Low cost miniaturized spectrometer for mid infrared sensing

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LOW COST MINIATURIZED SPECTROMETER FOR MID INFRARED SENSING

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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The contributions of the co-authors are as follows:

- I prepared the manuscript drafts.
- The manuscript was revised by Prof Tan and Prof Lee.
- I co-designed the study with Li Lynn Shiau and performed measurement in NTU and NUS. I also analyzed the data.

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- I co-designed the study with Li Lynn Shiau and performed all the laboratory work in NTU and NUS. I also analyzed the data.
- Chen Nan facilitated with the FTIR measurement in NUS

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- I prepared the manuscript drafts.
- The manuscript was revised by Prof Tan and KaiLiang. KaiLiang provided suggestion for improvement.
- I designed the study myself and performed all the laboratory work in NTU and also analyzed the data.
- Tina facilitated with the optical setup and measurement done in NTU

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Date

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Simon Goh

This thesis is dedicated to my loved ones, my wife, Claire and my
naughty but adorable baby, Emmanuel.

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Summary

Mid-infrared (MIR) spectroscopy is an attractive technology for the detection of molecules. It enables compounds to be identified rapidly. One main issue plaguing MIR sensing is that most equipment is bulky and is often laboratory-based. Hitherto, a miniaturized counterpart is facing several technological limitations: low power requirement, suitable optical filter for field use, uncooled detector operation at elevated temperature and the utilization of an appropriate packaging that confers physical and chemical protection. Because of the limitations, samples have to be brought back from the field for analysis. Often, it is challenging to survey samples with fast deterioration. To address the current limitations, a field operable miniaturized MIR spectrometer is proposed in this thesis. The scope of this thesis covers the fabrication and characterization of filters, mirrors and detectors. Specifically, as an optical filter is considered the heart of a spectrometer, it is given greater emphasis in this work. In particular, interferometric filters are discussed. Interferometric filters are arguably considered to be superior to other kinds of filters.

In this thesis, linear variable optical filters (LVOF) for MIR sensing are fabricated for two different modes of operation. Normal incidence cross-plane LVOF is constructed by sandwiching photoresists (PR) pillars by two Si-SiO₂ distributed Bragg reflector (DBR) coated Si substrates. By using PR with different thicknesses, the transmitted response is theoretically and experimentally proven to be affected by the taper angle. That is, an increase in taper angle results in a larger full width half maximum and greater attenuation in the transmission signal. The concept of substrates mated LVOF is further developed by replacing PR with low temperature deposited SiO₂ patterned

by liftoff in O₂ plasma. Low pillar height variation between samples indicates excellent process control. Complementary holes, tilted at an angle, are etched in the other substrate. The mated LVOF is explored as a volatile organic contaminant sensor. The LVOF has a full width half maximum of 230 nm measured at 3500 nm.

While cross-plane operation is the norm, the addition of a gas cell to the already bulky construction hampers further miniaturization. To address the challenge, in-plane LVOF, fabricated by deep etching on Si wafer, is investigated. To achieve that, low contrast SU-8 PR is patterned on Si with electron beam lithography. It has been qualified that by imposing a 2 hours post-exposure delay, a ten times improvement in resist contrast can be achieved. Thereafter, vertical Si pillars are formed by an optimized reactive etching process. Subsequently, the Si-air DBR Fabry-Perot interferometer and LVOF are subjected to poly-Si deposition. The treatment results in the broadening of Si pillars. By manipulating the increase and decrease in Si linewidth and spacing by 194 nm, respectively, the transmitted peak redshifted by 140 nm. The concept is proposed to repair erroneously made samples. It is further proposed that two wafers with a center cavity, containing the LVOF, is bonded. While the LVOF is fabricated on the bottom substrate, the top substrate contains the emitter and detector modules. Finally, the intracavity space in the wafer packaged LVOF acts as a gas cell.

The in-plane LVOF located on the bottom substrate requires a parallel to the substrate light path. Without waveguides, vertical free space propagated light is generated by the emitter on the top substrate. Therefore, vertically propagated light has to be redirected. Thus, Si (110) plane as an on-chip mirror for 90° light redirection is

demonstrated. KOH wet etching is carried out in the presence of tensioactive Triton X- n ($n = 45, 100$ and 405) molecules. Using contact angle measurement, it is shown that Triton preferentially adsorbs on (110) due to the higher packing density of Si atoms. Shorter Triton can be surface adsorbed due to lower steric repulsion between molecules. On the contrary, due to the presence of ether bonds, the long Triton hydrophilic chain is capable of forming hydrogen bonds with ionic reactants and products. This delays ions transport and slows down the rate of reaction in the following order ($X-45 > X-100 > X-405$). As such, the presence of long chain Triton produces smooth (110) surfaces which is essential for the fabrication of mirrors.

Given that present MIR thermal detectors have a low figure of merit ($FOM < 0.05$), graphene as detector with better FOM (> 1) is investigated. Chemical vapor deposited grown graphene is transferred onto a SiO_2/Si substrate. Subsequently, metal nanoparticles are reduced onto graphene's surface (G-Au, Ag and Pt), assisted by ultraviolet irradiation. The fabricated device shows an increase in the thermoelectric power factor (TEPF). A decrease in sheet resistance is as follows ($G-Au > G-Ag > G-Pt$). While a 25% decrease in the Seebeck coefficient is observed for G-Au due to localized thermal cooling, the system offers a three times improvement in the overall TEPF. The G-Au reveals the highest TEPF amongst the tested metals.

The results shown above suggest new methodologies for cross-plane and in-plane MIR LVOF fabrication. Pillars formed with PR and oxide grant the formation of precise and tunable taper angles. On the other hand, in-plane LVOF allows further miniaturization of compact spectrometers with 2D materials as thermal detectors;

while cavity space can be explored as a gas cell. The concepts and design rules presented in this thesis pave ways for the manufacturing of highly precise fixed filters. The methodology presented can be leveraged upon for the creation of next-generation hyperspectral sensors with enhanced infrared sensitivity.

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1 Introduction

1.1 Motivation

In recent years, scores of negative events, both natural and man-made, have shaken the entire world. For example, rampant release of toxic wastes into rivers and tributaries, volcanic activities around the Pacific ring of fire, fake food produce, substandard pharmaceutical pills, factory fires, security threats, etc [1]. Lacking the right field-deployable detection tool, much time is wasted in bringing samples back to analysis laboratories. Furthermore, the current crisis containing methodology requires careful and selective testing of samples. Although it is effective in determining the situational root cause, such practice is unable to provide a mere more than satisfactory statistical estimate of the immensity of the issue.

Over the past decades, different tools have been designed for the presence detection of chemical molecules. These include, mass spectrometer, gas chromatography, Raman spectrometer, optical spectrometer, terahertz spectrometer and electrochemical sensors as shown in Table 1 [2]. While mass spectrometer provides high resolution and detection, it is costly and sample destructive. Although gas chromatography has high sensitivity, it requires typically long elution time. Moreover, different columns have to be installed for the detection of different chemicals. Raman spectrometer is capable of high precision, non-destructive and rapid sample measurement. Its benefits are often over-shadowed by high false alarm rate. Moreover, alloys and metals cannot be evaluated by Raman spectroscopy. Terahertz spectroscopy is gaining popularity lately because of its ability to penetrate deeper into

opaque materials. However, its use is limited to water-free samples as water is highly absorbing in the terahertz regime. Infrared spectroscopy is a rapid, non-destructive, high accuracy material evaluation tool. It is disadvantaged by the need to be equipped with a suitable infrared transmission window with low absorption. Currently, many ongoing research are focusing on miniaturizing infrared spectrometer for the detection of chemical molecules.

Table 1 show the comparison of various detection techniques

Technique	Advantages	Limitations
Mass spectrometry	Highly accurate High resolution	Destructive High maintenance cost
Gas chromatography	Accurate	Long analysis time
Electrochemical sensor	Highly accurate Highly specific	Single use Affect by humidity and temperature
Raman spectrometry	No sample preparation Fast response	Cannot use for metals/alloys High rate of false alarms
Thz spectrometer	Penetration of opaque material Non-destructive	Short distance use Penetration affected by water content
Infrared spectrometry (IR)	Qualitative and quantitative analysis Repeatable	Indoor use Suitable IR window
Miniaturized IR spectrometer	Simple, lightweight, low cost No calibration needed	Short optical path length

With the advent of advanced microfabrication technology, many of such detection tools can be miniaturized and incorporated into existing detection platforms. These platforms, with a multitude of miniaturized detection units, can be field deployed in “always on” mode, ready to pick up signatures that signal impending threat. One such detection tool is the mid-infrared (MIR) spectrometer. MIR is defined to be between 2.5 – 25 μm . For sensing application, most molecules absorb strongly between 3-5 μm . As shown in Fig 1 below, these molecules include, H_2O , N_2O , CH_4 , CO_2 , etc. Many of the listed molecules within this range are greenhouse gases. As the gases are largely released due to human activities. It is therefore important to be

able to detect them in order to manage the release of such gases into the atmosphere to curb global warming. The advantage of MIR spectroscopy is that all molecules have clear and distinct fundamental vibration signatures in the MIR.

Figure 1 shows the chemical species and their absorption wavelength[3]

Currently, state-of-the-art compact spectrometers operate in the near-infrared (NIR) regime. Unlike MIR, a variety of photodetectors exist to support NIR detection. Some of these detectors can be operated in uncooled mode, rendering it an attractive option for remote sensing purposes. On the other hand, MIR spectrometers are commonly paired up with mercury cadmium telluride (MCT) photodetector array. Major disadvantages of MCT incorporation include high acquisition cost and the strict requirement of liquid nitrogen cooling during operation. This fact cripples the use of low-cost miniature MIR spectrometer for remote sensing.

On a positive note, two-dimensional (2D) materials, with their extraordinary electronic, optical and thermal properties, could be purported as the next-generation photon / thermal detector. When properly fabricated, their performance has been predicted to surpass that of today's detectors. Additionally, with a smaller footprint, more detector array can be packed per area. This could translate to achieving a higher resolution and sensitivity detector unit. Moreover, it has been shown that 2D materials are

sensitive to a small change in temperature even when working at room temperature. This assures that 2D material based detectors can be operated uncooled. As such, this holds promise that miniature low-cost MIR spectrometers can be widely deployed like “stardust” with minimal human intervention for background sensing and beyond.

1.2 Aim and objectives

This work aims to design, build and manufacture an all-in miniaturized mid-infrared optical absorption-based spectrometer using wafer level processes. The intended MIR spectrometer is designed to require low power as well as minimal calibration. Currently, most of the commercially available miniaturized spectrometers are still bulky and costly. To overcome the issues, the future spectrometers have to low power as well as three dimensionally integrated at wafer level. In this thesis, greater emphasis is placed on the discussion to realize wafer level fabricated interferometric based LVOF besides the fabrication of mirrors and MIR detectors.

1.3 Organization of the thesis

In chapter 1, spectrometry techniques, spectrometers are presented and compared. Specifically, optical filters and interferometers and their working principles are discussed. Linear variable optical filter for spectroscopy is introduced. Present methodologies to realize working LVOF are described.

In chapter 2, non-movable linear variable optical filter (LVOF) will be presented. Normal incidence LVOFs are fabricated using photoresist pillars to prop the top mirror

a distance away from the bottom mirror as well as to stick the mirrors together. The study on the effect of a variation in taper angle on optical transmission is carried out. LVOF placement in a microspectrometer package with respect to the location of a detector array will be discussed.

In chapter 3, the LVOF realized in chapter 2 is made to be more robust. In this chapter, thin film SiO_2 deposited on a substrate using high density chemical vapour deposition with photoresist for liftoff. Tilted holes are created in the other substrate by Bosch process. The two substrates are put together to form a LVOF. Its optical performance is evaluated with acetone vapour as volatile organic contaminant sensing.

In chapter 4, the concept of an integrated gas cell is explored. To achieve that, an in-plane Si-air LVOF construction is proposed. During this work, tunability to vertically etched LVOF by linewidth compensation and de-compensation using LPCVD poly-Si and buffered oxide etch to manipulate the Si line width. It is able to red / blue shift the passband depending on process undertaken. It has been shown that the proposed technique is able to tune the fabricated samples for specially targeted applications.

In chapter 5, 45° mirrors etched into Si (110) plane is investigated. The mirrors are important for the realization of on-chip in-plane and normal incidence spectrometers. Special focus has been placed on the utilization of different Triton with varying tail length to manipulate the concentration of hydroxyl ions on Si for etching. In the final part, a mirror for MIR spectrometer is realized.

In chapter 6, the partially completed work on the realization of a 2D material detector is reported. Metal nanoparticle decorated graphene have been characterized and screened. It has been shown that Au functionalized graphene provides the most significant decrease in sheet resistance. In all, a three times improvement in thermoelectric power is reported. The integration of interferometers described in chapter 2,3 and 4 with mirrors and detectors within a wafer level packaging are described.

1.4 Major contribution from this thesis

Major contributions as follows

- 1) In chapter 2, the relationship between LVOF taper angle and transmission passband has been derived and shown experimentally. Excellent control over photoresist heights have been demonstrated on 4" wafer and between sample batches. Later the resist pillars are showcased to adhere to similar mirror coated Si wafers to form a LVOF.
- 2) In chapter 3, low temperature deposition of thick SiO₂ using high density chemical vapour deposition and subsequent liftoff using negative photoresist is demonstrated. Later, technique for tilt etching of holes is carried out using resist pillar deposited on wafer backside. Finally, the lock in place pillar and holes realized the formation of a LVOF

- 3) In chapter 4, the effect of post exposure bake is evaluated and shown that by introducing a delay of 2 hours, well defined near-micrometer sized patterns can be obtained. By subjecting Si pillars created using optimized Bosch process to low pressure CVD (LPCVD) poly-Si at 625 °C, conformal growth of poly-Si is achieved. The decrease/increase in linewidth can blue/red shift the transmission passbands.
- 4) In chapter 5, Triton X-45, X-100 and X-405 are evaluated as tensioactive materials in KOH etchant. The concentration of the Triton in use is varied up to 1000 ppm. It has been reasoned that longer Triton hydrophilic tail blocks the effective arrival of hydroxyl ions on Si surface. Also, Si (110) surface smoothness depends on Triton length. The Si packing formation in Si (100) and (110) affects the number of surface adsorbed Triton, affecting the etch rate and surface roughness.

2 Spectrometer under evaluation and spectroscopy

2.1 Spectrometer under evaluation

This thesis informs readers about the development of an absorption-based spectrometer for the analysis of gas samples. The spectrometer will be operated in transmission mode.

2.2 Introduction to spectroscopy, spectrometer and spectrometry

Broadly, spectroscopy refers to the study of certain radiation energy interacting with matter over a range of wavelength or frequency. Spectrometer is a tool that enables and reports the detection of such phenomenon. Finally, spectrometry is the analysis of gathered data.

2.3 Theory of spectroscopy

Spectroscopy involves the measurement of radiated energy emanated from a subject. Sources of such energy include, electromagnetic wave, thermal de Broglie wavelength, acoustic wave, and dynamic mechanical wave. For electromagnetic wave spectroscopy, the spectrometer setup differs when assessing different energy sources which include, infrared, visible, terahertz, x-ray and ultraviolet. This will be covered in more details in subsequent sections.

2.4 Examples of matter-energy interaction

Many spectroscopic methods have been developed since the discovery of dispersible of visible light with a prism. These methods are capable of detecting a varieties of interactions. A non-exhaustive list of such nature of interactions is summarized in Table 2.

Table 2 shows the different types of spectroscopic methods, their descriptions and examples

Spectroscopy technique	Details	Examples
Absorption	Amount of energy absorbed by a body	Michelson Interferometer
Emission	Release of energy from a body	Fluorescence spectroscopy
Inelastic scattering	Kinetic energy lost through interaction results in wavelength/frequency shift.	Raman spectroscopy
Coherent	Quantized interactions involving molecular excitation where certain parameters like dipoles and magnetic field remain the same throughout	2D coherent spectroscopy

2.5 Infrared Spectrometry

Of special interest, pertaining to chemical signature detection, is in the wavelength range of infrared in the electromagnetic spectrum [4, 5]. Chemical signatures can be obtained from gases, liquid or solids using different apparatus. Therefore, qualitative and quantitative analysis of the analyte can be obtained. Normally, spectrometer acquired data contains information concerning the vibrational frequencies of molecules in question and the associated absorption wavelength. Therefore, IR spectrum is considered the fingerprint of a substance. For this, structural and chemical composition information of a substance constituents can be unravelled [6]. The principle of IR absorption is presented in the following section. It is omitted in this section. Broadly speaking, infrared is classified into the following segments: near infrared (NIR 0.8 – 2.5 μm), mid infrared (MIR 2.5 – 25 μm) and far infrared (FIR > 25 μm).

Fundamental vibration absorption band of chemical molecules are found in the MIR region. In this case, most molecules present in the sample mix can be easily identified. However, broad –OH peak due to atmospheric water moisture at approximately 3300 cm^{-1} shadows the presence of absorption peaks such as –NH₂. Thus, it is always necessary to calibrate the equipment prior to measurement.

Classically, MIR IR technique is useful for identification of pure samples. Today, its usefulness has been extended to identify membrane proteins / DNA in complex biological matrices, complementary solid constituents analysis in conjunction with X-ray diffraction, etc [7].

NIR spectrum can be subdivided into three sections: 4000- 5500, 5500 – 8500 and 8500 – 13500 cm^{-1} . In comparison to the MIR range, NIR range is considerably narrower. NIR spectroscopy analysis differs from that of MIR. Both electronic and harmonic behaviour exists for both vibrational and harmonic / anharmonic molecular movements. NIR absorption comprises combinations and overtones [8]. There are generally more combinations than overtones. Although NIR allows deeper depth probe, broad and overlapping peaks are at times difficult to interpret. Also, the presence of water moisture peaks further hinder data acquisition. Thus it is important to design appropriate post processing tools to extract useful information from noise [9].

2.6 Absorption-based spectroscopy and market forces

Amongst the types of spectroscopy developed so far, the most common spectroscopy technique familiarly used by many is an absorption-based spectrometer. Given its straightforward operation as well as its ability to perform elemental composition analysis, it is utilized in industries ranging from food and beverage (F&B), pharmaceutical, biotechnology to defence. The US market was reported to be worth US\$4.9 billion in 2009 was projected to increase with a cumulative annual growth rate (CAGR) of approximately 5% until 2023 [10, 11]. Some of the major market players include, Perkin Elmer, Rigaku, Hitachi and Brukers.

2.7 Principles of molecular absorption and absorption-based spectrometers:

Benchtop and miniaturized models

Spectrometers are the hearts of spectroscopy data. These spectrometers allow the measurement and comparison of intensity of incidental wavelength package in the presence and absence of analytes. The loss in wavelength intensity is then attributed to absorption by the sample. Generally, the rule of the thumb is that T (transmission), R (reflection) and A (absorption) sums up to unity as shown by Eq 1. In a given system where T and R can be sufficiently measured and concluded, A can be assigned to absorption by the sample.

$$T + R + A = 1 \quad (1)$$

Moreover, the intensity of absorption is governed by the Beer-Lambert Law such as Eq 2.

$$A = \epsilon L[c] = \log_{10} \frac{I_0}{I} \quad (2)$$

Where ϵ is the molar extinction coefficient, L is the length of the sample cell and $[c]$ is the concentration of the analyte. From Eq (2), it can be seen that absorption is proportional to the length of the measurement cell which contains the sample as well as the sample concentration. Thus, the absorption is related to the volume of specific molecules present in the sample cell. It is noteworthy to know that in certain circumstances, nonlinearity between A and $[c]$ would exist.

The absorption spectroscopic phenomenon is attributed to that of molecular vibration. This is where all molecule above absolute zero (0 K) temperature would assume a vibration, rotational or translational periodic movement. Therefore, atoms move in

relation to that of adjacent atoms. In the case of a planar ethene molecule ($\text{CH}_2=\text{CH}_2$), the $-\text{CH}_2$ it displays an assortment of vibrational coordinates: symmetrical stretching, asymmetrical stretching, bending, rocking, wagging, and twisting. Typically, it is accepted that a linear and non-linear molecule has $3N-5$ and $3N-6$ vibration modes, respectively. N refers to the number of atoms present in the molecule. The subtracted numerical digits represent the total number of translational and rotational movements [12].

When a molecule absorbs a quantum of energy, it is excited from the ground state to the fundamental mode. When the next quantum energy is absorbed, it is excited to the first overtone. As more quanta energy are absorbed, the molecule is excited to even higher overtones. The energy absorbed is related to the energy of the incidental light as follows

$$E = h\nu \quad (3)$$

Where E is quantum energy, h is Planck constant and ν is the molecular vibration frequency

Molecular frequencies and absorption intensity are sensitive to changes in the local environment. These external perturbations include concentration, temperature, and pressure. Also, they are subjected to alternations in, local structure, orientation and physical state. When the absorption frequencies across a broad spectrum of wavelength is acquired, the IR fingerprint of the sample is made known. At this moment, the spectrum is compared against the library of reference spectra. This would identify the presence of molecules. On the contrary, specific chemical functionalities can be made known by noting the absence or presence of specific molecules when there is no close match of the spectrum to that of the library.

Although IR spectroscopy is a powerful technique, it could even be challenging for trained spectroscopists to dissect the presence of multiple chemicals in a sample mix. Lately, complex computation involving statistics such as multiple regression and principle linear analysis, etc are widely researched for revealing subtle and even occluded chemical signatures.

