Carbon-based materials for thermal management applications

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**CARBON-BASED MATERIALS FOR THERMAL
MANAGEMENT APPLICATIONS**

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SCHOOL OF ELECTRICAL AND ELECTRONICS ENGINEERING

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Carbon-Based Materials for Thermal Management Applications

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Abstract

The scaling down of device sizes and the increasing in power dissipation make heat transport and removal a major technological impediment to the future development for electronic applications. Limited heat conduction within devices causes severe localized self-heating problems. Temperature increase significantly degrades the device performance, and the thermal stress caused by the mismatch in the coefficient of thermal expansion shortens the device lifetime drastically. To solve these issues, the development of highly effective heat transfer materials, such as heat sinks, heat spreaders, and thermal interface materials, has received extensive attention. Carbon-based materials, such as carbon nanotubes (CNTs) and diamonds, become attractive for thermal management applications due to their superior thermal properties. In this dissertation, I have focused my attention on the thermal property investigation of polycrystalline diamonds (PCDs) and CNTs for thermal management applications. For the PCD and CNT thermal property investigation, it includes the growth of PCDs and CNTs, the thermal measurement (technique development), the building up of the thermal model, and the thermal conductivity fitting based on the thermal model.

Diamonds have been proposed as advanced heat spreaders and heat sinks for high power density devices. Polycrystalline diamond stands out among all diamond isotopes for its versatility, low production cost and high

thermal conductivity. However, due to the evolutionary growth mode of PCDs, the thermal properties of the top surfaces (growth surfaces) and the bottom surfaces (nucleation surfaces) are different. Besides, a limitation in PCDs as thermal management materials is the dependence of their thermal properties on defects. In this study, the thermal conductivity comparison between top and bottom surfaces of PCDs due to various defects has been investigated. For the top surfaces, the heat transport is limited by the presence of the Ns^0 defect. For the bottom surface, the non-diamond carbon phase, Si vacancy, C-H stretch and Ns^0 defects all lead to an obvious reduction in the thermal conductivity. The correlation between the thermal conductivity and the optical transmission of a PCD is studied, making the fast estimation of thermal conductivity by optical inspection available.

Carbon nanotubes show a high potential for a thermal interface material (TIM) due to its high thermal conductivity and mechanical compliance. A novel three dimensional carbon nanotube (3D CNT) network has been proposed to improve the thermal performance of currently used CNT-based TIMs. The 3D CNT network is comprised of vertically aligned CNT arrays (primary CNT arrays) bridged with randomly-oriented secondary CNTs. These linkages between the primary CNTs can be postulated to enhance the thermal performance of CNT-based TIMs.

Because of the large surface roughness of the CNT array (in micrometers), the thermal characterization of the CNT array using state-of-the-art techniques remains a challenge. In this dissertation, two novel thermal characterization techniques, (1) the free-standing sensor-based 3ω technique and (2) the infrared thermal imaging technique, have been well developed for the characterizations of the cross-plane and the in-plane thermal conductivities of the CNT-based TIMs. Both of the theoretical thermal models and the experimental investigations have been reported. The cross-plane thermal conductivity of the 3D CNT network has been measured to be 56% higher than that of the primary CNT array when the array density is $5.6 \times 10^8/\text{cm}^2$. The in-plane thermal conductivity of the 3D CNT network has been estimated to be 5.4 W/mK, which is more than 50 times higher than that of the CNT array alone.

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List of Abbreviations

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AC	Alternating current
AlN	Aluminum nitride
BeO	Beryllium oxide
CH ₄	Methane (gaseous)
C ₂ H ₂	Acetylene (gaseous)
C ₂ H ₄	Ethylene (gaseous)
CNT	Carbon nanotube
CO	Carbon monoxide
Cr	Chromium
CTE	Coefficient of thermal expansion
CVD	Chemical vapor deposition
DC	Direct current
ESR	Electron spin resonance
FTIR	Fourier transform infrared spectra
FWHM	Full width at half maximum
H ₂	Hydrogen (gaseous)

HF	Hydrofluoric acid
HNO ₃	Nitric acid
IR	Infrared
K	Kelvin
MD	Molecular dynamics simulation
MPCVD	Microwave plasma-assisted chemical vapor deposition
MWCNT	Multiwall carbon nanotube
N ₂	Nitrogen (gaseous)
NP	Nanoparticles
Ns ⁰	Single substitutional nitrogen
N-V ^{0/-}	Neutral and charge nitrogen vacancy
PCD	Polycrystalline diamond
PECVD	Plasma Enhanced Chemical vapor deposition
PL	Photoluminescence
PMMA	Polymeric methyl methacrylate
PPR	Pulsed photothermal reflectance
RF	Radio frequency
RMS	Root mean square
SCD	Single crystalline diamond
SEM	Scanning electron microscope

Si-V	Silicon vacancy
Si ₃ N ₄	Silicon nitride
SWCNT	Single-wall carbon nanotube
TCR	Temperature coefficient of resistance
TDTR	Time-domain thermoreflectance technique
TEM	Transmission electron microscopy
Ti	Titanium
TIM	Thermal interface material
TiN	Titanium nitride
UV	Ultraviolet
UV-Vis	Ultraviolet-visible spectroscopy
VACNT	Vertically aligned carbon nanotube

Chapter 1: Introduction

1.1 Background and motivations

For the past decades, enormous effort has been invested in the electronic industry to improve the efficiency and functionality of electronic systems. To achieve this goal, the development of miniaturized, fast response electronic devices with high processing speeds is crucial [1-3]. However, as the device size is reduced, heat transport and removal from the device become a major challenge [4-6]. The miniaturization of devices increases the power density within the device, which leads to the generation of high heat density and causes severe heat conduction issues. This can lead to serious localized device-level self-heating problems [7-10] such as degradation of the device performance and thermal-induced failure caused by discrepancy in the coefficient of thermal expansion (CTE) at interfaces resulting in thermal stress accumulation within the device [11]. To solve these issues, developing high efficiency heat transfer materials with superior thermal conductivity is essential. Among the reported studies on advanced heat transfer materials, much attention has been focused on the application of carbon-based materials for thermal management due to their extraordinary thermal properties [12-16].

Among the reported carbon-based materials, diamond has been proposed to be a promising heat spreader for high power density devices [17-20]. The thermal conductivity of diamond can reach up to 2200 W/mK [21], which is a factor of five higher than that of the pure copper [22] and over a factor of 10 higher than commonly-used thermal dissipaters, such as aluminum nitride (AlN) or beryllium oxide (BeO) [23]. To reduce the cost in the usage of diamond for thermal management, the chemical vapor deposition (CVD) technique has been developed to synthesize high-quality diamond films, making it possible for diamond to be used in commercial applications [24, 25]. Among the CVD grown diamond forms, polycrystalline diamond (PCD) stands out for its lowest cost and highest compatibility with Si based devices and systems [26]. Furthermore, recent advancements in CVD deposition have enabled PCDs to reach a thermal conductivity of 2100 W/mK, which is comparable with that of a high quality single crystalline diamond.

Despite the promising possibilities of using PCDs as heat spreaders, their thermal conductivity is strongly dependent on grain size, crystal orientation, lattice defects and impurities [27-30]. In addition, due to the evolutionary growth of PCD [31], the thermal properties of the top and bottom surfaces of PCDs are different. Previous studies attributed this thermal conductivity difference to the grain size discrepancy between the top and bottom surface of a PCD [26, 32], and they neglected considering the influence

from other kinds of defects, such as impurities. It should be noted that, when the grain size is comparable or larger than the phonon mean free path within a diamond, the influence from impurity scattering is much stronger than that from the grain boundary scattering [26]. Therefore, systematic studies regarding the thermal properties difference by analyzing various defect scatterings on top and bottom surfaces are needed.

Besides diamond, carbon nanotube (CNT) is another carbon-based material that receives much attention for thermal management, especially its application as a thermal interface material [33-35]. The thermal conductivities for individual single-wall CNT (SWCNT) and multiwall CNT (MCWNT) have been measured to be 3500 W/mK [36] and 2586 W/mK [37], respectively. Besides, CNT is also chemically and thermally stable, which enables its usage in harsh environments [38]. Numerous studies have reported on the development of CNT-based thermal interface materials (TIMs), especially on the CNT/polymer composite [39] and CNT array [33]. Among the findings, the vertically-aligned CNT (VACNT) array stands out for its thermal conductivity advantage [33, 40, 41]. The thermal conductivity of the VACNT array is reported to be 15 to 250 W/mK [42-44], which is much higher than that of conventional TIMs, such as thermal greases and phase change materials [4, 45, 46]. Moreover, the VACNT array possesses high mechanical strength and

mechanical compliance [41]: solving the issue of thermal stress caused by the CTE mismatch between two contacting surfaces.

However, compared with the exceptionally high intrinsic thermal conductivity of CNTs, which has been predicted to be 6600 W/mK [47], the thermal conductivity of VACNT array is much lower. The limited thermal performance of VACNT array is due to the poor heat transport between adjacent CNTs. The air gaps between adjacent CNTs largely increase the thermal resistance of the overall VACNT array, which is undesirable for effective thermal dissipation. In addition, the thermal conductivity of a VACNT array is highly anisotropic. Che *et al.* has predicted from molecular dynamics (MD) simulations that the in-plane thermal conductivity of VACNT array is only 0.056 W/mK [48]. Limited by the poor in-plane thermal properties, a VACNT array cannot make full use of all individual CNTs within the array structure, as the air gap hinders the heat transfer between adjacent CNTs. The limitation in the in-plane thermal conductivity of CNTs becomes more prominent as the devices and their corresponding heat source shrink, where the heat spreading property is expected for the applied thermal interface materials. Hence, the development of a novel VACNT array-based TIM with both high in-plane and high cross-plane thermal conductivities is significant.

Another barrier in the development of VACNT array-based TIM is the technical difficulties involved in carrying out appropriate thermal

measurements on a VACNT array. Regarding the cross-plane thermal conductivity characterization for samples with thin film geometry, the state-of-the-art thermal measurement techniques can be divided into two categories: (1) thermoreflectance measurement techniques based on thermoreflectance and (2) 3ω measurement techniques based on the electrical response in the frequency domain.

In thermoreflectance techniques, the sample surface is heated up by a laser pulse, and the temperature change of the sample is monitored by the reflected laser light from the sample surface. The Time-Domain Thermoreflectance (TDTR) technique [49] and the Pulsed Photothermal Reflectance (PPR) technique [50] both belong to this category. However, in order to achieve a reflected monitoring laser light with a high signal-to-noise ratio, a mirror-like sample surface is required, which is not available in VACNT arrays due to their high surface roughness (in micrometers). Direct deposition of other materials on top of the sample surface is usually applied in the sample preparation for TDTR or for PPR measurements to minimize the surface roughness. However this method is also not suitable for VACNT arrays, since the deposited material fills in the air gap between VACNTs and changes the thermal property of the VACNT film. Yang *et al.* [51] has proposed a method to cover the VACNT array with a gold foil to achieve a reflected laser light signal. However, as this technique involves the manual covering of gold foil

onto CNTs, possible inconsistencies may occur in every measurement: resulting in low accuracy.

The other art-of-the-state technique for cross-plane thermal conductivity characterization is based on the electrical response in the frequency domain. The representative technique under this category is the 3ω technique [52]. In this technique, a metal wire is deposited on top of the sample surface and acts as a heater and a thermometer. In a conventional 3ω measurement, a smooth sample surface is required to ensure the continuum of the deposited metal wire. Because of the high surface roughness of the VACNT array, direct deposition of the metal wire on top of the VACNT array is not available. Hu *et al.* [44] proposed a modified 3ω technique, which involves pressing down the CNT films onto a metal heater deposited on a glass substrate, and detecting the thermal signal of the CNT film from the temperature oscillation of the metal heater. To extract the thermal conductivity from the obtained thermal signal, Hu *et al.* applied one-dimensional (1D) heat conduction approximation and assumed that the contact resistance between the CNT and glass only contributes a fixed offset to the temperature oscillation as a function of frequency. However, solid theory support about when the 1D heat conduction approximation is valid was not provided. Furthermore, the assumption that the contact resistance only contributes a fixed offset is questionable. Thus, a theoretical analysis of the heat

conduction in this modified 3 ω method is lacking and certainly worth investigating.

In addition to the difficulty in the cross-plane thermal conductivity characterization of VACNT array-based TIMs, the in-plane thermal conductivity characterization of VACNT array-based TIMs is also a challenge. A VACNT array cannot be freestanding or in a suspended geometry, which is required for state-of-the-art in-plane thermal characterization techniques, such as the opto-thermal Raman technique [53] and the thermography technique [54]. So far, few studies have reported experimental data for the in-plane thermal conductivity of VACNT array-based TIMs due to the technical problems in thermal characterization. Thus, developing an in-plane thermal characterization technique for VACNT array-based TIMs is necessary for further investigation.

1.2 Objectives

This research proposes potential carbon-based material for thermal management applications and develops novel thermal characterization techniques for thermal property analysis. The thermal properties of carbon-based materials (PCD and CNT) are investigated. The main objectives are to:

- 1) Study the thermal conductivity difference between the top and bottom surfaces of PCDs due to different kinds of defects.
- 2) Provide fast estimation of PCD thermal conductivity based on its optical properties.
- 3) Explore novel in-plane/cross-plane thermal characterization techniques for the thermal property evaluation of carbon-based materials.
- 4) Explore a novel VACNT array-based TIM structure with improved in-plane and cross-plane thermal properties.
- 5) Investigate the thermal properties of the novel VACNT array-based TIM.

1.3 Major contributions of the thesis

The major contributions of this thesis are:

1. Polycrystalline diamonds with different crystalline quality and impurity concentrations are grown by micro-wave plasma chemical vapor deposition (MPCVD). The defects of diamond in the form of single substitutional nitrogen (Ns^0), C-H stretch bonds, neutral and charge nitrogen ($\text{N-V}^{0/-}$) vacancies, silicon vacancies (Si-V) as well as grain boundaries are analysed in detail concerning their impact on thermal conductivities. The thermal conductivity differences between the top and bottom surfaces of PCDs due to different defects have been investigated. A well-fitted equation is given to estimate the thermal conductivity of PCD by optical transmission.
2. A novel three-dimensional (3D) CNT network is proposed for thermal interface material application. A VACNT array is grown by plasma enhanced chemical vapor deposition (PECVD). Randomly-oriented secondary CNTs are then grown from the sidewall of primary VACNTs with the help of Ni catalysts by thermal chemical vapor deposition (TCVD): forming a 3D network structure. This novel 3D CNT network structure increases the interface contact area significantly and fills the air gap between adjacent primary CNTs. The in-plane thermal conductivity of the 3D CNT network is estimated to be more than 50 times higher than that of the bare VACNT array. For the perpendicular direction, with a primary CNT

array density of $5.6 \times 10^8/cm^2$, the cross-plane thermal conductivity of the 3D CNT network is 56% higher than that of a bare VACNT array.

3. A freestanding sensor-based ω technique is developed for the characterization of cross-plane thermal conductivity. The freestanding sensor is a metal bridge encapsulated between a polymeric methyl methacrylate (PMMA) substrate and a silicon nitride (Si_3N_4) interfacial layer. As a good thermal insulator with a thermal conductivity of 0.19 W/mK, PMMA blocks the majority of the probing heat signal and ensures a high sensitivity for thermal conductivity evaluation. Since the metal wire is more than five times larger than the thin film thickness, the thermal signal is only sensitive to the cross-plane thermal conductivity of thin film. A full numerical solution of the two dimensional (2D) heat diffusion equations is developed to increase the accuracy in the extraction of cross-plane thermal conductivity.
4. An in-plane thermal conductivity characterization method for thin film samples has been developed based on infrared thermal imaging analysis. The thin film is heated up by a metal heater underneath. The temperature distribution of the thin film surface is recorded by a high-resolution infrared thermal camera. By suspending the “thin film on heater” structure by a side-clipped holder, the surface temperature profile of thin film is only sensitive to the in-plane thermal conductivity. To extract the in-plane

thermal conductivity of a 3D CNT network from the “thin film on substrate” structure, a 3D finite-element model is developed to enable a numerical fitting of the obtained temperature profile.

1.4 Organization of the thesis

The thesis consists of seven chapters:

- *Chapter 1* provides the background, motivation, objectives, major contributions, and organization of the thesis
- *Chapter 2* presents an extensive literature review on carbon-based materials and thermal characterization techniques. It provides the information of the growth and properties of diamond and CNT. The theoretical basis for the 3ω technique and the infrared thermal imaging are also described in detail.
- *Chapter 3* discusses the influence of optically active defects on the thermal conductivity of PCD. Based on the relationship found between thermal conductivity and the optical transmission of PCDs, a fast way to evaluate PCD thermal conductivity is reported.
- *Chapter 4* proposes a novel freestanding sensor-based 3ω technique to characterize the cross-plane thermal conductivity of a thin film sample. The determination of thermal conductivity based on this new characterization method is verified both theoretically and experimentally.
- *Chapter 5* proposes a novel 3D CNT network structure for thermal interface material. The cross-plane thermal conductivities of 3D CNT networks with different primary CNT array densities are characterized by a freestanding sensor-based 3ω technique.

- **Chapter 6** demonstrates the in-plane thermal properties of a 3D CNT network. A novel thermal characterization method based on infrared thermal imaging is developed.
- **Chapter 7** provides the conclusions and recommendations for future research.

The diagram of the thesis structure is shown in Fig. 1-1.

Fig. 1-1 Diagram of the thesis structure.

Chapter 2: Literature Review

2.1 Diamond properties and growth

2.1.1 Diamond structure

Diamond was first demonstrated as an allotropic form of carbon by Tenet in 1797. Since then, researchers have attempted to synthesize diamond due to the high cost and scarcity of natural diamond, which makes contribution to the comprehensive understanding of a diamond structure and related properties.

Diamond has two basic crystal structures [55]: (1) a cubic symmetry (Fig. 2-1(a)) and (2) a hexagonal symmetry (Fig. 2-1(b)). For both structures, each carbon atom is strongly connected with its neighboring four atoms in a tetrahedral arrangement by sp^3 bonding with an equal angle of $109^\circ 28'$ between each atom. However, the cubic structure is the dominant structure in both natural and synthesized diamond, since the cubic structure has a lower energy and is more stable than the hexagonal one. The cubic structure can be seen as two interpenetrating face centered cubic lattices, one of which is displaced by $(1/4a, 1/4a, 1/4a)$, where ' a ' is the lattice constant with a value of $3.567 \text{ \AA}$. The stacking sequence for the cubic structure in the $\langle 111 \rangle$ direction is ABC ABC ABC.... The bond length of the C-C covalent bonding is $1.54 \text{ \AA}$ and the bond

energy is 711 kJ/mol [56]. Compared to the cubic structure, the hexagonal structure is much rarer and is found in the mineral lonsdaleite. The stacking sequence for the hexagonal structure is AB AB AB.....with a closer bond length of 1.52 Å between adjacent atoms compared to the cubic structure. The lattice constants for the hexagonal lattice in the a and c directions are 2.52 Å and 4.12 Å, respectively.

Fig. 2-1 Schematic diagram showing diamond structures: (a) in cubic symmetry and (b) in hexagonal symmetry. This figure is reproduced with the permission from the copyright holder [55].

Diamond also has a layered-structure isomer: graphite. Graphite is the most common and most stable allotrope of carbon under ordinary conditions. In each layer, carbon atoms are arranged in a hexagonal lattice by sp^2 bonding with a bond length of 1.42 Å. The distance between each layer is 3.35 Å. A

simplified phase diagram of carbon is shown in Fig. 2-2 [57]. According to the diagram, diamond is the most stable form of carbon at a high temperature and high pressure. However, under ordinary conditions, when the pressure is less than one atmosphere and the temperature less than 1000°C, although diamond is not the minimum energy state, it is also not an unstable state, because in some cases, like during CVD deposition, diamond can be synthesized without converting to graphite spontaneously. Thus, diamond is considered as a metastable state under ordinary conditions.

Fig. 2-2 Sketch of the carbon phase. This figure is redrawn based on the data from Ref [57].

2.1.2 Diamond properties

Due to its strong sp^3 C-C bonding force, diamond has unique mechanical, thermal, electrical, optical and chemical properties. The properties of CVD single crystalline diamond and natural diamond are listed in Table 2-1 [58].

