured by AFM was approximately 45 nm for 8 min, resulting in

Table 2.5: Composition of a few Au electroless plating solutions [97, 99]

Component	Solution A	Solution B	Solution C	Solution D
<i>Metallic salt</i>	$HAuCl_4$ $1.27 \times 10^{-3}M$	$HAuCl_4 \cdot 4H_2O$	$Na_3Au(SO_3)_2$ 0.01M	$Na_3Au(S_2O_3)_2$ 0.01M
<i>Reducing agent</i>	NaH_2PO_2 $2 \times 10^{-2}M$	30% H_2O_2	KH_2PO_4 0.04M	Na L-ascorbate 0.05M
<i>Complexant</i>	$NaH_2CH_2CH_2NH_2$ $8.32 \times 10^{-2}M$	-	$EDTA \times 4H_2O$	Citric Acid 0.4M
<i>Accelerator</i>	-	APTMS for adhesion	-	-
<i>Buffer</i>	KOH	-	-	KOH
<i>pH</i>	9 - 9.5	-	7.0	6.4
<i>Temperature</i>	65°C	Room temperature	65°C	70°C
<i>Deposition rate</i>	2.4 μ/hr	0.34 μ/hr	25 μ/hr	0.76 μ/hr

a deposition rate of about 0.34 μ/hr . The plating reaction in this case is [99]:

There are, however, other chemicals that can be the metal sources for Au electroless plating, such as the Au(I) sulfite complex and Au(I) thiosulfate complex [97]. Table 2.5 summarizes the compositions of the most suitable non-cyanide-based Au electroless plating solutions.

Fabricating micro-coils with HAR conductors that are vertically oriented and buried in the substrate is not without problems, mainly because void-free filling of HAR trenches by copper electroplating is challenging. The features and challenges of electroplated copper used in Damascene processing for typical multi-layer interconnections in integrated circuits or different types of copper corrosion in microstructures filled with Cu have also been characterized in detail previously [50–52]. Furthermore, the mechanism of copper electrodeposition, effect of different external parameters, effect of seed layer and over-potential in electrodeposition of copper inside trenches have also been detailed [53–57]. However, all these reports are associated with Through-Silicon Via (TSV) structures or typical vias and metal interconnects which are isolated cylindrical via trenches and not continuous long blind trenches as in the case of our micro-coils. Hence, the

challenges and solutions proposed in these reports might not necessarily extend to micro-coils in HAR trenches.

2.3 Copper removal

It is well known that copper cannot be dry etched; hence wet etching and Chemical Mechanical Polishing (CMP) of copper are the only two options to remove excess copper. Each of these processes has its own advantages and disadvantages, which are This has been introduced and discussed in the following subsection.

2.3.1 Copper wet etching

Wet etching of copper has been well-known for a long time and reported in detail earlier [100–103]. Choi *et al.* have reported controlled wet etching of copper overburden obtained from electroplating of TSVs, their etching solution using sulphuric acid solution in a special capsule chamber [102]. Furthermore, their process was based on the existence of differential etch rates between Cu protrusions from TSVs on one hand, and the Cu overburden outside TSVs on the other hand, in order to achieve the desired selectivity. A comparative table for existing Cu wet etchants given in [100] shows that the most common Cu etchants, $FeCl_3$ and $CuCl_2$, are used at temperatures well above the room temperature. Also, among the two most common Cu wet etchants, viz. $FeCl_3$ & $CuCl_2$, although $FeCl_3$ has a higher etch rate it produces a rough surface, while for $CuCl_2$ the toxicity is high and its etch rate drastically reduces with time [101]. Mayer *et al.* reported a novel but rather complex Cu etching solution consisting of organic complexing agents, peroxide and acids [103].

The major advantage of wet etching of Cu is that it is much faster than the removal rate of Cu using CMP, which is on average of around 10 nm/min [104]. As it will be detailed later, in Chapter 5 of this Thesis, we have developed a novel wet etch procedure of Cu, which does not have the constraints of the common Cu etchants mentioned above and does not need any type of toxic or corrosive reagents.

2.3.2 Chemical Mechanical Polishing (CMP)

Chemical Mechanical Polishing (CMP) is a very well established conventional way of planarizing surfaces and removing excess material on substrates. Initially introduced in the 1980's by IBM for SiO_2 surface planarization, the subsequent application of CMP has increased by leaps and bounds, although the process is not free from challenges like dishing, erosion and corrosion [105]. Despite being initially employed for silica, CMP was also introduced for copper removal in the microelectronic fabrication of advanced modern integrated circuits (ICs) [106] as well as for the damascene process [104], due to the difficulty of removing copper using dry etching and/or uncontrollability issues of its wet etching. A detailed analysis on the chemical process involved in the CMP of Cu indicates that the Cu removal occurs in two stages; first mechanical abrasion followed by chemical dissolution of copper [107]. The slurries most often used are silica-based [108] and alumina based. A comparison between these slurries' performance has been made by Caprio *et al.* with nitric acid and ammonium hydroxide as the oxidizing agents. Another study of these two slurries concluded that the removal rate for alumina-based slurries increased with pressure and velocity of the polishing pad, which was not true for the silica-based slurry. Also, the alumina-based slurry had a higher tendency to adhere to copper lines more than the silica ones [104]. The effect of the oxidizing agent has also been studied and it was found that although hydrogen peroxide-based slurries were slower compared to ferric nitrate-based ones, the former produced better planarization [109]. A detailed analysis of the process parameter interaction has been given by Kim *et al.* [110], as well as others who have discussed the process parameters influence onto the removal rate and uniformity [111, 112]. Another major disadvantage of CMP is dishing; the effect of process parameters on dishing for a generic CMP process has been studied thoroughly and modeled by Chang *et al.* [113] with closed form analytical expressions. The dishing issue for Cu CMP has been reported by Nguyen *et al.* [114], who highlighted the effect of removal rate and slurry chemistry.

2.4 Carbon Nanotubes (CNTs)

As it has been discussed, achieving planar micro-coils using Cu filling of HAR trenches followed by CMP to remove the excess Cu is extremely challenging. Therefore, it was worth looking into alternatives which can help achieve easy filling of HAR trenches. One such option is to use CNTs. The growth of CNTs using various methods is amply detailed in previous reports [115–119] which give detailed insight of different methods of synthesis of CNTs, their structure and characterization. Also, the possibility of growing CNTs in HAR trenches has been explored by Xie *et.al.* [120]. However, the issue with employing CNTs grown in HAR trenches as conductive material for micro-coils is that there is no lateral electrical conduction possible between adjacent CNT bundles. Bhuvana *et al.* suggested contiguous petal-like carbon nanosheet outgrowths from graphite fibers using plasma under a CVD process [121]. We have used a similar procedure to cement adjacent CNT bundles to create a continuous structure which gives a path for lateral electrical conduction. For this purpose, an Aixtron BM system was used to grow the CNTs using a growth recipe documented in literature [122, 123], followed by our novel recipe to cement the adjacent CNT bundles. Raman spectroscopy has been used to investigate the resulting hybrid structure [124, 125]. Although previous theoretical analyses of CNT based interconnects [126, 127] documented their effect of increasing the inductance and Q values at different high frequencies, in our work it was measured for the first time at low frequencies. Existing literature [128–131] indicates the presence of ferromagnetic iron carbide particles as an interstitial compound within the carbon-based materials. An initial iron seed layer is used as catalyst for the subsequent growth of CNTs and, these Fe particles are gradually converted into iron carbides (Fe_3C , Fe_7C_3) during the CNT growth process. These iron carbides are ferromagnetic materials with high magnetic saturation. Their presence consequently results in higher inductance values, which ultimately lead to higher Q values despite of higher resistances compared to those obtained for Cu micro-coils of same dimensions.

2.5 SU8 and PDMS processing

In the last chapter, the design of a cryogenic system for enhancement of SNR of an NMR micro-probe is presented. It uses polymers that have low thermal conductivity and are also compatible with current silicon microfabrication process technologies. Two such polymers are SU8 and PDMS that have a thermal conductivities of 0.2 W/mK [132] and 0.15 W/mK [133], respectively. SU8 has been successfully proven to be compatible with existing microfabrication processes and can be used to realize HAR as well as multilayer complex structure [134–137]. It is even possible to etch SU8 using existing conventional technologies [138]. Polydimethylsiloxane (PDMS), on the other hand, is a very versatile and easy-to-use material, widely used for soft lithography, and it has numerous reported applications, including for such channels [139–141]. One important advantage of PDMS is that, in principle, it can easily adhere to almost any material, including glass. However, to improve the adhesion force and especially reliability, the surface chemistry of the PDMS and/or of the surface it should adhere to must be modified in an oxygen plasma. This greatly enhances its adhesion and promotes a much easier and stronger bonding [142, 143], which can thus be used for good quality long-term sealing of micro-channels.

2.6 Summary

This chapter gives a detailed description of the available literature relevant to the work presented in the Thesis. First, the SNR calculation in NMR experiments is reviewed, followed by a detailed report on the micro NMR probes available in the literature. Their comparison shows that no proper probe design approach was suggested until now. Consequently, there is a need to propose a procedure for easy, direct one-to-one comparison of the NMR micro-probes' performance using a common metric, and which would also significantly ease their design.

Second, the literature review indicated that, until now, no planar micro-coils embedded in HAR Si trenches have been used in NMR microprobes. Various micro-fabrication processes utilized in the fabrication of our device were then presented. The smoothening of the scalloped DRIE walls is first reported. This is

followed by a detailed review of electrodeposition of Cu into trenches. However, most of them were related to realization of 3D micro-coils using TSVs or TPVs filled up with strictly bottom-up electroplating techniques. In contrast, our micro-coils employ very long, blind Si trenches in which the electroplating of Cu takes place not only vertically from the bottom, but also laterally from the side walls.

Third, the literature available on (CMP) was studied to provide an insight regarding the development of recipes for copper removal.

Next, we explored the usage of CNTs as a replacement for the Cu used in the micro-coil conductors. For this purpose, the previous literature reports relevant to CNT growth, their analysis and process of cementing CNT bundles through graphitization were discussed.

Lastly, the key features of the most important polymers used in micro-fabrication technologies were discussed, highlighting their suitability for the design of a cryogenic system that would enable SNR enhancements for a MR micro-probe.

Highlights of Chapter 2

- The thorough literature review of probes for MR experiments performed in this chapter shows micro-probes clearly have an advantage when it comes to cost of mass production through micro-fabrication and portability.
- Comparison of exiting micro-probes shows there exists no comprehensive guide for micro-probe design. There does not exist any parameter which quantifies the performance of the probe structure only, independent of the external MR measurement setup or type of the sample used. Currently, SNR is the only parameter which quantifies the performance of an NMR experiment, but it depends on both the measurement setup and the sample type used.
- The main component of a MR micro-probe is a micro-coil structure. Hence, a thorough literature review compared the various micro-coil fabrication techniques. Planar micro-coils with high aspect ratio inside Si trenches seemed to be most advantageous and least reported.
- We also weighed the pros and cons of the generic CMP process used for Cu removal with that of Cu wet etching procedures reported in the literature. The comparison showed that CMP is a rather slow but controllable process while wet etching -although fast- requires higher temperature, was less controllable and often required a complex combinations of wet etchants to be used.
- Lastly, a literature review showed that CNTs can be easily grown inside HAR trenches and had good longitudinal electrical conductivity, but the lateral conductivity between the CNT bundles was very poor due to random entanglement.

Chapter 3

Definition of a novel performance factor P

3.1 Introduction

A MR micro-probe for *ex vivo* applications may consist of at least one micro-coil, which can be used as the oscillating Magnetic Field (MF) generator as well as receiver coil, and a sample holder, with a volume in the range of nanoliters to micro-liters, placed near the micro-coil. The first generic expression for the signal-to-noise ratio (SNR) for an NMR experiment was formulated almost 40 years ago by D. Hoult *et al.* [17]:

$$SNR = \frac{K\eta(\frac{B_1}{i})\omega_0 M_0 V_s}{\text{Sample Noise} + \text{Thermal noise from coil}} \quad (3.1)$$

where K is the inhomogeneity factor of the MF generated by the coil, η is the filling factor which indicates the extent of coupling of the magnetic energy generated by the coil with the sample, B_1 is the time-varying MFS which lies in the plane perpendicular to the direction of B_0 , i is the current generating the RF MF of strength B_1 , ω_0 is the Larmor frequency, M_0 is the strength of the magnetization vector which depends on B_0 and the sample under investigation, and V_s is the sample volume. As it can be seen from eqn. 3.1, and as was indicated in

previous Chapter 2 with examples from literature, the SNR of such a probe is, however, dependent not only on its design but also on the measurement setup, and the measured sample. Equation (3.1) indicates the parameters involved in the calculation or optimization of SNR, but it may need to be modified (or some of its components recalculated) depending on the specifics of the used system. Here, in this Chapter, we are mainly interested in estimating the SNR of miniaturized micro-scale NMR probes for which the sample's noise is not significant owing to its small volume (nL - μL).

3.2 Outline of the original contribution

This Chapter focuses on the theoretical study of various factors affecting SNR of a MR micro-probe that consists of a planar micro-coil with conductors buried in its substrate, and an adjacent microfluidic structure with which the sample is manipulated and/or placed in the vicinity of the micro-coil. Most importantly, our approach defines a micro-coil performance factor P that enables one to optimize the SNR performance of the MR micro-probe, independently of the external setup and the proton density of the measured sample. The literature review summarised in Chapter 2 and specifically the data detailed in Table 2.1, indicated clearly that it is very difficult to directly compare the performance of all the various types of coils used in different NMR/MRI probes and especially to understand which are the key parameters influencing their SNR. Therefore, P defined here could serve as a quantitative performance indicator that would aid the design and optimization of MR micro-probe. This is necessary because it is very difficult to make a one-to-one comparison for different setups even when the SNR values are reported since in each case the experiments were carried out with a different set-up, different strengths of DC magnetic flux density and different bio-chemical samples having different proton densities. Additionally, the work here details the analysis and calculation of the main components of P , namely the filling factor η and the inhomogeneity factor K . The factor P can help the design of planar micro-coil-based MR micro-probes with a given sample volume in order to provide an optimal performance independent of the external setup used for the MR experiment(s).

3.3 NMR micro-probe performance factor P

For the case considered here, when the sample noise is quite negligible compared to the thermal noise from the micro-coil, eqn. (3.1) reduces to

$$SNR = (M_0 V_s \omega_0) \cdot \left(\eta \cdot \frac{K(\frac{B_1}{i})}{\sqrt{T_c R}} \right) \cdot \frac{1}{\sqrt{4k\Delta f}} \quad (3.2)$$

where T_c and R are the temperature and the electrical resistance of the micro-coil respectively, Δf is the bandwidth of the pre-amplifier, k is the Boltzmann's constant, and B_1 is the average value of the magnetic flux density (i.e. magnetic field strength MFS) generated by the micro-coil.

Equations (3.1) and (3.2) show clearly that the SNR is improved by maximizing the corresponding numerator value. Since both the magnetization vector M_0 and the Larmor frequency ω_0 are directly proportional to B_0 , they can both be enhanced by boosting B_0 and consequently improve the SNR. This explains the adoption of increasingly stronger superconducting (electro)magnets in NMR/MRI machines in the last decade.

Unfortunately, the choice of increasing B_0 is not always available to the user: once set in place, the value of B_0 is a given, dictated by the characteristics of the NMR/MRI machine available to the researcher and cannot be further increased. Therefore, another way of improving the SNR is to optimize the other remaining parameters in the numerator: the MF's inhomogeneity factor K , the filling factor η , the average value of B_1 within the sample volume V_s , and the sample volume itself. This Thesis examines all these factors and their influence on the final value of the P factor, and, hence, on SNR.

The first term ($M_0 V_s \omega_0$) in eqn. (3.2) is a sample-dependent term and indicates the number of proton spins of the particular element of interest to be detected within the total sample volume at the DC MF B_0 and at the Larmor frequency ω_0 . It can be shown that this term's value depends on the number of spins present in the sample under investigation and on the gyro-magnetic ratio (γ) of the element in whose NMR spectra one is interested.

The second term in the right-hand side of eqn. (3.2) represents solely the coil

performance in an MR experiment, since the numerator is proportional to the spatial homogeneity and strength of the MF generated by the coil, and to the filling factor η which represents the time-varying MF's effective coupling with the sample, while the denominator is the thermal noise due to the micro-coil's electrical resistance. Therefore, this second term in eqn. (3.2) is independent of both the proton spin density γ and DC MFS and, hence, can be defined as a 'performance factor' P characterizing only the micro-probe itself. eqn. (3.2) can thus be re-written as

$$SNR = (\text{term dependent on sample type and external sample setup}) \cdot P \cdot \text{constants} \quad (3.3)$$

where P is given by $\left(\eta \cdot \frac{K\left(\frac{B_1}{i}\right)}{\sqrt{T_c R}} \right)$, as indicated by the second term in the right hand side of equation (3.2).

Consequently, P can be used to calculate and compare the performance of various MR micro-probes by quantitatively assessing a probe's efficacy independent of proton spin density and external DC MFS. However, although the factor P does not explicitly include the sample volume term V_s , all of its numerator parameters do depend on V_s . Thus, V_s indirectly influences P and hence the determination of an optimal sample volume, or at least studying how P varies with the volume of the sample, is extremely important and is to be determined foremost.

3.4 Mean magnetic flux density (B_{z-mean}) and inhomogeneity factor (K)

The three most important factors influencing both P and SNR are the spatial homogeneity of the MF reflected in the parameter K (which takes into account the inhomogeneity of the time-varying field within the sample volume), the MFS (which can be represented by the mean value of its dominant component within the sample volume B_{z-mean}), and the filling factor η . The magnitude of B_z within the sample volume depends on the micro-coil dimensions and number of turns, and also on the distance of the sample from the coil (but which is fixed in our case,

for all micro-coil variants). The inhomogeneity factor K shows how much the MF varies, i.e. how inhomogeneous it is compared to (as a fraction of) the mean value of its strength. Previously, K has been discussed only qualitatively by Hoult *et al.* [17]. We define the inhomogeneity factor K as

$$K = 1 - \frac{\sigma}{B_{z-mean}} \quad (3.4)$$

where σ is the standard deviation of the MFS within the sample volume. For an ideal MF that is perfectly homogeneous within the sample volume, $\sigma = 0$ and $K = 1$. On the other hand, the smallest possible value of K is 0.

Hence, eqn. 3.4 is valid as long as σ is smaller than the mean value of the MFS B_{z-mean} , or else $K \leq 0$, resulting in impractical negative values of P . The values of the standard deviation σ and of B_{z-mean} for all probe variants presented in this work were extracted from electromagnetic simulations using CST for the useful maximum sample volumes.

3.5 Filling factor (η)

The filling factor η determines the extent of coupling between B_1 and the sample volume that will induce the sample response. It is defined as [17]:

$$\eta = \frac{\int_{\text{sample volume}} B_1^2 dv}{\int_{\text{all space}} B_1^2 dv} \quad (3.5)$$

Thus, η is the ratio of the magnetic energy contained within the sample volume to the magnetic energy in all space:

$$\eta = \frac{\text{Magnetic energy in the sample volume}}{\text{Magnetic energy over the entire space}} \quad (3.6)$$

The denominator of eqn. 3.6 essentially represents the inductance of the micro-coil, which for a unit current can be expressed as

$$L = \frac{1}{\mu_0} \int_{all \ space} B_1^2 dv \quad (3.7)$$

which can be rearranged as

$$\int_{all \ space} B_1^2 dv = \mu_0 L \quad (3.8)$$

If B_1 is perfectly spatially homogeneous over the sample volume, then the numerator of eqn. (3.6) can be simplified as the product of B_1^2 and the volume of the sample V_s . In reality B_1 always has a spatial variation in all three directions of spaces, x , y , and z . Also since B_z is the dominant MF component for a planar spiral micro-coil placed in the xy plane, eqn. (3.8) can be further written as:

$$\int_{sample \ volume} B_1^2 dv = \int_{sample \ volume} B_z^2(x, y, z) dv \quad (3.9)$$

Hence, the analytical expression for the filling factor η for a sample holder with the length aligned along the z axis is:

$$\eta = \frac{\int_{sample \ volume} B_z^2(x, y, z) dx dy dz}{\mu_0 L} \quad (3.10)$$

Therefore, in order to evaluate the filling factor η analytically, it is necessary to first deduce the expression of $B_z(x, y, z)$ that gives the MFS variation along the x , y & z axes. Alternatively, both the energy stored in the sample and that over the entire space can be extracted from electromagnetic simulations of each micro-coil and sample placement, and then used to evaluate η according to eqn. (3.6).

The approach described above for determining the filling factor η based on electromagnetic simulations must first be verified, especially since this method has not been reported previously in the literature. For this purpose, we use as a reference the approximate closed form expression of the filling factor η for a sample

Figure 3.1: 3D simulation model for planar micro-coil inside water sample [144]

kept inside the core of a solenoid [17]:

$$\eta_{solenoid} \approx \frac{V_s}{2V_c} \quad (3.11)$$

where V_s is the sample volume and V_c is the cylindrical volume occupied by the solenoidal coil. Considering a generic solenoidal coil with the sample in its core along the z axis and the corresponding values of V_s and V_c of 0.021 pL and 0.15 pL, respectively, the filling factor value results as $\eta = 0.07$ using eqn. (3.11).

Next, we also simulated in CST the 3D model of the same solenoidal coil and a value of 0.06 was obtained for the filling factor η . This result is close to the analytically calculated value of 0.07 with a variation of only 14.28%. This demonstrates the validity of our approach to calculate the filling factor η using energy extraction from simulations.

3.6 P factor comparison with literature

In order to verify the P factor defined by us and the approach described in the previous two sections for the calculation of each term of the P factor, the P factor for a planar coil reported by Armenean *et al.* [144] was calculated using this approach. Armenean *et al.* [144] clearly mentioned all the parameters and the measurement setup details which can be used for the theoretical calculation of SNR using eqn. (3.1). Using CST, a 3D model of the same planar coil immersed in 5 μL of water sample was built, exactly as described in Armenean *et al.* [144]. The 3D model is shown in Figure 3.1.

The CST simulation results were used to extract average value of MFS within

the sample volume, the K factor and η as well as the resistance R , followed by the calculation of the P factor. Next, this P factor was used to calculate the SNR according to the measurement parameters and, the volume of the sample. The resulting values are given in Table 3.1 along with the measured value reported by Armenean *et al* [144]. However, the SNR equation cited in Armenean *et al* [144] does not consider the effects of K and η which are essential in the calculation of SNR. In order to have a direct one-to-one comparison with Armenean's system, the P value thus calculated by us is also devoid of K and η values.

While the two SNR values have the same order of magnitude, they still differ by a factor of ≈ 3.5 . This difference mostly stems from the fact that the investigated zone of sample around the micro-coil mentioned by Armenean *et al* [144] is an approximate volume of $5 \mu L$ surrounding the micro-coil immersed in a larger volume of 0.33 cm^3 water. This uncertainty in actual volume will result in a change of the mean value of MFS inside the sample volume and also of the number of protons present under the influence of the magnetic field. In summary, the P factor proposed here appears to predict the SNR value reasonably well.

Table 3.1: Value of SNR derived from the P factor calculated by us for the planar coil reported by Armenean *et al.* [144] and its experimentally reported SNR

Performance factor P for Armenean's [144]'s planar coil $(mT)/(\Omega \cdot K)^{1/2}$	SNR value calculated from the P factor determined by us	Experimental value reported by Armenean <i>et al.</i> [144]
0.045	27	95

3.7 Conclusion

In order to be able to compare micro-probes that may be operated in different MR experiments that use very different operating parameters, in this chapter we defined and used a sample- and setup-independent performance factor P . We showed how through electromagnetic simulation we can calculate the different terms of the P factor, namely the mean value of the B field generated by the micro-coil inside the sample volume. We also defined the inhomogeneity factor K quantitatively. Using the mean value and standard deviation of the magnetic field inside the sample obtained from the electromagnetic simulations, the K value can

be determined. Lastly, we proposed a way of estimating the filling factor from its definition. Using the details of a coil already reported in the literature, we estimated its P factor, followed by the derivation of its SNR. This SNR value obtained from our P factor calculation was close to the reported value, confirming that our P factor can predict the SNR reasonably well.

Highlights of Chapter 3^a

- In this chapter we defined a novel performance parameter $\mathbf{P}$ to characterize the performance of the MR micro-probe. Unlike the conventional SNR used to characterize MR systems, this $\mathbf{P}$ factor is independent of the external MR measurement setup details and proton density of the sample under test. Hence, this $\mathbf{P}$ factor is of paramount importance for NMR micro-probe designers.
- We defined a clear closed mathematical expression for the inhomogeneity factor $\mathbf{K}$ which is an important parameter in the definition of $\mathbf{P}$ factor. Following its definition we also introduced a way to calculate it from CST electromagnetic simulations of 3D models of MR micro-probes.
- Next, we introduced an approach to calculate the filling factor η from CST electromagnetic simulations of 3D models of MR micro-probe using magnetic field energy extraction.
- Finally, we calculated the value of the $\mathbf{P}$ factor for existing micro-probe design in the literature and compared it with the both theoretical SNR as well as the experimental SNR value. This comparison gave us confidence in our P -factor calculation approach; showed SNR can be extrapolated from our P factor using the technique outlined in this chapter and the method is pretty close to the experimental value reported in the literature.