Typically, a spectrometer has the following components: light source, optical filter, and detector.

In many standard MIR spectrometer, the prime material choice for thermal emitter is made of silicon carbide [13]. On the other hand, tungsten filament and Si nanorods are employed as an emitter for NIR spectrometer [14]. Optical filter technology will be further elaborated in later chapters. Currently, both photodetectors (PDs) and thermal detectors are in use. MIR PDs are made of wide working spectral range mercury cadmium telluride HgCdTe. Furthermore, lower costs TDs such as thermopile, bolometer, pyrodetectors are alternatives to PDs. NIR detectors are generally PDs as InGaAs, PbS, etc. Depending on the spectrometer's build, other components such as mirrors, beam splitters, waveguides, aperture, lenses, etc would have to be integrated.

So far, a few classifications of spectrometers have been developed. Broadly speaking, they can be segregated into two different categories: Dispersive and interferometric spectrometers.

2.7.1 Dispersive (Diffraction) monochromator spectrometers

Gratings and prisms are choiced main optical components for separating light to its constituent wavelengths as shown in Fig 2. (In this thesis, these monochromators are considered as filters as they enabled the dispersion of light). Since the 1960s, mechanically ruled gratings have been incorporated into many units of spectrometers. With better rulers, ghost effects such as Rowland and Lyman had been eliminated [15]. Woods' anomalies remain a concern when the incident beam is perpendicular to the grating grooves. The phenomenon was described properly by Fano later to be the presence of surface plasmon polariton (SPP) on the surface of the periodical metalized grooved grating [16]. Generally, the grating is ruled into lamellar or echelle grating for specific purposes [17]. The general working principle of an optical grating is illustrated in Fig 2 (Inset) and the general grating design is as follows in Eq 4:

$$\frac{m\lambda}{d} = 2 \cos\left(\frac{\phi}{2}\right) \sin\left(\frac{\phi}{2} - \varphi\right) \quad (4)$$

Where ϕ is the incidental beam angle, φ is the diffracted beam angle, d is the groove spacing, m is the order for wavelength, λ .

Spectral resolution of a diffraction grating monochromator is given to be Eq 5.

$$R = \frac{\lambda}{\lambda_o} = m \frac{W}{d} = mN \quad (5)$$

Where W is the width of the grating groove and N is the number of grooves

Figure 2 illustrates a diffraction based spectrometer which includes light source, diffraction grating as filter, aperture, detector and mirrors. Inset: pictorial explanation of diffraction

Miniaturized diffraction-based spectrometers are one of the first to be fabricated and reported. Being simple with fewer components for assembly, the Czerny-Turner monochromator, as shown in Fig 3, is widely reported as a compact spectrometer [18, 19]. One of the requirements for diffraction based optical spectrometer during operation is the need for volumetric space. The space is needed for proper propagation and focus of light. An example of a compact spectrometer is illustrated below.

Figure 3 shows a Zemax simulated Czerny- Turner of A) existing design and B) proposed astigmatism-free design [18].

Some of the disadvantages associated with the dispersive filter element are as follows. Due to the working principle of a dispersive element, the individual wavelength of light has to be dispersed. This results in a low amount of light reaching the detector. To enhance the signal, a longer scan time is needed. Furthermore, the use of a slit further reduces the light intensity. The slit is required to be small in order to resolve highly complex signature. Light is further attenuated internally given the use of several reflective mirrors.

The above challenges are no longer the major issues in interferometric spectrometers.

2.7.2 Classical Interferometric spectrometers

A classic example of an interferometer is the Michelson interferometer (MI). It was invented in 1887 by Albert Michelson and Edward Morley [20]. The device consists of two mirrors, one that is stationary (M1) and another that could be translated along the axis of light propagation (M2) as shown in Fig 4. Furthermore, it has a beam splitter, light source and a detector. The light source, typically a laser source, emits a beam that is split at the beam splitter. Half of the light travels to M1 while the half travels towards M2. The beams are then recombined and read by the detector. Depending on

mirror alignment and tilt, coherent length of light source and path length difference, regular interference fringes are obtained. An illustration of the Michelson interferometer is shown in Fig 4. To ensure proper tracking of the position of mirror, M2, a dedicated laser alignment is used.

Michelson interferometer is the heart of a Fourier transform infrared interferometer (FTIR). So far, FTIR has been adopted for biological samples testing, gravitational wave LIGO project, amongst many different applications [21, 22].

Figure 4 illustrates a schematic diagram of a Michelson interferometer where the mirror M1 is fixed while the mirror M2 tracks along the direction of the light beam to change the optical path length

Another classic example of an interferometer is the Fabry-Perot interferometer (FPI) as shown in Fig 5. As compared to the MI configuration, the FPI does not have a beam splitter. Similarly, it has two mirrors for reflecting light in the internal cavity. To replace the function of the beamsplitter, one of the mirrors is purposely made to be lossy. In

this case, light is allowed to leak from the cavity in the general propagative direction and is focused by a lens. Eventually, interference patterns are formed at the detector.

The optical phase change of an FPI is according to Eq 6.

$$2d \cos\theta = m\lambda \quad (6)$$

Figure 5 shows a schematic drawing which illustrates the working principle of a Fabry-Perot interferometer

With geometrical analysis and with reference to Fig 5, the path difference (OPD) is seen to be (Eq 7)

$$OPD = 2AB - CD \quad (7)$$

Thus, Eq 6 and 7 can be written together to express Eq 8.

$$2AB - CD = 2 \cos \vartheta = m\lambda \quad (8)$$

Similar to MI, FPI possesses high quality fringes which allows high accuracy measurement to be made. This is possible due to its resolvable resolution as shown in Eq 9.

$$\frac{\lambda}{\Delta\lambda} = \frac{m\pi\sqrt{R}}{1-R} \quad (9)$$

Where m is the mode, R is the reflectance of the mirror and $\Delta\lambda$ is the spectral resolution

And according to Eq 10,

$$m \sim \frac{2d}{\lambda} \quad (10)$$

Due to small angle approximation, Eq 10 can be streamlined to become Eq 11.

$$\Delta\lambda = \frac{\lambda(1-R)}{m\pi\sqrt{R}} \quad (11)$$

It can be seen that in Eq 11, the resolution of the interferometer depends on the mode as well as the fact that $\Delta\lambda$ is larger at longer wavelengths.

With the Rayleigh criterion satisfied, the free spectral range (FSR) of the FPI is made known to be as revealed in Eq 12.

$$FSR = \delta\lambda = \frac{\lambda^2}{2nd} \quad , \text{ since } \cos\Phi \sim 1 \quad (12)$$

Figure 6 shows the working principle of an FPI and the corresponding transmission passband which depends on the standing wave profile [23].

By tuning the resonator gap, d , different wavelengths can be selected as shown in Fig 6. FSR is determined by the spacing between two transmission peaks with the same d gap. Depending on use cases, broad FSR is required for scanning of a range of wavelengths in the case of non-specific spectroscopy. However, FSR can be made narrower for a more specific detection. One thing for sure is, FSR is determined by propagation mode, m . This would mean that, at lower m , peaks are generally broader with a larger FWHM. Usually, higher modes improve FWHM, but the filter is limited by a narrow FSR.

2.7.3 Miniaturized interferometric spectrometers

Given the favorable and ever-improving microfabrication techniques, previously bulky and heavy sensors and detectors are being made smaller. With a small footprint, these microelectromechanical systems (MEMS) can be incorporated directly into devices for real-time tracking, measurement and reporting. Many such MEMS are made using CMOS-compatible wafer level processes. Recently, a broad area of interest includes artificial intelligence, deep learning, machine learning, memory, processes, communication, wireless networking, biomedical and photonics.

An example of a miniaturized MEMS FPI filter fabricated by Infratec GmbH is as shown in Fig 7. The wafer-wafer bonded microfabricated electrostatic operated FPI (Fig 7A) was mounted onto a pyroelectric single element thermal detector. Each mirror layer has already been coated with the desired DBR layers. The unit was then assembled on a TO can (Fig 7B).

Figure 7 shows the A) schematics of a MEMS FPI, B) an assembled FPI module on a TO package and C) tested working range of the FPI [24].

Despite being made smaller than before, the filter is capable of high finesse transmission passband with broad FSR. The working principle of a MEMS FPI is as such: a voltage is applied across the top and bottom mirror. Similar to a parallel-plate capacitor, the electrostatic actuation force causes the distance between the top and bottom mirrors to decrease. The mirror layers are hinged to the rigid substrate by means of stiffness regulated cantilevers. One important consideration is the effect of pull-in at reasonably high driving voltage. During pull-in, the top and bottom layers collapses inwardly resulting in stiction and / or permanent damage to the unit. If the FPI has not been driven beyond pull-in voltage, the unit can be actuated continuously until total failure. The working conditions of an electrostatic MEMS FPI can be designed by the following rules

By balancing the electrically induced forces with the countering mechanical response modeled by springs at equilibrium as can be seen in Eq 13. (To cite Foundation of MEMS)

$$F = 0.5 \frac{\epsilon A}{(d-x)^2} V^2 = kx \quad (13)$$

Where A is the area of the parallel plate, d-x is the travel distance. Eq 13 can be solved for the maximum travel distance until pull-in shown in Eq 14

$$x = \frac{d}{3} \quad (14)$$

Eq 15 could be then derived by substitution Eq 14 in Eq 13 for the maximum working voltage

$$V = \sqrt{\frac{8}{27} \frac{k d^3}{\epsilon A}} \quad (15)$$

As shown in Fig 6C, each FPI has a working range of up to 1.3 μm . As described by Eq (15), the operating range depends on 1) maximum voltage before pull-in and 2) design of blocking range by DBR.

Apart from electrostatic actuated FPI, thermal actuated FP have been fabricated as well. Principally different, thermal FPI relies on joule heating and subsequent thermal expansion to achieve actuation [25]. Although large travel distance can be achieved, thermal FPI suffers from a slower response than electrostatically actuated FPI.

2.7.4 Linear Variable Optical Filter (LVOF)

Despite being robust, both MI and FPI contain moving parts that require precise movement tracking and special care to prevent pull in, respectively. In this light, it is relatable that rugged, low maintenance cost miniaturized and long service life spectrometer should be constructed with robust materials that would not jeopardize sensing operation in any way.

Therefore, LVOF has been actively pursued as a rugged, fixed mirrors alternative to FPI. The LVOF, although at first look, appears different from an FPI, are designed using the same set of approximation. An example of parallel-plate LVOF FP approximation is shown in Fig BBB. Using reasonable boundary considerations, that is, mode of propagation, $m < 3$ and reflectivity, $R > 95\%$, FPI model can be used for LVOF approximation [26]. At $m > 3$ as well as $R < 95\%$, Fizeau approximation should be undertaken [27]. Although more complicated, Fizeau approximation is able to account for intensity loss due to the introduction of a taper angle. One significant difference between FP and Fizeau approximations is that the passband transmission at higher wavelength is always lower than that of shorter wavelength counterparts. This effect is typically known as the “walkaway” [27]. In the case that $m < 3$, Fizeau approximation can also be utilized. It is noteworthy to know that those approximations do not account for light absorption, reflection at Si substrate- air interfaces. Moreover, fabrication errors could lead to a shift in passbands as well as broadening of transmission peaks. Therefore, some authors chose to use the simpler approximation purely or design purposes only.

Figure 8 shows the schematic illustration of an LVOF with a detector array positioned directly below the filter. Specific light wavelength is selectively transmitted through the LVOF which depends on the resonator gap, L .

As shown in Fig 8 above, an LVOF is first presented as a triangular shaped block. The top mirror is tilted with respect to the bottom mirror. The angle between the mirrors is denoted as α . By merit of FP approximation, parallel plates, designated by the rectangular blocks, are used to instill parallel-plate top and bottom mirrors. Apart from mirror reflectivity and mode, it can be observed that the taper angle could have an effect on the accuracy of this model as well. Smaller α would ensure that the top slope mirror is approximated as much as possible by the rectangle. In the case of a large angle, an appropriate increase in the number of rectangular blocks have to be put in place.

LVOF, a modified fixed-fixed Fabry-Perot structure, does not require movable components for wavelength scanning. Rather, lateral movement along the length of

the filter is sufficient to select a different passbands. For effective measurement, an LVOF is always coupled with a detector array. The periodical absorber or active centers on the detector would detect signal transmitting through different passbands which depend on the length of the cavity, L . One essential element in an LVOF spectrometer setup is the need for generating a collimated incidental beam. Given the lack of fabrication tools for geometrical lens fabrication in NTU, the collimator lens is not realized in this dissertation. However, the general design and simulation of a lens will be discussed in a later chapter.

2.8 Comparing different optical interferometric filters

An attempt to compare the different optical filters that could possibly be incorporated in a microspectrometer package. As mentioned earlier, MI, FPI and LVOF are some of the most promising candidates given their fabrication demands, general reception among users and manufacturers as well as their ability to support end applications [28-30]. A comparative table between MI, FPI and LVOF is shown in Table 3.

Table 3 shows a comparison between MI, FPI and LVOF

	MI	FPI	LVOF
Tuning range	Broad	Narrow	Narrow
Resolution	High	High	High
Technique	Electrostatic	Electrostatic	Fixed
Principle	Optical path length difference	Resonator length	Resonator length
Mirror	Reflection only	Reflection and transmission	Reflection and transmission
Fabrication requirement	Flat mirror and precision tracking	Cantilever	Taper angle
Noise	Insensitive to source noise	Sensitive	Sensitive
Vibration sensitivity	Yes	Yes	No
On-chip fabrication	Difficult	Some difficulty	Easiest
Ownership Cost	High	Moderate	Low

MI = Michelson interferometer

FPI= Fabry-Perot interferometer

As described in Table 3, MI is capable of a very wide scanning range. Typically, a benchtop FTIR MI has an operating range from 2.5 – 25 μm . on the flip side, FPI and LVOF, due to design limitation, the operating range is generally between 500 nm to a few microns. However, the tuning range of FPI and LVOF is always tailored and targeted for specific applications. This eliminates the need for a long tuning range. As illustrated in Table 3, both FPI and MI are disadvantaged by their susceptibility to mechanical vibration due to the presence of tunable mirrors. This also poses a

significant fabrication challenge for a micro-sized package. For LVOF, overall packaging is much simpler as the mirrors are fixed and the filter is typically affixed on top of a detector linear array. A clear advantage of an LVOF is that it is not prone to vibration issues, allowing it to be mounted on any vehicle. This also means that an LVOF powered microspectrometer can be produced cheaper with lower ownership costs.

For FPI and LVOF, depending on needs, there could exist the need for out-of-band suppression. The phenomenon of out-of-band could be visualised in subsequent chapters 3-5. To accomplish that, some techniques have been developed and are widely adopted. Typically, bandpass filters can be incorporated into the optical filter design. Multiple alternating dielectric high and low refractive index layers ($\lambda/4$) and gaps ($\lambda/2$) would be presented as a vertical stack. By overlapping the bandpass filter operation wavelengths, a narrow bandpass can be achieved. Furthermore, the use of fibre Bragg grating design have been reported to apodize the output signal. The aperiodic grating can be used to selectively reject unwanted transmission signal. The Bragg grating is capable of high attenuation (~30 dB) coupled with relatively broadband operation (~200nm) [31].

In all, LVOF optical engine use in a microspectrometer package is highly advantageous. Thus, this dissertation is presented on LVOF design, construction and characterization. In the subsequent section, the design of an LVOF is presented.

2.9 LVOF: Background

LVOF construction and design are based largely on that of the F-P principle. The main difference between an FPI and LVOF is that the mirror pair in an FPI is constructed

parallel to each other. For the latter, both mirrors are fixed and one of the mirrors is tilted at an angle with respect to the other. In order to tune the transmission passband, the gap between the mirrors is modulated by electrostatic tuning. For LVOF, different passbands are achieved by spatial translation along the length of the filter.

The design and fabrication of an LVOF can be further segmented into a few parts.

- 1) Design of the mirror: metal, metal-dielectric, dielectric-dielectric, plasmonic, others
- 2) Design of the resonator

2.9.1 Metallic mirror

For the design of the mirror, it depends largely on the materials to be deposited. Traditionally, full or partial metallic mirrored films have been reported [32]. In this case, a blanket deposition of metal coating of specific thickness is done by electron beam deposition, evaporation or sputtering. Metallic coating enables one to achieve broadband reflection with excellent reflectivity >95% even in the infrared regime. Common metals reflectivity are plotted against wavelength are plotted in Fig 9 [33]. However, due to high reflectivity in the cavity gap, the transmission intensity is generally low. This results in the need for longer integration time to improve the signal. Therefore, there is a shift to other types of mirrors as described below.

Figure 9 shows the reflectivity of common metals plotted against wavelength ranging from ultraviolet to infrared. (Adapted from [33])

The reflectivity of the metal species depends on the extinction coefficient value. In this case, the amount of reflectance depends on the excitation frequency, ω , with respect to the metal intrinsic plasma frequency, ω_p . In this case, ω_p is dependent on the metals electron density. When $\omega < \omega_p$, and $\varepsilon < 0$, then reflectivity will be close to unity ($R=1$). When $\omega > \omega_p$, and $\varepsilon > 0$, which corresponds to $k=0$, reflectivity decreases. Now, the reflectivity is described as $0 < R < 1$. At higher than $\omega > \omega_p$, the metal is transparent to the incidental light. Typically, such transparency is observed in the ultraviolet region.

Material absorption of light can occur resulting in 1) electron excitation from valence band to an unoccupied conduction band and 2) lattice vibration. Generally, mirrors

are typically made of d-band metals. With Cu metal as an example, when excited by a 2 eV incident light, the d-bands electrons are excited to the conduction band. Light of energy 2 eV corresponds to a wavelength of 620 nm. Because of that, copper appears to have a red hue.

2.9.2 Dielectric-metal and dielectric-dielectric mirrors

Instead of a single layer of metal coated mirror, both dielectric-metal and dielectric-dielectric mirrors have been reported [33]. For dielectric-metal mirror, a multilayer stack of [metal-dielectric]_n – substrate (n being the repeating number of metal-dielectric layers) had been reported to improve the quality factor of the intended mirror [34]. Depending on the construction thickness of the various layers, the refractive index can be manipulated. For example, when the thicknesses of the layers are subwavelength, a negative real refractive index can be obtained [35, 36]. The design of the metal-dielectric layer can be designed using the following equations which described the effective tensors in Eq 16 and Eq 17. To achieve hyperbolicity, $\epsilon_{\perp}\epsilon_{//} < 0$.

$$\epsilon_{\perp} = \frac{m \frac{d_m + \epsilon_d d_d}{d_m + d_d}}{\epsilon_m + \epsilon_d} \quad (16)$$

$$\epsilon_{//} = \frac{\frac{d_m + d_d}{\epsilon_m + \epsilon_d}}{\epsilon_m + \epsilon_d} \quad (17)$$

Such construction has also been explored for many applications such as the design of waveguide and fiber-based lasers [37]. Despite the different use of terminology which depends on the fields the readers are in, the metal-dielectric metasurface is a class of hyperbolic metamaterial/surface [38, 39]. Typical metal-dielectric configurations are shown in Fig 10.

Figure 10 shows the typical metal-dielectric construction. A) layer by layer, b) lens, c) fishnet with nanohole array, d) nanorod, e) surface micromachined pyramidal-shaped and f) graphene-interlayered layer by layer [39]

2.9.3 Plasmonic mirror

Lately, the plasmonic-based mirror is gaining popularity [40, 41]. This is likely a case of a better understanding of harnessing the effect of surface polaritons [42]. One advantage of the utilization of the meta-atom unit cell for plasmons generation is that the passband transmission intensity is dependent on the design of the nanohole array [43]. Thus, the wavelength selection depends on its period and diameter of the nanohole. The former would decide on the specific wavelength while the latter affects the intensity of the specific passband intensity. Although larger diameter holes are preferred, the wavelength selection specificity diminishes with a change in the diameter [44]. As mentioned, one main disadvantage of the described method is that the mirror allows a narrow wavelength to pass through. This is highly undesirable for broadband applications (> 500 nm) [45].

2.9.4 Dielectric-dielectric mirror

Dielectric- dielectric mirror is commonly known as the distributed Bragg reflector (DBR). In this instance, the selected wavelength transmission or reflection profile depends largely on the materials for the dielectric materials [46]. Typically, a high refractive index layer is always paired up with a low refractive index layer. Typically, high refractive index [H] layer materials are silicon (Si), germanium (Ge), etc while low refractive index [L] materials are, air, SiO₂, etc. The construction of a DBR generally requires the fulfillment of the quarter-wave requirement [47]. The formula for the quarter-wave stack is as follows in Eq 18.

$$n t = \frac{m\lambda}{4} \quad (18)$$

Where n is the refractive index, t is the thickness of the thin film, m is the propagation mode and λ is the interested passband. While the relationship describes the stipulated passband for an FPI, the formulation is overly general. It has to be used in tandem with the descriptor of a half-wave as shown in Eq 19.

$$n_c t_c = \frac{m\lambda}{2} \quad (19)$$

Where n_c is the refractive index, t_c is the thickness of the thin film, m is the propagation mode and λ is the interested passband. Eq 19 is used for the design of the resonator cavity sandwiched in between two DBRs.

2.9.5 Tapered resonator design

The merit of an LVOF belies on its tapered wedge configuration. In a typical LVOF construction, the top mirror set is tilted at an angle with respect to the bottom mirror set. In this setting, the resonator length changes along the length of the filter. Thus, it allows the selection of different wavelengths of light at a specific section of the filter. It

should be noted that, like an FPI, multiple wavelengths can be selected in tandem. Therefore, it is imperative that proper design of the resonator and DBR (FSR) to be carried out. This would assist in preventing the issues of overlapping transmission peaks in the operating range.