Table 2-1 Properties of CVD (single crystalline) and natural diamonds [58].

Properties	CVD Diamond	Natural Diamond
Density (gcm^{-3})	2.8-3.51	3.515
Thermal capacity at 27°C($\text{J/mol}^{-1}\text{K}^{-1}$)	6.12	6.195
Thermal conductivity at 25°C($\text{Wm}^{-1}\text{K}^{-1}$)	2100	2200
Thermal expansion coefficient at 25-200°C($\times 10^{-6}/^{\circ}\text{C}$)	2.0	0.8-1.2
Band gap(eV)	5.45	5.45
Electrical resistivity($\Omega \times \text{cm}$)	10^{12} - 10^{16}	10^{16}
Dielectric constant at 45MHz to 20GHz	5.6	5.7
Dielectric strength(Vcm^{-1})	10^6	10^6
Saturated electron velocity($\times 10^7 \text{cm s}^{-1}$)	2.7	2.7
Carrier mobility($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)		
Electron(n)	1350-1500	2200
Positive hole(p)	480	1600
Young's modulus(GPa)	820-900 at 0-800°C	910-1250
Compression strength(GPa)		8.68-16.53
Poisson's ratio		0.1-0.16
Coefficient of friction in air	0.035-0.3	0.05-0.15

Vickershardness(GPa)[varies with crystal orientation]	50-100	57-104
Index of refraction at 10μm	2.34-2.42	2.40

Diamond is the hardest natural material known in the world. For example, the Vickers hardness of diamond is 57-104 GPa, while the value for casehardened steel is approximately 4 GPa. Diamond also has the highest elastic modulus and the lowest compressibility among all known natural materials. However, diamond is brittle and can break along well-defined cleavage planes, even though the cleavage strength of diamond is stronger than the tensile strength of tungsten wire. Regarding thermal properties, diamond has the highest thermal conductivity among all natural materials. It has been reported that its thermal conductivity would be many times higher if the purity of the ^{13}C isotope, which always acts as phonon scatters in the diamond structure, is well controlled [59]. However, the specific heat capacity and thermal expansion of diamond are low, which increase the difficulty in using diamond in thermal management applications.

For electrical properties, diamond has a wide indirect band gap of 5.45 eV at 300 K. Its dielectric constant and electrical resistivity were measured to be 5.7 and $10^{16} \Omega\text{cm}$ respectively, which indicate that diamond is a good insulator at room temperature. Concerning optical properties, pure diamond has the

largest optical transmission bandwidth, from ultraviolet (UV) to microwave range. Besides, pure diamond almost has no optical absorption, while the absorption spectrum could be altered greatly by impurities in both natural diamond and CVD diamond. Diamond also has a large refractive index of 2.4, so the reflection coefficient for diamond is large. As a result, the angle for total internal reflection is small.

Regarding chemical properties, diamond is chemically inert at ordinary conditions due to its strong C-C covalent bonds. Nonetheless, diamond was reported to start graphitization at 1800 K in an inert atmosphere, and to start oxidation at 900 K in the presence of oxygen [57]. Diamond also reacts with several kinds of metals, such as tungsten, titanium and nickel, and it forms carbide at high temperatures [60], which property is also applied to increase the adhesion between the diamond coating and metal tools.

For polycrystalline considerations, the properties of polycrystalline CVD diamonds are similar to that of single crystal diamonds. Nevertheless, tiny differences exist. First, the fracture strength of polycrystalline CVD diamond was reported to be less than 10% of single crystal diamond [33]. Second, polycrystalline diamond films were reported as p-type surface conductivity and have a higher carrier mobility than single crystal diamond [16]. Third, polycrystalline CVD diamonds do not have well-defined cleavage planes as

single crystal diamonds do. Therefore, polycrystalline CVD diamond cannot be used for traditional gem applications.

2.1.3 Microwave plasma-assisted chemical vapor deposition (MPCVD)

Microwave plasma-assisted chemical vapor deposition (MPCVD) is the most frequently used method for diamond growth in industrial production due to its high energy efficiency, stability, and potential of depositing large-area diamond substrates. The MPCVD system [61] consists of a gas flow rate control subsystem, vacuum pumping subsystem, discharge chamber subsystem, microwave power supply subsystem, and microwave applicator subsystem.

The working mechanism of MPCVD can be described briefly as four steps. First, the discharge chamber is pumped down to 10-100 torr by the vacuum pumping system and the substrate in the discharge chamber is heated up to 800-1000°C. Then a hydrogen-methane mixture (typically 0.2-2vol.% CH₄ in H₂) is introduced into the discharge chamber surrounded by the microwave applicator. Next, a 2.45 GHz microwave radiation waveguided from the microwave supply discharges the gas mixture (CH₄ and H₂) under low pressure into atoms (H), chemical radicals (CH₃, CH₂, CH), electrons and ions (H⁺). These further react and lead to diamond nucleation and growth on the heated substrate.

The MPCVD diamond deposition process can be treated as gas-phase non-equilibrium happening near the deposition substrate. Simplified surface reactions are given to explain the surface chemistry occurring during the diamond growth [39]. As mentioned above, the microwave discharges molecular hydrogen into atomic hydrogen and dissociates molecular methane into CH_3 , CH_2 , and CH . Since the atomic hydrogen exceeds the carbon incorporation rate by a factor of 10^4 [62], the entire surface is bounded by atomic hydrogen: forming surface terminating hydrogen. The growth mechanism is described as:

- (i) An open site is formed once the surface-terminating hydrogen is abstracted by atomic hydrogen. C_dH means a hydrogenated surface site and C_d^* means the open site with the terminating hydrogen removed.

- (ii) Atomic hydrogen or carbon-containing radicals, such as CH_3 , would be absorbed on the open site by covalent bonds.

- (iii) Once the carbon-containing radical is bonded on the surface, two chemical reactions may conduct. One is thermal desorption, which means the carbon containing radical is desorbed and the surface returns to an open site.

The other is the abstraction of hydrogen from the carbon species, incorporating the carbon species into the diamond structure.

In conclusion, diamond deposition is a process of hydrogen abstraction and carbon incorporations. High atomic hydrogen coverage (nearly 100%) is required to ensure that carbon-containing radicals are deposited in a diamond structure. Lower hydrogen coverage leads to the deposition of graphite or other sp^2 phase carbon material.

Besides CH_4 and H_2 , oxygen (O_2), nitrogen (N_2) and inert gas are sometimes added to the deposition chamber to improve the growth properties. It has been reported that the inclusion of oxygen at a lower substrate temperature, either as molecular O_2 or as CO or CO_2 , can increase the deposition rate or reduce the secondary nucleation, which increases the grain size and reduces sp^2 incorporation in diamond films [63, 64]. The addition of N_2 also influences the CVD synthesis of diamond films. Jin *et al.* demonstrated that a high N concentration results in nanocrystalline structures and black films containing sp^2 phase carbons, like graphite or amorphous carbon, while a lower concentration of N leads to a smoother and more stable film texture [49]. Sometimes, a large quantity of argon (Ar) is also added to the chamber. It has

been presented that the discharge of argon with relatively small amounts of CH₄ and H₂ leads to very smooth diamond film surfaces [50].

2.2 CNT properties and growth

2.2.1 CNT structure

Carbon nanotube (CNT) is a kind of crystalline carbon allotrope in the form of seamless cylinders. Since its first discovery in 1991 by Iijima [65], CNT has attracted tremendous interest from both the academic community and industry researchers and engineers. Due to its superiority in electrical, thermal and mechanical properties, CNT is considered a promising material in various applications, such as highly conductive and strength composites, nano-sized electronic devices, interconnects and thermal management components.

Similar to graphene, CNT belongs to the family of carbon with sp^2 hybridization. Graphene is formed by one-atom-thick planar sheets of sp^2 bonded carbon atoms that are densely packed in a honeycomb crystal lattice. While a single wall CNT (SWCNT) can be conceptualized by wrapping a graphene nano ribbon into the structure of a seamless cylinder, the rolling up direction of a graphene sheet (the chirality) of a SWCNT has dramatic influence on some of its properties. As depicted in Fig. 2-3, chirality is defined by a chiral vector:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \quad (2-6)$$

where $|\vec{a}_1| = |\vec{a}_2| = a = 0.246 \text{ nm}$, which is the lattice constant of two-dimensional graphene.

The diameter of the SWCNT is obtained as:

$$D = \frac{|\vec{c}_h|}{\pi} = \frac{a}{\pi} \sqrt{n^2 + nm + m^2} \quad (2-7)$$

The chiral angle is defined as:

$$\theta = \cos^{-1} \left(\frac{\vec{c}_h \cdot \vec{a}_1}{|\vec{c}_h| \cdot |\vec{a}_1|} \right) \quad (2-8)$$

Based on this scheme, SWCNTs can be categorized into three different types. If $m = 0$ ($\theta = 0^\circ$), the nanotubes are called zigzag nanotubes, and if $n = m$ ($\theta = 30^\circ$), the nanotubes are called armchair nanotubes. Otherwise, they are called chiral.

Fig. 2-3 Definition of chirality of SWCNTs. $\vec{a}_1$, $\vec{a}_2$ are the unit lattice vectors. The insets are the illustration of armchair and zig-zag SWCNTs. The figure is reproduced with the permission from the copyright holder [66].

Multi-walled nanotubes (MWCNTs) consist of multiple concentric shells of carbon cylinders. The distance between adjacent shells is approximately 0.34 nm, which is close to the distance between graphene layers in graphite.

2.2.2 CNT properties

The unique sp^2 bonds and honeycomb crystal lattice, along with cylinder structures result in the superiority of the properties of CNT. They exhibit ballistic properties in both electrical and thermal transport. Exceptionally high Young's modules and a very large aspect ratio have also been observed [67].

(a) Thermal properties

Heat transfer in crystalline carbon is dominated by phonons, or lattice vibration [68]. Both theoretical [47, 48, 69] and experimental [36, 70-72] works show that CNT possess high thermal conductivities. It has been predicted that the thermal conductivity of an individual CNT can reach up to 6600 W/mK at room temperature [47]. Due to the effect of additional intertube scattering, the thermal conductivity of MWCNTs is lower than that of SWCNTs [73]. The thermal conductivities of an individual SWCNT and MWCNT have been measured to be 3500 W/mK [36] and 2586 W/mK [37], respectively.

The phonon thermal conductivity of CNT can be defined as $K = \sum_p C_p v_p l_p$, where C_p is heat capacity; v_p is the group velocity of phonons (or velocity of sound); and l_p is the phonon mean free path [47, 70, 74]. The seamless cylinder structure and honeycomb lattice formed by strong sp^2 bonds guarantee the super stiffness of the CNTs: resulting in the high speed of sound [75]. Moreover, a large phonon mean free path makes the thermal transport nearly ballistic inside the CNT systems [70, 76-78]. The phonon mean free path consists of two contributions:

$$l^{-1} = l_{st}^{-1} + l_{um}^{-1} \quad (2-9)$$

where l_{st} and l_{um} are the static and Umklapp scattering lengths, respectively [70, 79]. Static scattering is also called as elastic scattering, which means the energy will not change due to the scattering process [80]. At low temperatures, where Umklapp scattering is negligible, l keeps almost constant as l_{st} . Therefore, K increases with temperature T following the trend of C_p . At high temperature, l drops significantly due to the onset of Umklapp phonon scattering. Therefore, K shows a peak at $l_{st} = l_{um}$, before falling at higher temperature [69, 71, 74, 81].

The thermal conductivity K of CNT has been found to be insensitive to chiralities [69, 79, 82]. However, K is dependent on the length L of CNT and follows the L^α law. The factor of α is determined by the ratio of the CNT length L and the mean free path l . When the length of a CNT is much larger than the mean free path l , the dependence of thermal conductivity on length is no longer

significant [77, 78, 83, 84]. K was also found to decrease with diameter in both SWCNTs and MWCNTs [71, 84, 85]. Besides the influence from the CNT geometry, the thermal conductivities of CNTs show a strong dependence on the defects [86-90]. The impurities and vacancies of CNTs have a remarkable impact on the thermal properties and lead to a large discrepancy among the experimental results [91-93]. Therefore, the thermal conductivity of CNT in a practical case can be as low as 15-250 W/mK [42-44], which is much smaller than the simulation results.

Bulk CNT materials, including mat, bundles and arrays, are of higher interest for practical applications. Despite the extraordinary high values in individual CNTs, the thermal conductivities of CNTs in bulk forms are much lower [94-96]. Thermal transport inside these materials is significantly hindered by the high resistive thermal junctions and weak coupling between the tubes. As a result, the measured results of a CNT mat are usually over two orders lower than the intrinsic values of an individual CNT [85]. Hone *et al.* obtained a value of 35 W/m·K at room-temperature for a densely-packed SWCNT mat, using a comparative method [97]. Highly aligned CNT bundles or arrays may offer higher thermal conductivities along the axis, which are comparable to those of the best metals [94, 95, 98]. The thermal conductivity of highly aligned CNT bundles was measured to be 200~250 W/m·K at room temperature by Hone *et al.* [99].

(b) Mechanical properties

CNTs are one of the strongest and stiffest materials. Both experimental work and theoretical investigations have shown the remarkable mechanical properties of CNTs, such as an exceptionally high Young's modulus [66, 75, 100], large elastic strain and fracture strain sustaining capability [101, 102]. This strength comes from the covalent sp^2 bonds between adjacent carbon atoms and the seamless cylinder structure.

The Young's modulus of individual nanotubes was estimated in the terapascal (TPa) range, by Treacy *et al.* through measuring, in TEM, the amplitude of the intrinsic thermal vibrations [75]. The results were later confirmed by direct measurements developed by Wong *et al.* [100] and Salvétat *et al.* [103], through the atomic force microscopy (AFM) technique, and Yu *et al.* [104] via stress–strain measurements in electron microscopy.

On the other hand, regarding the value of strength, Wong *et al.* obtained an average bending strength of 14 GPa [100]. In agreement with their results, Yu *et al.* [104] managed to measure the CNT fracture strains of up to 12 % and strengths in the range of 10–63 GPa [105].

2.2.3 CNT growth

Chemical vapor deposition (CVD) is a technique widely used in industries and laboratories for the synthesis and functionization of various

materials. However, the CVD method was not utilized for the fabrication of CNTs until 1993 [106]. So far, no published theory or model can explain the exact mechanism for CNT growth completely. However, it is generally accepted that the reaction processes take place as follows:

- (i) During the CVD process, the catalyst film on the substrate transforms into nanoparticles (NPs) after annealing.
- (ii) At the growth temperature, reactive carbon atoms are dissociated from the input carbon feedstock with the catalyzation of the catalyst NP.
- (iii) The resulted carbon atoms then dissolve into the catalyst NPs. Catalyst NPs are eventually saturated owing to continuous supply of carbon feedstock.
- (iv) Finally, carbon atoms precipitate onto the surface of the catalyst NP, which leads to the formation of tubular carbon structures that are in a low energy state.

The growth of CNTs can be categorized into two modes: tip-growth mode and base-growth mode as shown in Fig. 2-4 [107] with respect to the location of the catalyst NPs after growth. The difference between the two modes derives from the adhesion between the catalysts and the substrate. The tip-growth mode happens when the condition of the catalyst-substrate adhesion is relatively weak. Carbon feedstock is fed to the tip of the growing CNT, the interface between CNT and the catalyst NP. As a result, the catalyst is lifted up

from the substrate, and it is carried all the way by the CNT during the growth. In contrast, in the base-growth mode, strong interaction to the substrate anchors the catalyst NP onto the substrate during the growth. The base part of growing CNTs remains reactive during the growth, where new tubular structures are formed.

Fig. 2-4 CNT growth modes: (a) tip-growth mode and (b) base growth mode.

The figure is reproduced with the permission from the copyright holder [107].

In the CVD growth of CNTs, the catalyst is one of the most important factors for the formation and final properties of the CNTs. A variety of materials can catalyze the growth of CNTs. Among them, metallic materials, especially transition metals, such as Fe, Co, Ni, Cu, have been found to be the most efficient and are now widely used. It was also reported that noble metallic NPs, such as Au, Pd, and Pt, and Si-based nonmetallic NPs, such as Si, SiC and

SiO₂ are also able to serve as catalysts. The catalyst has a great influence on the growth rate, density and quality of CNTs. Regarding the carbon sources, the choice of catalyst need to be well considered. The first material used for CNT growth was CO. Nowadays, hydrocarbon gases, such as C₂H₄, C₂H₂ and CH₄ or alcohols are the most common choices.

A typical CVD process involves three steps. First, the sample is mounted on the heater, which is heated up to the annealing temperature under inert (such as N₂ and Ar) and annealing gas (such as NH₃ or H₂) atmosphere. The catalyst film or particles are annealed and/or reduced to be reactive NPs. In the following growth step, carbon sources are introduced into the chamber and generate the growth of CNTs. When carbon sources are cut off, the CNTs growth finishes. Finally, the chamber is cooled before the sample is taken out of the chamber.

Besides the classical CVD process, plasma can be introduced to promote the growth of CNTs. This is known as PECVD technology. Plasma energy helps the nucleation of catalyst film into particles and accelerates the dissociation of carbon feedstock into active carbon atoms. Moreover, the activity of the catalysts can be maintained during the growth as the plasma etches away the byproducts such as amorphous carbon. Besides, the electrical field brought-in by the radio frequency (RF) power guides CNTs to align into

an array. Through the PECVD process, large area vertically-aligned CNT arrays can be achieved.

Compared to the arc-discharge and laser-ablation technologies, CVD is able to produce high-purity MWCNTs and SWCNTs. Besides, the CVD system is easier to handle and is relatively low-cost as it does not require high vacuum, high temperature or high power laser. Moreover, in a CVD process, CNTs can be directly grown on a substrate with their location, orientation, density, diameter, and length controlled by simply controlling the CVD parameters. The advantages of CVD make it a suitable and ideal method to grow CNTs for a variety of applications.

The material cost of CNTs dictates its practicability in various commercial applications [108]. Nevertheless, the price of CNTs has been reduced significantly from \$45000/kg to \$100/kg over the last 10 years [109], and further reduction in CNT price can be speculated in the near future. Thus the development of CNT-based technology can pair up with the continuous price reduction in CNTs, which may give promising potential in the commercialization of CNT-based applications.

2.3 3ω technique

2.3.1 3ω theory

The 3ω method was first developed by Cahill and Pohl to measure the thermal conductivity of amorphous solids in 1987 [110], and then it was extended for the thermal characterization of thin films and bulk material [111, 112]. In this method, a narrow metal wire is deposited on the sample surface with good thermal contact, which functions as both a heater and a thermometer. An alternating current (AC) at a frequency of ω is applied to the metal wire, which causes a temperature wave at a frequency of 2ω to diffuse into the sample due to the Joule heating effect. Since the electrical resistivity of metal increases linearly with temperature, the generated heat leads to a metal resistance oscillation at a frequency of 2ω . As a result, the voltage drop across the metal wire oscillates at a frequency of 3ω . Based on the temperature oscillation measured at the sample surface, the thermal properties of the sample can be deduced. The advantage of the 3ω method is its insensitivity to radiative heat losses. It has been reported that the error caused by black-body radiation is less than 2% [113].

(a) 3ω measurement for bulk material

The generic side view of a 3ω measurement for bulk material is shown in Fig. 2-5. A metal wire with a width of $2b$ is deposited on the substrate.

Fig. 2-5 Side view of the 3ω measurement for bulk material.

The exact solution of the temperature oscillation $\Delta T(r)$ caused by an infinitely narrow line source on a semi-infinite substrate is given by Carslaw and Jaeger [114]:

$$\Delta T(r) = (P/\pi l k) K_0(qr) \quad (2-10)$$

where $r = \sqrt{x^2 + y^2}$ is the distance from the line heat source, k is the thermal conductivity of the substrate, P is the amplitude of power applied to the metal wire, l is the length of the metal wire, K_0 is the zero order modified Bessel function, and $1/q$ is the thermal penetration depth or wavelength of the diffusive thermal wave. The thermal wave is exponentially damped in the radial direction.

$$1/q = \sqrt{\alpha/i2\omega} \quad (2-11)$$

In Eq. 2-11, α is the thermal diffusivity as

$$\alpha = k/\rho C \quad (2-12)$$

where ρ is the density of the substrate and C is the specific heat capacity of the substrate.

