Ordered hybrid nanoneedle arrays for gas sensing

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NANYANG
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**ORDERED HYBRID NANONEEDLE ARRAYS
FOR GAS SENSING**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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ORDERED HYBRID NANONEEDLE ARRAYS FOR GAS SENSING

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ABSTRACT

This thesis presents ordered hybrid nanoneedle arrays for gas sensing application. The ion milling process on the metal/silicon material system is investigated in depth, in order to fabricate iron/silicon and platinum nanocrystallites/silicon hybrid nanoneedle array. The field ionization gas sensors using those unique highly ordered nanoarrays are prototyped and studied, which achieve the high gas sensitivity under an ultralow operation voltage.

A hybrid nanostructure is a material system consisting of two or more components, which brings about the significant improvement of the property of the individuals. More recently, the capability of hybrid nanostructures has drawn the growing attention worldwide. However, the control during their assembly is rather challenging, especially for the one-dimensional metal/semiconductor hybrid nanomaterials.

In the present thesis, a novel ordered metal/silicon hybrid nanoneedle array is fabricated using an ion beam that patterns the metal/silicon substrate producing a pillar array followed by the self-organization of hybrid nanoneedles. Each nanoneedle consists of a nanoneedle with a nanodot sitting on its top. The nanodot is an alloy of Ga and initially deposited metal. However, such ordered hybrid nanoneedles are not formed on the pure silicon substrate. Nor are the hybrid nanoneedles produced on the silicon surface coated with a thin metal that has a very high sputtering rate, such as Au and Ag. A mechanism of nanoneedle formation is proposed considering the alloying process during incident

gallium ion irradiation to the silicon substrate coated with a thin layer of a sufficient low sputter rate.

Iron, is a metal which has a pretty low sputtering rate and allows the formation of a perfectly ordered hybrid nanoneedle array on the surface of Fe/Si substrate. This unique nanostructure has been demonstrated to be highly sensitive to various types of gases, including air, nitrogen, hydrogen and carbon monoxide. And it also has ability to differentiate the same gas with various concentrations. Moreover, the sensitivity can be significantly enhanced when Fe metal is replaced by Pt nanocrystallites. In this case, a lateral electric field is applied across the nanoneedle array rather than a vertical electric field that is engaged during the evaluation of the Fe/Si gas sensing device. The breakdown voltage of nitrogen for Pt/Si comes up with only ~ 7 V in contrast to ~ 30 V, which is required to N_2 discharge for Fe/Si hybrid nanoneedle array. It is also found that the homogeneous silicon nanoneedles failed to generate any gas sensing signal.

Based on the insightful analysis of gas ionization currents, such anomalous high field ionization efficiency has been attributed to the superimposed effects to the one-dimensional nanoneedles. For example, iron/silicon nanoarray provides abundant surface states for efficient gaseous electron tunneling, and polarized platinum nanocrystallites enhance the local electric field sufficient to direct ionization, respectively. Added by these experimental results and theoretic analysis, the previous physical scenarios of field ionization in a gaseous electronics system have been extended at nanoscale.

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CHAPTER 1: INTRODUCTION

This chapter covers an overview of hybrid nanoneedle array followed by the motivation, objectives, importance and novelty of its application as a field ionization gas sensing device. The scope, problems, methodology and significant findings from this research are also presented.

1.1 Nanostructure array: overview of gas sensing

Nanostructure arrays show unique properties which are quite different from their bulk substrates. They are widely applied in the field of renewable energy [1-4], quantum dot superlattices [5], light-emitting [6, 7], magnetic data storage media [8, 9] and self-cleaning coating [10]. One-dimensional nanomaterials (ODNM), in particular, such as carbon nanotube, zinc oxide nanowire or silicon nanowhisker, allow the extensively application as the ideal field ionization devices [11-14]. In this case, when the applied voltage is raised up to a certain value, the ambient gas will generate conductive plasma to bridge the tips of ODNM and counter-electrode [11, 15-19]. Therefore, a steep increment of ion current can be detected immediately in the measurement circuit. Such current “spike” detected from a field ionization gas sensor has a “fingerprinting” property, which is unique to a certain ambient gas. The threshold voltage, where the ion current avalanche is ignited, represents the characteristics of the tested gas, *e.g.* the type, concentration or pressure.

The ODNM field ionization gas sensor has been compared with a couple of traditional nanosensors based on gas chemical adsorption process, as listed in Table 1.1 [11, 20, 21]

Table 1.1 Three typical mechanisms of nanomaterial gas sensors.

Type	Device setup	Advantages	Disadvantages
field ionization		<ul style="list-style-type: none"> • High sensitivity • Stable and reversible • Ubiquitous to diverse gases • Fast response and recovery 	<ul style="list-style-type: none"> • High working voltage and energy consumption • Complex fabrication and difficult arrangement of nanomaterials, especially for low-voltage devices
resistance		<ul style="list-style-type: none"> • Straightforward fabrication • Sensitive to specific types of gases • Fast response 	<ul style="list-style-type: none"> • Adsorptive layer needed • Detectable gas species determined by sensitive coating • Long recovery time due to slow desorption
capacitance		<ul style="list-style-type: none"> • Low cost • Class-specified gain to gas sensing signal • Low power • Fast response 	<ul style="list-style-type: none"> • The chemoselective coating needs replace from poison frequently • Difficult to capture or process the capacitance signal

Darker contrast electrode is conductive while brighter one is for insulator, and red dot stands for the tested gas molecule; field ionization and resistance-based sensor is conducted by voltage bias sweep for direct current (DC) signal, while capacitance based sensor is stimulated by voltage of alternating current (AC) for impedance response.

The comparison shows that the ionization gas sensor has many advantages, including higher sensitivity and stability, but shorter response or recovery time. These unique properties of field ionization gas sensor are mainly attributed to the scale effect of individual ODNM and their optimized organization. For an individual one-dimensional nanostructure, it has the high aspect ratio that results in a flux convergence effect of electric field (geometry effect), to enable a dramatic reduction of the voltage bias required for gaseous field ionization [22-27]. However, even having this scale effect of ODNM, the previous reported field ionization devices still suffer a high operation voltage issue. Table 1.2 shows some examples of metallic nanotips as field ionizers in specific ambient gases, which generally work at high voltages.

Table 1.2 Field ionization on various metallic nanotips.

Year	Tip Materials	Tip Radius (nm)	Work Voltage	Current (A)	Gas	Ref.
1975	Ge	250	17.8 kV	6.3×10^{-14}	Ar	[28]
1975	Ir	80-150	15 kV	10^{-10}	H ₂	[29]
2004	β -W	0.1-0.2	3-4 V	$\sim 10^{-10}$	Ar	[16]
2005	Ir	100	12 kV	4.0×10^{-10}	H ₂	[30]
2006	W	atomic	1.6 kV	-	N ₂	[31]
2008	Au	90	250 V	$\sim 10^{-10}$	Ar	[27]

Meanwhile, even the individual nanotips listed in Table 1.2 are mainly loaded by such high voltages; the generated ionization currents are still too weak to be detected for the practical gas sensing application. To improve the gas sensing signal, one approach is to assemble the sharp ODNM into an array, in order to capture the collective current signals from individuals at a low operation voltage. This innovation brings about the considerable electric field enhancement and increases discharge current density simultaneously. In this case, it is critical to align the ODNM of uniform topography with proper separation. Otherwise, the insufficient spacing between adjacent nanostructures will cause electric field shielding effect and consequently reduce the efficiency of field enhancement [11, 26, 32, 33]. On the other hand, the nanostructures with quite different profiles are vulnerable to result in device failure. For example, the long nanowires may cause short circuit by connecting to the counter electrode, where the induced thermal energy during gas test can destroy the whole device immediately. Some typical ODNM grown on plate as electrode in field ionization gas sensing device are compared and shown in Table 1.3, including gold nanorod, zinc oxide nanowire, carbon nanotube and copper oxide nanorod.

Table 1.3 Typical nanowire grown on plate electrode for field ionization.

Material	Profile	Gas Sensing Property	Limitations of Use	Ref.
gold nanorod		Breakdown of Argon at 170 V, 1 nA . Nanorods separated well by template.	Aspect ratio of gold nanorod is too low to enhance the electric field significantly.	[34]
zinc oxide nanowire		Breakdown of Helium at 175 V, 250 μA . High stability with moderate voltage.	High density of nanowire increases the working voltage due to shielding effect.	[35]
carbon nanotube		Prebreakdown voltage of NH ₃ at 100 V, ~100 pA . Sensitive to change of concentration.	The electrodes pair has to be separated widely for variety of nanotube lengths, which increases the working voltage.	[22]
copper oxide nanorod		Surface ionization of Acetone at 300 V, ~100 pA . Greatly reduce the working temperature.	Low ionization efficiency due to the randomly distributed blunt nanorods.	[36]

Due to the limitations of use as presented these prevalent one-dimensional nanowires merely shrink operation voltage from several kV to around 100 V based on geometry effect. Such working voltage is still unsafe to human body, which hinders the portability of these miniaturized gas sensing devices. To pursue lower power consumption and safer operation condition (especially for application in handy equipments), a novel “hybrid nanostructure” has been introduced to the ionization gas sensor.

1.2 The motivation: ordered hybrid nanoarray for ionization gas sensing

A hybrid nanostructure is a material system which consists of at least two nanocomponents, in order to bring about significant property improvement of individual nanostructures [37-42]. Table 1.4 shows some typical metal-semiconductor hybrid nanomaterials and their different applications.

Table 1.4 Typical hybrid nanomaterials and their applications.

Hybrid Materials	Structure	Advantage	Principle	Ref.
CNT-Au-CNT		<ul style="list-style-type: none"> •Improved CNT/metal contact •Junction still in nanoscale 	High adhesion of the junction at the interface of carbon nanotubes and metal.	[40]
Fibre-ZnO NW-Au		<ul style="list-style-type: none"> •High flexibility of both components •Enhancement by fibre bundling 	A “coupled piezo-electric and semi-conducting property” due to interaction of Au/ZnO array and pure ZnO.	[37]
MnO ₂ -CNT		<ul style="list-style-type: none"> •Improved Lithium battery capacity •Remarkable cyclic stability •Enhanced conductivity 	A dual Lithium storage in both CNT and MnO ₂ and well-oriented 1D route of conduction along the coaxial interface.	[41]
Ag-Si-Pt		<ul style="list-style-type: none"> •High photo-electric efficiency •Photocatalyst in a wide range •Stable across the whole solar spectrum 	Schottky diodes at two metal/semiconductor interfaces with enhanced photovoltaic and photocatalyst effect.	[39]

The hybrid nanostructures are applied in a variety of fields, as shown in Table 1.4, whereby each heterojunction between semiconductor and metal plays a crucial role in the specific application. It is believed that certain hybrid structures of ODNM may also further enhance the field ionization property. However, due to the complexity of fabrication, the application of hybrid nanostructures on field ionization gas sensing is still quite limited.

Table 1.5 Three hybrid nanostructure schematics for gas ionization.

Hybrid Materials	Profile	Structure	Mechanism	Ref
Metal on Semi-conductor Nanoneedle		Assembly of contacted particles or metallic cap on the tip of semiconductor nanoneedle, which provide surface states.	The surface states related to impurities in metal modify the band bending potential, which assists to tunnel into the valence band.	[11]
Semi-conductor on Metal Nanoneedle		The top of metal nanowires coated by semiconductor shell or dots, which is close or lower than zero electron affinity, e.g. alumina or diamond.	A coupling of scale effect and electric field reinforcement of Schottky diode, where electrons are able to tunnel through semiconductor easier.	[33, 43]
Metal Nanoparticles on Insulator		A cluster of isolated metallic nanocrystals as separated centers for polarization on the top of insulator.	Each insulated metallic nanocrystal can be polarized to generate high local electric field, combined with geometry effect.	[44]

Dark: semiconductor, yellow: metal and grey: insulator.

Currently there are mainly three approaches integrating nanocomponents into ODNM to form a hybrid field ionization structure, as shown in Table 1.5. All these listed hybrid nanostructures are created based on a metal-semiconductor material system. However, the different structures result in their respective gaseous ionization mechanisms.

For example, gold nanoparticles are commonly used as catalysts to grow nanowires, such as silicon. The Au/Si nanowire is a typical hybrid metal/semiconductor nanostructure system [11]. In the gas sensing device using Au/Si nanowires, a detectable gaseous ionization current ($\sim$ nA) can be generated at an extremely low voltage bias ($\sim$ 6V). However, these high-density nanowires are randomly distributed, which will cause a severe shielding effect leading to a significant decrease of field enhancement. In addition, the semiconductor nanowire growth is also restricted by the availability of metals that are able to be used as catalysts, which hinders the wide application of this hybrid nanostructure.

The semiconductor/metal is another hybrid material system for gas field ionization. Alumina/gold is a typical combination, where alumina from anodic aluminum oxide template after removal is still remained on top of the grown gold nanowire [33, 45]. In this case, amorphous alumina is chosen due to its electron affinity close to zero, which brings about higher electron tunnelling efficiency of electron through Schottky barrier [43]. Compared to the metal/semiconductor structure of gold nanodots on silicon whisker, this semiconductor/metal nanostructure array shows better overall regularity. But the field ionization property is lower due to the intrinsic contamination within the alumina cap during fabrication [33, 45].

In contrast, the metal nanocrystals on insulator increase local electric field intensity by polarization mechanism [44]. However, the fabrication of such hybrid nanostructure is very challenging. First, the high precision process at nanoscale is needed, in order to perfectly align the well-separated nanoneedles. Second, the nanocrystals should be controlled in extremely small size, in order to provide a strong scale effect. Third, the

insulating matrix is crucial for isolation of each nanocrystal, which enhances the polarization effect of individual nanocrystallite, in order to generate the detectable field ionization signals.

The hybrid nanoneedle structures for gas ionization, regardless of the different superimposed mechanism types, are depending on the shape of underlying nanoneedles. The overall profile of one-dimensional nanoneedle is essential to supply a sufficient background field enabling the supplementary enhancement from the functionalized tip. In order to integrate the hybrid nanoneedle array into a field ionization sensor, an effective fabrication method has to be explored.

1.3 The problem: challenging hybrid nanoneedles fabrication

The hybrid nanoneedle structure is promising to reduce the working voltage which the traditional ionization gas sensors required (more than 1 kV). However, it is difficult to fabricate the satisfying hybrid field ionizers at nanoscale. For each individual hybrid nanoneedle, the challenge of fabrication comes from the control of its internal composition to the overall profile. Furthermore, these nanoneedles are difficult to be arranged into an ordered array.

The prevalent Micro Electronic Mechanical System (MEMS) process is capable of fabricating the ordered silicon nanoarray. It usually takes advantage of anisotropic wet etching along different crystallographic planes. However, the geometry is restricted to a low aspect ratio and a fixed separation. Additionally, only homogeneous silicon pyramids are available on the substrate where there is no hybrid structure on the tip [6].

There are some other bottom-up methods to align the grown ODNM into ordered arrays using templates [46-52]. For example, anodic alumina membranes (AAM) [3] or anodic alumina oxide (AAO) [27, 53], can be coated on the catalyst layer to isolate the growth of nanowires against the shielding effect. However, the pattern of template is usually imposed by a high density, resulting in the insufficient separation of grown nanowires. Additionally, the template material is difficult to be removed completely, which in turn deteriorates the gas sensing property severely.

A thin layer of SiC [54] and SiO₂ [10, 52] can serve as the alternative masks in the top-down technique to obtain nanoneedles of high aspect ratio. These nanoparticles, also referred as “self masks”, fade away with a considerably lower rate during corrosive plasma etching, to protect the underlying substrate. A hybrid nanoneedle structure is self-organized, with tip covered by the remained protective insulating nanoparticles. Even though this method is able to achieve a desirable high aspect ratio, these high-dense nanoneedles are still randomly distributed. Meanwhile, the insulating residuals on each tip can hardly contribute to gaseous field ionization. Nevertheless, this approach suggests another top-down methodology, which uses ion beam to etch the semiconductor substrate coated with a metal protective layer producing a metal/semiconductor hybrid nanoneedle array.

1.4 The solution: focused ion beam patterning on metal/silicon

There are various useful nanostructure arrays fabricated by the focused ion beam (FIB) system [14, 55-59]. It takes a rapid straightforward ion milling technique without any mask or pre-patterned layer; meanwhile, integrated with a scanning electron microscope (SEM), the process precision can be *in situ* monitored with a resolution down to

submicron. Based on the flexibility and controllability, FIB system is in particular favourable to fabricate a prototype of nanodevice for theoretical verification at nanoscale before the bulky production [56, 57].

The previously reported nanostructures formed by ion beam irradiation are mainly accomplished on the homogenous substrates [55, 60, 61]. Recently, FIB system with Ga ion source successfully assembles some hybrid nanoneedle arrays on III-V compound, including GaSb [62, 63] substrate and InAs/InP [64] or InSb/GaAs [65] heterostructure. During the ion beam bombardment, the metal with low melting point will be separated from the decomposed substrate. These hybrid nanoarrays are formed by the migration of released metallic nanodots along the sidewall of nanoneedle towards the top, serving as the self masks [62, 65-67].

The challenges in the cost, process adjustment and conductivity control of III-V compounds hinder their gas sensing application. Alternatively, silicon is a better substrate for electronic nanodevice; however, so far the understanding of silicon-based hybrid nanoarray fabrication is still rather insufficient.

1.5 Objective, importance and novelty

The primary objective of this research includes the fabrication, characterization, and gas sensing evolution of ordered hybrid nanoneedle array on a silicon substrate. The mechanism of hybrid nanoneedle array formation will be proposed combining the *in situ* observations and ion irradiation calculation. Microscopy techniques will be used to examine the overall profile associated with the geometry effect, and internal microstructures which determine the superimposed enhancement of field ionization. At

last, prototypes of gas sensors will be created and then evaluated in a gas sensing test platform. Delivery of a novel field ionization gas sensor with a high sensitivity at ultralow working voltage is the main target in this work.

Many efforts have been made previously in order to reduce the working voltage of ionization gas sensors. However, the sensing nanodevices still need hundreds of volts to ionize gases until the invention of hybrid nanoneedle arrays [11]. The significance of this project involves the formation of a novel hybrid metal/silicon nanoneedle using ion beam sputtering for gas sensing, followed by the finding of the criterion for metal selection. In the thesis, a hypothesis of self-organization procedure towards three-dimensional hybrid nanostructures is proposed. The ordered nanoarrays were discovered to be very sensitive to various gases under ultralow voltages, due to their surface states or polarization enhancement. The creation of such special hybrid nanostructures should contribute to the research in the field of gaseous electronic, for example developing the next generation of gas sensors for various applications.

This thesis introduces a series of selected metal/semiconductor material systems to form a unique ordered hybrid nanoneedle array. A theoretic model of novel nanocrystallites' polarization gas sensor has been practically produced in this work. An extended physics scenario of gaseous electronics has been set up eventually based on the observed anomalous field ionization phenomenon of the hybrid nanoneedle arrays. The novelty will be insightfully detailed in section 1.8 of Methodology.

1.6 Scope

The scheme of this thesis is illustrated in Figure 1.1.

Ion beam in FIB system carries high energy enabling the materials removal from the substrates through ion sputtering [68-71]. This beam incident to the substrates can also rearrange the atoms to form different topographic structures on the surfaces. In this thesis, metal/silicon material systems are selected in order to produce the expected hybrid nanoneedle array. This system includes a series of metallic thin layers deposited on the silicon substrates, which are then subject to ion irradiation with gradually increased dose.

A nanodot located on the silicon nanoneedle, is formed on the substrate of iron/silicon system as a result of ion sputtering. In contrast, ion sputtering of the surface coated with Pt leads to a hybrid nanoarray where the nanocrystalline platinum is preserved on top of nanoneedle. Their geometries and microstructures are described in details.

Several types of gases in various concentrations were used for gas sensing test. The working voltage and the current signal from these hybrid nanoneedle arrays were evaluated. After theoretical analysis of these gaseous ionization signals, additional hypothesis of gas field ionization mechanisms are integrated into the classical gaseous electronics theory at nanoscale. We also pursue the extended applications of hybrid nanoneedle array as a base, on which the nanowires are grown to form the nanowire/nanoneedle nano-hetero-structures.

Purpose: Study of ordered hybrid nanoneedle array for gas sensing

Figure 1.1 A flow chart of the general approaches within this research.

1.7 Hypothesis

The formation of hybrid nanoneedle array is determined by the intrinsic sputter rate of metallic layer on silicon substrate. The low-sputtering-rate metal will preserve and alloy with incident ion, to provide abundant surface states for higher field ionization efficiency. On the other hand, platinum deposited locally in FIB system can be patterned as nanocrystals cluster sitting on the top of each nanoneedle, to enhance gas ionization by the polarization effect.

1.8 Methodology

The thin metallic layers are deposited on the surface of silicon substrate by pulse laser deposition (PLD) for iron and sputtering deposition for others, including aluminum, titanium, chromium, cobalt, zinc, molybdenum, silver, indium, tin, hafnium, tantalum, tungsten, gold as well as bismuth. These metal layers deposited on silicon substrate constitute a material matrix for hybrid nanoneedle fabrication. In order to provide isolated metallic nanocrystals, a chemical vapor deposition (CVD) of platinum is conducted by ion irradiation with a gas injection system (GIS) [72].

Ion beam is rastering in a pattern consisting of a series of squares with gradually increasing dose on each substrate in the metal/silicon materials matrix, in order to find the correlation of profile and material properties, *e.g.* melting point, density or sputter rate. Then the substrates are subject to the square mesh patterning to fabricate the hybrid nanoneedle arrays. The profiles after rastering and mesh patterning are compared to explore the hybrid nanoneedles formation mechanism. Then the iron/silicon hybrid nanoneedle array is used as one electrode of parallel-plate ionization gas sensor, which generates a local electric field of high intensity. On the other hand, a novel gas sensor

using platinum nanocrystallites places a pair of stripes on either side of nanoneedle array, which provides a lateral electric field. These nanoneedles are characterized in detail after fabrication. The geometrical parameters are measured using SEM, which include the aspect ratio, tip radius, and separation space. A column of nanoneedles in each array is retrieved by lift-out technique and thinned down for observation in a transmitted electron microscope (TEM), where the nanoalloys, metal/semiconductor junction or metallic nanocrystallites are characterized precisely.

A gas test platform is set up to investigate the sensitivity of both hybrid nanoneedle arrays. Nitrogen is used as a carrier gas, to deliver the tested gases into the vicinity of nanoarrays. A group of mass flow controllers (MFC) integrated into this platform can adjust the flow rate ratio between the target gas and carrier, which allows a series of precisely controlled gas concentrations. This platform is attached to a semiconductor parameter analyzer, which generates sweeping voltage bias and collects the ionization current signal simultaneously.