An example of an FDTD simulated transmission passband is as shown in Fig 11. During the simulation setup, the top mirror set is placed parallel to the bottom mirror set. This is similar to the FPI configuration. It can be seen that as the gap between the mirrors widens, the passband redshifted. Also, another prominent issue is that the FWHM increases at a longer wavelength. Similar effects are observed in fabricated LVOF and will be discussed in later sections.

Although LVOF modeling is a well-accepted, simple and logical approach to simulate the response of an LVOF, it has some disadvantages. These disadvantages include areas such as [48], 1) The inability to compensate for the “runaway” lossy light effect due to the taper angle, 2) Attenuation of transmission intensity for longer pass wavelengths.

Figure 11 shows an FDTD simulated transmitted passband based on FPI principle with varying resonator gap

2.9.6 Transfer Matrix Method (TMM)

In a typical FPI or LVOF DBR, a multilayer stack thin film material possessing different refractive index is expected. Given that light incident vertical or at an angle α with respect to the surface normal, a one-dimensional stratified model can be used. One assumption that is presented here is, the layers must be non-homogenous with uniform and constant refractive layers within each thin film layer. A schematic illustration of such design is shown in Fig 12. Normal incidence is presented in Fig 12. This is presented as vertically stacked FPI and LVOF are preferred mode of operation.

Figure 12 shows an illustration of a multilayer, non-homogenous build-up of a DBR. The notations show the electric field at the interfaces of materials with different refractive index

With reference to Fig 12, the notations in use are defined as follows. E represents the vector of the electric field in the material. The superscript denotes the directionality of the field such, the subscript describes the specific layer's refractive index. The use of the prime is reserved for the notation used on the right-hand side only.

In this case, the summation of a pair of the electric field vector (E_{total}) in any medium can be generically written as such

$$E_{\text{total}} = E_{x+} + E_{x-} \quad (20)$$

Taking the interfacial electric field between layers m^{th} and $m-1^{\text{th}}$, the field amplitudes observed in Eq 21 can be written in the form of a matrix.

$$\begin{pmatrix} E_{m-1}^+ \\ E_{m-1}^- \end{pmatrix} = \mathbf{D}_{m-1}^{-1} \mathbf{D}_m \begin{pmatrix} E_m'^+ \\ E_m'^- \end{pmatrix} \quad (21)$$

Where the $\mathbf{D}_{m-1}$ and $\mathbf{D}_m$, both dynamical matrices represent the complex expression of the Fresnel reflection and transmission. In this case, they can be separately expressed as Eq 22

$$D_{m-1}^{-1} = \frac{1}{t_{m-1,m}} \quad (22)$$

And Eq 23,

$$D_m = \begin{bmatrix} 1 & r_{m-1,m} \\ r_{m-1,m} & 1 \end{bmatrix} \quad (23)$$

Thus, Eq 21 can be conveniently expressed as Eq 24 with the expanded D_{m-1} D_m product with a [2 x 2] matrix

$$\begin{pmatrix} E_{m-1}^+ \\ E_{m-1}^- \end{pmatrix} = \frac{1}{t_{m-1,m}} \begin{bmatrix} 1 & r_{m-1,m} \\ r_{m-1,m} & 1 \end{bmatrix} \begin{pmatrix} E_m'^+ \\ E_m'^- \end{pmatrix} \quad (24)$$

On the other hand, the amplitudes of the electric fields at the $(m-1)$ th bulk layer can be expressed as in Eq 25,

$$\begin{pmatrix} E_{m-1}^+ \\ E_{m-1}^- \end{pmatrix} = \mathbf{P}_{m-1} \begin{pmatrix} E_m^+ \\ E_m^- \end{pmatrix} \quad (25)$$

Where $\mathbf{P}$ is the propagation matrix in the bulk $(m-1)$ th layer

In this case, $\mathbf{P}$ can be expanded to be a [2 x 2] matrix with the following terms in Eq 26

$$\mathbf{P}_{m-1} = \begin{bmatrix} e^{i\delta_{m-1}} & 0 \\ 0 & e^{-i\delta_{m-1}} \end{bmatrix} \quad (26)$$

Where $\delta_{m-1} = 2\pi\sigma n_{m-1}d_{m-1}$. δ_{m-1} represents the phase change in accordance to the material thickness of the bulk $(m-1)$ th layer, σ is the wavenumber of the incidental ray, n is the refractive index and d is the thickness

Therefore, Eq (25) can be expressed as

$$\begin{pmatrix} E_{m-1}^+ \\ E_{m-1}^- \end{pmatrix} = \begin{bmatrix} e^{i\delta_{m-1}} & 0 \\ 0 & e^{-i\delta_{m-1}} \end{bmatrix} \begin{pmatrix} E_m^+ \\ E_m^- \end{pmatrix} \quad (27)$$

Finally, the system TMM methodology could be used to elucidate the overall field amplitude of all the multilayers

$$\begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix} = \mathbf{D}_0^{-1} [\prod_{m=1}^N \mathbf{D}_m \mathbf{P}_m \mathbf{D}_m^{-1}] \mathbf{D}_{N+1} \begin{pmatrix} E'_{N+1}^+ \\ E'_{N+1}^- \end{pmatrix} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} \begin{pmatrix} E'_{N+1}^+ \\ E'_{N+1}^- \end{pmatrix} \quad (28)$$

2.10 Miniaturisation of optical microspectrometer as gas sensors

Industrial emission has been a major worldwide problem for many countries. These toxic chemicals are often released into the environment by illegal activities without regard for the health and safety of human and environmental health [49]. This situation is particularly grim for developing countries where laws are often difficult to enforce due to poor enforcement control. It is a known issue that exposure to many such chemicals are detrimental to human health. These effects are often chronic and have been shown to contribute to early mortality.

Although a proper framework for law enforcement is critical to stem environmental pollution, the need for monitoring tools is equally important. Some of these tools, gas chromatography with mass spectrometry, infrared spectrometer, terahertz spectrometer, etc. Among those tools, infrared (IR) spectroscopy technique has been proven to be the next-wave low-cost, easy field deployment equipment with potentially low setup cost. Given the easy adoption of the associated system, IR systems have been readily deployed a sensors network to support Industry 4.0 [50], indoor and outdoor pollution tracing and quantification [51, 52], smart cities and living such as human pedestrian detection [53].

Linear Variable Optical Filter (LVOF) and Fabry-Perot Interferometer (FPI) are commonly employed optical engines for the detection of analytes which include gases, liquids and solids. Typically, LVOF and FPI have been reported for the detection of gases in NIR and MIR ranges [54]. Moreover, commercial products which include compact spectrometers have been manufactured [55]. Many of such devices have high ownership cost due to low manufacturing yield imposed by high technology demand [56]. Therefore, the current challenge for LVOF and FPI is to further miniaturized into a smaller footprint package that is vibration safe and can be manufactured by existing standard manufacturing tools.

2.11 Normal incidence LVOF

Principally, the LVOF top mirror is tilted at a small angle with respect to the bottom mirror. This creates a varying resonator length along the length of the filter. The filter is then mounted directly on a filter array. In this configuration, collimated broadband light will be selected by the design of the Bragg mirror and the resonator length. Therefore, each detector element on the linear detector array will “see” a narrow range of wavelengths. This is by far the most commonly adopted optical spectrometer configurations. Normally incidence miniaturized LVOFs will be shown in chapters 3 and 4.

2.12 In-plane LVOF

While most spectrometers are constructed to receive normal incidence light, the vertically stacked configuration require a large headspace. Undesirably, it translates

to a large volumetric space requirement. For further miniaturization of an on-chip spectrometer, a radical transformation to the overall design has to be carried out.

A viable solution to overcome the mentioned is to fabricate an in-plane LVOF with the bulk micromachined cavity as the gas cell as demonstrated in chapter 5. A highly reliable tool for bulk micromachining is the deep reactive ion etching (DRIE). The dry process was perfected in the 1990s to replace certain wet etching process [57, 58]. As compared to wet etching, DRIE does not depend on crystal orientation and offers excellent pattern transfer without the need for mask compensation [59]. Widely considered as an “IC- compatible” process, since its recognition as a process tool, DRIE has been utilized for the fabrication of micro (Opto)electromechanical systems (MEMS, MOEMS). To a large extent, the introduction and development of the DRIE process have revolutionized many microfabrication techniques and processes [60]. Some of these areas of interest include on-chip accelerator, gyroscope, bulk micromachined mirrors and cantilever and Fabry-Perot optical interferometric filter (FPI) [61-65]. So far, bulk micromachined FPI and LVOF have been demonstrated [66].

DRIE is a highly anisotropic etching technique. However, depending on the level of process optimization, there is a chance that the etched structure dimension deviates from the original design [67]. On-chip optical design, specifically, in-plane optical filters, are heavily dependent on the quality of the vertical etching step [68]. Specifically, the transmission or reflection profile depends on the line width and line spacing [69]. If a deviation from the design pattern(s) occurs, transmission and

reflection profiles will also deviate from expected. Typically, the peaks might 1) red or blue shift and 2) intensity will increase or decrease depending on the severity of the situation. Typical challenges pertaining to vertical etch are as follows. 1) Suboptimal lithography step preceding etching process, 2) Under-optimized DRIE process. Under ideal conditions, photoresists (PR) patterned on substrate would form a vertical side slope (“digital” sidewall). However, it is very common for PR to reflow during the hard bake step [70]. This would result in the PR forming a positive slope. Now, the volume of on-site resists is no longer consistent across the entire area. That is, there will have more resist in the center than at the boundary. Such a profile can be modeled by Young’s equation, Eq 31. During etching, PR is removed together with the substrate albeit at a slower rate [71]. As the etching step progresses, the PR covered area decreases due to PR loss at the edge. Eventually, the overall linewidth will be less than that from design. One probable method to resolve such an issue is to estimate the amount of linewidth loss per etching time. Then, the iteratively-found parameters are used for photomask compensation [72]. Although practical in nature, it is an expensive process where photomasks have to be made to obtain the “perfect” desired pattern parameter. Also, the PR pattern can be transferred onto a hard mask such as SiO₂. Typically, oxides are etched using a non-Bosch process which increases the difficulty in achieving a highly vertical etch profile to preserve the intended linewidth [73]. Finally, metal masks made of aluminum is an attractive low etch rate mask for deep etching [74]. However, it is prone to micro-masking effect as well as the fact that not all foundries accept metal masks for DRIE.

To overcome all the possible errors incurred during the fabrication of an in-plane LVOF, a linewidth compensation step will be introduced after the deep etching step.

As it can be seen in chapter 5, by using poly-silicon, the overall linewidth can be tuned in accordance to the thickness of the poly-Si. Furthermore, by manipulating the poly-Si deposition time, LVOF with different working range can be obtained.

2.13 Conclusion

This chapter presents a broad overview of the types of spectrometers. These spectrometers, which are founded on different principles, can be useful for the complementary quantification and qualification of unknown samples. A comparison was made between commonly-utilized interferometric spectrometers. LVOF is deemed to be suitable for use in high vibration applications as it is mechanically robust. Finally, design parameters concerning distributed Bragg reflectors are mentioned in tandem with the derivation of the transfer matrix method.

3 Normal incidence Die Attached Linear Variable Optical Filter for Volatile Organic Contaminants Detection

3.1 Motivations

Different methodologies have been explored for the fabrication of the LVOF component have been reported. These techniques include the use of shadow masking with controlled translation and rotation during electron beam deposition as well as reactive sputtering [75, 76]. One advantage of the deposition method is that it is a well-established process adopted by the optics coating industries [77]. On the flip side, the method is disadvantaged in the following areas:

- 1) Frequent mask replacement due to film accumulation
- 2) Small sample size per run
- 3) Redesigning of mask to complement new designs

Given the stringent need for the taper angle formation, a simple, robust and reliable must be developed. In the following sections, a new method for milli-degree taper is proposed.

In this instance, the top mirror is elevated a distance from the bottom mirror by photoresists (PR) pillars. One advantage of this method is that the PR height can be precisely controlled by modulating the spin speed. Thereafter, by subjecting the PR to a temperature above its glass transition temperature (T_g), the PR can function as an adhesive to bond the mirrors together.

3.2 Methodology

Silicon (Si) and silicon dioxide (SiO₂) thin films were alternatively deposited onto an isopropanol-acetone triple cleaned 6" Si wafer. As shown in Fig 13, a layer of SiO₂ was deposited by plasma-enhanced chemical vapor deposition (PECVD). Following that, Si was sputtered using a 3" 99.999% Si target. The deposition steps were repeated once more to attain a profile of Si substrate – oxide – Si - oxide – Si. Thereafter, half of the wafer was mechanically diced into samples of dimension 10 mm x 10 mm. The rest were diced to dimension of 8 mm x 5 mm. In subsequent sections, 10 mm x 10 mm samples are designated as bottom substrate while 8 mm x 5 mm substrates are later known to be top substrate.

The bottom substrate was spin-coated with a layer of PR (In this case, PR in used were AZ 5214E, AZ 9260 and AZ 4620). 2 pillars stumps of diameter 400 μm were then lithographically patterned using ultraviolet lithography (UVL).

Subsequently, the top substrate was carefully flipped onto the bottom substrate. The device was then heated on a covered hot plate at 150 °C for 30 mins.

Lithography parameters for the different PRs are as follows.

AZ 5214E – The PR was dispensed and spin-coated at 300 rpm. Then, it was heated on a 105 °C hot plate for approximately 120 s for 2 min. After exposure, it was developed in AZ developer diluted with 2 parts deionized water (DI).

AZ 9260 – The PR was spin-coated at 6000 rpm for 30 s and then baked at 105 °C for 200 s. Subsequently, the PR was developed in an undiluted AZ developer.

AZ 4620 – The PR was thawed at room temperature first. Thereafter, it was spin-coated for 60 s at 2000 rpm. The wafer was then hot baked for 180s at 130 °C. Finally, it was developed in an undiluted AZ developer after exposure.

For ethanol vapor characterization, the setup was carried out as follows. An amount of absolute ethanol was dispensed onto a glass petri dish. Thereafter, the lids were tightly clamped to each other. The petri dish was then placed on a hot plate and heated at 80 °C for approximately 1 – 2 min until all ethanol had vaporized. Finally, the dish was then placed right above that of the LVOF for effective wavelength absorption during FTIR measurement.

Figure 13 reveals a schematic diagram for the die attach fabrication process. A) Si wafer was properly cleaned in acetone, isopropanol and water. B) Deposition of thin film Si and SiO_2 layers via sputtering and PECVD. C) Deposition of PR stumps via lithographic process. D) Stacking of similar DBR-profiled Si-DBR. E) Proposed assembly of the completed die attach LVOF

3.3 Characterization

The surface micromachined, thin film deposited, Si substrate was probed by ellipsometry to elucidate the refractive index, extinction coefficient and the thickness of the associated thin films. Measurements were carried out at 55°, 65° and 75° on a JA Woollam's variable angle ellipsometer (VASE). Atomic force microscopy (AFM) was performed to probe the surface roughness of the deposited DBR. The measurement window per AFM run was 100 μm x 100 μm with scan rate set to 1 Hz. In all, 512 lines were acquired. Field emission electron microscopy (FESEM) was carried out to image the surface and cross sectional profile of the DBR. In order to prevent any charging effect from occurring, the acceleration voltage was pre-set to 5 KV. For the measurement of PR pillar height, the Detak XT surface profiler was carried out with tip traversing the surface at 50 $\mu\text{m/s}$ for a total travel distance of 1000 μm . X-ray diffraction (XRD) was carried out at a grazing angle to obtain maximum surface information from the amorphous Si (a-Si) top layer while minimizing signal from the bulk Si substrate. Raman spectroscopy was conducted with a 532 nm laser source with a measurement readout by the UHTS300 Raman spectrometer from Witec. The transmission profile of the LVOF was probed by a Fourier transform infrared spectrometer (FTIR) with a microscope capability. In this case, an onboard microscope objective lens was used to reduce the aperture size to 100 μm x 100 μm . FTIR measurement was carried out between 2-8 μm .

3.4 Results and Discussion

Lumerical FDTD simulation software was used to facilitate the fabrication of a suitable quarter-wave stack DBR construction [78]. A DBR comprises pairs of alternating high

refractive index layer (H, n_H) and low refractive index layer (L, n_L). In a typical DBR, $[HLHL]_n$ is required for the formation of a reflective mirror surface. In this case, n refers to the number of HL pairs. An increase in HL pairs is preferred for achieving near-digital transmission/reflection profile. However, the increase in HL pairs would result in lower transmission intensity as well as the fact that additional thin film stress could be introduced into the device [79]. Such stress could contribute to early device failure.

A viable solution to design feasible DBR is to construct one with high Bragg contrast. In this case, n_H/n_L value should be as large as possible [80]. In this case, few mirror layers are needed. One typical example would be $a\text{-Si} = n_H$ and $\text{SiO}_2 = n_L$. In this instance, a Bragg contrast of about 2 could be achieved in the mid-infrared region of $3 - 5 \mu\text{m}$. In this work, a [HLH] DBR was constructed to demonstrate the concept of on-chip LVOF.

On the other hand, the design of the half-wave resonator length is of equal importance to DBR construction. In a typical LVOF, the taper angle is generally milli-degree in angle. This allows such LVOF to be modeled as an FPI or a Fizeau interferometer (FI) [27]. The former model which considers the top and bottom mirror to be parallel is significantly simpler than FI. However, it does not account for transmission/reflection intensity loss due to the taper angle. In this case, the FI model would account for the decrease in intensity at longer transmission wavelength. FI model is most useful for reflection (R) $< 95\%$ and propagation mode, m , of more than 3. In this work, both DBR and resonator are designed with $m = 1$ and $R > 95\%$ [26]. The simulated FPI model is as shown in Fig 14. The cavity gap was varied with an interval of $0.25 \mu\text{m}$ from 1.50

to 2.50 μm . It can be observed that by increasing the resonator cavity results in the red-shifting of transmission wavelength. In this instance, the designed LVOF is capable of operating between 3.3 and 4.7 μm .

Figure 14 shows the simulated $[\text{Si-SiO}_2]_{1.5} - \text{Si}$ with resonator gap varying between 1.5 and 2.5 μm

Despite the fact that the model is unable to provide sufficient information concerning transmission intensity change with respect to wavelength, such data is informative at its best. The transmission intensity depends on DBR fabrication integrity, reflection at Si substrate – air interfaces, etc which would affect the ultimate transmission intensity. Thus, it would be more sensible to conduct the experiment (to be described in subsequent sections) physically to elucidate the true nature of transmission characteristics.

X-ray diffractometry was carried out on the deposited a-Si as shown in Fig 15A which shows that the deposited film is highly amorphous. Cross sectional profile of the deposited film can be observed in Fig 15B. The ellipsometric analysis was conducted to study the properties of the thin film DBR as shown in Fig 15E. The data obtained from this ellipsometric was inputted for FDTD computation. Calculated refractive index and extinction coefficient for a-Si layer was projected to be 2.8 and 0, respectively, at $3.5\ \mu\text{m}$ since the light source and detector are designed for measurement up to $1.7\ \mu\text{m}$ [81] and the results obtained is similar to previous reports [82]. The value deviated from that of crystalline Si due to changes in polarizability and atomic density. This relationship is described by the Clausius-Mossotti effect [83]. To prevent complications, one Si – SiO₂ layer was deposited on a cleaned Si substrate. Moreover, a-Si and SiO₂ layers were modeled to be about 350 and 770 nm thick, respectively. To cross check the validity of the ellipsometric results, cross sectional FESEM was carried out. The image measured thin film thicknesses corroborate to that of ellipsometric measurement.

Raman spectroscopy was carried out on a-Si to understand the nature of the sputtered Si. The acquired spectrum is shown in Fig 15E Peaks between 100 and 700 cm⁻¹ were studied. The peaks present corresponded to transverse acoustic (TA) and transverse optical (TO) at 150 and 460 cm⁻¹ [84]. The amorphous nature of the sputtered Si could be inferred by the absence of a peak at 520 cm⁻¹.

Figure 15 shows the characteristics of the sputtered Si layer by A) XRD, B) Raman spectroscopy, C) cross-section FESEM, D) AFM and E) Ellipsometry

AFM was performed to determine the topmost deposited a-Si surface roughness. From the topography data shown in Fig 15D, the calculated root mean square surface roughness (R_q) is 4.1 nm. This translates to an optical flatness of $\lambda/800$.

Conventionally, optical flatness is calculated by dividing the surface roughness by the shortest operating wavelength. Surface irregularities, often measured by Rq , is needed to be kept as low as possible. This is because high surface roughness leads to surface scattering of light contributing to propagation loss and the broadening of FWHM of transmission peaks [85]. Thus, it is always necessary to decrease surface roughness of all interfaces as much as possible.

Photoresists from the AZ – series were used to explore the effects of resist pillar height on taper angle difference and its consequences on transmission profile and intensity. As mentioned earlier, AZ 5214E, AZ 4260 and AZ 9620 were used in this case. Based on the spin coating, exposure and developing conditions, the heights of the pillars measured by surface profiling are as such, 2.5, 5.4 and 9.6 μm for AZ 5214E, AZ 9620 and AZ 4260, respectively. The taper angle of the fabricated LVOF is calculated to be 0.0205°, 0.0442° and 0.0786° when AZ 5214E, AZ 9620 and AZ 4260 PRs were in use as pillar stumps. The diameter of the PR, as well as their associated height profiles, are shown in Fig 16A. In this case, as shown in Fig 16B stumps of diameter 400 μm were deposited on the surface.