In practical measurements, the metal wire is not infinitely narrow but has a width of $2b$. However, once the thermal penetration depth $1/q$ is large compared to the heater half width b , that is

$$1/q \gg b \quad (2-13)$$

the heater can be approximated as a line source. Equation 2-10 can be simplified as [51, 113]:

$$\Delta T = (P/\pi l k) \times \left(\frac{1}{2} \ln(\alpha/b^2) - \frac{1}{2} \ln(\omega) + \eta - i\pi/4 \right) \quad (2-14)$$

where η is a constant.

Based on Eq. 2-14, the thermal conductivity can be deduced either from the real part or from the imaginary part. Cahill *et al.* showed that using the slope of the real part versus $\ln(\omega)$ is more reliable [115].

In the derivation of Eq. 2-14, the thermal boundary resistance between the metal wire and the substrate is ignored. Swartz found that the boundary resistance between evaporated metal films and dielectric crystals is small (equivalent to the thermal resistance of a 20 Å a-SiO₂ layer) [116]. Thus, the assumption is valid for the 3ω measurement.

Another limitation for using Eq. 2-14 is the assumption of a semi-infinite substrate, which holds if the thermal penetration depth $1/q$ is small compared to the substrate thickness d_s . That is

$$1/q \ll d_s \quad (2-15)$$

It has been reported that if $qd_s > 5$, the error of using the semi-infinite assumption is less than 1% [117].

(b) 3ω measurement for thin films on substrates

The 3ω method can be further applied to measure film-on-substrate systems to deduce the thermal properties of thin films [118]. The generic side view of the 3ω measurement for thin films is shown in Fig. 2-6. A one-dimensional (1D) heat conduction model is usually used to analyze the heat flow across the system. To ensure that the 1D heat conduction model is valid, the following conditions must be satisfied: first, the thermal conductivity of the substrate k_s should be much larger than the thermal conductivity of the films k_f . Second, the metal wire width $2b$ should be much larger than the film thickness d_f and the film anisotropy should be small to minimize the heat spreading effects inside the film. Third, the metal wire width $2b$ should be smaller than the thermal penetration depth $1/q$ to make sure the line source approximation is valid.

Fig. 2-6 Side view of the 3ω measurement for thin film geometry.

We can deduce the thermal properties of the thin film further by one of two ways: (1) the slope method and (2) the differential method. For the slope method, the thin film is treated as a simple thermal resistance and it would add a frequency-independent temperature oscillation to the film-on-substrate system. The experimental temperature rise of the entire system could be written as [119]:

$$\Delta T_{s+f} = \Delta T_s + \Delta T_f \quad (2-16)$$

$$\Delta T_f = \frac{P d_f}{2b l k_f} \quad (2-17)$$

where ΔT_s is the temperature rise of the substrate, and can be calculated using Eq. 2-15. Then the thermal conductivity of the thin film could be deduced using Eq. 2-17. Since ΔT_s is a calculated value, the thermal properties of the substrate (or the layers below the interest layer) must be known in order to subtract their influence on the entire temperature rise measured in the experiment.

For the differential method, a reference sample without the film of interest is needed. The temperature oscillation of the film-on-substrate system and the reference sample are measured at the similar power input (P) through the similar metal wires deposited on the surfaces. Then the thermal properties of the film of interest could be deduced by the temperature rise difference between these two samples:

$$k_f = \frac{d_f}{2} \left(\frac{b l T_{r+f}}{P} - \frac{b l T_r}{P} \right)^{-1} \quad (2-18)$$

where T_r is for the reference sample and T_{r+f} is for the initial film-on-substrate sample.

The advantage of the differential method is the insensitivity to the influence from the substrate or other additional films, which have all been subtracted by the measurement of the reference sample. Thus, the differential method is also extended to measure the thermal conductivity of conductive films, because it is insensitive to the influence from the substrate and the insulating layers [120].

2.3.2 3ω sensor

The temperature oscillation on the sample surface is measured through the $V_{3\omega}$ signal collected from the deposited metal wire [62]. An alternating current at a frequency of ω is applied to the metal wire:

$$I(\omega) = I_0 \cos(\omega) \quad (2-19)$$

The power P diffusing into the sample can be written as:

$$P = RI^2(\omega) = \frac{1}{2}RI_0^2 + \frac{1}{2}RI_0^2\cos(2\omega t) \quad (2-20)$$

where R is the resistance of the metal wire. It would cause a continuous temperature variation ΔT_{DC} and a 2ω temperature oscillation $\Delta T_{2\omega}$. Since the electrical resistivity of metal increases linearly with temperature, the generated heat would lead to a metal resistance oscillation at a frequency of 2ω :

$$\Delta R_{2\omega} = R_0 \times TCR \times \Delta T \cos(2\omega t) \quad (2-21)$$

where TCR is the temperature coefficient of resistance for the metal wire. As a result, the voltage drop across the metal wire is obtained as

$$\begin{aligned} U = IR = I_0 \cos(\omega t) \times R_0 (1 + TCR \times \Delta T \cos(2\omega t)) &= I_0 R_0 \cos(\omega t) + \\ \frac{1}{2} I_0 R_0 \times TCR \times \Delta T \cos(\omega t) + \frac{1}{2} I_0 R_0 \times TCR \times \Delta T \cos(3\omega t) & \\ (2-22) \end{aligned}$$

Thus the temperature oscillation ΔT is obtained as:

$$\Delta T = 2 U_{3\omega} / (TCR \times U_0) \quad (2-23)$$

2.3.3 Sample preparation

Figure 2-7 shows the process of the sample preparation for the 3ω measurement. The gold wire pattern is 1 mm long and 10 μm wide. By a lithography process with photoresist AZ5214, the gold wire pattern is transferred to the sample surface. Then 20 nm Ti and 100 nm Au are deposited on the top of the sample with photoresist patterns using E-beam deposition. The purpose of the Ti layer is to improve the adhesion between the gold layer and

the sample surface. After that, the wire is released after a lift-off process in acetone. The resistance of gold wire is measured as around 20 to 50 Ω at room temperature. After the gold pattern deposition, the sample is attached to a 28-pin integrated circuit (IC) package using thermal epoxy. The electrical connections are further achieved by a gold wire bonding process.

Step 1: gold wire pattern

Step 2: lithography

Step 3: E-beam deposition

Step 4: attach to IC package

Step 5: gold wire bonding

Fig. 2-7 Sample preparation process for the 3ω technique: (a) gold wire pattern; (b) photoresist pattern on top of the sample; (c) Ti/Au deposition on the top of the sample by E-beam deposition; (d) sample attached to the 28-pin IC package by thermal epoxy; and (e) gold wire bonding to enable electrical connections.

2.3.4 Experimental set-up and calibration

Figure 2-8 shows the schematic view of the 3ω system setup. The sample is loaded in the vacuum chamber, which can provide a vacuum of 10^{-6} torr. A sinusoidal signal is supplied from the lock-in amplifier (LI 5640). A Wheatstone bridge is applied to detect the weak 3ω voltage signal. The metal heater (R_h) is one branch of the Wheatstone bridge. The other three branches are two fixed-value resistances ($R_1=50.12\ \Omega$, $R_2=500\ \Omega$) and a variable resistance R_3 . The cancelation of 1ω voltage is done by tilting the variable resistance R_3 until the 1ω voltage signal is the minimum (around 1mV). The output third harmonic signal $V_{3\omega} = V1 - V2$ of the Wheatstone bridge is measured further using a lock-in amplifier with an output impedance of $50\ \Omega$. The relationship of the Wheatstone bridge output $V_{3\omega}$ is related to the 3ω voltage of the metal heater $U_{3\omega}$:

$$V_{3\omega} = \frac{R_1}{R_1 + R_h} U_{3\omega} \quad (2-24)$$

The temperature coefficient of the resistance (TCR) of the metal heater is measured using the prober station (Keithley 4200-SCS). Figure 2-9 shows a typical resistance of metal wire versus temperature (for gold wire). The TCR is further calculated further using:

$$TCR = \frac{1}{R} \times \frac{dR}{dT} \quad (2-25)$$

The TCR value for gold wire is measured to be $0.00199\ \text{K}^{-1}$.

Fig. 2-8 The schematic view of the 3ω technique.

Fig. 2-9 Resistance of the deposited metal wire as a function of temperature.

The 3ω system has been calibrated using materials with known thermal conductivities. Figure 2-10 shows the real part of the temperature oscillation for calibrated bulk materials. Table 2-2 exhibits the fitting results of the thermal conductivity based on Eq. 2-14. The uncertainty of the thermal conductivity measurement of bulk material is mainly related to the uncertainty in the measurement of the three harmonic voltage $U_{3\omega}$ (0.09%), the power density per length P applied to the metal wire (4.1%), and the temperature coefficient of resistance TCR (1.5%). After considering all the related uncertainties, the total uncertainty for the thermal conductivity measurement is calculated to be about 6.3% by Eq. 2-26.

$$\frac{\delta K_{\text{bulk}}}{K_{\text{bulk}}} = \sqrt{\left[\frac{\partial f(K_{\text{bulk}})}{\partial U_{3\omega}} \delta U_{3\omega} \right]^2 + \left[\frac{\partial f(K_{\text{bulk}})}{\partial P} \delta P \right]^2 + \left[\frac{\partial f(K_{\text{bulk}})}{\partial TCR} \delta TCR \right]^2} \quad (2-26)$$

Fig. 2-10 The real part of the temperature oscillation for calibrated bulk materials: PMMA, glass and quartz.

Table 2-2 Thermal conductivity of bulk material measured with the 3ω technique at room temperature compared with the thermal conductivity reported in related studies [121, 122].

Thermal	PMMA	Glass	Quartz
Conductivity			
Measured(W/mK)	0.190 ± 0.004	1.112 ± 0.031	1.764 ± 0.08
Handbook (W/mK)	0.1922	1.060	1.71

Besides the measurement of the bulk material, we also calibrated the 3ω system with a SiO_2 thin film on a Si substrate. The thermal conductivity was obtained as 1.44 W/mK using a 3ω differential method. It is consistent with the results reported by related studies [123]. Figure 2-11 shows the temperature oscillation as a function of frequency for a SiO_2 film on the Si substrate. The thermal conductivity of the SiO_2 thin film is calculated using Eq. 2-17. Similar to the uncertainty analysis with the bulk material, the uncertainty analysis is mainly related to the uncertainty in the measurement of the three harmonic voltage $U_{3\omega}$ (0.09%), the power density per length P applied to the metal wire (4.1%), the temperature coefficient of resistance TCR (1.5%) and the thickness of the thin film d_f (2%). The total uncertainty for the thermal conductivity measurement is calculated to be about 7.1% by Eq. 2-27.

$$\frac{\delta K_{\text{film}}}{K_{\text{film}}} = \sqrt{\left[\frac{\partial f(K_{\text{film}})}{\partial U_{3\omega}} \delta U_{3\omega}\right]^2 + \left[\frac{\partial f(K_{\text{film}})}{\partial P} \delta P\right]^2 + \left[\frac{\partial f(K_{\text{film}})}{\partial TCR} \delta TCR\right]^2 + \left[\frac{\partial f(K_{\text{film}})}{\partial d_f} \delta d_f\right]^2} \quad (2-27)$$

Fig. 2-11 The real part of the temperature oscillation for the calibrated SiO₂ thin film sample.

2.4 Infrared thermography theory

2.4.1 Black body radiation

The presence of thermal radiation outside the spectrum of visible light was first discovered by Herschel in 1800. Thermal radiation is the electromagnetic radiation generated due to an object's temperature. Any object radiates (or absorbs) thermal radiation when its temperature is above absolute zero. The thermal radiation covers the entire electromagnetic waves. The near to far infrared is from $0.75\ \mu\text{m}$ to $1000\ \mu\text{m}$ (see Fig. 2-12). The intensity of thermal radiation in a certain wavelength is quantified by the term "spectral radiance". The concept of a black body is the physics basis for thermal radiation, as the thermal emissions of all objects are deviated from the ideal black body extensively. A black body is an ideal object that absorbs all incident electromagnetic radiation. The radiation properties for a black body can be described by three laws [124]: (a) Planck's law, (b) Wien's law, and (c) Stefan-Boltzmann law:

Fig. 2-12 Infrared wavelength range from $0.75\ \mu\text{m}$ to $1000\ \mu\text{m}$

(a) Planck's law

The spectral density of thermal radiation emitted by a black body is described by Planck's law:

$$\frac{dR(\lambda, T)}{d\lambda} = \frac{2\pi hc^2 \lambda^{-5}}{\exp(hc/\lambda kT) - 1} \quad (2-28)$$

where $\frac{dR(\lambda, T)}{d\lambda}$ is the spectral radiance; $h = 6.6256 \times 10^{-34}$ Js is the Planck's constant; $k = 1.38054 \times 10^{-23}$ J/K is the Boltzmann's constant, $c = 2.998 \times 10^8$ m/s is the speed of light; and T is the absolute temperature with a unit of Kelvin (K).

In the case of short wavelengths, that is $\lambda T \ll hc/\lambda kT$, an approximation is applied as:

$$\exp\left(\frac{hc}{\lambda kT}\right) - 1 \sim \exp\left(\frac{hc}{\lambda kT}\right) \quad (2-29)$$

Then it tends to Wien's law, that is:

$$\frac{dR(\lambda, T)}{d\lambda} = \frac{2\pi hc^2 \lambda^{-5}}{\exp(hc/\lambda kT)} \quad (2-30)$$

which is valid for $\lambda T < 5000 \text{ } \mu\text{mK}$.

In the case of long wavelengths, that is $\lambda T \gg hc/\lambda kT$, an approximation is applied as:

$$\exp\left(\frac{hc}{\lambda kT}\right) - 1 \approx \left(1 + \frac{hc}{\lambda kT} + \dots\right) - 1 \approx \frac{hc}{\lambda kT} \quad (2-31)$$

Then it tends to Rayleigh-Jeans law:

$$\frac{dR(\lambda, T)}{d\lambda} \approx 2\pi c k T \lambda^{-4} \quad (2-32)$$

which is valid for $\lambda T > 5000 \text{ } \mu\text{mK}$. However it is in significant disagreement in the ultraviolet range, as the spectral intensity tends to be infinity.

(b) Wien's law

By differentiating Planck's law with respect to λ , the displacement of the maximum radiation intensity as a function of temperature is described by Wien's displacement law:

$$\lambda_{max} = \frac{b}{T} \quad (2-33)$$

where T is the absolute temperature with a unit of Kelvin (K) and $b = 2898 \text{ } \mu\text{mK}$ is the Wien's displacement constant. It states that the wavelength peak of the black body radiation at different temperatures is inversely proportional to the temperature.

(c) Stefan-Boltzmann law

By integrating Planck's law from $\lambda = 0$ to $\lambda = \infty$, Stefan-Boltzmann law is obtained as:

$$R_t = \sigma T^4 \quad (2-34)$$

where the σ is Stefan's constant as :

$$\sigma = 2\pi^5 k^4 / 15c^2 h^3 = 5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4 \quad (2-35)$$

It gives the total thermal radiation of a blackbody at a given temperature T .

2.4.2 Emissivity

An approximation realization of a black body is a very small hole to a cavity with a large enclosure. Ordinary objects are not generally black bodies.

The thermal radiation intensity at a certain wavelength and temperature depends on the emissivity of the object's surface. Emissivity is defined as the ratio of the energy radiated from an object's surface to that from a blackbody:

$$\varepsilon(\lambda) = E_{\lambda}/E_{b\lambda} \quad (2-36)$$

where $\varepsilon(\lambda)$ is named as the spectral emissivity. For a black body, $\varepsilon(\lambda) = 1$.

Non-black bodies only absorb a fraction of the incident radiation. The other incident radiation is reflected or transmitted. Thus:

$$A(\lambda) + R(\lambda) + T(\lambda) = 1 \quad (2-37)$$

where $A(\lambda)$ is the absorption; $R(\lambda)$ is the reflectance; and $T(\lambda)$ is the transmittance.

When it is under thermodynamic equilibrium, the energy emitted is equal to the energy absorbed:

$$\int \varepsilon(\lambda) d\lambda = \int A(\lambda) d\lambda \quad (2-38)$$

For non-black bodies, Planck's law is described as:

$$\frac{dR(\lambda, T)}{d\lambda} = \varepsilon(\lambda) \frac{2\pi hc^2 \lambda^{-5}}{\exp(hc/\lambda kT) - 1} \quad (2-39)$$

2.5 Summary

In this chapter, the structure and properties for diamond and CNT were reviewed. The growth mechanisms of diamond and CNT using CVD methods were introduced briefly. Furthermore, the theoretical bases for the thermal characterization techniques (the 3ω technique and the thermal imaging technique) were presented.

Chapter 3: Thermal Conductivity of Polycrystalline Diamond

3.1 Introduction

Diamond has the highest thermal conductivity (2200 W/mK) among all known materials [125]. Due to the high cost in acquiring natural diamond, techniques in synthesizing diamond by MPCVD have been developed to significantly reduce the cost of diamond, and make it commercially available for thermal management applications [126]. Due to diamond's excellent thermal conductivity, numerous studies have been reported on the advantages of using it as the heat spreader for high power density devices [12, 127, 128]. The usage of diamond as a thermal management material is especially irreplaceable in applications where electrical isolation or optical transparency is required.

Among diamond isotopes, much attention has been focused on polycrystalline diamond (PCD) due to its capability in large wafer size growth on various substrates [129] and its low fabrication cost. From the reported studies, the thermal conductivity of PCDs can reach up to 2200 W/mK [130], which is nearly identical to the thermal conductivity of pure single crystalline diamond. The versatility, low production cost, and high thermal performance

of PCD position it as a promising candidate for advanced thermal management. However due to the evolutionary growth mode of PCDs [129], the thermal properties of the top surfaces (growth surfaces) and the bottom surfaces (nucleation surfaces) are different. Besides, a limitation in PCD as a thermal management material is the dependence of its thermal properties on its structural properties where the thermal conductivity is highly affected by the presence of defects [131]. In state-of-the-art technology, it has been reported that the diamond grain size correlates with its thermal conductivity, where the discrepancy in the top-down grain size of diamond results in their corresponding difference in thermal conductivity [26, 32]. However, as the grain size is comparable or larger than the phonon mean free path within diamond, the dependence of thermal conductivity on grain size is relatively insignificant compared with other kinds of defect scattering [26]. Therefore, systematic studies on investigating the thermal properties difference by analyzing defect scattering on the top and bottom surfaces are highly required.

In this chapter, the thermal conductivity comparison between the top and bottom surfaces of PCDs is investigated. The degree of crystallinity and the presence of non-diamond carbon phase within PCDs are further evaluated. Meanwhile, the various defects of diamond, such as single substitutional nitrogen (N_s^0), C-H stretch bonds, the neutral and charge nitrogen ($N-V^{0/-}$)

vacancies, and silicon vacancy (Si-V), are analyzed in detail concerning their impact on thermal conductivity.

3.2 Experimental details

3.2.1 PCD sample preparation

Polycrystalline diamond samples are prepared in Iia Technologies Pte Ltd using the MPCVD system. Polycrystalline diamonds are grown on 1 cm× 1 cm Si substrates under different growth parameters namely: temperature, pressure and C/H/O/N ratio. After growth, the Si substrates are dissolved using a mixture of nitric acid (HNO₃) and hydrofluoric acid (HF). Figure 3-1 shows the scanning electron microscope (SEM) images of one freestanding PCD sample after the removal of the Si substrate. The PCDs are then polished mechanically to a surface roughness less than 10nm on both their top and bottom surfaces. The PCD samples show a thickness ranging from 0.25 mm to 1 mm after polishing. The grain sizes are estimated after H₂/O₂ etching of the surfaces, and the range is from 2 μm to 200 μm.

Fig. 3-1 SEM images of one freestanding PCD sample after the removal of the Si substrate: (a) cross-section; (b) top surface (growth side); and (c) bottom surface (nucleation side).

