Thermal characterization and thermal tuning in nanostructured materials

Majid Kabiri Samani

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Thermal Characterization and Thermal Tuning in Nanostructured Materials

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School of Electrical & Electronic Engineering

2014

Thermal Characterization and Thermal Tuning in Nanostructured Materials

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Summary and Abstract

In this dissertation, the experimental investigation of the heat transport in crystalline nanostructured materials is studied. Different methods to reduce their thermal conductivity to create user-specific materials are presented as well. It is shown that by using different methods such as the incorporation of additional elements in the crystalline structure, controlling the deposition and embedding metallic nanoinclusions in the semiconductor matrix, it is possible to reduce the thermal conductivity. Thermal conductivity measurements have been conducted by using pulsed photothermal reflectance (PPR) and 3ω techniques at room temperature. The materials studied in this work include Ti-based hard coatings, multilayer TiN/TiAlN coatings and n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ thermoelectric films.

Firstly, the effect of the incorporation of Al on the thermal conductivity of TiAlN coatings prepared by a lateral rotating cathode arc (LARC) technique has been investigated. To study this, a series of TiAlN coatings were deposited on stainless steel substrates and the thermal conductivity of the coatings was measured by the PPR technique. The Microstructure of the coatings was analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). These techniques reveal that TiN coating shows a clear columnar structure with a predominant (111) preferential orientation. With the incorporation of Al, the columnar structure of the coatings is disrupted, the grain size of the coatings is decreased and the dislocation density is increased. A significant decrease in thermal conductivity was found with increasing Al content and a minimum thermal conductivity of about 4.63 W/mK was obtained

at the Al/Ti atomic ratio of around 0.72. The decrease in thermal conductivity of the TiAlN coatings is explained in terms of increased phonon scattering due to the decrease in the grain size and increasing dislocation density.

The effect of the incorporation of Al and Si on the thermal conductivity of the TiAlSiN nanocomposite coatings prepared by the LARC technique has been studied. A series of TiAlSiN nanocomposite coatings were deposited on stainless steel substrates and the room temperature thermal conductivity of the coatings was measured by the PPR technique. A significant decrease in thermal conductivity was found with increasing Al and Si contents and it was shown that the thermal conductivity of the TiAlSiN nanocomposite coatings is about 1.8 W/mK at a (Al+Si)/Ti atomic ratio of around 1.76. The decrease in thermal conductivity of the TiAlSiN nanocomposite coatings can be attributed to the reduced grain size and the formation of a nanocomposite structure which consists of crystalline nanograins embedded in a disordered, lower thermal conductivity than TiAlN, amorphous SiN_x matrix.

In order to study the effect of a multilayer structure on the thermal conductivity, a series of multilayer [TiN/TiAlN]_n coatings with different bilayer numbers *n* were deposited on stainless steel substrates by the LARC technique. The PPR technique was employed to measure thermal conductivity of the coatings at room temperature. TEM observation and microstructure analysis of multilayer coatings show a lattice mismatch and misfit dislocations at the interfaces between TiN and TiAlN layers, and a decrease of the grain size with increasing number of layers. Results show that the thermal conductivity of the multilayer coatings reduces with increasing bilayer number *n*. Phonon scattering is

increased at the interfaces and grain boundaries due to the existence of misfit dislocations and to the decreasing grain size, respectively.

For the study of the effect of metallic nanoinclusions in thermoelectric (TE) film on the thermal conductivity, textured *n*-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ thin films with Pt nanoinclusions were successfully prepared via pulsed laser deposition. The thermal conductivity of the TE films was measured by the 3ω technique. The TEM observation shows that the Pt nanoinclusions are embedded at the grain boundaries of the semiconductor matrix. By introducing Pt nanoinclusions, the thermal conductivity is reduced due to scattering phonon at the grain boundaries.

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Chapter 1: Introduction

1.1 Background and Motivation

The electron was discovered by Thomson in 1898 and electrical conductivity of materials has been an attractive research field during the last century. Researchers focused their efforts on tuning and controlling the electrical conductivity of materials. There has been considerable progress in electronic systems and now it is difficult to imagine the world without electronics. Research efforts were focused on tuning the electrical conductivity by controlling electron concentration due to doping, electron mean free path by crystal imperfections and the quantum effect of electrons [1; 2]. The transistor is an important invention of the 20th century and is an example of tuning electrical conductivity.

The invention of fire was a starting point of the history of thermal transport and recalls primitive human efforts, such as straw for insulation, specific heat of

stone for warmth, etc. The range of thermal conductivity at room temperature spans about four orders of magnitude: from polymers (0.1 W/mK) to diamond (10^3 W/mK). An investigation of thermal transport in materials has been underway for several decades compared to the much longer investigation of its electrical conductivity. There are some critical issues in many technologies because of the lack of attention to thermal transport [3; 4]. The current inability to control thermal transport has limited the development of cutting edge technologies both in industry and microelectronics as illustrated below.