^a“Design of planar microcoil-based NMR probe ensuring high SNR”, Zishan Ali, Daniel Poenar, and Sheel Aditya, AIP Advances, Volume 7, 095107 (2017)

Chapter 4

P factor-based design of NMR micro-probes

4.1 Introduction

As discussed in the previous Chapter, a MR micro-probe consists of a planar field generating and/or pick-up structure, and a sample holder in its close vicinity. Since existing literature provides no concrete approach on how to design an MR micro-probe a thorough procedure was devised based on the usage of the performance factor P which was explained in detail in previous Chapter 3. This Chapter introduces the different novel designs for NMR micro-probes that have been developed using this approach. Literature shows that NMR microprobes have been mostly implemented using planar spiral micro-coils. Our probe designs have not been restricted by using only planar, spiral micro-coils but other planar structures were also considered and their SNR performance is compared through the approach described in Chapter 3.

4.2 Outline of the original contribution

- Several novel planar NMR micro-probe designs are first proposed and then their performance is compared to select the best probe structure.
- The design considered not only different planar conductive structures but

different sample holder shapes were also investigated

- Criteria for determining the optimal sample volume were developed, based on maximizing the component homogeneity of the magnetic field B_1 .

4.3 Proposal of different micro-probe structures

The various micro-probes designed in this work differ in the shapes of both their micro-coils and their sample holders. For the micro-coil, 3 planar conductive structures were considered viz. spiral, meander and concentric semi-circles. For the sample holder, 2 shapes were considered for each micro-coil type. A first generic sample holder sits on the top of the structure covering its entire surface area, and another type of sample holder mimics the shape of the underlying conductive structure. 3D models of the proposed microprobe designs were built in the software package ‘Computer Simulation Technology’ (CST) to perform electromagnetic simulations. An unit current was passed through the structure which generates the magnetic field. Considering the planar structures to lie in the xy plane, the dominant magnetic field is then B_z . As described in the previous chapter, the mean value of B_z is first extracted, the K value is calculated as introduced earlier and then the filling factor η is also computed using the energy extraction procedure. All the resulting values for B_z , K and η are subsequently used to calculate the performance factor P .

In the first design step, trace width optimization was performed for each probe design with both generic and mimicking sample holder. Considering the optimum trace width thus obtained, next the optimum number of turns was decided through simulations. After deciding between the performance of generic and mimicking sample holder, next the aspect ratio of the conductive structure was optimized by changing the trench depth while monitoring the effect on the P factor. For the generic sample holder we also additionally imposed a condition for an optimum sample volume.

4.3.1 Generic sample holders

For all the designs presented here, a generic sample holder was first considered, i.e. of cylindrical shape placed right on top of the micro-coil and covering its entire surface area. The first planar micro-coil which was examined had a spiral shape with an internal radius of $25\ \mu\text{m}$ and a rectangular conductor cross-section etched $20\ \mu\text{m}$ deep inside a silicon substrate with an inter-turn spacing of $15\ \mu\text{m}$. The sample holder sits on top, covering the entire micro-coil surface. The design is shown in Fig. 4.1. The trace width and the number of turns were varied to compare the SNR performance for various dimensional parameters.

Other considered micro-probe designs include two variants of concentric semi-circular conductors. In the first, all the conductive semi-circles are connected in parallel and have equal trace width, as shown in Fig. 4.2, in the other design the semi-circles have increasing widths to ensure equal resistance, as shown in Fig. 4.3. The advantage of the latter variant is that the resistance is the same for all the semi-circles, hence the equal current flow through them will produce uniform magnetic field, unlike the former structure where maximum current flows only through the innermost semi-circle due to its smallest resistance. Fig. 4.4 shows the last micro-probe design considered: a planar meander structure.

For comparison, the ‘magnetic performance’ was first calculated for each micro-probe, as given by the numerator of the P factor defined in Chapter 3:

$$\text{Magnetic performance} = B_{z-\text{mean}} \cdot K \cdot \eta \quad (4.1)$$

The variation of the resulting magnetic performance with the trace width is shown in the Fig. 4.5. For the semicircle design with equal resistance, no trace width

Figure 4.1: Planar micro-coil based microprobe design with generic holder

Figure 4.2: Planar concentric semi circular based micro probe design with equal trace widths and generic holder

Figure 4.3: Planar concentric semi circular based micro probe design with equal resistance for all the semi circles and generic holder

Figure 4.4: Planar meander based micro probe design with generic holder

variation is necessary since its trace widths are fixed by the equal resistance criterion and the width of the innermost semi-circle is fixed at a minimal value of width $50 \mu\text{m}$. Therefore, the results of this design are not included in Fig.4.5.

First of all, it is seen from Fig. 4.5 that the magnetic performance of the spiral micro-coil is the best. Secondly, as expected, the magnetic performance reduces with increasing the trace width of the planar structures. This is due to both a reduction in the mean value of B_z over a larger sample volume (since the surface

Figure 4.5: Magnetic performance with the variation in trace width for the spiral structure with 3.5 turns, semi circular and meander micro-coils respectively with generic sample holders

area of the micro-coil increases with the trace width) and also a reduction of the K value due to poorer magnetic field homogeneity over the larger surface area. The reduction of these two factors negates the increase in the filling factor due to the corresponding larger sample volume. For the semi-circular structure, however, the magnetic performance slightly increases with trace width; this can be mainly attributed to the increase in filling factor. For the meander structure, the magnetic performance is the poorest and remains almost constant; this is due to the very low value of the magnetic field it generates.

For the spiral micro-coil, the number of turns was also varied. The magnetic performance is shown in Fig. 4.6. Since a $25\ \mu\text{m}$ trace width showed the best magnetic performance for the 3.5 turns spiral micro-coil (from Fig. 4.5), this was the trace width value used when varying the number of turns. In Fig. 4.6 the plot shows that the magnetic performance first increases up to 5.5 turns and then starts decreasing with larger number of turns. This is again due to the fact that

Figure 4.6: Magnetic performance variation of spiral micro coils with generic sample holder as the function of the number of turns and $25\mu\text{m}$ trace width

the surface area of the micro-coil increases with the number of turns and, hence the mean B_z value falls. Consequently a number of 5.5 turns is the optimum value for which the mean B_z , K and η are all sufficiently high to provide the best magnetic performance. Thus, having a larger number of turns and/or larger sample volume does not necessarily mean a better magnetic performance when it comes to SNR of a MR micro-probe.

4.3.2 Mimicking sample holders

Similarly, the magnetic performance of the micro-probes with mimicking sample holders was also analyzed. The idea behind such a design was to have better coupling of the B_z component of the MF generated from the current flowing inside the traces with the sample present exactly above the location of the traces. The structures are shown in Figs.4.7 - 4.9. The conductive structures are exactly same

Figure 4.7: Planar spiral micro-probe design with mimicking sample holder

Figure 4.8: Planar semi-circular micro-probe design with mimicking sample holder

Figure 4.9: Planar meander micro-probe design with mimicking sample holder

as before, with the sample holder sitting on top of the structure mimicking the shape of the conductors. Just as in the previous case, electromagnetic simulations were carried out for all the probe designs with mimicking sample holders to extract the B_{z-mean} , K and η and then these values were used to calculate the magnetic performance for various trace widths as well as number of turns in case of the micro-coils. The results are shown in Figs 4.10 & 4.11.

Compared to the results of the previous case, the magnetic performance of the structures with mimicking sample holder is lower for all trace widths and also in the case of spiral micro-coils for all number of turns. The variation of the magnetic

Figure 4.10: Magnetic performance with the variation in trace width for the micro-coil structure with 3.5 turns, semi circular structure and meander structure with mimicking sample holder structure

performance with respect to both the trace width of the micro-coils and the number of turns for the spiral micro-coils has a similar behavior with that of the generic sample holder designs, but with some important differences. Again, Fig.4.11 shows it is not necessary to have a large number of turns for the mimicking sample holder as well.

For the variation in trace width, the mimicking sample holder designs show smaller values (roughly half of those the generic holder) for the magnetic performance (after comparing Fig. 4.5 with Fig. 4.10) of all the designs. However, the slope is different since the drop in the values for the spiral coils is now only 1.5 mT compared to ≈ 4 mT for the generic sample holder structures. In contrast, the semi-circular micro-coil with mimicking holder shows an increased slope for its variation with the trace width. The meander micro-coil remains the poorest performer and again, its magnetic performance has an almost constant value.

Figure 4.11: Magnetic performance variation of micro coils having mimicking sample holder on the top with different number of turns and $25\mu\text{m}$ trace width

For the magnetic performance of spiral micro-coils as a function of the number of turns, again the qualitative behavior seen in the graph of Fig. 4.11 is similar to that shown in Fig. 4.6 for the structures with generic sample holders but different quantitatively. For the structures with mimicking sample holder, the peak is much clearer defined as the curve starts from a much lower level (relative to the peak value). The peak value is ≈ 11.5 mT (vs 18 mT for the case with generic holder) and then decreases with 39% to the lowest value vs 44% for the structures with generic sample holder.

4.3.3 Comparison between generic and mimicking sample holder

The plots shown in Figs. 4.5, 4.6, 4.10 & 4.11 clearly indicate that the magnetic performance of the probes with mimicking sample holder is inferior to that of those with to the generic sample holder. The same conclusion applies for the P factor, since the magnetic performance as described earlier in equation (4.1) is the numerator of the P factor as defined earlier in eqn.s (3.2) and (3.3). The P factor values can then be calculated by dividing the magnetic performance value with the square root of the product RT of the resistances of the conductive structures (R) and the temperature (T), which represents the noise component. Since both the probe designs employ identical conductive structures, their resistance is the same and, hence, at the same temperature they will yield the same noise component value. Therefore, the values of the P factor for the mimicking holder structures will be smaller than those for the structures with generic holders. Consequently, the probes with generic sample holders are the logical choice for further analysis, as will be detailed in the next section. Furthermore, it should be noted again that the spiral micro-coil performs much better than any of the other structures discussed here. Hence, only spiral micro-coils will be hitherto used in all the subsequent designs. The plots in Figs. 4.5, 4.6, 4.10 & 4.11 also clearly show the numbers of $25\ \mu m$ for the trace width and 5.5 for the number of turns as the optimal design parameters for the spiral micro-coils. We will, however, continue to compare their performance with that of micro-coils with a large number of turns to get a clear picture on how much will the inductance change affect the MR performance. These analyses are carried out in the following section.

4.4 Micro-probe designs

Based on the above analysis, the spiral micro-coil having an aspect ratio (AR) value of 1 : 1 with generic sample holder was chosen for the micro-probe design. However, the analysis was further extended now to the high aspect ratio (HAR) of 3 : 1 where the depth was chosen to be $75\ \mu m$ inside the silicon substrate. The motivation to have such HAR micro-coils was to reduce the surface area of the

micro-coils such that miniaturization is achieved and the resistance is lowered to obtain a lower thermal noise and, hence, increase the SNR. However, for a full comparison from the design point of view, we run the analysis for three aspect ratios viz. 3 : 1 (HAR), 1 : 1 and 1 : 3 (less challenging from the fabrication point of view). The details of all the micro-coil variants are given in Table 4.1

Table 4.1: Dimensions of the different micro-coil variants analyzed in this paper

Number of turns	3.5			5.5			15.5		
Aspect ratio of the micro-coil conductor	1:3	1:1	3:1	1:3	1:1	3:1	1:3	1:1	3:1
Height of the micro-coil conductor (μm)	8	25	75	8	25	75	8	25	75
Width of the micro-coils conductor (μm)	25								
Radius of the innermost turn of the micro-coils (μm)	25								
Inter turn spacing (μm)	15								

4.5 Determination of maximum permitted sample volume

Since the spiral micro-coil is located in the xy plane, the dominant component of its generated MF is along the z axis, B_z . For any MR analysis, if we consider the external DC MF B_0 to be oriented along the x axis (hence perpendicular to B_z), then in order to tip the M_0 vector within the zy plane only one of the B_z or B_y components must be dominant. Although for a planar micro-coil B_z is usually considered dominant within the entire sample volume, we need to carefully check that this is indeed correct and that there are no areas where B_y is stronger. In order to determine this, we considered the angle θ between B and B_y along the x and y axes for different values of z . B_z is considered stronger than B_y in the regions where $\theta \geq 75^\circ$. The angle criterion of $\theta \geq 75^\circ$ ensures that the component B_y can be neglected within the sample volume. The height of the sample along z

axis was restricted to 10 μm since the magnitude of B_z along the z axis falls as $\approx \frac{1}{z}$, as given by Equation A.1 obtained through modification of a similar relation given in literature [145]:

$$B_z = \frac{\mu_0 \mu_r N I}{2e} \cdot \left(\frac{a_0}{\sqrt{z^2 + a_0^2}} - \frac{a_0 + e}{\sqrt{z^2 + (a_0 + e)^2}} + \ln \frac{a_0 + e + \sqrt{z^2 + (a_0 + e)^2}}{a_0 + \sqrt{z^2 + a_0^2}} \right) \quad (4.2)$$

where $e = Nw + (N - 1)s$, w & s are the conductor trace width and inter-turn spacing, respectively, I is the current and a_0 is the internal radius of the coil.

Figure 4.12 shows one set of such angle variation plots for a spiral micro-coil with 5.5 turns and 3 different CAR values. The extent along the x and y axes where the angle is below 75° was estimated from these plots, thus indicating the largest region in which the sample could be situated. The same procedure was repeated, for spiral micro-coils with 3.5 and 15.5 turns and all the different conductor CAR values, to determine the maximum extent of the sample volume for which $\theta \geq 75^\circ$ and the resulting values are tabulated in Table 4.2. In all cases it was considered that the height (i.e. thickness) of the sample is held constant at a value of 10 μm along z axis.

As can be seen from Table 4.2, the sample volume extent along the x axis increases with the number of turns while the change is insignificant along the y

Table 4.2: The maximum permitted extent of the sample volume along x and y axes satisfying the angle criterion $\theta \geq 75^\circ$ for all micro-coil variants

micro-coil variant: number of turns & CAR value	Along x axis	Along y axis
3.5; 1 : 3	−140 μm to 170 μm	−52 μm to 35 μm
3.5; 1 : 1	−140 μm to 170 μm	−50 μm to 35 μm
3.5; 3 : 1	−140 μm to 170 μm	−50 μm to 35 μm
5.5; 1 : 3	−220 μm to 210 μm	−50 μm to 40 μm
5.5; 1 : 1	−220 μm to 220 μm	−50 μm to 40 μm
5.5; 3 : 1	−220 μm to 220 μm	−50 μm to 40 μm
15.5; 1 : 3	−550 μm to 550 μm	−50 μm to 45 μm
15.5; 1 : 1	−550 μm to 550 μm	−50 μm to 45 μm
15.5; 3 : 1	−550 μm to 550 μm	−50 μm to 45 μm

Figure 4.12: Angle variation along x , y and z axes for all conductor aspect ratio (CAR) values of a 5.5 turn coil at different heights ($2\ \mu\text{m}$, $5\ \mu\text{m}$, $10\ \mu\text{m}$, $15\ \mu\text{m}$, $20\ \mu\text{m}$) from the micro-coil surface.

axis, and the CAR value also has little to no effect. The maximum permitted sample volume resulting from these plots for each micro-coil variant was then used to determine the average values of B_z , the inhomogeneity factor K and the filling factor η , with the results shown in the next section.

4.6 Performance factor calculation

Using the maximum permitted sample volume and B_{z-mean} , K and η , the P factor values have been calculated for different micro-coils and these results are tabulated and discussed in the following sub-sections.

4.6.1 Performance of the micro-coils with the maximum permitted sample volume

First we consider the maximum sample volume determined for each micro-coil variant using the angle condition $\theta \geq 75^\circ$, as described in section 4.5. The resulting values are tabulated in Table 4.3 along with the total resistance of each micro-coil.

As can be seen from Table 4.3, for a micro-coil with a given number of turns, the B_{z-mean} value increases with decreasing CAR value, with the largest variation for the smallest micro-coil (3.5 turns). This happens since more of the MF is distributed within the sample placed above the coils as the CAR value decreases (or the conductor height decreases), and, therefore, the MF-generating currents

Table 4.3: Calculated values of B_{z-mean} , K , η , P and electrical resistance for the maximum permitted sample volume for each micro-coil variant

Micro-coil variant: number of turns & CAR value	Mean MFS B_{z-mean} [mT]	Inhomogeneity factor K	Filling factor η	Resistance [m Ω]	Performance factor P (mT)/($\Omega \cdot K$) ^{1/2}
3.5; 1:3	13.5	0.45	0.01	4.3	0.053
3.5; 1:1	12.3	0.46	8.9×10^{-3}	1.4	0.077
3.5; 3:1	9.6	0.47	4.3×10^{-3}	0.46	0.05
5.5; 1:3	14.5	0.43	0.01	6.8	0.044
5.5; 1:1	13.4	0.42	0.01	2.2	0.07
5.5; 3:1	11.6	0.5	6.9×10^{-3}	0.73	0.087
15.5; 1:3	11.9	0.3	3.5×10^{-3}	19.5	0.0052
15.5; 1:1	11.7	0.3	3.14×10^{-3}	6.2	0.008
15.5; 3:1	11.3	0.33	3×10^{-3}	2.06	0.001

are closer to the chip surface and hence to the sample. This phenomenon also affects the filling factor η . Since the micro-coil CAR value has no effect over the magnetic energy over the entire space but does influence (as mentioned above) the magnetic energy within the sample volume, the micro-coils with same number of turns have lower filling factors as the CAR value increases due to the lowering of B_{z-mean} values within the sample volume. However, increasing the CAR value reduces the resistance for a given number of turns and constant conductor width since it results in an increased conductor cross-sectional surface area through which the current flows.

As the number of turns increases from 3.5 to 5.5, the increase of the mean MFS within the sample volume B_{z-mean} is larger than the increase of the magnetic energy over the entire space and, consequently, the filling factor η also increases. However, for the bigger micro-coils, the inhomogeneity factor K suffers due to an increased variation of the MF distribution across a larger micro-coil (and hence within the sample volume as well), and so does the resistance which increases due to an increased conductor length.

Contrary to expectations, the results deteriorate when the number of turns is further increased to 15.5 turns. Although the larger number of turns allows a larger sample volume, the MFS B_{z-mean} is quite low compared to micro-coils with less turns and this reduces the filling factor η while the micro-coil resistance increases. Consequently, the performance of the micro-coil with 15.5 turns is quite poor in all aspects and is reflected in a smaller P value, as shown in the last column of Table 4.3.

4.6.2 Performance of the coils with the minimum common volume

The previous section discussed the performance of the micro-coils when the maximum permitted volume was used. Now, in order to get an idea about the effect of the sample volume on the P factor values, we selected the smallest volume for which the angle condition $\theta \geq 75^\circ$ is simultaneously satisfied by *all* micro-coil variants. This volume is the volume corresponding to the largest permitted volume for the 3.5 turn coil since this volume is lower than the largest volume allowed

Table 4.4: Calculated values of B_{z-mean} , K , η , P & electrical resistance for the smallest volume common for all the micro-coil variants.

Micro-coil variant: number of turns & CAR value	Mean MFS B_{z-mean} [mT]	Inhomogeneity factor K	Filling factor η	Resistance [m Ω]	Performance factor P (mT)/($\Omega \cdot K$) ^{1/2}
3.5; 1 : 3	13.5	0.45	0.01	4.3	0.053
3.5; 1 : 1	12.3	0.46	8.9×10^{-3}	1.4	0.077
3.5; 3 : 1	9.6	0.47	4.3×10^{-3}	0.46	0.05
5.5; 1 : 3	18.6	0.66	9.8×10^{-3}	6.8	0.084
5.5; 1 : 1	17.4	0.7	8.33×10^{-3}	2.2	0.125
5.5; 3 : 1	14.5	0.7	4.85×10^{-3}	0.73	0.11
15.5; 1 : 3	24	0.78	2×10^{-3}	19.5	0.015
15.5; 1 : 1	23.8	0.8	1.9×10^{-3}	6.2	0.26
15.5; 3 : 1	21.4	0.85	1.3×10^{-3}	2.06	0.03

for the 5.5 and 15.5 turn coil variants. Then we recalculated the values of all the parameters (B_{z-mean} , K , η) and, of course, that of the P factor, and the results are given in Table 4.4.

In Table 4.4 the first 3 rows are the same as in Table 4.3 since the lowest common volume is the same as the largest allowed volume for the 3.5 turn coil. However, for the rest of the coil variants the MFS as well as the homogeneity of the MF have improved, since the volume considered now is lower than the maximum allowed volume, while on the other hand the filling factor η has reduced for the same reason. Another conclusion which can be drawn from Table 4.4 is that the effect of an increased micro-coil CAR for a particular number of turns is still the same as before: it reduces the B_{z-mean} , which in turn affects the values of both K and η .

4.6.3 Comparison of results for P for different volumes

The values of the performance factor P , calculated using the values of its components and listed in Table 4.3 & 4.4 are also plotted in Fig. 4.13 for a better comparison. Fig. 4.13 can thus be used to draw some useful conclusions for the design of micro-coil-based NMR probes.

- The sample volume reduction from the maximum allowed volume to lowest common volume has improved both B_{z-mean} and K , as reflected by the K factor values closer to 1 for the larger number of turns. However, the

Figure 4.13: Comparison of the values of the performance factor P for all micro-coil variants in two cases: for maximum allowed sample volume and for the lowest common sample volume

opposite is true for the filling factor η : its value reduced considerably since the minimal sample volume is very low, especially for the micro-coil with 15.5 turns. Thus, although this latter micro-coil has the strongest B_{z-mean} and better MF homogeneity within the sample, its smaller filling factor and higher resistance reduce the value of P .

- The micro-coil's CAR has a major effect on resistance. In terms of magnetic performance, however, its increase only reduces the MFS within the sample which in turn lowers the filling factor value. Additionally, conductors with high aspect ratios are more difficult to fabricate/fill in using copper electroplating.
- Increasing the number of turns initially, i.e. for a relatively small number of turns of, e.g., up to 5...6, enhances the MFS inside the sample and also may

be necessary to accommodate a minimal sample volume. This is because a too small sample volume, although characterized both by a large B_{z-mean} and a high K value, would have a very small filling factor that would reduce drastically the value of the entire performance factor P . However, increasing excessively the number of turns of the planar spiral micro-coil would increase the maximum permitted sample volume (i.e. for which the angle condition $\theta \geq 75^\circ$ is satisfied). Although having the largest possible sample volume may seem desirable to maximize the SNR (see Equations 3.1 & 3.2), in fact it would have only negative effects in this case. The average MFS would be reduced within the larger sample volume, hence the filling factor η decreases, and the MF homogeneity worsens too. Additionally, the micro-coil resistance also rapidly increases with the number of turns and contributes considerably to the rapid reduction of the performance factor value. Consequently, an optimum compromise has to be found (also see next point), with the smallest number of turns that would accommodate the required sample volume (considering a sample holder of fixed height and as close as possible to the micro-coil surface) but which would still generate the strongest MF without increasing R .

- Our data obtained for planar spiral micro-coils variants with 3 different CARs (1:3, 1:1 and 3:1) and with 3 different numbers of turns (3.5, 5.5 and 15.5) indicate that the optimum performance factor value is obtained for an aspect ratio of 1:1 and 5.5 turns. 5.5 turns seem to be a compromise between low and high number of turns and so does a 1:1 CAR where the field B_{z-mean} is stronger than that of the 3:1 variant and the resistance is less than that of the 1:1 variant.

4.7 Solenoidal coil analysis

Since the solenoid is one of the most conventional structures used for NMR analyses of small samples, we simulated a set of solenoidal coils whose dimensions were chosen such that the cross-sectional area of their wires were identical with those

Figure 4.14: 3D model of a solenoidal coil with sample placed inside its core

of our micro-coils with the different CAR values of 1:3, 1:1 and 3:1. Thus, from the Equation

$$\pi \cdot r_0^2 = h \times w \quad (4.3)$$

where r_o is the radius of the solenoid wire, $h/w = \text{CAR}$ & $w = 25 \mu\text{m}$, three values of r_0 can be obtained, corresponding to each CAR. The inter-turn spacing is taken to be the same as for our micro-coils, with a total number of turns of 5. The radius of the core of the solenoid is also taken the same as the radius of the innermost turn of the micro-coils, i.e. $25 \mu\text{m}$. The sample is placed inside the core of the micro-coil and, hence, its volume is that of the cylinder the solenoidal coil

 Table 4.5: Comparison of P values for solenoids having same coil cross-sectional area, 5 turns and the same inner core radius as that of the planar micro coil of 5.5 turns

Solenoid wire radius (r_0) for different CAR of our planar micro coils [μm]	Mean MFS $B_{z-\text{mean}}$ [mT]	Inhomogeneity factor K	Filling factor η	Resistance [m Ω]	Performance factor P (mT)/($\Omega \cdot K$) ^{1/2}
8 (1:3)	37	0.845	0.12	87	0.72
14 (1:1)	26	0.846	0.08	34	0.55
24.4 (3:1)	17.5	0.847	0.05	14	0.35

encompasses. Table 4.5 tabulates the different component values for the solenoidal coils along with their calculated P factor values. As can be seen, the P factor value falls as the cross-sectional area of the solenoidal coil increases. The reduction in mean value of B_z (we considered the solenoid to be oriented along the z axis and hence the dominant field is B_z) when increasing the wire cross-section seems to be the main culprit for the reduction of the P factor despite the fact that the resistance decreases. The reduction in B_z value is due to the fact that the length, and hence the volume of the cylinder encompassed by the solenoid, increases with the cross-sectional area of the solenoid's wire, ultimately reducing the mean value of B_z and also the filling factor.