3.2.2 Thermal characterization

The thermal conductivities of both the top and bottom surfaces of PCDs are measured at room temperature (25°C) using the 3ω technique [62]. The direction of thermal conductivity measured by the 3ω technique is determined by the ratio of the width of the heater to the thickness of the sample underneath [132]. In our measurement, the width of the heater is only 8 μm , which is much smaller than the average thickness of the PCD samples (500 μm). Thus, the heater can be treated as a line heater, and the measurement is more sensitive to the in-plane thermal conductivity of the PCD samples. The thermal conductivity obtained for each sample is the average value measured from five different points on the sample surface. The obtained measurements show that the standard deviation is less than 10%: indicating a high consistency in

measurement data. The thermal conductivity of a high quality SCD with no detectable defects is measured as $K_0 = 2300$ W/mK as a reference.

3.2.3 Defect characterization

Micro-Raman and photoluminescence (PL) spectra are applied to measure the PCD samples using Ar⁺ laser (514.5 nm) excitation of a Renishaw inVia Raman microscope. The laser spot size is estimated to be approximately 1 μm using a 50× microscope objective with a numerical aperture of 0.75. Fourier transform infrared spectra (FTIR) are obtained by a Nicolet 6700 spectrometer (Thermo Scientific) using a KBr beam splitter and a DTGS KBr detector. Ultraviolet-visible spectra are collected by a UV 2600 spectrophotometer (Shimadzu) with an ISR-2600 integrating sphere attachment.

3.3 Results and discussion

3.3.1 Photoluminescence (PL) and Raman analysis

Figure 3-2 shows the PL and Raman spectra (inset) for one PCD sample. The intensities have been normalized to the diamond first-order Raman peak at 552 nm (1332 cm^{-1}). The PL spectrum for a high-quality single crystalline diamond (SCD) with no detectable defects is shown as a dashed line.

Fig. 3-2 PL and Raman spectra (inset) for the top and bottom surfaces of one PCD sample. The PL spectrum for one high quality SCD sample is shown as a dashed line for reference.

For the bottom surfaces, a strong Si-V peak appears at 738 nm, which is a result of the interaction between the growth gases and the Si substrate. For the

top surfaces, the typical zero phonon lines for NV^0 and NV^- show up at 575 nm and 637 nm, and there is no Si-V peak. A background luminescence from 560 nm to 900 nm is observed on both the top and bottom surfaces. We can estimate the defect concentration from this luminescence since for high quality and pure single-crystalline diamond, the PL background is almost zero [133]. A non-diamond phase band is observed from 1350 cm^{-1} to 1650 cm^{-1} on the bottom surface. From the bottom to the top surface, the FWHM of the diamond peak drops from 5.17 cm^{-1} to 2.43 cm^{-1} , which indicates an increase in the degree of crystallinity after growth.

As shown in Fig. 3-3, the bottom surfaces show a higher intensity of the non-diamond carbon phase (I_{ND}) as compared to the top surfaces. As I_{ND} increases, the thermal conductivity on both the top and bottom surfaces decreases. However, when I_{ND} is very small (see the grey-shaded region in Fig. 3-3), the thermal conductivities on the top surfaces distribute randomly.

Fig. 3-3 Thermal conductivity versus the integrated intensity of the non-diamond carbon phase band from 1350 cm^{-1} to 1650 cm^{-1} .

This indicates the non-diamond carbon phase is not the main contributor to the reduction of the thermal conductivity on the top surface, and the influences from other defects are more dominant. For the bottom surfaces, the influence from the non-diamond carbon phase is more prominent due to its higher defect concentration. As shown in Fig. 3-4, the top surfaces show a lower PL background intensity I_{PL} than the bottom surfaces. This reflects that the defect densities decrease as the diamond grows. As I_{PL} increases, the thermal conductivity on the top and bottom surfaces decreases. This occurs because higher defect densities lead to a higher phonon scattering rate, which

lowers the thermal conductivity. For all PCD samples measured, the Si-V peak only appeared on the bottom surface. The Si-V peak intensity is picked out from the PL background by curve fitting to eliminate the background noise. Similarly, as the intensity of the Si-V peak on the bottom surfaces increases, the thermal conductivity decreases (see Fig. 3-5), which is in good agreement with the molecular dynamic simulation work [134].

Fig. 3-4 Thermal conductivity versus the integrated intensity of the background luminescence from 560 nm to 900 nm.

Fig. 3-5 Thermal conductivity versus the intensity of the Si-V peak.

3.3.2 FTIR analysis

The FTIR absorption spectrum for a typical PCD sample, as well as a defect-free single crystalline diamond, is shown in Fig. 3-6. The spectra are normalized by scaling the sample thickness to 1 cm. As shown in Fig. 3-6(a), the intrinsic diamond absorption is observed in two-phonon (1332 cm^{-1} to 2665 cm^{-1}) and three-phonon (2665 cm^{-1} to 4000 cm^{-1}) regions. Beyond 4000 cm^{-1} , there is no detectable absorption. For perfect diamonds without any lattice distortion, no single phonon absorption is expected. In Fig. 3-6(b), although TO(L) and O(Γ) modes are observed in the single phonon region, the absorption is very low (less than 1 cm^{-1}). No nitrogen related absorption band is detectable in the single phonon region. Thus, our PCD samples are mostly Type IIa

diamonds [135]. The CH_x stretching band is observed in the region from 2760 cm^{-1} to 3030 cm^{-1} (see Fig. 3-6(c)), which is a superposition of several CH_x vibration modes [56].

Fig. 3-6 (a) The FTIR absorbance spectrum from 400 cm^{-1} to 5000 cm^{-1} for one PCD sample, (b) the FTIR single phonon absorption region, and (c) the FTIR CH_x absorption band.

The CH_x absorption α_{CH_x} is integrated from 2760 cm^{-1} to 3030 cm^{-1} . As shown in Fig. 3-7(a), for the bottom surface, the thermal conductivity decreases as α_{CH_x} increases. The data fits well with the model reported in Ref [130]. For the top surface, the dependence of thermal conductivity on α_{CH_x} is not as significant as that on the bottom surface (see Fig. 3-7(b)). One possible reason is that FTIR is a through-plane characterization. Thus, α_{CH_x} collected by FTIR does not directly reflect the CH_x concentration on the top or the bottom surface, but the CH_x concentration through the whole sample. From a reported study [136], the CH_x concentration shows a linear correlation with the concentration of the non-diamond carbon phase for CVD diamonds. Consequently, it is reasonable to use the surface intensity of the non-diamond carbon phase characterized by Raman to estimate the surface CH_x concentration.

Fig. 3-7 (a) Integrated intensity for CH_x absorption from 2760 cm^{-1} to 3030 cm^{-1} versus thermal conductivity on the bottom surface; and (b) integrated intensity for CH_x absorption from 2760 cm^{-1} to 3030 cm^{-1} versus thermal conductivity on the top surface.

Figure 3-8(a) shows the correlation between the through-plane CH_x absorption and estimated surface CH_x intensities. Linear correlations are observed for both the top and bottom surfaces. The slope for the bottom surface is much larger than that for top surface, which indicates that the concentration of CH_x on the bottom surface is much higher than that on the top surface. The standard fitting error for the slope of the top surface ($\pm 84\%$) is much higher than that of the bottom surface ($\pm 11\%$). This implies that the CH_x absorption collected by FTIR is not sensitive enough to reflect the CH_x concentration on the top surface. As shown Fig. 3-8(b), the thermal conductivity difference ΔK increases as α_{CH_x} increases. This demonstrates that hydrogen impurities affect the bottom surface more than they affect the top surface.

Fig. 3-8 (a) The correlation between through-plane CH_x absorption and estimated surface CH_x content and (b) thermal conductivity difference ΔK ($K_{\text{top}} - K_{\text{bottom}}$) versus CH_x absorption.

3.3.3 Ultraviolet-visible spectroscopy (UV-VIS) analysis

The PCD samples studied in this work are in a wide range of optical transmission (see Fig. 3-9). The UV-Vis spectra for the high quality SCD with no detectable defect is also shown in Fig. 3-9 as a reference. It almost overlaps the transmission limit. From the obtained UV-Vis spectra of PCDs, as the wavelength exceeds the fundamental cut-off at 220 nm, the optical transmission rises quickly in the UV region. Then it smoothly reaches a limit in the visible region.

Fig. 3-9 The UV-Vis transmission spectra for PCDs with the highest, medium, and lowest transmission at 800 nm. The transmission spectra for a high quality

single crystalline diamond and transmission limit are shown by dashed lines for reference.

Reported electron spin resonance (ESR) studies on MPCVD diamonds suggest that nitrogen is incorporated within the diamond lattice as single substitutional nitrogen atoms Ns^0 [137]. The concentration of Ns^0 absorption can be extracted at 270 nm absorption from UV-Vis spectra using the method described by Nistor *et al.* [29]. Figure 3-10(a) shows the correlations between the Ns^0 absorption coefficients α_{Ns^0} at 270 nm versus thermal conductivities on the top and bottom surfaces. The increase in the Ns^0 concentration leads to a decrease in thermal conductivity due to the presence of excessive phonon scattering. Unlike CH_x defects, the ΔK between the top and bottom surfaces presents no dependence on Ns^0 concentration. The reason could be that Ns^0 distributes evenly on the top and bottom surfaces because the nitrogen gas concentration is kept constant during the entire growth of PCDs along with other growth parameters. Thus, the impact of Ns^0 is not significant on the observed difference in the thermal conductivity between the top and bottom surfaces.

Fig. 3-10 (a) N_s^0 absorption coefficient $\alpha_{N_s^0}$ at 270 nm versus thermal conductivity, and (b) optical transmission (%) at 633 nm versus thermal conductivity.

As no obvious absorption features are observed in the visible region (see Fig. 3-9), it is more reasonable to use optical transmission in the visible region for thermal conductivity estimation, instead of using it in the UV region. Figure 3-10(b) shows a strong dependence of thermal conductivity on optical transmission at 633 nm. The optical transmission is normalized by scaling the sample thickness to 0.5 mm. The pictures of the PCD samples with the optical transmissions of 22.5%, 45.2% and 65.2% at 633 nm are also shown in Fig. 3-10(b) for reference. The correlation between thermal conductivity K and optical transmission T is fitted using [138]:

$$K = \frac{K_0}{1 + A \ln\left(\frac{T_r}{T}\right)} \quad (3-1)$$

where ‘A’ is a constant and K_0 is the thermal conductivity of pure and defect-free diamond. In this work, we used the measured thermal conductivity for a high quality SCD with no detectable defect as $K_0=2300$ W/mK. After fitting, $A_{top}=0.7775$ and $A_{bottom}=0.3476$ are obtained for the optical transmission at 633nm. As the optical transmission decreases, the thermal conductivity of the bottom surface drops more drastically than the thermal conductivity of the top surface, which is due to the presence of more defects (such as CH_x , Si-V and smaller grains) on the bottom surface. The trendlines of thermal conductivity on the top and bottom surface intersect at 2300 W/mK

when the optical transmission reaches the transmission limit of 70.75%, which is the value for the high quality SCD with no detectable defects.

Compared with the above mentioned defects (non-diamond carbon phase, Si-V, CH_x , or Ns^0), the R-squared value of thermal conductivity versus optical transmission is much closer to 1, as presented in Table 3-1. This result indicates a stronger dependence of thermal conductivity on optical transmission, because optical transmission not only gives information about defects densities but it also gives information about the lattice dislocation and grain boundaries, which influence thermal conductivity as well. Therefore it is reasonable to use optical transmission to obtain a more comprehensive estimation of the thermal conductivity for PCD diamonds.

Table 3-1 R-squared values for the correlations between thermal conductivities and different optical characterizations

Dependence of thermal conductivity on:	R-squared for top surface (W/mK)	R-squared for bottom surface (W/mK)
Optical transmission at 633 nm (T)		
	0.885	0.742
Non-diamond carbon phase		
	0.101	0.372

(I _{ND})		
PL background intensity		
(I _{PL})	0.513	0.448
Si-V intensity (I_{SiV})	-----	0.469
CH_x absorption (α_{CHx})	-----	0.346
Ns⁰ absorption (α_{Ns^0})	0.382	0.570

In fact, a strong dependence of thermal conductivity on optical transmission is observed at any wavelength in the visible region, not only at 633 nm. We also found that Eq. 3-1 fits well on any wavelength in the visible to near IR (450 nm to 800 nm) regions. A linear increase in the fitting value of ‘A’ is observed for both the top and bottom surfaces as the wavelength increases (see Fig. 3-11). This justifies the dependence on the optical absorption coefficient α towards its corresponding wavelength. The linear behavior is due to the almost linear change of the refractive index for PCDs from 450 nm to 800 nm. The fitting value of ‘A’ and the slope ($\Delta A / \Delta \lambda$) on the top surface are smaller than those on the bottom surface, because the top surface has lower defect densities than the bottom surface. For pure diamonds ($T \cong T_r$) with no detectable defects and a uniform thermal property throughout its thickness, the

thermal conductivity K reaches up to K_0 , and the fitting value of 'A' approaches zero.

Fig. 3-11 Fitting value of 'A' under wavelengths from 450 nm to 800 nm.

3.3.4 Grain size analysis

Due to the polycrystalline structure of PCDs, the properties of PCDs are dependent on their grain sizes. For all the PCDs observed in this study, the top surfaces always exhibit larger grain sizes than the bottom surfaces. Since defects tend to be concentrated at grain boundaries [139], the larger grain size at the top surface results in a lower defect density than the bottom surfaces, which

is in good agreement with the results described in Fig. 3-4. As a result, for a single PCD sample, the top surface always shows a higher thermal conductivity than the bottom surface. However, comparing multiple PCD samples with various grain sizes, no correlation is observed between thermal conductivity and grain size (see Fig. 3-12). As reported by Simon *et al.* [26], at room temperature, the phonon mean free path within diamond is less than 10 μm , which implies that the thermal conductivity reduction due to grain boundary scattering is not significant unless the grain size is comparable to or less than 10 μm . This gives a good explanation of the random distribution of thermal conductivity when grain sizes are from tens to hundreds. However, as shown in the inset of Fig. 3-12, even for the range of small grain size (from 2 μm to 18 μm), no clear dependence of thermal conductivity on grain size is observed. This is because the defect scattering difference caused by varying growth conditions is more significant compared with the grain size effect. After all, at room temperature, the rate of grain boundary scattering is much smaller than other types of phonon scattering rates, such as impurities [59]. Therefore, for PCDs with a grain size comparable or larger than the phonon mean free path within diamond, the influence of grain boundary scattering is no longer significant.

Fig. 3-12 Thermal conductivity versus grain size for the top and bottom surfaces. The inset is the zoom-in image for the grain size range from 2 μm to 18 μm .

3.4 Summary

In this chapter, the influence of optically active defects on thermal conductivities was studied systematically for polycrystalline diamonds. The thermal conductivities of both top and bottom surfaces were characterized using the 3ω technique. The defects of polycrystalline diamonds in the form of single substitutional nitrogen (Ns^0), C-H stretch bonds, neutral and charge nitrogen ($N-V^{0/-}$) vacancies as well as silicon vacancy (Si-V) were analyzed in detail concerning their impact on thermal conductivity. The thermal conductivity difference between the top and bottom surfaces of PCDs was investigated due to the above-mentioned defects.

It was found that the top surfaces of PCDs show lower defect densities and higher thermal conductivity than the bottom surfaces. For the top surfaces, Ns^0 is the main factor limiting the heat transport. The influence from the non-diamond carbon phase and the C-H stretch is not significant because of the low concentrations of the related defects. For the bottom surfaces, the non-diamond carbon phase, Si vacancy, C-H stretching bonds and Ns^0 defects all lead to an obvious decrease in thermal conductivity. A strong dependence of thermal conductivity on optical transmission in the visible region was observed. A simple fitting equation was established to estimate thermal conductivity using any wavelength in the visible region. This equation enables a fast and reasonable estimation of thermal conductivity by optical inspection.

Chapter 4: Freestanding Sensor-Based 3ω Technique

4.1 Introduction

In the 3ω technique, a metal heater is deposited on top of the sample surface to function as both a heater and thermometer (see Fig. 2-9). To ensure the continuum of the metal wire, the sample surface requires a high smoothness (less than 100 nm). For example, in Chapter 3, we apply the 3ω technique to characterize the thermal conductivities of PCDs on both the top and bottom surfaces. In the sample preparation for the 3ω thermal characterization, the PCDs are mechanically polished to achieve a surface roughness less than 10 nm.

However, this requirement for high surface smoothness in the sample preparation limits the adaptability of the 3ω technique in the measurement of samples with rough surfaces, such as CNTs. Figure 4-1 presents the SEM image of the gold wire pattern on CNT. It is not possible to form a continuous gold layer on the top of the CNT surface due to the high roughness of the surface (in micrometers).

Fig. 4-1 SEM image of the gold wire pattern on CNT.

To extend the 3ω technique to characterize the thermal properties of samples with rough surfaces, a novel design of the freestanding sensor-based 3ω technique is proposed. Figure 4-2 shows the schematic diagram using the freestanding sensor for thermal characterization. The freestanding sensor is a gold bridge encapsulated between a sensor substrate with a high surface smoothness (less than 100nm) and a thin electrical insulating layer (around 300nm). The gold bridge is connected to the 3ω system. During the thermal measurement, the freestanding sensor is pressed on the top of the sample surface with a controlled pressure. The gold wire is then sandwiched between the sensor substrate and the sample. By analyzing the temperature oscillation of

the gold wire heater as a function of frequency, the thermal property of the sample contacted with the freestanding sensor can be extracted.

Fig. 4-2 The schematic diagram of the freestanding sensor measurement.

As reported by Moon *et al.* [110], when two different materials are on opposite sides of the heater, the heat diffuses to both sides unequally. If the half width of the gold wire is much larger than the heat penetration path, the temperature rise of the heater is obtained as:

$$\Delta T = \frac{P/2b}{\sqrt{2\omega C_p k_g} + \sqrt{2\omega C_p k_s}} e^{-\pi i/4} \quad (4-1)$$

where the subscripts g and s stand for the freestanding sensor substrate (PMMA) and the sample, respectively; P is the heat generation rate per length for the metal heater; b is the half width of the metal heater; ω is the frequency of the AC current applied to the metal heater; C_p is the material heat capacity; and k is the material thermal conductivity.

For a line heater, if the boundary mismatch is neglected, the problem can be written as a combination of two separate heat diffusions. By defining $F(x) \equiv -\ln x + \eta$, $\eta = 0.922$ as a constant, Equation 4-1 can be further written as:

$$\Delta T = -\frac{P}{\pi(k_s + k_g)} F(q_s b) \times \left[\frac{1}{1 + \left[\frac{k_s}{k_s + k_g} \right] \left(\frac{F(q_s b)}{F(q_g b)} - 1 \right)} \right] \quad (4-2)$$

where k_s and k_g represent the thermal conductivity of the sample measured and that of the freestanding sensor substrate. b is the half width of metal wire, and q is the reciprocal of the thermal penetration depth, which is defined as:

$$q = \sqrt{\frac{i2\omega C_p}{k}} \quad (4-3)$$

Thus, if we know the thermal properties of the sensor substrate, we can further extract the thermal properties of the sample measured from the heater temperature oscillation using Eq. 4-2. Thus, developing a freestanding sensor based 3ω technique for thermal conductivity characterization is theoretically feasible.

However, the analytical solution provided in Eq. 4-2 has limitations. First, it ignores the thermal contact resistance between the sensor and the sample. For solid samples, the thermal contact resistance is in the order of 10^{-5} m²K/W, which is equal to the thermal resistance of 10 μ m SiO₂ [123]. A significant error will be induced if the thermal contact resistance is ignored, especially for the characterizations of samples with thermal resistances that are

comparable with the thermal contact resistance or less. Besides, Eq. 4-2 is only applicable for liquid or bulk materials, since it assumes there is a single kind of material on each side of the heater. Thus, the “thin film on substrate” structure that we are interested in in this research cannot be evaluated using Eq. 4-2. Yet, the thermal conductivity extraction from the thermal signal obtained by the freestanding sensor is certainly worth investigating.