In addition, to study the gas field ionization mechanism, the geometry impacted Laplacian electric field distribution is calculated by the finite element method (FEM).

1.9 Significant findings

- a. Silicon substrate deposited by thin metal layers of low sputter rate can result in the formation of hybrid nanoneedle array using ion beam patterning. This hybrid nanostructure is composed of an alloyed metallic nanodot sitting on the silicon nanoneedle. In contrast, high-sputter-rate metals will be removed during ion meshing and lead to the formation of pure silicon nanotips with nanodot free.

-
- b. After ion beam patterning, the platinum deposition can be reserved on top of each nanoneedle in the array. Meanwhile, the as-deposited isolated nanocrystals in the insulating frame can be preserved as well. These platinum nanocrystals have extremely small dimension of around ~5 nm in diameter generally.
 - c. The iron/silicon hybrid nanoneedle array shows excellent field ionization sensitivity to various gases in ultralow working voltages (~ 30 V). The metallic nanodot of alloy (~20 nm in radius controlled by ion dose) on each nanoneedle is believed to play an essential role in the gaseous ionization process. Its significance is proved by the absence of ionization current signal from pure silicon nanoneedle array.
 - d. The platinum/silicon hybrid nanoneedle array is able to operate in even lower voltages (~ 10 V) with remarkable gas sensitivity. The polarized metallic nanocrystal on the tip of each nanoneedle is crucial to the gaseous ionization. Without these nanocrystals, only leakage current can be detected, without any sensing signal as responses to the gases.
 - e. The metal coating, which is able to form hybrid nanoneedle array under ion milling, can also serve as a protective shelter to other functional layers. This methodology can extend ion beam patterning to those materials which are vulnerable to ion sputtering.

1.10 Organization of thesis

This thesis is organized as six chapters:

Chapter 1 introduces the background and motivation of hybrid nanoneedle array for ionization gas sensing, followed by the challenges from its complicated fabrication process and high working voltages. The solution is proposed by the ion beam patterning on selected metal/silicon material system. The general scope, hypothesis, methodology and a list of the significant results are also described.

Chapter 2 reviews the classical gas ionization theory together with recently proposed mechanisms of superimposing enhancement. The fabrication techniques for nanostructure array are compared in this chapter, in order to find a suitable methodology to produce the hybrid nanoneedle arrays with enhanced ionization efficiency.

Chapter 3 presents the metals/silicon material systems in a matrix and their respective responses to the ion beam bombardment. The criterion for selecting the suitable metals to fabricate hybrid nanoneedles has been proposed, along with the qualitative interpretation of geometrical and compositional evolution.

Chapter 4 describes the design, test methodology and gas sensing property of hybrid nanoneedle array on Fe/Si substrate, followed by another novel ionization gas sensor based on isolated platinum nanocrystallites.

Chapter 5 discusses the fundamental mechanisms of these hybrid nanoneedle array gas sensors after the analysis of experimental results. The principle of the field ionization enhancement at nanoscale is discussed, and then integrated into the classical gaseous electronic ionization category.

Chapter 6 draws the conclusions of this work and recommends a framework for future research based on the current findings.

CHAPTER 2: BACKGROUND

In this chapter, the gaseous ionization mechanisms for gas sensing are presented with emphasis on local electric field intensity. Novel surface-states and polarization effect superimposed on the geometry enhancement is able to further improve the ionization efficiency for the hybrid nanostructures. In order to fabricate the hybrid nanoneedle array, ion beam sputtering on a metal/silicon substrate is chosen, which has a lot of advantages over other fabrication methods.

2.1 Gaseous field ionization

An *ion* is defined as a particle (either molecule or atom) carrying unequal numbers of electrons to protons. When one particle absorbs enough energy, it will lose an electron and simultaneously carry an excessive positive charge to become a *positive ion*. This procedure is called as *gaseous ionization* when this phenomenon occurs at a gas particle. The gas molecules in an extremely high electric field may be directly separated as ion/electron pairs, which are then subject to multiplication by collisions with neutral gas particles until forming an electrical flow to bridge the interstitial gap, call as *gaseous field ionization*. On the other hand, if the electron is extracted by an applied electric field from a solid rather than a gas, it is well known as *electron field emission*, or simplified as *field emission*. Although the electron emission only happens on the surface of the cathode in a gaseous electronic system, it still contributes significantly to the indirect gas ionization in a secondary process.

2.1.1 Gaseous ionization methodology

Gaseous ionization is essentially caused by the transfer of external energy to the gas molecules. Besides the field ionization, there are also several other energy-transfer techniques leading to the occurrence of a gaseous ionization, including photo, X-ray, nuclear radiation as well as thermal ionization as shown in Table 2.1 [73].

Table 2.1 Gaseous ionization methods.

Type	Procedures	Annotation	Ionization properties
Photo	$h(\nu_1 - \nu_2) = W_e$ $h\nu_1 + A = h\nu_2 + A^*$ $A^* + A = A_2^+ + e$	<ul style="list-style-type: none"> • $h\nu_1, h\nu_2$ the energies of incident & emitted photons • W_e the gas excitation energy • Collision of atom A and its excited state A^* forming ionized gas molecule A_2^+ 	<ul style="list-style-type: none"> • Only work from 20 to 250 nm in wavelength • Energy is too low to ionize gas directly • An indirect step-ionization is required
X-ray	$h\nu = E_k + W_b$ $h\nu + A \rightarrow A^+ + e$ $e + A \rightarrow A^+ + 2e$	<ul style="list-style-type: none"> • $h\nu$ the incident X-ray energy • E_k, W_b the kinetic and binding energy of electron • A^+ ionized state of atom A 	<ul style="list-style-type: none"> • High-energy X-ray retracts and accelerates electrons to successive collisions to multiply gas ionizations
Nuclear radiation	$E_i = \frac{W_p}{n_c}$ $E_i + A \rightarrow A^+ + e$	<ul style="list-style-type: none"> • W_p, n_c The energy and collision count of incident nuclear particles • E_i the average energy transferred to atom A in collision for ionization to A^+ 	<ul style="list-style-type: none"> • Nuclear-irradiation-charged particles deliver their energy to gas molecules in multiple collisions with slow movement
Thermal	$E_t + A = A^*$ $A^* + B^* = A + B^+ + e$ $e + A \rightarrow A^+ + 2e$	<ul style="list-style-type: none"> • Thermal energy E_t changes atom A to excited state A^* • Excited atom A^* and B^* collides with each other generate ion B^+ 	<ul style="list-style-type: none"> • Collision of excited gas atoms with high kinetic energy from heating • Thermal emission induced photoionization

The methods listed above suggest that an applied high energy is crucial to the gaseous ionization, which takes effect through either the direct liberation of electrons from gas particles or indirect collisions between them. However, the efficiency of

photoionization is very low and the other three approaches demand bulky equipments with stringent protection.

The field gaseous ionization prevails over these traditional gaseous ionization techniques because of several advantages. For example, the establishment of ionization device is more straightforward. The source and ion generation process is safer with radiation free, and the ionization voltage-current signal is more dedicated to the gas property, which is essential to a gas sensor.

2.1.2 Classic gaseous field ionization theory

Field ionization was first observed in 1953 by Müller in a field-emission tube but loaded with a positive voltage bias on the tip [74-76]. Subsequent researches indicated that field ionization is not necessarily related to adsorption, and all particles approaching to the anode can be ionized if the applied electric field is strong enough [75-77]. Researchers later confirmed that field ionization is essentially a gaseous electronics phenomenon reversed to field emission (electron ejected off a solid), whereby there is an electron tunnelling from a gas molecule to the surface of positive charged electrode [75].

2.1.2.1 Tunnelling of electron in field of metal or semiconductor

The energy-band diagrams in Figure 2.1 illustrate the tunnelling of electron into metal and semiconductor surface respectively. As shown in Figure 2.1 (a), in a given electric field F_{VAC} , a gas particle with an ionization potential of U_I emits one valence electron. Subsequently, this electron tunnels through a potential barrier to occupy a vacancy in the conduction band of a metal having a work function of ϕ . Due to the absence of vacant energy states below Fermi level of metal (E_F), the applied external field has to

raise the gaseous valence electron to E_F for tunnelling along the shortest route. By neglecting the weak variation of system energy after tunnelling, a *critical distance* d_c can be derived as

$$d_c \cong (U_I - \phi) / eF_{VAC}, \quad (\text{Eq. 2.1})$$

which defines a margin along the metal surface where the involved gas particle is unable to be ionized. Essentially, the critical distance represents the field ionization efficiency, characterized as *tunnelling probability* D and ion current I [30, 45, 78].

Figure 2.1 Energy-band diagrams for a field ionized gas particle in the vicinity of (a) a metallic tip and (b) a semiconductor surface [11], where E_F depicts the Fermi level, Φ and U_I defines the work function and gas ionization potential, F_{VAC} stands for the vacuum field intensity and d_c is the distance of E_F to the equal atom ground state, called as critical distance. For semiconductor, Φ_s indicates band bending cause by field penetration with depth of λ_c .

The image effect is usually negligible, and the tunnelling probability D can be approximately governed by the gas ionization potential U_I and the applied electric field intensity F_{VAC} as

$$D \cong \exp \left[-6.8 \times 10^{-7} \sqrt{U_I - 7.6 \times 10^{-4} (eF_{VAC})^{1/2}} d_C \right]. \quad (\text{Eq. 2.2})$$

Accordingly, the ion current can be calculated by Gomer's equation [33, 75] as

$$I = A 2 \pi R_m^2 e d_C D, \quad (\text{Eq. 2.3})$$

where A stands for a factor related to the gas feature (ionization potential, concentration *et al*), R_m is the curvature of metal tip and e represents the charge of an electron.

When a semiconductor replaces the metal to serve as the electrode, the fundamental field ionization mechanism of metal tip has to be revised considering the field penetration and band bending effect [28, 79-81]. On the surface of a semiconductor, the bent band provides empty energy states above E_F in valence band, which become the vacancies for electrons to tunnel into. Such band bending ϕ_s is determined by the penetration depth λ_c in the applied electric field F_{VAC} , reads

$$\phi_s = (eF_{VAC} / \varepsilon_r) \lambda_c, \quad (\text{Eq. 2.4})$$

where ε_r depicts the dielectric constant of the semiconductor. This upward bending raises the surface work function of semiconductor electrode, which in turn reduces the critical distance, as shown in

$$d_C^* \cong [U_I - (\phi + \phi_s)] / eF_{VAC}. \quad (\text{Eq. 2.5})$$

As expressed in Equation 2.2 and 2.3, both tunnelling probability and ion current are negative correlated to the critical distance. Thus, of a shorter d_C^* , the semiconductor generally requires a lower field for gaseous ionization, but generates a higher ion current overwhelming the metal, which is also experimentally confirmed in Ref [28, 79-81].

2.1.2.2 Electrical characteristics of gaseous field ionization

The typical current signal of gaseous field ionization under an increasing voltage bias is outlined in Figure 2.2. It can be captured from a well-known parallel-plate capacitor structure, whereby the gas acts as a dielectric layer, as shown in the inset. The entire current-voltage (I - V) curve can be divided into four successive stages, with various current characteristics as responses to the increasing electric field intensity [27].

Figure 2.2 A current-voltage curve of dielectric gas in the electric field of parallel plate electrodes pair [27], which is displayed as inset. The voltage loading is increased from zero to breakdown threshold voltage V_b .

In stage I, the applied electric field is very weak and thus the current is mainly governed by the diffusion of initial charged particles. Therefore the I - V curve is linear, showing an ohmic property which is independent to the gaseous characteristics. There will be more charges subject to recombination in stage II, leading to the depletion of effective current flow; hence the slope of curve becomes gradually flat. Loaded by an intermediate voltage, the current becomes saturated in region III. The number of generated carriers is

equal to the charges neutralized in the electrode. Stage IV is also called as *Townsend discharge*, where the current increases exponentially. The critical voltage V_b defines the requirement for the occurrence of gaseous breakdown, where a “spike” is visible on the I - V curve. Only in this region, the applied electric field is sufficient to generate a detectable current signal for the practical gas sensing applications. At the same time this Townsend discharge and/or gas breakdown signal is strongly correlated to the gas properties, which is crucial to the gas sensitivity.

2.1.2.3 Townsend discharge and gas breakdown

At the beginning of last century, J. S. Townsend commenced to study the gaseous electrical behaviour above the saturation region of I - V curve (after stage III in Figure 2.2) [82, 83]. He led his students to overcome many difficulties, such as equipment limitation and deficiency of knowledge regarding the atomic structure at that moment. However, they successfully explained many gaseous ionization phenomena using arguments based on “collision”, some of which are still valid in certain conditions till today.

In order to understand a field ionization discharge signal, it is particularly important to evaluate how many electron/ion separations one electron can cause by collision to gas particles on its pathway. In the electric field direction, the amount of newly liberated electrons by electron-particle collisions per unit length is designated as *Townsend's first ionization coefficient*, α . In Townsend discharge region, the externally initialized electrons (*e.g.* radiation) will migrate from cathode towards anode in a constant electric field to form a current i_0 . On their pathway with length of x , the current will be propagated to $i = i_0 e^{\alpha x}$. The details of theoretic calculation are interpreted in Appendix

A. Such multiplication in the current, however, will turn off as soon as no start-up electron “seed” is supplemented, which is also known as *non self-sustained* current. In practical gas sensing applications, such exponential I - V curve is less distinguishable compared to the steep perpendicular spike by gaseous breakdown. The breakdown current, in contrast, does not need the external stimulus to retain the ionization current, therefore known as the *self-sustained* current. The sudden boost of self-sustained current has to take the *secondary process* into account, which mainly originates from the positive ion collision.

The positive ions move slowly towards the cathode, which may cause two secondary processes: ion collision (β -process) and cathode process (γ -process). Herein β represents *Townsend's second ionization coefficient*, the count of electrons generated by ion-particle collision per unit length and γ indicates the probability of liberating a secondary electron by each ion impinging to the cathode surface. Thus, if the distance of electric field is d , the ionization current based on β -process can be evaluated as

$$i = i_0 \frac{e^{\alpha d}}{1 - (\beta/\alpha) e^{\alpha d}}. \quad (\text{Eq. 2.6})$$

Similarly, γ -process superimposed ionization current is governed by

$$i = i_0 \frac{e^{\alpha d}}{1 - \gamma e^{\alpha d}}, \quad (\text{Eq. 2.7})$$

which only replaces β/α by γ but shares the same form to β -process. The derivation of these equations is detailed in Appendix B.

These two equations determine the condition for gaseous breakdown, in which

$1 - (\beta/\alpha) e^{\alpha d} = 0$ and $1 - \gamma e^{\alpha d} = 0$, known as the *Townsend's breakdown criterion*.

In perspective of the electrical signal, if either condition is satisfied the ion current will become infinite theoretically, but determined by the external circuit practically. From a different viewpoint of gaseous electronic physics, it reflects the formation of a plasma channel that bridges the anode and cathode [73].

2.1.3 Fingerprinting signal of gas field ionization

So far, the gaseous breakdown procedures by electric field ionization can be summarized as follows:

1. Electron tunnelling from gas particle in vicinity of either metal or semiconductor anode to form an initial ion current.
2. The propagation of ion-electron pairs by collisions between field-accelerated electrons and neutral particles (α - process).
3. Avalanche of electrical flow due to secondary processes (either β -process or γ -process depending on device structure and dimension).

Both the initial direct ionization and the successive collision-caused indirect ionization are correlated to the specified ionization potential U_i . To overcome this barrier for separating the positive ion from negative electron, characteristic voltage bias (threshold voltage), which is unique to a certain type of gas, is required to be loaded on the gas ionization device. This distinct breakdown voltage established at certain pressure and temperature condition provides the “fingerprint” for the gas under investigation [84-86].

Traditional bulky ionization gas sensing equipments always have the difficulties to be installed, because of the extremely high operation voltage and power consumption. For example, theoretically electric field up to 1.7×10^{10} V/m is necessary to directly ionize

nitrogen [11]. Therefore, the research of field gaseous ionization sensing is trudging until the introduction of nanotechnology.

2.2 Nanostructure enhanced ionization gas sensors

The first miniaturized gaseous ionization sensor was fabricated by Ashish Modi *et al.* using carbon nanotube in year 2003 [13]. Thereafter, many derivative works extensively improved the gas sensing performance by innovation of the geometry or optimization of the material (system), mainly in order to further decrease the working voltages.

2.2.1 Geometry enhancement

One straightforward method to increase the electric field of a parallel-plate is reducing the interstitial gap. However, this approach is inefficient in the case of uniformly distributed electric field. Taking nitrogen as an example, theoretically the plate electrodes pair with a gap down to 1 μm still needs a terrific voltage bias of 17 kV to cause ionization directly [11]. Fortunately the gas sensor only requires high electric fields to induce the detectable ionization signal locally, rather than the uniform current flowing across the entire gaseous space. Therefore, one alternative method is proposed, which roughens the surface of electrode in order to converge the local electric field around the “protrusions”.

2.2.1.1 Field convergence effect

With geometry at nanoscale, one-dimensional nanomaterials (ODNM) generate strong nonlinear electric field in vicinity of their tips [87-91]. This effect can be schematically illustrated in Figure 2.3 (in an arbitrary size) [92].

Figure 2.3 A simulation chart showing the electric field in vicinity of rods is enhanced by geometry effect [92].

In this model, it is obviously that the contour, which outlines the identical electrical field intensity, is dramatically distorted around the tip of each rod. The higher intensity in darker color is concentrated around each tip either. Decorating with a sharp one-dimensional nanomaterial, such as one single carbon nanofiber, a plate electrode is able to elevate the local field up to more than one thousand times higher by convergence of the electric field lines [92-94].

There are many ODNM of the high aspect ratio, of which the tip can work as an idea convergence center in the applied electric field [22, 24, 35, 95, 96]. One pioneer material is carbon nanotube (CNT), which is grown vertically on the anode of a parallel-plate device for the field ionization gas sensing application, as shown in Figure 2.4 [13].

Figure 2.4 The setup of an ionization gas sensor using CNT [13]: (a) vertical-aligned multiwalled CNTs decorated on the anode, (b) cathode of aluminum plate mounted on the glass insulators to form the discharge space and (c) a cross-sectional SEM image of CVD-grown CNTs film.

The performance of this CNT gas ionization sensor is quite impressive as plotted in Figure 2.5. Compared to the traditional devices of parallel-plates structure, with the same separation the overall breakdown voltages has been reduced from more than one kV to hundreds of volts. Furthermore, these breakdown voltages can even establish a spectrum containing the different gases, exhibiting a pronounced fingerprint property.

This creative work inspires many following exploratory researches using ODNM for field ionization. However, depending on its extremely sharp tip ($\sim 15\text{nm}$ in radius generally), carbon nanotube still dominates the field ionizer materials based on the geometry mechanism [13, 97]. There are few alternative nanomaterials employed in

2.2.1.2 Field shielding effect

The focus moving to the electric field shielding effect was initiated by a question that had been proposed for a long time: the field intensity around CNT tip would be extremely high due to its nanoscale curvature, why there is never visible discharge with illumination but usually the dark current instead [33, 34, 45, 73, 75, 84]? The preliminary answer is provided by Y. Zhang *et al.* using a three-dimensional finite element method (FEM) simulation [99]. For each volume of CNTs in the array, the field enhancement factor f is obtained as a ratio of the maximum field intensity $E_{\max}$ over the average one, as shown in Table 2.2 [99].

Table 2.2 Calculated electric field of increasing numbers of CNTs [99].

CNT number	170 μm gap		100 μm gap	
	$E_{\max}$ (V/nm)	f	$E_{\max}$ (V/nm)	f
1	0.248221	5.275	0.408811	5.110
9	0.182061	3.869	0.350994	4.387
25	0.14983	3.184	0.366453	4.581
49	0.119932	2.549	0.277499	3.469
81	0.11633	2.472	0.325183	4.065
121	0.134452	2.857	0.278052	3.476
169	0.137704	2.926	0.265815	3.323

The calculation suggests that even though a single CNT can distort the local electric field significantly, the field becomes uniformly low when the number of CNTs is increased to form a film of high density. In this case the field becomes equivalent to that of a macro parallel-plate structure, where the geometric effect of nanomaterials is negligible [35, 92-94, 98]. Another two-dimensional FEM simulation is carried out in order to investigate the electric field distribution, whereby both the geometry and shielding effect are clearly visible in Figure 2.6.

Figure 2.6 Plots of two-dimensional FEM electric field simulation (voltage bias of 30 V in vacuum: (a) (b) (c) gradually increased aspect ratios lead to the higher maximum electric fields while (d) the coupled electric field crossing the crowded tips of nanowires due to shielding effect. The inset in (c) and (d) presents the overall field distribution, where the square area is magnified respectively.

Figure 2.6 (a) and (b) compares the corresponding enhanced electric field around different curvatures of nanotip, whereby a maximum intensity of 1.879×10^8 V/m for 50 nm of radius and 4.746×10^8 V/m for 25 nm of radius respectively. Figure 2.6(c) and (d) represents a column of CNTs, having an individual tip radius of 15 nm but with different separation distances. If the space between adjacent nanowires is 500 nm, as shown in Figure 2.6 (c), the maximum electric field is elevated up to 5.998×10^8 V/m. However, the nanowires in Figure 2.6 (d) are bundled with a small gap of 50 nm, the maximum field has fallen to 1.241×10^8 V/m, which is even lower than that of blunt tips showing in Figure 2.6 (a). In this simulation, only the boundary of gaseous space is considered, regardless of the materials properties and surface charges.

2.2.1.3 Separation for one-dimensional nanomaterials array

There are mainly two approaches to separate the grown one-dimensional nanomaterials: catalyst pattern or template block, as schematically listed in Table 2.3 [33, 92].

Table 2.3 Two methods to separate one-dimensional nanomaterials [33, 92].

Type	Procedures	Example
catalyst pattern	<p>Catalyst layer on supporting substrate</p> <p>Patterning on catalyst</p> <p>Nanomaterials growth on residual catalysts</p>
template block	<p>Catalyst layer on supporting substrate</p> <p>Template on catalyst</p> <p>Nanomaterials growth on exposed catalyst then remove template</p>

blue: supporting substrate, dark: catalyst, red: nanomaterials and gray: template; the example of catalyst pattern: carbon nanofiber grown on lithography-patterned nickel catalyst [92-94] and the example of template block: gold nanowires grown through holes of anodic aluminum oxide (AAO) layer (top-viewed profile in the inset) [33].