Figure 16 shows the A) step profilometry measured height profile of pillars made with AZ 5214E, AZ 9260 and AZ 4620, B) SEM image of an AZ 5214E pillar stump

In this work, the PR pillar stump serves two primary purposes. 1) the pillars, due to differences in materials (such as viscosity) and fabrication parameters, will create

stumps of different heights. The height difference will induce a different taper angle.

2) PR, when heated above its glass transition temperature, will reflow and adhere to surfaces. Thus, it could also function as an adhesive to bond the top and bottom substrates together.

One of the main advantages of the discussed methodology is the creation of a highly precise batch to batch of LVOFs. In this case, the height profile can be properly and accurately controlled. This then enables the fabrication of a precise taper angle. Furthermore, one of the many benefits of this method lies in the fact that poorly manufactured LVOF can be easily reworked on. Simply, the PR can be cleaned off in solvents such as acetone. Such solvents would not have ill adverse effects on the underlying layers. Thus, a fresh PR coat can be applied subsequently.

To proof the claim, mask patterns were fabricated on 5" mask for lithographic patterning of 4" wafers coated with DBR layers. During this demonstration, AZ 5214E was used. Briefly, AZ 5214E was automatically dispensed onto a stationary wafer. The pattern size of all pillars were 400 μm . Then the coater would spin at the inputted speed and time. After all the pattern transfer lithography steps have been completed, the wafers were thermally annealed. Thereafter, a random inspection was carried out on the entire wafer to check for the fabrication tolerance. Ten randomly selected spots on the wafer were surveyed. The results of the calculated mean taper angles and standard deviation were as shown in Fig. From Fig 17, it can be seen that the taper angle is highly dependent on the spin speed. Higher spin speed results in the formation of thinner PR and vice versa. More importantly, regardless of spin speed utilized, the

spread in the taper angle is small. This suggests that spin coating is an excellent tool for even deposition of photoresist with excellent height control.

Figure 17 shows the calculated taper angles with indicated spread with respect to spin speed for AZ 5214E PR pillars

The major advantage of the proposed technique is that spin coating performed using planar chuck is capable of an uniform coating of PR on wafers with little batch to batch variation. This demonstration showcases that spin coating could be an effective toolkit for possible mass manufacturing of vertical integration of integrated circuits (ICs) chips. This will be covered in greater detail subsequently.

The PR profile after thermal annealing can be predicted by Young's equation [86]. The presentation of Young's equation is as shown in Eq 31.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \quad (31)$$

where γ_{sv} is the substrate – air interfacial tension, γ_{sl} is the substrate – PR interfacial tension and γ_{lv} is the PR – air interfacial tension. θ is the acute contact angle between substrate and PR.

The above equation suggests that the PR height post thermal annealing could be altered by the utilization of a different material in which the PR was dispensed and spin coated on. This is based on the assumption that the gaseous interface remained the same. As illustrated by Emadi *et al*, alterations to the gaseous compounds could affect the reflow profile [87].

During this laboratory scale demonstration, all top dies were flipped onto the bottom dies by hand aligned with a sharp tipped tweezer under low power magnification microscope. Despite that, a yield of greater than 90 % could be achieved. The rest of the dies were de-bonded during transport to the characterization facility due to rough handling.

The following tools are proposed for mass production. During actual mass manufacturing, automatic developer dispenser should be put in use. This would ensure that similar developer chemicals are dispensed for all wafers. Furthermore, with the wafer situated firmly on the flat chuck, all areas on the wafer will be evenly developed. This could further reduce the variation in PR pillar height. Subsequent stacking of top and bottom dies could be done on a professional die attach

instruments. Commercially available pick and pick die bonders (such as Nova Plus™ from ASM [40]) are capable of achieving placement accuracy better than 2.5 μm .

Due to equipment limitation, in this case, the top dies were manually flipped onto the broader bottom dies. Subsequent reflow at elevated temperature attaches the top and bottom dies together. The fabricated LVOF was then placed onto the FTIR sample mount stage. Prior to measurement, the alignment and focus laser was focused on the backside of the top wafer. The unpolished backside was used as the focal point. Following that, the sample was gently removed from the stage and the FTIR was set to transmission mode and was calibrated in the air in the absence of the LVOF sample. During LVOF measurement, the sample stage was manually translated at a step interval of 100 μm . Optical measurement was progressively taken from the filter side with shorter resonator length. The obtained measurements for LVOF constructed with three different PRs are as shown in Fig 18.

As observed from Fig 18A, B and C, the effective working ranges are 3.50 – 4.35 μm , 3.60 – 4.25 μm and 3.75 – 4.35 μm , respectively, for AZ 5214E, AZ 9260 and AZ 4620 PR pillared LVOFs. Effective working range is defined as the bandpass region straddled by two band stops where non-overlapping transmission peaks appear. On the other hand, the operating range of an LVOF is defined as the distance between two band stops measured at half intensity.

Figure 18 demonstrates the transmitted passbands for LVOF made with A) AZ 5214E, B) AZ 9620 and C) AZ 4260

As shown in Fig 18A, the operating range of AZ 5214E made LVOF is from 3.25 – 5.00 μm . However, the operating decrease when taller pillar height was put into use such as 3.50 – 4.75 μm for AZ 4620. Such occurrence can be explained by the concept presented in Eq 32 proposed by Garmire previously [47].

$$FPI \text{ operating range} = \frac{\frac{\lambda^2}{2 L_{opl}}}{1 - \left(\frac{\lambda}{4 L_{opl}}\right)^2} \quad (32)$$

Where L_{opl} is the optical path length of an FPI. Assuming that transmission passband is only selected by the cavity gap, then Eq 32 can be extended to Eq 33.

$$LVOF \text{ operating range} = \frac{\frac{\lambda^2}{2 x \tan \alpha}}{1 - \left(\frac{\lambda}{4 x \tan \alpha}\right)^2} \quad (33)$$

Where α is the acute LVOF taper angle, λ is the incidental wavelength, x is the total length of the filter. In this case, $x \tan \alpha$ is the optical path length as shown in Fig 19 below.

larger taper angle would constitute a smaller working range. Likewise, a small taper angle will increase the operating range. The mathematical expression confirms the experimentally obtained results. Enhancement to operating range is necessary for “stretching out” LVOF measurement. Such capability is useful under situations where there are chemical signatures present at either end of the operating range. In addition, it is also quintessential to strike a balance between the physical dimension of the LVOF in relation to other optical components, such as the detector array, in the spectrometer setup.

Furthermore, it can be observed in Fig 18 that the overall transmission intensity decreased with pillar height. Thus, measured transmission intensity can be arranged in the following sequence: (Highest) LVOF-AZ5214E > LVOF-AZ9260 > LVOF-AZ 4620 (Lowest).

Subsequently, the quality of the assembled optical filters was examined. In this case, peaks present at 3.70 μm were chosen due to the fact that no molecular absorption occurs at 3.70 μm which is commonly known as the atmospheric window [88]. This way, measurements performed will not be affected by the presence of certain chemicals present in the atmosphere, if any. As shown in Fig 20A, the FWHMs of the transmission peaks vary with the choice of PR, which, alter the pillar height and taper angle. Therefore, the measured FWHM of AZ 5214E, AZ9260 and AZ4620 are, 220 nm, 250 nm, and 320 nm, respectively. Meanwhile, an FDTD simulated FPI- modeled peak at 3.70 μm is shown in Fig 20B which serves a reference. The changes in FWHM and transmission intensity are a consequence of the introduction of a taper angle, α .

Given the high Bragg contrast between Si and air at multiple interfaces such as wafer backside, it is then expected that the transmission profile of any LVOF would be lower than what is expected during the simulation. Ideally, to overcome this issue, an anti-reflective coating should be introduced to the backside as well as the front side of the substrates. Additionally, upon determining the optimal distance between the LVOF and the FTIR light source, backside polished substrates should be used to construct an LVOF. This would resolve the effect of surface scattering.

Figure 20 shows the transmitted profiles of A) AZ 5214E-, AZ 9260- and AZ AZ 4260- pillared LVOF and B) FDTD simulation

In the following section, a geometrical analysis was performed on an LVOF with wedge angle, α . For simplicity, a single light ray of wavelength λ was incidence-d on the tilted top mirror at an angle θ as shown in Fig 19. Throughout the analysis, the refractive index of the cavity gap was assumed to be unity. It had been previously shown that the incident angle with respect to the non-tilted mirror would affect the subsequent rays propagation behavior [89]. When $\theta > 0$, the transmitted and reflected rays will diverge. When $\theta < 0$, the transmitted and reflected rays will converge. In the interest of designing a spectrometer engine, angle $\theta \leq 0$ is preferred. One can engineer an LVOF-detector system with transmitted or reflected light rays that could focus intensely on the detector element. Therefore, the study on $\theta > 0$ is omitted in this work.

Although multiple roundtrip internal reflections occur in the cavity gap, only the first and second transmission rays are taken into account in this analysis. This approach is possible as the first two rays are more intense than subsequent internally reflected rays due to transmission loss at every mirror interface. As shown in Fig 19, the acute angle at points T and R is 2α . T and R correspond to the transmitted and reflected focused points, respectively. The focus at points T and R is only dependent on the wedge angle.

As illustrated in Fig 19, the placement of the detector element is crucial. In order to maximize the capture of both transmitted and reflected light, the detector is required to be positioned at T and R, respectively. In the case of transmitted light, placement of detector at a position away from point T could results in a signal loss if the detector surface area is not wide enough to capture all incident light. Therefore, the decrease

in transmitted intensity with a larger wedge angle sample could be a result of a poorly placed detector.

On the other hand, the associated taper angle has an effect on the detector placement. It is important to position the array at an appropriate site which could maximum the absorption of light transmitted through the LVOF. Therefore, the proper alignment of the detector array could be approximated using the design rule formulated by Meyer [90]:

$$F \sim \frac{h\theta}{\alpha} \quad (34)$$

With reference to Fig 19, F is the focal point, h is the height of the resonator gap, θ is the light incidental angle and α is the taper angle.

A hypothetical example is presented. In this scenario, light is incidental at $\theta = 0.1^\circ$ and $\alpha = 0.022^\circ$ where $h = 2.50$ and $1.00 \mu\text{m}$. The approximated F value is 4.54 and $11.36 \mu\text{m}$. This relationship is rarely enforced due to the presence of large active areas found on most commercial detectors. However, such a relationship has to be properly validated in the future where a spectrometer system is dimensionally scaled down. In that case, the LVOF has to be tilted at an accurate angle with respect to the detector array. In the near future, it has been anticipated that devices would be further miniaturized such as the fabrication of micrometer size photodetectors [91]. Then, it would be necessary to factor in the distance from LVOF to detector element(s) with that of equation (34).

The designed and fabricated absorption-based LVOF is capable of molecular absorption in the mid-infrared region. With a strong transmission signal between 3.3 and 4.5 μm , it is particularly suited for the detection of hydrocarbon-containing molecules such as C-H. In this case, the design of volatile organic compounds (VOC) spectrometers can be realized. Equipped with a suitable high detectivity optical engine, hydrocarbons can be detected, qualified and quantified.

To showcase VOC detection, AZ 5214E pillared LVOFs were used. AZ 5214E was selected given its favorable operating range and highest transmission intensity amongst all LVOFs. To simulate VOCs presence, safe chemicals, in this case, ethanol, were used. Ethanol was dispensed into a borosilicate glass petri dish which acts as a gas cell using a micropipette which was rated up to 200 μl . The borosilicate glass affords optical transmission up to approximately 4.4 μm . It acts as a single pass gas cell. Upon ethanol dispensing, the lid and bottom of the glass gas cell were tight clamped. Thereafter, the gas cell was heated on a hot plate at 80 $^{\circ}\text{C}$ until all the ethanol had evaporated. To quantify possible ethanol loss to the environment, ethanol was measured under a controlled environment and was determined that 0.0001ml/s was lost to the atmosphere. The amount is lower than 1 volume % of the total amount of ethanol added. Therefore, it can be concluded that the loss is negligible. It was then disregarded for all future measurements.

On complete vaporization, the glass dish was placed in between the FTIR light source as well as the sample stage mounted LVOF. In the absence of ethanol, the transmission peak intensity is 15% at 3.5 μm . As the amount of added ethanol

increases, transmission intensity decreases accordingly as observed in Fig 21B. The transmission profiles in the presence of varying amounts of ethanol up to 0.152 ml, can be seen in Fig 21A.

The observed attenuation of transmission intensity is due to the absorption of light by the ethanol molecules present in the gas cell. Specifically, ethanol absorbs strongly at 3.5 μm . Slight red shifting of wavelength observed has also been reported before [92].

To further support the notion that optical intensity attenuation is due to the presence of more vaporized molecules, the simulation was performed at various temperatures. Therefore, the simulation temperature was set to 25, 50 and 80 $^{\circ}\text{C}$. A simulation was carried out between 25 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$, mainly to understand if a transient decrease in temperature during the experiment would alter its optical profiles. This experiment was done to due to the fact that the heated gas cell is cooling down progressively during optical measurement. Furthermore, between measurements, a different amount of time could be spent on different samples. This adds to the complexity of the issue.

As shown in Fig 21B, it can be taken that no shift in transmission wavelength and transmission intensity. No detectable peak profile change can be observed in all three cases, namely, 25, 50 and 80 $^{\circ}\text{C}$. Based on the simulation results, temperature up to 80 $^{\circ}\text{C}$, the temperature which is necessary to vaporize ethanol, will effect little interference on the optical measurement outcome.

Figure 21 A) Highlights the transmission characteristics of Az 5214E pillared LVOF in the presence of an ethanol-filled gas cell. Ethanol of volume up to 152 μl was tested. B) Plotted relationship of obtained transmission intensity against ethanol concentration.

The main purpose of this work is to showcase the possibility of constructing a precise, repeatable taper angle and optically flat LVOF. Although a total of two PRs pillars were lithographically patterned onto the bottom substrate, more pillars should be fabricated.

This would then improve its mechanical strength during field trials. Furthermore, mechanical and optical reliability tests should be carried out to determine the level of the ruggedness of such LVOF. One of the advantages of the proposed method over other fabrication methods is that new designs can be readily incorporated without the need to produce new masks. As such, LVOF for different applications and wavelengths can be readily manufactured. Since the pillars are made of PR, poorly fabricated dies could be identified and reworked on. This suggests lower manufacturing loss and overall costs.

While the top and bottom DBR dies were manually stacked in this work, die to wafer process can be developed with the use of a die bonder as mentioned in the earlier section. In this case, the bottom substrates were patterned with pillars. Diced top substrate into smaller dies was picked and placed onto the bottom substrate. The devices would then be subjected to thermal reflow.

The propose PR stacking method could be extended to on-chip vertical integration. It will be especially useful for the mounting of components that would not exceed emanate heat that exceeds the glass transition temperature of PR. Importantly, the proper selection of PR is essential. Components such as lens, optical filters, low power integrated circuits (ICs) for three-dimensional IC (3D-ICs) are purportedly suitable for stacking with PR pillars. Furthermore, electrically conductive PR could be put into use for the stacking of ICs where the PR could act as structural support as well as electrical bumps for vertical connection [93].

3.5 Conclusion

DBR coated Si wafers, propped by PR, have been demonstrated as LVOF in this work. By adjusting the spin coater set parameters, such as the spin speed, even the thickness of photoresists can be coated on wafers. The results have been shown to be consistent batch after batch. Using AZ 5214E, AZ 9620 and AZ 4260 PR, pillar heights (taper angles), 2.5 μm (0.0205°), 5.4 μm (0.0442°) and 9.6 μm (0.0786°) are formed. The fabricated LVOFs were optically measured at 3.7 μm to possess FWHMs of 220, 250 and 320 nm, respectively. Furthermore, the LVOF operating range, as well as measured overall transmission intensity, decreases with an increase in taper angle. AZ 5214E assembled LVOF was tested for EtOH vapor characterization. EtOH up to 152 μl could be detected.

In this chapter, normally incidence LVOF was fabricated with PR pillars to create a distance varying resonator gap. While that work described the fundamental effect of taper angle with respect to optical characteristics of LVOF, the construction of a working LVOF is far from robust. Two inherent problems with such construction are 1) Poor utilisation of overall LVOF area. In this case, only approximately 30% of the total LVOF length has been utilised for transmission band selection. 2) Photoresists are susceptible to attacks by many different kinds of chemicals. In the following chapter, highly reliable silicon oxide pillars deposited on one substrate were demonstrated to mate with the holes of the other substrate. The “lock and key” mechanism could improve its robustness and manufacturability.

4 Highly Compact Linear Variable Filter as Electronic Nose for Chemical Detection

4.1 Motivation

Normally incidence LVOF has been demonstrated previously in Chapter 3 with photoresist stumps to prop one end of the top die from the bottom die. Despite best effort, much of the LVOF is wasted as the useful transmission area for the required wavelength is up to 30%. Therefore, there is a need to explore the fabrication of pillars of different heights. By managing the height difference between the top and bottom dies, the half-wave resonator length can be tuned according to the wavelengths of interest.

In Chapter 3, two wafers with similar DBR profiles were flipped and stacked together with photoresists. The substrates were separated by deposited PRs. Although precise pillar height can be achieved, the polymer based PR pillars are prone to chemical attack. Moreover, the PR pillars have a working temperature ceiling.

In this chapter, LVOF with deposited SiO₂ pillars is reported. The low temperature high plasma chemical vapor deposited (HDCVD) SiO₂ is chemically inert and possesses a high working temperature ceiling. Holes with corresponding tilted angles were etched on the other wafers. The pillars and holes were mated together to form an LVOF using a flip-chip bonder.

Commonly, reported end uses of electronic nose systems have been demonstrated for use in breath analysis [94], agricultural produce analysis [95], and air pollution monitoring [96].

4.2 Fabrication methodology

The process flow for the fabrication of an LVOF is as shown in Fig 22. The bottom die is fabricated as such. A) Alternating layers of Si and SiO₂ thin films were deposited via sputtering and CVD onto a Si wafer. B) A thick layer of negative photoresist MaN-1440 was spin coated onto the DBR wafer. C) HDCVD SiO₂ was coated at steps of 500 nm per run until it has attained a thickness of 1.5 or 2.5 μm . Right after deposition, the PR was then “liftoff” by O₂ plasma ashing. The entire process was repeated to deposit another set of pillar of a different height. For the top die, the process flow is as described. E) On the front side of another DBR-substrate, patterns corresponding to the pillars are patterned by a negative PR ma-N 1440. F) On the wafer backside, PR pillars with a height of 1 μm were patterned with AZ 5214E. G) The wafer in (E) was then frontside etch into Si until the stop etch on the subsequent SiO₂ layer using deep reactive ion etching. G) Both wafers were then flip-chip attached to each other.

Figure 22 shows the process steps to realize a mechanical LVOF for bottom die where A) Si-SiO₂ DBR was first deposited onto a cleaned Si wafer, B) deposition of 1st set of oxide with PR as mask for liftoff, C) deposition of 2nd set of oxide PR for liftoff, D) further O₂ plasma for surface cleaning and removal of remnant hardened PR. For top die, E) lithographic patterning at front side of a new wafer, F) backside lithographic patterning, G) tilted etching of holes and F) integration of top and bottom wafers and H) mating of the top and bottom die.

After the LVOF was fabricated with the mating of the top and bottom DBR-substrate, it was characterized optically by a benchtop FTIR with an attached microscope. The

microscope unit allows areas as small as $12\ \mu\text{m} \times 12\ \mu\text{m}$ to be imaged and measured. In this case, the sampling aperture window was set to $50\ \mu\text{m} \times 50\ \mu\text{m}$. Surface topography was conducted on an atomic force microscope (AFM) with the tip set to tapping mode. To visualize the cross sectional profile of the DBR layers, the DBR was scribed by a diamond knife and was broken into two. The sample was mounted onto a vertical stage and viewed using a field emission scanning electron microscope (FESEM) at high magnification. A focus ion beam (FIB) using a Gallium source was utilized to provide precise ion milling of the deposited oxide pillar on DBR-substrate.

4.3 Results and discussion

As explained in Chapter 2, the Fabry-Perot interferometry (FPI) model approximation was favored over Fizeau approximation. This include the fulfilment of 1) reflectivity $> 95\%$ and 2) utilization of propagation mode, $m < 3$. However, the FPI model does not account for the change in transmission intensity at the longer wavelength. In the case where the transmission profile is affected by fabrication issues such as non-flat surface scattering and material absorption, transmission attenuation due to taper angle can be assumed to be trivial.

To decide the profile of the DBR, simulations were performed using Lumerical FDTD. As shown in Fig 23, alternating Si and SiO₂ thin films were simulated using FPI configuration. The two DBR windows were separated by a gap of $2\ \mu\text{m}$. To construct a DBR, high refractive index Si (H) was coupled with low refractive index SiO₂ (L). The number of [H] and [L] alternating layers were varied. It can be observed that the [HL] configuration yield poor transmission profiles. By increasing the number of repeating

[HL] layers, a distinct transmission peak appears at around 3.75 μm . The FWHM of the transmitted peak decreases with the increase in the number of alternating layers. On the flip side, it results in a decrease in transmission. In this work, [HLH]-gap-[HLH] was fabricated. Although it is preferable to increase the number of alternating layers, [HLH] was deposited in view of available deposition machine limitation.