The values of P for the solenoidal coils appear much larger than those for planar micro-coils in Tables 4.3 and 4.4. However, it is much more difficult to miniaturize solenoidal coils at micro-scales/on-chip. For the cross-sectional area equivalent to a CAR of 3:1 the solenoidal coil's diameter is about $48\ \mu m$, which is extremely small for a 3D solenoidal coil. Hence, in reality, for the solenoidal coils to be used by wounding them around capillary tubes of practical sizes, the solenoidal coils must have much larger diameters which will reduce the P factors significantly. This suggests that the comparatively bigger solenoids used conventionally will have a lower P factor compared to planar micro-coils unless other dimensional parameters are varied to nullify the effect.

4.8 Substrate analysis for the micro-coils

The Larmor frequency of hydrogen is as low as 42.56 MHz for $B_o = 1\ T$, and, hence, this should be the minimal operating frequency of any MR micro-probes. Hence, the previously introduced probe designs were simulated at frequencies up to 1 GHz in order to study the effect of the Si substrate's resistivity. For simplicity we first simulated the 3.5 turn model for all the 3 conductor aspect ratios. The simulations first used CST discrete ports, as shown in Fig. 4.15, and later waveguide ports were used.

At first the S_{11} parameter values for various port impedances were simulated, as shown in Figs. 4.16, 4.17 & 4.18. The best value of port impedance is considered the one which gives a S_{11} as low as $-20\ dB$ for all values of the frequency up to

1 GHz. Next, this port impedance was used to simulate the Q values for different substrate resistivities as tabulated in Table 4.6. The Q values for 42.58 MHz (H-frequency), 600 MHz and 1 GHz are shown in Fig 4.19.

(a) With Silicon substrate

(b) With Silicon substrate hidden

Figure 4.15: Discreet port model

Figure 4.16: S_{11} for aspect ratio 1:3

The Q values show that the loss increases with substrate resistivity, mostly due to eddy current losses, resulting in low Q values. The CST lossy model, which has an impractically high resistance, essentially behaves identically as the air substrate

 Figure 4.17: S_{11} for aspect ratio 1:1

 Figure 4.18: S_{11} for aspect ratio 3:1

model and, hence, the eddy current loss is very low. For the lossless CST model, there are no eddy current losses and, hence, the Q values are similar those of the lossy CST model. For the practical high resistivity wafer, the Q values are higher compared to those obtained for the low resistivity wafer.

Next, considering the high & low resistivity substrate, the coil was simulated using waveguide ports to check the effect of the pads for each aspect ratio. The waveguide port model in CST is shown in Fig. 4.20.

Table 4.6: Different Silicon substrates considered for the simulation

CST lossy Silicon	CST lossless Silicon	Low resistivity Si wafer	High resistivity Si wafer
$\rho = 400000 \text{ ohm-cm}$ $\sigma = 0.00025 \text{ S/m}$	Resistivity not considered	$\rho = 5 \times 10^{-3} \text{ ohm-cm}$ $\sigma = 2000 \text{ S/m}$	$\rho = 1000 \text{ ohm-cm}$ $\sigma = 0.1 \text{ S/m}$

Figure 4.19: Values of Q for different substrate types

Figure 4.20: Waveguide port model in CST

The variation of the Q value with frequency is shown in Fig. 4.21; the h values given in the legend correspond to the micro-coil height and, hence, indicate the different aspect ratio values of 1 : 3, 1 : 1 & 3 : 1 respectively.

(a) High resistivity Silicon substrate

(b) Low resistivity Silicon substrate

Figure 4.21: Simulated Q factor variation for micro-coils with 3.5 turns of different aspect ratios, as obtained from CST simulations using the waveguide port model

We can observe from the plots that the Q values of the high resistivity substrate are still higher than those obtained for the lower resistivity substrate although they have reduced due to the presence of the pads when compared to the discrete model.

Figure 4.22: Resistance variation with frequency for the micro-coil with 3.5 turns embedded in a high resistivity Si wafer

Figure 4.23: Inductance variation with frequency for the micro-coil with 3.5 turns embedded in a high resistivity Si wafer

Also, for the low resistivity wafer similar Q values were obtained for all the aspect ratios, while in the case of the high resistivity wafer the best performance was obtained with the 3 : 1 aspect ratio. The resistance and inductance variations with the frequency of all the 3 aspect ratios of the 3.5 turn micro-coil are shown in Figs. 4.22 and 4.23 respectively.

Figure 4.24: S_{11} parameter variation for micro-coil with 5.5 turns embedded in a high resistivity Si wafer obtained from the optimized simulation settings determined from simulations of the micro-coil with 3.5 turns

The 3.5 turn micro-coil was simulated first to optimize the mesh cell numbers and the port dimensions in order to get an idea how the micro-coil behaves at a higher resistivity Si substrate. These optimized simulation settings were then used to simulate the 5.5 turns micro-coil which was determined as the best design for MR micro-probe using the P factor based design approach, as discussed earlier in this Chapter.

Figure 4.25: S_{21} parameter variation for the micro-coil with 5.5 turns embedded in a high resistivity Si wafer obtained from the optimized simulation settings determined from simulations of the micro-coil with 3.5 turns

The results of the simulations provided the variation with frequency up to 100 MHz for the S-parameters of the 5.5 turns micro-coil, as shown in Fig.4.24 and

4.25. Q , resistance and inductance are shown in Figs. 4.26, 4.28. In each case, the precise simulated value at 42.58 MHz, the Larmor frequency of the hydrogen atom is shown.

Figure 4.26: Q factor variation of for the micro-coil with 5.5 turns embedded in a high resistivity Si wafer obtained from the optimized simulation settings determined from simulations of the micro-coil with 3.5 turns

As seen from the figures, the S-parameters showed a pretty good response in the low frequency range of up to 100 MHz. The S_{11} parameter is below -10 dB which indicates very little signal reflection, while the S_{21} parameter is only -3 dB indicating efficient power transfer between port 1 & 2 of the micro-coil.

Figure 4.27: Resistance variation with frequency for the micro-coil with 5.5 turns embedded in a high resistivity Si wafer, as obtained from the optimized simulation settings determined from simulations of the micro-coil with 3.5 turns

The latter plots of Q , inductance and resistances show that, as expected, the

5.5 turns micro-coil has both higher inductance and much increased resistance than those of the micro-coils with 3.5 turns (as shown in Fig. 4.23 & 4.22), resulting in a reduced Q value. From the above analysis, it is quite evident that the use of a high resistivity substrate is necessary to have good S parameter and Q values of the micro-coils. Hence for the fabrication, wafers with resistivity of 0.1 S/m were used.

Figure 4.28: Inductance variation with frequency for the micro-coil with 5.5 turns embedded in a high resistivity Si wafer, as obtained from the optimized simulation settings determined from simulations of the micro-coil with 3.5 turns

4.9 Conclusion

Here in this Chapter, the P factor design/analysis approach introduced in Chapter 3 was used to determine the best micro-probe design, which includes the optimum micro-coil structure as well as the sample holder design. Initially we proposed two types of sample holder designs viz.

- A generic sample holder occupying the entire surface on top of the micro-coil, and
- A mimicking sample holder, which follows exactly the shape of the micro-coil's conductor and sits on the top of it.

However, from the analysis it soon became clear that the generic sample holder performs much better. Next, we determined the trace width of the conductive

structures which, besides the spiral micro-coil, also included other types of micro-coils (meanders as well as semi-circular), all with generic sample holders. Once it was determined that the planar spiral micro-coils perform better compared to the other designs in terms of NMR performance, an optimal number of 5.5 turns was determined to provide the best performance. After the number of turns and the trace width were optimized, we imposed another condition for determining the optimal sample volume based on the homogeneity of B_z . Once the sample volume was determined, the aspect ratio of the micro-coils conductor was varied by changing their height inside the silicon trenches, and their P factor values were calculated. The resulting values were then compared to determine the best micro-probe design, which was found to be the micro-coil with 5.5 turns, a 1 : 1 conductor aspect ratio, and having a generic sample holder with the lowest common volume. Thus, the usage of the P factor enabled us to directly compare different designs and to ultimately find the best micro-probe, and its optimal dimensional parameters.

Next, in order to determine the resistivity of the Si substrate to be chosen in the fabrication of the micro-coils, the frequency responses of its S parameters were studied up to 1 GHz in CST models while variation of Q-factor values, inductance and resistance of the micro-coils with 3.5 and 5.5 turns were simulated up to 100MHz which well includes our frequency of interest, 42.58MHz . The resistivity of the Si substrate was also varied in these simulation models. The simulation settings were determined by simulating first the 3.5 turns micro-coil. Both discrete and waveguide port models were used to determine the best simulation performance. It was finally found that the high resistivity Si substrate performed better for both the 5.5 and 3.5 turns micro-coils at frequencies below 100 MHz, which is our frequency range of interest, since the Larmor frequency of the hydrogen atom for $B_0 = 1T$ is around 42.58 MHz. Hence, a Si substrate with conductivity of 0.1 S/m was selected for the fabrication of the micro-coils.

Highlights of Chapter 4^a

- Several micro-probe designs, which included planar, circular and spiral micro-coils in a Si substrate with sample holder sitting on the top of the micro-coils, have been developed and analyzed. However, ultimately only planar spiral micro-coils were considered since CST simulations revealed that they provided the best performance.
- Two sample holder shapes were considered. The first was a cylindrical holder which covered the entire surface of the micro-coil (generic sample holder), while the second holder had the same shape and size as the spiral micro-coil's conductor and followed it exactly (mimicking sample holders).
- Electromagnetic simulations showed that the generic sample holders exhibited superior magnetic performance compared to the mimicking sample holders.
- The optimum sample volume was determined based on the condition that the angle θ between B_z and B_y satisfied the condition $\theta \geq 75^\circ$
- Next, the P factor values were calculated for all the generic sample holder probe designs using the parameters extracted from the electromagnetic simulations for different trace widths and number of turns.
- Comparisons of the calculated P factor values highlighted the best micro-probe designs.
- Finally, RF simulations for low as well as high frequencies up to 1 GHz were run with the chosen probe designs and the necessary resistivity of the Si substrates were determined based on the S-parameters obtained around 42.5 MHz.

^a'Design of planar microcoil-based NMR probe ensuring high SNR', Zishan Ali, Daniel Poenar, and Sheel Aditya, AIP Advances, Volume 7, 095107 (2017)

Chapter 5

Fabrication of High Aspect Ratio (HAR) planar micro-coils embedded in silicon

5.1 Introduction

In a MR micro-probe, a pre-requisite condition for the micro-coil to efficiently act as the signal receiver is to have a resistance as low as possible in order to ensure low thermal noise during signal detection, and, hence, provide a high SNR. Using a conductor whose cross-sectional shape has a High Aspect Ratio (HAR) i.e. high ratio of height (or depth) to width, will ensure that the micro-coil's resistance is low as well as provide much more effective miniaturization. However, such HAR micro-coils have not been often used until now, especially for NMR signal detection and the challenges met in their fabrication have not been discussed at all until now. Their study and usage for such applications are justified and highly relevant because an area where the current aggressive miniaturization trend has been less successful is the miniaturization of inductive components, i.e. spiral mini- and micro-coils. The key reason for this is that the size of a planar mini- or micro-coil is typically dictated by the desired inductance, which in turn determines the outer diameter and number of turns.

However, fabricating micro-coils with such HAR conductors that are vertically

oriented and buried in the substrate is not without problems, mainly because void-free filling of HAR trenches by copper electroplating is challenging. Section 2.2 has indicated the various characteristics, problems and solutions for these problems, for Cu-filling using electroplating. However, as was also mentioned in that section, all these reports are associated with Through-Silicon Via (TSV) structures or typical vias and metal interconnects which are isolated cylindrical via holes that are filled only from bottom up. In stark contrast, our HAR micro-coils employ continuous long blind Si trenches in which Cu deposition takes place not only upwards from the bottom of the trench, but also laterally from the trench sidewalls. Hence, the challenges and solutions proposed in those reports may not necessarily extend to micro-coil trenches.

5.2 Outline of our contribution

This chapter will detail all the problems met along the fabrication steps of micro-coils with vertically oriented conductors realized in HAR trenches etched within a silicon substrate.

First, the photolithography step necessary to realize well defined trenches was optimized. This was followed by solving the crucial problem of the scalloping produced on the sidewalls of trenches etched in Si using DRIE which hindered continuous deposition of seed layer required for electrical connectivity during electroplating. The difficulties of the major fabrication step, the electrochemical deposition (ECD) of copper in long continuous spiral-shaped HAR blind trenches in silicon are next presented. Such challenges include optimization of the copper electroplating parameters (electroplating time and current density, effect of seed layer thickness) using an orthogonal Design of Experiments (DoE) to eliminate voids and achieve proper filling of the silicon trenches with copper. Unlike the Cu ECD optimization procedures reported in literature [146–148] in TSVs that modified the additive contents of the electrolyte, we have used only standard off-shelf pre-mixed electrolytic solution without any variation or modification of additive contents. The recipe that gave us best filling was obtained by modifying only the external non-chemical parameters determined by orthogonal DoEs and the Taguchi analysis method. Hence, our method is more straightforward, without

the need to change the composition of the electrolyte and/or its additives, or to perform frequent chemical analysis of the electroplating solution. To the best of our knowledge, as was also shown by the thorough literature survey as presented in Chapter 2, this is the first time when the challenges of filling up long continuous blind HAR trenches with a large volume of copper by electroplating are discussed in detail and solved.

After the trenches were filled with Cu, an entirely novel and original contribution is using wet etching with a sodium persulphate solution instead of conventional CMP to remove the post-electroplated copper overburden. This wet etching procedure has been compared with other existing wet etching processes of Cu and its advantages are highlighted. The process has also been optimized using an orthogonal DoE. Finally, once the micro-coils were realized, they were annealed in a hydrogen-rich ambient in order to enhance their conductors' conductivity. The final resistance values of the annealed devices were then compared with those reported in other works. Very few results can be found in literature, and those micro-coils have not been realized with HAR conductors and/or in trenches in Si. Consequently, as previously pointed out, they would have none of the advantages of our HAR micro-coils in Si related to miniaturization, surface planarization, heat dissipation and CMOS process compatibility, as elaborated by the previous comprehensive literature review detailed in Chapter 2.

5.3 Process flow and design

The micro-coils used in our first tests had an internal radius of $25\text{ }\mu\text{m}$, trace width of $7\text{ }\mu\text{m}$, height (i.e. trench depth) of $20\text{ }\mu\text{m}$ and inter-turn spacing of $3\text{ }\mu\text{m}$. Three micro-coils variants were realized, with 3.5, 15.5 and 40.5 turns, respectively. In the first step, the spiral shape of the micro-coils was patterned using photolithography and DRIE to define the HAR micro-coils trenches which are subsequently filled up with copper using ECD. Finally, the excess copper was removed to reveal the embedded micro-coils inside the silicon trenches. This fabrication process flow is shown in Fig 5.1. Since the process flow consists of multiple layers of oxide and metal, initial experiments of depositing multiple oxide and electroplated Cu layers were carried out prior the actual process in order to understand the stress behavior

Figure 5.1: Process flow steps for realizing the Si-entrenched HAR micro-coilss

of multiple films depositions on Si and find out the thickness of the layers to be used in the final fabrication process. The details and results of these preliminary tests are given in Appendix D.

5.4 Photolithography optimization

S1813 was the photoresist used to pattern our micro-coilss. A resist thickness of $1.8 \mu\text{m}$ provided good resistance to DRIE and produced well defined patterns for an exposure time of 9 sec. An exposure time longer than 9 seconds resulted in electrical shorts between adjacent turns. Fig. 5.2 summarizes the defects in the patterns that resulted from different over- and under-exposure situations. Fig. 5.3 shows the cross-sectional image of the trenches of a micro-coils with 15.5 turns, as it was obtained immediately after the optimized photolithography patterning and DRIE.

Figure 5.2: Examples of photolithography defects caused by: **a)** Under-exposure; **b)** Over-exposure; **c)** A too thin ($1.2\mu\text{m}$) photoresist; **d)** Striations due to improper PR disposal from the nozzle; and **e)** and **f)** Optimized photolithography resulting in successfully patterned trenches for the micro-coils with 3.5 and 15.5 turns, respectively.

5.5 DRIE and smoothening of scalloped DRIE-ed trench walls

Deep reactive ion etching (DRIE) is the most popular dry etching technique used to produce nearly vertical trenches in Si. This popularity is due to DRIE's intrinsic capabilities of etching at large depths and/or high aspect ratios, compatibility with using simple photoresist (PR) masks and of producing vertical sidewalls on silicon substrates of any crystalline orientation. One of the typical DRIE process is the so-called Bosch process, which consists of alternate polymer deposition-dry

etching steps [58,59]. However, scalloping is a well-known phenomenon that arises from DRIE of silicon substrates using the Bosch process [60] and is undesirable in many cases due to the negative influence it may have on subsequent process steps, e.g. filling up these trenches with metal by electroplating which in our case is relevant as we intend to fill up the DRIE-ed coil trenches with copper through ECD. Two basic approaches can be used to control, or at least to minimize, this undesired scalloping: modifying the DRIE etch process parameters, or carrying out additional post-etching processing of the etched trenches/features. A detailed literature survey on the techniques of reducing scalloping has been given in Chapter 2 earlier.

Here we describe an effective and CMOS-compatible post-DRIE roughness reduction method based on alternate oxidation and oxide removal cycles. By CMOS compatibility, we first and foremost mean that our smoothening process (consisting of identical oxidation+oxide removal cycles which can be repeated as desired) could be easily adopted in any CMOS cleanroom as it requires only CMOS-compatible fabrication tools.

Figure 5.3: Cross-section of DRIE trenches successfully etched into the Si substrate before filling up with Cu

Prior to experimentation, simulations were performed in Taurus TSUPREM-4 [149] to understand what effects can be expected from such multiple alternate oxidation and oxide removal cycles. These simulation results are reported in Appendix B.

5.5.1 Experimental setup: materials and methods

Standard CMOS silicon wafers of $\langle 100 \rangle$ orientation, 6 inch in diameter and of p -type doping with a resistivity of $0.001 - 0.009$ ohm-cm, have been thermally oxidized to grow an oxide layer of about $1.3 \mu m$ thick that would act as a hard-mask in the subsequent DRIE steps (to produce the desired trenches) together with the overlying layer of S1813 photoresist about $1.5 \mu m$ thick which was used to pattern this thick oxide layer. The mask which was used to dry etch the pattern on the silicon oxide consisted of a checker-board pattern made of alternate succession of 2 types of arrays: an array of 9×9 large squares (each square with a size of $100 \mu m \times 100 \mu m$) with a gap of about $100 \mu m$ between each square, alternated with an array of 85×85 small squares ($10 \mu m \times 10 \mu m$) with a $10 \mu m$ gap in-between each square. For the scalloping parameter measurements, only the small trenches were analyzed.

After the oxide patterning, the PR was not removed and the wafers underwent DRIE etching using a Bosch etching process in an STS machine. The etch parameters of the DRIE recipe used to etch the trenches are shown in Table 5.1. The

Figure 5.4: Scallop depth and pitch in a DRIE trench

depth of the trenches were $10\text{ }\mu\text{m}$, which results in an aspect ratio (A.R) value of 1:1. One wafer was removed from the entire batch at the end of the DRIE process for the characterization of the ‘as is’ etched trench, while the remaining wafers have been subjected to two subsequent cycles of alternative thermal oxidation growth and oxide removal using a wet etchant. Each oxidation was targeted to grow about 350 nm of thermal oxide by wet oxidation at 950°C for 120 min. In our recipe of thermal oxide growth firstly dry oxidation in oxygen was carried out for 5 minutes at 950°C . This was followed by a longer (120 min.) wet oxidation process at the same temperature obtained by combining hydrogen and oxygen flows that formed a pyrogenic steam ambient resulting in a more rapid thermal oxide growth. The process steps are detailed in Table 5.2.

After each oxidation, a sample wafer was removed from each lot at the end of each process step for inspection by SEM. More specifically, the selected wafer was sliced in halves: one half was left ‘as is’ while the other was etched in HF to strip all the grown SiO_2 , together with the rest of the wafers which continued their processing, with more iterations of oxidation-stripping sequences. The oxide wet etching was carried out using BOE with a 7 : 1 NH_4F (40%) : HF (49%) ratio. The SiO_2 vertical etch rate was found to be around 100 nm/min at room temperature (300K) with no significant agitation. Both halves of each extracted wafer were then examined under SEM to study the effects of the sequential oxidation and SiO_2 removal on the scalloping, namely to determine the values of the depth and pitch of the scallops (as illustrated in Fig.5.4) for the trench lateral walls.

Our key concern was to reduce the thermal budget as much as possible in order to maximize its attractiveness and compatibility/adoption, even when the described trench etching & filling is desired to be carried out as post-processing. However, a compromise must be reached between the thermal budget minimization requirement on one hand, and the process duration and oxide quality on the other hand. A temperature of 950°C was considered to provide this desired compromise: it is much lower than many other oxidation recipes, but choosing a lower temperature would significantly increase the oxidation time and at the same time reduce the quality of the grown oxide.

Table 5.1: DRIE etch parameters

Etch Parameters	Details
Etch:Passivation time (s)	11 : 8
$SF_6 + O_2$ flow rate (sccm)	130 + 13
$C_4F_8 + O_2$ flow rate (sccm)	85 + 0
Platten power (W)	20
Coil power (W)	600
Pressure ($\frac{etch}{pass}$)(mTorr)	$\frac{20}{11}$
Automatic pressure control (APC) angle (%)	75
Etch:Passivation ratio	1.375
$SF_6 : C_4F_8$ flow ratio	1.53

Table 5.2: Thermal oxidation recipe used in our scallop reduction process

Step Name	Oxygen flow rate (SLM)	Hydrogen,flow rate (SLM)	Nitrogen,flow rate (SLM)	Temperature ($^{\circ}C$)	Time (min.)
Dry Oxidation	6.8	No flow	No flow	950 $^{\circ}C$	5
Wet Oxidation (Pyrogenic steam)	5.0	8.5	No flow	950 $^{\circ}C$	120
Dry Oxidation	6.8	No flow	No flow	950 $^{\circ}C$	5
Anneal	No flow	No flow	8.0	950 $^{\circ}C$	5

5.5.2 Results and discussion

The values of the scallop parameters obtained from SEM photos of the etched trenches in 2 locations on the wafer were used to provide an average value of each

Figure 5.5: 10 μm deep silicon DRIE 'as-is' trench showing prominent scalloping. The numbers along the length of trench show the 14 points where we took the measurements (Wafer surface is at top in the figure)

characteristic scalloping feature defined in Fig.5.4. We measure the scallop depth and pitch at 14 different locations along the height of the trench with the point 1 being near to the bottom while point 14 is near the top. The following sub-sections describe the results obtained after each oxidation-oxide strip iteration, but first let's examine the features of the 'as is' trench etched using the BOSCH DRIE process.

The 'as is' etched trench

As can be seen in Fig.5.5, there is clear scalloping of the sidewalls even in this shallow (more accurately said, a non-etched-through-wafer) trench. The number of lateral etch depressions is equal to the number of etch cycles used to achieve the target etch depth. It can also be seen that, at the end of the DRIE process, the bottom horizontal profile is slightly narrower than the opening at the surface of the wafer. The average value for the scallop depth is $0.41\ \mu\text{m}$ with a standard deviation of $0.12\ \mu\text{m}$. As it will be seen in the subsequent sub-sections, these values improve correspondingly after each oxidation and SiO_2 removal step.

Figure 5.6: SEM photos of a $10\ \mu\text{m}$ deep 'as is' DRIE etched trench before (top) and after (bottom) the 1st oxide stripping in HF, still showing prominent scalloping.