In the case of carbon nanofiber synthesis, a titanium thin film is deposited on the substrate followed by a catalytic nickel membrane. Then a complicated photolithography process is introduced to split the catalytic nickel layer into 2 μm dots with 6 μm spacing. The intermediate Ti layer plays a critical role of a barrier against the diffusion of catalysts during subsequent nanofiber growth. Besides these complicated pre-patterning of catalysts, there are also several post-treatments after the nanowire growth. These processes, such as blocker removal and residue cleaning, probably deteriorate the overall field ionization performance [92-94]. In the second example of

gold nanowire growth, one AAO membrane is coated on the baking electrodeposited gold seed film. This thick AAO template ($\sim 60\text{ }\mu\text{m}$) is in a pattern of the uniform cylindrical holes of 180 nm in radius and 300 nm in separation. Within these holes, the gold nanowires are able to grow galvanostatically up to 10 μm controlled by an electrochemical system. Subsequently, the template is removed by immersion into a NaOH solution. As the image shown in the table, the elimination of AAO membrane is obviously incomplete with serious interstitial residual inside the nanowires array. Even though the preparation for nanowire growth is straightforward without lithography process in patterned catalyst case, the inconvenient template removal still causes severe defects, which hinder the application of grown nanowires.

Compared to the gas ionization sensor using CNTs of Modi *et al.* [13], template-blocked gold nanowires causes occurrence of argon ionization at a relatively lower voltage (162 V than 220 V) [34]. The sufficient separation between individual gold nanowires has compensated the disadvantages of its unfavorable blunt tips. However, it is disappointing that the working voltage is still too high to operate practically, for example in the field of the portable equipment. The research is required to explore other supplementary effects to increase the field ionization efficiency.

2.2.2 Hybrid nanostructure enhanced ionization

There are many hybrid nanostructures that are integrated in the conductometric gas sensors. Various functional nanoparticles are decorated on the sensitive nanomaterials to intensify the current signals [100-105]. However, such intensive chemical interaction between the gas particles and the sensitive nanostructure is undesirable in the case of field ionization gas sensing. These interactions are believed to extend the recovery time

cost by the desorption procedure. Meanwhile, the adsorption of gas particle may deteriorate the stability and reliability of local field ionization [24, 26]. Hence, it is challenging to find a proper material system and compatible process to fabricate a hybrid nanostructure for enhancing the field ionization. Currently, few theories or devices are proposed in this exploratory research field.

2.2.2.1 Surface-states enhancement

It is interesting that the concern of hybrid nanostructure enhanced ionization begins at the disadvantage of template block method [27, 33, 34, 45]. R. B. Sadeghian *et al.* found that a trace of amorphous alumina could survive on the tip of each gold nanowire after incomplete AAO template removal. The residual alumina exhibits a semiconductive character, forming a Schottky interface with the underlying gold nanowire. It can operate at a lower voltage than homogeneous metallic nanowires, which is consistent to the theoretical band diagram shown in Figure 2.1. In this case, the band bending of semiconductive alumina cap on the tip of each nanowire increases the surface work function, which yields a short critical distance, and in turn a higher ionization probability.

Subsequently, he continued to fabricate a reverse hybrid nanostructure for ionization gas sensing, which consists of a metallic nanocap on top of each semiconductor whisker, as the secondary electron images shown in Figure 2.7 [11]. In this case, a two-step vapor-liquid-solid (VLS) method is conducted on a highly conductive silicon wafer. At first VLS step, Si nanowire trunks are grown with gold particle as catalyst on the top. But then, HCl flow is introduced to suppress the growth of these trunks; at the same time, gold-silicon alloys begin to migrate from the tip and spread downwards

along the surface of the silicon nanowire. The whiskered silicon is subsequently grown based on these dispersed Au/Si nanoalloys, which eventually forms a “nanotree” after the second step of VLS growth.

Figure 2.7 SEM images of hybrid gold-whiskered silicon nanowires [11]: (a) silicon trunks annealed in HCL without whiskers; (b) a bundle of and (c) a single silicon nanowire with whiskers, where the gold nanoparticles of bright contrast are visible on each tip.

The typical current-voltage (I - V) signal for a single hybrid whisker is calculated as $I_i = 7 \times 10^{-22}$ A under voltage loading of 6 V. The researchers noticed this anomalous ultralow field and a dramatically weak current, which is inconsistent to mechanism regarding to the critical distance (d_c , refer to Figure 2.1). Based on their previous argument [45], a shorter d_c should have resulted in a higher tunnelling probability (lower required field for ionization) and larger ion current at the same time. In order to

explain this phenomenon, two hypotheses were proposed on this hybrid structure; both are quite different to the either homogenous metal or semiconductor material, as the energy band diagrams shown in Figure 2.8.

Figure 2.8 Energy-band diagrams of two possible mechanisms to explain the anomalous field ionization phenomena [11]: (a) metal has a triangle potential barrier (solid line) with work function ϕ_{metal} . However, work function of semiconductor $\phi_{semicond}$ superimposed by field-induced band bending ϕ_s , which encounters a trapezoidal barrier in a larger size (dash line). Herein field penetration is considered without impact to the critical distances, thus $d_{C-metal} = d_{C-semicond}$. (b) This model considers surface states effects. Even without the electric field induced surface inversion, the surface states still provide the vacancy for the electron tunnelling. In a strong field (solid line), the penetration probability is higher for closer state to valence band (shorter d_{c1}) than further one (longer d_{c2}). In case of a weak field F_{vac2} (dot dash line), electron can tunnel into the surface states. The intrinsic and p-type degenerate Fermi level is marked as E_F and E_F' respectively, while the vacuum field intensity is designated as F_{vac} . Diagram (a) and (b) are plotted in different scales.

Without consideration of surface states as shown in Figure 2.8 (a), a field penetration to semiconductor is assumed to modify the shape of potential barrier but retain the critical distance d_c [106]. In other words, the gas particle is probably ionized on the surface of

a semiconductor in a comparable electric field to the metal. The shape of barrier is changed from triangular of metal to trapezoidal of semiconductor, with an increased barrier height $\Delta U_{semicond} > \Delta U_{metal}$. Therefore, the barrier expansion suppresses the electron tunnelling probability, which is characterized as a weaker ion current [28, 30, 107].

In contrast, the mechanism illustrated in Figure 2.8 (b) involves the surface states [108]. Different to the previous viewpoints, electron from gas particle can also access these surface states rather than vacancy available in valence band only [30]. The location of surface state away from the valence band, which is positive correlated to the critical distance d_c , generally determines the probability of tunneling occurrence. For example, electron tunneling to surface state in level of E_F (blue curved box) is more probable than that around E_c (white curved box) with a lower critical distance ($d_{c1} < d_{c2}$).

Under a low voltage F_{VAC2} , the experimental results confirmed that surface states are in favour of electron tunnelling [11]. Furthermore, another measurement by Garnett E. C. *et al.* suggested that the majority of edge positions surprisingly prefer the tunneling of electrons from gas particles which are further away from solid surface [109]. In this condition, a long critical distance is illustrated as d_{c3} corresponding to the low voltage F_{VAC2} , where field ionization can start. In spite of this lower field requirement for gaseous ionization, the field ion current is still very weak due to the lower penetration probability (long d_{c3}).

It is believed that the second mechanism involving surface states is in agreement with the detected gas sensing signal (low field and weak current), as shown in Figure 2.9. The field ionization currents in Figure 2.9 (b) are absent in Figure 2.9 (a) after removal of gold caps on top of the nanowhiskers. Combining the proposed mechanism and electric test results, it can be deduced that the gold provides the crucial surface states. In a low field, it is believed that the ionization current is strongly correlated to gaseous ionization potential ([30, 75] see Eq 2.2, 2.3), which is the fundament to fingerprint various gases, as shown in Figure 2.9 (c).

Figure 2.9 Gaseous ionization current signals [11]: (a) no field ionization signal in I - V curves after gold cap removal from silicon nanowhiskers, (b) field ion currents of nitrogen under various pressures and (c) field ion currents of argon, helium, ammonia and nitrogen under a constant voltage bias of 2 volts. Gas sensitivity (S) is represented by ion current over partial pressure. A table as inset displays the relative sensitivity of various gases to that of N_2 .

This work was profound as a fundamental science research, which creatively proposed and carefully examined a gas ionization mechanism based on the surface states, to explain the observed anomalous field ionization phenomenon. However, the origin of surface states is only roughly discussed. The surface state is an important concept in

conductrometric gas sensor. Its working mechanism in this field ionization gas sensor requires more insightful discussion. Meanwhile, the silicon nanowires are grown randomly, and the following whiskered process is rather complicated. These irregular distributed hybrid nanostructures are unfavourable for the generation of a detectable gas sensing current (shielding effect).

2.2.2.2 Polarization enhancement

There is another novel field enhancement based on polarization of nanocrystals, which is still proposed as a theoretic model at the present stage [44]. Polarization is a procedure which redistributes the internal electrons of an object in an applied electric field. This effect behaves in different manners depending on the conductivity of material. For example, when a dielectric material is placed into an applied electric field, the electrons along the surface are rearranged through stretching or rotation within the atom or molecule. In contrast, the free electrons within a metal will flow across the entire surface under the electric field. The electron migration in metals charges one terminal of the conductor positively whereas the other negatively, resulting in a build-in electric field. Obviously, the efficiency of charge redistribution is much higher in metallic materials than semiconductors.

Z. Hou *et al.* fabricated a nanostructured sensor to detect atomized liquids combining both the field polarization and ionization effects, as shown in Figure 2.10 [110]. The atomized liquid is injected into an applied electric field whereby each droplet is polarized immediately. The charges in the droplets move in the opposite directions; herein, more positive charges accumulated on the lower edge towards the cathode of nanoneedles having an enhanced electric field (due to geometry effect) [92-94]. Hence,

the strong field in vicinity of nanoneedle is subject to further improvement by superimposition from the field of polarized charges. Therefore, the vaporized molecules from droplets are favourable to be ionized, causing a characteristic ion current.

Figure 2.10 A schematic diagram of polarization on field intensity simulation plot and characteristics of nanomaterials [110]: (a) polarization effects within atomized droplets induced by external electric field. The vaporized molecules ionization will happen in the high electric field formed by polarized droplets and nanoneedles. The electric field is simulated by finite element method. (b) and (c): bright-field transmitted electron images of a carbon nanotube and a carbon based one-dimensional nanostructure.

However, this work only qualitatively demonstrates the probability of integrating polarization and ionization together for gas sensing application, without a theoretic quantitative discussion. Moreover, the proposed enhancement on the atomized liquid droplets is unable to be directly implemented in the case of common dry gases. It is desirable to enable a one-dimensional nanostructure with the internal polarization enhancement to overcome this limitation. One promising method is introducing the polarisable nanomaterials, *e.g.*, metallic nanoparticles, on the top of insulating one-dimensional nanomaterials. In this hybrid nanostructure design, the isolation of polarisable particle is crucial for the charge accumulation; otherwise, charges will

uniformly disperse in a continuous potential, which may severely decrease the local charge density and weaken the field enhancement efficiency [24, 44].

The exploration of field ionization gas sensor based on polarization mechanism encounters a series of challenges, from the device design and fabrication technique to the electric field evaluation.

The traditional gaseous field ionization nanodevices always originate from the classical parallel-plate model (see Figure 2.2), where one or both electrodes have been decorated with nanomaterials [11, 13, 111]. This design is useful for field convergence of the nanotips with uniform surface charges distribution, for example a continuous positive layer on the anode without charge congregation. An alternative placement has to be proposed, which arranges nanomaterials (CNTs) into the interstitial gap between the electrodes pair rather than on the their surfaces, as shown in Figure 2.11 [112].

In this case, before the deposition of a catalytic nickel membrane, a layer of insulating silicon dioxide is coated on silicon substrate in order to isolate the growing carbon nanotubes. A gold layer on nickel patterned by lithography serves as the electrode, which defines the region for nanotube growth. The change of electric field direction during nanotubes growth results in their bent profile [113], while the straight CNTs will be obtained in a consistent field, as shown in the schematic comparison in Figure 2.11 (b) and (c).

Figure 2.11 Schematic diagrams of field ionization gas sensor using carbon nanotubes [112]: (a) process steps of growing bent CNTs between patterned electrodes and (b) the electrodes pair on the substrate is loaded by a direct current (DC) voltage bias, to generate an ion current flowing along the bent CNTs. (c) As a comparison, a traditional setup is outlined which employs CNTs as the anode to induce ion current towards the counter cathode plane.

The different placements of functional nanomaterials (between electrodes) determine its special voltage loading method (lateral rather than vertical). In the case of bent CNTs, the gaseous ionization field is restricted to the interstitial gap between adjacent nanotip and nanotube, which is exactly desirable for the polarization mechanism. Therefore, a pronounced field enhancement by bent CNTs is proved by the required working voltage as low as tens of volts, compared to the case of the straight CNTs around 400 V. However, the ion current generated by the bent CNTs array only shows an exponential increment with voltage sweeping, where the fingerprinting gas sensing signal is hardly distinguishable. This disappointing signal might be due to the leakage caused by the incomplete depletion of catalytic metallic layer of Ni, or the undesirable cross-linked CNTs [113].

The theoretic analysis of polarization suggests that each polarisable nanomaterial requires a strong field and a complete isolation for a considerable enhancement. The surrounding high field intensity can be easily provided by adjacent nanotips, *e.g.* the bent CNTs. However, the previous ODNM are usually formed continuously on the surface of electrode, which requires an overall high conductivity in order to deliver the generated ionization current. For example, a metallic seed layer is usually necessary to grow nanowires but it may cause severe leakage of the polarized charges [22, 27, 35]. The semiconductor nanomaterial does not suffer from the serious leakage issue because of the intrinsic high resistance, like zinc oxide nanowire [35]. However, a semiconductor in an applied field is partially dielectric polarized, which means the internal charges are redistributed insufficiently.

A simplified polarization model was established by Z. Hou *et al.* to estimate the surface accumulated charge density σ_p in vacuum. In this model, an array of isolated metallic nanorods is placed between a parallel-plate electrodes pair. The surface charge density reads [44]:

$$\sigma_p = \frac{\varepsilon_o h r M}{A_e^2} \left[\frac{2A_e}{s} + \frac{M(N-1)rh}{s} + \frac{(M-1)sh}{d-2s} \right] \times V, \quad (\text{Eq. 2.8})$$

where ε_o stands for vacuum dielectric constant, h and r defines height and radius of each nanorod, M or N is the number counting parallel or perpendicular to the electrode of equivalent area A_e , d and s measures gap of the electrode and space between nanorods and V represents the voltage bias. In this formula, the first item presents the surface charge density based on classic parallel-plate capacitor model. A following expression in the square brackets represents the amplification effect provided

by the inserted nanorods array. A corresponding schematic diagram is outlined in Figure 2.12 (a), compared to the traditional design originating from parallel plates setup (b).

Taking these surface charges into consideration, it is feasible to use the finite element method to estimate the electric field distribution by solving the coupled Laplace equation [92-94, 110].

Figure 2.12 (a) A schematic diagram of polarization effect in metallic nanorod array compared to (b) traditional parallel plane setup for ionization gas sensing. The charges within nanorods move towards opposite electrodes and accumulate on the surface. Herein, the number of nanorods M and N is 3 and 4 respectively.

2.2.2.3 Top-down fabrication for nanoneedle array

Heretofore, in summary the one-dimensional nanomaterials for field ionization are mainly assembled by growth on the surface of electrode. Templates or patterned catalysts are introduced to separate these nanomaterials orderly to overcome the shielding effect in field convergence or charge leakage issue during polarization. The metallic catalyst or template residual has to be preserved carefully on top of each nanotip to form the hybrid nanostructure with superimposed effects (surface states or polarization effect). Although there are many progresses in bottom-up approaches to form hybrid nanoarrays, neither the overall regularity nor the internal component

control is satisfying currently. In contrast, the alternative top-down fabrication techniques for nanoarrays drew more and more attentions recently [7, 10, 46, 114]

Different to the bottom-up processes with a manner of “addition”, the top-down methods generally shape the structure through “subtraction” within the substrate [10, 54, 115]. In particular, the shaped structure in the form of nanoneedle has a high aspect ratio, which is particularly desired for gaseous ionization application. Unfortunately, only wet-etch integrated with lithography on homogenous single crystalline substrate, *e.g.* silicon is able to provide the periodic nanoneedle array [6]. The anisotropic etched silicon nanoneedle shows a low aspect ratio defined by the preferred etching crystallographic plane, which might be qualified as an anti-reflection coating for optic applications but unable to induce sufficient electric field for gaseous ionization [54, 116-120].

Dry etching, as an isotropic process, fabricates nanoneedle array in one step with a pronounced higher aspect ratio particularly incorporated with surface mask layer [10, 52, 54]. One typical example is illustrated in Figure 2.13, whereby the gas-assisted electron cyclotron resonance (ECR) plasma is etching various substrates and the silicon carbide (SiC) nanomask.

The mixed reactants in terms of ECR plasma contained two couples of gases for the corresponding purposes in sequence: assembly of SiC nanocluster as mask (reaction of silane and methane) [121] followed by etching of unmasked region of substrate selectively (erosive argon and hydrogen).

Figure 2.13 Schematic diagrams of nanoneedles formation and secondary electron images of nanotips array fabricated on three different substrates [54]: (a) a mixture of reactive gases is introduced to form plasma; (b) the reaction of silane and methane plasma synthesizes the silicon carbide nanoclusters, which subsequently distribute on the surface of substrate uniformly; (c) argon and hydrogen plasma etches the substrate selectively where no protective SiC particles exists. (d), (e) and (f) display the morphology of nanotips produced on substrate of single crystal silicon, polycrystals silicon and gallium nitride (GaN) on sapphire respectively.

With the higher rigidity and chemical stability, the SiC nanoclusters were able to protect the underlying substrate and form a nanoneedle array of high aspect ratio. The mechanism of the nanomask deposition and preservation was still unclear. However, the final profile and distribution of nanoneedles varied on different substrates, as shown in Figure 2.13 (d), (e) and (f). This phenomenon can be partially explained by the different

intrinsic physical stabilities of substrate against the bombardment of argon plasma and chemical inertness to reactive etching by hydrogen plasma.

Besides silicon carbide, other nanomaterials can also work as mask layer of which the resistivity to etching reactant is high, such as silicon dioxide [52, 53]. Unfortunately, the metal layer in dry etching is usually quite unstable [122-124]. Therefore, if a metal/semiconductor material system is etched in order to fabricate a hybrid nanoneedle structure, the metallic cap will be eliminated immediately, even in prior to the formation of semiconductor nanoneedle. Therefore, the massive plasma irradiation etching is unfavourable to form the desired hybrid nanoneedle array for field gaseous ionization. Alternatively, a more precise nanofabrication technique, focused ion beam (FIB) milling, is promising to overcome such challenges, particularly adopting the merit of mask layer [9, 125, 126].

2.3 Focused ion beam system

In the last three decades, focused ion beam (FIB) system plays a significantly important role in semiconductor industry, by means of transmission electron microscopy (TEM) sample preparation and cross-sectional observation on integrated circuit [57, 127, 128]. Meanwhile, in materials research area, the FIB patterning on substrate is prevalent for nanodevice prototyping; in particular the three-dimensional nanoneedle array [56, 67, 129, 130].

2.3.1 FIB installation

FIB system is usually integrated with a scanning electron microscope (SEM), which allows the *in situ* observation during ion beam fabrication as shown in Figure 2.14.

Figure 2.14 (a) A dual-beam focused ion beam system [131] and (b) a schematic diagram showing the structure of two columns in chamber [132].

A focused ion beam system is mainly consisting of an ion source, an ion beam column, a beam deflector and a sample stage in sequence, as shown in Figure 2.15 (a). Gallium is commonly selected as the liquid metal ion source (LMIS) [123, 124] with advantages of low melting point, volatility and vapor pressure but high discriminability from other elements. [133]. The gallium ions (Ga^+) are extracted from the liquid source tip and then collimated by an upper lens into a parallel beam. A following optic column beneath the source filters out the ions of undesired mass-charge ratio or deviated to the vertical direction [56]. The lower lens with a deflector is critical to further focus the beam and then defines the final landing position onto the substrate [57]. A multi-channel plate (MCP) is right above the projected substrate surface, to collect the ion-induced secondary electrons emitted from sample for imaging [134]. There is an auxiliary gas nozzle quite closed to the substrate delivering gases which are reactive to the incident ions, to allow either deposition or accelerated etching. Therefore, these components incorporating with focused ion beam realizes three different functions: imaging, milling and deposition, as shown in Figure 2.15 (b), (c) and (d) respectively [134].

Figure 2.15 (a) A schematic diagram of components in FIB system [56] and the principles of its main functions [134]: (b) imaging, (c) milling and (d) deposition. In image mode, a fine ion beam with lower current and small spot scans the sample surface, to generate secondary electrons/ions which are then collected by a MCP for imaging. In milling mode, a stronger ion beam sputters the material out from substrate. While if during the beam irradiation there is precursor gas molecules injected, there will be a film deposited along the projected area.

2.3.2 Ion milling

Localized ion beam milling becomes one of the most important applications of FIB system in nanotechnology research. This nanofabrication technique that forms a nanostructure actually involves a series of processes including material sputtering, redeposition and swelling. There are many experimental or theoretic works carried out to study the relationship between these effects and synthesized nanostructures [56, 57, 62, 63, 65, 68, 70, 71, 127, 135, 136].

2.3.2.1 Ion sputtering

In general, sputtering is essentially a sublimation process in which an atom is ejected from the surface of solid into the gaseous space. Hence, a high-energy (*e.g.* 30 keV) ion beam impinges onto the surface of low-binding-energy material allows a rapid material removal. However, if the beam energy is ultrahigh, for example 100 keV, ions will prefer penetration and embedment into substrate deeply to sputtering materials off [57]. Beside the characteristics of ion beam and substrate, the design of milling pattern is equally significant to the formation of nanoneedle array [136].

Figure 2.16 (a) A schematic diagram showing pixel-by-pixel style in FIB trench milling, where there is an overlap between adjacent pixel to permit a uniform dose distribution along the direction of beam movement [56]. **(b)** Corresponding cross-sectional SEM images illustrating evolution of V-shape nanostructure, where the reflected ions at sidewalls from tail of beam (red lines) enhance the removal around the bottom corner [129].

In a FIB system, a pattern is directly “written” on the substrate by deflecting ion beam in a manner of accurate pixel-by-pixel shift as shown in Figure 2.16 (a). In each pixel, the incident ions yield a Gaussian distribution, where more doses are concentrated in the center of beam with a weak tail in the outer-ring zone [65, 70, 71]. An example of a

trench nanostructure formed is shown in Figure 2.16 (b) [129]. During the fabrication, irradiation always causes the removal of materials within the corner region (doubled dose) being moved faster than the center area on top of each nanopillar. This preferential material removal is due to the effective reflection of the beam tail on sidewalls ($\sim 70\%$ ions reflected from a sidewall of 2° – 5°) [129].