Figure 23 shows the simulated passbands of Si and SiO₂ FPI structures with varying numbers of layers. The resonator gap was fixed at 2 μm . Inset shows the snippet of the Lumerical FDTD simulation window.

In this work, low temperature thick SiO₂ pillars (1.5 and 2.5 μm) were successfully deposited with PR as a mask. Previously, some groups had attempted in depositing silicon nitride or silicon oxide with PR as a mask. However, most reported works involved sub-micron thickness oxide or nitride layers [97, 98]. One of the main challenges in attempting “liftoff” for oxide, nitride and amorphous hydrogenated silicon thin film is the burden of the temperature ceiling of PR. Typically, PECVD deposition takes place at 300 °C [99]. LPCVD working temperatures are always higher than that.

However, with the development of HDCVD in recent years, lower deposition temperature is made possible [100]. This enables the use of a suitable PR as a deposition mask. The glass transition temperature determines the highest working temperature for the PR. As an example, polymethyl methacrylate (PMMA) has a reflow temperature at around 130 °C while SU-8 reflows at approximately 225 °C [101]. For HDCVD deposition with deposition temperature between 80 – 150 °C, a number of PR can be used.

After oxide pillar deposition, the resist can be stripped away by various methods. Although resist liftoff in acetone is usually the norm in foundries, PR subjected to an elevated temperature for an extended period of time could be difficult to be removed. In this work, resist removal by a combination of acetone and O₂ plasma has been found to be effective. The powdered resists was removed under a gentle N₂ gas stream after the ashing step. Alternatively, other methods to remove hardened resist have been described widely in the literature as well [102, 103].

After the “liftoff” process, the integrity of the deposited pillar was characterized. As mentioned in Chapter 3, pillar height is crucial for the formation of a die attached LVOF. In this work, the control over the deposition of the oxide pillar has to be optimized and perfected. This way, pillar deposited at-will would possess the height characteristics determined by design. FIB was carried out Pt strip deposited prior to ion milling to improve the charging effect. As shown in Fig 24, the oxide pillar is firmly attached to the surface of the DBR with uniform height seen. The height of the pillar was measured

using the on-screen ruler to be 2.5 μm . Later, surface profiling confirmed the height of the pillar. At the same time, the underlying DBR layers can be observed.

Figure 24 shows the FIB ion milled cross section image of the oxide pillar on DBR layers

Surface contamination of the topmost DBR layer could affect the measurement. Thus, it is imperative to remove those contaminants prior to the final device fabrication step. As mentioned earlier, due to the difficulty in removing hardened resist, there exists a probability that resists could be retained on the surface. To ascertain that, optical measurement performed using FTIR spectroscopy could be carried out. In the event that polymers were retained on the surface, absorption pertaining to that chemical would be registered on the FTIR measurement. The results of the FTIR measurement could be seen in Fig 25. As shown in Fig EEE, the sample which had been subjected to O_2 ashing cleaning for the “liftoff” of oxide has similar chemical composition as that of freshly prepared DBR on Si substrate. In this case, the peaks present at 450, 720, 810 and 1100 cm^{-1} are attributed to Si-O, Si-Si, Si-O and Si-O-Si bonds. These peaks are associated with the DBR deposited Si and SiO_2 layers as well as the Si substrate. Without carbon peaks at 1000 - 1400, 1266 - 1342, 1380 - 1385, 1638-1648 and 1705

– 1725 cm^{-1} which correspond to absorption peaks of C-F, C-N, C-H, C-C and C-O, respectively, it can be suggested that carbon-containing residues are absent. This concludes that the O_2 plasma treatment is highly effective in removing carbon residue.

Figure 25 demonstrates the FTIR acquired spectra of DBR on the Si surface before the oxide deposition process and post O_2 plasma cleaned surface.

AFM was carried out to determine the surface topography before and after the oxide deposition and removal processes (steps B and C in Fig 21). The topographical change can be observed in Fig 26. The calculated root mean square surface roughness (R_q) are 4.5 nm and 55 nm. It can be inferred from the AFM image that the increase in surface roughness is due to the presence of micro-deposits carbon residues. Despite that, their presence was not detected on the optical transmission profile. Therefore, no further cleaning step was carried out. However, for better consistency such as during mass manufacturing, it is essential that as much carbon residues have to be removed as possible. Proven methodology for carbon removal

including ashing and chemical as described previously could be employed. Additionally, lower oxide deposition temperature should be further investigated. Whilst it can prevent resist hardening, there is a chance that under optimized low temperature deposition process could results in poor oxide – surface adhesion [104]. This is attributed to the lack of energy for reaction and surface diffusion of chemical species to take place.

Apart from its ability to measure topological change due to the presence of residue deposited on the surface, it can be used to quantify the smoothness of an optical surface. Such a tool could be indispensable given the trend in the miniaturization of optical components.

Figure 26 reveals the surface topography of DBR on Si surface A) before the oxide deposition process and B) post O₂ plasma cleaned surface.

The formation of a possibly robust and mechanically rigid LVOF requires the use of mechanical interlocks. Apart from the formation of oxide pillars on one wafer frontside, holes corresponding to the dimension and location of the pillars are etched on another substrate. The final assembly of the LVOF would require the tilting of the top substrate with respect to the bottom substrate. To allow proper mating of the parts while enabling the tiling of the top substrate, the holes have to be tilted at an angle. Therefore, stumps of height $\Delta t = (t_1 - t_2)$, which is the height difference between the pillars deposited on the bottom substrate, were deposited on the wafer backside of the top substrate. During etching, the stump props the substrate asymmetrically on the chuck. This creates a slanted etching profile upon the removal of the stump at the backside. To visualize the results of such etching better, pillars of the linewidth of $5\text{ }\mu\text{m}$ with line spacing of $10\text{ }\mu\text{m}$ were deep etched using an optimized high verticality recipe. The cross sectional profile of the etched features was imaged at high resolution as shown in Fig 27.

Figure 27 shows the cross sectional FESEM image of tilted pillar and holes fabricated on a $5\text{ }\mu\text{m}$ line width and $10\text{ }\mu\text{m}$ spacing pattern which was vertically etched with an optimized DRIE recipe.

Mating of the top and bottom substrates was performed using a flip-chip bonder. With that, the LVOF was optically characterized using a benchtop FTIR spectrometer equipped with a microscope objective capable of altering the aperture between 20 and 200 μm . Throughout this work, the aperture was set to 100 μm x 100 μm . Due to equipment limitations, the sample mount stage is manually translated along the length of the LVOF. Prior to testing, background calibration was conducted in the air in the absence of the LVOF.

The response of the fabricated LVOF is shown in Fig 28A. The measured transmission band is between 3.25 and 4.60 μm . For hydrocarbon sensing, the required wavelength detection range is from 3.30 μm to 3.70 μm . The measured FWHM of the peak at 3.50 μm is 230 nm. As shown in Fig 28B, the simulated at 3.50 μm is approximately 220 nm. The difference between the simulated passband profile and the actual measured profile is likely attributed to 1) fabrication error and 2) reflection at the Si-air interfaces due to the high Bragg contrast effect.

Hydrocarbon sensing is demonstrated using acetone vapor. Electronic grade acetone obtained from the chemical supplier was used directly without further purification. An amount of acetone was dispensed into a custom-made gas cell and was heated on a hot plate. Upon acetone vaporization, the gas cell was placed in between the LVOF and the FTIR IR light source. Signal attenuation due to the presence of acetone molecules can be seen in Fig 29A. As shown in Fig 29A, the decrease in transmission peak intensity distinctly at 3.31 μm tallies with the increase in the amount of acetone present in the gas cell. In this case, acetone up to 200 μl was evaluated.

Figure 28 shows A) measured optical transmission profile of fabricated LVOF and B) simulated passband of an FPI model with a varying resonator length

Figure 29 shows the A) transmission response in the presence of vaporized acetone between 3.2 and 3.5 μm and B) relationship of T_1/T_0 vs acetone concentration (up to 200 μl).

In order to properly quantify the presence of acetone, a relationship between acetone-free (T_0) and with-acetone (T_1) is established. By taking the ratio of (T_1 / T_0) plotted

against acetone concentration, a non-linear relationship is attained as shown in Fig 29B. The fitted best fit trendline achieved a good correlational factor of $R_2 = 0.972$. The author believes that this method is superior to the usual case when absolute transmission % is plotted against acetone concentration. The results obtained from the latter are affected by changes to measurement conditions such as aperture size, light source intensity, etc.

To accomplish an even higher correlational factor, alteration to acetone dispensing technique should be explored. In the future, acetone should be vaporized in a heated collection tank. Then, its vapor can be continuously purged into the gas cell using a pump with a low pressure head. This technique could reduce the incidence of acetone loss during pipette transfer.

4.4 Conclusion

In this work, a normally incidence LVOF was fabricated and characterized. The use of HDCVD silicon oxide enables the use of photoresist for subsequent liftoff. Depending on the thickness of the photoresist, thick oxide could be deposited onto the DBR-coated LVOF surface. Unlike previously proposed LVOF fabrication methodology, no etching of the LVOF surface is needed. This method preserves the smooth DBR surface quality which is necessary for achieving a good transmission profile. An LVOF with a working range between 3 – 5 μm has been presented for acetone sensing. With acetone concentration varying between 10 and 200 μl , a R_2 of 0.972 was calculated.

In chapters 3 and 4, the reported propagation mode of broadband light is normally incidental on the LVOF. Thereafter, vertical transmission of a selected wavelength of light arrives onto the linear array detector chip positioned below the filter. Many such compact spectrometers for gas sensing applications have been reported in the literature. Amongst them, many have been commercialized [105, 106]. One main issue of such construction is that the device, with an incorporated gas cell, would not be able to scale smaller than the size of a human thumb. This is so when considering a gas cell that affords the necessary number of optical passes through a volume of trapped gas mixture. In chapter 5, an in-plane LVOF will be presented. The proposed LVOF could reduce the overall volumetric space of a microspectrometer. With a smaller dimension, the device could be easily integrated onto a variety of platforms.

5 In-plane on-chip Linear Variable Optical Filter for Gas Sensing

5.1 Motivation

By convention, compact spectrometers are always vertically integrated. Interferometric based spectrometers can be made dimensionally smaller than diffractive optical engine spectrometers. However, in view of the need to incorporate a multi-pass gas cell, size benefits offered by the various types of optical engines are often nullified. Simply said, a gas cell often occupies the largest volumetric space amongst the components found in a spectrometer. Thus, further miniaturization of a spectrometer using conventional technology will not be suited. This calls for a new inventive technique to incorporate the gas cell with other components of a spectrometer.

Linewidth loss due to DRIE is almost inevitable. However, linewidth loss can be mitigated by compensating the deposition of low pressure CVD (LPCVD) poly-Si to tune the linewidth. The proposed method is cost effective and allows customization. Furthermore, to develop this idea further, samples were tested before and after the deposition of LPCVD poly-Si with different measured optical passband characteristics.

The proposal discussed in this chapter could be subjected to wafer level processing to form the etched cavity as an on-chip gas cell. The technique described in this work could have wider applications for the development of other MEMS devices.

In this chapter, novel experimental and theoretical works leading up to the characterization of an in-plane vertically etched LVOF will be presented. Firstly, the emphasis on FDTD simulation to design the Si-air DBR will be discussed. Thereafter, primary work concerning the qualifying of SU-8 as electron beam lithography (EBL) resist will be mentioned. Subsequently, deep reactive ion etching (DRIE) parameters and their influence will be presented. Finally, the fabricated LVOF is then characterized by a benchtop FTIR spectrometer.

5.2 FDTD simulation of Si-air DBR

Si-air pair was chosen for high [H] and low [L] refractive index materials, respectively [107]. Given the high Bragg contrast between Si and air, fewer pairs of [HL] are needed to form a sufficiently reflective mirror. As shown in Fig 30A, simulated reflection efficacy depends on the number of [HL] pairs. It can be observed that for a [HL] single pair mirror, a poor mirror reflection is achieved. Between 3.5 and 4.5 μm , more than 40% of light transmitted through the mirror. By doubling the mirror pair to [HLHL], a reasonable amount of incident light would be reflected. Also, the band stops at 3.5 and 4.5 μm become apparent. Further increase in the number of pairs results in digital band stops as in the case of [HLHLHL].

For the proper simulation of an LVOF, two mirrors with a similar number of [HL] pairs were spaced by a void. This way, the top mirror was simulated to be parallel to the bottom mirror-like in the case of an FPI. As shown in chapter 2 as well as reported by Ayerden *et al* previously, FPI approximation is valid for LVOF fabrication. The simulation results can be seen in Fig 30B. It can be observed that with an increase in

the number of [HL] pairs, FWHM of the transmitted peak at 3.70 μm improves. A two-fold decrease in FWHM from 200 nm to 90 nm when an additional pair of [HL] is added to [HL]-[HL] to form [HLHL]-[HLHL]. On the flip side, an increase in finesse brings about a decrease in transmission intensity. This is the outcome of the highly reflective DBR which prevents light from entering as well as transmitting through the cavity resonator. Based on the simulated results, [HLHL]-[HLHL] structure was thought to be the best compromise between transmission intensity and FWHM.

Figure 30 shows the simulated profile of A) a Si-air mirror different number of layers and B) $[\text{Si-air}]_2 - \text{gap} - [\text{Si-air}]_2$ FPI model

5.3 Experimental work

In this section, the full fabrication process comprising 1) electron beam lithography, 2) deep reactive ion etching and 3) low pressure chemical vapor deposition of poly-Si is presented. A schematic illustration of the work done is shown in Fig 31.

Figure 31 illustrates the steps for the formation of on-chip LVOF. The process flow is as follows. A) Patterning of SU-8 2000.5 using EBL, B) deep etching by Bosch process and C) compensation of linewidth using LPCVD poly-Si at 625 °C

5.3.1 Electron Beam Lithography (EBL)

EBL utilizes expensive resists such as ZEP-50 which is not viable for high volume patterning. Therefore, throughout this work, Microchem SU-8 was used. In particular, SU-8 2000.5 was specifically selected. For consistency, SU-8 2000.5 will be referred to SU-8 in subsequent sections in chapter 4. An amount of SU-8 was dispensed onto triple ultrasonically cleaned Si wafers in acetone and isopropanol. The resist was spin coated at 500 rpm and soft baked at 95 °C for 1 min. During exposure, patterns were written with exposure dose set to 5.5 $\mu\text{C}/\text{cm}^2$ with an acceleration voltage set to 100

KeV. Thereafter, the resist was developed in SU-8 developer for 1 min and was then hard baked at 200 °C for 30 mins in an enclosed hotplate.

5.3.2 Deep Reactive Ion Etching (DRIE)

Prior to etching, the DRIE chamber was cleaned to remove possible contaminants from previous etching requested by other users as well as to improve the etching performance. In addition, the chamber was cleaned after every 10th etching cycle. SF₆ and C₄F₈ gas concentration and time were optimized in order to obtain the best parameters to achieve vertical etching. During etching, the chamber pressure was maintained at 120 mTorr.

5.3.3 Low Pressure Chemical Vapour Deposition (LPCVD) of poly-Si

Etched samples were horizontally loaded into the dedicated quartz-lined tube oven. Prior to deposition, the oven was programmed to evacuate to a base pressure of 12 mTorr. Then, the oven temperature was raised to 625 °C. Subsequently, SiH₄ gas was continuously purged at a flow rate of 25 sccm throughout and poly-Si deposited was conducted at 250 mTorr atmospheres. Sample after the process was allowed to cool down to 500 °C before removing the sample from the oven.

5.4 Characterization

Structures fabricated by EBL were screened using an optical microscope. Samples with improperly developed resists were discarded. The step height of developed patterns was measured using a surface profiler with a 5 mg exertion force. Deep

etched structures were visualized using FESEM. Etched samples were cleaved using a diamond scribe. The sample was broken into two parts by exerting a firm force on the substrate. X-ray diffraction (XRD) was performed with Cu-K α x-ray source where the corresponding wavelength is 1.541Å. 2θ was scanned from 20-80° with an interval of 0.02°. The XRD equipment was operated at 40 KV and the current was set to 40 mA. Raman spectroscopy was carried out with a 532 nm excitation laser. A 100X objective lens was used to focus the incident beam onto the sample surface. Grating density was set to 1800 g/mm. FTIR testing was conducted with the following parameters. Scan range was set to 2-8 μm with resolution 16 cm^{-1} . Aperture was set to a size of 20 μm x 50 μm . The background was taken in air.

5.5 Results and Discussion

5.5.1 Post Exposure Delay (PED) – Enhancement of feature

One of the main advantages of using SU-8 is that it can be patterned using a low exposure dose. Typically, exposure dose ranges from 1 to 10 $\mu\text{C}/\text{cm}^2$. In comparison, popular EBL resists such as polymethylmethacrylate (PMMA) which requires dose in thousands of $\mu\text{C}/\text{cm}^2$ [108]. Due to its low dose requirement, the writing of patterns can be done in a fraction of seconds. However, SU-8 is an uncommon resist for EBL. This is largely due to its low contrast nature as well as the need to perform lithography under yellow light [109, 110]. One advantage of using SU-8 is due to its high etch resistance during DRIE.

In the first part of this work, the SU-8 exposure dose was verified. Dose test was carried out by patterning 200 μm x 200 μm squares using a dose ranging from 1 – 30

$\mu\text{C}/\text{cm}^2$. At the same time, the concept of gap time was introduced to increase the time interval between resist exposure and developing. As shown in Fig 32, different slopes were obtained when the samples were withheld from being developed. With an increase in PED, the slope becomes steeper. Slope steepness is directly related to resist contrast by Eq 35.

$$\gamma = \frac{1}{\log \frac{D_{100}}{D_0}} \quad (35)$$

Where γ is the resist contrast, D_{100} and D_0 are the maximum and minimum dose to clear the resist, respectively.

In this instance, a 10 min interval between sample retrieval from EBL station to pattern development at a wet bench was intentionally introduced to simulate the shortest time for one sample to be developed. For other PED duration, samples removed from EBL were stored in clean wafer carriers for the stipulated time.

As observed in Fig 32, PED performed immediately after lithography results in low contrast patterns. When PED was increased from 10 min to 1h, the contrast γ , improves by 10 times from 0.015 to 0.03 $\text{cm}^2/\mu\text{C}$. It is therefore preferred to store samples for at least 1 h before PEB. Between PED 1 h and 2h, contrast γ increased from 0.03 to 0.06 $\text{cm}^2/\mu\text{C}$. Given that the increase in contrast decreases with longer delay, storage time of longer than 2 h was not performed. Also, it makes no economic sense to keep samples on the production floor for a long holding period which could result in sample loss and cross-contamination.

Figure 32 demonstrates the normalized height profile of the patterned SU-8 structure with spin coated SU-8 thickness plotted against the exposure dose set during EBL. Fabricated samples were held in the air briefly before developing in SU-8 developer

From the results gathered, it can be suggested that PED is a plausible route to improve the contrast of SU-8 as well as other chemically amplified photoresists. There is a strong correlation between the loss of photogenerated acids and PED. During the holding period, the acids could be degenerated through evaporation, diffusion and neutralization by base found in the environment [111].

As photogenerated photoacids possess short diffusion length, the acids should be largely concentrated in the vicinity of lithography exposed areas. Using Fick's law, the diffusion coefficient, D , of the photogenerated acid can be explained as presented in Eq 36 [112].

$$D = \frac{\sigma \kappa T}{[H] q^2} \quad (36)$$

Where σ is the acid ion conductivity, κ is the Boltzmann constant, T is the ambient temperature, $[H]$ is the concentration of photogenerated acid and q is the acid ionic charge.

With the diffusion coefficient known, diffusion length, L , can be computed with the following relationship as shown in Eq 37.

$$L = \sqrt{2Dt} \quad (37)$$

In this case, t refers to the total diffusion time. From Eq 36 and Eq 37, it is possible to deduce the relationship that L is proportional to the square root of D and t . This implies the direct correlation between PED and diffusion length on the assumption that acid concentration is fixed. Therefore, all subsequent EBL patterned samples were held for 1 h in air before PEB.

5.5.2 DRIE parameter optimization

EBL patterned samples were individually loaded into the etching chamber. Pre-set Bosch process recipes for high aspect ratio Si were trialed as a start. During the etching process, an alternating etch and passivate process were cycled to create a vertically etch structure. Typically, for Si etching, SF_6 and C_4F_8 were utilized as the etchant and passivation gas, respectively. Both etching and passivation steps are controlled by gas flow rate, process time, temperature and power [113]. Furthermore, etch density and required etch depth could influence the outcome as well. Given that slight deviation could alter the etch outcome, parameters are normally individually investigated. Thus, many samples are required to optimize an etching recipe. At the

conclusion of each trial set, the samples were scribed for cross sectional FESEM analysis. Depending on the required etch profile, DRIE parameters were tuned in the following sequence:

Gas flow rate → etch and passivation time → power → repeat

A brief optimization process can be seen in Fig 33. Fig 33 shows only significant progress improvement. As such, incremental improvement to structure morphology is omitted. Etching with the pre-set recipe resulted in structures highly delineated from expected. The Si pillars were over-etched. This is a result of excessive etch process without sufficient passivation material to protect previously etched regions. Therefore, it resulted in excessive removal of Si at the top. When the SF₆ flow rate was decreased by 10 % while C₄F₈ flow rate was increased by 10 %, more protection was afforded to the top part of the Si pillars. The Si pillars appear to be more vertical except at the top 1/5 portion of the structure. To overcome the issue, a “break” process was introduced to the recipe. During the “break”, higher SF₆ flow rate and higher power were allowed to remove unwanted Si. Finally, both etching and passivation timings were fine tuned to create deep vertical Si pillars. On closer inspection, DRIE scallops with diameter of 30 nm were observed from the top to the bottom of the pillars. Regular scalloping along the length of the pillars indicates excellent etching control as improperly etch pillars would have scallops of increasing size and the presence of kinks.