Figure 5.7: Values of scallop depth measured at 2 locations on the wafer before (top) and after (bottom) 1st oxide strip

Figure 5.8: Values of scallop depth measured at 2 locations on the wafer before (top) and after (bottom) 2nd oxide strip

Figure 5.9: SEM images of scallops with each oxidation showing smoothening after each step

Figure 5.10: Final average values of scallop depth of the as-is trench ('No oxidation') and after each oxidation

After the 1st oxidation and SiO_2 stripping cycle

Next, after etching the trench, a first sequence of oxidation and SiO_2 stripping in HF was carried out, and another test wafer was removed from the wafer lot

and underwent the same examination and analysis procedure mentioned earlier. Figure 5.6 shows SEM photos of an etched trench before and after the removal of the grown silicon dioxide film. The data obtained from SEM photos show that the average depth of the lateral walls' scallops before and after the growth of the 1st oxide were of about $0.41\ \mu m$ and $0.38\ \mu m$, respectively. As expected, no substantial change in pitch occurred and the measured pitch maintained its average value at around $0.64\ \mu m$, with a standard deviation of $0.05\ \mu m$. This is shown in Fig. 5.7.

After the oxide had been stripped, the average scallop depth was found to be $0.22\ \mu m$ with a standard deviation of $0.04\ \mu m$. This is a clear improvement over the initial wafer as the vertical sidewalls are now smoother (the average scallop depth has been almost halved in comparison with the value for the 'as-is' etched trench).

After the 2nd oxidation and SiO_2 stripping cycle

The plots shown in Fig 5.8 present the results before and after the 2nd oxide has been stripped away. The measured average depth of the lateral trench walls' scalloping after the 2nd oxidation (but before the 2nd oxide strip), and after the 2nd oxide strip were $0.16\ \mu m$ and $0.08\ \mu m$, respectively.

Conclusions of DRIE trench tests

The as-is trench showed prominent scalloping that is unfavorable for subsequent filling of the etched trenches with electroplated Cu which in our case would form the turns of a micro-coil. It was, therefore, necessary to perform this sequence of oxidation-oxide etching to test how this significant lateral wall roughness can be diminished, in order to allow proper subsequent electroplating with Cu (i.e. full filling of the trenches with Cu without voids) as well as to avoid an increase in the resistance of the coil's turns (due to an increase in roughness of the trench which can become relevant for the metal's resistance at high frequency due to the skin effect, which is manifested at the surface of the metal). For such applications, the paper of Filipovic *et al.* [61] already has detailed how such trench wall roughness reduction helps in reducing capacitance, resistance and EM-induced stress after the trenches have been filled by copper through electroplating, hence we shall not

Table 5.3: Summary of the scallop parameters before and after each oxidation and SiO_2 removal cycle

Process Cycle	When measurement was performed	Scallop depth	
		Average Values (μm)	Standard Deviation (μm)
As-is DRIE Trench	Before Oxidation	0.41	0.12
Cycle #1	Before SiO_2 strip	0.38	0.09
	After SiO_2 strip	0.22	0.04
Cycle #2	Before SiO_2 strip	0.16	0.04
	After SiO_2 strip	0.08	0.04

repeat this information.

All the results obtained from these experiments are summarized in Table 5.3. They clearly show that our sequential oxidation and oxide strip cycles are able to diminish the magnitude of scalloping by reducing by $\sim 80\%$ the depth of the scallops, from $0.41 \mu m$ to $0.08 \mu m$ on average. Fig.5.9 shows clearly this scallop reduction with each oxidation step. The plots in Figure 5.10 compare the scallop depth values for the non-oxidized DRIE trenches with those obtained after consecutive oxidation and oxide strip steps. These results show that the undercut ratio, defined as

$$Undercut\ ratio = \frac{Average\ scallop\ depth}{Average\ scallop\ pitch} \quad (5.1)$$

has also been reduced by 80% from 0.65 to 0.13. The parameters ‘scallop depth’ & ‘scallop pitch’ are as defined in Fig. 5.4, measured according to Fig. 5.4 and their average values used in equation 5.1 are those indicated in Table 5.3.

Figure 5.11: Average values of the DRIE etched trench's lateral wall scalloping undercut ratio

This is clearly shown in Figure 5.11, which illustrates that each oxidation and oxide strip cycle has improved significantly the undercut ratio of the sidewalls, and thus their roughness. This improvement is due to the reduction of depth of the scallops (the oxidation and oxide stripping cycles have limited or no effect on their pitch), since the oxidation occurs faster, and, therefore, the rate of consumption of the silicon is faster, at the peaks of the scallops, thus reducing significantly their magnitude. Finally, the silicon dioxide is stripped away, resulting in a new, flatter lateral trench wall surface.

Comparison with similar reported works

As discussed in Section 5.5, the proposed sidewall roughness reduction using alternate oxidation and oxide removal cycles belongs to the 2nd category. Compared to all the other reviewed works, our process is definitely repeatable, suitable for mass production, robust and CMOS-compatible. If the same structure is adopted by other users (i.e. based on Cu-filled trenches *a priori* etched into the substrate) to realize their devices, then the entire smoothening process can be carried out

Table 5.4: Comparison of our work with similar reported works (N.R: Not reported)

Report	Peak-to-valley roughness		RMS roughness		Roughness reduction	Remarks
	<i>Before</i>	<i>After</i>	<i>Before</i>	<i>After</i>		
Juan <i>et al.</i> 1996 [75]	N.R.	N.R.	29.95 nm	5.93 nm	80.2%	Did NOT use DRIE to etch initial trenches and for smoothening used only one cycle of oxidation at 1100°C for 135 min and oxide etch
Seng <i>et al.</i> 2003 [76]	60 nm	30 nm	N.R.	N.R.	50%	Experimented on SOI wafer with only one cycle and no detailed analysis given
Le <i>et al.</i> 2009 [77]	320 nm (at top) 280 nm (middle) 240 nm (at bottom)	160 nm (at top) 150 nm (middle) 110 nm (at bottom)	N.R.	N.R.	50% 46.42% 54%	The values given are at different positions along the height of the trench. Initial roughness was reduced by optimizing DRIE process followed by 3 different cycles of oxidation at 1000°C and oxide etch
Our work	410 nm	80 nm	-	-	80.5%	No optimization of DRIE was carried out. Only 2 cycles of post-DRIE oxidation (950°C, 120 min.) and oxide removal were used

BEFORE any CMOS process, hence its thermal budget would have zero impact on subsequent devices. The trenches can be easily filled initially with another material (e.g. polysilicon or oxide), planarized (if CMP is undesired even a simple blanket back-etch of the trench filling material can be performed since now it is a non-critical step), and after that the wafer can undergo any desired CMOS processing, so that the trenches filling with copper and its CMP planarization can take place only after the CMOS process is finished. Indeed, this is one of the key reasons why the trench-based process was selected for our micro-coils: since it is buried in the substrate it provides excellent planarity, thus enabling easy subsequent processing of other devices in the wafer (even on top of it after the Cu filling) and excellent thermal dissipation thus allowing the injection of large currents to generate stronger magnetic fields [20, 21].

Even when compared with reports that used the same procedure of alternate oxidation and oxide etch cycles [75–77], our work not only provides a detailed analysis of the process steps but also shows better performance. A full comparison of our work with these previous reports is presented in Table 5.4. The work which used for the very first time the alternate oxidation and oxide etch procedure employed non-DRIE etched trenches seemingly devoid of scallops and whose initial sidewall roughness was much smaller [75]. The second work which used the same method also started from a much smaller initial roughness, did not describe in detail the smoothening process and performed just a single cycle [76]. Lastly, Le *et al.* have used a 3-fold approach to minimize the sidewall roughness, which included modification/optimization of the DRIE etching process already giving

them a reduced initial peak-to-valley sidewall roughness below 300 nm at the bottom of the trench. This resulted in barely any scalloping at the top and middle portion of the trenches. For the lower portion of the trench Le *et al.* did a ‘post-DRIE’ alternate oxidation and oxide etching cycles [77] to reduce the scalloping. In contrast, we did not modify any DRIE parameters and relied exclusively on the oxidation+oxide removal cycles to achieve a superior roughness reduction of 80%, compared to maximum 54% obtained by Le *et al.* [77] only in the best case. It can also be noted from Table 5.4 that their initial peak-to-valley roughness was smaller than that in our work: max. 320 nm vs. 410 nm in our case. Even for the smallest initial roughness of 240 nm (much smaller than our initial 410 nm) their final result (due to their significantly smaller percentage roughness reduction) is 110 nm, larger than our final value of 80 nm [77].

In contrast to all these previous reports, we did not optimize the DRIE trench etching process, started with the largest initial sidewall peak-to-valley roughness, relied exclusively on oxidation and oxide etch cycles for roughness smoothening and obtained the best roughness reduction efficiency after using only 2 cycles at a peak to valley value of only 80 nm compared to an average value of 150 nm as obtained by Le *et al.* [77]. This significant roughness reduction with 80% using post-DRIE alternative oxidation and oxide etching cycles with such a rigorous analysis is reported here for the first time. Furthermore, our oxidations are carried out at a lower temperature of 950°C.

Our approach is much more flexible as it allows multiple degrees of freedom for the user to be adapted as necessary. For instance, if a trench wall roughness reduction greater than 80% is desired, then one can easily modify the temperature and/or duration of oxidation and/or increase the number of oxidation + oxide removal cycles as desired until the targeted sidewall planarity is achieved. Moreover, in another possible version, our process may also be used before the actual CMOS process, hence having no thermal budget impact upon the devices fabricated subsequently. This was also the case for our specific process, in which no initial devices were present in the wafer and it continued being processed after the realization of the micro-coils. Nevertheless, even if our process were to be used after the fabrication of CMOS devices, its thermal budget would still be better, namely with $\sim 20\%$ smaller than that of the method used by Le *et al.* Finally,

our structures are not similar with those used in the work of Le *et al.* who used through-wafer etching to produce vias much deeper than our trenches (hence much more difficult to be filled with electroplated copper if they were to be used in a similar application as ours), but with a much smaller initial roughness, as was highlighted above.

5.6 Electrochemical deposition of copper

The very first initial electroplating tests were carried out in a simple DIY type of setup which is discussed in Appendix C. These first tests were used to optimize the initial Cu depositions on flat wafers and enable us to begin to gain knowledge about the electroplating process. Subsequently, all the other experiments described below were carried out in a standard electroplating bath.

Copper sulphate was used in our ECD work, as it is the most common commercially available electrolyte used in copper electroplating and it is also cheap, non-toxic and has a high throwing power. The solution used for copper ECD typically consists of copper sulphate pentahydrate, sulfuric acid, hydrochloric acid and organic additives. Copper sulphate provides the copper ions, the sulphuric acid enhances the conductivity of the solution, and the hydrochloric acid provides chlorine ions which help in the uniform dissolution of the copper anode. The additives generally consist of organic compounds that are denominated by the industry as levelers and brighteners. The levelers are needed for electroplating in trenches as they reduce the probability of void formation, while the brighteners are used to increase plating uniformity.

The experiments and the final electroplating in our case were done using 6 inch silicon wafers and the electrolyte used was the commercially available PC 81 solution from Slotocoup. PC 81 comes with a pre-mixed concentration of additives and its composition is given in Table 5.5.

Table 5.5: Composition of the commercially available PC 81 electrolyte

Constituents of PC 81 electrolyte	Concentration
Copper sulphate	75 gm/L
Sulphuric acid	180 gm/L
Chlorine ions (from HCl)	60 mg/L
Additives	2 ppm
Total plating bath volume	8 L

Table 5.6: Different levels of the selected process variables; experiments with shorter time (above), experiments with longer time (below)

Exp #	Current (A)	Time (min)	Temp °C	Agitation (rpm)
1	0.01	30	25	0
2	0.01	45	40	100
3	0.01	60	65	300
4	0.1	30	40	300
5	0.1	45	65	0
6	0.1	60	25	100
7	0.05	30	65	100
8	0.05	45	25	300
9	0.05	60	40	0

Exp #	Current (A)	Time (min)	Temp °C	Agitation (rpm)
1	0.01	60	25	0
2	0.01	90	40	100
3	0.01	120	65	300
4	0.1	60	40	300
5	0.1	90	65	0
6	0.1	120	25	100
7	0.05	60	65	100
8	0.05	90	25	300
9	0.05	120	40	0

(a) Shorter time

(b) Extended time

Figure 5.12: The variation of mean SNR values with to each control parameter for the 2 categories of the performed experiments

5.6.1 Orthogonal DOE of ECD - analysis using Taguchi method

The orthogonal design of experiments (DoE) followed by statistical analysis through Taguchi method have been introduced and used previously to optimize complex multi-dimensional processes, e.g. to determine the optimal recipe for dry etching parameters. Similarly, we used an orthogonal DoE followed by Taguchi analysis to optimize the electroplating process parameters [150]. An orthogonal array L_3^4 for 4 control parameters with 3 levels each was used for our experiments. The four main control parameters considered for the DOE were current density, temperature, agitation of the solution in the bath and plating time. However, two sets of experiments were planned using DOE; one with plating time of up to 60 min. and the other up to 120 min. The different levels for all these parameters are detailed in Table 5.6 for both sets of experiments. All these experiments were carried out using the Slotocoup PC 81 electrolyte, on 6 inch silicon wafers with a copper seed layer of 100 nm on 20 nm of Ti acting as an adhesive layer. For each combination of control parameters represented in the rows of Table 5.6 we carried out three experiments and measured the average thickness of deposited copper, hence calculating the deposition rate. From these values, a mean value of so-called Signal-to-Noise Ratio (SNR) of the i^{th} experiment was calculated using the equation,

$$SNR_i = -10 \log \left[\frac{1}{N_i} \cdot \sum_{u=1}^{N_i} \frac{1}{y_u^2} \right] \quad (5.2)$$

where y is the performance characteristic of the experiment, which in our case is the plating rate. N_i is the number of trials for the i^{th} experiment as indicated in the 1st column of Table 5.12 and u is the trial number. For our case, for each experiment (i) we have 3 trials, hence $N_i = 3$ and $u = 1, 2$ and 3.

The results with the calculated SNR values for the measured variation of each control parameters are shown in Fig 5.12. Next, for each of these parameters the difference between the maximum and minimum values of SNR is plotted in Fig. 5.13. The largest values Δ in SNR for a certain parameter indicate that it is the most influential control parameter in controlling the electro-deposition

Figure 5.13: Difference in mean SNR values for each parameter in the copper electro-deposition experiment with orthogonal design and analyzed using Taguchi method

rate. As expected, current (or current density) has the highest influence on the electro-deposition rate followed by the plating time. However, Fig 5.13 shows that the deposition rate's dependence on the plating current is smaller for the longer plating time, indicating a slight saturation effect. Both agitation and temperature are the least important parameters and, therefore, may have a significant effect only if the experiment runs for a longer time, otherwise their effect is negligible for a short plating time.

5.6.2 ECD of Cu into trenches

For filling up the trenches of actual micro-coils, we started with the highest current of 100 mA selected from the control parameter values introduced in Table 5.6 in order to promote faster plating. No increased temperature and agitation were used since they had little influence over the deposition rate. Initially a seed layer of 20 nm Ti (acting as an adhesive layer) and a 100 nm Cu layer were deposited

Figure 5.14: Deposition of copper only at the top of the trenches indicating lack of Cu seed layer inside the trenches

through e-beam evaporation before performing the ECD of Cu into the trenches. The resulting deposition is shown in Fig. 5.14. The copper has grown only at the top of trenches with no deposition at the bottom or from the trench side walls. Subsequent investigations showed that this was due to poor seed layer coverage throughout the trenches, since unlike TSVs, in our case the trench is a blind via in which the electrical connection is ensured by good coverage of the seed layers over both the trench walls and the bottom of the trench. This led to the deposition of copper on the top of the trench walls with almost no deposition inside the trenches where the seed layer was almost absent, resulting in the mushroom-like formations at the top of trenches. Additionally, because there was very little bottom-up growth, it was suspected that the electrolyte was having difficulty in accessing these HAR trenches since no agitation was provided.

For the second iteration, a thicker Cu seed layer of 300 nm was used, together with agitation at 100 rpm during electroplating using a magnetic stirrer. This solved the problem of the trenches being unfilled; however, voids still appeared, as shown in Fig. 5.15. These voids are due to unequal potential distribution caused by varying seed layer thickness along the trench length. The Cu deposition

Figure 5.15: Filled trenches after using a thicker seed layer with agitation during ECD, but voids were still present inside the filled trenches

rates are higher at the places with a larger potential drop, such as at the edges and the corners at the top of the trench, where the seed layer thickness is thinner than at the trench sidewalls. The lateral growth at the mouth of the trenches is thus faster resulting in sidewall growth at the mouth of the trench that pinches off the trench and finally causes the void at the center. To solve the problem of poor coverage resulting in varying resistance, the seed layer deposition was done using sputtering instead of e-beam evaporation. Additionally, the thickness of the seed layer was also increased to 500 nm to ensure a more conformal deposition with better step coverage. Properly filled trenches were finally obtained, as shown in Fig. 5.16. This recipe guaranteed balanced lateral and bottom growth causing proper filling up of the trench walls.

In order to further accelerate the deposition rate it was decided to increase the current to 500 mA, but this again caused internal voids, as shown in Fig. 5.17. This can be again attributed to higher deposition rates at the top opening of the trenches which have increased now due to the higher current (which translates in a higher current density). However, it can be noticed in Fig. 5.17 that the voids are now near the top of the trenches. This indicates that, although initially the bottom and lateral growth was quite balanced for most of the trench depth, near the top the lateral growth was higher due to higher current (density) thus resulting in the observed voids.

5.6.3 Wet etching to remove the Cu overburden

The removal of excess of Cu resulting after electroplating is generally done through Chemical Mechanical Polishing (CMP) with a Cu removal rate of around 10

Figure 5.16: Properly filled trenches after increasing the Cu seed layer thickness to 500 nm

Figure 5.17: Voids re-appear once the current value is increased to 500 mA

Table 5.7: Different levels of the selected process variables and their combination used in orthogonal DoE employed to determine the wet etching rate of copper using sodium persulphate

Exp #	Persulphate Concentration (gm/L)	Temperature (°C)	Agitation	Volume of HCl (ml)
1	10	<i>RT</i>	0	0
2	10	50	<i>M</i>	5
3	10	80	<i>H</i>	10
4	20	<i>RT</i>	<i>M</i>	10
5	20	50	<i>H</i>	0
6	20	80	0	5
7	30	<i>RT</i>	<i>H</i>	5
8	30	50	0	10
9	30	80	<i>M</i>	0

nm/min [104]. However this process requires complex optimization of many parameters, is time consuming and cannot be used by those who do not have a CMP setup at their disposal. Here we present a novel procedure of Cu overburden removal using industry grade sodium persulphate, with an etching rate as high as 3 to 8 nm/sec, depending on the specific process parameters, as will be seen later. The reaction involved in the etch process is given by

However, due to lack of literature in wet etching of copper using sodium persulphate, first the optimum recipe to etch Cu in this solution was determined using orthogonal DoE. The DoE was carried out by considering 4 input parameters, as seen in Table 5.7, and the etching rate was determined by noting the time of etching for a Cu layer 2 μ m thick. For the agitation 3 levels were set, viz. no agitation (0), medium agitation (*M*) and high agitation (*H*). The value of *M* is half of the maximum rotational speed of the magnetic stirrer that was possible and *H* is the highest speed. The results obtained from this orthogonal DoE using Taguchi method is given in Fig. 5.19. It shows the difference between the SNR of etching rate resulted for the different values considered for the control parameters used in the DoE. As seen from Fig. 5.19, agitation has the least effect on the etching rate,

Figure 5.18: Mean SNR value corresponding to each control parameter

while the addition of HCl and temperature have the second and third strongest effects. The persulphate concentration (gm/L) has the highest effect, as expected.

Unfortunately, any microvoids present in the Cu filling of the trenches allowed seeping in of the etchant causing enlargements of the voids and dissolving the Cu traces. This was due to the fact that the highest level of persulphate concentration was chosen along with the highest concentration of HCl from Table 5.7 and the solution was heated at $80^{\circ}C$. This aggressive etching, although fast, also removed the copper inside the trenches, as shown in Fig. 5.20. In order to eliminate this problem, the HCl addition was avoided, amount of persulphate was reduced to 10 gm/L (the lowest level as in Table 5.7), and the temperature was kept constant at $80^{\circ}C$. Still, due to the agitation and the high temperature, the persulphate solution seeped into any voids or cracks present in the copper filled trenches as shown in Fig. 5.21. Next, only room temperature was used, which yielded good results with controlled etching and well defined traces for the micro-coils with 3.5 and 15.5 turns, as shown in Fig. 5.22. Chapter 2 already reviewed the other Cu wet etching procedures that have been reported in literature. However, our Cu

Figure 5.19: Difference in SNR values for the parameters of the persulphate wet etching DoE results evaluated through the Taguchi method

Figure 5.20: Uncontrollable over etching by Sodium Persulphate inside coil trenches

Figure 5.21: Wet etch through existing holes or voids on the Cu trace

(a) 3.5 turn coil

(b) close up of 15.5 turn coil

Figure 5.22: micro-coils after successful wet etching removal of the copper overburden

wet etch procedure is the first one that reports Cu wet etching using sodium per-sulphate solution alone, avoiding the usage of any toxic or acidic agents. Choi *et al.* have reported controlled wet etching of copper overburden but their etching solution consisted of sulphuric acid and also required a special capsule chamber for the Cu etching process [102]. However, in our case we avoided the use of any acid and no special apparatus and/or equipment set up was required. Our process

involves simple immersion of the wafer in the etchant solution and taking out the wafer after a specific time, followed by thorough rinsing. Furthermore, the process described by Choi *et al.* [102] relies on the differential etch rate between the Cu protrusions from TSVs and the Cu overburden outside TSVs to achieve the desired selectivity. In our case the scenario is totally different: a blanket universal cover of Cu overburden is formed over the Cu micro-coil and this has been removed by sodium persulphate etching, the parameters of which have been determined precisely using the orthogonal DoE. The common Cu etchants such as $FeCl_3$ and $CuCl_2$ are heated at temperatures well above the room temperature [100], while in our case the etch process was successful and controlled at room temperature. Therefore, compared to the reported Cu wet etching processes, our procedure is extremely simple, controlled, non-toxic with formation of copper sulphate as the by-product, and successfully achieved at room temperature.

5.6.4 Comparison with ECD of copper inside through silicon trenches

Electro-deposition of copper inside blind and very long trenches like our micro-coil structure differs greatly from realizing spiral micro-coils through filling up of through silicon trenches [36, 37] or deep but small and isolated TSVs. To re-iterate, (as was also mentioned in Chapter 2), those micro-coils were obtained by strictly bottom-up Cu ECD that used an extra ‘contact’ wafer with seed layer pasted on the backside of the ‘device’ wafer in which the micro-coils were realized. This is an extension of the TSV filling technique reported earlier in literature [48, 56] where it is clearly shown that the deposition proceeding vertically, from the bottom up. This procedure makes TSV, or through silicon trench, filling less challenging since the bottom seed layer is more or less uniform resulting in uniform resistance and equipotential distribution and only one-directional bottom-up copper deposition. However, in our case, unless special measures are taken in ECD of Cu inside blind trenches (as described previously), the seed layer thickness may not necessarily be uniform at the trench bottom and/or along the trench walls. This varying thickness causes a varying potential drop throughout the trench and hence the lateral growth rate is different compared to the bottom-up growth rate,

resulting in void formation. Yung *et al.* also analyzed this difference [49]. However, this analysis was again performed for isolated vias, not long HAR trenches as those in our micro-coilss for which no experimental analysis has been reported previously. Other authors reported [146–148] modifying the additive contents to achieve modified ECD inside through-wafer trenches. In our case, we have used only pre-mixed electrolytic solution without any variation or modification of its additive contents. The recipe that gave us best filling was obtained by modifying only the external non-chemical parameters determined by orthogonal DoEs and the Taguchi analysis method.

5.7 Electrical characterization of HAR micro-coilss

I-V measurements were performed on micro-coils with both 3.5 and 15.5 turns. A first set of I-V measurements were done under SEM through nanoprobeing, as shown in Fig. 5.23. The measurements were carried out both before and after annealing at 400°C in presence of argon and hydrogen, which would chemically reduce any copper oxide present and also enlarge the grain size. Previous reports [151, 152] documented the formation of copper (II) and (I) oxides in deposited copper which significantly increase its sheet resistance to high values in range of $10^6 - 10^8$ ohm/square. Hence, hydrogen was selected to reduce the copper oxide present in the electroplated copper and at the same time anneal it at a higher temperature to enlarge its grain size [153].

However, it has also been reported that at higher temperatures the diffusivity of hydrogen inside Cu is very high, leading to hydrogen inclusion inside Cu voids [154–156]. Therefore, it was decided to use a lower temperature for our anneal treatment in a hydrogen-rich ambient. Thus, Konishi *et al.* suggests a temperature of 400°C and an argon environment in order to prevent hydrogen from forming excess voids through reaction with the trapped oxygen and formation of water which expands while vaporizing, after which it escapes from the copper [157]. Also, argon helps in keeping a passive environment in presence of flammable hydrogen in the chamber. Hence, in our annealing treatment, the hydrogen flow rate was kept low and linearly increased from 10 sccm to 50 sccm while the argon flow rate was kept constant at 100 sccm and the temperature was ramped up to 400°C for

90 min. The plot in Fig.5.24 shows the average resistance of each variant before and after annealing.