In this chapter, a freestanding sensor-based 3ω technique is proposed. This modified 3ω technique enables the thermal characterization for samples with rough surfaces. To investigate the sensor response to thin film samples, a finite-element model is developed using COMSOL Multiphysics. By finite-element simulations, the temperature oscillation due to the Joule heating of the metal heater is calculated in the frequency domain. Based on these calculations, the understanding for the dependence of temperature rise on the thermal conductivity of thin film materials is developed. This freestanding sensor-based 3ω technique is further implemented experimentally. The determination of the cross-plane thermal conductivity of materials in thin film geometry is discussed in detail.

4.2 Freestanding sensor fabrication

The freestanding sensor is based on polymeric methyl methacrylate (PMMA). The surface roughness of PMMA is less than 50 nm, which ensures the continuous layer of a 200 nm thick metal bridge. The metal bridge is a gold line 8 mm long and 60 μm wide with four-wire electrical connects. Polymeric methyl methacrylate is a good heat insulator, which enables the majority of the heat generated to pass through the sample and increase the sensitivity of the sensor to the sample thermal properties. The Si_3N_4 interfacial layer enables the electrical insulation between the gold bridge and the CNT samples.

Figure 4-3 shows the fabrication process of the freestanding sensor. First, PMMA is sunk in deionized water and cleaned by ultrasonic bath for 15 mins to remove contaminants. By a lithography process with photoresist AZ6130, the metal bridge pattern is transferred to the PMMA surface. Then 10 nm Cr and 200 nm Au is deposited on the top of PMMA using E-beam deposition. Since acetone dissolves PMMA, a dilute alkali solution is applied instead for the lift-off process. The Si_3N_4 layer is further deposited on top of the PMMA by PECVD. After the Si_3N_4 protection layer deposition, the four contact pads of the metal bridge are connected to the 3ω system by silver paste bonding. Figure 4-4 contains a photo of the free-standing sensor.

Fig. 4-3 Fabrication process of the freestanding sensor.

Fig. 4-4 Photograph of the fabricated freestanding sensor (inset is the zoom-in view of the metal bridge).

4.3 Finite-element model

4.3.1 Theoretical basis

Since there is no analytical solution available for the “sensor/heater/thin film” structure, a numerical analysis based on a finite-element model is applied to investigate the sensor response to the thin film material. The partial differential equations of heat diffusion are solved in the frequency domain using COMSOL Multiphysics. The following derivation is based on a general thin film/substrate structure. For bulk material, it can be treated as thin film/substrate geometry with a thin film thickness of zero.

As the length of the metal wire is much greater than the thermal penetration depth, the temperature is assumed to be uniform along the length of the wire. Thus, a two-dimensional (2D) heat diffusion model in a plane perpendicular to the axis of metal wire (with a half width of b) is valid. Besides, as the gold wire is located in the middle of the sample surface, with the help of a symmetry plane Γ_1 (see Fig. 4-5); the modeling can be restricted to half of the whole structure.

Fig. 4-5 A schematic view (not to scale) of the 2D thermal model with a symmetry plane Γ_1 .

In Fig. 4-5, the gold wire is the heat source and is sandwiched between PMMA and thin film/substrate structure. An alternating current at a frequency of ω is applied to the gold wire:

$$I(\omega) = I_0 \cos(\omega t) \quad (4-4)$$

The power P generated from the gold wire due to Joule heating can be written as:

$$P = RI^2(\omega) = \frac{1}{2}RI_0^2 + \frac{1}{2}RI_0^2 \cos(2\omega t) \quad (4-5)$$

where R is the resistance of the gold wire.

The governing heat equations for the heater, the freestanding sensor (PMMA), the thin film and the substrate are:

$$\frac{\partial}{\partial x} \left(K_H \frac{\partial T_H}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_H \frac{\partial T_H}{\partial y} \right) + P = \rho C \frac{\partial T_H}{\partial t} \quad (4-6)$$

$$\frac{\partial}{\partial x} \left(K_{PMMA} \frac{\partial T_{PMMA}}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{PMMA} \frac{\partial T_{PMMA}}{\partial y} \right) = \rho C \frac{\partial T_{PMMA}}{\partial t} \quad (4-7)$$

$$\frac{\partial}{\partial x} \left(K_{film} \frac{\partial T_{film}}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{film} \frac{\partial T_{film}}{\partial y} \right) = \rho C \frac{\partial T_{film}}{\partial t} \quad (4-8)$$

$$\frac{\partial}{\partial x} \left(K_{sub} \frac{\partial T_{sub}}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{sub} \frac{\partial T_{sub}}{\partial y} \right) = \rho C \frac{\partial T_{sub}}{\partial t} \quad (4-9)$$

where P is the heat generating rate of gold wire, K is the thermal conductivity, ρ is the density, and C is the heat capacity. The heat capacity of PMMA has been measured to be 1260 J/kg · K. Due to the volume influence, the thermal capacitance of PMMA sensor substrate is much larger than that of the sample ($\sim 10^4$ times). Therefore, the sensor is not sensitive to the heat capacity and density of the sample.

By assuming that the boundary surfaces (Γ_3 and Γ_4) are under adiabatic conditions, so that:

$$-\vec{n} \cdot \vec{q} = 0 \quad (4-10)$$

where

$$\vec{q} = -K \Delta T \quad (4-11)$$

as the substrate is placed on a copper plate during experiments, the temperature of the bottom surface of substrate (Γ_2) is fixed to ambient temperature T_0 in the thermal model:

$$T = T_0 \quad (4-12)$$

Because of the air gap between the contacting surfaces of the thin film and the sensor, a thermal contact resistance R_c exists and causes a heat flux across the contacting surfaces as:

$$-\vec{n} \cdot \vec{q} = -\frac{1}{R_c} (T_{sensor} - T_{film}) \quad (4-13)$$

Besides, the thermal resistance of the protecting layer Si_3N_4 for the gold wire ($\sim 10^{-4} \text{ cm}^2\text{K/W}$ [140]) can also be treated as a part of the contact resistance. Thus, the 300 nm Si_3N_4 film does not need to be drawn separately in the model geometry. The oscillating temperature $\Delta T_{2\omega}$ of the heater is obtained by calculating the mean oscillating temperature averaged over the heater width.

For the finite-element analysis, we fix the dimensions of the sample and the sensor, which are known in the experiment, and we investigate the sensor response to the parameters unknown, such as the thermal properties of the thin film. Based on study of the sensor's responses to different parameters, we further develop a way to extract the thermal conductivity of the thin film from the freestanding sensor signal. Table 4-1 lists the fixed dimensions of the thermal model used in Section 4.2.

Table 4-1 Sample dimensions used in simulations.

Geometry	Width	Height
PMMA	5 mm	3 mm

Gold wire	60 μm	200 nm
Thin film	5 mm	5 μm
Substrate	5 mm	350 μm

4.3.2 Sensitivity optimization

Theoretically, there are two methods to improve the sensor sensitivity to the thin film thermal conductivity. One is to apply a high heat source power density to heat up the thin film sample: resulting in a strong thermal signal from the thin film. The other is to apply a sensor substrate with a low thermal conductivity, which can prevent the heat from dissipating through the sensor substrate and ensure the majority of the heat transfer through the thin film sample.

To compare the sensor sensitivity to the thin film thermal conductivity, we compare the temperature oscillation signal (ΔT) difference between the thin films with thermal conductivities of 1 W/mK and 5 W/mK. If the ΔT difference is higher, it is easier to distinguish the thermal signals between the thin film with a thermal conductivity of 1 W/mK and the thin film with a thermal conductivity of 5 W/mK. Thus, the sensor sensitivity to the thin film thermal conductivity is higher. The detailed simulation results for these two methods are listed as:

(a) High heat source power density

Figure 4-6 shows the simulation results of the sensor sensitivity to the thermal conductivity of thin film under different heat source power densities per length (2 W/m, 6 W/m, and 10 W/m). The power densities are chosen based on the applicable power density range that our 3ω system could support. During the simulation, the contact resistance between the sensor and thin film is set as a constant of $5 \times 10^{-5} \text{ m}^2\text{K/W}$; the thermal resistance of the substrate is set as a constant of $1.75 \times 10^{-4} \text{ m}^2\text{K/W}$; and the sensor substrate thermal conductivity is set as a constant of 0.19 W/mK.

Regarding the high frequency region (1 Hz to 4000 Hz), the ΔT value increases as the frequency value decreases. At the low frequency region (lower than 1 Hz), the ΔT curve is saturated, and turns out to be independent of the frequency change. This is because at low frequencies, the thermal wave penetration length is much longer than the sample thickness (it can be calculated from Eq. 4-3), and the detected thermal signal is mainly from the large copper plate on which the sample is placed. Due to the superior thermal conductivity of the copper plate [141], the temperature of the large copper plate is maintained at room temperature. As a result, the ΔT value will no longer increase with the decreasing frequency value.

As presented in Fig. 4-6, as the heat source power density increases from 2 W/m to 10 W/m, the ΔT difference between the thin film with a

thermal conductivity of 1 W/mK and the thin film with a thermal conductivity of 5 W/mK increases from 0.12 K to 0.59 K. Thus, a higher heat source power density leads to a larger ΔT difference, resulting in a higher sensitivity to the thermal conductivity of thin film. This is because under a higher heat source power density, more heat dissipates through the thin film material and results in a stronger thermal signal.

Fig. 4-6 Simulation results of the sensor sensitivity to the thermal conductivity of thin film under different heat source power densities per length (2 W/m, 6 W/m, and 10 W/m).

(b) Low sensor thermal conductivity

Figure 4-7 shows the simulation results of the sensor sensitivity to the thermal conductivity of thin film under different sensor substrate thermal conductivities (0.19 W/mK, 0.8 W/mK, and 2 W/mK). The substrate thermal conductivity values are chosen based on the thermal properties of currently commercial available sensor substrates. During the simulation, the contact resistance is set as a constant of $5 \times 10^{-5} \text{ m}^2\text{K/W}$; the thermal resistance of substrate is set as a constant of $1.75 \times 10^{-4} \text{ m}^2\text{K/W}$; and the power density per length is set as a constant of 10 W/m.

As the sensor substrate thermal conductivity decreases, the ΔT difference increases dramatically, and the sensitivity of the freestanding sensor to the thin film thermal conductivity increases. This result occurs because the sensor substrate with a low thermal conductivity blocks the majority of the heat generated from the metal heater, and enhances the sensitivity as a result. Based on this reason, PMMA is chosen as the sensor substrate, and its thermal conductivity is measured to be as low as 0.19 W/mK.

Fig. 4-7 Simulation results of the sensor sensitivity to the thermal conductivity of thin film under different sensor substrate thermal conductivities (0.19 W/mK, 0.8 W/mK, and 2 W/mK).

4.3.3 Determination of thin film thermal properties

As shown in Fig. 4-5, after the heat is generated from the gold wire, it dissipates into two ways: (1) through the sensor substrate or (2) through the contact resistance between the sensor and thin film and then into the thin film and sample substrate. Thus the temperature oscillation signal is determined by the synthetic effect of the thermal properties of the sensor substrate, contact resistance, the thin film, and the sample substrate together. By now, we only know the thermal conductivity of the sensor substrate (PMMA) as 0.19 W/mK.

The other three parameters (thin film thermal conductivity, contact resistance, and substrate thermal resistance) are all unknown. To check whether it is possible to extract the thin film thermal conductivity from this combining signal, the sensor response to these three unknown parameters should be investigated. During the simulation study, we control the metal heater power density as 10 W/m and the PMMA thermal conductivity as 0.19 W/mK, respectively.

(a) Thin film thermal conductivity

Figure 4-8 presents the simulation results of the sensor heater temperature oscillation ΔT as a function of frequency f under different thin film thermal conductivities (1 W/mK, 5 W/mK, and 10 W/mK). The contact resistance is set as a constant value of 5×10^{-5} m²K/W; and the thermal resistance of the substrate is set as a constant value of 1.75×10^{-4} m²K/W. Three distinct regions are observed in the behavior of temperature oscillations: an overlapped region ($f > 100$ Hz), a linear region ($100 \text{ Hz} > f > 1$ Hz) and a planar region ($1 \text{ Hz} > f$).

In the high frequency range ($f > 100$ Hz), the temperature oscillation curves for three different thermal conductivities are overlapped. Due to the short thermal wave penetration depth into the sample in the high frequency range, the temperature oscillation signal is only sensitive to the sensor substrate thermal conductivity and the contact resistance. Thus, the change in the thin

film thermal conductivity cannot lead to a difference in the temperature oscillation curves in the high frequency region, resulting in the overlapping. As the frequency decreases to 100 Hz, the temperature oscillation curves start to separate from each other and enter the “linear region”. The difference in the slope of the “linear region” is due to the difference in the thin film thermal conductivities. At around 1Hz, all these three temperature oscillation curves start to turn into a “planar region” where ΔT is no longer dependent on the frequency change due to the fixed temperature of the large copper plate. According to the discussion above, the thin film thermal conductivity can be extracted due to the slope in the “linear region”.

Fig. 4-8 Simulation results of the heater temperature oscillation ΔT as a function of frequency f under different thin film thermal conductivities (1 W/mK, 5 W/mK, and 10 W/mK).

(b) Substrate thermal resistance

Figure 4-9 shows the simulation results of the sensor heater temperature oscillation ΔT as a function of frequency f under different substrate thermal resistances ($3.5 \times 10^{-4} \text{ m}^2\text{K/W}$, $1.75 \times 10^{-4} \text{ m}^2\text{K/W}$, and $0.7 \times 10^{-4} \text{ m}^2\text{K/W}$). The

contact resistance is set as a constant value of $5 \times 10^{-5} \text{ m}^2\text{K/W}$; while the thermal conductivity of the thin film is set as a constant value of 1 W/mK .

Similar to the simulation results of the samples with different thin film thermal conductivities, there is an overlapped region in the high frequency region ($f > 100 \text{ Hz}$) for samples with different sample substrate thermal resistances, which is due to the controlled thermal properties of the sensor substrate and the contact resistance. As the frequency decreases to 100 Hz , the temperature oscillation curves turn away from each other and enter the “linear region”. The slope difference in the “linear region” is due to the differences in the sample substrate thermal resistances. As the frequency continues to decrease, the temperature oscillation curves start to turn into the “planar region”.

However, one feature can distinguish the influence of sample substrate thermal resistances from the influence of thin film thermal conductivities in the temperature oscillation curves. Unlike the samples with different thin film thermal conductivities, the samples with different sample substrate thermal resistances present a difference in the frequency when the temperature oscillation curve turns from the “linear region” into the “planar region” (called the “turning point”). The lower the substrate thermal resistance, the higher the frequency of the turning point. Thus, the substrate thermal resistance can be extracted from the frequency of the turning point.

Fig. 4-9 Simulation results of the heater temperature oscillation ΔT as a function of frequency f under different substrate thermal resistances ($3.5 \times 10^{-4} \text{ m}^2\text{K/W}$, $1.75 \times 10^{-4} \text{ m}^2\text{K/W}$, and $0.7 \times 10^{-4} \text{ m}^2\text{K/W}$).

(c) Contact resistance

Figure 4-10 shows the sensor heater temperature oscillation ΔT as a function of frequency f under different contact resistances ($7 \times 10^{-5} \text{ m}^2\text{K/W}$, $5 \times 10^{-5} \text{ m}^2\text{K/W}$, and $3 \times 10^{-5} \text{ m}^2\text{K/W}$). The thermal conductivity of the thin film is set as a constant value of 1 W/mK ; while the thermal resistance of the substrate is set as a constant value of $1.74 \times 10^{-4} \text{ m}^2\text{K/W}$.

As mentioned above, the temperature oscillation in the high frequency range is sensitive to the thermal conductivity of the sensor substrate and the contact resistance. Since the thermal conductivity of the sensor substrate is set

as a constant of 0.19 W/mK , the difference of the slope in the high frequency region is only attributed to the contact resistance difference. Thus, the contact resistance can be extracted from the slope in the high frequency region ($f > 100 \text{ Hz}$). Besides, the frequencies of the turning points where the temperature oscillation curves turn from the “linear region” into the “planar region”, are the same under three different contact resistances, which verifies the statement that the turning point frequency is only attributed to the substrate thermal resistance.

Fig. 4-10 Simulation results of the heater temperature oscillation ΔT as a function of frequency f under different contact resistances ($7 \times 10^{-5} \text{ m}^2\text{K/W}$, $5 \times 10^{-5} \text{ m}^2\text{K/W}$, and $3 \times 10^{-5} \text{ m}^2\text{K/W}$).

To summarize, the three thermal parameters (thin film thermal conductivity, contact resistance, and sample substrate thermal resistance) are all unknown during experiments and need to be extracted from the temperature oscillation curves. The contact resistance can be extracted from the slope at the high frequency region, and the sample substrate thermal resistance can be extracted from the turning point frequency. The slope of the temperature oscillation curve in the “linear region” is determined by the synthetic effect of the thin film thermal conductivity and the sample substrate thermal resistance. Thus, once the sample substrate thermal resistance is obtained due to the turning point frequency, the thermal conductivity of the thin film can be further extracted from the curve slope in the “linear region”. Therefore, we extract the thermal conductivity of the thin film material using the freestanding sensor-based 3ω technique.

Since the thermal properties of the thin film material may be anisotropic, we further study the sensitivity of our freestanding sensor to the in-plane and cross-plane thermal conductivity of thin film material, as shown in Fig. 4-11. According to the simulation results, the freestanding sensor is able to distinguish thin films with different cross-plane thermal conductivities (see Fig. 4-11(a)), while we cannot distinguish thin films with different in-plane thermal conductivities (see Fig. 4-11(b)). This is because the width of the heater ($60\text{ }\mu\text{m}$) is much larger than the thin film thickness. Thus, the freestanding sensor-based

3ω technique is only sensitive to the cross-plane thermal conductivity of thin film material [142].

Fig. 4-11 (a) Simulation results of the heater temperature oscillation ΔT as a function of frequency f under different cross plane thermal conductivities (the

in-plane thermal conductivity is fixed as 1 W/mK); and (b) simulation results of the heater temperature oscillation ΔT as a function of frequency f under different in-plane thermal conductivities (the cross plane thermal conductivity is fixed as 1 W/mK).

The sensor sensitivity dependence on frequency is due to the thermal penetration depth of the metal heater (see Eq. 2-11). Under the “high frequency region” ($f > 100$ Hz), the thermal penetration depth of the metal heater can only reach the contact region between the sample and the sensor, thus the temperature oscillation curve of the metal heater is only sensitive to the contact resistance. As the frequency decreases, the thermal penetration depth of the metal heater increases. The temperature oscillation curve of the metal heater will be further sensitive to the thin film thermal conductivity and the sample substrate thermal resistance as a result.

4.4 System calibration and uncertainty analysis

Figure 4-12 shows the schematic view of the freestanding sensor-based 3ω technique. The freestanding sensor is attached to a stage that is adjustable in the X, Y, and Z directions. The heater on the freestanding sensor is further connected to the 3ω system. The temperature coefficient of resistance (TCR) of the metal wire is measured as 0.00199 K^{-1} .

Fig. 4-12 The schematic view of the freestanding sensor-based 3ω technique.

This freestanding sensor-based 3ω technique has been calibrated using both thin film materials with known thermal conductivities. These fitting results are compared with the thermal conductivity result measured using a

conventional 3ω technique, which is depositing metal wire directly on top of the sample surface. Figure 4-13 shows the temperature oscillation profiles of different thin films measured using this technique. The thermal conductivity is obtained by numerically solving Eq. 4-6 to Eq. 4-13 due to the 2D thermal model in Section 4.3.1 by COMSOL Multiphysics. As shown in Fig. 4-13, the experimental data match well with the fitting curves.

Fig. 4-13 Temperature oscillation as a function of frequency measured by freestanding sensor.

Figure 4-14 shows the temperature oscillation curves measured using a conventional 3ω differential method. The thermal conductivities of the thin film can be obtained based on Eq. 2-14. Table 4-2 compares the fitting results using these two methods. The thermal conductivity results characterized using the freestanding sensor-based 3ω technique are in good agreement with the results obtained by the conventional 3ω technique, and are consistent with the results reported in related studies [47, 123].

Fig. 4-14 Temperature oscillation as a function of frequency measured by the freestanding sensor.

Table 4-2 Thermal conductivity results characterized using the freestanding sensor-based 3ω technique and a conventional 3ω differential method.