Figure 2.17 (a) A 4×4 nanopillar array developed by preliminary square mesh patterning on 500 nm InAs thin film on InP substrate. (b) A nanospike array fabricated by long-term repetitive scanning of an identical pattern [64].

The sidewall of a nanotrench usually has a considerable slope (up to $\sim 80^\circ$) as a result of Gaussian ion beam, which is desirable to form the profile of a nanoneedle structure with a high aspect ratio. This characteristic of ion beam allows each pillar in the array pattern (Figure 2.17 (a)) [64] to be transformed into a nanospike when this pillar pattern is subject to the sufficient ion irradiation, forming a nanoneedle array (Figure 2.17 (b)).

2.3.2.2 Redeposition

The sputter process, whereby atoms are ejected from substrate surface into the gas phase, is not a thermodynamic equilibrium state. Thus the ion sputtered particles probably recoil back onto the solid causing a redeposition [57]. The effect will complicate the estimation of milling rate, because the volume of redeposition is not only

impacted by both the pattern or sputtered geometry, but also the material properties, such as sticking coefficient and binding energy [56, 68]. In case of fabrication of a nanoneedle array, the material accumulation on the ridge, rather than the total material removal during engraving, has to be emphasized, as shown in Figure 2.18 [137].

Figure 2.18 (a) A cross-sectional profile of a channel created by one single FIB milling pass, where ‘A’ and ‘B’ stands for ridge and mouth width, while ‘C’ and ‘D’ the channel and ridge height respectively. (b) According geometry measurements of channel with increasing dwell time [137].

The measured dimensions by ion milling of one single scan plotted in Figure 2.18 (b) suggests that due to the more severe redeposition with longer irradiation dwell time, the growth of ridge is approximately linear to elapsed time (D) but the trenching process is decelerated (C). To eliminate the redeposition inside the trench, ion milling is usually implemented by repetitive pass instead of single pass [65]. The volume of redeposition in each pass of repetitive routes is rather small; and meanwhile, the piled-up material is removed partially by the subsequent scan. In addition, the extension of trench mouth (A and B) confirms that the beam tail is able to accumulate enough dosage for effective sputtering, which is crucial to create the sharp tip of a nanoneedle.

2.3.2.3 Swelling effect

If the dose and energy of incident ions is insufficient during ion beam bombardment, the swelling effect will dominate in the irradiated region on the substrate instead of materials removal [127, 130, 135].

Figure 2.19 AFM measurements of a square FIB milling pattern on a silicon substrate of (a) a low dose swelling by 30keV, $5 \times 10^{15} \text{ cm}^{-2}$ and (b) a high dose sputtering by 30keV, $5 \times 10^{16} \text{ cm}^{-2}$ irradiation. (c) Total volume changes of silicon from swelling effect to material removal stage with the increasing 30 keV Ga^+ dose projection [135].

The swelling effect expands local irradiated substrate mainly by two approaches: implantation and amorphization. The impinged ions in the form of cascade may penetrate into the crystalline target and then occupy the lattice positions of the substrate material by driving the original atoms to the ambient area. However, the implantation mechanism is too insufficient to cause the significant change of nanostructure geometry [138, 139]. On the other hand, the energy transferred from the incident beam may cause the amorphization of crystal substrate. Due to the relatively higher density of crystal than amorphous, such as silicon [140], the volume undergoes considerable increase after

amorphization. The measured topography change due to swelling is on the level of tens of nanometers [57], the amorphization is deduced to dominate over implantation [129, 130, 135]. One example is shown in Figure 2.19, where the ion dose is more than two orders of magnitudes lower than that of effective sputtering (10^{15} versus 10^{17} cm⁻²) [57, 129, 135].

In summary, all these four effects are critical to the fabrication of nanoneedle array in a focused ion beam system:

- An ion beam with either an extremely high energy or ultralow dose causes implantation and amorphization instead of an efficient sputtering.
- Trench-type structure under square mesh patterning can create a sharp nanoneedle array with steep sidewalls.
- Scanning of repetitive ion pass is able to decrease redeposition effect inside the trench, which results in a nanoneedle of higher aspect ratio.
- The tail of incident beam is crucial to the formation of nanotip due to both redeposition and swelling effect.

After understanding these effects, the fabrication recipe of ion beam milling for hybrid nanoneedle array can be designed successfully.

2.3.3 Hybrid nanoneedle array fabrication

The hybrid nanoneedles composed of semiconductor and metal are believed to perform improved gas sensitivity in ionization gas sensing application. Some preliminary works related to metal/semiconductor hybrid nanoneedle array fabrication, in particular on III-V compounds have been obtained, which are overviewed as below.

2.3.3.1 Hybrid nanoneedle of III-V compound

K. A. Grossklaus et al. summarized the mechanism highlighting the metallic nanodots assembled on substrates of InAs, InP and GaSb under Ga^+ irradiation in FIB system [141-144]. For these III-V compounds, group V elements are preferentially sputtered out of the substrate surface, whilst the remaining group III elements aggregate in the form of nanodots. In general, the group III element is characterized to have a low melting point, but a high surface tension and diffusion coefficient, which is critical to the generation and nucleation of adatoms [145, 146]. Thereafter, many researches take advantage of these unique metallic nanodots, mainly gallium and indium, as “self-sustained masks” to fabricate hybrid nanoneedles [62-65]. One hybrid nanoneedle array with gallium metal caps formed in GaSb substrate by Ar^+ sputtering is shown in Figure 2.20 [62], which is quite similar to the case of SiC coated GaN in Figure 2.13.

Figure 2.20 (a-c) AFM images and schematic diagrams showing an evolution of GaSb substrate by increasing ion rastering time [62]. Region 1: the original substrate coated by an intrinsic oxide layer. Region 2: After ion milling by 30 seconds, Ga droplets coalescence occurs with separation filled by oxides. Region 3: nanopillars are formed with a protective gallium nanodot on each top. (d) A schematic diagram illustrating the Ga re-supplies mechanism. Ion beam induces Ga or Sb peeled off the substrate or nanotip (hollow arrow) and Ga diffuses along the sidewall of nanoneedle upward to supplement the metallic nanocap (black arrow).

The original surface of GaSb substrate covered by a uniform oxidation layer is flat before sputtering. After 500 eV Ar⁺ ion bombardment for 30 seconds, many Ga droplets start to appear due to the depletion of Sb. The substrate is then subject to more irradiation for 600 seconds until a nanoneedle array is formed where the gallium droplet still remains on top of each nanotip. During this stage, the continuous incident ions separate the Ga droplets and suppress their coalescences. Each Ga nanodot sitting on the surface layer plays a critical role as a hard mask, to shelter the underlying pillar of GaSb from being sputtered off [63-65]. On the other hand, the ion sputtering decomposes GaSb and causes a region enriched with gallium on the sidewall of each nanoneedle, where the Ga is successively supplemented towards the nanotip [147, 148]. At the same time the ion beam is also tapering the mask of Ga nanodot. Therefore, a dynamic equilibrium of Ga element on top of each nanoneedle can be sustained as shown in Figure 2.20 (d). Similar phenomena are also visible on substrates of other III-V compounds, such as InAs, InP and InSb, but a heavier source of Ga⁺ is required.

2.3.3.2 Metal/III-V compound heterostructure

In the case of GaAs substrate, a widely used typical III-V compound, the Ga⁺ direct irradiation fails to create the self-sustained hard mask. Instead, there is only random coalescence of gallium droplets dispersed across the substrate surface rather than the formation of nanoneedles, as shown in Figure 2.21 (a) [125].

Figure 2.21 (a) A SEM image of Ga droplets viewed in an oblique angle of 45 °, which is formed by ion rastering on pure GaAs substrate. (b) EDX mapping in a bright field TEM image of a Fe/GaAs nanoneedle along [100] as inset diffraction pattern (green: Fe, red: Ga and yellow: As). (c) 45 ° viewed SEM images showing the evolution of random Fe/GaAs nanoneedle fabrication, along with corresponding schematic outlines [9, 125].

To overcome this problem, a thin metallic layer of iron is epitaxial grown on the GaAs substrate creatively. This iron layer is expected to play the role of self-supplied Ga droplets in the case of Ar^+ irradiated GaSb [9, 125, 126]. It is proposed that the much lower sputtering rate [125] than GaAs is responsible for iron to retain on the tip all the time, as an element mapping shown in Figure 2.21 (b) [9]. A morphology evolution of Fe/GaAs substrate under ion patterning is demonstrated in Figure 2.21 (c) with the corresponding schematic diagrams [9, 125, 126].

At the beginning of sputtering, the iron layer is roughened by ion cascade, where many Fe atoms are ejected out from the surface. With more ion doses along with coalescence of iron particles, the beam cut through the metal film to expose the GaAs substrate. Additional ions selectively mill the exposed regions without protection of residual iron clusters, which results in the separation of many small pillars. The iron nanodots

become gradually smaller to shelter a decreasing area, which leads to the formation of tapered nanoneedle structure finally (similar to the evolution shown in Figure 2.20).

In this case, the rastering of ion beam can only provide an irregular segregation of Fe masking nanodots, which turns into a random distribution of formed nanoneedles. A pre-pattern of square mesh similar to Figure 2.17 can be applied to split the mask layer into an ordered array in order to arrange the nanopillars. Subsequently, a uniform rastering is applied to the entire substrate of Fe/GaAs. A highly ordered nanoneedle array is self-organized as shown in Figure 2.22 [9].

Figure 2.22 (a) A SEM image from top view showing a well-aligned nanopillar pattern engraved by FIB scanning. (b) A SEM image viewed in 45 ° with magnified inset, which display a highly ordered nanoneedle array by tapering the nanopillars shown in (a) through additional rastering irradiations [9].

In these two examples on Fe/GaAs substrate, no gallium self-mask is available on the surface during ion sputtering. Instead, a thin metallic layer seems to serve as hard masks, which results in the successful formation of Fe/GaAs nanoneedle array. This experimental result implies that a metallic element is not necessary to originate from the intrinsic substrate for the formation of hybrid nanoneedles, *e.g.* indium from InAs substrate. With a proper metal deposition, it is still possible to assemble a similar

ordered hybrid nanoneedle array in another semiconductor substrate to replace III-V compound, in order to produce a field ionization gas sensor. This is because, in the perspective of fabrication, III-V compound wafer is facing difficulties in elimination of the impurity during manufactory; in addition, it is challenging to adjust the ion milling recipe on III-V substrates due to their intrinsic high sputter rate [9, 56, 124, 125, 149]. As materials used in electronic devices, III-V compounds usually have relatively wide bandgaps and high electric resistivity, and is therefore not suitable to capture the weak current signal in an ionization gas sensor [150]. Silicon, a ubiquitous material applied to produce nanoelectronic devices, is a prospective candidate. However, the ion milling recipe of silicon substrate needs some modifications to that of GaAs due to their different sputter rate [123, 124]. This problem can be solved by incorporation of silicon with proper metal layer to prototype hybrid nanostructure array using ion beam fabrication technique.

2.3.3.3 Platinum gas deposition in FIB system

As discussed in Figure 2.15, a FIB system can also perform an additive metal deposition process besides the subtractive etching technique [134, 151-153]. A gas nozzle is necessary to be equipped into FIB system for the purpose to introduce the organometallic reactant gases above the desired location. Then the incident focused ion beam decomposes the delivered gaseous precursor into metal atoms and volatile gases respectively [57, 151, 153]. These metallic atoms are then deposited on the specific area and the volatile are pumped away from the substrate surface by vacuum system. An example of Pt deposition by ion-irradiation is schematically illustrated in Figure 2.23 (a) [153].

Figure 2.23 (a) A schematic diagram of ion beam induced Pt deposition process, whereby the decomposition occurs to the introduced organometallic gas [153]. Subsequently the reaction products are eliminated by vacuum system and metallic nanoparticles land onto the substrate surface. (b) Bright field cross-sectional TEM images of Pt coating on SiO₂ substrate [152]. The dark contrast regions in the high magnification image indicate the metallic nanoparticles embedded in the brighter insulator matrix, and the inset displays the entire profile of Pt deposition.

The typical metals deposited in FIB system are tungsten and platinum, which use the organometallic gas W(CO)₆ and C₉H₁₆Pt as precursor, respectively [57, 154, 155]. In practice, due to relatively higher deposition efficiency compared to tungsten, platinum deposition is more prevalently applied in structural patterning, circuit edit and TEM sample preparation [56, 57, 127, 154]. A bright field TEM image of cross-sectional Pt layer on SiO₂ substrate is illustrated in Figure 2.23 (b) [152]. EDX compound analysis is conducted to the darker contrast regions, which are averaged as Pt (31%), Ga (50%), C (10%) with remained content of Si and O [152]. The Pt-Ga particles of dark contrast with diameters below 10 nm in average are visible in TEM images, which are immersed in the insulation medium of bright contrast formed by elements of silicon, carbon and oxygen.

Previous researches suggested that the platinum by ion beam irradiated CVD usually encounters low conductivity issue at nanoscale in electrical connection applications [72, 152]. The high electrical resistance mainly originates from the damage within platinum

strip due to the ion bombardment and its intrinsic impurity (a mixture of platinum nanocrystallites within some non-conducting organics). However, this non-conductivity gives rise to the excellent isolation that is favorable to enhance local electric field by polarization effect [24, 44, 110]. Therefore, by optimizing the device structure and adjusting the process recipe, it is possible to fabricate a novel ionization gas sensor integrated with Pt nanocrystals deposited in FIB system.

2.4 Summary

The gaseous ionization theory provides the intrinsic fingerprinting property through gas breakdown voltages and highlights the critical field intensity. Surface states and polarization can respectively further enhances the local electric field superimposing on geometry effect. To fabricate the hybrid nanostructures with those unique enhancements, various materials with bottom-up or top-down processes are analyzed and compared. Finally, FIB system is selected as the tool to fabricate two different types of hybrid nanoneedle arrays for ionization gas sensing. Accordingly, the metal/silicon material system is chosen as the substrate to fabricate the hybrid nanoneedle array for ionization gas sensing application.

CHAPTER 3: HYBRID NANONEEDLE FABRICATION

Based on the observation of the self-masking effect of iron on GaAs substrate during FIB milling, a material system of iron coated silicon substrate is proposed in this thesis and proved to be favourable for fabricating a hybrid nanoneedle array. Apart from iron, a series of other metals were coated on the silicon substrate and their responses to ion irradiation were investigated. Combining these experimental results and theoretical calculations, the hybrid nanoneedle formation mechanism is explored.

3.1 Metal thin film deposition

Any inorganic material can be deposited on various substrates with desired features by *physical vapor deposition* (PVD) [156]. Based on their corresponding mechanisms, PVD can be categorized into *Pulsed Laser Deposition (PLD)*, *Sputter Deposition*, and *Evaporative Deposition*. In this project, iron layer is deposited using PLD. Meanwhile, a series of other metallic membranes is deposited on silicon wafer by Sputter Deposition.

3.1.1 Iron coating by PLD

The gaseous ionization current is generally rather weak ($\sim$ nA), which requires an effective collection and conduction in gas sensing device. Therefore, the high-conductivity material is essential to the parallel electrodes pair. In this project, p-type (100) silicon wafers with ultralow resistivity ($0.015\sim 0.021\ \Omega\cdot\text{cm}$) are used as the substrate for subsequent metal coating and ion beam milling.

Figure 3.1 (a) A PLD system used in this work and (b) a schematic diagram showing the operation mechanism [157]. A laser beam is focused to strike the target (iron) placed in a vacuum chamber. The emitted metallic particles will then form a thin film on the substrate facing the target.

An iron thin film is deposited onto the surface of silicon substrate by a PLD system, as shown in Figure 3.1. The vacuumed chamber is integrated with a laser of Continuum Surelite Nd:YAG (532 nm, 10 ns, 10 Hz). This laser with an energy density of 1.3 J/cm^2 ablates one iron target provided by Angstrom Science.

Figure 3.2 The dual-beam FIB system used in this work for hybrid nanoarray fabrication and TEM sample preparation.

To investigate the microstructures of the coated layer, one cross-sectional TEM sample from iron/silicon substrate was prepared by lift-out technique in a Ga⁺ FIB system, as shown in Figure 3.2 (FEI Nova Nanolab 600i, 30 keV) [127, 158].

Figure 3.3 The field emission gun TEM attached with an EDX detector applied in this work for nanostructure characterization.

The TEM sample was then placed into a field emission TEM (JEOL 2100F, 200 keV) attached with an EDX detector (EDAX TEAMTM EDS System) as shown in Figure 3.3, for detailed characterization.

Figure 3.4 (a) is a bright field TEM image, where a thin layer of iron membrane (~5nm) is visible as a thin dark line between the protective Pt layer and silicon substrate. The elements of sample are determined by the spectra from EDX point analysis (Figure 3.4 (C-E)).

Figure 3.4 (a) and (b) TEM bright field images showing an original silicon substrate (b) coated by a thin Fe layer (a). (c), (d) and (e): EDS point spectra originating from the protective Pt layer (Point 1), the Fe layer (Point 2), as well as the Si substrate (Point 3), respectively.

3.1.2 Metallic layer deposition by Sputter Deposition

A thin film deposition system (PVD 75TM from Kurt J. Lesker[®]) is used to deposit the metallic layer on the surface of silicon wafer as shown in Figure 3.5.

Figure 3.5 (a) A PVD system for metal layer deposition and (b) a schematic diagram showing the procedures of sputter deposition. A gas flow (usually Argon) in the vacuumed chamber to provide the ions, which are then controlled by a magnetron to sputter metal materials off the target. Subsequently the metallic atoms lands onto the surface of substrate (silicon) to form the thin film.

Sputter deposition is selected as thin film growth method due to its wide application range (including high-melting-point material), high adhesion between coated layer and substrate, as well as few contaminations or thermal problems.

Table 3.1 Sputter deposition of metals.

Metal	Atomic number	Relative atomic mass	Deposition condition
Al	13	27.0	5 min, 300 W
Ti	22	47.9	5 min, 400 W
Cr	24	52	11 min, 200 W
Co	27	58.9	11 min, 200 W
Zn	30	65.4	8 min, 100 W
Mo	42	95.9	4 min, 300 W
Ag	47	108	1.5 min, 300 W
In	49	115	8 min, 100 W
Sn	50	119	4 min, 150 W
Hf	72	178	8 min, 100 W
Ta	73	181	8 min, 200 W
W	74	184	5 min, 200W
Au	79	197	1.5 min, 300 W
Bi	83	209	8 min, 100 W

In order to select the proper metal-silicon material system for hybrid nanoneedle fabrication, a series of commonly-used metallic materials are selected and have been

deposited on the silicon surface in the PVD system. A lot of these metals are presented in Table 3.1. The deposition thickness of each metallic material with distinct sputter rate can be aligned around 30 nm by adjusting the sputtering parameters, such as the power and elapse time.

The lift-out TEM sample is prepared from the metal-silicon substrate in order to examine the quality of metal layer by sputter deposition. As an example, the bright field TEM image and EDX elemental mapping of chromium/silicon is shown in Figure 3.6. The thickness of chromium layer between protective Pt coating and silicon substrate is measured as 28 nm. Meanwhile, it is observed that the as-deposited chromium is crystalline, which is confirmed by the Fast Fourier transform (FFT) shown as inset.

Figure 3.6 (a) A bright field HRTEM image of chromium deposited on silicon substrate, with inset of a FFT taken from the squared area. (b) The corresponding EDX mapping of (a), where cyan: silicon, red: chromium and green: protective platinum.

3.2 Hybrid nanoneedle array fabrication

The successful fabrication of nanoneedle array using Fe as a protective layer on GaAs encourages its application as a shelter on silicon substrate. To facilitate the

low-sputter-rate silicon, a new sputtering style of continuous square meshing is introduced. Based on the process results within the metal/silicon materials matrix, a mechanism of hybrid nanoneedle formation is proposed and one application by making use of this method to pattern gold nanoparticles/silicon nanoarray for ordered nanowires growth is presented.

3.2.1 FIB rastering on metal-silicon substrate

As discussed in last chapter, ion beam irradiation on GaAs substrate only leads to the coalescence of gallium droplets, failing to form the desired nanoneedles. However, protected by the Fe thin layer, the surface is gradually roughened by the preliminary passes of scanning, which eventually leads to the self-organization of Fe/GaAs nanoneedles [9, 125, 126]. This suggests that the early stage of substrate evolution subject to ion beam bombardment is critical to the successful formation of hybrid nanoneedle array. Due to the low ion sputter rate of silicon (3-4 times lower [9] than GaAs), the topography of metal-coated silicon by Ga^+ irradiation at an energy of 30 keV with the beam current of 2.8 nA is rather different from the resulted surface appearance of GaAs, as shown in Figure 3.7. For each metal/silicon substrate, there are nine rastering squares ($1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ in size) with gradual increasing irradiation doses from left to right, top to bottom, by setting the etching depth from $0.01\text{ }\mu\text{m}$ to $0.09\text{ }\mu\text{m}$ ($0.01\text{ }\mu\text{m}$ interval).

These metal/silicon material systems can be categorized into two types as frame-coloured in Figure 3.7, *i.e.* the ones with sustainable nanodots under immediate ion dose projection (red) and the others where the metal is sputtered off with few irradiations (yellow). The different responses may originate from the intrinsic physic

stability (depending on atomic number or weight and surface potential U_s), which can be characterized as their respective *sputter rate* (averaged volume of sputtered materials per charge) or *sputtering yield* (the count of emitted atoms by one single incident ion). Some available data by theoretic calculations are collected and listed in Table 3.2 [124, 159-162]. The reference table and detailed equation can be found in Appendix C.

Figure 3.7 SEM images captured in an oblique angle of 52° showing gradually increasing ion dose to various metals coating on silicon substrate. Metal materials from left to right, top to bottom: Al, Ti, Cr, Fe, Co, Zn, Mo, Ag, In, Sn, Hf, Ta, W, Au and Bi. The scale bar is 500 nm.

Table 3.2 Sputter rate/ yield under 30 keV Ga⁺ irradiation.