Figure 5.23: Nano probing of 15.5 turn micro-coil under SEM

From the available micro-coil dimensions reported previously [27, 30, 31, 39, 40] we have calculated the different values of conductor cross-sectional area and volume in each case. Next, the measured values of the reported coils as well as our coils were divided by the conductive cross sectional area and volume to normalize the resistance values with respect to these better parameters, and the obtained results are represented in Fig. 5.25. It can be seen that all the values reported in the literature are larger than those for our micro-coils except [40] and [39]. However, these coils had smaller aspect ratios of 1 : 5 and 3 : 10, respectively, as compared to our AR of 3 : 1, and also did not use a silicon substrate as in our case.

The measured results were then compared with the simulated and analytical values, as shown in Table 5.8. The simulated values were extracted from simulation. The discrepancy between the measured and the analytical values of the resistances may be contributed to the presence of voids inside the electroplated copper. Moreover, the resistivity of the copper used to calculate and simulate the

Figure 5.24: Resistance values of micro-coils with 3.5 and 15.5 turns before and after annealing at 400°C in Ar and H_2

Figure 5.25: Comparison of normalised resistances of our micro-coils with the values obtained for other planar coils reported in literature

Figure 5.26: Measured Q-factor values of 15.5 and 3.5 turn micro-coils

coil structure is the ideal bulk value while the resistivity of electroplated copper is different, as determined from the sheet resistance measurement. Additionally, we did also measure the values of Q of these coils at low frequencies up to 5 MHz, as shown in Fig. 5.26 for both the micro-coils with 3.5 & 15.5 turns.

Table 5.8: Measured resistances compared with the analytical values

Coil turns	Analytical Resistance Ω	Resistance extracted from CST model Ω	Measured Resistance Ω
3.5	0.108	0.126	0.43
15.5	1.18	1.25	3.52

5.8 Conclusion

This chapter discussed all the critical steps in the fabrication of our HAR micro-coils. Specifically, as mentioned in Section 5.5, this work focused on solving the

challenges faced in the following process steps:

- Scalped side walls after DRIE of trenches in the Si substrate
- Improper seed layer deposition
- Copper overburden
- High resistance due to voids and copper oxide within the Cu film deposited inside the HAR trenches

Each of these problems has been highlighted previously, followed by the solutions proposed and successfully applied practically. The scalloping of the trench sidewalls was minimized using an efficient iterative oxidation and oxide removal technique, the seed layer deposition was optimized, copper was electro-deposited inside HAR blind Si trenches using DC current, followed by developing a novel method of wet etching of copper which is faster compared to conventional CMP. Finally, an annealing treatment has been used to further reduce the resistance of the micro-coils through reduction of any non-conductive copper oxide present and increase of grain size. As a result of all these measures, HAR planar Cu micro-coils in silicon blind trenches have been realized. The target was to achieve low resistance in order to minimize the micro-coil's thermal noise and, thus maximize its SNR.

Highlights of Chapter 5^{a b}

- This chapter detailed both the challenges of the key fabrication steps of our HAR micro-coils, and the found solutions which ensured their realization with low resistance resulting in low thermal noise and, thus, high SNR.
- HAR micro-coils in the existing literature, are obtained through strict bottom up ECD of Cu which involves an extra complicated fabrication step of attaching and removing a seed layer wafer underneath the device wafer. Compared to these coils, our micro-coil is obtained by ECD of Cu inside long blind trenches in Si substrate by lesser and simpler steps through careful balance of bottom-up and lateral Cu deposition.
- The effect of the key external parameters on the Cu electroplating was first studied through an orthogonal DoE using Taguchi statistical analysis and the final recipe was used for Cu electroplating in DRIE trenches etched in Si.
- Scalping on DRIE-ed side trench walls of Si trenches caused discontinuous coverage of seed layer necessary for the subsequent Cu electroplating inside the trenches. This problem was solved using repetitive oxidation and oxide removal steps which resulted in smooth trench walls giving continuous seed layer coverage. When compared to literature our process is more effective and has a less thermal budget.
- A novel Cu wet etching procedure was developed using sodium persulphate and was then optimized using an orthogonal DoE. The merits of this simple etching procedure, which can replace CMP for small thicknesses of overgrown Cu, is compared to others that are reported in the literature.
- Our HAR micro-coils were annealed in a hydrogen environment which lowered the resistance by almost 3 time. This resistance has been compared with the existing micro-coils in the literature.

^a‘Smoothering of scalloped DRIE trench walls’, Zishan Ali Syed Mohammed, M.A.S Olimpo, D.P. Poenar & Sheel Aditya, Materials Science in Semiconductor Processing, Volume 63, 1 June 2017, Pages 83-89

^b‘Fabrication of Silicon Embedded Low Resistance High Aspect Ratio Planar Copper Microcoils’, Zishan Ali Syed Mohammed, Poenar Daniel Puiu, Sheel Aditya; Journal of Micro/Nanolithography, MEMS, and MOEMS (JM3), Volume 17(1), 014501, 9 January 2018

Chapter 6

Fabrication of micro-coils for magnetic field generation in NMR micro-probes

6.1 Introduction

This chapter details the fabrication process for the micro-coil designs finalized in Chapter 4. Although it was found that the micro-coil with 5.5 turns with aspect ratio of 1 : 1 was the best design, we also fabricated the micro-coil with 3.5 turns for comparison and investigation purposes. Moreover, we also fabricated wide meander structures for easier visual analysis of fabrication.

The fabrication process flow is shown in Fig. 6.1. Four inch silicon wafers of conductivity 0.1 S/m with crystallographic orientation of $\langle 100 \rangle$ were used as the starting substrates. First, photolithographic patterning defined the micro-coil structures according to the design dimensions decided in Chapter 4, using the same optimized recipe reported in Chapter 5. This was followed by DRIE to define the trenches of aspect ratio 1 : 1. Next, ECD of copper was used to fill up these trenches, then a combination of CMP & Cu wet etching removed the excess copper. Lastly, a 1 μm thick PECVD (TEOS) Si oxide was deposited and patterned to open the windows of the connecting vias, followed by sputtering of aluminum and its patterning using RIE in order to define the bonding pads.

Figure 6.1: Process flow of the NMR micro-coils to be fabricated

6.2 Outline of our contribution

The micro-coils fabricated now had an AR value of only 1 : 1, because the P-factor-based optimization described in Chapter 4 had shown that the 5.5 turns micro-coil with an AR of 1 : 1 would provide the best performance for a MR micro-probe. Because of the smaller AR, in order to provide a significantly lower resistance -and, hence a better SNR- the conductors of these micro-coils had a wider trench opening of $25\ \mu\text{m}$, which dictated a few significant changes in the fabrication process.

Firstly, the filling up of the long blind trenches could not be achieved using the conventional constant value DC electroplating which had been used previously. Instead, progressive Cu electroplating had to be used, in which the current density is increased at specific intervals of time to ensure that the Cu ECD process is uniform and void-free. However, just as in the previous case, usage and/or optimization of progressive ECD for blind long trenches, where lateral growth is significant and

unavoidable, has not been explored and is studied here at length for the first time. Another significant difference is that the final overgrowth of Cu obtained at the end of the ECD (which would need to be removed in the subsequent step) had a much increased thickness compared to the previous case (25 μm vs 40 μm).

Additionally, due to the same wider trench width used in this case, the possibility of copper wet etchant seeping inside the trenches is higher, compared to the HAR micro-coils reported in the previous chapter where the trench opening was only 7 μm wide. A combination of chemical mechanical polishing (CMP) and wet etching had to be employed to successfully remove the significantly thicker excess electroplated copper.

This chapter will detail the DoE optimization of the CMP recipe, the results of which showed that the chemical polishing part of CMP is the most crucial component in the efficient removal of Cu. Finally, the same anneal treatment in hydrogen environment (as described in the previous chapter) was applied to these low AR and wide micro-coils. This was followed by measurements of the micro-coils' resistances and of the magnetic field generated by them. The dependence of the generated MFS on magnetic field variation with the resistance of the micro-coils is also investigated at the end of this Chapter.

6.3 Electrodeposition of copper

Since the steps prior to ECD of Cu are the same with those used in the optimized process steps reported in the previous Chapter, this section will discuss about optimizing the ECD of Cu in the wider trenches of the micro-coils with a CAR of 1:1, followed by subsequent fabrication steps until the pads are realized. To optimize the Cu ECD recipe for these micro-coils with wider trenches, 2 variants of electroplating were studied:

- DC electroplating
- Variable time DC electroplating

The ECD has been done in an electroplating setup available in the school of Mechanical and Aerospace Engineering of NTU, using the procedure described and

Figure 6.2: Electroplating setup with 4 inch wafer holder as used by Dixit *et. al.* [48]

detailed by Dixit *et. al.* [48]. This setup is shown in Fig. 6.2. The image on the left side shows the wafer holder immersed inside the electrolyte which is constantly circulated, and underneath the wafer holder is the Cu anode. The wafer holder is capable of rotating, hence facilitating the access of electrolyte inside the trenches. The image on the right side of Fig. 6.2 shows a wafer with seed layer mounted inside the wafer holder just before putting it inside the electrolytic bath. Prior to electroplating, the wafer was momentarily immersed for 120s in a dilute sulphuric acid solution (10 : 1) to remove any copper oxide on the seed layer that had been produced due to atmospheric oxidation [158, 159]. The wafer rotation rate was kept constant at 100 rpm for all the experiments.

The content of the electrolytic bath was prepared as suggested by the supplier company, Atotech S.E.A Pte. Ltd. The plating solutions' components and their description are given in Table 6.1

However, the depletion rate of the different additives in the electroplating process of our wafers were different from the literature data, and they have been

Table 6.1: Initial electroplating bath constituents as suggested by Atotech

Component	Description	Recommended Concentration
Cuprabase 55	Acidic copper electrolyte	55g/L
Spherolyte Cu200 Brightener	Plating accelerators which promotes Cu deposition from bottom to top of the trench	12ml/L
Spherolyte Carrier 11	Primary plating inhibitors that inhibit lateral growth of Cu inside trenches	12ml/L
Spherolyte Leveller UF2 MOD	Secondary plating inhibitors that acts at macro-level to inhibit Cu deposition at the trench edges and corners and on wafer surface to reduce Cu overburden and prohibiting keyhole void formation	10ml/L

replenished periodically in order to keep constant the concentration of the additives in the solution, as suggested by Atotech in Table 6.1. The depletion rate (ml/Ah) for each additive is given in Table 6.2. As it will be seen later in this Chapter, its value will be estimated after each deposition session in order to calculate the total depletion of each additive in the electrolyte and, hence, to determine the replenishment amount for each component.

6.3.1 DC electroplating

Steady state DC was first studied and used to perform Cu electroplating for 1 : 1 aspect ratio micro-coils using the Cuprabase 55 electrolyte from Atotech. The composite seed layer consisted of a 20 nm Ti film and a 500 nm Cu film, both

Table 6.2: Additive depletion rate for each additive as suggested by Atotech

Additive	Depletion rate ml/Ah
Spherolyte Cu200 Brightener	1.5
Spherolyte Carrier 11	0.5
Spherolyte Leveller UF2 MOD	0.8

Figure 6.3: 1 : 1 wafer electroplated at 0.4 mA/dm^2 DC current density for 1hr

of which were deposited using magnetron sputtering. The thickness values and deposition technique used for the composite seed layer were chosen based on the previous electroplating results that were detailed in Chapter 5.

The standard Cu deposition rate stated by Atotech was approximately $0.22 \text{ } \mu\text{m/min}$ per unit current density. In order to study the effect of the current density on the ECD process, a first test was carried out at a value of 0.4 mA/dm^2 for around 1 hr. The top surface SEM results are shown in Fig. 6.3. As can be seen from Fig. 6.3, the Cu has been deposited only on the walls and there is no bottom to top growth. Also, the timing was assumed to be insufficient and the wafer was hence plated again for 2 more hours. These results are shown in Fig.6.4. As seen

Figure 6.4: The previous 1 : 1 wafer electroplated at 0.4 mA/dm^2 DC current density for further 2 more hours

Figure 6.5: Cross sectional view of the copper deposited at 0.4 mA/dm^2 DC current density for further 2 more hours.

the lateral deposition dominates and even after 3 hrs of plating the trenches were not filled. This wafer was diced in order to study the cross-section under SEM as shown in Fig. 6.5. Compared to the previous 3 : 1 micro-coil structure, this design has a lower aspect ratio of with wider trench opening and hence from Fig. 6.3 - 6.5 it was seen that it is difficult to fill the wider trenches using only DC electroplating. The primary reason behind this is that, since it is a wide blind via, deposition on lateral walls cannot be avoided and hence a balance between the bottom to top and lateral growth has to be achieved as it was done previously for the 3 : 1 AR micro-coils. However, in this case, because the blind trench is wider than that used in our previous HAR coils it is difficult to achieve a balanced growth both from bottom to top and from lateral walls. The wider trench means the lateral deposition needs to be as slow as possible compared to the bottom to top growth, in order to avoid void formation at the trench opening and this will greatly reduce the plating rate inside the trenches. In order to solve this problem it was necessary to optimize the plating recipe using progressive electroplating and changing the additive content, as detailed in the subsequent sections.

6.3.2 Variable time DC electroplating

The progressive DC electroplating tests using different recipes were performed on 5 Si wafers of 4 inch diameter, in which micro-coil trenches with aspect ratio 1 : 1

Figure 6.6: Cross sectional SEM showing the trenches are not filled with copper and has higher Cu deposition at the corners of trench mouth (which will later seal off the opening) after the first recipe

had initially been realized. The results for each wafer are presented below and will be denominated as iteration $\#i$ for i^{th} wafer.

Iteration #1

The details of the electroplating recipe used in this case are shown in Table 6.3. The tests started with lower current density values of 0.4 A/dm^2 for the longest period of time, and then the current density was increased for progressively shorter durations. The final thickness of the deposited copper was calculated based on the rate provided by Atotech, which is 0.22 μm/min for 1 A/dm^2 . The electroplating continued until the deposited copper had a thickness equal to the height of the trench i.e. 25 μm . The results were then examined through visual analysis under SEM, as shown in Fig. 6.6. Additionally, a profilometer was used to verify if voids still remained in the trench after electroplating. Only the wider meander structure was used in this test, since the profilometer accessible to us did not have a narrow tip. The obtained results are shown in Fig. 6.7. From the plot it can be deduced

Table 6.3: Recipe 1 for wafer #1

Current density (A/dm^2)	Time (mins)	Expected Thickness (μm)	Current (mA)
0.4	60	5.28	314.2
0.8	45	7.92	628.3
1.2	30	7.92	942.5
1.5	12	3.96	1178.1

(a) Region of profilometer scanning

(b) Profilometer plot

Figure 6.7: Profilometry to analyze presence of void in electroplated coil trenches

that a central void around $13 \mu\text{m}$ wide still exists despite of the progressive electroplating.

The above figures indicate two things: i) The plating time to fill up the trench is insufficient but in the meantime the final Cu overburden increases, and ii) overall Cu growth rate inside the trench is quite slow compared to the growth rate suggested by Atotech. The latter must be just the vertical growth rate when Cu electrodeposition takes place on a bare planar surface, e.g. a blank wafer, but that is not the case here. Furthermore, the profile of Cu deposited inside the trenches,

as shown in Fig. 6.6, indicates that if further deposition were carried out the copper deposition at the mouth will pinch-off the trench opening and result in the inclusion of a void in the trench center.

Three possible Cu deposition profiles are illustrated in Fig. 6.8. Fig. 6.8(a) shows the ideal ECD of Cu inside a blind via in which the seed layer is present on both the sidewalls as well as the trench bottom. In this ideal case, the Cu deposition rate is same everywhere i.e. at the bottom, on the sidewalls and on the top flat surface outside the trenches. However, this profile is not observed practically due to both an unequal current distribution along the seed layer and reduced accessibility of electrolyte inside the trenches. The observed resulting profile (Fig. 6.6) resembles the case illustrated in Fig. 6.8(b) where continued Cu deposition would pinch off at the top and results in a big central void. Fig. 6.8(c) shows the desired trapezoidal shape (or V shaped) of the Cu deposition profile. In this case, the Cu deposition rate is (more) suppressed on the side-walls and at the corners near the trench mouth, which prevents the trench from getting sealed off and allows ECD of Cu inside the trenches. The following iterations focused on producing the desired trapezoidal profile rather than the present profile, such that proper Cu filling of the trenches would be obtained.

(a) ideal Cu deposition inside blind Si via

(b) Unwanted trench profile as in Fig. 6.6

(c) Desired trapezoidal (or 'V') Cu deposition profile inside trench

Figure 6.8: Copper deposition profiles inside Si trenches

Figure 6.9: Cross sectional SEM showing 17 μm of Cu deposition within the coil trenches

Iteration #2

To solve the above problem, first it was decided to increase the leveler concentration and made it equal to that of the brightener. The carrier concentration was also increased at twice the concentration of the brightener to further suppress the growth on the sidewalls. These increments in the concentrations of the electroplating solution's chemicals were performed by adding larger amounts of leveler and carrier during the additive replenishment stages. Thus the replenishment was done such that now *leveler* = *brightener* and *carrier* = $2 \times \textit{brightener}$. The reason for modifying the concentrations of the plating chemicals instead of increasing the plating time can be easily deduced from the deposition profile shown in Fig. 6.6: it is evident that if the deposition continued for a longer duration, the lateral growth would still continue at the same rate as that of the vertical deposition. Therefore, in order to obtain a better deposition profile, it is imperative to suppress the lateral deposition on the side-walls and ensure that bottom plating is predominant and has a much larger deposition rate than the lateral one. Once this regime is established, finer tuning can be carried out by adjusting the plating time in the subsequent iterations. The results obtained after the modification of the recipe are presented in Fig. 6.9. As it can be seen from Fig. 6.9, the deposition profile is now trapezoidal, which indicates lesser lateral growth and increased bottom-up

Figure 6.10: Cross sectional SEM showing 21.49 μm of Cu deposition within the coil trenches after modification of recipe #1 and extra additives

deposition with tapered top corners. Consequently, since we reached our desired goal, in the next iteration the same electrolyte bath concentration was used and we attempted to enhance the plating rate.

Iteration #3

Table 6.4: Recipe 3 for wafer #3 with extra added additives as previous iteration

Current density (A/dm^2)	Time (mins)	Expected Thickness (μm)	Current (mA)
0.4	120	10.56	314.2
0.8	105	18.48	628.3
1.2	30	7.92	942.5
1.5	12	3.96	1178.1

In this iteration plating time was increased for low current densities viz. 0.4 A/dm^2 & 0.8 A/dm^2 , as summarized in Table 6.4 and the results are shown in Fig. 6.10. It can be seen that, although the result is better than in the previous case, the trench is still not filled completely. Nevertheless, a Cu layer 21.49 μm thick has been plated, indicating that the increase in electroplating time has been effective. The obtained trapezoidal profile also looks good, indicating that the bottom-top growth was still enhanced while the lateral one was suppressed, and no pinch off is

observed at the top of the trench. Hence, in order to completely fill up the trenches, further plating was carried out for a supplementary duration at the higher current density as detailed in the next sub-section.

Iteration #4

The same plating recipe was used here as in the previous iteration, but the plating time was now extended with 30 more minutes at the increased current density of 1.2 A/dm^2 as listed in Table. 6.5, and the obtained results are shown in Fig. 6.11. It can be seen that narrow voids are formed in this case, due to a larger lateral

Table 6.5: Recipe 4 for wafer #4 with increased plating time for current density of 1.2 A/dm^2

Current density (A/dm^2)	Time (mins)	Expected Thickness (μm)	Current (mA)
0.4	120	10.56	314.2
0.8	105	18.48	628.3
1.2	60	15.84	942.5
1.5	12	3.96	1178.1

deposition at the top corners near the trench openings during the end phase of ECD. This is a similar phenomenon with that which was also observed for our HAR micro-coils in previous Chapter 5. Therefore, it was decided to carry out the deposition at lower current densities.

Iteration #5

Instead of using a much larger current density, in this case the electroplating was carried out at a lower current density, namely 0.6 A/dm^2 (between 0.4 A/dm^2 & 0.8 A/dm^2). Hence, the revised recipe now is as shown in Fig. 6.6 with an extra low current density step of 0.6 A/dm^2 and eliminating the higher current density steps at 1.2 A/dm^2 & 1.5 A/dm^2 .

The plating results are shown in Fig. 6.12, where it can be seen that trenches were fully filled and no voids were visible. Therefore, recipe 5 which had lower density deposition steps though took a longer time produced the best results.

Figure 6.11: Cross sectional SEM showing 25 μm of Cu deposition with voids within the coil trenches after modification of recipe #3

Table 6.6: Final electroplating recipe 5 for wafer #5 with the current density of all its steps having values below 1 A/dm^2

Current density (A/dm^2)	Time (mins)	Expected Thickness (μm)	Current (mA)
0.4	240	21.12	314.2
0.6	120	15.84	471.2
0.8	60	10.56	628.3

All the SEM images in Figs 6.6 - 6.12 were taken after initial wet etching since it was extremely difficult to dice the wafers covered by a thick Cu layer deposition at top for SEM sample preparation.

6.4 Removal of Cu overburden

With the filling of the trenches, a very thick excess Cu layer would also be deposited on top of the wafer surface, with thickness expected to be around the value given in the third column of Table 6.6. Hence, for the final optimized recipe, according to Table 6.6, the thickness of the copper layer on the wafer surface was around

Figure 6.12: Cross sectional SEM showing 25 μm of Cu deposition without any voids within the coil trenches after modification of recipe #4

47.52 μm . Such a heavy overburden is not possible to be removed using wet etching only, as it has been done previously in the case of our HAR micro-coils. The reason for this is two fold. First, the removal of 47.52 μm of Cu will take a long time during which the Cu layer above the filled trenches will also be exposed to the etching solution. Second, the trenches are much wider now, at 25 μm . Due to both these factors, there is a much higher probability for the wet etchant to seep into the fine cracks, or micro-voids (if any) and, hence, etch completely the Cu inside the trenches (or, in the best case, create non-uniform voids inside the micro-coil's conductors). Consequently, it was decided to reduce the overburden initially using the wet etching only in an initial step for a limited duration, which had to be followed by CMP that not only removes the Cu but also planarizes the surface for subsequent process steps.

Therefore, after electroplating the wafer was immersed in sodium persulphate solution and the effect after 30 mins of wet etching is shown below in Fig. 6.13. An average wet etching rate of 10 μm in 30 mins was observed for persulphate with the concentration of 25g/L, no agitation and at room temperature.

Figure 6.13: Wafer undergoing wet etching before CMP to remove overburden of Cu

6.4.1 CMP

Chemical mechanical polishing (CMP) of Cu has been elaborately discussed in Chapter 2. Here we optimize the CMP process for the removal of the excess Cu covering the entire Si wafer with micro-coil trenches embedded underneath. This is quite novel and the details of such a recipe have not been provided in literature until now.

Our tests were carried out on a Logitech ORBIS machine, which is shown in Fig.6.14. The image was taken while CMP was underway and the blueish residue on either side is the copper sulphate solution produced as a result of chemical reaction of the slurry with the Cu. This blue residue serves as an excellent visual aid to indicate if the removal of Cu is taking place or not, as will be discussed later. Epoch C8902 alumina-based slurry with peroxide oxidizing component was purchased from CabotCMP to use along with a 24 inch IC 1000 polishing pad. The alumina-based slurry due to its excellent selectivity to SiO_2 , as it is imperative for the polishing to stop as soon as the Cu/Ti is removed and the CMP polishing pad touches the thermal oxide surface on the wafer. As suggested by the datasheet of Epoch C8902, the slurry was prepared with a 1:9 volumetric ratio between raw slurry and DI water, with the addition of 1% hydrogen peroxide to promote the oxidation of Cu that would make the removal due to mechanical action easier.

Figure 6.14: Logitech ORBIS CMP setup with blue copper sulphate residue on either side during CMP indicating copper removal is effective

The overall removal rate of a layer due to CMP action is given by Preston's equation, which states that the removal rate is proportional to the product of pressure and relative speed between the wafer carrier & polishing pad, as given by the equation (6.1):

$$\frac{dz}{dt} = -k_p \cdot P \cdot v \quad (6.1)$$

where z represents the thickness of layer removed in time t under the pressure P and the relative velocity of v between the wafer carrier and the rotating polishing pad. k_p is the Preston's constant.

However, this equation has been modified quite often in order to predict the actual removal rate of various layers under different CMP conditions, such as slurry rate, pattern density, etc. [160, 161]. Although eqn.6.1 may seem to suggest that theoretically it is necessary to increase the pressure and polishing speed in order to increase the polishing rate, our experimental results proved that this was not

the case in practice.

Initial CMP experiments

In order to optimize the CMP process, the first experiments were run on a 4 inch wafer. The wafer was covered with seed layer prior to electroplating except the central area, which was protected using a scotch tape during the sputtering of Cu seed layer, as illustrated in Fig. 6.15. Consequently, when electroplating was performed later on, the central region with no seed layer did not have any copper deposited through ECD. These wafers were used for the following CMP experiments in order to optimize and study the Cu removal process.