Although Si width of 1.45 μm and an air gap of 1.00 μm are desired, the measured Si width is about 1.25 μm. The decrease in Si linewidth is attributed to the fact that low contrast SU-8 formed a positively sloped resist pillar [114]. The formation of a positive sloped resist is likely due to the acid loss effect. In which, the effect is more

pronounced at the top of the PR than at the bottom. It happened when freshly developed SU-8 was exposed to alkali contaminants found in the cleanroom. It occurs during transfer and PEB [115]. The concentration of the alkali can be estimated using Eq 38.

$$A = A_o \operatorname{erfc} \frac{z}{\sqrt{2d}} \quad (38)$$

Where alkali concentration, A_o , is modeled to be constant in the environment as well as the top of the PR, z is the diffusion depth of alkali into PR and d is the diffusion length of the alkali in the PR.

Although it was hard baked prior to etching, loss of SU-8 during etching resulted in Si linewidth loss. Deviations from expected structural dimension would impact the finesse of the optical output. Such data will be presented in later section. A better alternative that can be explored would be to use a hard mask such as thermal SiO_2 which has much higher Si: mask etch ratio.

Figure 33 shows the development phase to achieve the optimized recipe for deep etching via the Bosch process. A) original recipe. B) Increase C_4F_8 by 10%, decrease SF_6 gas flow rate by 10%. C) introduce a two-step etch process with the initial process

targeted in “breaking” the topmost 100 nm Si layer and D) Further optimization of process with 15% change to etching, passivation and “break” parameters. E) High magnification of D) and F) High magnification of DRIE scallop formed due to Bosch process

5.5.3 LPCVD linewidth compensation with poly-Si

As explained earlier the decrease in eventual Si pillar linewidth is due to the loss in resist structural integrity during etching. Few methods have been proposed previously. These include, 1) use of hard mask instead of photoresists, 2) selecting almost digital shaped resists, and 3) photomask compensation. However, these methods have their limitations. Firstly, the etched dimension of the hard mask is dependent on the patterned photomask as well a subsequent dry etch pattern transfer step. Secondly, digital shaped resists are typically much more expensive. Depending on fabrication technique and handling, truly digital shaped resists are difficult to develop. Thirdly, photomask compensation is an expensive process. It includes multiple iterations of photomask and lithography process to obtain the desired resists dimension. To further complicate the matter, such iterations have to be performed whenever the pattern dimension changed.

For the first time, LPCVD deposited poly-Si is explored as a compensation agent for increasing the dimension of Si pillars. One of the main advantages of using the LPCVD process is that the deposited poly-Si vary proportionally with deposition time. The thickness of deposited poly-Si was measured on a SiO₂/Si wafer monitor.

The development process of poly-Si is shown in Fig 34.

Figure 34 shows the cross section FESEM profiles of A) in-plane LVOF fabricated using optimized DRIE, B) high magnification of DRIE scallops, C) LPCVD poly-Si compensation leading to widening of linewidth and D) high magnification of sidewall profile after LPCVD poly-Si deposition

The sample prepared using optimized DRIE recipe from section 5.5.2 was used as-is. A representative FESEM image of such a sample is shown in Fig 34A. Higher magnification of one of the pillars is shown in Fig 34B. Subsequently, the sample was deposited with poly-Si as shown in Fig 34C. It can be observed that the Si pillars are broader than before. A closeup of the pillar showed in Fig 34D revealed that the surface morphology of the pillars was modified by poly-Si.

In order to better showcase the quality of the deposited LPCVD poly-Si, etched samples (Fig 35A) were deposited with a thin layer of thermal oxide (Fig 35B). The thermal oxide was prepared by dry oxidation at 950 °C for 30 min. This will enhance the contrast of deposited poly-Si as shown in Fig. As shown in Fig 35C, a conformal layer of poly-Si was deposited on top of the insulator layer. It can be seen that poly-Si was evenly deposited on all surfaces. The zoomed in image in Fig 35D further shows that approximately 87 nm of poly-Si was deposited. As shown previously in Fig, poly-Si thickness can be altered by changing the deposition time. This would allow on-demand linewidth compensation of Si pillars.

Figure 35 displays the FESEM images demonstrating the development of highly conformal LPCVD poly-Si deposition. A) Freshly etched FPI structure. B) deposition of dry thermal oxide. C) Deposition of LPCVD poly-Si at 625 °C. D) Close-up FESEM which shows highly conformal poly-Si wrapped on the thermal oxide

The nature of the LPCVD poly-Si was probed by XRD, Raman spectroscopy and ellipsometry. The results of the above tests are shown in Fig 36A. XRD conducted on the wafer monitor reveals the presence of peaks at 28.5°, 47.4°, 56.2°, 69.4° and 76.8° by selecting detector scan mode with theta offset to 1°. According to JCPDS card 00-027-1402, the peaks correspond to Si (111), (220), (311), (400) and (312), respectively. Crystal size was estimated using Scherrer formula as revealed in Eq 39.

$$B = \frac{K\lambda}{L\cos\theta} \quad (39)$$

Where B is the FWHM of the peak, K is the Scherrer constant with a typical value of 0.9, λ is the wavelength of the X-ray source, L is the crystallite size and θ is the angle of peak-of-interest.

Although the peak presents at 28.5° is suitable for crystallite size analysis, the presence of SiO₂ signal, due to the presence of the underlying SiO₂ layer could complicate analysis. Therefore, the peak at $2\theta = 47.4^\circ$ was used instead. Utilizing Eq 39, a crystallite size of 10 nm was approximated. This suggests that nanocrystalline Si was deposited [116]. Due to the possibility of light scattering at grain boundary, larger Si grain is generally desired. Larger Si grains can be obtained by increasing LPCVD growth temperature (> 625 °C) or by subjecting the sample to temperature greater than 1000 °C [117].

Figure 36 shows the characterization of deposited LPCVD poly-Si layer by A) XRD, B) Raman spectroscopy and C) Ellipsometry

To confirm the quality of the deposited Si, Raman spectroscopy was carried out with a 532 nm laser excitation source. A 100X objective scope was used. As shown in Fig 36B, the poly-Si is centered at 520 cm^{-1} . This shows that the LPCVD poly-Si has low internal stress [118]. As reported earlier, poly-Si typically has higher Raman intensity and the FWHM is broader than that of crystalline Si [118, 119]. Broader FWHM reveals the presence of grains. The asymmetrical 50 cm^{-1} peak shows the nonlinearity nature of the sample.

Ellipsometry was conducted using an IR-VASE with extended source and detector up to 37.0 μm . This is likely the first time that poly-Si ellipsometric analysis was performed

beyond 1.70 μm . Based on Fig 36C, the refractive index of poly-Si ($n_{\text{poly-si}}$) at 3.9 μm is 3.46. On the other hand, the refractive index of crystalline Si (n_{si}) is 3.42 [120]. Slight variation in electronic band structure in poly-Si could have contributed to higher n value than Si. The value is expected because refractive index of amorphous Si ($n_{\text{a-si}}$) is much higher than that of Si because of differences in electronic band structure [121]. As expected, the refractive indices can be arranged in the following order (high to low): $(n_{\text{a-si}}) > (n_{\text{poly-si}}) > (n_{\text{si}})$.

AFM, as shown in Fig 37, was performed to understand the change in surface topography before (Fig 37A) and after LPCVD (Fig 37B) deposition. Unlike typical topography measurements, a high aspect ratio AFM tip was utilized in this case. To ensure that the surfaces are properly measured, the sample was mounted on a wedge stage to “open” up more sampling areas. Finally, the acquired image was flattened using the supplied post analysis software. As the samples were etched using Bosch process, it resulted in the formation of scallops. The measured root mean square surface roughness (R_q) is 12.0 nm. High R_q is probably due to the presence of scallops. However, when LPCVD poly-Si layer was deposited, the R_q increased to 27.2 nm. This is due to the presence of grain boundary as well as other microstructures introduced during poly-Si deposition [122].

A

B

Figure 37 shows the surface topography of the pillar sidewall profile probed by a high aspect ratio AFM tip with sample mounted on a tilted stage. A) Before and B) after LPCVD poly-Si deposition

5.5.4 Optical measurement

Etched samples were individually mounted on a customized stage prior to FTIR measurement. A typical setup is shown in Fig 38. The sample is first affixed vertically on to a customized jig which is then placed on to the movable sample stage. The stage is controlled using a joystick and is controlled by a servo motor. The onboard 100X objective scope was used to focus on the topmost etch Si pillars. Once it is done, background reference was performed in air. Subsequently, sample transmission characteristics were performed between 2 – 8 μm . Every sample was translated horizontally by 50 μm until the entire length of the filter was scanned. A total of 64 scans were taken per run to improve the signal output.

Figure 38 illustrates the mounting of the in-plane LVOF on a custom stage and the subsequent focus of light beam on the top of the pillars using the onboard microscope for optical characterization on the Cary FTIR (Agilent, right)

In this work, both FPI and LVOF were fabricated. FPI samples were used primarily to optimize DRIE parameters. Etched FPI filters were also utilized in the following ways.

1) Optimization of LPCVD process and 2) benchmark of FTIR signal. As shown in Fig

39A, FPI performance was simulated. At the same time, FPI samples subjected to a string of processes were evaluated. As-fabricated FPI was plotted as “original”. LPCVD compensated FPI were designated as “LP + 194 nm” and “LP + 170 nm”. For “LP + 194 nm” sample, 97 nm of poly-Si was deposited on each side of the pillar. In the case of “LP + 170 nm” sample, 85 nm of poly-Si was deposited. An illustration of its optical characterization is shown in Fig 39C.

Figure 39 shows the A) simulated transmission passband of a Si-air FPI, B) measured transmission profiles of FPI with (194 nm and 170 nm poly-Si) and without LPCVD poly-Si linewidth compensation and C) illustration of a FPI component

It can be visualized in Fig 39B that as-fabricated FPI has low transmittance. Both stop bands as well as transmitted band intensity were weak. The high loss in transmission band could be attributed to under-optimised fabrication technique and process control [123].

When FPI was subjected to poly-Si growth, it can be observed that the stop bands intensity improves. Transmitted passband red shifted in addition to an increase in peak intensity. The passband red-shifted from 3.45 to 3.54 and 3.57 μm when 85 nm and 97 nm of poly-si were deposited, respectively. This way, the deposition of poly-Si increases the effective linewidth of [H] structures while decreases the line spacing proportionally.

Prior to poly-Si compensation, the transmission peak intensity was measured to be 0.2 %. It was enhanced three times (0.5 %) and seven times (135 %) when the pillars were compensated with a total of 170 nm and 194 nm of poly-Si, respectively. The enhancement in passband intensities is likely a result of regaining linewidth and spacing in accordance with simulated structures. Although signal improvement can be observed, lower than expected signal output could be due to the following reasons. 1) Rough sidewall due to Bosch process can contribute to surface scattering effect leading to signal attenuation. 2) Lower than expected transmission intensity can be a result of grain boundary scattering and absorption caused by nanocrystalline poly-Si [124]. 3) High Bragg contrast at Si-air interfaces results in high reflection.

With reference to Fig 39B, the slight change in linewidth and spacing affects the transmission profile of the device. FWHM of “original”, “LP + 170 nm” and “LP + 194 nm” peaks were measured to be 80 nm. Transmission peak FWHM remained unchanged at 80 nm reveals the fact that the deposition of poly-Si is highly conformal. In the event of uneven deposition along the height of the pillars, the FWHM value will increase.

The work done on on-chip FPI evaluation was used directly for the development of on-chip LVOF. The reason why LVOF could not be developed in tandem with FPI is because of the difficulty in scribing all trial samples at the same spot along the structures. Because of the linearly varying cavity gap, it is difficult to optimise etching recipe without proper control of other parameters. Logically, FPI evaluation preceeds development of LVOF.

Therefore, LVOF etching was based on optimise FPI parameters. The only difference between them is a slight change in cavity etch depth along the length of the filter. This is due to the phenomenon of RIE lag. The performance of before and after poly-Si deposition on LVOF can be seen in Fig 40A and B.

Figure 40 shows the transmission profile of Si-air LVOF A) before LPCVD poly-Si deposition and B) after LPCVD poly-Si deposition and C) schematic drawing of a in-plane LVOF with linearly selective transmission passband along the length of the filter

The optically measured characteristics of the fabricated LVOF can be seen Fig 40 A and B. The fundamentally working principle of a LVOF is illustrated in Fig 40C. From Fig 40A, it can be observed that LVOF has an operating range from 3.0 to 3.9 μm. After subjecting it to 194 nm of poly-Si deposition, the operating range redshifted to 3.3 to 4.5 μm. In all, the operating range increased from 900 nm to 1200 nm.

5.6 Conclusion

This work showcases a concept that can be widely adopted by various microelectronics fabrication stakeholders. The featured technique can be used to

compensate and repair MEMS/MOEMS friction worn out Si components. In the field of Si photonics, the concept can be used to compensate imperfectly etched structures.

This technique allows manufacturers to smoothen DRIE scallops which formed as a results of Bosch process. The following steps are suggested. Firstly, fabricated samples are dry or wet oxidized to form a layer of oxide. Subsequently, dry hydrogen fluoride (HF) gas. HF molecules will etch away the oxide layer. The samples are then oxidized and etch in HF. The process will iterate until the required Rq is met. Finally, the samples are compensated with poly-Si to achieve the needed linewidth.

Photoresists are commonly used for the fabrication of many MEMS and MOEMS devices. In particular, positive resists are deposited on substrates for pattern transfer via etching. Due to the issue of under optimised lithographic processes, hardbaked photoresist might form a larger than expected slope angle. This could translate to resist that could contribute to uneven DRIE. As shown in this work, improperly etched structures suffered from decreased linewidth. To overcome the issue, a commonly adopted method is to perform compensation for designs on photomask. Although such method can resolve the said issue after a few trial iterations, it is unable to resolve batch to batch variations. Thus, an alternate method involving the deposition of poly-Si via LPCVD was showcased in this work. This versatile tool is capable of recovering loss Si linewidth.

In this work, both FPI and LVOF were fabricated and evaluated. It was demonstrated that LPCVD poly-Si was conformally deposited on the entire depth of the Si-air pillars.

The intended design was recovered after poly-Si deposition. Moreover, transmission peaks were red-shifted from 3.45 μm to 3.54 μm and 3.57 μm when 170 nm and 194 nm of poly-Si were deposited, respectively. Furthermore, transmission intensity was enhanced three times and seven times, respectively.

6 Formation of on-Chip Silicon Mirror for Mid Infrared

Applications

6.1 Introduction

An important optical sub-component is the on-chip mirror. Mirrors are essentials for directing light from source through lens, filter, analyte and eventually onto a detector. Therefore, mirrors are integral components of the overall build of a spectrometer. Given its importance, mirrors are found in virtually all spectrometers today.

As the working space of an on-chip spectrometer is highly compact, it is necessary to explore avenues to increase headspace. In particular, the miniaturization of gas cell which consumes the bulk volume of a spectrometer. In this work, fabricated on-chip mirrors are explored as reflectors to redirect free space propagated light to create an on-chip gas cell.

6.2 Background

On chips MEMS –based micromirrors are utilized in directing free space propagated light [125]. Bulk micromachined on-chip mirrors are an important feature in many MEMS and MOEMS devices [126]. Normally, they can be dry or wet etched, laser ablation, molding and dicing [127-133]. For dry etched mirror, deep etching using deep reactive ion etching (DRIE) are typically employed for the fabrication of vertical mirror. One main challenge for such mirror fabrication is the formation of DRIE scallops. Depending on process, the scallops formed on the etched surface could cause propagation loss through surface scattering.

On the contrary, wet etching is able to micromachine smooth surface on Si. The creation of the etch profile depends on the crystal orientation of the substrate, orientation of masking as well as the use of certain chemicals in the wet etching bath. So far, different kinds of micromirrors have been demonstrated. Examples of wet etching include, 90° (100) sidewall and 45° Si (110) and 54.7° (111) on Si (100) substrate.

Among them, 45° micromirrors are highly sought after for use as reflectors for optical beam steering [134]. In this case, vertically or horizontally propagation beam can be directed to be in plane or out of plane depending on its specific use cases. To date, both movable MEMS. Although tunable MEMS mirror allows the flexibility of fine tuning, it is prone to mechanical vibration. On the contrary, such vibration will not affect fixed mirrors. Fixed mirrors are typically realized by wet etching in tetramethylammonium hydroxide (TMAH), potassium hydroxide (KOH) and ethylene diamine (EDA) [135, 136]. In particular for Si (110) micromirrors, tensioactive alcohol additives like isopropanol (IPA) are added to decrease Si (110) etch rate. This way, Si (110) plane which is sloped at 45° with respect to Si (100) plane is retained. Given that IPA has lower boiling point than the temperature required for etching, alcohol has to be replenish regularly [137]. This is critical as alcohol concentration has to be controlled to be between 3 – 5 M. It has been reported previously that lower IPA concentration will increase Si (110) etch rate.

Non-alcohol based tensioactive ingredients have been explored as well. These substances include non-ionic amphiphatic polymers like Triton X[™] (Isooctylphenoxy polyethoxyethanol) and NCW (polyoxyethylene alkyl phenyl ether) [138]. Comparing Triton and NCW to alcohol, part per million amount of Triton and NCW is needed to retain Si (110) plane [139]. Moreover, both Triton and NCW have higher boiling point than IPA. This case, etching can be done at higher temperature which guarantees smoother etched surface. Among the two surfactants, Triton-based etch bath, is the most commonly reported. Studies investigating etching temperature, magnetic stirring speed, surfactant and etchant concentration have been widely reported [140-144]. Amongst different etchants, TMAH-Triton is well-known to produce the smoothest Si (110) plane. The most common combination reported so far is TMAH/Triton X-100 [145]. However, TMAH system suffers from rougher Si (100) surface than KOH [146]. This ill effect limits (100) from further processes without incurring additional smoothing processes. Also, TMAH is an expensive and dangerous chemical which is highly toxic for human operators. A noteworthy TMAH alternative is KOH with Triton X.

6.3 Motivation

As reported previously, Triton molecule has a hydrophobic head and a hydrophilic tail. The hydrophobic moiety had been known to interact with hydrophobic surfaces [147-149]. First principle studies using Fourier Transform Infrared spectroscopy (FTIR) and water contact angle measurement revealed that Triton X hydrophobic head interacted with hydrophobic Si (100) [150]. However wet etching in KOH-Triton etchant with different Triton moiety has not been reported before.

This chapter aims to shed light on Triton X-n molecular interaction with Si (100) and (110) surfaces during etching. Therefore, Triton X-n ($n = 45, 100, 405$) were examined. While a mechanistic insight will be presented, fabricated Si (110) sidewalls were demonstrated as on-chip reflector at 1.55 and 3.80 μm .

6.4 Experimental Procedure

6.4.1 Si wafer preparation

P-doped Si wafers were cleaned in Acetone and IPA under agitation. The wafers were then subjected to wet thermal oxidation at 1000 $^{\circ}\text{C}$ to form a 1 μm thermal oxide as hard mask. During lithography, the wafers' flats were tilted 45 $^{\circ}$ with respect to the mask pattern without special alignment. The primary flat location error tolerance is rated to be $\pm 1^{\circ}$ when manufactured in accordance to the M1-0302 standard set by SEMI. An addition of an alignment step could improve alignment errors to be less than 0.1 $^{\circ}$ [151]. However, it is not needed in this case due to the following reasons: 1) Alignment errors are minimized at long etching time (this case, 3 hours) with rapid removal of (100) where etch rate of (100) $\gg$ (110). Thus, etching is "etch stopped" on (110) with a self-eradication of error after extended etching time. 2) Even in the event of mirror misalignment, it can be easily compensated by adjustment made to the subsequent ebeam lithography to align the Si-air pillars (LVOF type 3) accordingly. 3) In the case of a slight mirror tilt with respect to the LVOF, incidental light will propagate at an angle. It will affect the focal point of light incidental on the detector. In which, the detector array can be displaced accordingly. Furthermore, other authors have found that the use of a reliable primary flat is suffice for the creation of 45 $^{\circ}$ (110) mirrors [152]. Thereafter, the oxide hard mask was dry etched to reveal the Si bulk.

6.4.2 Wet etching

Triton X-n, obtained from Sigma Aldrich, were used without additional purification. Triton-KOH bath was prepared fresh prior to all etching session. A volume of Triton was measured and make up with deionized (DI) water under vigorous stirring. Thereafter, KOH pellets were cautiously added under mild stirring. The experimental setup can be viewed in Fig 41A. Etching was performed at 80 °C. Si wafers were suspended in the etching bath which was stirred at 250 rpm for 2 h. After that, the etch samples were dried under dry N₂ stream.

6.4.3 Dielectric distributed Bragg Reflector (DBR)

Si (320 nm) and SiO₂ (770 nm) thin films were deposited onto the etched samples to improve the mirror reflectivity at 3.80 μm. Si was sputtered while SiO₂ was deposited using plasma enhanced chemical vapor deposition method.