Metal	Atomic number	Relative atomic mass	Sputter yield [124]	Sputter rate [124]	Sputter yield [160]	Sputter rate [160]
Al	13	27.0	1.290	0.134	1.476	0.153
Si	14	28.1	0.734	0.092	0.689	0.086
Ti	22	47.9	1.119	0.122	0.798	0.087
Cr	24	52	1.712	0.130	---	---
Fe	26	55.8	1.720	0.127	1.278	0.094
Co	27	58.9	1.715	0.118	1.998	0.138
Zn	30	65.4	20.392	1.942	---	---
Mo	42	95.9	1.195	0.117	1.279	0.125
Ag	47	108	7.255	0.773	4.982	0.531
In	49	115	---	---	---	---
Sn	50	119	7.015	1.185	---	---
Hf	72	178	2.617	0.364	1.495	0.208
Ta	73	181	1.694	0.191	---	---
W	74	184	1.420	0.141	1.044	0.104
Au	79	197	8.385	0.888	4.625	0.490
Bi	83	209	---	---	---	---

“---” : not available. Sputter yield in a unit of [atoms/ion] and sputter rate in a unit of [$\mu\text{m}^3/\text{nC}$]

It is obvious that the metal materials with a lower sputter rate (or yield) are able to preserve on the surface of silicon substrate in the forms of ridge or droplet after several ion scans. However, due to the even lower sputtering efficiency of silicon than all the listed metals, the substrate fails to form silicon nanoneedles before the elimination of metal nanocaps by long-term projection. In contrast, irradiation to the iron-coated surface of GaAs substrate, which has a very high sputter rate, results in self-organized nanoneedles as mentioned in last chapter [9, 125, 126]. Thus, a new route should be developed in order to form hybrid nanoneedle array in the silicon based material system.

3.2.2 Hybrid nanoneedle array on iron/silicon substrate

The Gaussian distribution of incident beam, as shown in Figure 3.8 (a), suggests that each pixel of ion milling can be divided into two regions: the strong center circle and the weak ring of tail. Due to the high physical stability of silicon in ion sputtering (low sputter rate), the intense center ions are responsible for cutting through the substrate to form the nanopillars. At the same time, the ion dose of tail plays the role in tapering the nanopillars into nanoneedles. Therefore, a square pattern of ion milling for ordered nanoneedle array can be designed, as shown in Figure 3.8 (b) [26].

Figure 3.8 (a) A schematic diagram of Gaussian distributed ions (green arrows) bombardment onto a silicon substrate (dark contrast with brighter oxidation surface) coated by a metal layer (yellow), expecting a nanoneedle structure with metallic nanodots on the tip (orange). **(b)** A dose mapping of designed square mesh pattern, where the intensity increases towards the cross from blue to red [26].

A typical evolution of metal/silicon substrate under continuous ion meshing is *in-situ* observed by the SEM integrated in the FIB system, as the self-organized Fe/Si nanonipple array shown in Figure 3.9. During first stage within 5 seconds, an array of square pillars ($1\ \mu\text{m} \times 1\ \mu\text{m}$) is patterned on iron/silicon substrate using a Ga^+ beam (30 keV, beam current of 2.8 nA, dwell time of 1 μs , 50% overlap). After additional ion sputtering of 5 seconds, a “volcano-like” structure appears on each pillar, where the

corners aggregate more materials than the center. With further milling of half a minute, the residuals on the top of each pillar begin to move towards the center, forming a trajectory of “X-shape”. A unique hybrid nanonipple structure is finally produced with another 70 s of ion dose, which consists of a nanodot sitting on top of each nanoneedle after this self-organization process.

Figure 3.9 SEM images showing an evolution of ordered hybrid nanoneedle array on the surface of iron/silicon substrate [26]: (a) a pillars array patterned by 5 seconds ion milling. (b) The top surface of each pillar is roughed by a subsequent 5 s cutting, where there is a peak formed at each corner. (c) Additional 20 s ion beam bombardment drives these peaks immigrate from corner into the center trough in an X-shaped feature (as the inset of top view). (d) A hybrid nanonipple array accomplished within total 100 seconds, where the nanodot on each tip has a much higher curvature than the nanoneedle (detailed in the inset).

The microstructure of this novel nanonipple is characterized by TEM observation and EDX elemental point analysis, as illustrated in Figure 3.10. A bright field TEM image of Figure 3.10 (a) demonstrates the overall profile of a nanonipple, which is retrieved from an array using lift-out technique in the FIB system. This nanonipple structure is composed of a nanodot in dark contrast, separated by a uniform amorphous layer in

bright contrast to the grey crystalline silicon nanoneedle. Figure 3.10 (b) is a magnified image of the square region marked ‘1’ in (a), where the nanodot can be confirmed as amorphous through a FFT pattern taken from the white square area.

Figure 3.10 Detailed characterization of one single nanonipple structure [26]: (a) A low magnification bright-field TEM image of a hybrid nanonipple. (b) An amplified bright field image showing the square area signed as 1 in (a), with inset of FFT for the squared region above the interface. (c) A HRTEM image indicating the crystal/amorphous interface in square region signed 2 in (a). (d) EDX signal curves display the elemental distribution along the line in (a) from “O” to “A”.

Figure 3.10 (c) magnifies the area marked as square 2 in Figure 3.10 (a). In this high-resolution TEM image, a clear crystalline contrast is visible below the flat interface similar to the original surface of silicon substrate. This suggests that the metal layer acts as a shelter to block or moderate the destructive ion bombardment to

underlying silicon. The elemental signals of an EDX line scan starting from “O” to “A” in Figure 3.10 (a) are plotted in Figure 3.10 (d), which indicates the dark nanodot of alloy is rich in gallium and iron.

3.2.3 Hybrid nanoneedle matrix

The iron coating is believed to be essential in the formation of the hybrid nanoneedle array. It can be simply proved by the failure of hybrid nanoneedles fabrication through a comparative trial on a bare silicon substrate, as shown in Figure 3.11. With the same ion milling recipe to that of iron/silicon substrate, an array of silicon nanoneedles instead of hybrid nanonipples is turned out.

Figure 3.11 SEM images captured in an inclined angel of 52° during an evolution of nanoneedles formation on pure silicon substrate [26]: (a) pillars array by 5 s ion beam patterning, inducing a smooth top but rough trough (see the top-viewed inset). (b) An array of nanocylinder with additional 5 s milling. (c) The aspect ratio of these nanocylinders increases by another 20 s of sputtering and (d) final homogenous nanoneedle array with uniform secondary electron contrast after total 100 seconds meshing.

Figure 3.12 SEM images viewed in an oblique angle of 52° showing the nanoneedle array patterned on various metals/silicon substrates. The distance of adjacent nanotip is ~ 700 nm. Metal materials from left to right, top to bottom: Al, Ti, Cr, Fe, Co, Zn, Mo, Ag, In, Sn, Hf, Ta, W, Au and Bi. The scale bar is 500 nm.

Figure 3.12 shows a matrix of nanostructure arrays formed on various surfaces subject to ion beam milling through the procedures as described above. It is apparent that only the metal layers with sufficiently low sputter rate are able to preserve nanodots under ion irradiation and result in a hybrid nanoneedle array. This conclusion is in agreement with our previous experiment (Figure 3.7).

The microstructures of some hybrid nanoneedles are also selected to be characterized in TEM, along with EDX element mapping (Figure 3.13). All hybrid nanoneedles share the same profile, morphology and element distribution as nanoneedles formed on the iron/silicon surface. Each hybrid nanoneedle consists of an alloyed Ga/ metal amorphous nanodot located on top of the protected underlying silicon nanoneedle.

Figure 3.13 Bright field TEM images and diffraction patterns from nanodots of the hybrid nanoneedles on substrate: (a) Cr/Si; (b) Co/Si; (c) Ta/Si; (d) W/Si. And the corresponding EDX elemental mappings (e-h), where cyan: silicon, green: gallium and red: (e) chromium, (f) cobalt, (g) tantalum and (h) tungsten.

3.2.4 Hybrid nanoneedle formation mechanism

The mechanism study is based on the differentiated ion irradiations towards the trough (between adjacent nanoneedles) and the metallic nanotip (on top of each nanoneedle).

The non-uniform milling efficiencies are responsible to different responses from the projected regions in the substrate.

For the incident ion beam, the Ga^+ current density J [$\text{A}\cdot\text{cm}^{-2}$] on each pixel yields a two-dimensional Gaussian distribution, which can be expressed as

$$J = \frac{I}{2\pi\sigma^2} \exp\left(-\frac{r^2}{2\sigma^2}\right) [\text{A}\cdot\text{cm}^{-2}], \quad (\text{Eq. 3.1})$$

where I stands for the total beam current, r represents the distance of the concerned point to the beam center on sample surface, and σ is the statistic deviation. In the process condition of this work (a beam current up to 2.8 nA), σ is evaluated as 66 nm from the FIB controlling system, and the tail radius can be assumed to be 5σ [70], which just covers the tip position of nanoneedles. For each pixel, the dwell time t_d is 10^{-6} sec as default. Based on these settings, it is calculated that there are totally 4192 repetitive passes (N_p) required to achieve the hybrid nanoneedle array. Hence, Eq. 3.1 can be converted into the format of charge transported from ion beam to the substrate:

$$J = \frac{I}{2\pi\sigma^2} \exp\left(-\frac{r^2}{2\sigma^2}\right) \times N_p \times t_d [\text{C}\cdot\text{cm}^{-2}]. \quad (\text{Eq. 3.2})$$

Additionally, one Coulomb is approximately equivalent to 6.242×10^{18} charges. Therefore, it can be calculated that the total density of incident ions from the beam tail to the nanotip until nanoneedle formation is in the order of 10^{19} cm^{-2} . As discussion in Chapter 2, previous reports assume that dose density over 10^{17} cm^{-2} will cause material removal rather than amorphization or swelling [127, 129, 130, 135]. A consistent experimental result can be found in this work as shown in Figure 3.11, whereby the blunt nanoneedles are formed by efficient tapering of the pure silicon substrate.

Subject to the same ion dose distribution, the silicon substrate coated with low-sputter-rate metal layer is shaped into a hybrid structure. Combining the *in-situ* SEM observation during Fe/Si hybrid nanoneedle self-organization procedures (see Figure 3.9) and the corresponding sputter rates of different metals, a mechanism is proposed and schematically outlined in Figure 3.14.

When the Gaussian distributed beam irradiates to the surface of metal/silicon substrate (red/grey in Figure 3.14 (a)), many metal particles in the vicinity of high dose area are sputtered out, part of which are subsequently redeposited onto the edges of the trenches, forming ridges (orange) by alloying with the incident gallium ions as shown in Figure 3.14 (b). However, the as-deposited metallic layer is too thin to stop the incident ions entering the c-Si substrate across the intrinsic a-Si layer. Thus, the interaction between incident gallium ion and c-Si results in the further transition from silicon crystal to amorphous uniformly. With additional ion bombardment, the trench opening pushes these nanodroplets immigrating from the corners towards the center on top of each nanorod. This coalescence procedure has been ever *in-situ* observed as an “X shaped” pattern during the ion evolution of Fe/Si nanoneedles (Figure 3.9 (c)) [26]. Such topography change enables a thicker layer to buffer, absorb or even scatter the projected ions which successfully preserve the silicon form removal, as illustrated in Figure 3.14 (c). Along with additional ion dose of meshing, the metallic nanodot is subject to tapering instead of pilling up. At this stage, the decreasing nanodot alloy protects a gradually shrinking region towards the center of each nanoneedle, which is essential to the large curvature and high aspect ratio, as shown in Figure 3.14 (d).

Figure 3.14 Schematic diagrams illustrating the procedures for metal/silicon hybrid nanoneedle array assembly. (a) The metal (red)/ silicon (grey) substrate subjects to the ion beam patterning, of which the current density J yields a Gaussian distribution. (b) The metal and silica layer (bright grey) projected to the center region of beam is cut through as a channel with preliminary dose, while alloying process (orange) of incident gallium and metal layer occurs around the bank of trench. (c) The coalescence of Ga/metal nanodots forming nanocaps to protect the underlying silicon from being sputtered off, while the materials in the channels is fast removed by direct milling. (d) With more ion irradiation, the metallic nanodots shrink and shelter gradually decreased region, which results to the high aspect ratio of hybrid nanoneedles.

3.2.5 Protective application of the metal layer

The survival of silicon/metal interface through the formation of alloyed nanodots suggests that the selected metal coatings may shelter the underlying fragile functional film which is intrinsically vulnerable to ion pattering process. For example, gold particles which commonly serve as catalyst are critical for the nanowires growth [163]

[164]. However, due to their intrinsic high sputter rate, it is challenging to arrange them ordered through ion beam patterning [165]. Especially in case of the three dimensional nanostructure of a high aspect ratio where excessive ion milling is necessary, the preservation of gold becomes more difficult. A failed example is shown in Figure 3.12.

In order to solve this problem, a protective layer of iron is superimposed onto the gold film, as shown in a bright field TEM image and EDX mapping inset in Figure 3.15 (a). By ion irradiation in the same square mesh patterning to the case of Fe/Si (Figure 3.9), a highly ordered hybrid nanoneedle array is created as shown in Figure 3.15 (b). The profile and contrast is similar to that of Fe/Si hybrid nanoneedle array; however, a characterization of microstructure by TEM suggests that the retained gold in dark contrast actually is crystalline instead of amorphous, as the FFT pattern taken from the squared area in Figure 3.15 (c). In Figure 3.15 (d), the EDX elemental mapping indicates that the iron is in the form of a shell covering the entire gold nanodot rather than a cap preserving on the top constantly, which is in agreement to the schematic diagrams of evolution shown in Figure 3.14 (b-d). In the proposed mechanism, the alloyed nanodot formed by diffusion or redeposition plays a critical role. The successful formation of hybrid gold/silicon nanoneedle array enables the growth of other semiconductor nanowires (such as gallium arsenide) on top of each nanoneedle, where the gold nanodot serves as the catalyst. As the secondary electron image shown in Figure 3.15 (e), a few GaAs nanomaterials are visible on the nanoneedles after 5 minutes' growth with precursors of a V/III ratio as 14.2, at 430 °C in the 10 mbar hydrogen atmosphere. A magnified image in Figure 3.15 (f) illustrates that the GaAs on each nanoneedle actually is in the form of a bundle of nanowhiskers, which have a diameter smaller than 10 nm in average.

Figure 3.15 A protective application of Fe coating for nanowire growth on Au nanodots. (a) A bright field TEM image showing the silicon substrate coated by a gold layer (~ 50 nm) followed by a thin iron film (~ 40 nm). The inset displays corresponding elemental mapping, where cyan: silicon, yellow: gold, red: iron and green: platinum. (b) SEM image viewed in 52° of a nanoneedle array with metallic nanodot on each tip. The distance between adjacent nanoneedles is 700 nm. (c) A bright field TEM image of a metallic nanodot in the form of crystal confirmed by the inset of FFT pattern. (d) The corresponding EDX elemental mapping indicates the nanodot is consisting of gold core covered by a thin iron shell. (e) A secondary image of the nanoneedle array with grown GaAs nanowhiskers and a magnified image (f) in the center region.

In addition, it is found that nanowhiskers are grown on top of each nanodot only, while no GaAs nanomaterial is grown on the sidewall of nanoneedle or the region of

as-deposited metallic film. Such precise arrangement for nanowire growth is crucial for the specific applications, for example the localized field emission devices [12, 13, 97, 166-168].

3.3 Platinum/silicon hybrid nanoneedle array

The previous field ionization gas sensors mainly place nanomaterials on either plate of a parallel-electrodes pair. In contrast, the hybrid nanoneedle array integrating with platinum nanocrystallites has a more straightforward fabrication method, which prepares the nanoarray and electrodes in one single step.

3.3.1 Pt/Si hybrid nanoneedle array formation

As discussed in Figure 2.23, the FIB system allows the platinum deposition on the surface of substrate in the form of isolated nanocrystals. Herein, ion patterning for hybrid nanoneedle array is used for two purposes: (1) separating each nanoneedle to provide the lateral gap as the gaseous ionization space; (2) tapering the platinum nanodot for improved geometrical field convergence effect. In order to effectively isolate the platinum nanodots for the polarization enhancement, a silicon wafer with an insulating SiO₂ layer (~300 nm in thickness) has been chosen as the substrate.

An evolution of Pt/Si hybrid nanoneedle array is *in situ* observed by SEM during ion meshing, as shown in Figure 3.16 (a-d). At the beginning, a thin (200 nm) platinum rectangle (7 μm $\times$ 3.5 μm) is deposited on SiO₂ substrate by the ion irradiation to organometallic gas C₉H₁₆Pt. With 30 seconds' ion square mesh patterning (~700 nm periodically) an array (3 $\times$ 10) of thin Pt nanopillars is formed between two parallel

stripes. By additional ion irradiation for 50 seconds, more substrate material is removed, and the nanopillars are transformed into a visible nanorod array.

Figure 3.16 SEM images viewed in an inclined angle of 52° showing the evolution of Pt/Si hybrid nanoneedle array structure: (a) Pt rectangle deposition, (b) 30s (c) 80s and (d) 12s ion mesh patterning respectively. The formation of comparative bare silicon nanoneedles: (e) no Pt deposited between two electrode stripes and (f) an array of homogenous silicon nanoneedles formed within stripes.

With further ion tapering for 40 seconds, the aspect ratio of each nanorod increases, creating an array of nanoneedles with Pt nanocaps on the tip which have the diameters down to ~ 100 nm. As a comparison, there is no metallic nanodot sitting on the tip of each nanoneedle without platinum pre-deposition, as shown in Figure 3.16 (e) and (f).

3.3.2 Characterization of Pt nanocrystals

The morphology of each Pt/Si nanoneedle in the array is characterized by TEM. Three identical nanoneedles are retrieved from an array through FIB lift-out technique, of which a bright field TEM image is shown in Figure 3.17 (a).

The height of each nanoneedle is around 800 nm equally, which has a separation of 700 nm to the adjacent nanoneedle, as the design of mesh pattern. The nanodot with dark contrast is isolated to the crystalline silicon by a thick layer of silicon dioxide, as illustrated in a higher magnified image of one single nanoneedle in Figure 3.17 (b). The radius of nanodot is tapered as small as 50 nm in average, preserved on the insulating SiO₂ layer with a thickness of 300 nm as the original substrate. There is a uniform bright featureless layer covering the sidewall of crystalline silicon nanorod, which is essentially caused by the redeposition of sputtered silicon or direct amorphization during ion milling, as discussed in section 2.3.2.3. An EDX elemental mapping confirms the preservation of platinum, which constitutes a small nanocap, as shown in Figure 3.17 (c). Furthermore, a detailed high resolution TEM image in Figure 3.17 (d), which magnifies the square region in Figure 3.17 (b), suggests that the platinum is in the form of nanocrystallites as expected. These platinum nanocrystallites of the size down to around 5 nm in the insulating matrix are promising to perform unique field gaseous ionization property.

Figure 3.17 TEM observation of Pt/Si hybrid nanoneedles: (a) a bright field TEM image showing the overall profile of three nanoneedles in a column. (b) A magnified bright field image of a single nanoneedle, consisting of three segments from top to bottom: platinum nanodot, silicon dioxide layer and crystalline silicon, which is examined by (c), the EDX elemental mapping correspondingly (red: platinum, blue: oxygen and green: silicon). (d) A high resolution TEM image in the squared region of (b) indicates that the nanodot is constituted by many isolated Pt nanocrystallites.

3.4 Summary

In this chapter, a series of metal/silicon material systems have been settled to explore the mechanism of hybrid nanoneedle array formation in ion milling. It is experimentally confirmed that only the low-sputter-rate metallic coating on silicon substrate is able to fabricate the hybrid nanoneedle array by ion patterning. Additionally, a hybrid Pt/Si nanoneedle array is successfully fabricated in the FIB system, which is in the form of

desired nanocrystallites embedded into an insulating matrix on top of nanoneedle. Each hybrid nanoneedle array is the ideal structure to be integrated into the field ionization gas sensor, as detailed in next chapter.

CHAPTER 4: FIELD IONIZATION GAS SENSING

The fabricated hybrid nanoneedle arrays are desirable structure for making an ideal field ionization gas sensor due to their high aspect ratio and regularity. In this chapter, the design, fabrication and gas sensitivity test methodology are included. The excellent gas sensitivity is demonstrated for both Fe/Si and Pt/Si hybrid nanoneedle arrays.

4.1 Gas sensing device

There are two different structures of ionization gas sensing devices presented in this thesis, including hybrid metal/silicon nanoneedles formed on parallel plate and platinum nanocrystallites/silicon nanoarray.

4.1.1 Hybrid nanoneedles on parallel plate for ionization gas sensing

As schematically shown in Figure 4.1, an ionization gas sensor is prototyped as a derivation of a classic parallel-plate capacitor structure. One electrode of a high-conductivity silicon substrate is integrated with the metal/silicon hybrid nanoneedle array (herein Fe/Si as the example). On both sides of this nanofabricated substrate, there are a couple of identical polished insulating SiO₂ spacers. A flat silicon wafer coated by a conductive metal is employed as the counter electrode opposite to the nanoneedle array, which is supported by the spacer pair. Apparently, the interstitial gap between the tip of nanoneedles and the counter electrode defines the gas ionization and discharge space (herein, 10 μm in length).

Figure 4.1 A schematic diagram of the hybrid nanoneedle array ionization gas sensor. The silicon substrate with Fe/Si nanoneedle array is separated to the counter electrode by a couple of SiO₂ spacers. Two electrical test probes are connected to the counter electrode and silicon substrate of nanoarray respectively, to generate an electric field for gaseous ionization. The ion current, is subsequently collected and processed by the external circuit.

4.1.1.1 Nanoneedle separation

One unique advantage of this ordered nanoarray is the precise control of the separation between adjacent nanoneedles, in order to avoid the electric field shielding effect. The arrangement of nanoneedle array is determined by the parameters of the FIB milling process. It is well accepted that a current of 2.8 nA of 30 keV is preferred to sputter the materials off the substrate, as recommended in Ref [131].

M. Rommel *et al.* recently suggest that the tip of each nanoneedle in an array can be properly tapered with the periodic separation only in a certain range [169]. The examples in last chapter with separation from 700 nm to 1 μm are favourable for hybrid nanoneedle array assembly. The periodic separation of 700 nm fabricated by 2.8 nA ion milling is chosen to form the gas sensing device (as shown in Figure 3.9).

4.1.1.2 Nanodot size control

As discussed in Chapter 2, the geometry effect (or “tip effect”) is crucial to provide the converged local electric field. This enhanced background field is also the basis for the

superimposed surface-state ionization mechanism. The finite element method simulation suggests that a large curvature (sharper tip) of a one-dimensional nanostructure produces a high electric field in the vicinity of the tip (see Figure 2.6 in section 2.2.1.2). Therefore, the metallic nanodots staying on the top of nanoneedle is expected to be as small as possible.

Figure 4.2 A bright-field TEM image of the hybrid nanoneedle array with gradually decreasing radii of tips from left to right column (75 nm, 50 nm and 20nm). The size of metallic nanodots is controlled by the projected ion dose in terms of irradiation time [26].