Figure 6.15: Wafer with central region void of any electroplating for CMP process optimization

The initial recipe for the removal was suggested by Logitech Orbis. This is given in Table 6.7. The recommended recipe was subsequently modified in order

Table 6.7: Initial CMP recipe to start with as suggested by Logitech

Polishing pad speed (rpm)	Carrier speed (rpm)	Down load pressure (psi)	Back pressure (psi)	Slurry rate (ml/min)
50	30 (counter clockwise)	2	25	20

to optimize its parameters so as to obtain the fastest removal rate. Two parameters, viz. rotation speed and the down load pressure (the down ward pressure exerted when the wafer holder with the wafer in it presses against the polishing pad) on the wafer, were varied and the Cu removal rates were measured. First the downward pressure was changed at a particular rotational speed of 50 rpm and then, when the maximum pressure was reached (8 psi), the rotational speed were increased. Both the rotation speed and pressure was increased to accelerate the Cu removal rate as predicted by eqn. (6.1). The values of these parameters are shown in Table 6.8. During the experiment, each session is run for 10 min. The copper thickness on the wafer is measured before and after the CMP using a profilometer at 4 points (denoted by point 1, 2, 3 & 4) at the edges of the central non-electroplated region, shown in Fig. 6.15. As seen from Table 6.8, the removal rate, R , slowly falls as the pressure increases at a particular rotational speed. Next, we increased the polishing pad speed to 75 rpm and finally 100 rpm, while maintaining the downward polishing pressure of 8 psi. At both of these increased polishing speeds the removal rate dropped drastically. Particularly at 100 rpm the Cu removal rate R was so minuscule that it was not practically measurable. This vanishing removal rate was visually indicated by significantly much less bluish residue formation during CMP.

This reduction of the removal rate R when increasing both pressure and rotational speed is extremely counterintuitive from what one would expect. At first, it was assumed that the peroxide-based oxidizing component in the slurry, (being unstable) must have been degrading with time and hence the removal rate R reduced, as this was limiting the conversion of the Cu layer into its oxide required for its subsequent removal. Hence, to make sure the oxidation would take place a more concentrated slurry was made, but this time with double concentration of raw slurry and hydrogen peroxide, and the same experiment was then repeated. The results are tabulated in Table 6.9. Here again, we see the same issue of reduction in removal rate with pressure and very minute removal at the higher rotational rates.

Table 6.8: Removal rate for different pad rotation speed and pressure with the standard slurry recipe suggested by Logitech

Pad rotation speed <i>rpm</i>	Down load pressure <i>psi</i>	Total elapsed time <i>mins</i>	Removal rate $\mu m/min$
50	2	10	0.2
	4	20	0.1
	6	30	0.1
	8	40	0.07
75	8	50	0.012
100	8	60	<i>Minute removal</i>
	2	70	<i>Minute removal</i>

However, the values of the overall removal rate have increased compared to those obtained previously when using just the standard slurry. For direct comparison of both the results, the plot showing the variation in time of the removal rates for both the slurries is shown in Fig. 6.16. This plot clearly shows that, although the removal rate obtained for the concentrated slurry exhibits increased absolute values, it also has a higher variation/faster reduction in time despite the fact that the downward polishing pressure had been steadily increased in time, as is clearly indicated in Tables 6.8 & 6.9.

From the data in Fig. 6.16 it becomes clear that, although increasing the concentration of the slurry increases the removal rates, their values would still fall

Table 6.9: Removal rate for different pad rotation speed and pressure with the slurry recipe modified by us to make higher peroxide and raw slurry concentration

Pad rotation speed <i>rpm</i>	Down load pressure <i>psi</i>	Total elapsed time <i>mins</i>	Removal rate $\mu m/min$
50	2	10	0.223
	4	20	0.173
	6	30	0.153
	8	40	0.121
75	8	50	0.02
100	8	60	<i>Minute removal</i>
	2	70	<i>Minute removal</i>

Figure 6.16: Removal rate comparison between recommended slurry and concentrated slurry with time

steadily in time as pressure increases. This suggests that the chemical reaction between the slurry and the copper is the most important factor that determines the copper removal, followed by the mechanical abrasion. The removal rate is being primarily dependent on the chemical reaction, hence the Cu removal rate, R , is then dictated by the concentration of the slurry that reacts with the Cu. Additionally, the Cu removal rates fall steadily with time in spite of the pressure increase and simultaneous increase of the pad's rotational velocity. This is most probably because the increasingly higher pad rotational speeds would gradually spill more and more slurry due to the correspondingly increased centrifugal force. This would result in a diminished replenishment of the consumed slurry, and, hence, in less and less removed Cu as time advances, as was proven by our experimental results shown earlier. It is also evident that the polishing pressure has no influence on the chemical reaction between the slurry and the Cu layer but is a key factor in the mechanical removal of the metal, while the opposite is true for the slurry replenishment rate. Consequently, we can once again conclude that our experimental results clearly indicate that the Cu-slurry chemical reaction is the crucial factor dictating the CMP removal rate in our case.

In order to further study in more detail the effect of the chemical reaction over that of mechanical abrasion, two more wafers were prepared. On these two wafers, different thicknesses of Cu films, viz. 10 μm and 20 μm , were electrodeposited, keeping again the center of the wafer copper-free, as was shown in Fig. 6.15. Both these wafers then underwent CMP at 50 rpm and 8 psi pressure. After 10 min. the thickness of remaining copper was measured as before, and the removal rate R was calculated. The variations of both Cu thickness and the removal rate with time are shown in Fig. 6.17 and 6.18, respectively. From the plots, it can be seen that the wafer with thick copper (around 20 μm) had a removal rate which did not show any systematic decrease with time, namely it was around 0.25 $\mu\text{m}/\text{min}$ with a variation between 0.2 $\mu\text{m}/\text{min}$ and 0.3 $\mu\text{m}/\text{min}$. For comparison, the removal rate of the wafer with a Cu layer 10 μm thick strongly reduced from 0.2 $\mu\text{m}/\text{min}$ to 0.05 $\mu\text{m}/\text{min}$ after around 30 min. of polishing, when the removal rate reduced abruptly. The plot of the Cu thickness at every 10 mins also gives an idea of how fast the Cu thickness reduced with time (the slope of the plots in Fig. 6.18(a) & Fig. 6.17(b)). The chemical reaction in the Cu removal by CMP can be written in a very simplified form as

Two important observations can be made from the plots shown in Figs 6.18 & 6.17. Firstly, the reduction of removal rate, R , with time shows that the concentration of at least one of the initial reactants is rapidly decreasing in time. Since the slurry is the only element whose concentration can indeed vary in time, it means that its reaction with the Cu layer proceeds extremely fast. The slurry's concentration is dictated not only by the initial amount of slurry in the starting solution, but also by its replenishment rate vs. its consumption rate. The replenishment rate is determined by the slurry's flow rate which, on its turn, also depends on the pad's rotational speed, which thus becomes another key limiting factor of the removal rate besides the slurry concentration.

The fact that the Cu-slurry chemical reaction is the dictating factor for the removal rate is indeed confirmed by two facts:

- The usage of a more concentrated slurry did increase the removal rate, and

(a) Thickness variation with time

(b) Removal rate variation with time

Figure 6.17: Copper thickness and removal rate variation with CMP at 50 rpm and 8 psi for thicker Cu layer with thickness above $20 \mu\text{m}$

(a) Thickness variation with time

(b) Removal rate variation with time

Figure 6.18: Copper thickness and removal rate variation with CMP at 50rpm and 8psi for a $10\ \mu\text{m}$ thick copper

- This removal rate also gradually decreased in time as the reaction progressed and more and more slurry was consumed, as shown by the red bars in Fig. 6.16.

Consequently, because of the effects caused by both phenomena, namely the very fast rate for the Cu-slurry reaction and the gradually decreased replenishment rate of the slurry with increased rotation rates in time (as explained above), the removal rate would flatten out sooner or later.

Thirdly, another phenomenon was also observed: removal rate is not constant throughout but starts falling after a particular time. From the plot in Fig. 6.17, it can be seen the Cu removal rate is more or less constant around $0.25 \mu/\text{min}$ till around 50 min. For the experiment with wafer with less thicker Cu of 10μ shown in 6.18, as long as the Cu thickness is greater than a certain critical/threshold thickness (which we can denote by z_0), the removal rate, R is quite steady with insignificant variation, and, hence, independent of time. As soon as the thickness goes below z_0 , R reduces with time. This indicates the rather peculiar -and hitherto unreported- the fact that the chemical reaction rate reduces not only due to the rapid consumption of the slurry and its diminished replenishment rate, but also because the Cu layer thickness decreases under the critical value z_0 .

The thickness z of the Cu layer at a particular time $t = t_1$ depends on the chemical reaction rate between $t = 0$ and $t = t_1$. As time progresses, the concentration of the slurry and, hence, the chemical reaction rate also slows down. Additionally, we also noticed that if at $t = t_2$, (where $t_2 > t_1$) the Cu thickness becomes smaller than the critical value, i.e. $z(t_2) < z_0$ the Cu removal rate will also be much slower and decreases in time. Consequently, from our experimental observation the removal rate is best described by two Preston's equations, one for each operating regime. Thus, the Cu removal rate R in the initial part of CMP must be given by a modified Preston's eqn. (6.1) that is time independent of time for $z > z_0$, i.e. until z reaches z_0 at time t_0 , as can be deduced from the plots in Fig. 6.17 & Fig. 6.18. For remaining Cu thickness below z_0 i.e. for $t \geq t_0$, the removal rate falls with time. Hence, Preston's equation (6.1) can be split and

modified as:

$$\begin{aligned} R &= -k_p \cdot [P]^b \cdot [v]^c; \text{ for } z > z_0 \text{ or } t < t_0 \\ R &= -k_p \cdot [t]^a \cdot [P]^b \cdot [v]^c; \text{ for } z \leq z_0 \text{ or } t \geq t_0 \end{aligned} \quad (6.3)$$

where from our experimental plot in Fig. 6.18(b) $a \approx -1$ for $t > 25$ mins (t_0), which gives the critical thickness in our case as $z_0 = 6 \mu\text{m}$. Above this thickness, for $z > z_0$ and $t < t_0$, the removal rate is independent of time for a given pressure and rotational speed as observed in the plot of Fig. 6.17-b. Hence, for the wafer under CMP with Cu thickness of $20 \mu\text{m}$, even after $t = 50$ min the thickness z has not yet reached the critical value of z_0 . Next, in the second part of the CMP, when the remaining Cu thickness has decreased below the critical value, i.e. $z < z_0$ at $t \geq t_0$, the phenomenon is modeled by the $[t]^a$ factor in eqn. 6.3, with $a \approx -1$. This phenomenon is observed in Fig. 6.18-b. The physical meaning of the fact that $c < 0$ can be deduced from both Tables 6.8 & 6.9 is that increasingly higher rotational speeds would indeed gradually reduce the removal rate, as most of the slurry is spilled from the rotating pad due to the correspondingly increased centrifugal force. This decrease of removal rate with time due to the reduction of the Cu thickness and/or increase in rotational speed (that spills away the slurry) concludes the fact that chemical removal is the primary removal mechanism. Its absence beyond t_0 leaves mechanical abrasion as the sole removal phenomenon,

(a) Wafer after CMP with only partial removal of Cu (b) CMP-ed wafer with the entire Cu overburden removed

Figure 6.19: Wafer that have undergone CMP

resulting in a correspondingly drastic reduction of the Cu removal rate.

Consequently, our recipe optimization for the CMP process led to the following major conclusions:

- The Cu-slurry chemical reaction process is the key determinant factor that dictates the Cu removal in a CMP process using an alumina-based slurry with peroxide oxidant.
- Increasing the rotational speed of the polishing pad does not lead to an increase of the Cu removal rate, R , but has an opposite effect. This is because the higher centrifugal force spills the slurry away from the pad. It also reduces the replenishment rate of the slurry, and, hence, its concentration present on the polishing pad usable for the Cu removal process. Moreover, a higher rotational speed reduces the time and amount of slurry in contact with the wafer during polishing, which in turn reduces the effectiveness of the chemical reaction between copper and the slurry.
- The downward pressure between the wafer and the polishing pad may increase R by proportionally boosting the mechanical removal rate of Cu. However, due to the much more predominant influence of both the Cu-slurry reaction rate and of the slurry replenishment rate, its individual effect on R is difficult to segregate and quantify, especially before the critical time t_0 as explained above.
- The removal rate R is independent of the time t down to/until a critical (or minimal) thickness z_0 at $t = t_0$, below which its value sharply decreases and becomes dependent on time.

the Al was deposited, MASK #03 was used to pattern the pads. However, this time the photoresist AZ 9260 (5 μm thick) was used, since the Al RIE in a BCl_3 chemistry (with a removal rate of 2 μm in ≈ 15 min) might very quickly remove the standard photoresist. Finally, the photoresist was removed by immersing the wafer in acetone to reveal the pads. Fig. 6.22 shows the final device wafer.

6.6 Measurements

Two sets of measurements were first performed viz. electrical characterization and magnetic field measurement, and the obtained results were compared with the simulated values. We measured the micro-coils with 3.5 and 5.5 turns from 2 different wafers. The devices were considered fully operational if the measured resistances had values in the order of a few ohms. The resistance was measured using a high precision multimeter capable of measuring resistances below 0.1 Ω , unlike a probe station where the tungsten probe resistance alone is around 2 Ω .

The magnetic field measurement was performed using Coliy G91 Gauss-meter with a 3D movement platform which allowed us to precisely position its magnetic

Figure 6.22: Complete devices realized on a wafer

field probe over the tested device at a height of desired 2 μm when a current of 1A was injected in it. The values of the measured resistance and magnetic field values are given in Table 6.10. Box plots of these measured resistances and magnetic field strengths (MFSs) are shown in Fig. 6.23 where the mean value is represented by the dot in middle; the bottom and top of the box are the first and third quartiles, and the band inside the box is the median value.

As seen from this plot in Fig. 6.23 the magnetic field has a lower deviation from the mean value for both the micro-coils with 3.5 and 5.5 turns obtained from all the wafers. The fact that the resistance variation is quite high due to the variability in the filling of the trenches with ECD Cu, and as it was observed before in the case of HAR micro-coils, detailed in the previous chapter.

It can be seen from Table. 6.10, that MFS decreases rapidly with the increase in resistance. A probable explanation for this can be the presence of micro-voids in the trenches of the structures with high resistances (which are, in fact, the causes of the high resistance). When a current is injected in the micro-coils with less voids and lower resistances, trenches that are better filled with ECD Cu. In contrast, for the higher resistance coils, considering that the voids exist near the top (mouth of the trench) as it was seen earlier that could be the (most probable) case for the wide trenches, the majority of the current flows only near the filled bottom of the trench where the resistance is low. This uneven current distribution with most -if not all- of the current further away from the top of the micro-coil will result in a drop of the MFS measured at the surface. However, it is difficult to quantify accurately this effect since it requires the knowledge of the exact physical

Table 6.10: Measured magnetic field and resistances for 3.5 and 5.5 turn micro-coils

3.5 turns		5.5 turns	
Mean Magnetic field (mT)	Resistance (Ω)	Mean Magnetic field (mT)	Resistance (Ω)
0.04	0.7	0.12	1.4
0.08	0.5	0.15	0.7
0.1	0.4	0.18	0.55
0.11	0.25	0.22	0.4
0.14	0.17	0.21	0.4
0.14	0.16	0.24	0.38
0.15	0.15	0.26	0.35

(a) 3.5 turn micro-coil

(b) 5.5 turn micro-coil

Figure 6.23: Box plots for measured magnetic field and resistances

Table 6.11: Comparison of best measured value of the magnetic field and the resistance with simulated values

Micro-coils	Measured MFS (mT)	Simulated MFS (mT)	Measured Resistance (Ω)	Simulated Resistance (Ω)
3.5 turns	0.15	0.22	0.15	0.124
5.5 turns	0.26	0.38	0.35	0.2

distribution of voids/micro-voids and thickness, thickness uniformity and density of the Cu at the filled bottom of trenches, all of which are very challenging to obtain.

The best values of magnetic field from Table. 6.10 was compared to the simulated results, where the models are simulated considering same measurement setup. The results are shown in Table 6.11. According to eqn. (A.1) the magnetic field the micro-coil with 5.5 turns should be around $\frac{5.5}{3.5} = 1.57$ times larger than the micro-coil with 3.5 turns. Indeed, values of 1.73 and 1.6 are obtained for the ratio of measured and simulated values of magnetic field, respectively. The differences between these values and the theoretical one is due to the fact eqn. (A.1) refers to the field along z axis at a particular point and not to the mean value over a given volume which is the case for the measured or simulated results.

6.7 Conclusion

This chapter first details the fabrication process of wide ($25\ \mu\text{m}$) and low AR (1 : 1) micro-coils which have been determined to provide optimal performance for MR microprobes (see Chapter 4). This is followed by the electrical characterization of the fabricated micro-coils.

The process flow used DRIE trenches in Si realized with the same process used for the previous HAR micro-coils described in Chapter 5 and, hence, is not elaborated here again.

Electroplating had to be optimized for filling up such low AR (1:1) trenches since this time commercially available industrial grade electrolyte from Atotech and their additives were used with a standard plating bench. Moreover, although the aspect ratio in this case was lower than that of the previous HAR micro-coils,

filling up these trenches with electroplated Cu still remained equally challenging since it is required to precisely control both the lateral copper deposition (which is unavoidable in blind vias) and the bottom to top growth. DC plating was initially employed, but it proved to be slow and it was replaced by variable time DC plating which was subsequently optimized in 5 iterations that involved increasing the leveler and carrier concentrations with respect to that of the brightener. As a result, the overburden has been reduced and a slower sidewall copper deposition was achieved to provide balanced vertical-to-lateral Cu deposition inside the trenches. It was once more realized that lower current densities are preferable even in variable time plating, in order to prevent void formation at the opening of the trenches, provided that the additive concentration is optimum.

Next, a combination of wet etching and CMP was applied to remove the Cu overburden. The CMP process has also been optimized in several iterations which indicated that the chemical reaction of the slurry with the copper is the most important factor dictating the removal rate, followed by mechanical polishing which alone has dramatically reduced impact.

Once the excess Cu was removed, the bonding pads were defined using aluminum sputtered on previously patterned silicon dioxide; metal RIE was then used to etch off the sputtered Al in order to pattern the pads.

Finally, the fabricated micro-coils with 3.5 and 5.5 turns were characterized by measuring the electrical resistance and magnetic field strength (MFS) for over 3 different wafers. The results show a decrease of magnetic field with increase in resistance. The very large measured resistance values are due to incomplete Cu filling, i.e. voids inside the trenches. Hence, compared to the ideal MFS and resistance values, a micro-coil with a non-ideal copper filling (which is the practical case) will have larger resistance as well as less intense magnetic field generated than those for the ideal micro-coil with 100% copper filling.

Highlights of Chapter 6

- The micro-coils designed in Chapter 4 using the ‘P’ factor approach to provide the optimal performance of an MR micro-probe, were fabricated in this chapter.
- Unlike the HAR micro-coils in the previous chapter, these coils had an AR of 1 : 1 and their filling up with ECD Cu was performed using commercially available solutions and a standard bench. Hence, a different Cu ECD procedure was implemented compared to the previous one that had been used for the HAR structures.
- A progressive DC electroplating technique was developed which included using different values of plating current for different intervals of time. The additive concentration was also adjusted to ensure a proper balance between lateral & ‘bottom-up’ Cu deposition rates such that no voids would be observed in the trenches after Cu ECD..
- In order to get rid of the excess Cu overburden, a new procedure consisting of wet Cu etching and Cu CMP was developed. Detailed step by step analysis of Cu CMP showed that the Cu removal rate varied as the CMP progressed.
- Finally, generated MFS and the resistance of the micro-coils were measured and the measurement results were then compared with the simulated values.

Chapter 7

Future work for SNR improvement

7.1 Introduction

The major drawback of any Magnetic Resonance (MR) micro-probe consisting of a micro-coil in comparison to a macroscopic solenoid is lower Signal-to-noise ratio (SNR) due to both the reduced volume sample, poor magnetic coupling of the sample with the micro-coil and the thermal noise from the resistance of the micro-coil. Consequently, the SNR of such a micro-probe can be enhanced by following measures:

- Reduce the electrical resistance of the coil by cooling it, which in turn reduces the thermal resistance and increases both the SNR and its Q .
- Increase the magnetic coupling by keeping the coil and the sample in close proximity and using the most suitable sample holder.
- Maximize the sample volume by enlarging both the coil and the holder sizes.

In this Chapter, two new methods are proposed to address the challenges highlighted above. Firstly, a micro-coil realized with a CNT-graphitic heterostructure material (CNT-GHM) is demonstrated. It exhibited a large Q value and, hence, a very good magnetic field generation capability. Second, a design which incorporates cryogenic cooling at micro-dimensions is presented.

Cryogenic cooling for reduced electrical resistance (in this case in order to minimize the thermal noise) is a very well-known technique that has been used for a

very long time. However, its miniaturized application, especially for on-chip devices, is very novel and has rarely been attempted, and never at micro-scale. Very little information about such miniaturized systems for cryo-cooling of NMR probes can be found in literature. One such report, by Koo *et al.* [162], describes a planar coil for NMR, embedded in PMMA and cryogenically cooled using liquid nitrogen (LN). However, in this case, the entire structure has dimensions on the order of mm, and the most important factor from our point of view is the extremely large distance of 2.1 mm between the sample and the coil surface.

The major difficulty in realizing such a cryo-cooled design at micro-scale is given by the need to impose/compromise contradictory requirements: on one hand, the micro-coil should be cryo-cooled at the LN temperature (77K), but on the other hand, the biological sample must be kept not only as close as possible to the micro-coil (to enhance the A.C. MFS and thus maximize the SNR), but also to be kept alive at a reasonable temperature (i.e. of minimum 4°C) in order to avoid freezing and destroying it.

7.2 Outline of our contribution

In order to boost the intensity of the low MFS generated by conventional micro-coils, devices using a novel CNT-graphitic heterostructure material (CNT-GHM) instead of Cu were fabricated and tested. Employing the CNT-GHM instead of using just CNTs as the conductive material was necessary because, as is well known, the electrical conductivity in CNTs is very anisotropic with the conduction happening only along the length of the CNT and not between adjacent CNT bundles. This is a major problem given that the growth of the CNTs will proceed vertically, but the current flow takes place along the patterned micro-coil, i.e. transversally across the vertical CNTs. The CNT-GHM proposed and used here results in significantly increased lateral electrical conductivity. The aspect ratio of these micro-coils were also 3 : 1 and the CNT growth in these HAR trenches is very much easier compared to their filling by ECD of metals like copper. This chapter describes the fabrication procedure, and measurement results of such structures.

In contrast, the key target of the second proposed method is to design an on-chip cryo-cooled MR probe structure. For this purpose, the simplest solution

is to flow the LN through a micro-channel realized by anisotropic wet etching of the Si on the backside of the Si wafer, and then sealing it using PDMS, glass, or any other suitable material. A very complex and time-consuming FEA design process has been carried out using COMSOL in order to design an appropriate sample holder which could provide the necessary thermal insulation between the cryo-cooled Si substrate that contains the micro-coil and the sample, both of which should nevertheless be situated as close as possible to one another. This Thesis reports for the first time, a cryo-cooled design in which the distance between the sample and the micro-coil is $150\ \mu\text{m}$ - $200\ \mu\text{m}$ and freezing of the biological sample is avoided.

7.3 CNT-graphitic coils

Planar micro-coils have been extensively used as inductive components in on-chip circuits. One way to enlarge the Q value of such an on-chip inductor is to increase the aspect ratio AR ($\text{AR}=\text{height}/\text{width}$) of its conductor. This ensures low resistance through increase in the cross-sectional area of the micro-coil's conductor. However, the fabrication of high aspect ratio (HAR) on-chip micro-coils is not trivial, and uniformly filling up HAR features with copper through electroplating is an additional difficulty, as discussed in previous Chapters.

In contrast, CNTs are fairly easy to grow even in HAR features like trenches or vias. However, CNTs exhibit high electrical conductivity only along the length of the nanotubes, i.e. in the longitudinal direction. If one defines a spiral planar coil-like pattern using CNTs, since the CNTs will be mostly oriented vertically, the current flow through the micro-coil will not be oriented along the CNTs but normal onto them, hence facing a much smaller conductivity due to lack of proper electrical connectivity between adjacent CNT bundles. This drawback can in principle be eliminated by using the solution reported by Bhuvana *et al.* [163], namely enhanced adjacent connectivity through conversion of CNT bundles into CNT-graphene fused heterostructures.