6.5 Characterization

Root mean square (Rq) roughness was measured using atomic force microscopy (AFM). Both Si (100) and (110) surfaces were measured. Contact angle measurement (Static sessile) was performed using DI and Triton on cleaned Si surfaces. Mirror reflectivity studies were performed at 1.55 μm and 3.80 μm using the setup shown in Fig 41. The experiment was conducted using lasers at the two wavelengths. Firstly, a sample was mounted on a rotation stage with a single mode fiber (SMF-28) fiber placed as close to the (110) surface as possible. To collect the reflected light, 20X DIN and LFO-5-6 lenses were placed a distance away from the surface. The lenses were used for NIR and MIR quantification, respectively. Finally, the light was terminated at

an InGaAs photodetector and thermopile with an integrated sphere for NIR and MIR measurement.

Figure 41 shows the setups for A) wet etching, B) actual optical setup and C) schematic diagram where the input fiber is situated perpendicular with respect to a 45° rotated sample. Light reflected from sample surface is collected by a 20X lens which is collected by an InGaAs photodetector or the CCD camera for imaging

6.6 Results and Discussion

6.6.1 Etching characteristics

Up till now, different kinds of shapes such as circle, square, rectangle, etc have been bulk micromachined in Si substrate by KOH-Triton. To showcase the micromachining of on-chip mirrors, long rectangular shaped mesas were fabricated on (100) Si surface.

As a comparison, etching speed (rate) in a KOH bath with different Triton X was compared. For a fair comparison, Si was etched in KOH without added Triton. It achieved a maximum etch removal speed of $75 \mu\text{m} / \text{h}$ as shown in Fig 42. In this case, the (110) plane was rapidly etched leaving the presence of (100) sidewall highly visible. Over etching of the process resulted in the formation of Si stumps as shown in Fig 43. Therefore, KOH only wet etching is not suitable for the preservation of (110) plane. However, when a small amount of Triton was added, (110) plane could be observed. To study the effect of Triton X-n on etch rate, Triton X-n concentration was varied between 0 and 1000 ppm in KOH. As shown in Fig 42, with the addition of Triton, etch rate decreases. The rapid decrease in etch rate could be observed above 10 ppm in all three cases. With the Triton concentration fixed at 10 ppm, the etch rates for X-45, X-100 and X-405 are 74, 55 and $37 \mu\text{m}/\text{h}$, respectively. Therefore, the hydrophilic tail length influences the etch rate. At very concentration, the vertical etch rate is approximately $10 \mu\text{m}/\text{h}$. Since the amount of Triton could affect the selective removal of (100) and (110), it is imperative to decide on the concentration of Triton X-n to be added for etching.

Figure 42 shows the etch rate ($\mu\text{m/hr}$) for varying Triton chain lengths in different concentration

Observation of surface morphology of etched samples in different Triton X-n at different concentrations can be seen in Fig 43. Without Triton, rapid etching of Si was observed in Fig 43A. Striated patterns perpendicular to the rectangular patterns were observed in all three Triton X-n. The striation happened at low Triton concentration as shown in Fig 43B, C, D. The phenomenon disappeared at higher Triton concentration for X-100 and X-405 as observed in Fig 43E, F, G. It persisted for X-45. The appearance of the “caterpillar-like” legs could be a result of the revelation of high order planes where the adsorbed Triton interacted with the Si surfaces. Similar to previous reports by Tanaka *et al* and Rola *et al*, the Si (100) surface was observed to be the roughest at Triton X-n 10 ppm [142, 153]. The (100) plane was observed to be

smoother at higher Triton X-n concentration. At low Triton X-n concentration, the etching behavior parallels that of KOH-only etchant. However, at higher Triton X-n concentration, the Triton loses its propensity in protecting high order planes, resulting in gradual removal of Si and the formation of smooth (100) plane.

Figure 43 shows the SEM images for rectangular mesas etched in KOH – Triton X-n at different Triton concentration

Although smooth structures are preferred, a balance between etching run time and material quality have to be evaluated and compromised. In this case, it has been determined that 10 ppm Triton X-n is advantageous over other concentrations in KOH. In this case, the etch rate is sufficiently quick for all three Tritons. Thus, in subsequent sections, Si substrates etched in the solution containing Triton X-n 10 ppm – KOH will be evaluated.

	Root means square (R_q) surface roughness (μm)		
Si facets	X-45	X-100	X-405
100	0.275	0.444	0.88
110	1.31	0.221	0.186

Figure 44 reveals the root mean square surface roughness and surface topography of Si (100) and Si (110) etched in various Triton X-n at different concentration

To evaluate the effects of Triton X-n polymer chain length on surface roughness, AFM was performed to probe the (100) and (110) surfaces. As shown in Fig 44, root means square surface roughness (R_q) for Si (100) surface worsens with an increase in Triton X-n chain length. On the contrary, R_q for Si (110) improves with the use of longer Triton X-n chain length from 1.31 μm to 0.186 μm for X-45 – KOH to X-405 – KOH, respectively. The attainment of smooth (110) plane is critical for the fabrication of micromirrors where output efficiency is largely determined by its surface roughness. Rough surfaces attribute to surface scattering resulting in severe attenuation of signal. Because of that, Triton X-100 and X-405 are possible candidates as tensioactive agents to be used in KOH etching bath.

Due to the possible planes in close association with either (100) or (110), these planes could be exposed in the course of etching. As such, surface roughness for (100) differs from that of (110) with the former more granulated while the latter is more striated in nature [145]. It is highly plausible that the striated appearance is a result of accidental exposure of high order (551) plane. The phenomenon was previously reported by Sato

et al [154]. Surface roughness measured in this work was within the same order of magnitude as reported in [154]. Striation appears to be more prominent for samples etched in X-45 – KOH than other Tritons (X-100 and X-405) as shown in Fig 43. The striated appearance disappears when more X-45 was added.

It concurs that the rate of reaction depends on the accessibility of the Si surface and reactants. To conduct a thorough investigation on the effect of Triton X-n interaction with Si substrate, a contact angle study was carried out. Prior to contact angle measurement, Si wafers were cleaned in buffered oxide etch (BOE). However, one of the main constraints faced in this work is that a layer of native oxide forms rapidly on cleaned Si wafers [155]. As suggested by [155], the thickness of the native oxide on Si wafers will increase rapidly 100 min after exposure to air. Therefore, it is imperative that all characterization works have to be conducted and concluded within the stipulated time. In this work, to ensure consistency across measurements, all characterizations were carried out up to 60 min after BOE. Triton X-n was dispensed using a custom-made glass body syringe. Deionized water was used as a control. As such, a contact angle of 75° was observed on Si. The data corroborates with previous work [156].

6.6.2 Si-Triton interface

Triton X-100 adsorption on Si was reported by Pal and co-workers. The work was carried out using infrared spectroscopy [157]. The study concluded that more Triton X-100 were adsorbed on Si (110) plane than (100) plane. However, the study required a complicated setup. To further understand the interaction of Triton X-n with Si

surfaces during etching in KOH, static sessile drop method has separately experimented on Si (100) and Si (110) commercial grade wafers. Triton X-n, between 1 and 1000 ppm, was prepared in deionized water. Throughout the experiment, 3 μ l of Triton was dispensed onto BOE cleaned wafers. The results of this set of solid-liquid contact angle measurements are shown in Fig 45 conducted on Si (100) and Si (110) wafers.

It can be observed from Fig 45 that contact angle decreases with an increase in Triton X-n concentration for both Triton – Si (100) and Triton – Si (110). In view of higher Si atomic packing density, (110) plane affords greater wetting. This is so when more Triton molecules can readily interact with the hydrophobic Si atoms. Moreover, it can be observed that shorter Triton molecules afford smaller contact angles than longer molecules. This could be due to the presence of repeating ethyl hydrophilic tail. With the increase in chain length such as in the case of Triton X-405, steric repulsion occurs at the hydrophilic moiety. This repulsion force prevents effective packing of molecules on the Si surfaces.

Figure 45 reveals the contact angles of Triton X-n dispensed on A) Si (100) and B) Si (110) surfaces

6.6.3 Triton X-n – H₂O interface

Triton tail moiety is hydrophilic in nature due to the presence of repeating ether units.

The ether – O – is capable of forming hydrogen bonding with adjacent ether or with

that of water. This calls for an investigation to understand the interaction between Triton X-n tail and H₂O. The effects of Triton chain length on hydrogen bonding with water will be evaluated. OH⁻ from dissociated KOH etchant was previously shown to be non-interactive with the ether group along the Triton tail [158]. One of the assumptions the authors made in this part is that Triton molecules are presumed to assemble on Si surface the moment Si wafers made contact with Triton X-n in the etch bath. It is further assumed that the spontaneous interaction of Triton precedes that of etching. Based on the assumptions made, Triton X-n was first dispensed and spun onto Si (100) and (110) wafers. To parallel the thought process, Triton X-n was dried on Si when the substrate was subjected to heating on a hot plate at 80 °C. Deionized water was carefully dropped onto the surface. With due consideration given to the danger of using KOH in a non-standard workplace, all contact angle testing was conducted in water. The justifications are as such, 1) safety over the handling of corrosive nature of KOH and 2) KOH would introduce surface roughness due to surface etching. It is imperative to recognize that effect of surface roughness on contact angle [159]. Also, the presence of micro-fabricated features such as by wet etching would affect contact angle as well [160, 161]. Furthermore, it was revealed in a previous study that the addition of KOH would not alter the contact angle measured in water [162].

As shown in Fig 46, longer Triton X-n demonstrates greater wettability than shorter Triton X-n in the following sequence: X-405 > X-100 > X-45. When Triton X-n molecules are dispersed in aqueous media, the ether groups readily form hydrogen bonds with water and OH⁻ molecules [163]. Therefore, it can be postulated that longer

chain Triton X-n are effective in shielding the underlying Si surface from rapid etching. This case, Triton molecules decrease etch rate of Si (110) removal.

Figure 46 showcases the contact angles of water dispensed on Triton X-n of various concentration on A) Si (100) and B) Si (110)

6.6.4 Molecular mechanism insight

As explained in earlier sections, the Triton X-n chain length affects the etch rate. This is due to the presence of repeating ether bond units along the length of the hydrophilic tail. It is highly plausible that the ether forms hydrogen bonds with adjacent ether or with hydroxyl ions and water molecules. In this case, the ether unit acts as a hydrogen acceptor [164]. Because of that, longer chain Triton possesses higher solubility in aqueous solvent. As shown in Fig 47, Triton X-405 easily solubilizes fully in water while Triton X-45 forms a turbid suspension.

Figure 47 shows the dispersibility of Triton X-n in water. Triton X-100 and 405 are fully solubilized in the water while Triton X-45 forms a colloidal suspension due to a decrease in solubility

While the ether bonds would interact with the aqueous solvent, it also readily forms hydrogen bonds with the hydroxyl ions contributed by dissociated KOH. By the same convention, the ether groups can temporarily “trap” OH⁻, preventing easy access of OH⁻ to Si surface. This explains the observation that longer Triton decreases etch rate. Moreover, the ether bonds have the propensity to “trap” SiO₂(OH)₂⁻, a product of the Si wet etching process. With reference to Eq (39), the decrease in rate of removal of

SiO₂(OH)₂²⁻, due to trapping by the ether bond affects the forward reaction in accordance with Le Chaterlier's principle as shown in Eq 40 [165, 166].

The overall reaction for Si wet etch in OH⁻ is as such:

Given the preferential etching which results in the preservation of Si (110) plane, it is obvious that the number of Triton adsorbed on a surface depends on the atomic packing density as well as the surface energy. In earlier work, ellipsometry analysis was carried out to quantify the thickness of the Triton layer on Si (110) and (100) surfaces [158]. In this case, the hydrophobic head interacts with the Si whilst the hydrophilic tail dangles in the aqueous environment. Between the Triton X-n with differences in chain lengths, shorter X-n such as X-45 is capable of more compact arrangement on the Si surface. This is due to the lower steric repulsion between the chains. This effect is viewed by a decrease in contact angle. Despite that, the shorter chain length is not able to confer sufficient protection to decrease the etch rate for producing cleaner 45° mirror. In contrast, longer Tritons experience larger steric repulsion resulting in lower packing density. However, the longer tail affords more "stopping power" for molecular influx. This results in slower surface etching by hydroxyl ions. The entire mechanistic insight is illustrated in Fig 48.

Concerning the difference in packing arrangement between that of Si (100) and (110), (100) plane is expected to have fewer anchoring Triton. Because of that, unprotected Si surface sites are more prone to etching than Triton adsorbed Si. Extended etching time results in the formation of granules. This postulation must be evaluated

experimentally to verify the claim in the future. Higher Triton concentration preserves smoother (100) and (110) surfaces. With regards to longer Triton's affinity to an aqueous solution, longer Triton X-n is easily removed that its shorter counterpart. This would be beneficial for device fabrication using long chain polymer for post fabrication cleaning.

Figure 48 shows a schematic drawing of products and reactants, possible adsorption of molecules on Si surfaces during KOH-Triton X-n wet etching

6.6.5 Optical characterization of 45° mirrors

Optical measurement conducted using 1.55 μm lasers as sources for NIR measurement. The setup was prepared as shown in Fig 41. SMF-28 fibers were used throughout the experiment. An uncooled InGaAs photodetector with an attached integrating sphere was used to measure power output. For this work, a long pillar design was lithographically transferred onto a wet thermal oxide grown Si wafer. Etching in KOH bath with 10 ppm Triton X-n was carried out. Specifications required for subsequent measurement using SMF-28 fibers are as follows: the fiber was stripped to expose the cladding revealing a 125 μm diameter cladding with an 8 μm

core. In order to allow the cladding to make contact with the Si (100) surface, a minimum vertical etch of more than 80 μm is needed. This allows light emitted from the fiber tip to be reflected by the Si (110) surface. A 20X objective lens was positioned a distance from the (110) surface to focus the reflected light onto the InGaAs detector. The sample was mounted onto a rotating holding.

During operation, all optical setup as shown in Fig 40 were fixed in place with the exception of the mounted sample. The sample was rotated until a reasonable output has been acquired. The optical measurement results performed at 1.55 μm have been summarized in Fig 49. Prior to measurement, power output from the tunable laser at 1.55 μm was measured to be 5.43 mW. Due to absorption and reflection, the amount of transmitted power from the lens was 3.68 mW. Thereafter, a polished Si (100) wafer with surface roughness ($< 5 \text{ \AA}$) was fitted on the rotating jig. The sample was rotated 45°, in order to simulate a 90° light reflection. The total final output power measured is 1.25 mW. It is noteworthy to mention that low reflectance is expected on uncoated Si at NIR region. In particular, only 40 % of the light is reflected at 1.55 μm from the surface of an uncoated Si wafer. With regards to the reflected power of Si (110) constructed using different Triton precursors, it is observed that KOH- Triton-100 / 405 affords higher measured reflected power. It has been further confirmed by images taken by an extended range charged coupled device (CCD). Highly focused light spot taken from KOH-Triton X-100 and X-405 etched surface indicates that the (110) surface is smooth and planar. The optical measurement corroborates with the SEM images shown earlier. That is, KOH Triton-405 produces the smoothest surface which

ensures high reflectivity and no possible distortion of (110) surface which could result in convergence or divergence of reflected light.

Figure 49 describes the propagation loss at different components with light source supplied by a 1.55 μm lasers. It has been measured that the absolute power output reflected from the surfaces of sample etched in KOH – Triton A) X-45, B) X-100 and C) X-405 are 0.58, 0.76 and 0.72 mW, respectively. The images of the corresponding beam spot were taken with the CCD camera.

The success of the fabrication and characterization of 45° Si (110) as on-chip micromirror at NIR was further processed for characterization at the MIR range. In this case, dielectric distributed Bragg reflector comprising alternating layers of Si and SiO₂ was deposited onto the sample. The simulated and measured transmission profiles are shown in Fig 50 below. Although complete reflection could not be achieved at this

moment, more layers of Si and SiO₂ could be deposited in the future to enhance the mirror reflectivity. At present, the prepared mirror is capable of reflecting light with reasonable efficacy between 3.5 and 4.5 μm . The reasons for the decrease in reflectivity as well as a narrower working range are as such. Deposited Si thin film is in actual fact amorphous Si. The measured refractive index of the amorphous Si possesses smaller refractive index. This leads to a smaller Bragg contrast ratio with SiO₂ which affects the working range. Furthermore, with a smaller refractive index, light transmits more readily through the thin films and the subsequent substrate. This explains why the fabricated mirror has lower reflectance.

Figure 50 compares the A) measured [Si-SiO₂]₂ DBR mirrored Si (110) reflectance with that of simulated

Thereafter, the mirror was subjected to similar testing using a 3.8 μm laser as the light source. The setup is similar to measurement in NIR range. In this case, the photodetector was replaced with an uncooled single pixel thermopile detector from Newport Corporation. Given the ease of Si (110) etching in KOH-Triton X-100 than X-

405 in view of slower etch rate for the latter, only data for X-100 etched Si samples were presented. The measured results are displayed in Fig 51. Propagation loss amounted to $[(22-16)/22]$ 27 % due to the sample DBR imperfections, fiber, as well as the lens, was registered. Although other Triton-KOH etched sample was not tested, it can be estimated that KOH-Triton X405 should have similar reflection profile. KOH-Triton X-45 sample would likely display lower reflectivity due to surface irregularities. Slight improvement in reflectivity should be expected as the surface micromachined thin films would improve overall surface roughness [167].

Figure 51 shows the measured reflected output from a KOH – Triton X-100 etched sample as well as losses from other components. The light source was powered by a 3.8 μm laser.

6.7 Conclusion

In this chapter, the wet etching of Si substrate in KOH – Triton X-n was presented. Specifically, Triton with different hydrophilic chain lengths (X-45, X-100 and X-405) were investigated. AFM probed surface roughness revealed that X-405 produced the smoothest (110) plane but roughest (100) plane. This is thought to be due to the length of the hydrophilic tail. Triton's tail which contains repeating units of ether could slow down etch rate by modulating the flow of hydroxyl ions to Si surface. The ether group has the propensity to interact with the ions via hydrogen bonding. During contact angle measurement, lower water contact angle was measured for longer Triton due to its greater ability to form hydrogen bonding. Due to the difference in atomic packing density between (100) and (110) as revealed by contact angle, more Triton may be present on (110). This results in greater occurrence of Si etching on (100) plane. For (110) surface, surface roughness can be classified in the following sequence: (Smoothest) X-405, X-100, X-45 (roughest). Finally, etched (110) mirror was tested in the NIR and MIR wavelength bands. Triton with longer chain length affords higher power reflectivity. Si-SiO₂ DBR surface micromachined KOH-Triton X-100 etched sample proffers reflected power to be higher than 73 %.

7 Metal decorated - graphene as thermal detector

7.1 Introduction

The previous four chapters summarize the core works performed in realizing an on-chip MIR spectrometer. Firstly, the design, fabrication and characterization of interferometric filters were described. As such, two primarily different propagation modes for detection were presented: Out – of – plane transmission LVOF and in-plane transmission LVOF. Secondly, the fabrication and characterization of wet etch Si (110) was presented as on-chip micromirrors for 90° light bending. The utilization of such a mirror system further enables the miniaturization of the overall spectrometer package. The eventual on-chip miniaturized spectrometer can be realized effectively with the incorporation of a detection system, light source and possible inclusion of lenses.

Presently, there is a severe shortage of suitable MIR detector systems available. In many systems, mercury cadmium telluride (MCT) photodiode is a popular choice [168]. However, MCT is prohibitively expensive to be incorporated into a micro spectrometer. Moreover, MCT requires liquid nitrogen cooling which demands constant liquid top-up for continuous operation.

On the other hand, heat detection based thermal detectors have been explored as a suitable detector for field-based spectrometers. The pyroelectric detector is a prime choice given its sensitivity in the MIR – far infrared (FIR) range. However, all pyroelectric based detector requires a chopper to regulate the receiving heat inputs. Typically, a mechanical chopper can be incorporated into the on-chip device at the

expense of additional power utilization and volumetric space. More importantly, the material with the highest reported pyroelectric coefficient is lead zirconium titanate (PZT). With the looming concerns about lead poisoning effect on human health and environmental pollution, led by the European Union directive on lead-free directive [169], PZT is destined to be replaced or minimized in use in the near future. Although collectives of PZT alternatives such as lithium tantalate (LiTa) and potassium-sodium doped niobate (KNN) have been rigorously researched on, their performance is still a far cry from that of PZT [170, 171].

The next in line class of infrared detectors is based on the principle of thermoelectricity. Thermopile, a collection of thermocouples, detects heat signatures by comparing the change in temperature between the hot and cold junctions. By merit of its intrinsic Seebeck coefficient, the induced potential drop can be read by an on-board microcontroller. The wavelength of the light or temperature could then be identified. Currently, most commercially available thermopile is made by n- and p- doped poly-Si. However, the figure of merit (FOM) for Si is low ($ZT = 0.02$) [172].

7.2 Motivation

Two dimensional (2D) materials could be explored as possible next-generation TE materials. One of them is graphene. Like silicon, graphene based microfabrication is CMOS compatible. More importantly, graphene has been reported to possess much higher FOM ($ZT > 1.4$) [173].

In this chapter, metal nanoparticles functionalized graphene TE material were made. Their Seebeck coefficient and thermoelectric power factor (TEP) were characterized

and reported. Thereafter, the device level integration of an LVOF, lens and detector will be presented and discussed.