Figure 4.2 is a bright field TEM image showing three columns of hybrid nanoneedles with different metallic nanodots in radii (75 nm, 50 nm and 20nm from left to right). It proves that if other parameters are held constant, the size of nanodot can be precisely controlled by the irradiation ion dose (milling time). The more ion dose, the sharper the hybrid nanoneedle formed. In the case of this work, for each 20×20 nanoarray with 700 nm as the distance of adjacent nanoneedle, 120 seconds ion irradiation at a current of 2.8 nA will bring about the nanodots that have a radius down to around 20 nm.

4.1.1.3 Counter-electrode consideration

As illustrated in Figure 4.1, there is a counter electrode mounted on top of two insulating spacers. The metallic layer on silicon wafer is responsible to load the ground potential and conducting the ion current to external circuit for measurement. The Joule heating will be generated during the gaseous breakdown, which may cause the damage to both nanoneedles and the counter electrode. One example of this accident was found on Au-coated silicon counter electrode after keeping gaseous breakdown current at 10 μA for 30 seconds, as shown in Figure 4.3. To avoid this failure, a sweep voltage mode with compliance current protection was introduced into the measurement circuit, which will be detailed in section 4.2.3. In addition, a much stable metal material, **aluminum**, is chosen to be deposited on the surface of silicon plane to form the counter electrode.

Figure 4.3 Secondary electron images of a hybrid nanoneedle array and surface of Au/Si counter electrode which has undergone large gaseous ionization current (10 μA) for half a minute. (a) A corner of the nanoarray is damaged and some spherical droplets (gold) distributed in the vicinity of nanoneedles. (b) An explosion occurs on the surface of Au/Si substrate, which is responsible to the disaster region of nanoneedle array. The nanodroplets emitted from the explosion point disperse on the surface of both electrode and nanoarray.

4.1.2 Pt/Si hybrid nanoneedles array for ionization gas sensing

The nanoneedles formed on the surface of electrode in the parallel-plates structure have a high aspect ratio, which allow a convergence effect to enhance vertical electric field.

In contrast, the platinum nanocap on top of each nanoneedle consists of many nanocrystallites, which act as polarization centers in a lateral electric field instead. Therefore, the structure of Pt/Si hybrid nanoneedle array is quite different to the previous ionization gas sensors.

Figure 4.4 (a) A schematic diagram of an ionization gas sensing device integrated with Pt/Si hybrid nanoneedle array. A pair of perpendicular Au electrodes (yellow) is pre-patterned by photolithography on the surface of a thick SiO₂ substrate (bright grey). An array of Pt/SiO₂ is fabricated between a pair of parallel Pt stripes (cyan), which is connected to the Au electrodes. (b) A secondary electron image of squared region in (a), which shows viewed the topography of the hybrid Pt/Si nanoneedle array.

To generate a lateral electric field for polarization of the platinum nanocrystals, a voltage bias is required to be loaded onto the electrodes pair. However, due to the limited dimension of nanodevice in several micrometers, it is necessary to connect the electrodes to a large pad for probing, such as the prevalent wire-pad pattern through standard microelectronics process [23, 24, 167]. As schematically illustrated in Figure 4.4(a), two wire-pad gold patterns were prepared by standard lithography on the surface of a SiO₂ coated silicon substrate. These two gold electrodes are perpendicular to each other with a separation of few micrometers around their intersection. An array of ordered Pt/Si hybrid nanoneedles within a pair of Pt stripes is then fabricated in FIB

system, as shown in Figure 4.4(b). Since the wire-pad pattern is able to load the external voltage to generate a lateral electric field, the gas sensing detection can be carried out.

4.2 Gas sensing test platform

A gas sensing test platform is designed and installed to evaluate the performance of these two types of hybrid nanoneedle gas sensors. This gas sensing test system contains two segments, the gas delivery system and ion current measurement.

4.2.1 Gas delivery system

As the schematic diagram shown in Figure 4.5, there are four cylinders available to provide the test gases, including pure air, nitrogen, and carbon monoxide or hydrogen diluted in nitrogen. Additionally, four mass flow controllers (MFC) are connected in series to the tube of each cylinder, with the resolution down to one standard cubic centimetre per minute (1 sccm). MFC is responsible to adjust the concentration of the mixed gas delivered into the test chamber, through controlling the relative flow rate between the target and carrier gas, as listed in Table 4.1.

Before each test, a mechanical pump attached to the test chamber will operate, in order to reduce the residual ambient gas or space charge generated by the previous detection. Subsequently, the carrier gas of pure nitrogen will be introduced to sweep the internal space of the chamber, to initialize and stabilize the gas detection status [170].

Figure 4.5 A schematic diagram showing the gas sensing test platform. Before each test, the pump will vacuum the chamber, followed by the sweep of background nitrogen flow. When a gas is under test, the valves of corresponding cylinder and carrier gas of nitrogen will open. Then the gas flows are controlled by the MFCs, which dynamically adjust the concentration of target gas in background nitrogen.

Table 4.1 Gas concentrations controlled by gas flow rates.

Target gas	Concentration [ppm]	Cylinder gas		Carrier gas	
		MFC	Flow rate [sccm]	MFC	Flow rate [sccm]
Air	---	#1	1000	---	---
N ₂	---	#2	1000	---	---
CO	200	#3	200	2	800
H ₂	200	#4	200	2	800
H ₂	100	#4	100	2	900
H ₂	50	#4	50	2	950
H ₂	10	#4	10	2	990

4.2.2 Device installation

As outlined in Figure 4.1, two electrical test probe needles are connected to the nanoneedle substrate and counter electrode, respectively. These probes are responsible to load a voltage bias on the nanoneedles from the external circuit, which generates a local high electric field around the nanotips, which is perpendicular to the substrate. If the field intensity is sufficient to ionize the target gas, a discharge current will be collected by the external measurement equipment.

In contrast, the Pt/Si hybrid nanoneedle array is subject to a different voltage loading and therefore different electric field direction compared to the Fe/Si hybrid nanoneedle array. As outlined in Figure 4.6, a hybrid Pt/Si nanoneedle array is fabricated between two parallel Pt stripes, which define the gaseous ionization space. The voltage loading is achieved by probing the gold pad patterns connected to the Pt stripes and electric field direction is a horizontal to the substrate.

Figure 4.6 A schematic diagram of Pt/Si hybrid nanoneedle array ionization gas sensing device. The probes are connected to the gold pads, which is linked to the parallel platinum strips. During the gas sensing test, a voltage bias will be loaded on the stripes to polarize the Pt nanodots (nanocrystallites), which enhance the local electric field in vicinity to induce gaseous ionization.

4.2.3 Electrical measurement

Since the field ionization signal is too weak (usually low to $\sim$ nA), the proper setting of voltage sweep along with the reasonable analysis of ionization current have to be concerned, as well as device protection.

4.2.3.1 Voltage sweep

A precision semiconductor parameter analyzer Agilent® 4156C as shown in Figure 4.7 (a) is used to supply voltage and capture the generated ion current. In order to locate the fingerprinting voltage for the tested gas, a current-voltage (I - V) measurement is implemented in the “sweep” mode. As plotted in Figure 4.7 (b), the sweep step is set as 0.2 V in this work with an interval of 0.15 second. For each step of stimulus voltage, there is a corresponding current to be detected simultaneously.

Figure 4.7 A precision semiconductor parameter analyzer (a) used in this work, which conducts a voltage bias on gas sensor in a sweep style (b). The step is set to 0.2 V at regular interval of 0.15 sec.

4.2.3.2 Signal assessment

As shown in Figure 2.2, the gaseous ionization current-voltage curve is typically a flat ground followed by a steep spike, where the inflection point corresponds to the fingerprinting threshold voltage. One example of practical measurements is plotted in Figure 4.8, where a hybrid Fe/Si nanoneedle array generates a breakdown current under ~ 15 V in the ambient air.

Figure 4.8 A typical I - V curve of air ionization in the electric field of hybrid Fe/Si nanoneedle array.

However, care must be taken as far as the concerns below:

- Leakage

This phenomenon happens mainly on Pt/Si hybrid nanoneedle array. During FIB patterning, there might be a conductive layer formed on the sidewall along the insulator of SiO_2 , through the redeposition of sputtered platinum nanoparticle and implantation of incident gallium [57, 127]. Therefore, the current will flow through the silicon substrate instead of the plasma bridge by gaseous ionization, as shown in the schematic diagram (Figure 4.9 (a)). A typical Schottky leakage current is plotted as an I - V curve in Figure 4.9 (b), which has a characteristic of an exponential shape. Such I - V curves have appear similar to Townsend discharge currents (see Figure 2.2), which may cause confusion during the signal analysis. Fortunately, the leakage can be reduced greatly by beam cleaning the surface of device using low energy ion beam, to eliminate the conductive media [127, 158].

Figure 4.9 (a) A schematic diagram of a leakage current flowing through the insulator layer and silicon substrate and (b) the captured I - V curve with a Schottky characteristic in air of atmospheric pressure.

- Short circuit

In the case of leakage, the substrate is connected to the electrodes by redeposition during ion milling. However, if the sputtered conductive media covers the nanoneedles resulting in the connection between the adjacent individuals, a short circuit will occur as illustrated in Figure 4.10 (a).

Figure 4.10 (a) A schematic diagram showing the short-circuit current along the conductive surface, resulting the linear I - V curves in (b), where even a weak voltage bias (lower than 1 volt) is able to cause a high current (tens of μ A).

The charges prefer to immigrate along the low-resistance surface rather than the substrate or gaseous space. Even though the voltage bias is very weak, a high current is detectable which shows a typical Ohmic characteristic (Figure 4.10

(b)). In order to eliminate this effect, a sufficient gap between adjacent nanoneedles is necessary, in addition to the ion cleaning using low energy beam before gas sensing test.

- Space charges

One important advantage of ionization gas sensor is the shorter recovery time. However, the space charge, which is generated by the previous gas ionization process, plays a critical role of “seed” in the subsequent test [23, 110, 171]. As shown in Figure 4.11 (a), it is the space charge colliding with gas particle or electrodes generates the detectable ion current, instead of the fingerprinting charges produced by field ionization. If the charges created by the previous test are remained in the space, the successive gas ionizations will become easier.

Figure 4.11 (a) A schematic diagram space charges enhanced gaseous ionization, where residual gas ion or electron collision multiplies the ion current. (b) Without space charge removal, the successive test (red and green) exhibits lower threshold voltages than the initial test (black).

Such phenomenon is characterized by the gradually decreasing gas breakdown (threshold) voltages, as plotted in Figure 4.11 (b). This “memory” effect deteriorates the repeatability of ionization gas sensing and misleads the signal judgment. Fortunately, it can be greatly alleviated by a vacuum system to

remove the space charges and deplete them under a low voltage bias. In a constant weak electric field, the ion or electron can drift to the cathode or anode for neutralization, rather than the multiplication of charges by collision.

4.2.3.3 Device protection

In addition to the problems reported above, a high ion current flowing in the gas sensing device for a long term generates Joule heating, which causes the severe device failure (as illustrated in Figure 4.3). Such effect was also observed in previous ionization gas sensing device using carbon nanotubes [35], as discussed in section 2.1.2.3. When the gas breakdown occurs, the ion current is practically determined by the external circuit [73]. Therefore, the gas sensing measurement can introduce a compliance current value, beyond which the voltage stimulus will stop immediately to cease the ionization current flow. As shown in Figure 4.8, the typical I - V curve of gaseous ionization is started with weak background current followed by a sudden spike at the fingerprinting threshold voltage. Therefore, the value of compliance current can be assigned in the range of the breakdown current. Herein, the compliance current is set as 2 nA for the gas sensing device integrating Fe/Si while 100 nA for Pt/Si hybrid nanoneedle array.

4.3 Gas sensing property

Table 4.2 shows the definitions of some important gas sensing parameters, including selectivity, sensitivity, repeatability, and stability [172]. As a ubiquitous sensor to diverse gases, the selectivity of a field ionization gas sensor is interpreted by the fingerprinting property. The gas sensing performance of ionization gas sensors, including the fingerprinting, sensitivity, repeatability and reliability, has been evaluated in the gas sensing test platform. Both hybrid nanoneedle arrays show excellent gas sensitivities under the ultralow operation voltages.

Table 4.2 Definitions and comparison of important gas sensing parameters [172].

Gas sensing parameters	Definition	Comparison	
		Chemical gas sensor	FI gas sensor
Selectivity	The ability of a sensor can respond selectively to a specific type of gas or gas group.	Depending on the specified adsorptive layer for the certain type of gas.	Fingerprinting property (V_{th}) to various types of gases universally.
Sensitivity	The change of detected signal per gas concentration unit.		
Repeatability	The variation of measured signal from the same gas under the same condition (e.g. pressure and temperature).	The adsorptive layer is usually degraded due to saturation or poisoning.	Reproducible signals without chemical interaction, but has Joule heat of ionization current.
Stability	The resistance to sudden change (deteriorate) of functional material or structure during gas sensing test.		

4.3.1 Gas sensitivity of Fe/Si hybrid nanoneedle array

The ion current-voltage signals detected from a Fe/Si hybrid nanoneedle array device in various gases are plotted in Figure 4.12, including air, nitrogen, and diluted hydrogen or carbon monoxide in nitrogen.

For each I - V curve, the current retains at a small value around zero when the applied power is weak. When the voltage bias rises up to a certain level (fingerprinting threshold voltage) for a specified gas (e.g. 14 volts for air), the measured current ramps up suddenly, which reflects the occurrence of gas breakdown. These I - V curves with distinct thresholds in different gases are in an order which is consistent to the previous works [11, 13, 27, 33-35, 45, 111]. However, compared to the reported ionization gas sensors, the operation voltages have been decreased dramatically from hundreds of volts to around 30 V.

Figure 4.12 Four ionization current-voltage curves captured from the Fe/Si hybrid nanoneedle array gas sensor in atmosphere of air, CO/N₂, H₂/N₂ and N₂. The responses to various types of gases are clearly separated.

Figure 4.13 *I-V* curves of three successive gaseous ionization tests of hybrid nanoneedle array device in nitrogen, where the variation of threshold voltages is less than 1 volt.

In order to identify the reliability of the gas sensitivity measurement, there are several successive tests for each target gas. For example, three successive nitrogen discharge

currents are collected and plotted in Figure 4.13, which shows an excellent repeatability with a very little variation around the threshold voltage.

The sensitivity of Fe/Si hybrid nanoneedle array is evaluated in a series of hydrogen concentrations carried by nitrogen, ranging from 10 to 200 ppm by adjusting the gas flow rate as listed in Table 4.1.

Figure 4.14 *I-V* curves (a) and respective threshold voltages chart (b) of hybrid nanoneedle array to various hydrogen/nitrogen concentrations [26].

Figure 4.14 shows a series of *I-V* curves demonstrating the gradual increase of ionization voltages in response to the decrease of H₂/N₂ concentrations. These differentiated signals confirm that such hybrid nanoneedle array is able to detect both the type and the concentration of a gas.

As a comparison, the gas sensitivity of a homogenous silicon nanoneedle array is investigated. These nanoneedles have a similar geometry to that of Fe/Si hybrid nanoneedles, as shown in Figure 3.11 (d). However, there is no alloyed nanodot staying on the tip of each nanoneedle. The *I-V* curves of the silicon nanoneedle array measured in the gas test platform are plotted in Figure 4.15. Instead of field ionization, there are

only noisy currents detected with increasing voltage in various ambient gaseous environments. Thus it fails to differentiate any tested gas.

Figure 4.15 The ion current signals of silicon nanoneedle array responding to various gases, including air, CO/N₂, H₂/N₂ and N₂. These *I-V* curves remain at zero as background noise when voltage sweeps, showing no gas sensitivity [26].

The simple comparison of the profiles of the same hybrid nanoneedle array before and after ionization gas sensing test suggests that there is no damage to the hybrid nanoneedles after several field ionization tests (Figure 4.16). The high stability of the chosen material system and careful protection during measurement (see section 4.2.3.3) ought to be responsible for this.

Figure 4.16 SEM images viewed in an oblique angle of 52° showing an area of Fe/Si nanoneedle array (a) before and (b) after the field ionization gas sensing test, where is no change observed.

4.3.2 Gas sensitivity of Pt/Si hybrid nanoneedle array

The typical ionization I - V curves detected from the Pt/Si hybrid nanoneedle array in various gases are plotted in Figure 4.17 [32].

Figure 4.17 Three ionization current-voltage curves captured from the Pt/Si hybrid nanoneedle array gas sensor in air, H_2/N_2 and N_2 . These curves share a similar shape to that of Fe/Si parallel-plate nanodevice, but in a much larger scale of current with a lower voltage bias [32].

When the voltage bias is low to provide a weak electric field in gaseous space, the current detected is increasing quite slowly in a manner of smooth slope. However, if the voltage sweeps approaching a certain threshold for the specific gas, a spike is visible immediately on the I - V curve. These fingerprinting signals are clearly differentiated, which is corresponding to various environments of air, nitrogen and hydrogen diluted in nitrogen respectively. Compared to the previous ionization gas sensing devices and Fe/Si hybrid nanoneedle array in this work, this Pt/Si nanosensor shows similar discharge I - V curves but provides an ultralow operation voltage (less than 10 V).

Traditional ionization gas sensor, which normally requires up to hundreds of volts for gas breakdown, where the variation of breakdown voltages (*e.g.* several volts) is usually insignificant [11, 13, 27, 33-35, 45, 111]. However, this platinum/silicon hybrid nanoneedle array requires a much lower voltage (~ 10 V) to ionize gases. Therefore, the repeatability issue becomes crucial within such a small range.

Figure 4.18 Three successive air ionization I - V curves measured from Pt/Si hybrid nanoneedle array gas sensing device, where the repeatability is confirmed by variation of less than 0.25 V.

Likewise, the reliability of Pt/Si hybrid nanoneedle array is evaluated. One example of the measured successive I - V curves in ambient air is shown in Figure 4.18. The bundled I - V curves suggest the occurrence of air breakdown at the bias around 3.75 V with a derivation of ± 0.25 V.

Thus, the considerable repeatability of ion current signals encourages us to use this Pt/Si field ionization sensor to detect the various gas concentrations, in addition to the different gas type differentiation. The sensitivity of Pt/Si nanoneedles to a series of H_2 concentrations diluted by N_2 was examined in the gas sensing test platform. The result is presented in Figure 4.19 [32], where the occurrence of gaseous ionization is measured to be lower at higher concentration of hydrogen. This response is in agreement with the gas ionization of previous reports works [11, 13, 27, 33-35, 45, 111] as well as the Fe/Si hybrid nanoneedle array [26], although much lower threshold voltage is needed (around 6 V only) in current case.

Figure 4.19 I - V curves (a) and threshold voltages chart with linear fitting (b) of Pt/Si hybrid nanoneedle array to hydrogen/nitrogen in a series of concentrations, including 10ppm, 50ppm, 100 ppm and 200 ppm.

The design of this Pt/Si hybrid nanoneedle array gas sensing device is on the basis of polarization-enhanced field ionization. Therefore, the platinum nanocrystallites embedded into the insulating matrix as the centers of charge accumulation and field convergence play a critical role. A comparative experiment of the gas sensing signals detected from Pt/Si hybrid and pure silicon nanoneedle array was conducted. The homogenous silicon nanoarray was fabricated next to the hybrid Pt nanoneedles, as shown in Figure 4.20(a). The comparison results of gaseous ionization currents in the ambient air are plotted in Figure 4.20(b). A steep jump can be clearly observed in the I - V curve of Pt/Si hybrid nanoarray at around 4 volt. In contrast, the pure silicon nanoneedle array comes up with a typical Schottky I - V curve, which remains as a leakage current even under a higher voltage bias.

Figure 4.20 (a) A secondary electron image showing the Pt/Si hybrid nanoneedle array (lower left) and homogeneous silicon nanoneedle array (lower right) fabricated around the same substrate for gas sensing comparison. (b) Two I - V curves showing the different responses to ambient air for silicon nanoneedles with (black) or without (red) platinum nanocrystallites on each nanotip [32].

There is also a concern about the stability of the metallic nanodots after the ionization gas sensing tests, especially for this Pt/Si device having a much higher compliance of discharge current (as high as ~ 100 nA). In order to check the impact of ion current flow to the nanodots, the secondary images of a Pt/Si hybrid nanoneedle array after gaseous

ionization tests were taken and shown in Figure 4.21. There is no obvious change or visible damage on the nanodots after several ionization gas sensing tests. The stability of Pt/Si hybrid nanoneedles might be partially due to the measurement methodology, which turns off the voltage loading as soon as the current exceeds the compliance. Meanwhile, the unique polarization mechanism that enhances ionization efficiency may also contribute to the survival of the nanodots as detailed in next chapter.

Figure 4.21 SEM images illustrating a Pt/Si nanoneedle array after the field ionization gas sensing test, where no visible change occurs to the electrodes and junctions (a) or the hybrid nanoneedles (b).

4.4 Summary

This chapter focuses on the concerns which have to be considered during the design and fabrication of the hybrid nanoneedle array for ionization gas sensing application. A gas sensing test platform is set up to evaluate the sensitivity of these two types of novel gas sensors. The remarkable sensitivity, stability of the hybrid nanoarrays and the significance of nanodots are highlighted, in comparison with the pure silicon nanoneedle array.

CHAPTER 5: FIELD IONIZATION MECHANISMS

This chapter studies the fingerprinting gaseous ionization current in the gas sensing devices by integrating with either Fe/Si or Pt/Si hybrid nanoneedle array. The differentiated I - V curves for various gas types and linear or nonlinear responses to the gas concentration are insightfully discussed. Based on the experimental results, the different field ionization mechanisms of the hybrid nanoneedles are explored and compared. At last, an extended category of ionization mechanisms is created by adding these two novel ionization gas sensors at nanoscale.

5.1 Fe/Si hybrid nanoneedle array gas sensing mechanism

As discussed in last chapter, a Fe/Si hybrid nanoneedle array is employed as the anode of a parallel-plate field ionization gas sensing device. Compared to the previous gaseous ionization nanosensors, this hybrid nanoneedle array exhibits a competitive sensitivity and requires a much lower operation voltage. Meanwhile, we found that the homogeneous silicon nanoneedles with metallic nanodots free fail to detect any gases. In this section these experimental results will be analyzed in detail, followed by a discussion on gas sensing mechanisms.

5.1.1 Study of fingerprinting I - V curves

The process of gaseous ionization could be classified into two successive categories in the perspective of electrodynamics: 1) the separation of charges of gas particle (atom or molecule) followed by 2) the movement of collective charges within the applied electric field [44].