However, graphene does not have a large mechanical strength and thus may not be a suitable material with which to realize a micro-coil. Our novel solution was to fuse the CNT bundles into a more rigid and sustaining structure of graphite

Table 7.1: CNT-graphitic micro-coil growth parameters

Plasma power	Plasma Treatment		Remarks
	<i>Activation time (min)</i>	<i>Acetylene flow & Graphitization time</i>	
700W	10	10 sccm & 30 min.	Slight graphitization at CNTs periphery
		25 sccm & 30 min.	More visible graphitization along the CNT bundles
		50 sccm & 30 min.	Over-graphitization closing inter-turn gaps to form a disk

rather than one made of flimsy graphene. In this chapter, we first describe the procedure to fabricate micro-coils with a HAR conductor (with an $AR = 3 : 1$) made of CNT-graphitic fused heterostructures and realized on a Si wafer. The dimensions of the micro-coils considered are same as those previously described and studied in Chapter 5. The resulting devices were then examined under SEM and also by Raman spectroscopy. Measurements showed that these micro-coils exhibited unexpectedly larger Q values despite higher resistances compared to those of identical copper micro-coils. Finally, subsequent investigations carried out to find the possible reasons for this behavior and the obtained results will also be presented.

7.3.1 Fabrication of CNT-graphitic micro-coils

CNT-based micro-coil structures of $3 : 1$ aspect ratio were successfully grown on Si substrates with an Aixtron BM system using the procedures outlined in literature [122, 123]. The catalyst used for CNT growth was iron sputtered on a 1nm aluminum oxide layer obtained through Atomic Layer Deposition (ALD). This was followed by lateral cementing of adjacent CNT structures using graphitic growth under plasma treatment and acetylene. The flow rate of acetylene was varied to study its effect on graphitization, while keeping the plasma power constant at 70 W. All the CNT growth parameters are shown in Table 7.1. The effects of the graphitization can be seen in Fig 7.1. For the lower acetylene flow rates of 10

Figure 7.1: CNT coils (left) and CNT-graphitic coils (right)

scm the graphitization is seen to take place only at the periphery, while at the higher rate of 25 sccm the graphitization happens within inner CNT bundles as well. These two cases are also shown in more detail in Fig 7.2. At higher acetylene flow rates beyond 25 sccm over-graphitization occurs. Initial over-graphitization starts with secondary growths connecting adjacent micro-coil traces resulting in electrical shorts as shown in Fig. 7.3. At 50 sccm and above fully graphitized discs form within the micro-coil structure, as shown in Fig. 7.4.

The presence of graphitic structure was verified by Raman spectroscopy as shown in Fig. 7.5. The presence of distinct D and G peaks at 1360 cm^{-1} and 1580 cm^{-1} along with a low intensity G' peak at 2700 cm^{-1} confirm the presence of multiwalled CNT structures [124]. The spectra exhibit a split G' peak of low intensity (less compared to graphene but higher compared to CNT-only structures), which proves the presence of graphitic structures in these cases [125].

Figure 7.2: Graphitization of CNT micro-coils at different acetylene flow rates

Figure 7.3: Start of secondary growths connecting adjacent coil traces at higher acetylene flow rates

7.3.2 Measurements of Q factor and resistance

First, I - V characteristics were measured using nano-probes under SEM. This yielded the resistance values of the micro-coil structures with both CNT and CNT-GHM with 3.5 and 15.5 turns each. Table 7.2 shows the resistance values of each type of micro-coil, which confirm that the resistance falls with increase in graphi-

Figure 7.4: Disc formation due to higher acetylene flow rates

Figure 7.5: Raman plot for CNT coil with different acetylene flow

tization at higher acetylene flows. The I - V plots in Fig. 7.6 show excellent linear proportionality between current and voltage confirming the pure ohmic characteristic of the CNT-based micro-coils.

Next, the Q values of the micro-coils were measured up to 5 MHz, and the obtained results are shown in Fig. 7.7 where the Q values of the CNT-GHM device are compared with those of a copper micro-coil of exactly same design dimensions reported in Chapter 5. It can be seen from Fig. 7.7 that the Q values

Figure 7.6: I-V characteristics of the micro-coil structures with 15.5 turns

of the CNT-graphitic micro-coils are much larger than that of the similar copper micro-coil with the same number of turns and the same dimensions, despite the fact that the CNT-graphitic micro-coils have larger resistances compared to their copper counterparts.

Extensive electromagnetic simulations have then been carried out using CST in order to understand the reason behind such a high inductance. A model was built considering the CNTs having anisotropic conductivity while the graphite surrounds the periphery of the CNTs. The conductivity along the CNT length, i.e. the z axis, was taken to be around 10^7 S/m (a standard value for CNT). The electrical conductivity value along the x and y directions was taken according to the resistance value that was obtained from the I-V characteristic measured by nano-probing, namely around 0.17 S/m. Initially only CNTs define the micro-coil structure, however, under the action of the carbon precursor the outer regions of the CNTs become converted into thin graphitic layers. The outer periphery

Table 7.2: Resistance values of CNT and graphitized micro-coils as obtained through nano-probing

Coil turns	Probe Resistance	CNT-only	CNT-graphitic with 10 sccm Acetylene flow	CNT-graphitic with 25 sccm Acetylene flow	Remarks
3.5	9Ω	135KΩ	(205 – 9)Ω = 196Ω	(66 – 9)Ω = 57Ω	With graphitization the resistance drops remarkably
15.5		376KΩ	(276 – 9)Ω = 267Ω	(134 – 9)Ω = 125Ω	

is considered to be of graphite, which has a standard model in CST. Since it is difficult to understand the extent of graphitization inside the CNT structure, in the CST model a bulk graphite structure defining the entire coil is first built and this was followed later on by an anisotropic model of CNTs slowly replacing the interior of the micro-coil cross-section. The CNT height within the micro-coil is gradually increased along with the increase in the width of the CNT structure. Hence, at the height of $20\ \mu\text{m}$ and width of $7\ \mu\text{m}$ the entire micro-coil material was transformed entirely into a CNT structure. Electromagnetic simulations were then performed at 1V potential difference for each height and width of the CNT structure to obtain different values of the generated magnetic energy. For this purpose, a custom material profile was generated and used in CST in order to cater for the anisotropy of the CNT-based material present in our fabricated micro-coils. The CST model for anisotropic CNT is shown in Fig.7.8. Fig.7.9 shows the 3 possible micro-coil models made in CST for our CNT-based micro-coils. Fig.7.10 shows the dependence of the magnetic energy generated by a CNT-based micro-coil on the height h_2 , of the CNTs inside the micro-coil, for different values of the width w_2 occupied by the CNTs inside the micro-coil. When $h_2 = 20\ \mu\text{m}$ and $w_2 = 7\ \mu\text{m}$

Figure 7.7: Q factor variation with frequency of CNT-graphitic and copper micro coils with 15.5 turns and same design dimensions

the entire coil is made of as-deposited CNTs and no graphitization is present (in red Fig.7.9-a).

Figure 7.8: The anisotropic model of CNT as defined in CST

Figure 7.9: Possible combinations of CNT-graphitic micro-coils

Fig. 7.10 shows that the micro-coil made of a fully graphitized material (shown in Fig.7.9-c) exhibits a low magnetic energy compared to those generated by other configurations that comprise when both CNT and graphitic material ($0 < h_2 < 20 \mu m$; $0 < w_2 < 7 \mu m$). Hence, magnetic energy decreases with expanding the volume occupied by pure as-deposited CNTs (i.e. when both h_2

Figure 7.10: Magnetic field energy variation for different height (h_2) and width (w_2) combinations of CNT inside graphitized periphery

and w_2 increase). When the as-deposited CNTs occupy the entire width of the micro-coil but still with a graphite layer of variable thickness on the top surface ($w_2 = 7 \mu\text{m}$ and $h_2 < 20 \mu\text{m}$), the generated magnetic energy is much lower than that of an entire graphitic coil or of any other type of coil. Moreover, the magnetic energy constantly decreases as h_2 increases, until it becomes zero for a micro-coil entirely made of as-deposited CNTs ($w_2 = 7 \mu\text{m}$ and $h_2 = 20 \mu\text{m}$). In this last case, there is neither any current conduction in the xy plane due to the anisotropic conductivity of the CNTs, nor vertically, along the z axis, since it is not included or a part of any closed circuit.

Consequently, our extensive CST simulations clearly highlighted that the distribution of current inside the CNT-graphitic structure is not responsible for the measured high inductances. Hence, another plausible explanation for this observed phenomenon had to be searched. A literature review revealed that the most plausible explanation for the much higher magnetic field energy stored by the CNT-based micro-coils is the presence of ferromagnetic iron carbide particles as an interstitial compound within the carbon-based materials. Iron is used as catalyst for CNT growth, and these Fe particles get converted into iron carbides (Fe_3C , Fe_7C_3) during the CNT growth process. These iron carbides are ferromagnetic materials with high magnetic saturation [128–131]. Their presence consequently results in larger inductance values which cause the measured higher Q values despite of the larger resistances compared to those of the Cu micro-coils of same dimensions.

Figure 7.11: Proposed model for cryogenic cooling of NMR micro-probe

This higher Q value could result in better magnetic performance of a CNT based micro-coils if it were used as the magnetic field generator in a NMR micro-probe. However, it is much better to use a HAR copper micro-coils of low resistance as a second, signal receiver micro-coil, which will ensure a low thermal noise and, hence, a large SNR. This is a totally original and novel NMR micro-probe structure which has never been used or suggested by anyone until now.

7.4 Cryogenic cooling of NMR micro-probes

The proposed micro-probe structure consists of two blocks. One block contains the micro-coil structure, RF feed lines and ground planes, along with a fluidic channel micromachined in a silicon substrate for the flow of liquid nitrogen (LN). The second block consists of a microchannel for air flow along with the imaging plane at the top. These two individual blocks are thermally isolated by an air gap supported on micro-pillars at four corners. The design is shown in Fig. 7.11.

The polymeric materials used in this design have been chosen based on their low thermal conductivity and ease of realizing microchannels using microfabrication. The two polymers considered were PDMS and SU8 for their low thermal

conductivity and ease of fabrication of micro-fluidic channels. However, each of them has disadvantages of its own, as discussed in Chapter 2. SU8 was considered for the initial proposed model due to the large thickness of the patterned structures which needs to be realized, and which can be easily achieved and controlled using SU8. The 4 micro-pillars located at each corner, as shown in the Fig. 7.11, act as spacers and thermally isolate the second block from the silicon substrate. The sample is kept on the imaging plane above the air channel. Realizing these micro-pillars on the Si substrate at desired heights between 10 μm to 20 μm using SU8 is quite feasible, as has been reported previously in literature, as discussed in Chapter 2.

7.4.1 Thermal modeling

In this case, a conjugate heat transfer model that included both fluid and solid domains has been built and simulated. Our structure can be modeled as a heat exchanger at micro-scale, in which the silicon block is cooled due to the flow of liquid nitrogen and the flow of air in the polymeric block prevents the biological sample from freezing as heat is exchanged between the fluids flowing through the parallel microchannels. Considering the fluid flow in y direction, the operation of a heat exchanger can be described by the equations

$$J_1 \frac{dT_1}{dy} = \gamma(T_2 - T_1) J_2 \frac{dT_2}{dy} = \gamma(T_1 - T_2) \quad (7.1)$$

where J_i is the thermal mass flow rate of fluid i given by $J_i = \text{heat capacity } (c_i) \times \text{fluid flow rate } (j_i)$ and γ is the parameter that models the thermal connection between the two fluid channels and depends on the thermal properties, such as the heat capacity and thermal conductivity k of the material separating the fluid channels. Equations in (7.1) shows that the change in temperature due to fluid flows is proportional to the difference in temperature between the fluids in the two channels, which is controlled by the flow rate (j_i), the heat capacity of the fluids, and the thermal properties of the material separating the channels.

Figure 7.12: Temperature variation of the imaging surface with variation in pressure across the air channel. The straight line at 277K (or 4°C) represents the lowest possible temperature at which the sample can still be maintained while remaining viable

7.4.2 Thermal simulations

Detailed thermal analysis clearly showed that the air flow rate within the polymer air channel is the key parameter which determines the specific temperature of the imaging surface/sample, and not the LN flow rate. We simulated a wide range of pressure differences across the air channel compatible with the micro-pump initially intended to be used. The corresponding pressure simulated in the LN backside micro-channel is much lower as most of the commercially available LN delivery systems have low pressure ratings, of up to 100 mBar. Fig.7.12 shows the temperature variation of the imaging surface at a height of 150 μ m from the micro-coil surface with a variation of air pressure difference from 100 mBar to 1 bar between the inlet and the outlet of the air channel. As seen from the plot in Fig. 7.12, an air pressure over 700 mBar ensures that the temperature of the imaging surface remains above the desired target value.

To further extend the study, a temporal variation of the temperature of the image surface at 1 bar pressure has also been performed. Fig.7.13 shows that the temperature falls very rapidly with time and attains a constant value just above 277 K after only 500 seconds. The 1 bar pressure considered here is based on the simulations above and on the capability of commercially available micro-pumps

Figure 7.13: Temporal variation of temperature of the imaging surface for a 1 bar pressure difference at the air inlet

which can provide such a pumping pressure difference.

The height of the micro-pillars, or spacers, that determine the width/height of the air gap between the air flow micro-channel and the underlying Si chip, are another essential factor that strongly influence the sample's temperature. A subsequent set of simulations were carried out to choose the optimum spacer height that can provide a viable temperature for the sample. Figure 7.14 shows how the sample temperature varies as a function of the air flow rate in the air micro-channel for different spacer heights. As expected, for thicker spacers the temperature remains in the accepted range. Hence, $20\text{ }\mu\text{m}$ thick spacers were chosen in this design. The simulations results in Fig. 7.14 were obtained using SU8, but better ones are obtained if SU8 is replaced by PDMS since the thermal conductivity of SU8 is $0.2\text{ W/m}\cdot\text{K}$ which is still higher than that of PDMS' ($0.15\text{ W/m}\cdot\text{K}$). This makes PDMS a better thermal insulator and all the criteria reported above will surely work for a PDMS structure. However, in order to determine the structural feasibility of the final structure, detailed simulations in the mechanical domain are

Figure 7.14: Temperature of the sample for various spacer heights made of SU8

also required to be performed in the future, in order to ensure that the polymeric block has both low stress (thermal and structural) and no (or little) deflection (sagging).

7.4.3 Proposed fabrication steps

Fig. 7.15 presents schematically the fabrication of the entire polymer-based structure which should be constructed atop the entire Si chip containing the micro-coil. Up to this moment only initial tests were done, intended to optimize the realization of micro-channels in polydimethylsiloxane (PDMS) which could be applied for the air flow in the complete polymeric structure. As described earlier, the polymeric block with the air-flow micro-channel can be fabricated using either SU8 or PDMS, and each has its own advantages and disadvantages, as follows:

- SU8 can be used to build both the micro-pillars and the channels. It can be easily patterned using photo-lithography even when deposited in thick layers [137], although in this case care must be taken to avoid its cracking.
- PDMS can also be used to build the micro-channels. However, PDMS cannot be used for the micro-pillars as it is a very soft material and thus it may bend

Figure 7.15: Schematic illustration of the fabrication process for the polymeric insulating structure & sample holder necessary when the micro-coil chip is cryocooled

(sag under its own weight) when/after the PDMS micro-channel structure is placed over the micro-pillars. Besides, building micro-channels out of PDMS is complicated. It is first necessary to construct a SU8 mould over which the PDMS is poured, then cured, and finally peeled off to define the micro-channels. The advantage of a PDMS micro-fluidic channel is that it can be very easily sealed using another PDMS film: once the PDMS surfaces are

activated in oxygen plasma and then joined, a leakage-proof irreversible seal results.

7.5 Conclusion

The CNT-graphitic micro-coil structure proposed and demonstrated in this work exhibits a larger inductance, and hence, better magnetic performance than its Cu-based counterpart, but it also has a very large resistance and therefore cannot be used as the receiver micro-coil. However, it could be used as the MF emitter in a dual coil micro-probe that would also employ a HAR Cu micro-coil as signal receiver. The larger resistance of these CNT-based micro-coils will, however, have the disadvantage of increased Joule heating, making it difficult to inject high currents. Therefore, further investigation is required to lower the resistance of such CNT graphitic structures. Also, further studies into the effect of the ferrous nanoparticle are also required, eg. to find out how to increase their concentration.

In the second part of this chapter, a totally original structure for cryogenic cooling of micro-coils has been proposed and simulated. When its elements' dimensions are carefully designed, it can ensure that the imaging surface (or the sample holder) is in a very close proximity to the micro-coil, much closer than others reported in the literature, while at the same time, makes sure the temperature of the sample holder is at a viable temperature for any living bio-organism under investigation. This is achieved through introducing double thermal insulation by an air gap & an air flow channel and heat exchange at micro-scale. Exhaustive thermal simulations shows it is possible to keep the micro-coil cooled at cryogenic temperature while at the same time the imaging surface remains above 277 K for quite a long time, long enough to run NMR experiment on the sample. In the proposed structure, the two most influential factors noticed were the air flow rate inside the air channel and the spacer heights. Further studies of the mechanical feasibility of the structure are necessary in order to make sure it will not be distorted at the end of the fabrication process.

Highlights of Chapter 7^{a b c}

- This Chapter gives 2 possible methods of improving the SNR of NMR micro-probes that can be explored further in the future.
- A novel micro-coil was developed using carbon nanotubes (CNTs); the vertically grown CNTs were fused together using acetylene which enabled flow of current along the length of the micro-coils in between adjacent CNT bundles. When measured at low frequency, these micro-coils showed high inductance compared to other conventional micro-coils reported in the literature.
- Another design of a NMR micro-probe was presented in this Chapter that involved cryogenic cooling of the micro-coil to lower the thermal noise while keeping the sample at a viable temperature as well as ensuring good magnetic coupling. The design proposed here is based on the principle of heat exchangers at micro-scale and thermal simulations were done in COMSOL. Initial results show our proposed design with dimensions in the micrometer range achieves good thermal isolation and magnetic coupling compared to similar reported micro-cooling structure for NMR micro-probe whose dimension is in the range of mm. A possible fabrication flow of this micro-probe design is presented using polymers, such as PDMS and SU8, which are Si compatible and at the same time have a poor thermal conductivity.

^a'Fabrication of CNT-based Planar Micro-Coils on Silicon Substrate', Zishan Ali, Kaushik Ghosh, D.P. Poenar & Aditya Sheel; IEEE Transaction on Nanotechnology - *Revised and re-submitted after receiving positive reviewer comments*

^b'Lateral Conduction within CNT-based Planar Microcoils on Silicon Substrate', Zishan Ali, Kaushik Ghosh, D.P. Poenar, and Sheel Aditya; 2017 IEEE 12th Nanotechnology Materials and Devices Conference (NMDC), Singapore, 2017, pp. 83-84.

^c'Design of an NMR microprobe with a cryogenically cooled planar micro-coil in close proximity of biological sample', Zishan Ali Syed Mohammed, Xintong Zhu, Poenar Daniel Puiu, and Sheel Aditya, Proceedings 6th International Conference in Nano-Electronics 2014 (INEC 2014)

Chapter 8

Conclusion

This thesis began with a brief introduction of the MR analytical methods, the micro-probes reported in literature which can be used in such methods for analysis at micro-scales, as well as on the usage of SNR to measure the performance of such probes. It was highlighted that there is no coherent information in the literature about how to design a MR micro-probe. For an easy micro-probe design and to compare setup independent performance of various probes, a novel performance factor P was defined. The components of the P factor were then defined and their values for a few practical designs were calculated using electromagnetic simulations. The detailed analysis of this P factor and how can it be applied to characterize and compare probes reported in literature has been described in Chapter 3.

Next, in Chapter 4 the P factor has been used to study a few proposed micro-probe designs. Unlike most of the probes in literature, the effect of additional elements in the NMR micro-probe structure have also been considered and studied. For example, a so-called mimicking sample holder design was proposed in addition to the generic cylindrical sample holder and then the probe performance of these MR probe designs were compared. The results indicated that the micro-coil with generic sample holder design performs the best. Hence the design of these probes was optimized in the next step. First, the optimal trace width and then the best number of turns for the micro-coils have been determined. Surprisingly, the design optimization revealed that a larger (increasing) number of turns does

not mandatorily translates to a better magnetic performance. The micro-coil with 5.5 turns had the best magnetic performance, which will then deteriorate when further increasing the number of turns. Hence, a 5.5 turns micro-coil with a 25 μm trace width was chosen for the probe design.

Next, the effect of the conductor's aspect ratio on this micro-coil's performance was analyzed in detail using the P factor and compared with that of the micro-coils with 3.5 and 15.5 turns. Furthermore, a novel criterion was introduced for comparing the performance of various structures. It is based on the values of the angle between the B_z component of the magnetic field and the $B_{resultant}$ and indicates what are the maximum and minimum volumes allowed for each micro-probe structures. It was concluded that the micro-coil with 5.5 turns, minimum allowed volume and 1 : 1 conductor aspect ratio performs the best in terms of SNR in a MR experiment, as deduced after comparing the values of the P factors calculated for the various proposed designs. Lastly, a substrate analysis determined how would the Si substrate resistance affect the performance when the injected current has a frequency of 42.58 MHz, the Larmor frequency of the hydrogen nucleus (or proton). This analysis showed that, as expected, a higher resistivity wafer shows a better performance in terms of S-parameters and of Q values.

Chapter 5 describes the fabrication process and the challenges faced in realizing HAR copper micro-coils entrenched in a Si substrate. The key target here was to fabricate low resistance planar micro-coils in trenches realized in Si using a single photolithography step that can be used as signal receivers. The literature review showed that the reported HAR coils were either 3D coils with TSVs that required double (simultaneous) top and backside photolithographic alignment and patterning, or employed thick polymers. In either case, nobody else realized NMR micro-coils in Si trenches. The advantages of using Si as a substrate and a single lithography step to define the HAR Cu coil structure make our micro-coil the first of its kind to be reported.

Next, the challenges associated with filling up such blind HAR Si trenches, and how hydrogen annealing further reduced the resistance of the micro-coils were also presented. These micro-coils were electrically characterized and the resistance values of the HAR micro-coils were measured under SEM using nano-probing. Their low frequency quality factor Q was measured up to 5 MHz. These measured resis-

tance values were then normalised with respect to the conductive cross-sectional area and volume. Comparison with values for other coils reported in literature showed that our micro-coils had the normalised lowest resistance among all the other coils realized in HAR Si trenches.

Chapter 6 reports the fabrication of the micro-coils designed in Chapter 4 by first using copper electroplating. This was followed by copper removal through a combination of Cu CMP, which was optimized after a series of experiments, and wet etching of Cu using sodium persulphate, a novel process described in previous Chapter 5. The electroplating employed here involved time dependent DC electroplating to finally create successful void-free Cu deposition in blind Si vias. Although the trenches for the optimal MR performance have a lower aspect ratio of 1 : 1, filling them up with ECD Cu in a void-free manner was still challenging. This is because the Cu deposition in this case is due to both vertical bottom-to-top Cu growth and lateral growth on the side-walls, between which a balance had to be realized. The electrical resistance and generated magnetic field by these micro-coils were then measured and their variability across 3 different wafers was investigated. These values were also compared with the simulated values in the CST model developed in Chapter 4.

The last chapter discussed two more possibilities to improve the SNR of the NMR micro-probe. One such possible solution is to use HAR micro-coils with CNT-graphitic heterostructure whose measured inductance values are larger than those of similar Cu micro-coils. This ensures stronger magnetic fields generated by these micro-coils, recommending them as potential magnetic field emitters in more complex MR probes. The next solution proposed cryogenic cooling for the micro-coils while at the same time keeping the bio-sample at an ambient temperature by realizing a heat exchanger at micro-scale. The proposed design ensures the micro-coil remains at the very low cryogenic temperature, which reduces the thermal noise, while at the same time keeps the biological sample at a viable temperature. Thanks to the thermal insulation achieved in such an arrangement, the model ensures the sample and the micro-coil are placed as close as possible to provide good magnetic coupling between the two.

In conclusion, this Thesis reports a novel design procedure for micro-coils for NMR micro-probes, solving the challenges faced in their micro-fabrication process

and measuring their electrical characteristics. Finally, two other original structures were proposed which can further improve the SNR of MR micro-probes in the near future.

Appendix A

Initial CST simulations

In order to gain confidence, optimize the FEM parameter setting and reduce the simulation time in CST in subsequent, more complex optimizations, first initial simulations were performed as described below.

A.1 Field comparison

A first series of magnetic simulations were conducted to calculate the magnetic field, its inhomogeneity and filling factor. In the simulations, the top of the micro-coil was considered to be in the xy -plane, hence the magnetic field component along the z direction should be the dominant one. This assumption is supported by simulation results which indicate (as shown in Fig. A.1 for the micro-coil with $N = 3.5$ turns) that B_z is the most significant component. For this reason, henceforth, whenever the MF generated by micro-coil and/or its effects are presented and discussed, it will be assumed that it is the B_z component.