In the industry application, for instance, hard coatings on machining tools (cutting and forming tools, etc.) and thermal barrier coatings on gas-turbine (jet engines, turboprop engines, etc.) are being used as a protective layer to increase their service life and improve efficiency and performance [3; 5]. Temperature in the tool-chip interface in metal cutting is high and was reported at approximately 1150° C at the end of the process for the cutting speed of 925 m/min [6]. High cutting temperatures have an influence on tool wear, tool service life, thermal deformation and softening of the cutting tool, tool oxidation rate, tool hardness and the friction condition of the tool-chip interface [6-8]. A coating with low thermal conductivity is desired to act as a heat-insulating layer to redirect heat flow into the chip and reduce heat transport to the metallic components, thereby protecting the tools against thermal overload [9-11]. It was reported that the life-time and performance of the tools coated by lower thermal conductivity coatings improve significantly [11; 12].

In microelectronics, there has been a noticeable progress of integrated circuit technology during the past two decades in which there is a shrinking of the size of electronic devices and increasing electronic elements in a chip. Since high density of electronic elements in the chip increases power density, more heat is generated [13-15]. Figure 1-1 shows the exponential increase of power density of microprocessor (CPU) versus the year and expected power density increases to reach the power density of the surface of the Sun in 2015 [4]. This indicates that the tuning thermal transport is a desperate need to dissipate heat from microelectronic components for further technological development. Thus, controlling thermal transport will be a big challenge for the microelectronics industry in the future.

Figure 1-1. Near-exponential growth and the expected power density of microelectronics components (CPU) versus year [4].

Thermoelectric (TE) effects are direct conversions between thermal and electrical energy by using holes and electrons as energy carriers. These effects have a useful potential for thermal management of microelectronics and

biological systems and waste heat recovery [16]. TE devices convert heat to electricity using charge (power generation devices) or using electricity to pump heat from cold to hot (refrigeration devices), both without using any bulk fluids and moving parts. The former refrigerators had environmental problems due to containing the hazardous chemical compound, chlorofluorocarbon (CFC) refrigerant. TE devices already exist; they are environmentally benign and do not have problems such as gas or liquid leakage, failure of moving parts in the compressor, or high electricity consumption. Currently, the use of TE devices is limited because their efficiency is low compared to the efficiency of a compressor-based refrigerator and generators [17]. The efficiency of TE devices is measured by ZT , which is called the thermoelectric figure of merit is defined as $ZT = S^2 \sigma T / K$, where S , σ and T are the Seebeck coefficient, electrical conductivity and absolute temperature, respectively, and K is the thermal conductivity. Materials with low thermal conductivity and high electrical conductivity have enhanced thermoelectricity [18]. High electrical conductivity and low thermal conductivity are desired to decrease Joule heating and sustain large temperature differences, respectively. Therefore, material selection is an important step to have highly efficient thermoelectric energy conversion. Materials with $ZT > 3$ can compete with conventional refrigerators and generators [19]. Since 1950, the room temperature ZT of bulk semiconductors increased slightly from around 0.6 to 1.0. Increasing of ZT is challenging due to the fact that the three parameters S , K and σ are interdependent and changing one of them alters the others. The effective way to increase ZT is to reduce

thermal conductivity without affecting S and σ , and this improvement can be achieved by using semiconductors of high atomic weight and alloying [19]. High atomic weight reduces the speed of sound and alloying increases phonon scattering in the materials and thereby decreases thermal conductivity. So the efficiency of a TE device is dependent on the materials used to fabricate the device, and tuning thermal transport is one of the efficient mechanisms of making it possible to use thermoelectricity as an energy conversion device [17].

1.2 Objectives

The points mentioned above and many other practical problems attracted much attention worldwide, and a huge effort has been focused on tuning thermal transport in the materials to make them user-specific. Therefore, the main objective of this work is to examine and understand the role of nanostructure in low dimension materials as a way of tuning thermal conductivity. Pulsed photothermal reflectance (PPR) and 3ω techniques are employed to measure thermal conductivity of the coatings and thin films. Particularly, the objectives of this thesis are:

- To reduce the thermal conductivity of Ti-based hard coatings such as TiN, TiAlN, TiAlSiN, and TiN/TiAlN multilayer. This is attempted through studying the influence of microstructure on the thermal conductivity of the coatings.
- To boost the ZT of thermoelectric film. The influence of Pt dopant on microstructure and thermal conductivity of n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ thin film is investigated.