In this work, fingerprinting I - V curves as shown in Figure 4.12 are essentially determined by three factors: 1) the function of charges distribution $F_C(x, y, z, t)$, 2) the electric field distribution $F_E(x, y, z, t)$ and 3) the characteristics of convective, drift and diffusion procedures of the generated plasmas $\sigma(x, y, z, t)$, where x, y, z represent the three-dimension position and t stands for the elapsed time. In this project, the fabrication process with high precision allows the exactly same hybrid nanoneedles constituting an ordered array. Therefore the discussion of gaseous electronics mechanism can be simplified as a one-dimensional model, which ignores the difference between individual nanoneedles within the nanoarray [110], as shown in Figure 5.1. Correspondingly, only the perpendicular distance z to the hybrid nanoneedle array has to be considered (x and y ignored). If the interstitial gap between the electrodes pair is d , then after an interval time of t the ionization current $I(t)$ can be deduced by integration along the electric field direction as the Equation 5.1:

$$I(t) = \int_0^d F_E(z, t) F_C(z, t) \sigma(z, t) dz. \quad (\text{Eq. 5.1})$$

In this equation, the electric field distribution factor $F_E(z, t)$ is a combination of two different effects, in terms of Laplacian field distribution function, $F_E^L(z, t)$ and field of charges distributed in the space $F_E^s(z, t)$:

$$F_E(z, t) = F_E^L(z, t) + F_E^s(z, t). \quad (\text{Eq. 5.2})$$

Figure 5.1 A schematic diagram showing the different factor which determines the gaseous field ionization current: 1) The gaseous charge separation in the vicinity of hybrid nanoneedles, where Laplacian distributed field $F_E^L(z,t)$ is dominative (pink region). 2) The positive-ion bombardment to cathode for secondary electron emission γ -process (green region). 3) Space charges $F_E^s(z,t)$ generated by emitted electron collision (α -process) or ion collision (β -process) to gas particles (yellow region).

As discussed in Chapter 2, the Laplacian distribution is determined by the geometry of nanomaterials, which takes effect mainly in the vicinity of nanotips to enhance the local electric field. And the charges distributed in the space generate a superimposed field to the background, which can further intensify the local electric field.

The charges distribution $F_C(z,t)$ in the electric field between hybrid nanoneedles and the counter-electrode is collectively determined by four processes (see the section of “Townsend discharge and gas breakdown” at section 2.1.2.3):

- Direct field ionization around the tip of hybrid nanoneedles.
- Separated charges by positive ion collision to gas particle “ β -process”.
- Secondary electrons emitted by positive ion impact to cathode “ γ -process”.

-
- Charges generated by electron collision ionization “ α -process”.

As soon as the applied voltage exceeds a certain threshold, the gas particles around the tip of the hybrid nanoneedle are probably to undergo the field ionization process. This charge separation phenomenon mainly occurs in an electron-tunnelling manner under local ultrahigh electric field. Subsequently, the drift of generated positive ions along the direction of electric field is able to ionize the gas molecules by ion-gas particle collision (β -process). Additionally, the accelerated ions impinging to cathode can further eject electrons as the secondary process (γ -process). The emitted electron, always having a high velocity, is able to collide with gas particles in turn for further multiplication (α -process).

It is obvious that the direct field ionization determines the $F_C(z, t)$ by providing the “seed” charges. For all the I - V curves measured from this Fe/Si hybrid nanoneedle array, an increasing voltage bias raises the overall Laplacian distribution $F_E^L(z, t)$ and boosts the amount of charges $F_C(z, t)$ if it exceeds the threshold. Theoretically, the *Townsend’s breakdown criterion* is satisfied at this moment, which is expressed as $1 - (\beta/\alpha)e^{\alpha d} = 0$ for α -process and $1 - \gamma e^{\alpha d} = 0$ for γ -process respectively. The coefficient of ionization by electron collision α in these equations is given by

$$\alpha = pAe^{-Bp/E}, \quad (\text{Eq. 5.3})$$

where p stands for the pressure of the gas in an electric field E and A is a constant related to gas density while B approximately equals to the product of A and the specific gaseous ionization potential U_i (see section 2.1.2). If these secondary processes (β and γ) in a

similar form are combined and designated as an equivalent collective factor δ , then the criterion of Townsend self-sustaining discharge can be revised into a new form:

$$1 - \delta(\beta, \gamma) \left[e^{d p A \exp(-Bp/E)} + n_{FI} \right] = 0, \quad (\text{Eq. 5.4})$$

where we can find a new item of n_{FI} , adding to the exponential term of electron collision as the upgraded first ionization factor. n_{FI} represents the number of charges (ions or electrons) generated by the direct field ionization [26, 32, 110]. In this formula, the value of constant B directly depends on the type of the ambient gas. Meanwhile, as the discussion in section 2.1.2, the direct field ionization is strongly correlated to the gas composition, in terms of gas ionization energy eU_I . Additionally, the coefficient of ionization by positive ions collision to gas particles β/α is also determined by the characteristic of gas. Therefore the critical fingerprinting property of hybrid nanoneedle array for gas sensing is mainly derived from the charge distribution $F_C(z, t)$, which is composed by these gas-related factors. As the dominant item, the variation of $F_C(z, t)$ with applied voltage sweep provides the detectable ion current signal for gas sensing.

Another essential factor to the gaseous ionization current is the movement of charged gas particles. The generation of charges in the gaseous space is already interpreted by $F_C(z, t)$, whilst their individual mobility is expressed in the current function as $\sigma(z, t)$. The distribution of space charge $F_E^s(z, t)$ can be established on the basis of these two complementary factors ($F_C(z, t)$ and $\sigma(z, t)$). Thus the electric field of space charges is also correlated to the ability of charge transportation in the gaseous ionization system [44, 173, 174]. As a result, there are subtle differences between the gaseous breakdown I - V curves visible in Figure 4.12 (various slopes of spikes beyond the threshold).

The initial ions in the vicinity of hybrid nanoneedles, combining with the field distribution and gas mobility, collectively bring about the fingerprinting I - V curves. Meanwhile, the compatible form of Townsend's breakdown criterion of Eq.5.4 emphasizes the significance of field intensity and ionization efficiency, which is detailed in next section.

5.1.2 Ionization enhancement mechanism

The experimental result of the comparative gas sensing tests between the hybrid Fe/Si and homogenous silicon nanoneedles (Figure 4.12 vs. Figure 4.15) emphasizes the crucial role of the metallic nanodots in field ionization. In this section, the ionization enhancement is proposed as a collective mechanism of three associated aspects: geometry effect, surface-state and "Malter effect".

5.1.2.1 Geometry effect

The classic geometry effect is usually described as the electric field distortion by solving the Laplace equation (Figure 2.3 in section 2.2.1). The gaseous electronics theory suggests that if the distorted electric field is sufficiently high, the compressed potential barrier in the solid-gas interface allows the electron tunnelling into either surface of metal or semiconductor anode, where the positive/negative charges in gas particles are separated (see Figure 2.1 in section 2.1.2). The previous researches mainly focus on the role of a single one-dimensional nanostructure, especially the direct charge separation procedure [16, 27-31]. However, based on the finite element method (FEM) simulation, there is no effective electric field distortion that is caused by the nanorods array in a vertical distance above 0.36 μm , as shown in Figure 5.2 [25]. A similar FEM calculation is adopted to solve the Laplacian equation with nanodot having a radius of

about 20 nm and nanoneedles with height of approximately 1 μm in Figure 5.1. The result indicates that more than one half of field distortion (enhancement) is concentrated in the range of a vertical distance around 300 nm, which is consistent to the result shown in Figure 5.2.

Figure 5.2 The simulation results by finite element method showing the various levels of electric field distortion, where the y axis represents the relative deviation of field intensity (E) from its maximum value (E_m) at a series of vertical distances from the nanorod array [25].

The interstitial gap between nanotips and counter electrode is set as 10 μm in the gas sensing device in this work. This gap provides a large space so that majority of positions along the vertical axis (z) will not be enhanced by the field convergence effect directly. In other words, the uniform nanoneedle array can be assumed as a collective integration around the tips instead of independent individuals, as so-called “convergence band” [25]. The characteristic width of this convergence band can be referred to as the effective enhancement range, with 300 nm of axis distance herein.

If only geometry effect is included (in the case of homogeneous silicon nanoneedles as Figure 3.11(d)), the calculated local enhanced field around nanoneedles in this work is still too weak ($\sim 10^7$ V/m at most) to separate the charges inside the gas particles directly. Therefore, with this condition the direct field ionization (n_{FI}) has to be removed from Eq. 5.4 and a compatible breakdown criterion to this case becomes

$$1 - \delta(\beta, \gamma) \left[e^{d p A \exp(-Bp/E)} \right] = 0. \quad (\text{Eq. 5.5})$$

The exponential term in Eq. 5.5 is resulted from the first ionization (α -process). However, the mean free path of one electron in the ambient air is approximately 200 nm, which means that there are probably only few charges can be generated by the seldom effective electron-gas particle collisions within the interstitial gap before the electron neutralization on the anode [175, 176]. There might be more opportunities for electron to collide with gas particles in the space of the weaker electric field (yellow region in Figure 5.1). However, the active electrons in this region originate from γ -process, which demands the sufficient ions bombardment into cathode. Thus if a gaseous breakdown is detected, the improved secondary process $\delta(\beta, \gamma)$ is responsible for compensation to the absence of direct field ionization, based on the revised formula of Eq. 5.5.

With the deficient initial charges, the positive ion-gas particle collision (β -process) will dominate the secondary processes in the convergence band (pink region in Figure 5.1). Previous observation suggests that a much higher energy is required for positive ion to liberate the electron from the gas molecule (at least $3U_i$) due to the lower energy transfer efficiency [73]. However, the mean free path of air (68 nm [177]) and N_2 (63 nm [73]) in atmospheric pressure hinders the initial positive ion to obtain the sufficient kinetic energy in such a weak field between successive collisions. It can be concluded

that without the supplementary ions generated from gas, the secondary process $\delta(\beta, \gamma)$ is deficient to satisfy the Townsend's breakdown criterion. Therefore it is difficult for such geometry-based nanoneedles to independently induce a detectable sustainable breakdown current for the fingerprinting gases [73].

Consistent with the experimental results from the homogeneous silicon nanoneedles in this work (see Figure 4.15), the geometry effect fails to play the critical role exclusively. However, the hybrid nanoneedles with additional direct field ionization through surface states enhancement are able to overcome this problem.

5.1.2.2 Surface-states ionization

The enhancement of ionization by surface states is theoretically introduced in section 2.2.2.1, with an example of the gold nanodot/whiskered silicon hybrid nanostructure [11]. The hypothesis of surface states mechanism is generally in agreement with the experimental results of gas sensing device in this work. However, this surface states mechanism has to be further examined in this case of Fe/Si hybrid nanoneedle.

1) The intrinsic surface states

From the viewpoint of solid electronics, surface state is one type of intrinsic electronic states that is located at material surface, where a steep transition happens in the band structure at the interface of bulk and vacuum [178]. As illustrated in Figure 3.10, the metallic nanodot sitting on top of each nanoneedle is covered by a thin metal oxide surface layer. Before the movement of electrons, the surface states of acceptor are provided by the positive metallic ions, which tend to accept electrons. In contrast, the surface states of donor originate from negative oxygen ions, which prefer to release

electrons, as shown in Figure 5.3 (a). Based on the EDX point scanning results, this metal oxide layer is rich in metallic compositions (Ga or Fe) where contrarily the oxygen vacancies will be located. As outlined in Figure 5.3 (a), the excessive metals prefer to release the electrons jumping into the conduction band, which should have been associated to oxygen. As a result, oxygen vacancies become the primary donor and this thin layer can be characterized as an n-type semiconductor.

Figure 5.3 Energy band diagrams showing surface states of the n-type superficial metal oxide layer on the nanodot. (a) The metallic (Ga, Fe) ions and oxygen ions provide the acceptor and donor surface states respectively. The transition of extra electrons from donor energy level (E_d) to the conduction band (E_c) causes the ionization of oxygen vacancies. (b) The electrons from conduction band to lower surface states of acceptor, along with the fixed ionized oxygen vacancies, form a build-in field which bend the band structure in the gas-solid interface.

As shown in Figure 5.3 (b), when the migration of charges occurs, the excessive electrons in metal oxide are favorable to shift from conduction band into the lower surface states of the acceptor. This charge transfer results in the acceptor surface states becoming partially occupied. A “double-layer” region is composed by these negative electrons staying at surface states and positive charges in terms of oxygen vacancies within semiconductor. Inside this double layer, there is a depletion space where the movable charges are separated in either side to form a build-in electric field, which is

responsible for the bending of energy band at the gas-surface interface, even without an applying an external electric field.

2) Surface states on anode in an electric field

In gas sensing research, the surface states play a crucial role in the adsorption of external gas species on the surface of semiconductor [179]. The surface states mechanism proposed in Ref. [11] is based on the ionization in vacuum of extremely low pressure (few gas particles in vicinity of nanowires), which ignores the contribution of interaction between gas particles and metallic nanotip. In this project, the gas sensing test environment is under atmospheric pressure whereby more essential gaseous electronics processes will take place on the surface of nanodot.

The gas-metal oxide interaction is comprehensively studied in conductimetric sensors (see “resistance type” in Table 1.1). Except for the surface states, three other common interactions are negligible in the case of field ionization, including: “gas particle adsorption, semiconductor redox and ion exchange” [180], which derives from the physical or chemical adsorption, electrochemical reduction and oxidation and replacement of metal oxide atoms respectively. The surface states interact with the ambient gas particles in a manner known as “ionosorption”, where there is an electrostatic interaction between the charged solid surface and the polarized gas molecules [179]. When an ionosorption occurs, the electrons and holes on the metal oxide surface redistribute and potential barrier is distorted, to improve the field ionization efficiency of gas particles around the nanoneedles [180].

At the same time, the nanodot on top of each Fe/Si hybrid nanoneedle is subject to a positive voltage bias, which causes an “inversion layer” and brings about holes on the surface [181], as the band diagram drawn in Figure 5.4 (a).

Figure 5.4 (a) A band diagram showing the inversion of n-type metal oxide surface, where the applied electric field allows the electrons transiting from valence band to surface states of acceptor. This process provides the additional holes for gaseous electron tunnelling. (b) A schematic diagram of interactions between gas particles and the tip of hybrid nanoneedle. In clockwise: electron tunnelling from gas particle (blue) to generate positive ion (yellow); ionization at critical distance (dash line) after the successive bounds to deplete the kinetic energy [11]; adsorption of gas particles [180] and ionosorption transferring charges from polarized gas molecule to cause ionization [179].

The external electric field bends the energy band structure greatly, so that the electron moving from valence band has the access to the surface states of the acceptor. Therefore, extra holes emerge on the surface even though the intrinsic metal oxide is n-type, which provides the desirable additional sites for electron tunneling from gas particles. Thus, with a higher probability of electron tunneling, the electric field performs increased ionization efficiency in the vicinity of the nanodot surface. As summarized in Figure 5.4 (b), the gaseous ionization occurs in a manner of surface-state enhanced electron tunneling and separation of charges by electrostatic interaction.

In Ref. [11], the surface states are deduced to be located in gold nanodots presumably, experimentally proved by the absence of field ionization after removal of Au catalyst. Similar results have been obtained in the comparison of gas sensing responses between Fe/Si hybrid nanoneedle array and pure silicon nanoneedles. Furthermore, in this section the intrinsic and extrinsic surface states in electric field is compared and the operation principle is discussed. Taking advantage of the crucial surface states located on the nanodot, the initial charges are continuously supplemented for the occurrence of subsequent fingerprinting gaseous breakdown.

5.1.2.3 Malter effect of cathode process

Based on the breakdown criterion of Eq. 5.4, the presence of current spike requires a collective improvement of both the first process (n_{FI} and α -process) and the secondary processes (β and γ). Besides the supplementary enhancement of surface states and Laplacian (geometry) field enhancement, it is suspected that the γ -process (green region in Figure 5.1) may also introduce an additional contribution to the current avalanche.

As outlined in Figure 5.1, the positive ions flow in the direction of the applied electric field toward the cathode for neutralization. However, if there are oxide particles (*e.g.* alumina herein) staying on the surface of cathode, the positive ions will probably accumulate on these contaminations. Thus an extremely high field can be formed locally in the order of 10^8 V/m magnitudes, due to the ultrathin insulating layer [181-184]. Subsequently the electrons are ejected from the cathode in terms of field emission. With the high kinetic energy, these emitted electrons are usually able to pass through the positive charged contaminations. A small amount of electrons that are

moving in the gaseous space is sufficient to bring about the supplementary ions landing onto the charged particles of the cathode. This process becomes self-sustaining and is well known as “Malter effect” under the name of the first observer [73, 182].

However, the Malter effect will vanish as soon as the electrical or mechanical removal of metal oxide particles from the cathode surface [182]. Therefore, this secondary effect can only serve as a complementary enhancement to ion current, rather than the dominating factor. Interestingly, this effect is quite revealing to the Pt/Si hybrid nanoneedles sensor based on the polarization mechanism, which will be detailed later.

5.1.3 Study of responses to hydrogen/nitrogen mixture

A series of I - V curves from Fe/Si hybrid nanoneedle array representing H_2/N_2 ionization are plotted in Figure 4.14 as an example of the sensitivity to the gas concentrations [26]. It is observed that the threshold voltage of carrier gas (N_2) decreases dramatically when a trace concentration of H_2 (10 ppm) is mixed. However, the relationship between the threshold voltage and H_2 concentration is not linear, where the curve measured in this lower H_2 proportion (10 ppm) is separated from those higher ones (50, 100 and 200 ppm).

These gaseous electronics phenomena can be explained using the “Penning Effect” [73], which concerns an excitation or metastable population [23]. In the convergence band of the nanoneedle array, the enhanced electric field may also induce the gaseous excitation besides the direct ionization in the vicinity of nanotips. The nitrogen, as the majority of background gas, has a higher probability to generate metastable gas particles compared to the trace hydrogen. A number of nitrogen particles may have energy levels of

metastable states (*e.g.* $N_2(A_3\Sigma_u)$ around 6.21 eV [185]), which is higher than the ionization potentials of some hydrogen species [186]. Therefore, a Penning process may occur, *i. e.* the metastable N_2 transferring the energy to ionize the hydrogen. In such condition that the concentration of H_2 is ultralow, the Penning effect is responsible to essentially improve the ionization process. This is the reason why introducing such a trace content of H_2 results in a dramatic decrease of the breakdown voltage for N_2 . However, when more H_2 (*e.g.* 50 ppm) is diluted into N_2 , the convergence band will preferentially excite the hydrogen species themselves into the metastable states. With even higher proportion, the overwhelmed hydrogen will dominate the subsequent procedures, where the ionization mainly occurs within the hydrogen species. As a result, a shift of I - V curve from trace concentration (10 ppm) to moderate one (50 ppm) is still visible. With the further increasing hydrogen (100 ppm and 200 ppm), it fails to bring about any significant signal change.

So far, the fundamental gas ionization mechanism of Fe/Si hybrid nanoneedle array has been studied through the analysis of gaseous electronic signals. The proposed ion current equations and associated enhancement mechanisms are reflected to the remarkable gas sensitivity of nanoarray. Besides, another Pt/Si hybrid nanoneedles gas sensor with a different structure and even better signals will be insightfully discussed in the next section.

5.2 Pt/Si hybrid nanoneedle array gas sensing mechanism

As mentioned in previous chapter, a Pt/Si hybrid nanoneedle array is fabricated between the electrodes pair to form a novel gas sensor loaded by a lateral electric field. In addition to the geometry effect, the platinum nanocrystallites within the hybrid

nanoneedles are subject to a superimposed polarization effect. In this section, the field ionization mechanism discussion starts with the comparison of the ionization signals of Pt/Si to Fe/Si hybrid nanoneedles.

5.2.1 Study of gas sensing signals

As outlined in the fingerprinting I - V curves (*e.g.* Figure 4.20 and 4.22) from Pt/Si hybrid nanoneedle array, there is a background current clearly visible before the gas breakdown. In fact, these exponential curves are caused by the inevitable leakage crossing the substrate (see Figure 4.9), which are consistent to the current signal from homogenous Si nanoneedles (see Figure 4.21). Neglecting such leakage background, comparing to the Fe/Si device there are mainly two significant differences regarding the ionization signals of the Pt/Si gas sensor. First, I - V curve is much smoother with a sudden spike at each threshold voltage. The second advantage is the improved resolution of the responses to the various H_2 concentrations in N_2 . These developments can be attributed to a different mechanism of ion current generation in the unique device structure.

In the case of vertical Fe/Si hybrid nanoneedle gas sensing device, the surface states enhance the generation of positive ions. However, the overall background electric field ($\sim 10^7$ V/m) is far from the theoretic gaseous ionization energy ($\sim 10^{10}$ V/m [11]). Additionally, the direct ionization with surface states and secondary processes $\delta(\beta, \gamma)$ is necessary to compensate the deficiency of field strength for self-sustaining breakdown. Unfortunately, such mechanisms become unsuitable to the Pt/Si hybrid nanoneedles. As schematically illustrated in Figure 5.5, the surface of nanodot sitting on the top of each nanoneedle is polarized in the applied lateral electric field (simplified by ignoring the

isolation of each Pt nanocrystallite). In a gaseous electronic system, the separated charges drift towards the opposite directions at a constant electric field. As governed by the ion current formula of Eq. 5.1, the detected I - V signals are determined by the electric field distribution, generation of charges and ion/electron movement crossing the nanoneedle array. In this gaseous ionization device, the small gap between electrodes pair (2-3 μm) and distance of adjacent nanodots (~ 700 nm) may bring about rather different contributions from these effects.

Figure 5.5 A schematic diagram of probable gaseous ionization mechanism for Pt/Si hybrid nanoneedle array, where the surface of each nanoneedle is polarized into positive (red) and negative (yellow) sides. The electron or ion collision to gas molecule is absent due to the limited space.

First, the generated ions/electrons travel a much short path along the field, and thus there will be fewer recombinations between the opposite charged particles. As a result, the corresponding subtle fluctuations in I - V curves from Fe/Si device vanish in the case of Pt/Si hybrid nanoneedles. Instead, the direct conduction of charges to either nanodots

or electrode induces a smooth curve. From the perspective of ion current (Eq. 5.1), the charge drift factor σ becomes less important to the redistribution of field and overall current. Therefore, during the analysis of gaseous ionization in Pt/Si hybrid nanoneedle array, the electric field can be considered as a stationary factor, which is different to that of Fe/Si. On the other hand, there is insufficient space for the acceleration or collision of charges to cause secondary population $\delta(\beta, \gamma)$. Without these indirect supporting processes, further improvement in direct ionization efficiency is required to allow a rapid spike of current independently. When it happens, the proposed Penning process reflected in Fe/Si gas sensor will be absent in this Pt/Si device. Alternatively, the direct ionization of higher priority occurs, prevailing to the step charges separation in the form of metastable state. The changed mechanism is correlated to the linear responses to the various H_2/N_2 concentrations.