Calibrated thin films	Freestanding sensor-based 3ω technique	Conventional 3ω technique
Amorphous carbon	0.25	0.27
SiO ₂	1.35	1.44
Nanocrystalline graphite	2.29	2.39

The uncertainty of the thermal conductivity measurement is mainly related to the uncertainty in the measurement of the three harmonic voltage $U_{3\omega}$ (0.09%), the power density per length P applied to the gold wire (4.1%), the temperature coefficient of resistance TCR (1.5%), and the thermal conductivity of the sensor substrate (2%). After considering all the related uncertainties, the total uncertainty for the thermal conductivity measurement is calculated to be 7.4% by Eq. 4-14 based on the finite-element model [120].

$$\frac{\delta K}{K} = \sqrt{\left[\frac{\partial f(K)}{\partial U_{3\omega}} \delta U_{3\omega}\right]^2 + \left[\frac{\partial f(K)}{\partial P} \delta P\right]^2 + \left[\frac{\partial f(K)}{\partial K_{\text{sub}}} \delta K_{\text{sub}}\right]^2 + \left[\frac{\partial f(K)}{\partial TCR} \delta TCR\right]^2} \quad (4-14)$$

4.5 Summary

In this chapter, a novel design of the freestanding sensor-based 3ω technique was proposed to characterize the cross-plane thermal conductivity of the samples in “thin film on substrate” geometries. This technique was analyzed both theoretically and experimentally. By applying the sensor to detect the thermal signal on sample surfaces, it enables the thermal characterization of samples with rough surfaces, and extends the adaptability of a conventional 3ω technique.

The freestanding sensor is a metal bridge encapsulated between a PMMA sensor substrate and a Si_3N_4 insulating layer. The sensitivity of the freestanding sensor is dependent on the heater power density per length and the thermal conductivity of the sensor substrate. Higher power density and the lower thermal conductivity of the sensor substrate lead to a higher sensor sensitivity to the thermal conductivity of thin film. The determination of the sample thermal properties was conducted by numerical fitting of 2D heat diffusion equations. The total uncertainty was calculated to be 7.4%.

This chapter provides a theoretical support for Chapter 5, where the freestanding sensor is applied to characterize the cross-plane thermal conductivity of CNT-based thermal interface material.

Chapter 5: Cross-Plane Thermal Conductivity of 3D CNT Network

5.1 Introduction

The scaling down of device sizes and the increasing need for power dissipation make heat transport and removal a major technological impediment to the future development of electronic applications. As the device size decreases, the power density increases exponentially: leading to a drastic temperature increase. This huge temperature increase will significantly degrade the device performance and shorten the device lifetime. Among the state-of-the-art studies reported on the thermal management of devices, the development of thermal interface material (TIM) between the heat source and heat sink becomes a hot topic due to its significant role and current bottleneck in heat removal. Thermal interface materials can dramatically decrease the thermal resistance between two contacting surfaces by forming an effective heat conducting path between the heat source and the heat sink [143]. However, conventional TIMs, such as thermal greases or phase change materials, show low thermal conductivities in the range of 0.4 to 5 W/mK [60], which fail to satisfy the requirement for modern high power density devices [33].

To improve the thermal performance of TIMs, carbon nanotubes (CNTs) have been proposed be a promising candidate for TIM due to their high intrinsic

thermal conductivity [16, 144]. Attributed to its unique atomic structure, the thermal conductivities for individual CNT can reach up to 3500 W/mK [36]. Numerous studies have been reported on the development of CNT-based TIMs, specifically on CNT/polymer composite [39] and CNT array [33]. Among the reported studies on CNT TIMs, VACNT array stands out for its advantage in thermal conductivity [33]. Besides, VACNT possess high mechanical compliance, which is beneficial in solving the mismatches in the coefficient of thermal expansion (CTE) of two contacting surfaces [41].

However, one of main obstacles in VACNT TIMs practical applications is the poor heat transport between adjacent CNTs. The air gap between adjacent CNTs dramatically increases the thermal resistance of VACNT TIM, which is undesirable for effective thermal dissipation. To resolve the inter-CNT gap issues, a novel 3D CNT network structure is proposed. Randomly oriented secondary CNTs are grown from the sidewall of the primary vertically aligned CNT array: filling the air gap within CNT array and bridging adjacent CNTs together. These secondary CNTs can be postulated to improve the thermal conductivity of VACNTs by forming a thermal conductive pathway between them.

To measure the thermal properties of the novel 3D CNT network, the freestanding sensor-based 3ω technique is applied for the thermal characterization, as proposed in Chapter 4. A similar method has been reported

by Hu *et al.* [145] to measure the thermal conductivity of VACNT on silicon. Hu *et al.* apply one-dimensional (1D) heat conduction approximation and assume that the contact resistance between CNT and glass only contributes a fixed offset to the temperature oscillation as a function of frequency. However, solid theory support about when the 1D heat conduction approximation is valid has not been provided. At the same time, the assumption that the contact resistance only contributes a fixed offset is also questionable. To increase the accuracy in the extraction of CNT film thermal conductivity, a fully numerical solution of the 2D heat diffusion equations is developed to replace the reported approximate analytical solution in this work.

5.2 Experimental details

5.2.1 Growth of a 3D CNT network

1) Growth of the primary CNT array

First, a SiO₂ thin layer with a thickness of 380 nm is thermally grown on a 6-inch Si wafer. Then, 20 nm Ni is deposited on the top using e-beam evaporation as catalyst for CNT growth. The wafer is diced further to 1 cm×1 cm substrates. The primary CNT array is grown using an Aixtron Blackmagic PECVD system. In a typical PECVD process, the chamber pressure is kept as 5 mbar. A RF electric field is applied and biased at 700 V in the chamber with a power of 90 W. The temperature is ramped up and kept at 625°C with 250 sccm NH₃ for pre-growth annealing. In this study, the pre-growth annealing time period was varied from 5 mins, to 10 mins, 20 mins and 30 mins. After pre-growth annealing, the CNT growth is then conducted at 750°C with 250 sccm NH₃ and 50 sccm C₂H₂ for 30 mins.

2) Growth of secondary CNTs

The growth process of secondary CNTs is shown in Fig. 5-1. The catalysts supported on the primary CNTs are prepared by impregnating the CNT array with 0.01 mol/L Ni(NO₃)₂·6H₂O in acetone at room temperature. The secondary CNT is synthesized further by a thermal chemical vapor deposition (TCVD) system with a quartz furnace and an ethanol bubbler. The

furnace is heated up from room temperature to 700°C with a temperature increment of 15°C per minute under 100 sccm Ar gas flow. Once the chamber temperature reached 700°C, 50 sccm H₂ is introduced into the furnace to transform the precursor into Ni particles, as described in Eq. 5-1 and Eq. 5-2:

The Ni particles attached on the sidewall of the primary CNT array act as catalyst particles for secondary CNT growth. By switching the gas flow through the ethanol bubbler, ethanol is added to the gas flow, providing a carbon source for the secondary CNT growth. The growth is carried out at 700°C for 10 mins, followed by the system cooling down under 200 sccm Ar gas flow to room temperature.

Fig. 5-1 The growth process for the secondary CNTs: (a) the primary CNT array grown by PECVD; (b) the Ni catalyst attached on the sidewall of the primary CNT array; and (c) the formation of the secondary CNTs.

5.2.2 Thermal characterization using the freestanding sensor-based 3ω technique

Thermal characterization is performed using a self-developed freestanding sensor-based 3ω technique at room temperature. This technique is only sensitive to the cross-plane thermal conductivity of thin film material, as demonstrated in Chapter 4. The schematic diagram of the freestanding sensor measurement is shown in Fig. 5-2. The freestanding sensor is a metal bridge encapsulated between a PMMA substrate and a Si_3N_4 protecting layer. The gold bridge is further connected to a 3ω system. The electrical circuit of the freestanding sensor-based 3ω system is shown in Fig. 4-12.

Fig. 5-2 The schematic diagram of the CNT thermal characterization using the freestanding sensor-based 3ω method.

To extract the sample's thermal properties and contact resistance from the sensor temperature rise signal detected by the freestanding sensor, a 2D thermal model is developed using COMSOL Multiphysics (see Fig. 4-5). The governing heat diffusion equations and the boundary conditions for the freestanding sensor based- 3ω technique have been described extensively in Section 4.3.1. During the experiments, the root mean square (RMS) power per length applied to the gold wire is around 0.1 W/cm, causing a maximum temperature increase of 23 K in the gold wire, and causing less than 0.3 K on the boundary surfaces of the sample and the sensor (Γ_3 and Γ_4 in Fig. 4-5). The heat loss from natural convection ($\sim 1.9 \times 10^{-4}$ W/cm) and radiation (9×10^{-5} W/cm) on the boundary surfaces (Γ_3 and Γ_4 in Fig. 4-5) are three orders of

magnitude lower than the heat source. Thus, it is valid to assume that the boundary surfaces (Γ_3 and Γ_4 in Fig. 4-5) are under the adiabatic condition. The in-plane thermal conductivity of the CNT film and the contact resistance between the sensor and the CNT film are varied iteratively until the simulation matches the experimental data based on the least mean-square fitting using the COMSOL optimization solver.

The uncertainty of the thermal conductivity measurement of CNT films is mainly related to the uncertainty in the measurement of the three harmonic voltage $U_{3\omega}$ (0.09%), the thickness t of CNT films (9.1%), the power density per length P applied to gold wire (4.1%), the temperature coefficient of resistance TCR (1.5%), the sensor substrate thermal conductivity (2.0%). After considering all the related uncertainties, the total uncertainty for the thermal conductivity measurement is calculated to be 12.1% by Eq. 5-3 based on the finite-element model [120].

$$\frac{\delta K_{CNT}}{K_{CNT}} = \sqrt{\left[\frac{\partial f(K_{CNT})}{\partial U_{3\omega}} \delta U_{3\omega}\right]^2 + \left[\frac{\partial f(K_{CNT})}{\partial P} \delta P\right]^2 + \left[\frac{\partial f(K_{CNT})}{\partial t} \delta t\right]^2 + \left[\frac{\partial f(K_{CNT})}{\partial TCR} \delta TCR\right]^2} \quad (5-3)$$

5.2.3 Effect of loading pressure

As presented in Fig. 5-2, external pressure is applied to the freestanding sensor to enable good contact between the sensor and the sample surface. Since the pressure will reduce the air gap between the sensor and the sample surface, the thermal resistance measured using the freestanding sensor varies due to the pressure applied. Figure 5-3 shows the relationship between the thermal resistance and the loading pressure for the calibration sample. The pressure is measured using a FSR 402 force sensitive detector which is attached to the bottom surface of the sample substrate. As shown in Fig. 5-3, as the pressure increases, the thermal resistance decreases due to the improved contact between the sensor and the sample surface.

However, when the contact pressure increases to a certain range (127 kPa to 165 kPa), the thermal resistance stops decreasing and turns to be independent on the increasing value of pressure. Therefore, it can be inferred that the thermal signal measured by the freestanding sensor is independent on the loading pressure in this pressure range. Based on the above analysis, the measurement is performed under the pressure range of 127 kPa to 165 kPa to minimize the influence from the loading pressure. The SEM images of a typical CNT sample before pressing and after pressing are shown in Fig. 5-4 (at 165 kPa). From the SEM images, it can be observed that no mechanical damage has been induced to the CNT sample under this pressure range. As the geometrical

shape of CNTs does not show significant difference upon mechanical pressing, it can be presumed that the thermal properties and the geometry of CNT samples are supposed to remain the same [145].

Fig. 5-3 Evaluation of measured thermal resistance and loading pressure for the freestanding sensor.

Fig. 5-4 SEM images of a CNT sample before pressing (a) and after pressing (b) at the pressure of 165 kPa.

5.3 Results and discussion

5.3.1 Material characterization analysis

Figures 5-5(a) and (b) present the SEM images of the top view and cross-sectional view for the primary CNT array. As shown in Fig. 5-5(b), the primary CNT array grown by the PECVD technique exhibits a higher degree of vertical alignment, similar to the PECVD-grown CNTs as reported by Abdi *et al.* [146]. The air gaps between the CNTs are observable, which is also expected for the PECVD-grown CNTs [146]. To fill the inter-CNT gaps, secondary CNTs can be grown to establish physical connections between primary CNTs: forming a 3D CNT network comprising of primary and secondary CNTs. Figures 5-5(c) and (d) present the SEM images for the top view and the cross-sectional view for the 3D CNT network. As observed in Fig. 5-5(d), secondary CNTs are randomly oriented and bond the primary CNT together: filling up the gap within the CNT array. The secondary CNTs form a mat covering the CNT array and thus enable physical connections between primary CNTs.

Fig. 5-5 (a) SEM image of the top view of the primary CNT array, (b) SEM image of the cross-sectional view of the primary CNT array, (c) SEM images of the top view of the 3D CNT network, and (d) SEM images of the cross-sectional view of the 3D CNT network.

To investigate the morphological properties of the 3D CNT network further, we perform TEM imaging on the primary CNT array and 3D CNT network, as shown in Fig. 5-6. According to Fig. 5-6(a), the diameter of the primary CNT is around 150 nm and the diameter of the secondary CNT is

around 20 nm. From the magnified TEM image, both the primary and secondary CNTs show a multi-walled structure, as presented in Fig. 5-6(b). To investigate the epitaxy of the walls in both primary and secondary CNTs further, the zoom-in image of the red rectangle region in Fig. 5-6(b) is further shown in Fig. 5-6(c). As demonstrated in Fig. 5-6(c), the spacing between each wall is 0.34 nm for both primary and secondary CNTs, which is in agreement with the wall spacing in MWCNTs [147]. From the interface between the primary and the secondary CNT shown in Fig. 5-6(c), it can be observed that the growth epitaxy of CNT walls in secondary CNTs shows a smooth continuation from the primary CNT walls. At the primary-secondary CNT interface, the wall structure of the secondary CNT is embedded into the wall pattern of the primary CNT. The smooth continuation of CNT walls on both primary and secondary CNTs provides direct proof that the secondary CNT is grown directly from the sidewall of the primary CNT. This justifies the suggested growth mechanism where secondary CNTs are grown directly from the Ni catalytic particles on CNT walls, as discussed in Section 5.2.1.

Fig. 5-6 (a) The TEM image of the 3D CNT network, (b) the HRTEM image of the rectangular region in (a), and (c) the HRTEM image of the rectangular region in (b).

Figure 5-7 shows the relationship between primary CNT density and the pre-growth annealing time. The densities of the primary CNTs are estimated by counting the number of CNTs per area in the SEM images. The density values under different pre-growth annealing times range from $5 \times 10^8/\text{cm}^2$ to

$9 \times 10^8/\text{cm}^2$, which is in agreement with the range typically reported for CNT growth by the PECVD mode [148]. There is no obvious influence of annealing time on CNT diameter, which has reported to be determined by the thickness of the Ni catalyst film [114]. The filling factor of the CNT array is estimated further to be from 6.3% to 9.3% by treating CNT as a cylinder with an average diameter measured from SEM images. According to Fig. 5-7, as the pre-growth annealing time increases, the array density decreases, and the filling factor of CNT decreases, which is the result of the etching effect of NH_3 plasma on the Ni catalyst [149]. Therefore, by varying the pre-growth annealing time, primary CNT arrays with different array densities (or filling factors) are obtained.

Fig. 5-7 Array density (filling factor) versus pre-growth annealing time.

Figure 5-8 presents the Raman spectra acquired at 523 nm excitation and collected from CNT arrays before and after secondary CNT growth. G band is observed around 1580 cm^{-1} , which is assigned to the in-plane vibration of the C-C bond for sp^2 carbon material [150]. D band is observed around 1350 cm^{-1} , the intensity of which is proportional to the amount of disorder in the graphene structure [151]. Under different pre-annealing times, the Raman spectra of CNTs overlap with each other. There is a red-shift of the D peak after the growth of secondary CNTs due to the presence of smaller diameter secondary CNTs [152]. The pre-annealing time shows little influence on the I_D/I_G ratio, which means the structure quality of the CNTs is not affected by the CNT array density. At the same time, the higher I_D/I_G ratio of the 3D CNT network than pristine primary CNTs shows that the presence of secondary CNTs induces defects in the primary CNT array structure.

Fig. 5-8 Normalized Raman spectra for primary CNT array and 3D CNT network under different pre-annealing times of primary CNT array.

5.3.2 Thermal conductivity characterization

Figure 5-9 shows the temperature rise of the freestanding sensor as a function of the frequency for primary CNT arrays and 3D CNT networks under different array densities. The solid points are measured data and the dotted lines are fitting curves by the finite-element model as shown in Fig. 4-5. The geometry parameters and the thermal property parameters used in the finite-element model are listed in Tables 5-1 and 5-2. The experimental data

match well with the fitting curves as shown in Fig. 5-9. The fitting results are listed in Table 5-3. The contact resistances are fitted out to be from 0.67 to 0.78 $\text{cm}^2\text{K/W}$, which are in the same order of magnitude as reported by Hu *et al.* [145].

Fig. 5-9 The temperature rise of the freestanding sensor as a function of the frequency for primary CNT arrays and 3D CNT networks under different array densities.

Table 5-1 Geometry parameters used in the finite-element model.

Geometry	Width	Thickness
PMMA	5 mm	3 mm
Sample substrate	5 mm	350 μm
Gold wire	60 μm	200 nm
5 mins* 3D CNT network	5 mm	4.8 μm
10 mins* 3D CNT network	5 mm	4.5 μm
20 mins* 3D CNT network	5 mm	7.1 μm
30 mins* 3D CNT network	5 mm	6.7 μm
5 mins* primary CNT array	5 mm	6.2 μm
10 mins* primary CNT array	5 mm	5.3 μm
20 mins* primary CNT array	5 mm	6.7 μm
30 mins* primary CNT array	5 mm	5.9 μm

*Pre-growth annealing time

Table 5-2 Thermal property parameter used in the finite-element model.

Thermal property	Value used in finite-element model
PMMA thermal conductivity	0.19 W/mK

Table 5-3 Fitting results from the finite-element model.

Sample			Thermal property	Fitting result
5 mins* 3D CNT network			CNT film thermal conductivity	9.3 W/mK
			Sample substrate thermal resistance	1.29 cm ² K/W
			Contact resistance	0.67 cm ² K/W
10 mins* 3D CNT network			CNT film thermal conductivity	11.3 W/mK
			Sample substrate thermal resistance	1.52 cm ² K/W
			Contact resistance	0.78 cm ² K/W
20 mins* 3D CNT network			CNT film thermal conductivity	17.6 W/mK
			Sample substrate thermal resistance	1.52 cm ² K/W
			Contact resistance	0.71 cm ² K/W
30 mins* 3D CNT network			CNT film thermal conductivity	19.8 W/mK
			Sample substrate thermal resistance	0.88 cm ² K/W
			Contact resistance	0.76 cm ² K/W
5 mins* primary CNT array			CNT film thermal conductivity	20.3 W/mK
			Sample substrate thermal	0.58 cm ² K/W

		resistance	
		Contact resistance	0.67 cm ² K/W
10	mins*	CNT film thermal conductivity	16.8 W/mK
primary array	CNT	Sample substrate thermal resistance	0.87 cm ² K/W
		Contact resistance	0.65 cm ² K/W
20	mins*	CNT film thermal conductivity	13.8 W/mK
primary array	CNT	Sample substrate thermal resistance	1.40 cm ² K/W
		Contact resistance	0.67 cm ² K/W
30	mins*	CNT film thermal conductivity	12.7 W/mK
primary array	CNT	Sample substrate thermal resistance	1.16 cm ² K/W
		Contact resistance	0.67 cm ² K/W

*Pre-growth annealing time

The thermal conductivity results for primary CNT arrays and 3D CNT networks are further shown in Fig. 5-10. From the thermal conductivity measurement, it is found that the thermal conductivity of the pristine vertically aligned CNTs increases with increasing array density. The measured thermal conductivity for a vertically aligned CNT array ranges from 12.7 W/mK to 20.3

W/mK. The measured thermal conductivity is the effective thermal conductivity of the vertically aligned CNT array, which combines the contribution from the intrinsic thermal conductivity of CNT and the thermal conductivity of the air gap between CNTs:

$$K_{\text{CNT}} = \phi K_{\text{int,CNT}} + (1 - \phi) K_{\text{air}} \approx \phi K_{\text{CNT}} \quad (5-4)$$

where ϕ is the filling factor of CNT, K_{CNT} is the effective thermal conductivity of CNT array, and $K_{\text{int,CNT}}$ is the thermal conductivity of CNT. The filling factors of primary CNT arrays under different array densities can be found in Fig. 5-7. The $K_{\text{int,CNT}}$ is further estimated to be 208.3 ± 7.1 W/mK, which is in the same order of magnitude as Yang *et al.* [51].