7.3 Graphene – metal nanoparticle synthesis

Graphene grown using chemical vapor deposition and subsequent device fabrication is similar to a previous report [174]. The thermoelectric device is schematically shown in Fig 52. Metal precursors, HAuCl_4 , AgNO_3 and H_2PtCl_6 were purchased from Sigma-Aldrich and were used without further purification. The metal solutions were individually dissolved in deionized water and the metal basis concentration make up to 2 mg/ml. A drop of the solution was carefully dispensed onto the sample. It was then subjected to UV irradiation under a 400 W xenon lamp for two minutes. Thereafter, the sample was triply washed in deionized water and dried under a gentle N_2 stream. In subsequent section, G-Au, G-Ag and G-Pt abbreviation will be used for Au, Ag and Pt nanoparticles decorated graphene.

Figure 52 shows the schematic representation of a graphene thermoelectric device on SiO_2/Si substrate with Au microheater

7.4 Results and discussion

Visualization of graphene and surface functionalized metal nanoparticles (NP) using transmission electron microscopy (TEM). As shown in Fig 53, NPs size and dispersion are element dependent. For Au, Au NPs of 10 nm in diameter are deposited onto the graphene surface. They have a tendency to agglutinate into clusters. In contrast, Ag NPs are approximately 3 – 4 nm in diameter. These NPs are well dispersed and almost always observed as monodispersed particles. Pt NPs are spherical in shape and are roughly similar in size to Ag NPs. One difference between Pt NPs and Ag NPs is that the former has a larger size distribution.

Figure 53 shows TEM images of UV light reduced A, B) Au, C, D) Ag and E, F) Pt on graphene

To elucidate the nature of the graphene to metal NPs bonds as well as the oxidation state of metals, x-ray photoelectron spectroscopy (XPS) was performed. Critically, this technique would ascertain the possibility of reduction of metal_{n+} to metal_0 state by UV light. As revealed in Fig 54A, Au_{3+} was fully reduced to Au_0 . The peaks present at 83.9 and 87.8 eV belongs to $\text{Au}4f_{7/2}$ and $\text{Au}4f_{5/2}$ for Au_0 [175]. Peaks, shown in Fig 54B, are located at 368.4 and 374.9 eV which can be assigned to $\text{Ag}3d_{5/2}$ and $\text{Ag}3d_{3/2}$ for Ag_0 [176]. Although no Pt_{4+} peak is shown in Fig 54C, deconvoluted peaks at 72.1 and 75.4 eV, 70.5 and 73.5 eV can be assigned to $\text{Pt}4f_{7/2}$ and $\text{Pt}4f_{5/2}$ for Pt_{2+} and Pt_0 , respectively [177]. Complete photoreduction of Au and Ag were demonstrated. However, Pt was partially reduced with the presence of a 2+ oxidation state as indicated by XPS.

Figure 54 shows the XPS spectra for A) G-Au, B) G-Ag and C) G-Pt

Raman spectroscopy (RS) was undertaken to make known the effects of NPs on the chemical and physical properties of graphene as a supporting network. The defect (D)

peak located at approximately 1340 cm^{-1} , as shown in Fig 55A, D, G, was enhanced when Au and Ag NPs were reduced on graphene. The phenomenon has been reported previously and was due to the enhanced Raman scattering effect [178, 179]. Interaction of Pt^{2+} with the defect sites and the electron transfer at the metal- graphene interface likely contributed to the decrease in D peak intensity. From Fig 55B, E, H, the G peaks are observed to redshift (left shift) by 1.16, 0.76 and 0.76 cm^{-1} for G-Au, G-Ag and G-Pt, respectively. On the other hand, 2D peaks for G-Au, G-Ag and G-Pt red-shifted by 2.45, 6.36 and 4.40 cm^{-1} , respectively. Given that the calculated $\Delta 2\text{D} / \Delta \text{G}$ values are 2.11, 8.37 and 5.79 for G-Au, G-Ag and G-Pt, respectively, the peaks shifting phenomenon observed are results of multiple affecters. While it is commonly taken that in the case of a uni- or dual- axial strain, $\Delta 2\text{D} / \Delta \text{G}$ values should fall in between 1.9 – 2.5 [180]. However, higher than reported $\Delta 2\text{D} / \Delta \text{G}$ for G-Ag could be plausibly attributed to a local straining effect within the graphene lattice network as a result of large Ag NPs physisorbed on graphene. Furthermore, Ag NPs, being electron rich, are capable of electron charge transfer to graphene [181]. More fundamental studies should be carried out to deepen the knowledge and understanding concerning the effect of different perturbation factors on Raman signal shift.

Figure 55 shows the Raman spectra and shift for G-Au (A, B, C), G-Ag (D, E, F) and G-Pt (G, H, I) which correspond to the peaks for D, G and 2D peaks

The performance of a thermoelectric- based thermal detector is described by the FOM (ZT) formula as demonstrated in Eq 41:

$$ZT = \frac{S^2 \epsilon}{\sigma} \quad (41)$$

Where S is the Seebeck coefficient, ϵ is the electrical conductivity and σ is the thermal conductivity.

The numerator, $S^2 \epsilon$, describes the thermoelectric power factor (TEPF) [182]. To improve the ZT , it is necessary to increase the Seebeck coefficient as well as the

electrical conductivity. In this preliminary work, graphene was functionalized with metal NPs in an attempt to improve the TEPF. As such, TEPF was studied by normalizing with that of pristine graphene. Thus, a higher ratio is favored.

The TEPF of G-NP over that of pristine graphene can be expressed as shown in Eq 42.

$$TEPF \text{ ratio} = \frac{TEPF_{after}}{TEPF_{before}} = \frac{S^2_{after}}{S^2_{before}} \cdot \frac{R_{before}}{R_{after}} \quad (42)$$

Where R is the sheet resistance of graphene with (after) or without (before) metal NPs functionalization. Sheet resistance was measured using a four-point probe Van der Pauw's equation.

The details of the Seebeck, resistance and TEPF ratios are presented in Table 4.

Table 4 describes the Seebeck coefficient ratio, sheet resistance ratio and the TEPF for G-Au, G-Ag and G-Pt with respect to pristine graphene

	Seebeck ratio	Resistance ratio	
Sample	S _{after} / S _{before}	R _{before} / R _{after}	TEPF Ratio
G-Au / Pristine	0.76	5.26	3.04
G-Ag / Pristine	1.04	1.43	1.55
G-Pt / Pristine	0.94	1.33	1.18

A near 25 % decrease in the Seebeck coefficient ratio was observed in G-Au as compared to pristine graphene. This could be due to a localized thermal cooling effect contributed by the surface functionalized Au NPs [183]. No observable change was gathered for G-Ag and G-Pt. This shows that NP functionalization will not change the

Seebeck coefficient as it is an intrinsic factor of a material. Sheet resistance for functionalized graphene is better than pristine graphene. One likely explanation is that the NPs readily form at grain boundaries, defect sites bridging and facilitating charge transfer. So far, hybridization of graphene reveals a TEPF improvement factor of 3.0, 1.5 and 1.2 for G-Au, G-Ag and G-Pt, respectively.

In the future, in view of the cost associated with noble metals, non-noble metals such as first row transition metals should be explored. Some of these promising elements like Cr, Fe and Ni are possible candidates. Although p-type graphene has been demonstrated for use in a TE device, it is difficult to realize n-type graphene. Thus, the incorporation of graphene with another TE material is critical for the fabrication of a thermopile detector. N-type TE materials include MoS₂, Bi₂Te₃, etc. Alternating n- and p-type TE materials are necessary to form a thermopile. Finally, the hot junction of the thermopile is connected to an absorber (hot junction) and the other arm is in direct contact with the underlying Si (cold junction).

7.5 Conclusion

In this chapter, a monolayer graphene-based thermoelectric device had been presented. To improve the thermoelectric efficiency of the unit, different metals (Au, Ag and Pt) were photoreduced using UV. Subsequent four-point resistivity probe revealed that Au functionalized graphene had the lowest sheet resistance. Measured sheet resistance can be arranged in the following order: (Lowest) G-Au < G-Ag < G-Pt < pristine (highest). Although Ag and Pt decorated graphene did not observe significant change to its Seebeck coefficient, G-Pt observed a 25% decrease. This

could be attributed a thermal cooling effect caused by the presence of Au. Despite that, G-Au revealed the highest thermoelectric power factor enhancement of three times over that of pristine graphene.

8 Future works and Conclusion

8.1 LVOF structural improvement and reliability studies

Normally incidence LVOFs, presented in chapters 3 and 4, are meant for incorporation onto miniaturized spectrometer for small vehicles such as drones. Many a times, the components will be subjected to sudden acceleration / deacceleration and vibration. Therefore, LVOFs should be structurally reinforced prior to prototyping. This is because, the two diced substrates, secured by two to four pillars could easily collapse during use. This might cause the entire device to fail catastrophically. Therefore, it is imperative to redesign the LVOF.

One of the proposed methods is to replace the circular pillars with elongated pillars. The latter design will be extended along the entire width of the flipped die. The proposed structure will increase the total surface contact area between the top and bottom dies. To enhance the overall construction stability further, the cavity space between the top and bottom dies could be underfilled with an adhesive medium. One such consideration would be polydimethylsiloxane (PDMS) with low cure temperature. Unlike other polymers, PDMS possess minimum carbon-containing groups in its monomer. This results in limited light absorption by the polymer between 3 – 5 μm while maximizing light transmission. Having such construction would confer better structural reliability for maximizing long term operating lifespan.

8.2 Final spectrometer design

Two different spectrometer design has been proposed. Depending on the mode of operation, space constraint, etc, a suitable configuration can be adopted. In the first case, the light source and the 2D material based detector array would be fabricated on a Si wafer. On a separate wafer, 45° degree mirrors were wet etched using KOH-Triton X-100 10 ppm with the process flow as shown in Fig 56. Thereafter, SU-8 photoresist will be spray coated and EBL was performed to pattern SU-8 on the center stump. Later, DRIE will transfer the pattern into the Si for the formation of an in-plane LVOF. Si and SiO₂ DBR layers are deposited on the tilted mirror by sputtering. Finally, the top and bottom wafers are bonded together by wafer level processing involving wafer bonding. Then, individual dies were diced for further processing and integration.

Figure 56 shows the proposed process flow for the realization of a wafer level processed spectrometer with an internal cavity which acts as a gas cell

An impression of a possible spectrometer designed with the described interferometric filter described in chapter 5 is incorporated with the 45° mirror mentioned in chapter 6. In addition, the 2D material detector array would be designed on the other Si substrate. Ideally, in this configuration, an external gas cell can be replaced with an internal gas cell. The cavity space enclosed by two Si wafers acts as the gas cell. In this case, the eradication of an external gas cell would further decrease the volumetric dimension of the spectrometer. This is necessary for possible further miniaturization of the spectrometer.

Figure 57 shows a proposed in-plane LVOF with 45° (110) mirrors for the fabrication of a possible wafer bonded spectrometer

On the other hand, vertical, out of plane spectrometer can be realized with the interferometer mentioned in chapters 3 and 4. Although this configuration is easy to realize, it warrants a vertical integration of gas cell above or below the LVOF which

increase the overall size of the spectrometer. Clever positioning of mirrors at the top, while the light source and detector array are placed at the same plane, would halve the volume of the spectrometer. Moreover, careful integration of the different optical components as shown in Fig 58 is needed.

Figure 58 reveals potential gas sensors fabricated with a die attach LVOF in which the 2D material detector array is positioned beneath the LVOF

8.3 On-Chip lens

Apart from that, the incorporation of a collimation lens is necessary. Departure from the plane-wave restriction results in the FWHM broadening, decrease in transmission intensity and shift in expected transmitted beam position [184]. For that, a germanium

plano-convex lens (obtained from Edmund optics) was simulated using Zemax Opticstudio. Primarily, the simulation was carried out to understand the maximum size of a thermal emitter that can be collimated for use with the LVOF. During simulation, the thermal emitter of diameter (320, 640 and 1300 μm) are assumed to be a blackbody radiator with lambertian emission profile [185]. The results are as shown.

The blackbody is situated 22.5 mm away from the lens as stipulated by the manufacturer as shown in Fig 59. From ray trace, thermal emitter diameter of up to 640 μm is the limit to be used in the presence of the lens; the measured half cone angle is approximately 2-3°. As previously reported, a divergence angle of more than 2.5° would result in indistinguishable spread [184]. In this case, the position of the LVOF, as well as the detector array, should be within 100 mm of the lens. For which, it is more than sufficient when constructed in a wafer level packaging.

Figure 59 shows the Zemax Optistudio simulated ray trace profile of a Ge lens (Edmund optics). Thermal emitters of diameter A)320, B) 640 and C)1300 μm have been simulated

8.4 Miniaturized spectrometer construction and expected performance

A spectrometer comprises light source, detector, LVOF (In this case), mirrors and other components such as an on-board readout circuits. With respect to the LVOF demonstrated in chapters 3,4 and 5, a MIR responsive spectrometer with a detection range between 3-5 μm can be readily manufactured. Depending on the molecular species of interest, as shown in Fig 1, 6-8 μm range might be relevant. In that case, the quarter wave stack (material thickness) should be tuned accordingly.

In all cases, graphene-based thermoelectric detector can be utilized. Despite advancement in thermoelectric detector, it still suffers from lower sensitivity than other types of thermal detectors. Therefore, LVOF-graphene thermoelectric spectrometer presented in this thesis is not relevant for trace gas sensing. Rather, it is more suited for background, remote monitoring of industrial chemicals and/or chemical wastes effluent. Alternatively, the LVOFs described in this thesis can be paired up with pyroelectric detector for high sensitivity detection of molecular signatures.

A suitable on-chip light source has to be fabricated. The light source should be able to emit as high light intensity as possible. Thus, it might be necessary to use thin films made of high melting temperature materials such as SiC, Pt, etc.

8.5 Summary

This thesis has presented the design, microfabrication, and characterization of wafer level processed LVOF for an effective operating range between 3 – 5 μm . Similar to

an FPI, an LVOF is constructed by two distributed Bragg reflectors. The top mirror is tilted at a milli-degree angle with respect to the bottom mirror. In the first instance, a normal incidence LVOF is proposed. The mirrors are constructed by alternating layers of Si-SiO₂-Si-SiO₂-Si. The sputtered Si and PECVD deposited SiO₂ layers are approximately 320 and 700 nm thick. Later, the top mirror-Si die is flipped onto a bottom die with photoresists pillars. The pillars serve to create the desired taper angle. Demonstrated with different resists (AZ 5214E, AZ 9620 and AZ 4260), the top substrate is tilted 0.0205°, 0.0442° and 0.0786° from the bottom substrate. Furthermore, it has been suggested experimentally that the increase in taper angle from 0.0205° to 0.0786° increases the FWHM from 220 to 320 nm. On the other hand, it causes a decrease in transmission intensity and operating range from 15 to 10 % and 1.75 to 1.25 μm, respectively.

Later, to improve the overall physical reliability of the LVOF, HDCVD SiO₂ pillars are deposited in place of structurally-weak photoresists. The lowered oxide deposition temperature enabled the use of ma-N 1440 for liftoff. In this work, precise oxide of heights 1.5 and 2.5 μm were deposited 6 mm apart. The top mirror-Si substrate with tilt-dry etched holes was correspondingly mated with the pillars. The LVOF, with an FWHM of 220 nm, was used for the quantification of acetone vapor. Acetone volume up to 200 μl was evaluated at 3.31 μm. Subsequently, a relationship between acetone-free (T_0) and with-acetone (T_1) was established. By taking the ratio of (T_1 / T_0) plotted against acetone concentration, a good correlational factor of $R_2 = 0.972$ was achieved.

On the other hand, an in-plane Si-air DBR LVOF fabricated using electron beam lithography is presented. The design confers greater miniaturization due to the possible placement of an on-chip gas cell. During electron beam lithography, it is proven that the introduction of a post exposure delay improves the contrast of SU-8 photoresist by 10 times from 0.015 to 0.03 cm²/μC. Marginal improvement in resist contrast is observed for PED longer than 1 h. It has been shown that improved resist contrast is critical for proper deep etching of near 90° vertical pillars on Si substrate. By coating the LVOF pillars with 194 nm thick LPCVD poly-Si, the working range of the LVOF can be tuned from 3.0 - 3.9 μm to 3.3 - 4.5 μm. The FWHM, which remained at 80 nm, suggests that the deposition LPCVD poly-Si layer is highly conformal. This technique can be utilized for thickness compensation in the event of erroneous deposition step as well as for the fine tuning of fabricated devices.

In chapter 6, 45° rectangular- shaped micromirrors are fabricated on Si (110) wafers by wet etching. Wet etching was conducted using KOH-Triton X-*n* (*n* = 45, 100 and 405) solutions. KOH with Triton concentration between 0 and 1000 ppm are evaluated. In this case, 10 ppm Triton concentration is proven to be the optimized parameter for producing a deep mirror profile with reasonable surface roughness. Longer chain Triton has been shown to slow down etch rate from 74 μm/h (X-45) to 37 μm/h (X-405). As such, Triton X-100 is selected as a good balance between etch rate (55 μm/h) and surface quality (*Rq* = 0.221 μm). Triton X-100 (10 ppm) in KOH etched mirrors have been tested for light reflection at 1.55 and 3.80 μm with a measured reflectivity of 40 % and 48 %, respectively.

In order to realize a miniaturized spectrometer, a graphene-based (G) thermal detector is demonstrated in Chapter 6. Au, Ag and Pt are reduced onto the graphene surface using UV photoreduction method. All hybridized G- Au/Ag/Pt samples are then studied. The sheet resistances could be arranged in the following order: (Highest) pristine G (528.4Ω) > G-Pt (398.9Ω) > G-Ag (369.3Ω) > G-Au (100.4Ω) (Lowest). Hybridized graphene's Seebeck coefficient over that of pristine graphene is about 0.76, 1.04 and 0.94, for G-Au, G-Ag and G-Pt, respectively. In all, the thermoelectric power factor enhancement measured to be 3.0, 1.6 and 1.2 times over that of pristine graphene for G-Au, G-Ag and G-Pt, respectively.

Finally, the concept of an in-line or normal incidence spectrometer is presented. The sequential construction of a build-up spectrometer is showcased. In particular, the replacement of circular pillars with elongated pillars is proposed. Furthermore, the concept of underfilling the gap between the top and bottom substrates with PDMS is showcased. At the same time, the developmental work in progress on the on-chip lens is also presented. Although still primitive in nature, the simulation results indicate the geometrical parameters for achieving collimated light rays. With a $320 \mu\text{m}$ thermal emitter and a suitable collimating lens, the parallel light can achieve at least 100 mm in free space propagation with minimal spread.

List of Journal Publications

1. Graphene-Metal Nanoparticles for Enhancing Thermoelectric Power Factor, Li

Lynn Shiau, Simon Chun Kiat Goh, Xingli Wang, Minmin Zhu, Chuan Seng Tan, Zheng Liu, Beng Kang Tay, Transactions on Nanotechnology, 18 (2019)

2. Thermally Reflowed Die-attached Linear Variable Optical Filter for Mid-Infrared Volatile Organic Compounds Detection, Simon Chun Kiat Goh, Li Lynn

Shiau, Chengkuo Lee, Chuan Seng Tan, Journal of Microelectromechanical Systems 5, 28 (2019)

3. Deposited poly-Si as on-demand linewidth compensator for on-chip Fabry–Perot interferometer and vertical linear variable optical filter bandpass and

passband manipulation, Simon Chun Kiat Goh, Nan Chen, Li Lynn Shiau, Beng Kang Tay, Chengkuo Lee, Chuan Seng Tan, Journal of Micromechanics and Microengineering 4, 29 (2019)

4. Cu–Cu Bonding in Ambient Environment by Ar/N₂ Plasma Surface Activation and Its Characterization, Shen Lin Chua, Chan Marvin, Simon Chun Kiat Goh,

Chuan Seng Tan, IEEE Transactions on Components, Packaging and Manufacturing Technology 3, 9 (2019)

5. Formation of 45° Silicon (110) Surface Using Triton X-n Surfactants in Potassium Hydroxide for Infrared Applications, Simon Chun Kiat Goh, Tina Xin

Guo, KaiLiang Chuan, Chuan Seng Tan, ECS Journal of Solid State Science and Technology 12, 7 (2018)

6. Spiral Waveguides on Germanium-on-Silicon Nitride Platform for Mid-IR Sensing Applications, Wei Li, Anantha, Kwang Hong Lee, Hao Dong Qiu, Xin Guo,

Simon Chun Kiat Goh, Lin Zhang, Hong Wang, Richard Soref, Chuan Seng Tan, IEEE Photonics Journal 3, 10 (2018)

List of Conference Publications

- 1. Mid-infrared volatile Compounds detection using thermally reflowed flip-stacked die linear variable filter**, IEEE Sensors, 2019
- 2. First demonstration of gate voltage-less chemical vapour deposition graphene for non-vacuum thermoelectric study**, SPIE Commercial + Scientific Sensing and Imaging, 2018
- 3. Low cost rapid fabrication of vertical LVOF microspectrometer on-chip for MIR sensing**, SPIE Commercial + Scientific Sensing and Imaging, 2018
- 4. Two-Step Fabrication of Mid-Infrared Linear Variable Optical Filter Using SU-8 as Mask**, IEEE 13th Annual International Conference on Nano/Micro Engineered and Molecular Systems (NEMS), 2018
- 5. Effects of Triton X-n Surfactants on the Fabrication of Si (110) On-Chip Micromirrors**, International Conference on Optical MEMS and Nanophotonics (OMN), 2018

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