In contrast to the traditional setup of parallel-plates structure (*e.g.* Fe/Si hybrid nanoneedles gas sensor), the relatively small space provided by the Pt/Si device in this work gives rise to a direct rather than indirect ionization (collision and secondary $\delta(\beta, \gamma)$), to generate the fingerprinting currents. The mechanism is explored below.

5.2.2 Polarization enhancement

As discussed in Section 2.2.2.2, the isolated metallic nanocrystals (*e.g.* platinum in this work) are subject to polarization in an applied electric field. As a result, the positive or negative charges are tending to accumulate on the surface of each Pt nanocrystallites. Combining this surface charge concentration and geometry effect (see section 2.2.2.2), the polarization-enhanced electric field distribution can be evaluated.

Figure 5.6 The geometry parameters used in surface charge calculation and electric field FEM simulation.

The distance from Pt hybrid nanoneedles to the electrodes is in the range of submicron, where the “convergence band model” is no longer appropriate. In other words, each nanoneedle has to be considered as an individual in this nanoarray. Thus, Eq. 2.8 can be employed to estimate the density of charge accumulated onto each Pt-nanocrystal surface. Based on the characterization result from the SEM (Figure 3.16) and TEM (Figure 3.18) image, the geometric parameters are drawn in Figure 5.6 and defined as [32]: thickness h (30 nm) of Pt nanodot and equivalent radius r (400 nm) of nanoneedles in a separation s (575 nm), which form an M (10) $\times$ N (3) array placed into the gap d (2.6 μm) of the electrode pair with equivalent area A_e ($2 \times 10^{-15} \text{ m}^2$). If the loaded bias is set to be 6 V as the operation voltage based on Eq. 2.8, the effective surface charge density by polarization process can be calculated to be 0.847 C/m^2 [32].

The geometry parameters used in the finite element method simulation can also be found in Figure 5.6. Only the charged metallic nanocap is concerned in this model, which is definitely subject to a much higher electric field compared to the underlying insulating layer or silicon nanorod. The platinum nanocrystallites are outlined as a string

of separated beads in diameters of 10 nm, half-embedded into the surface of nanocap (see Figure 5.6).

Figure 5.7 Finite element method simulated electric field distribution superimposed by accumulated surface charges on Pt nanocrystals by polarization. (a) The significantly enhanced local electric field in the vicinity of Pt nanocaps, compared to the overall weak background field. (b) A line scan of field intensity across all these platinum nanocaps, which suggests that the maximum field strength can be found at the surface of Pt nanocrystallite and gaseous space.

After superimposing the calculated charge density of 0.847 C/m^2 on both sides of superficial nanocaps (nanocrystals), as illustrated in Figure 5.7 the polarization-enhanced electric field distribution can be obtained by solving the Laplacian equation. The simulation results suggest that the maximum electric field is located around the surface of platinum nanocrystallites (red region in Figure 5.7 (a) and

peaks in (b)). The intensity remains at an ultrahigh value in the order of 10^{11} V/m within a distance of 100 nm from the axis of each nanocap. Apart from this amplified region, the spaces between adjacent nanoneedles or the gap between nanoneedles and the electrodes undergoes a much weaker field without essential enhancement. These simulation results are consistent to the gas sensing signals, which implies the effective direct field ionization as the main mechanism rather than the collision or secondary processes.

Figure 5.8 Simulation result of electric field distribution for nanocrystallites on a nanocap after removal of surface charges. The electric field fails to be enhanced on the surface of nanocrystal, with less amplification to the background.

If the polarization effect is absent on the tip of each hybrid nanoneedle (similar to the condition of bare silicon nanoneedles), the Laplacian distribution of electric field fails to be efficiently improved by the independent geometry effect. As shown in Figure 5.8, in the same condition to Figure 5.7 but removing the surface charges, there will be no significant improvement on the surface of nanocrystals. The strongest field within this system is merely in the order of 10^6 V/m, which is quite close the overall background intensity. Such a low electric field is too weak to induce the direct gaseous field

ionization around the nanoneedles. Alternatively, the collision of electron (α -process) or ion-cathodes impinging (γ -process) in this field is responsible to generate the ion current. However, as discussion in last section, the limited space is insufficient to accelerate the charges or cause an electron avalanche [22, 23]. Therefore, only the leakage crossing the substrate rather than fingerprinting current signal can be captured from the silicon nanoneedle array without the presence of the platinum nanocrystallites.

5.3 Categorization of gaseous ionization mechanisms

Based on the detected ion current/voltage signals followed by the studies of various ionization enhancement methodologies, the fundamental ionization mechanisms can be classified into the corresponding physical scenario. These diverse gaseous electronics phenomena can be extensively summarized according to the level of electric field intensities, as following:

- Direct field ionization

This phenomenon happens mainly in an extremely high electric field (*e.g.* Pt nanocrystallites polarization enhanced) in the order of 10^{11} V/m magnitudes [32]. In such condition, the electron is able to tunnel from gas particles into the positive charged one-dimension nanomaterials. Without the successive secondary processes, a sudden boost of ionization current is observable in the external circuit. One example was presented by Goodsell in the literature [187], in which the direct field ionization occurred at low-temperature rubidium atoms in the presence of a high electric field around one single carbon nanotube.

- Field emission induced gaseous ionization

If the electric field decreases to the level of 10^9 V/m, the electric field emission will happen on the cathode. The ejected electron is subsequently accelerated along the field direction towards the anode. Along the pathway, several electron-gas particle collisions (α -process) are expected, which may induce the multiplication up to detectable gas ionization current level [73]. In the application of field ionizer based on one-dimensional nanomaterial, the cathode is always subject to the bombardment of heavier positive ions, which might cause the damage of nanostructure and ultimately the device failure [35, 188]. Meanwhile, a sufficient travelling route (interstitial gap between electrode pairs) is required to bring about the charge acceleration or collision [22, 23].

- Malter effect (surface contamination enhanced field emission)

The field emission efficiency can still be increased in a decreased field (10^7 to 10^8 V/m) [73], which is referred to “Malter effect” as discussed in section 5.1.2.3. The local electric field is further enhanced by the accumulated positive ions above the cathode surface, if there are certain types of contaminations there. The excessive energy provided from charge contamination initializes the emitted electron with a high velocity, which results to the high probability of electron avalanche.

- Surface-states enhanced direct ionization

Instead of increasing field strength above the ionization potential, the direct gaseous ionization can also be induced by providing abundant surface states for electron tunneling from gas molecules in a much lower electric field (10^7 V/m) [11, 26]. As shown in the example using Au nanodot/Silicon whisker and Fe

nanodot/silicon nanoneedle in this work, the surface states on the metallic nanotip are essential to separate the charges from the gas molecules. The background field is responsible to accelerate the generated positive ions to bombard the cathode for electron emission (γ -process) and subsequent charge multiplication.

- Ionization by electron collision (α -process)

Rather than a supplementary process for gaseous ionization, the electron-gas particle collision-induced ionization becomes predominated in an even lower field down to 10^6 V/m [22, 23]. In this condition, similar to the case of field emission, a large separation of counter electrodes pair with a long acceleration interval between successive collisions (mean free path) is required for effective collision ionization.

5.4 Summary

This chapter reviews the fundamental procedures for generation of fingerprinting I - V curves from hybrid nanoneedles. The collective ionization enhancements are proposed to explain the unique gas sensitivity of Fe/Si hybrid nanoneedle array, including geometry effect, surface-states ionization and Malter secondary process. On the other hand, polarization enhanced electric field of Pt/Si hybrid nanoneedle is confirmed by theoretic calculation, which is responsible to the prevailing gas sensitivity. Lastly, the category of classical gaseous ionization mechanisms is extended by the introduction of these two novel gas sensing devices at nanoscale.

CHAPTER 6: CONCLUSIONS AND FUTURE WORK

This chapter concludes the main work and findings in this thesis, together with the recommendation for future research.

6.1 Conclusions

This thesis presents the design, fabrication, characterization and gas sensing application of the novel metal/silicon hybrid nanoneedle arrays. It was found that the hybrid nanoneedles can only be successfully formed on the silicon substrates covered by a thin layer of low-sputter-rate metal. They were unable to be produced on a pure silicon substrate surface. Nor were ordered hybrid nanoneedle arrays formed on the surface of silicon coated with a high-sputter-rate metal layer. Fe, a very low sputter rate metal was chosen to be grown on the surface of silicon wafer. As a consequence of ion irradiation, a perfectly ordered nanonipple array was fabricated. Each nanonipple consists of a nanoneedle with a nanodot sitting on its top. The nanodot is a component alloyed between silicon and incident beam Ga^+ with a little amount of iron. This tiny nanodot is assumed to have abundant surface states that are considerably favourable for electron tunnelling. Such effects enhance the field ionization efficiency, which improve the gas sensitivity of nanoneedles to the types and concentrations of gases. The breakdown voltage was measured to be less than 30 V, far below the traditional gas sensors (normally over 1 kV). However, no nanodots were self-organized on the surface of silicon substrate if the thin Fe layer was replace by platinum thin film. Instead, a Pt cap is preserved on top of each silicon nanoneedle, which consists of a number of nanocrystallites (~ 5 nm). These nanocrystallites act as the polarization centers in a

lateral electric field, which enable to significantly reduce the gas discharge threshold down to ~ 7 V, an ultralow voltage.

The revised Townsend's breakdown criterion is compatible to the nanodevices in this work, with an additional consideration on the direct field ionization. The "convergence band model" suggested that the geometry effect was insufficient to cause a gas breakdown independently. Alternatively, the surface state located on the alloyed nanodot was supposed to be responsible for the effective field ionization. With an applied electric field, the inversion layer on the nanodot surface provided abundant vacancies for the gaseous electron tunnelling. The Malter effect and Penning step-ionization procedures might also act as the supplementary charge generation processes. In the case of Pt/Si hybrid nanoneedles, the smooth I - V curves and linear responses to concentration variations were attributed to the few secondary processes within limited gaseous space. Instead of the negligible collisions multiplication, the gaseous ionization mechanism was proposed to be generated by the direct ionization. The theoretic simulation indicated that the field around the polarized nanocrystallites was so strong that the approaching gas particles encounter to direct ionization.

6.2 Preliminary results for future work

The work at present was established a pioneer miniaturized research platform to provide local ultrahigh electric field at the nanoscale. Besides, there are some additional preliminary results obtained for the future work:

- 1) One-dimensional nanomaterials (ODNM) grown on hybrid nanoneedle array

As illustrated in Figure 3.15, the gallium arsenide whiskers were successfully grown on each preserved gold nanodot. With diameters of lower than 10 nm, these nanowhiskers were appropriate to act as an ideal field emitter or ionizer. Instead of gold-GaAs, there are many other combinations of catalyst-nanowire that can be introduced onto the top of hybrid nanoneedles, *e.g.* Au-Ge nanowire [189], GaN-ZnO nanowire [190] or Fe-carbon nanotube [191]. These highly ordered hybrid ODNM/nanoneedle arrays can be fabricated, which are promising to show the enhanced electrical and optical properties for various applications.

2) Treatment of hybrid nanoneedle array

As shown in Figure 3.10 and 3.13, the incident Ga^+ is alloyed with the metal coating to form the metallic nanodot. It is well-known that gallium has a low melting point ($\sim 29.8^\circ\text{C}$) [192]. Therefore as illustrated in Figure 6.1, the gallium can be partially separated out from the alloyed nanodot of Fe/Si hybrid nanoneedles, after the heat treatment of 30 minutes at 200°C in the argon gas atmosphere.

The gallium of exsolution is characterized as the spherical nanodroplet with an even smaller dimension (~ 15 nm in radius). Furthermore, from the EDX mapping and high-resolution TEM image, the gallium nanodroplet is confirmed to be in the form of a single crystal. Such miniaturized Ga nanodroplets are promising to serve as the matrix to assemble the functional compounds, *e.g.* GaN by nitriding for optics applications.

Figure 6.1 (a) A low magnification bright field TEM image showing a column of Fe/Si hybrid nanoneedles after heat treatment. (b) One single Ga nanodroplet emerges on each nanotip. (c) An EDX elemental mapping taken from the nanotip in (b), where cyan: Si, green: Ga and red: Fe. (d) A high resolution TEM image captured from red-squared region in (b) with its FFT pattern as the inset.

3) Nanowire-nanoarray gas sensing device

The hybrid nanoneedle array provided a platform at nanoscale with extremely enhanced electric field, where the other nanomaterials can also be introduced to improve their intrinsic properties. For example, a single silicon nanowire has been placed above the Pt/Si hybrid nanoneedle array, as shown in Figure 6.2.

This device constituted by a nanowire and a nanoarray is similar to that of a prevalent field effect transistor (FET) structure, where the nanoarray can serve as the back gate. As discussed in section 5.1.2.2 on the surface states, the applied electric field may charge the surface of nanowire on the top. These charges are able to enhance the

interaction between the gas and semiconductor, which in turn improves the conductimetric gas sensing signal on the silicon nanowire [179]. Herein, the nanotips play the role of field amplifier and, with even higher bias as a field ionizer or field emitter with the ability to produce additional gaseous electronic signals.

Figure 6.2 Secondary electron images showing the assembly of a gas sensing device consisting of a single nanowire on a nanoneedle array: (a) Fabrication of Pt/Si hybrid nanoneedle array on a silicon substrate. (b) A single silicon nanowire is transferred to the nanoneedle array by a nanomanipulator. (c) The silicon nanowire is landed right above the nanoarray and connected to the electrode. (d) The gap space between the tip of nanoneedle and the nanowire is measured as hundreds of nanometres.

APPENDIX

A: Evaluation of Townsend's first ionization coefficient α

It is significantly important to estimate the number of charges separated by an electron colliding with the neutral gaseous particles on its path from the cathode to anode. Therefore, an ionization coefficient, α , is introduced as the amount of electrons (ions) generated per unit distance of electron movement in the direction of electric field. It can be called as *Townsend's first ionization coefficient*, or simply *first ionization coefficient*.

The deduction of this factor is based on two assumptions [73]:

1. Each collision between the electron and neutral gas particle consumes all the kinetic energy from the incident electron. Therefore, during the interval between every successive collision events, each electron is accelerated from static (zero velocity).
2. All the electron-neutral gas collisions share an equivalent probability of ionization if the kinetic energy of electron is sufficient to separate the gaseous charges.

In a uniform electric field, as the case shown in Figure 2.2, an electron will be accelerated to move along the field direction from the cathode towards the anode. The electric field strength E can be calculated as V/d where V is the voltage loaded onto the electrodes pair with the interstitial gap d . The ionization by electron collision will increase the total electron amount in the field, where the newly generated electron is able to be accelerated for the successive ionization with the original electron. Therefore, the rapid multiplication process called as “electron avalanche” occurs with few initial electron seeds.

Figure A1 Schematic diagram of a parallel-plate electrodes pair for α evaluation.

As shown in Figure A1, at a distance x from the cathode there is a plate region (dash parallel lines) with a thickness of dx . When n electrons go through this region from left side, there will be dn newly generated electrons as governed by the Eq. A1:

$$dn = \alpha n dx, \quad (\text{Eq. A1})$$

at the beginning ($x=0$), there are n_o initial electrons in vicinity of cathode, and then we can change the form of Eq. A1 and integrate both sides of the formula from 0 to x :

$$\frac{1}{n} dn = \alpha dx, \quad (\text{Eq. A2})$$

$$\int_{n_o}^n \frac{1}{n} dn = \int_0^x \alpha dx. \quad (\text{Eq. A3})$$

In the uniform electric field, α can be assumed as a constant; therefore, Eq. A3 can be calculated as

$$\ln \frac{n}{n_o} = \alpha x \quad \text{and} \quad n = n_o e^{\alpha x}. \quad (\text{Eq. A4})$$

B: Townsend's break down criterion

In case of positive-ion collision (β -mechanism), the total ionization current should take the anode current as well [82, 83]. Supposed in unit cross section and unit time there are n_0 initial electrons moving starting at cathode similar to the α -process, p electrons will be generated from the cathode to the plate region dx (dash parallel lines) at position of x . As shown in Figure A2, q positive ions are approaching from anode to the plate region simultaneously.

Figure A2 Schematic diagram of a parallel-plate electrodes pair for β evaluation.

Therefore, the amount of electrons produced between the electrodes pair can be expressed as:

$$n = n_0 + p + q, \quad (\text{Eq. A5})$$

which equals to the number of electrons neutralized on anode and independent to the selected position of dx . Inside the plate region dx , the count of additional generated electrons can be represented as $(n_0 + p)\alpha dx$. At the same time, because β is defined

as the number of electrons created by ion-gas collision per distance in field, there are $q\beta dx$ electrons produced by ions within the plate region dx . Hence the total number of charge separation events (or number of newly generated electrons) inside dx equals to

$$dp = (n_0 + p)\alpha + q\beta dx. \quad (\text{Eq. A6})$$

Meanwhile, the number of ions q can be retrieved from Eq. A5 as $n - n_0 - p$, then dp can be revised to:

$$dp = [(n_0 + p)\alpha + (n - n_0 - p)\beta] dx. \quad (\text{Eq. A7})$$

On the cathode ($x = 0$), there is no electron where $p = 0$. After going through such collisions for multiplication, the number of electrons near the anode ($x = d$) becomes $p = n - n_0$ ($q = 0$ in Eq. A5). Therefore, by transforming the Eq. A7 and integrating its both sides, we can find

$$\int_{p=0}^{p=n-n_0} \frac{dp}{n_0 + p + n\beta/(\alpha - \beta)} = \int_{x=0}^{x=d} (\alpha + \beta) dx. \quad (\text{Eq. A8})$$

By calculating the left and right side in this formula and arranging the expression we can get:

$$n = n_0 \frac{(\alpha - \beta)e^{(\alpha - \beta)d}}{\alpha - \beta e^{(\alpha - \beta)d}}. \quad (\text{Eq. A9})$$

Considering the first ionization α (electron-gas collision) is more effective and significant than β (ion-gas collision), we can further simplify the Eq. A9 through replacing $\alpha - \beta$ by α as

$$n = n_0 \frac{e^{\alpha d}}{1 - (\beta/\alpha)e^{\alpha d}}, \quad (\text{Eq. A10})$$

which is similar to Eq.2.6 in the form of current in section 2.1.2.3.

Besides, the cathode process in terms of positive-ion bombardment (γ -process) also probably causes the considerable secondary electrons with the previous ones (α and β)

processes) [82, 83]. The probability of a positive ion to liberate a secondary electron after its arrival to cathode is signed as γ . As shown in Figure A3, in the plate region there are q positive ions impinging to the cathode to generate p secondary electrons, adding to the n_o initial field emitted electrons. Similar to the previous analysis, the total amount of electrons approaching to the anode equals to $n = n_o + p + q$.

Figure A3 Schematic diagram of a parallel-plate electrodes pair for γ evaluation.

Based on the definition of cathode process coefficient γ , the number of secondary electrons can be expressed as:

$$p = q\gamma = (n - n_o - p)\gamma. \quad (\text{Eq. A11})$$

Meanwhile, the movement of electrons from cathode to anode brings about their multiplications, in the form of Eq. A4 as:

$$n = (n_o + p)e^{\alpha d}. \quad (\text{Eq. A12})$$

The expression of p can be retrieved from Eq. A11 and substituted in Eq. A12, then

$$n = \frac{n\gamma + n_o}{1 + \gamma} e^{\alpha d}. \quad (\text{Eq. A13})$$

Subsequently the total number of generated electrons n can be solved as:

$$n = n_0 \frac{e^{\alpha d}}{1 - \gamma(e^{\alpha d} - 1)}. \quad (\text{Eq. A14})$$

In the condition closed to the gaseous breakdown, we can consider $e^{\alpha d}$ is much large than 1 and Eq. A14 can be further simplified as

$$n = n_0 \frac{e^{\alpha d}}{1 - \gamma e^{\alpha d}}, \quad (\text{Eq. A15})$$

which is similar to its current expression of Eq. 2.7 in section 2.1.2.3.

C: Sputter Rate

Based on Sigmund theory[159], for an incident ion energies of E , the total sputtering yield Y_t (sputtered atoms by per incident ion) is governed by [124]:

$$Y_t = \frac{0.42\eta S_n}{U_s} [\text{atoms} / \text{ion}], \quad (\text{Eq. A16})$$

where η is determined by the mass ratio of sputtered (M_s) and incident (M_i) atoms as:

$$\eta = 0.15 + 0.13 \frac{M_s}{M_i}. \quad (\text{Eq. A17})$$

S_n represents the elastic stopping power of the incident ion (nuclear stopping cross-section) and U_s is the sublimation energy of the target material. The related information related to the metals in the materials matrix of this work has been collected in Table A1.

The calculated sputter yield can also be converted into the sputter rate R_t following the equation:

TableA.1 Nuclear stopping cross-section of 30keV Ga⁺ to various targets.

Metal	Atomic number	Relative atomic mass	mass factor η	Sublimation energy (eV) [193]	Nuclear stopping cross-section [124]
Al	13	27.0	0.200	3.39	5.2
Si	14	28.1	0.202	4.63	4.0
Ti	22	47.9	0.239	4.85	5.4
Cr	24	52	0.247	4.12	6.8
Fe	26	55.8	0.254	4.28	6.9
Co	27	58.9	0.260	4.39	6.9
Zn	30	65.4	0.272	1.35	24.1
Ga	31	69.72	0.329	2.85	12.5
Mo	42	95.9	0.351	6.82	5.9
Ag	47	108	0.364	2.95	14.5
In	49	115	0.372	2.52	---
Sn	50	119	0.482	3.14	14.1
Hf	72	178	0.488	6.42	8.3
Ta	73	181	0.493	8.1	6.7
W	74	184	0.517	8.9	6.1
Au	79	197	0.540	3.81	14.7
Bi	83	209	0.202	2.15	---

“---”: not available.

$$R_t = \frac{Y_t \times 1.04 \times 10^{-14} \times M}{\rho} [\mu m^3 / nC], \quad (\text{Eq. A18})$$

where the incident beam containing charges of 1 nC equals to 1.04×10^{-14} mol ions. And then the volume of sputtered materials can be obtained by multiply the molar volume (atomic weight M [g/mol] over density ρ [$\text{g} \cdot \mu\text{m}^{-3}$]).

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