Fig. 5-10 Thermal conductivities of primary CNT arrays and 3D CNT networks under different array densities.

From Fig. 5-10, it is presented that the 3D CNT network shows a higher thermal conductivity than the primary CNT array when the CNT densities are $5.6 \times 10^8/\text{cm}^2$ and $5.9 \times 10^8/\text{cm}^2$. Growing secondary CNTs in primary CNT arrays with CNT densities of $5.6 \times 10^8/\text{cm}^2$ and $5.9 \times 10^8/\text{cm}^2$ enhances the thermal conductivity of primary CNT films by 56% and 27%, respectively. This enhancement can be attributed to the extra pathway for heat transfer provided by the secondary CNTs.

However, at higher array densities ($7.2 \times 10^8/\text{cm}^2$ and $8.2 \times 10^8/\text{cm}^2$), the 3D CNT networks show lower thermal conductivities than the pristine

VACNTs. One possible reason for the decrease in thermal conductivity for a high filling factor is that the growth of secondary CNT induces more defects in the primary CNT array. The presence of more defective secondary CNTs increases the overall intrinsic nanotube thermal resistance of the 3D CNT network, which is in good agreement with the Raman results as shown in Fig. 5-8.

In addition to the CNT intrinsic thermal resistance, the CNT-CNT intertube thermal contact resistance impacts the thermal performance of CNT-based TIMs[153]. As presented in Fig. 5-5(c) and (d), the growth of the secondary CNT largely increases the CNT-CNT contact points. These CNT-CNT contact points act as additional sites for phonon scattering, which leads to an increase in the tube-tube thermal contact resistance. This postulation can be further justified by previously reported studies on the super low thermal conductivities for randomly oriented CNT films due to high tube-tube contact resistance[117].

5.4 Summary

In this chapter, a novel 3D CNT network composing of a primary CNT array bridged with randomly oriented CNT was proposed. The cross-plane thermal properties of the 3D CNT network were characterized using the freestanding sensor-based 3ω technique. With an array density of $5.6 \times 10^8/\text{cm}^2$ for the primary CNT, the growth of secondary CNTs improved the thermal conductivity by 56%. The thermal conductivity enhancement of the 3D CNT network comes from the extra heat transfer path provided by the secondary CNTs. However, as the array density increased, the growth of secondary CNTs degraded the thermal performance of the CNT film due to the increased density of defects and the tube-tube contact resistance.

In Chapter 6, the in-plane thermal properties of this novel 3D CNT network will be investigated in detail.

Chapter 6: In-Plane Thermal Conductivity of 3D CNT Network

6.1 Introduction

Thermal interface materials (TIM) play a significant role in the packaging of high power density devices. They are generally positioned between heat generating devices and heat sinks to improve their thermal coupling via physical contact. By simply filling the air gaps between the heat source and the heat sink with thermal grease, the thermal resistance can be reduced by a factor of five [154]. Thermal conductivity is a key parameter to evaluate a TIM. For state-of-the-art TIMs, such as thermal greases or phase change materials, the effective thermal conductivity ranges between 0.4 and 5 W/mK [60]. Although it is much better than air (~ 0.026 W/mK), these thermal properties remain insufficient to satisfy the requirements of modern high power density devices [33].

Recent studies have focused on the investigation of CNT-based TIMs [15, 40]. Carbon nanotubes possess superior thermal properties due to their strong sp^2 carbon bonding and long phonon mean free path. The thermal conductivity of individual CNTs has been measured to be 600~3000 W/mK [155, 156]. Various kinds of CNT-based TIMs have been developed, such as CNT/polymer composites [39] and CNT arrays [33]. Among the reported

studies, vertically aligned CNT (VACNT) arrays stand out for their thermal conductivity advantages [14] coupled with high mechanical compliance [41], which help solve the issue of thermal stress caused by the mismatch in the coefficient of temperature expansion (CTE) between two contacting surfaces. Zhang *et al.* reported a reduction of 90% in the interfacial thermal resistance when replacing commercial TIMs with VACNT array-based TIMs in high brightness light-emitting-diodes [143].

Despite the promising potential of VACNTs as TIMs, the thermal conductivity of a VACNT array is highly anisotropic. The air gap within the CNT array reduces the heat transfer between adjacent CNTs, which limits the in-plane thermal conductivity of a VACNT array. From molecular dynamics (MD) simulations, Che *et al.* predicted that the in-plane thermal conductivity of a VACNT array is as low as 0.056 W/mK [157]. It reduces the applicability of VACNT as TIMs, as the in plane thermal conductivity plays a prominent role when the sizes of the devices and their corresponding heat sources decrease. However, compared with the cross-plane thermal measurements of VACNT-based TIMs, much less attention has been paid to in-plane thermal characterizations.

In this chapter, a novel VACNT array-based TIM is proposed to enhance the in-plane thermal properties. In this new structure, VACNTs are bridged together with randomly oriented secondary CNTs: thus forming a three

dimensional carbon nanotube (3D CNT) network. The secondary CNTs provide an extra path for heat conduction in the in-plane direction. The in-plane thermal conductivity of the 3D CNT network is characterized by an infrared thermal imaging technique coupled to numerical simulations. Real-time temperature maps of 3D CNT networks heated by a metal wire are recorded using an infrared thermal camera. A 3D finite-element model is then developed. The model enables the numerical fitting of the obtained temperature profiles, which finally yields the in-plane thermal conductivity of the 3D CNT network.

6.2 Experimental details

6.2.1 Sample preparation

Figure 6-1 shows the preparation procedure for the samples. Quartz is chosen as the substrate due to its good heat insulation (see Fig. 6-1(a)). The thermal conductivity of the quartz substrate is measured as 1.77 W/mK by the 3ω technique [62]. To serve as a heater, a metal bridge composed of a wire and two contact pads, is deposited on top of a rectangular quartz sample (15 mm $\times$ 20 mm) (see Fig. 6-1(b)). The metal bridge is made of 150 nm Ti and 30 nm TiN, and it is 6 mm in length and 40 μ m in width. The high electrical resistivity of Ti enables a large electrical resistance (up to 3000 Ω). TiN is deposited on top of Ti to protect Ti from oxidizing. A 20 nm Ni layer is then deposited on top of the sample as the catalyst for VACNT growth. The parts of the contact pads are protected with thermal tape during the evaporation. The resulting Ni catalyst layer is shown in Fig. 6-1(c).

The primary VACNT array is then grown by an Aixtron Blackmagic Plasma Enhanced Chemical Vapor Deposition (PECVD) system. The chamber pressure is kept at 5 mbar. A radio frequency (RF) electric field biased at 700 V is applied with a power of 90 W. After 5mins pre-growth annealing with 250 sccm NH_3 , the VACNT growth is then conducted at 750°C with 250 sccm NH_3 and 50 sccm C_2H_2 for 30 mins. The obtained “VACNT/heater/quartz” structure is shown in Fig. 6-1(d). For the preparation of the catalyst for secondary CNT

growth within the primary VACNT array, the primary VACNT array is impregnated with 0.01 mol/L $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in acetone and annealed in a furnace at 700°C under H_2 atmosphere. The Ni precursors contained in the above-mentioned solution are transformed into Ni particles. The reactive equations have been described in Eq. 5-1 and Eq. 5-2.

As can be seen in Fig. 6-1(e), the Ni particles attach on the sidewalls of the primary VACNT array and act as catalysts for secondary CNT growth. By switching the gas flow through the ethanol bubbler, ethanol is added to the gas flow and provides a carbon source for secondary CNT growth. The growth is then carried out under 700°C for 10 mins, and the 3D CNT network is formed (see Fig. 6-1(f)). The electrical resistance of the metal wire is measured before and after the growth process of the primary VACNT array and secondary CNTs. Little change ($<0.5\%$) has been observed in the metal wire resistance, which means that no electrical short circuit happens during the process or due to the presence of CNTs on top of the metal bridge.

Fig. 6-1 Sample preparation procedure: (a) the quartz substrate; (b) the metal bridge deposited on top of the quartz substrate; (c) the Ni catalyst layer deposition; (d) the primary VACNT array/heater/quartz substrate structure; (e) the Ni catalyst attached on the sidewalls of the primary VACNTs; and (f) the 3D CNT network/heater/quartz substrate structure.

6.2.2 Infrared thermography characterization

Figure 6-2(a) shows the schematic diagram of the set-up for the infrared thermal imaging of the samples. The temperature map of the sample surface is obtained using a FLIRX8400sc infrared camera equipped with a G1 lens and operating in the infrared wavelength range between 1.5 μm and 5 μm . This

system offers a spatial resolution of 15 μm and a temperature sensitivity of 25 mK. A black box surrounds the sample and the lens of the camera to minimize noise from the radiation of the surrounding objects. The image of the system-setup within the black box is shown in Fig. 6-2(b). The sample is suspended by an aluminum alloy holder. The two contact pads of the metal bridge deposited on the quartz substrate are further connected to a precision power supply (Keithley 2612B), as shown in Fig. 6-2(c).

Fig. 6-2 (a) Schematic diagram of the set-up of the infrared thermal imaging of the sample, (b) image of the system set-up within the black box, and (c) image of the sample with the electrical wire connection clipped by the holder.

A DC current is applied to the pads of the bridge so that the wire linking the pads acts as a heater by the Joule heating effect. The emissivities of the 3D CNT network and primary CNT array in the range of $1.5\ \mu\text{m}$ to $5\ \mu\text{m}$ are both measured to be 0.99. The emissivity measurement is conducted using an Perkin-Elmer Frontier FTIR system with an integrating sphere, and the

procedure has been well described elsewhere [158]. Temperature maps of the sample surfaces are recorded under three different heating powers: 23 mW, 47 mW and 99 mW. The temperature profiles corresponding to the thermal steady state are extracted for further thermal property analysis (see Section 6.3 for details).

6.3 Results part I: characterization results

6.3.1 Comparison between 3D CNT network and primary CNT array

Figure 6-3(a) shows the SEM images for the primary VACNT array. The primary VACNT array grown by the PECVD technique exhibits a high degree of vertical alignment. The air gaps between CNTs are observable, which is also expected for the PECVD-grown CNTs [146]. Figure 6-3(b) shows the SEM images of the 3D CNT network. The secondary CNTs are randomly oriented and bond the primary VACNTs together, filling up the gap within the primary VACNT array. Figure 6-3(c) shows the TEM image of the 3D CNT network. The secondary CNTs show a smaller diameter than the primary VACNTs, and the secondary CNTs are connected to the sidewall of the primary VACNT.

Fig. 6-3 (a) SEM image of the primary VACNT array, (b) SEM image of the 3D CNT network, and (c) TEM image of the 3D CNT network.

6.3.2 Thermal imaging characterization

A comparison of the high resolution thermal maps of the 3D CNT network and the primary VACNT array are shown in Fig. 6-4 for the inputting powers of 23 mW, 47 mW, and 99 mW. The temperature profiles along a segment perpendicular to the center of the wire heater (marked by the blue dotted line in Fig. 6-5(a)) are also extracted and shown in Fig. 6-5(b). Under

different heating powers, the temperature of the 3D CNT network is always lower than that of the primary VACNT array. This indicates that the 3D CNT network has a much better heat dissipation ability than the primary VACNT array. Compared to the primary VACNT array, the slopes of the temperature profiles for the 3D CNT network are much smaller, which indicates that the 3D CNT network has a lower thermal resistance than the primary VACNT array in the in-plane direction. At a distance of 6 mm away from the heater, the sample is clipped by the aluminum alloy holder, which corresponds to the heat sink for the heat dissipating system. Due to the high thermal conductivity of aluminum alloy, the temperature of the CNT film decreases to the ambient temperature. The temperature differences between the 3D CNT network and the primary VACNT array at the distance of 5.1 mm is partly caused by the differences in the ambient temperatures during thermal imaging measurements: 296.35 K and 295.45 K, respectively. Thus, the temperature of the 3D CNT network at the distance of 5.1 mm may be higher than that of the primary VACNT array due to the higher ambient temperature.

Fig. 6-4 (a) Primary VACNT array under 23 mW; (b) primary VACNT array under 47mW; (c) primary VACNT array under 99 mW; (d) 3D CNT network under 23 mW; (e) 3D CNT network under 47 mW; and (f) 3D CNT network under 99 mW.

Fig. 6-5 (a) The perpendicular bisector (blue dotted line) of the line heater in the region between the heater and the holder, and (b) the temperature profile as a function of the distance from the heater along the blue dotted line.

6.4 Results part II: extraction of in-plane thermal conductivity

6.4.1 Thermal model

To extract the in-plane thermal conductivity of the 3D CNT network further from the temperature profile given in Fig. 6-5(b), a finite element analysis is conducted using COMSOL Multiphysics. The governing 3D heat equations for the metal heater, the quartz substrate, the up and down parts of the aluminum alloy holder, and the CNT film are:

$$\frac{\partial}{\partial x} \left(K_H \frac{\partial T_H}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_H \frac{\partial T_H}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_H \frac{\partial T_H}{\partial z} \right) + P = \rho_H C_H \frac{\partial T_H}{\partial t} \quad (6-1)$$

$$\frac{\partial}{\partial x} \left(K_S \frac{\partial T_S}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_S \frac{\partial T_S}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_S \frac{\partial T_S}{\partial z} \right) = \rho_S C_S \frac{\partial T_S}{\partial t} \quad (6-2)$$

$$\frac{\partial}{\partial x} \left(K_{al} \frac{\partial T_{uh}}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{al} \frac{\partial T_{uh}}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{al} \frac{\partial T_{uh}}{\partial z} \right) = \rho_{al} C_{al} \frac{\partial T_{uh}}{\partial t} \quad (6-3)$$

$$\frac{\partial}{\partial x} \left(K_{al} \frac{\partial T_{dh}}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{al} \frac{\partial T_{dh}}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{al} \frac{\partial T_{dh}}{\partial z} \right) = \rho_{al} C_{al} \frac{\partial T_{dh}}{\partial t} \quad (6-4)$$

$$\begin{aligned} \frac{\partial}{\partial x} \left(K_{CNT,in} \frac{\partial T_{CNT}}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{CNT,in} \frac{\partial T_{CNT}}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{CNT,out} \frac{\partial T_{CNT}}{\partial z} \right) = \\ \rho_{CNT} C_{CNT} \frac{\partial T_{CNT}}{\partial t} \end{aligned} \quad (6-5)$$

In Eq. 6-1 to Eq. 6-5, the subscript H refers to the metal heater, S to the quartz substrate, al to the aluminum alloy holder, uh to the up part of the holder, dh to the down part of the holder, P to the heat generation rate of the metal wire, ρ to the density, C to the heat capacity, and K to the thermal conductivity. Since CNT shows high anisotropy in its thermal property [159], we apply $K_{CNT,in}$ and $K_{CNT,out}$ to represent the in-plane thermal conductivity and the cross-plane thermal conductivity of the CNT film separately. For the aluminum alloy holder,

the quartz substrate, and the metal heater, K_{al} , K_S , and K_H represent their isotropic thermal conductivities, since both metal and quartz are isotropic materials.

In the thermal steady state, the time derivatives of the temperature in the different domains are null; so the right-hand side of the Eq. 6-1 to Eq. 6-5 turns out to be 0. Therefore, the 3D heat diffusion equations under the thermal steady state are no longer dependent on the density (ρ) and the heat capacity (C) of the material.

Regarding boundary conditions:

- As the down part of the holder is placed on a large steel stage, the temperature of the bottom surface of the down holder is fixed at ambient temperature T_0 :

$$T = T_0 \quad (6-6)$$

- For all the remaining boundary surfaces, there is heat flux caused by natural convection. The heat flux $\vec{q}_c$ of natural convection is:

$$\vec{q}_c = h(T_0 - T) \quad (6-7)$$

where T_0 is the ambient temperature; T is the temperature at the boundary surface; and h is the heat transfer coefficient for natural convection.

- In addition to the natural convection, there is also heat loss due to the

radiation on all the remaining boundary surfaces. The heat flux $\vec{q}_r$ caused by radiation is described as:

$$-\vec{n} \cdot \vec{q}_r = \varepsilon \sigma (T_0^4 - T^4) \quad (6-8)$$

where ε is the sample emissivity; σ is the Stefan-Boltzman constant, and $\sigma = 5.67 \times 10^{-8} \text{W/m}^2\text{K}^4$. Since quartz is transparent in the mid-infrared range where the thermal camera operates, its emissivity in the mid-infrared range is extremely low and the radiation rate is negligible [160]. Based on our measurements, the temperature of the aluminum alloy holder is close to the ambient temperature T_0 . The radiation rate of the aluminum alloy holder is calculated to be around 10^{-3} mW, which is three orders of magnitude lower than the heat generation rate of the metal heater. Hence, the influence of radiation loss from the aluminum alloy holder on the temperature distribution is negligible. The radiation loss of the whole sample is thus dominated by the radiation from the CNT film.

- Since the sample is clipped by the aluminum holder, there is thermal contact resistance R_c between the sample surface and the holder. The heat flux $\vec{q}_c$ across the contacting surfaces is:

$$-\vec{n} \cdot \vec{q}_c = -\Delta T / R_c, \quad (6-9)$$

where ΔT is the temperature jump between the two contacting surfaces.

6.4.2 Parameter sensitivity check by numerical simulation

We perform the finite-element simulations solving Eq. 6-1 to Eq. 6-9 using COMSOL Multiphysics. The element size for simulation is set as 15 μm , which is the same as the resolution of the infrared thermal camera. Parametric simulations are done to investigate the sensitivity of the temperature profile to different parameters. The values for the parameters used in the simulations can be found in Table 6-1.

Table 6-1 Parameters used for the simulations in Section 6.4.

Geometry*	
Quartz width	15 mm
Quartz length	20 mm
Quartz height	1 mm
Up holder width	15 mm
Up holder length	1.5 mm
Up holder height	3 mm
Down holder width	15 mm
Down holder length	1.5 mm
Down holder height	5 mm
Metal wire length	6 mm
Metal wire width	4 μm
Metal contact pad length	12.5 mm
Metal contact pad width	1.8 mm
Metal layer thickness	200 nm
CNT film width	15 mm
CNT film length	10 mm
CNT film height	10 μm
Thermal property	

Quartz thermal conductivity	1.77 W/mK
CNT film in-plane thermal conductivity	1 W/mK
CNT film cross-plane thermal conductivity	20 W/mK
Aluminum holder thermal conductivity	200 W/mK
Contact resistance between the holder and sample	0.1 cm ² K/W
Natural convection coefficient	3 W/m ² K
Power supply	
Power	0.1 W

*The 3D geometry of the thermal model is shown in Fig. 6-5(a).

The surface temperature profiles along a segment perpendicular to the center of the wire heater (see the blue dotted line in Fig. 6-5(a)) are plotted as a function of the distance from the heater. The sensitivities of the surface temperature profiles due to various parameters are simulated by solving Eq. 6-1 to Eq. 6-9. The simulation results are presented as follows:

1) Thermal conductivity of the aluminum alloy holder

Figure 6-6 shows the simulation results of the surface temperature profiles under different thermal conductivities of the aluminum alloy holder. All the parameters are set as those in Table 6-1, except for the thermal

conductivity of the holder. The range for the thermal conductivity value is set based on the knowledge that the thermal conductivity of the aluminum alloy holder is in the range of 80~204 W/mK [161]. According to Fig. 6-6, the variation in the thermal conductivity of the aluminum alloy holder only leads to a very small shift of ΔT around 120 mK in the “linear region”. The slopes of the temperature profiles in the linear region remain the same.

Fig. 6-6 Simulation results of the surface temperature profiles under different thermal conductivities of the aluminum alloy holder.