1.3 Major contributions of the thesis

- Setup of the 3ω thermal conductivity measurement techniques. These systems are calibrated by measuring the known thermal conductivity of films and bulk materials.
- Studying the microstructure of TiN and the effect of incorporation of Al content in microstructure of TiN structure by X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) observation. Geometric phase analysis (GPA) is used to analyze the high resolution TEM micrographs to show the dislocations in the coatings. Thermal conductivity and diffusivity of TiAlN coatings were measured by pulsed photothermal reflectance (PPR) technique and they are found to be dependent on Al/Ti atomic ratio. The relationship between the microstructure (e.g. grain boundary effect, average crystallite size, preferential orientation) and thermal conductivity of these coatings has been studied. The reduction of thermal conductivity is described by increasing phonon scattering due to reducing grain size of the coatings and increasing dislocations in the coatings.
- Microstructure of TiAlSiN coatings with different (Al+Si)/Ti atomic ratios has been studied by XRD and TEM observation. Thermal conductivity and diffusivity of TiAlSiN coatings were measured by PPR technique. It is shown that the decrease in thermal conductivity of the TiAlSiN coatings could be attributed to the increased phonon scattering

due to the decrease in grain size of the coatings and formation of the nanocomposite structure, which consists of nano-crystalline TiAlN embedded in an amorphous SiN_x matrix.

- Thermal conductivity and diffusivity of [TiN/TiAlN]_n Multilayer coatings with different bilayer number n were measured by PPR technique. It is found that the thermal conductivity of the coatings depends on the number of bilayer and decreases by increasing n . In order to investigate the effect of the coating's microstructure and misfit dislocation at the layer interfaces on thermal conductivity, the microstructure and grain size of the coatings have been studied by XRD, TEM and HRTEM observation. Increasing phonon scattering at the interfaces between the TiN and TiAlN layers due to increasing misfit dislocation is responsible for reducing thermal conductivity of the coatings.
- Textured n -type Bi₂Te_{2.7}Se_{0.3} thermoelectric thin films with Pt nanoinclusions are prepared via pulsed laser deposition with different Pt content. Thermal conductivity of the thin films was measured by 3 ω technique. The TEM observation shows that the Pt nanoinclusions, with different size and distribution in a few to hundreds nanometer scale, are embedded at the grain boundaries of the semiconductor matrix. By introducing Pt nanoinclusions, the thermal conductivity is reduced and ZT is increased. The reduction in thermal conductivity can be attributed to increased phonon scattering due to increased grain boundaries.

1.4 Organization of the thesis

This thesis is structured into seven chapters. Chapter 1 gives a general background of thermal transport and discussion of how reducing thermal conductivity improves performance of hard coatings and thermoelectric materials. The motivation, objectives and major contribution of the thesis are stated in this chapter as well. In chapter 2, thermal characterization setup of pulsed photothermal reflectance and 3ω techniques are described in detail.

In chapter 3, the microstructure of TiN and TiAlN is studied and the relationship of the thermal conductivity of TiAlN coatings at different Al/Ti atomic ratios is reported. The effect of Al dopant in TiN coating is introduced as a method to reduce thermal conductivity of TiN. In chapter 4, the effect of incorporating Al and Si content in decreasing thermal conductivity of TiN and dependency of thermal conductivity of TiAlSiN coatings on (Al+Si)/Ti atomic ratio are studied.

Chapter 5 reports how the multilayer deposition and layer structure helps to decrease the thermal conductivity of the coatings. Thermal conductivity reduction in $[\text{TiN}/\text{TiAlN}]_n$ multilayer coating with different bilayer number (n) is described based on the coating structure. TEM and HRTEM observation and GPA are used to investigate the relation of thermal conductivity reduction and microstructure of the multilayer coatings.

Thermal conductivity of Pt-doped n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ thin films with different Pt content measured by 3ω technique is described in chapter 6. In this chapter,

the effect of nanoinclusions by introducing a Pt dopant in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ thermoelectric thin film is demonstrated as an efficient way to decrease the thermal conductivity as well. Finally, the last chapter provides the conclusions and recommendations for future research.

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Chapter 2: Thermal conductivity measurement

In this chapter, we will explain the techniques applied to measure thermal conductivity of the materials.

2.1 Pulsed Photothermal Reflectance technique

The technique used to measure thermal conductivity of Ti-based hard coatings such as TiN, TiAlN, TiAlSiN single layer coatings and [TiN/TiAlN]_n multilayer coatings is pulsed photothermal reflectance (PPR). Figure 2-1 shows the schematic diagram of PPR experimental setup. In this approach, thermal conductivity of the coatings is characterized in nanosecond regime by thermoreflectance technique. Keating applied the PPR technique first to measure thermal conductivity of SiO₂ thin films [20]. This technique is an optical and noncontact method consisting a pump laser and a probe laser. Before the measurement of thermal conductivity, a metal film, preferably gold

is deposited on top of the each sample surface for the purpose of enhancing heat absorption.