A.2 CST 3D model

Fig. A.2 illustrates the orientation of the DC and time varying MF for the micro-coil-based NMR probe considered in our model. The top of the micro-coil is in the xy plane, with the time-varying magnetic field B_1 oriented along the z direction, which is along the vertical axis of symmetry of the micro-coil. The external DC

Figure A.1: Magnetic field component comparison for the 3.5 turn micro-coil

MF B_0 is oriented along a direction perpendicular to the z axis, in this case along the x axis. Considering this orientation, the flux density of the axial component B_z at a distance z from the center of the N -turn micro-coil is given by [164]:

$$B_z = \frac{\mu_0 \mu_r N I}{2e} \cdot \left(\frac{a_0}{\sqrt{z^2 + a_0^2}} - \frac{a_0 + e}{\sqrt{z^2 + (a_0 + e)^2}} + \ln \frac{a_0 + e + \sqrt{z^2 + (a_0 + e)^2}}{a_0 + \sqrt{z^2 + a_0^2}} \right) \quad (\text{A.1})$$

where $e = Nw + (N - 1)s$, I is the current and a_0 is the internal radius of the coil. and s & w are the spacing between the micro-coil's conductors and the conductor width, respectively.

Figure A.2: Orientation of the dominant MF component B_z generated by a planar micro-coil

<i>Coil turns</i>	<i>Simulated Inductance</i>	<i>Simulated DC Resistance</i>	<i>Calculated DC Resistance</i>
3.5	4.58 nH	0.126 Ω	0.108 Ω
15.5	41.6 nH	1.25 Ω	1.18 Ω
40.5	540 nH	7.18 Ω	6.9 Ω

Table A.1: Characteristic parameters for micro-coils, as obtained from the CST magneto-static simulations of the 3D micro coil models.

A.3 Simplification of the model

It has been observed that the simulations give exactly the same results if we include the silicon substrate along with the micro-coil structure and the connection pads but the simulation time increases exorbitantly. Hence, in order to perform the simulations faster, the silicon substrate was excluded from the models. Further, the coil lengths used here are of the order of millimeters, which are much shorter than the wavelengths even at hundreds of MHz, which is the range for typical values for Larmor frequencies of common elements, such as hydrogen, oxygen, etc. for large B_0 values. For instance, the proton's Larmor frequency at 11.4 T is 485.3664 MHz, while that of deuterium is 74.50652 MHz. Therefore, wave propagation effects are negligible. Consequently, only magnetostatic CST simulations were used to determine the magnetic field.

A.4 Comparison between analytical and simulated model

Let us illustrate the variation of B_z with distance from the micro-coil surface for the previously mentioned designs. Each micro-coil was simulated using the magnetostatic module of CST in order to obtain the magnetic flux density variation when a 1 A current is injected through the micro-coil. Three coils were analyzed, two of which are the smaller coil designs of 3.5 and 15.5 turns embedded in HAR Si trenches, as mentioned in Chapter 5. To further gain confidence and better understanding of the trends of the obtained results, an additional fourth micro-coil with 40.5 turns was also considered. The resulting values are compared in Fig A.3 with those computed using equation A.1. It can be seen that the simulated results are in reasonable agreement with the analytical results but have slightly smaller peak values and are not symmetric about the coil axis. This is because the analytical expression in eqn. A.1 does not consider the thickness of the micro-coil structure and its impact upon the MF distribution, while the simulations using the 3D model consider the thickness of the conductor. Hence, the peak values are a bit smaller and shifted as they occur not at $z = 0$ but at a depth equal to half of the height/thickness of the micro-coil's conductor.

Figure A.3: Comparison of magnetic field variation between as obtained from existing analytical expression and CST simulation model

Appendix B

TSUPREM simulation of oxidation of DRIE trench walls

Prior to employing the alternate oxidation and oxide removal cycle to remove the DRIE trench scallops, 2D simulations were run in TSUPREM-4 to study the effect of such of oxidation and oxide removal on scallops. Essentially, we designed a 2D Si trench wall with scallops and defined the oxidation and removal recipe parameters to be same as those practically used in the fabrication of our devices. While defining the scallop walls, the scallop shapes were approximated as trapezoidal structures. For all the simulations, the VISCOELA model for oxide growth was used which also considers the viscoelastic flow of the oxide during oxidation. The movement of the oxide/silicon interface in this model is two-dimensional (movement is perpendicular to the interface), and the variation of crystal orientation along the interface is also taken into account. The VISCOELA model is also recommended for simulating 2D structures when details of the resulting oxide shape are important or when stress values are required.

B.1 Simulation results

Fig. B.1, shows the initial Si scalloped DRIE trench defined with an aspect ratio of 1 : 1. Thereafter, figures from B.2 to B.8 shows the results after each cycle comprising of an oxidation followed by the oxide removal. The simulations were

run until totally smooth vertical walls were obtained.

Figure B.1: Defining the scalloped DRIE walls in a Si substrate using T-Supreme employing trapezoidal approximations

Figure B.2: Cycle 1

Figure B.3: Cycle 2

Figure B.4: Cycle 3

At the end of the 7th cycle it was seen that the process produced vertical smooth Si walls without any scallops. However, the aspect ratio of the trench has also modified due to widening of the trench width from 10 μm to approximately 14 μm . This change in the shape of trenches is not acceptable in practice, and hence the simulation clearly indicated that it is necessary to restrict the number of cycles to a minimum in order to prevent the change in trench shape.

Figure B.5: Cycle 4

Figure B.6: Cycle 5

B.2 Comparison with experimental results

The results of simulation after two cycles were then compared with the experimental results. For measuring the change in scallop depth/height resulted from simulations, the region was zoomed in and the remaining scallop's magnitude was measured, in the same way it was done for experimental results from the SEM images as shown in Chapter 5. The obtained values and their comparison with the measured values is given in Table B.1, which shows very good agreement between the experimental and simulation results for both scallop depth and scallop width.

Figure B.7: Cycle 6

Figure B.8: Cycle 7

Higher polygonal scallop shapes were also attempted by defining curves in Matlab and importing the corresponding points to T-Supreme but the software failed to simulate these profiles.

Appendix B. *TSUPREM Simulation of Oxidation of DRIE trench walls*

Table B.1: Comparison of T-Supreme simulation results with experimental results after 2 cycles

Process Step	Average Scallop Depth (μm)		Average Scallop Pitch (μm)	
	<i>Experimental</i>	<i>Simulated</i>	<i>Experimental</i>	<i>Simulated</i>
After DRIE	0.41	0.41	0.64	0.64
After 1st Oxide Strip	0.22	0.27	0.67	0.7
After 2nd Oxide Strip	0.08	0.18	0.65	0.68

Appendix C

Initial Cu electroplating experiments

As was mentioned previously, Cu electroplating is another process vital for the realization of a micro-coil, and, therefore, of any MR micro-probe. In order to carry out Cu electroplating, a polypropylene electroplating bath was first manufactured, to hold the Cu electroplating solution, as illustrated in Fig.C.1. In order to build

Figure C.1: Bath used in our electroplating work, made of Polypropylene, for a volume of 8 liters of electrolyte

a copper plating system, the following items are required: Electrolyte, Cu anode bars, bath container, and power supply. The electrolyte provides the metal ions to the target, while the copper anode bar replaces the used copper ions deposited on the target. There are 4 main types of electrolytes that can be used for copper electroplating. They are detailed in Table C.1 below, which gives a clearer description of their main differences. In this project, copper sulphate was chosen as

Table C.1: Different copper plating electrolytes and their key features

Electrolyte type	Properties	Application
Copper cyanide	Highly Toxic, High adhesion, Very rapid plating	Wire plating, thick copper
Copper pyrophosphate	Ductile, High throwing power	Electroforming, Plating on plastic, PCB
Copper sulphate	High throwing power, economical, few waste treatment issues	PCB, Electronics, Semiconductor
Copper fluoborate	Rapid plating	PCB, electronics, Plastics, electroforming

the electrolyte for our experiments, since it was the most common electrolyte used in semiconductor electroplating. In addition, it is also cheap, safe and commonly found. Its typical composition consists of copper sulphate pentahydrate, sulfuric acid, hydrochloric acid and organic additives [91]. Copper sulphate provides the copper ions. The sulphuric acid enhances the conductivity of the solution. The hydrochloric acid provides the chloride ions which improve the uniform dissolution of the copper anode. The additives generally consist of organic compounds that are denominated by the industry as levelers and brighteners. The levelers are needed for electroplating in trenches as they help reduce the probability of void formation. Brighteners are used to increase surface uniformity. In addition, copper sulphate has higher throwing power compared to other electrolytes. Throwing power is defined as the ratio of the thickness plated halfway into the trenches to the average thickness plated on the surface [91]. A high throwing power is important in order to electroplate trenches uniformly without excess plating on the surface. Fig. C.2 shows the realized Cu electroplating system using the previously mentioned polypropylene bath. Once the set-up was completed, experiments had to be done to test the setup system. In these tests the bath composition was as follows: $CuSO_4 \cdot 5H_2O$: 40 g/liter, H_2SO_4 : 225 g/liter. The Si wafers were then sliced into different sizes and weighed both before and after the Cu electroplating.

Figure C.2: The Cu electroplating system with polypropylene bath container

The surface area of each piece of wafer slice can then be exactly calculated as:

$$Surface\ area = \frac{mass/Si\ density}{thickness} \quad (C.1)$$

The density of Si is well known ($2.33\ g/cm^3$) and so is the thickness of the silicon wafer ($625\ \mu m$). The surface area is needed to be calculated very accurately in order to determine the current density required during electroplating. In addition, this method also allows efficient use of Si wafer samples and of plating electrolyte to be used for numerous electroplating tests. The subsequent electroplating tests were conducted with and without plating additives added in the electrolyte, with plating times ranging between 2 to 10 mins. Only DC current was used, without pulsation. After each sample has completed electroplating, it was immediately removed from the bath and immersed in DI water for 1 minute. Thereafter, it was blown dry using a nitrogen gun. The surface finish for the Cu layers resulted from the multitude of these tests are shown in Fig.C.3. It can be seen that not all the samples have shiny surface finishes. Some are blueish, due to improper cleaning after electroplating. The left over $CuSO_4$ solution on the surface crystallized and formed the blueish layers seen in the photo. For a more detailed analysis, the samples were also investigated using SEM. Fig.C.4 shows the layer electroplated when the bath did not include any additives and used a current density $J = 19\ mA/cm^2$. It can be seen that the surface does not look good, it does not have a shiny finish and its surface -as revealed by the SEM photos- is very rough and grainy. It was also easily noticed after plating that the entire deposit, including the seed layer, peeled off after electroplating. Additionally, when wiping the surface of the wafer with a

Figure C.3: Various samples resulted after Cu electroplating with different conditions

Figure C.4: SEM photos of our resulted Cu layer plated without any additives: Zoom in & zoom out top views of the deposited layer (Top & Center); overall view of the electroplated sample (right)

Figure C.5: Cross sectional SEM photos of the Cu layer plated without any additives and a current density $J = 19 \text{ mA/cm}^2$

cleanroom paper, powdery copper deposits could be seen on the cleanroom paper, showing that poor adhesion was indeed a critical issue for this plated layer. The thickness of the layer was also very non-uniform. The largest value was as high as $16 \mu\text{m}$, but the overall average value was of about $7.61 \mu\text{m}$ as shown in Fig.C.5, resulting in an electroplating rate of about $1.522 \mu\text{m/min}$.

Figure C.6: Top view SEM photo (indicating the spot of the EDX measurement) & EDX measurement results of the Cu layer plated without any additives and at a current density $J = 19mA/cm^2$

Fig.C.6 shows the SEM photo and results of the EDX analysis carried out on the same sample. It can be seen that the layer is indeed pure Cu, with some traces of oxygen mostly due to the inherent exposure to environmental atmosphere. A subsequent sample was plated, this time with added additives and with a slightly larger current density of $22 A/cm^2$. It can be seen from the results shown in Fig.C.7 that the surface profile is smoother compared to the first one, although its structure (as revealed by the right-hand SEM photo of Fig.C.7) is still grainy. Moreover, its cross sectional profile is also relatively flatter. The surface finish is also shinier and brighter. This could, however, be also attributed to the fact that the thickness of the electro-deposited copper layer is thinner. The plating rate for this sample was of about $0.428 \mu m/min$. In this case, no peeling was observed, but the surface finishing has turned blueish. This was probably due to the improper cleaning of the sample after the plating, which caused the $CuSO_4$ leftover solution to crystallize on the surface. The EDX results, shown in Fig.C.8, indicate again that the layer was made of pure Cu, although a significant amount of Si can also be noticed, most probably due to the dust resulted when chipping off the sample for SEM. Finally, a last test was carried out at a smaller current density, since the deposition of any layer at smaller deposition rates usually results in better quality. Fig.C.9 shows SEM photos and the EDX results of such a sample deposited with added additives and at a current density of $7mA/cm^2$. It can be seen that, as expected, the thickness of the resulting plated layer is smaller ($2.47 \mu m$), resulting in a plating rate of about $0.247 \mu m/min$. Also as expected, the grains of the film are

Figure C.7: Optical photo and SEM cross-section & surface photos of the sample plated with additives at a current density $J = 22 \text{ mA/cm}^2$

Figure C.8: EDX result and SEM cross-sectional photo (indicating the spot of the EDX measurement) of the sample plated with additives at a current density $J = 22 \text{ mA/cm}^2$

Figure C.9: EDX results and SEM cross-sectional & top-view photos of the sample plated with additives at a current density $J = 7 \text{ mA/cm}^2$

smaller compared to those of the previous samples. Moreover, the thickness of the deposited layer is also more even and more uniform across the sample. However, as it can be seen from the SEM image, the Cu plated film is made up of 3 distinct layers. But the EDX measurements confirmed that all these 3 layers are Cu. The more serious issue observed after all these experiments was that the deposited copper was rather blackish and not at all shiny, with somewhat poor adhesion, especially when deposited at higher current densities. Hence, the next step taken was to clean everything thoroughly with DI water and IPA. Firstly, the copper bar was rinsed using DI water and dried using the N_2 gun. It was subsequently placed for 30 min. in a degreasing solution made using 15% NH_4OH [90,92]. Thereafter, it was rinsed again with DI water and thoroughly dried with the N_2 gun. Secondly, the target was also rinsed with DI water and IPA and then dried thoroughly with the N_2 gun. The plating bath itself was also cleaned thoroughly with DI water and IPA, and was then left on a hotplate at 95°C for 30 mins to ensure it would become completely dry. Finally, the electroplating solution was carefully filtered through a filter paper in a funnel and the filtrate was then used for the electroplating process. After all these steps, electroplating was then conducted with a current value of 0.1 mA. The final results are shown in Figs C.10 and C.11 below.

The average plating rate of the resultant films was of about 0.33 μ /min. The films had very good adhesion to the wafer and did not peel off easily. Similarly, the film was dense, with no porosity or visible granular structure and without any powdery deposits on its surface. In addition, upon wiping the surface with a cleanroom paper, there was no visible brownish coloration on the paper (as was the case with the previous low-quality deposits). In conclusion, these tests highlighted the extreme importance of cleanliness not only for the copper bar or wafer surface, but also for the electrolyte itself. Thorough cleaning and filtration must, therefore, be carried out before and after each electroplating in order to ensure a high quality of the plated Cu film. After electroplating, the electrolyte is again filtered through a filter paper and kept in a tightly sealed container for further use. The copper electrode is also rinsed with DI water and kept immersed in a container filled with DI water for future use. All the other items are rinsed with DI water and thoroughly dried with N_2 and left 15 mins on a hotplate at 95°C for drying before storing.

Figure C.10: A successfully electroplated target after proper cleaning

Figure C.11: SEM photographs of Cu electroplated wafers with a current of 0.1 mA after cleaning. (top: plating time = 30 min, bottom: 90 min)

In conclusion, all these initial tests produced a lot of relevant information useful for the subsequent finding of the optimal Cu electroplating. Firstly and most importantly, our setup worked at different current densities producing deposited copper on wafer surfaces. It became clear that reducing the electroplating rate results in smoother films, with more uniform and evenly distributed thickness across the sample, and without any peeling. Moreover, if high current density electroplating was carried out, bubbling was visible on the target sample. It also became clear that proper cleaning of the sample after electroplating is important to prevent unwanted crystallization on the surface of the plated copper film, degrading the surface finish and maintaining the cleanliness of both the wafer as well as of the Cu anode, all extremely important to produce good adhesion.

Appendix D

Stress analysis of thin films

Before fabricating the micro-coil embedded in the silicon substrate, the mechanical compatibility of the materials and the resulting mechanical properties & behaviour of the final micro-coil must be considered. One major concern is the residual stress of the metal conductors, which -if high enough- is possible to deform the structure of the micro-coil (assuming it would be released from the substrate) and thus interfere with the performance of the device. Even if not released, it is well known that high stress levels of thin films deposited on a wafer can distort the wafer which will become curved. The value of copper's residual stress can be found in the papers of Yoomin Ahn et al. [165] and H.M. Choi et al. [166]. In Yoomin's paper, 3 different plating solutions, detailed in the paper's Table 2.6.1, were used for copper electroplating, at current densities ranging from 10 to 20 mA/cm^2 , in order to examine its influence on the residual stress. The residual stress of the Cu film turned out to be compressive, in the range between 0 to 2000 MPa. Pulsed electroplating was also compared with DC electroplating. It was observed that pulse electroplating of Cu formed layers with lower residual stress, which was attributed to the higher mechanical strength caused by the smaller grain size resulted after pulsed plating.

In Choi's work [166], the Cu films were deposited on the silicon substrate by sputtering, with the working pressure fixed at 1 mTorr and DC bias voltage ranging from 0 to -200V and the observed residual stress turned out to be tensile, ranging from 0 to 400 MPa, dependent on the bias voltage. A lower bias voltage resulted in a more nonuniform, less dense and more porous films with high internal

stress, while sputtering at higher bias voltages resulted in densification and lower residual stress.

Stress characterization of various thin films was carried out as a first preliminary step for this Thesis work in order to study before optimizing the stress-dependent behavior (deformation/warping) of the final wafer at the end of the micro-coil processing. Three key factors would most probably influence significantly the mechanical deformation of the final wafer at the end of the process:

- The built-in stress of the trench-filling electroplated Cu
- The micro-coil parameters, such as the trench depth, trench width, number of turns etc
- The number and type of layers deposited on the front of the wafer after filling the micro-coil trenches with electroplated Cu

The stress of thin films deposited on wafers is calculated based on the wafer's radius of curvature measurement results before and after deposition, thickness and elastic modulus of substrate and thickness of that thin film, using equation (D.1). Thin films were deposited on bare blank test wafers whose curvature radii were measured a priori before deposition, then the specific thin film was deposited on each respective wafer according to the process split, after which the wafer radius measurements were done again using the available Tencor FLX-2320 thin film stress measurement equipment, while the deposited film thicknesses were measured using Filmetrics F20. For batch processes such as LPCVD nitride and TEOS, thin and thick thermal oxide, wafers underwent backside removal of thin films in RIE Oxford Plasmalab80 System before going for measurement of post deposition radius of curvature. For PECVD oxide and nitride processes, only one wafer was deposited for each kind of film.

$$\sigma = \frac{Eh^2(R_1 - R_2)}{6tR_1R_2} \quad (\text{D.1})$$

where σ = the average film stress in Pa, $R_{1,2}$ = the average wafer radius before and after the deposition of the thin film, respectively, in μm , E = bi-axial the elastic modulus of the substrate (1.805×10^{11} Pa for $\langle 100 \rangle$ Si), t = the film thickness in

Appendix D. Stress Analysis of Thin Films

Table D.1: Thin film stress measurement results. The meaning of the parameters is the same as in eqn. D.1

Thin film	#	R_1 [m]	R_2 (m)	t [Å]	Calculated stress σ [Mpa]	Average stress σ_{ave} [MPa]	Std.Dev of stress
LPCVD Nitride	4	-394.69	76.309	2600	764.5	1132.8	89.96
	8	529.499	42.302	2300	1202.0		
	9	-244.043	56.877	2550	1080.6		
	10	-211.598	59.849	2500	1089.8		
	12	-249.016	58.943	2100	1269.9		
	13	-187.529	63.892	2610	1021.9		
PECVD Oxide	15	-320.44	-80.719	10200	-115.5	-115.5	NA
PECVD Nitride	7	-334.29	-608.438	10200	16.8	16.8	NA
Thick Thermal Oxide (FOX)	11	-574.068	-44.892	7700	-338.9	-328.5	10.94
	16	-226.052	-43.26	7150	-332.3		
	17	-110.291	-34.615	8200	-307.3		
	18	-233.858	-43.797	7100	-332.2		
	19	-320.545	-46.192	7100	-331.7		
Thin Thermal Oxide	1	-262.015	-201.309	308	-474.9	-393.9	99.78
	2	-326.194	-234.891	315	-480.8		
	3	-6990	-756.663	325	-460.9		
	5	-372.445	-258.064	475	-318.4		
	6	-627.936	-412.87	450	-234.3		
LPCVD TEOS	1	-131.192	-97.455	4370	-97.4	-108.9	9.48
	2	-139.991	-95.937	4270	-123.9		
	3	-380.84	-188.085	4320	-100.4		
	4	-189.779	-120.065	4350	-113.4		
	5	-304.151	-159.01	4430	-109.2		
Electro-plated Cu	1	-758.246	96.031	80000	18.6	16.7	11.08
	3	-1040	257.395	100000	6.2		
	4	-660.452	39.595	100000	34.0		
	5	-776.198	403.949	60000	8.0		

μm and h = the substrate thickness in μm .

The stress measurement results are shown in Table D.1. It can be seen that, as expected, the difference in stress between thin and thick thermal oxide is relatively small and, again as expected, both are under relatively large compressive stress. Also as expected, the stoichiometric LPCVD nitride exhibits a high tensile stress. The stress in electroplated copper varies with film thickness as well as deposition rate, but despite these large variations, it is generally tensile and of a very low value. This shows that -most probably- the Cu-filled micro-coil trenches will have only a very small contribution to the overall stress & final deformation of the wafer. In this respect, an initial optimization can be done theoretically, using equation

(D.2) which provides the total overall stress for a multilayer structure of thin films:

$$\sigma_{Total} = \frac{\sum_i \sigma_i t_i}{\sum_i t_i} \quad (D.2)$$

where σ_i and t_i are the internal stress & thickness of the i^{th} layer/thin film, respectively. Then, with eqn.(D.2) one can easily determine the thickness of one layer if the stresses in all layers and the thicknesses of all the other layers are known. It is assumed, of course, that the stress levels of Table D.1 do not change with the thickness of the thin film. This is definitely true for the thermally grown oxides, for which the data have clearly shown very similar stress values for both thin & thick oxide layers. Thus, one can easily apply the equation to calculate, e.g., the thickness of a thick oxide underlying a 2500 Å LPCVD nitride layer in an oxide-nitride double film structure. Thus, in this case, using the average stress values from Table D.1, we have $\sigma_1 = 1133$ MPa and $t_1 = 0.25$ μm for the LPCVD nitride top layer, while for the bottom FOX layer we can consider $\sigma_2 = 320$ MPa and $t_1 = ?$ (unknown, to be determined using eqn.(D.2)). For σ_2 , a different value was considered instead of that indicated in Table D.1, in order to try and capture the slight dependence of the oxide film's stress on its thickness, i.e. the calculations will probably provide a thickness larger than that for the FOX films previously used in the stress measurements, hence with a slightly smaller stress, as indicated by the fact that the thin oxide layers have a larger average stress.

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Journals

- 'Fabrication of Silicon Embedded Low Resistance High Aspect Ratio Planar Copper Microcoils', Zishan Ali Syed Mohammed, Poenar Daniel Puiu, Sheel Aditya;
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- 'Design of planar microcoil-based NMR probe ensuring high SNR', Zishan Ali Syed Mohammed, Daniel Poenar, and Sheel Aditya, AIP Advances, Volume 7, 095107 (2017); DOI: <http://dx.doi.org/10.1063/1.5002721>
- 'Smoothing of scalloped DRIE trench walls', Zishan Ali Syed Mohammed, M.A.S Olimpo, D.P. Poenar & Sheel Aditya, Materials Science in Semiconductor Processing, Volume 63, 1 June 2017, Pages 83-89
DOI: <https://doi.org/10.1016/j.mssp.2017.02.006>
- 'Fabrication of CNT-based Planar Micro-Coils on Silicon Substrate', Zishan Ali, Kaushik Ghosh, D.P. Poenar & Aditya Sheel; IEEE Transaction on Nanotechnology - *Revised and re-submitted after receiving positive reviewer comments*

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Other relevant publications

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<https://doi.org/10.1109/TED.2018.2798575>
- ‘Field Emission Properties of SiO₂-wrapped CNT Field Emitter’, by LIM, YU DIAN; Hu, Liangxing; Xia, Xin; Syed Mohammed, Zishan Ali; Wang, Shaomeng; Tay, Beng Kang; Aditya, Sheel; Miao, Jianmin; Nanotechnology, Volume 29(1), p(015202), 2018
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Manuscripts under preparation for Journal

- ‘Modification of Preston’s equation for Cu CMP showing film dependence’, Zishan Ali Syed Mohammed, Sarthak Srivastava, Xin Xia, Sheel Aditya, Daniel Poenar
- ‘Fabrication of silicon embedded micro-coils for magnetic field generation for NMR micro-probes’, Zishan Ali Syed Mohammed, Daniel Poenar, and Sheel Aditya.

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