2) Contact resistance between holder and sample

Figure 6-7 shows the simulation results of the surface temperature profiles under different contact resistance values (10^{-4} ~ 10^{-5} W/m²K). All the parameters are set as those shown in Table 6-1, except for the contact resistance value. The range for the thermal conductivity value is set based on the reported studies about the contact resistance between the CNT film and the holder [162].

According to Fig. 6-7, the variation in the contact resistance will induce a constant change of ΔT in the “linear region”. The slopes of the temperature profiles in the linear region remain the same. The lower the contact resistance between the holder and the sample, the easier the heat dissipates away from the sample to the heat sink. Thus, the surface temperature of the sample is lower.

Fig. 6-7 Simulation results of the surface temperature profiles under different contact resistance values.

3) Ambient temperature

Figure 6-8 shows the simulation results of the surface temperature profiles under different ambient temperatures (293.15 K to 299.15 K). During the simulations, we control other parameters as listed in Table 6-1. The ambient temperature will induce a constant change ΔT in the “linear region”. The slopes of the temperature profiles in the linear region remain the same.

Fig. 6-8 Simulation results of the surface temperature profiles under different ambient temperatures.

4) Quartz substrate thermal conductivity

Figure 6-9 shows the simulation results of the surface temperature profiles under different quartz substrate thermal conductivities. During the simulations, all the parameters are set as those in Table 6-1, except for the quartz thermal conductivity value. The range for the effective thermal conductivity value is set based on the knowledge that the thermal conductivity of fused quartz ranges from 1.4 W/mK to 2 W/mK [163, 164].

According to Fig. 6-9, the difference in the thermal conductivity of the quartz substrate will lead to a difference in the slope of the temperature profile in the “linear region”. A quartz substrate with a lower thermal conductivity will prevent heat dissipating through the substrate. Thus, it leads to a larger slope and higher surface temperature.

Fig. 6-9 Simulation results of the surface temperature profiles under different quartz substrate thermal conductivities.

5) Natural convection coefficient

Figure 6-10 shows the simulation results of the surface temperature profiles under different natural convection coefficients. All the parameters, except for the natural convection coefficient, are set as described in Table 6-1. The typical range of the natural convection coefficient is from 5 W/m²K to 25 W/m²K [165], although values outside of this range have also been observed [166-168].

According to Fig. 6-10, as the natural convection coefficient increases, the heat flux dissipating into the surrounding atmosphere by convection increases, and the temperature on the sample surface decreases. Under a higher natural convection coefficient (like 25 W/m²K), the temperature profile under the “linear region” is no longer linear, but a curve. Due to Eq. 6-13, the heat flux by convection increases linearly with the surface temperature. Thus the heat dissipating rate due to convection along the perpendicular direction is not a constant, but it decreases as the distance from the heater increases. Consequently, when the natural convection coefficient is large enough and the dissipating rate is high enough, the temperature profile in the perpendicular direction turns into a curve in the “linear region”.

Fig. 6-10 Simulation results of the surface temperature profiles under different natural convection coefficients.

6) CNT in-plane and cross-plane thermal conductivity

Because of the tube-like structure of CNT, the thermal properties of CNT films are highly anisotropic [159]. Thus, we investigate the in-plane and cross-plane thermal conductivity of CNT separately.

Figure 6-11 shows the simulation results of the surface temperature profiles under different CNT in-plane thermal conductivities (0.01 W/mK to 5 W/mK). During the simulations, we control other parameters as listed in Table 6-1. According to Fig. 6-11, the difference in the in-plane thermal conductivity

of CNT will lead to a difference in the slope of the temperature profile in the “linear region”. Carbon nanotube film with higher in-plane thermal conductivity will help dissipate heat to the aluminum alloy holder. Consequently, it leads to a smaller slope and lower surface temperature.

Fig. 6-11 Simulation results of the surface temperature profiles under different CNT in-plane thermal conductivities.

Figure 6-12 shows the simulation results of the surface temperature profiles under different CNT cross-plane thermal conductivities (5 W/mK to 20 W/mK). During the simulations, we control other parameters as listed in Table

6-1. According to Fig 6-12, the surface temperature profiles of CNTs with different cross-plane thermal conductivities overlap. Thus, the surface temperature profile is not sensitive to the cross-plane thermal conductivity of the CNT film.

Fig. 6-12 Simulation results of the surface temperature profiles under different CNT in-plane thermal conductivities.

When the whole system is under the thermal steady state, the net heat flux in the CNT film happens in the in-plane direction. The heat flux flows from the heat source through the CNT film and dissipates into the aluminum alloy holder on the side of the sample, which acts as a heat sink. Thus, the

measured surface temperature profile is mainly governed by the in-plane thermal conductivity of the CNT film, and it is not sensitive to the cross-plane thermal conductivity of the CNT film.

7) Heating power

Figure 6-13 shows the simulation results of the surface temperature profiles under different heating powers. During the simulations, we control other parameters as listed in Table 6-1.

Fig. 6-13 Simulation results of the surface temperature profiles under different heating powers.

According to Fig. 6-13, the difference in the heating power will lead to a difference in the slope of the temperature profile in the “linear region”. The slopes in the linear region for different powers, as well as the comparison between the power ratio and the slope ratio, are listed in Table 6-2. As the heating power increases, the net heat flux through the sample increases. Thus, the slope of the temperature profile increases. From the comparison between the power ratio and the slope ratio, the slope of the temperature profile does not increase linearly with the heating power.

The reason for this nonlinear correlation is because, as the heating power increases, the surface temperature increases, thus the heat loss through convection and radiation will also increase. As a result, the net heat flux through the sample does not linearly increase with the heating power. Accordingly, the slope of the temperature profile is not linearly correlated with the heating power.

Table 6-2 The slopes of the temperature profiles in the linear regions under different powers.

Power	Slope in linear region	Ratio of the power to 0.06W	Ratio of the slope under the power to that under 0.06W
-------	---------------------------	--------------------------------	--

0.06 W	-2.05	1	1
0.08 W	-2.72	1.33	1.32
0.1 W	-3.34	1.67	1.62

8) Summary of simulation results

To summarize, the temperature profile responses to the different simulation parameters are investigated in detail. The variations in the holder thermal conductivity, contact resistance between the holder and the sample, and the ambient temperature only induce a constant shift of temperature by ΔT (see Fig. 6-6, Fig. 6-7, and Fig. 6-8). In contrast, variation of the quartz substrate thermal conductivity, the natural convection coefficient, the in-plane thermal conductivity of the CNT film, and the heating power will cause a change in the slope of the temperature distribution (see Fig. 6-9, Fig. 6-10, and Fig. 6-11). Note that the surface temperature profile is not sensitive to the cross-plane thermal conductivity of the CNT film (see Fig. 6-12).

6.4.3 Derivation of the in-plane thermal conductivity of the CNT film

As discussed in Section 6.4.2, variation in the CNT in-plane thermal conductivity will lead to a slope change in the surface temperature profile as a function of the distance from the heater (see Fig. 6-11). Thus, the in-plane thermal conductivity of the CNT film can be extracted due to the slope of the temperature profile. However, the value of the natural convection coefficient also has an influence on the slope of the temperature profile, which is unknown during the thermal imaging characterizations. Therefore, to extract the in-plane thermal conductivity of the CNT film and the value of the natural convection coefficient for each sample, at least two nonlinear-correlated temperature profiles are required.

As discussed in Section 6.3.2, we record three temperature profiles for each CNT film under different heating powers (23 mW, 47 mW, and 99 mW). As discussed in Section 6.4.2, the slopes of the temperature profile are correlated non-linearly with the heating powers. Thus, the three temperature profiles for each sample are in non-linear correlation. The in-plane thermal conductivity of the CNT film and the natural convection coefficient are varied iteratively until the simulation matches the experimental data under all three heating powers based on the least mean-square fitting using COMSOL Multiphysics parametric sweeps.

Note that the thermal conductivity of the aluminum alloy holder K_{Al} and the contact resistance R_c are also not known during the measurements. However, the simulations show that the changes in K_{Al} and R_c only induce a constant shift of the temperature by ΔT (as discussed in Section 6.4.2) and do not influence the slope of the temperature profile. As the extraction of in-plane thermal conductivity of the CNT film relies only on the slope of the temperature profiles, there is no impact on the final result.

6.4.4 Numerical fitting results

Figures 6-13(a) and (b) show the fitting curves of the temperature profiles for the 3D CNT network and the primary CNT array, respectively. Under different heat generation rates, the fitting curves match well with the temperature profiles obtained by the infrared thermal camera, with all the R-squared coefficient larger than 0.99.

(a)

(b)

Fig. 6-14 Numerical fitting of the temperature profile based on the 3D finite-element thermal model under the heating powers of 23 mW, 47 mW, and 99 mW for (a) the 3D CNT network and (b) the primary VACNT array.

The corresponding in-plane thermal conductivities for the 3D CNT network and the primary CNT array are obtained as 5.4 W/mK and 0.1 W/mK, respectively. The natural convection coefficients for the 3D CNT network and the primary VACNT array are both obtained as 2.0 W/m²K, since the conditions within the black box, which surrounds the samples, are well maintained during the thermal imaging measurements.

The uncertainty in the extraction of the in-plane thermal conductivity of the CNT films is mainly related to the uncertainty in the measurement of the quartz substrate thermal conductivity (1.2%) and the heat generating rate (1.6%), since the variation of these two parameters will lead to a change in the slope of the temperature profile (see Fig. 6-9 and Fig. 6-13). The total uncertainty for the thermal conductivity measurement can be calculated using:

$$\frac{\delta K_{CNT,in}}{K_{CNT,in}} = \sqrt{\left[\frac{\partial f(K_{CNT,in})}{\partial K_S} \delta K_S \right]^2 + \left[\frac{\partial f(K_{CNT})}{\partial P} \delta P \right]^2}, \quad (6-10)$$

where K_S is the thermal conductivity of the quartz substrate, and P is the heat generation rate. For the 3D CNT network, the total uncertainty is 17%. For the primary VACNT array, the total uncertainty is calculated to be 51%, which is due to the low sensitivity of the surface temperature profile to low $K_{CNT,in}$ around 0.1 W/mK. Despite the large uncertainties in the measurements, the improvement in the in-plane thermal conductivity is more than 50 times higher, which is significantly higher than the uncertainties in the measurements.

6.5 Summary

In this chapter, the in-plane thermal properties of the 3D CNT network structure was investigated. In the 3D CNT network structure, the primary VACNT array is bridged together by randomly oriented secondary CNTs. The temperature distributions of the 3D CNT network and the VACNT array heated by metal heaters are recorded in real time by an infrared thermal imaging system. Due to the temperature profile as a function of the distance from the heater, the surface temperature of the 3D CNT network is much lower than that of the VACNT array. The in-plane thermal conductivity of the 3D CNT network is further obtained by the numerical fitting of a 3D heat diffusion model. The thermal conductivity of the 3D CNT network is 5.4 W/mK, which is more than 50 times higher than the VACNT array. The 3D CNT network enhances the in-plane thermal conductivity of VACNT-based TIMs.

Chapter 7: Summary and Recommendations for Future Work

7.1 Summary

Carbon-based materials possess superior thermal conductivity and receive increasing attention for thermal management applications. The results of the experimental investigations on the thermal characterization of PCD and CNT in this thesis are:

- A systematic study has been carried out to investigate the influence of defects on the thermal conductivities of PCDs on both the top (growth) and the bottom (nucleation) surfaces. The thermal conductivities of PCDs on both surfaces are characterized with the 3ω technique. On the top surface, higher thermal conductivity and lower defect densities are obtained compared to the bottom surface. The influence from the non-diamond carbon phase and C-H stretch on top surface is not significant because of the low concentration of these defects on the top surface. However, the heat transport is still limited by the presence of the Ns^0 defect, which is the main contributor to lowering the thermal conductivities on the top surfaces. Regarding the bottom surface, the non-diamond carbon phase, Si vacancy, C-H stretch, and Ns^0 defects lead to an obvious reduction in the thermal conductivity. Furthermore, well fitted equations are obtained for the fast

estimation of the PCD thermal conductivities using optical transmission.

The equations are demonstrated to be valid at any wavelength in the visible region.

- A freestanding sensor-based 3D technique has been developed to characterize the cross-plane thermal conductivity for samples with rough surfaces, such as the CNT array. By applying a heat source with higher power density and a sensor substrate with lower thermal conductivity, the sensitivity of the freestanding sensor to the thin film thermal conductivity can be improved. Three distinct regions are observed in the behavior of the temperature oscillations from 0.01 Hz to 4100 Hz: (1) a high frequency region ($f > 100$ Hz), (2) a linear region ($100 \text{ Hz} > f > 1 \text{ Hz}$) and (3) a saturation region ($f < 1 \text{ Hz}$). The slope of the temperature oscillation curve in the high frequency region is determined by the contact resistance between the freestanding sensor and the thin film sample. The frequency (turning point) where the temperature oscillation curve turns from the linear region to the saturation region is determined by the thermal resistance of the sample substrate. The slope of the temperature oscillation curve in the linear region is determined by the thermal conductivity of the thin film. The determination of the thermal properties of the sample is conducted by the numerical fitting of 2D heat diffusion equations. The total uncertainty is calculated to be as low as 7.4%.

- A novel 3D CNT network is proposed for advanced thermal interface material. 3D CNT network is comprised of VACNT arrays (primary CNTs) bridged with randomly-oriented secondary CNTs. Primary CNTs are grown by the PECVD method. Secondary CNTs are then grown from the sidewall of the primary CNT array with the help of Ni catalysts by the TCVD method: thus forming the 3D network structure. The cross-plane thermal conductivities of the 3D CNT network under different primary CNT array densities are characterized using the freestanding sensor-based 3ω technique. With an array density of $5.6 \times 10^8/\text{cm}^2$ for the primary CNT array, the growth of secondary CNTs improves the thermal conductivity by 56%. The thermal conductivity enhancement of the 3D CNT network comes from the extra heat transfer path provided by the secondary CNTs. However, as the array density increases, the growth of secondary CNT starts to degrade the thermal performance of the CNT film due to the increasing defects and tube-tube thermal contact resistance.
- The in-plane thermal conductivity of the 3D CNT network is characterized by an infrared thermal imaging technique. The real-time temperature mapping of the 3D CNT network heated by a metal wire is recorded using an infrared thermal camera. To extract the in-plane thermal conductivity of

the 3D CNT network, a 3D finite-element model is developed to enable an accurate numerical fitting of the obtained temperature profile. We find the in-plane thermal conductivity of the 3D CNT network is 5.4 W/mK, which is more than 50 times higher than that of the VACNT array alone. The growth of secondary CNTs enhances the thermal coupling between the adjacent VACNTs in the 3D CNT network.

7.2 Recommendations for future work

Based on the findings and discussion in the thesis, four suggestions are made to explore the research topic further:

- In Chapter 3, the thermal properties of PCDs are investigated in detail. It is found that the thermal conductivities of PCDs with low defect densities can reach up to 2200 W/mK, which is five times greater than that of pure copper [22]. Polycrystalline diamonds show a high potential for the advanced heat sinks and heat spreaders in high power density devices. The recommended future work would be the integration of diamond heat spreaders or heat sinks into electronic devices and the investigation of the device performance improvement.
- A novel 3D CNT network is proposed in Chapter 5 and Chapter 6 to enhance the thermal properties of CNT-based TIMs. The cross-plane and in-plane thermal conductivities of the 3D CNT network are investigated. It would be interesting to study the improvement of device performance further by integrating the 3D CNT network into high power density devices as a thermal interface material. Besides, thermal contact resistance is an important factor for thermal interface material. The recommended future work would be to study the ways to reduce the thermal contact resistance between the 3D CNT network and the heat source/sink.

- An in-plane thermal conductivity characterization technique based on thermal imaging analysis has been proposed and demonstrated in Chapter 6. This method enables a non-detectable thermal characterization of thin film. Previously, no analytical solution is available for the thin film/heater/substrate structure as shown in Fig. 6-5(a). Although a fully numerical solution can be provided by a 3D finite-element model, the computing time is very long. By changing the geometry to a symmetric holding structure (see Fig. 7-1), the complex thermal model can be simplified into a 1D heat transfer model (see Fig. 7-2). The in-plane thermal conductivity of the thin film can be obtained as:

$$K_{film,in} = l / (2\Delta T / P - l / K_{sub,in}) \quad (7-1)$$

where $K_{film,in}$ is the in-plane thermal conductivity of the thin film; $K_{sub,in}$ is the in-plane thermal conductivity of the substrate; ΔT is the temperature between the heater and the heat sink (the aluminum alloy holder); and P is the heat generating rate from the line heater.

Fig. 7-1 Thin film sample suspended using a symmetric holding structure.

Fig. 7-2 Simplified 1D heat transfer model by treating the thin film and the sample substrate as thermal resistance values: R_{film} and $R_{\text{substrate}}$, respectively.

- There are other kinds of carbon-based materials that have potential for thermal management applications. Some of them do not have related thermal investigations, such as the graphene/CNT hybrid structure. The

fabrications of this hybrid structure and its electrical properties have been studied widely [169-171]. However, the thermal property of this hybrid has not been reported yet. Graphene and CNT are both materials with high thermal conductivities. The in-plane thermal conductivity of graphene has been predicted to be 2200 W/mK [172], and the cross-plane thermal conductivity of individual CNT has been predicted to be 6600 W/mK [157]. Thus, the in-plane and cross-plane thermal conductivities of this graphene/CNT hybrid structure are worth investigating further.

Author's Publications

Journal Papers

1. **Qinyu Kong**, Alvarado Tarun, Chuan Ming Yap, Siwei Xiao, Kun Liang, Beng Kang Tay, and Devi Shanker Misra, "*Influence of optically active defects on thermal conductivity of polycrystalline diamond*", *The European Physical Journal Applied Physics* 80.2 (2017): 20102.
2. **Qinyu Kong**, Laurence Bodelot, Bérengère Lebental, Yudian Lim, Li Lynn Shiau, Boris Gusarov, Chong Wei Tan, Kun Liang, Congxiang Lu, Chuan Seng Tan, Coquet Philippe, Beng Kang Tay, "*Novel three-dimensional carbon nanotube networks as high performance thermal interface materials*". *Carbon*, 2018. 132:0.359-369.
3. **Qinyu Kong**, Lin Qiu, Yudian Lim, Chong Wei Tan, Kun Liang, Congxiang Lu, Beng Kang Tay, "*Thermal conductivity characterization of three dimensional carbon nanotube network using freestanding sensor-based 3ω technique*", *Surface coatings and technology*, 2018. 345:p.105-112.
4. Yu Dian Lim, **Qinyu Kong**, Shaomeng Wang, Chong Wei Tan, Beng Kang Tay, Sheel Aditya, "*Enhanced field emission properties of carbon nanotube films using densification technique*", *Applied surface science, in press*, 2017.
5. Yu Dian Lim, Dmitry Grapov, Liangxing Hu, **Qinyu Kong**, Beng Kang Tay, Vladimir Labunov, Jianmin Miao, Coquet Philippe, Sheel Aditya "*Enhanced field emission properties of carbon nanotube bundles confined in SiO₂ pits*", *Nanotechnology*, 2018. 29(7):p.075205.

Conference Papers

1. **Qinyu Kong**, Beng Kang Tay “*Effect of grain size on the residual stress and defects of polycrystalline diamond*” the international Conference on New Diamond and Nano Carbons 2015, Shizuoka, Japan.
2. **Qinyu Kong**, Chuan Ming Yap, Siwei Xiao, Alvarado Tarun, Kun Liang, Beng Kang Tay, Devi Shanker Misra, “*Effect of impurities on thermal conductivity of polycrystalline diamond grown by microwave plasma-assisted CVD*”. International Conference on Diamond and Carbon Materials 2016, Montpellier, France.
3. Yu Dian Lim, **Qinyu Kong**, Beng Kang Tay, Sheel Aditya, “Enhanced field emission characteristics of carbon nanotubes film via surface modification technique.” The International Conference on Surfaces, Coatings and Interfaces 2017. Incheon, South Korea.
4. Beng Kang Tay, **Qinyu Kong**, Laurence Bodelot, Bérengère Lebental, Devi Shanker Misra, “ Thermal Characterization of Polycrystalline diamond using infrared thermal imaging measurement”, 8th IEEE International Nanoelectronics Conference, 2018, Kuala Lumpur, Malaysia.

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