The pump laser is a Nd:YAG (532 nm) laser pulse with a full width at half maximum of 7 ns, pulse repetition rate of 10 Hz, , and pulse energy of 5 mJ. The measurement starts with the pump laser pulse with spot size of 3 mm incident on the sample surface that induces the sample's surface temperature change over time. The heated surface induces a change in refractive index on the surface [21]. The probe laser is a 1 mW He-Ne laser (632.8 nm) focused at the center of the pump spot with a 20 μm spot size to monitor the changes in the beam reflected from the gold surface. The temperature excursion of metal surface is measured through the temperature dependence of metal's reflectivity. Since for most metals, the thermorefectance coefficient $C_{tr}=\Delta R/(R_0\Delta T)$ where R_0 and T are a reference reflectivity and the metal temperature respectively) is about constant [21], the intensity of reflected probe beam is inversely proportional to the gold surface temperature. The intensity of reflected probe beam is measured using a 125 MHz photodiode and pre-amplifier. Temperature excursion profile depends on the thermal properties of the underlying layers and thermal resistance between the layers. Because the effective thermal diffusion length on the gold surface $2\sqrt{\alpha_{Au}\tau_{exp}}$ (where τ_{exp} is the measurement duration in the experiment to detect the surface temperature excursion and α_{Au} is the thermal diffusivity of gold) is much smaller than the spot size of the pump beam, the measurement can be completed before any significant lateral heat diffusion occurs. Therefore, the heat conduction problem can be modeled as

one dimension vertical heat diffusion in the three-layer (Au/film/substrate) structure.

Figure 2-1. Schematic diagram of the pulsed photothermal reflectance technique.

By solving the heat diffusion equation analytically, the thermal properties of a film can be extracted from its thermal response captured by the PPR technique. For a multilayer sample, for example n -layer, we need to solve n differential equations with $2n$ coefficients. Computation of $2n$ coefficient using Laplace transform technique in the frequency domain is complicated. Ang et al [22] has suggested the use of Laplace transform method to obtain a solution for a three-layer structure. The analytical solution for one dimensional heat conduction in a multilayer structure by transmission line theory was introduced by Hui and Tan [23; 24]. By using the transmission line theory, the frequency domain solution for a multilayer sample can be obtained. Then, inverse Laplace transform can be used to obtain the time domain solution [25].

2.1.1 The Transmission-Line technique

The transmission-line technique is a powerful method to solve heat equation problem. The comparison between the electrical conduction and heat conduction was well presented [26]. Hui et al. [23] discussed the details of how the transmission-line equations can be extracted by this comparison. The temperature excursion $\varepsilon(z, s)$ is the temperature rise above the ambient. The voltage $V(z)$ is equivalent to the $\varepsilon(z, s)$ and the current $I(z)$ is equivalent to heat flux $-k\partial\varepsilon(z, s)/\partial z$ where K and s are the thermal conductivity and frequency, respectively. From these comparisons and the heat conduction equation in frequency domain, the transmission-line equations can be obtained as follow [23]:

$$\frac{dV(z)}{dz} = -\frac{1}{K} I(z) \quad (2-1)$$

$$\frac{dI(z)}{dz} = -\rho cs V(z) \quad (2-2)$$

Where ρ and c are the density and specific heat respectively. Equation (2-1) is the definition of the heat flux and equation (2-2) is the heat conduction equation in one dimension. Consider a transmission-line terminated by load impedance as shown in Figure 2-2.

Figure 2-2. Transmission-line terminated in a load impedance Z_L with current source $Q(s)$

After differentiating the above equation with respect to z , and substituting, a voltage wave and a current wave equation can be obtained as follow:

$$\frac{dV^2(z)}{dz^2} - \gamma^2 V(z) = 0 \quad (2-3)$$

$$\frac{dI^2(z)}{dz^2} - \gamma^2 I(z) = 0 \quad (2-4)$$

The voltage and current analog the transmission-line for $z < 0$ can be described as:

$$V(z) = V^+(0)(e^{-\gamma z} + \Gamma(0)e^{\gamma z}) \quad (2-5)$$

$$I(z) = \frac{V^+(0)}{Z_c}(e^{-\gamma z} - \Gamma(0)e^{\gamma z}), \quad (2-6)$$

$$Z_c = \frac{1}{(K\gamma)}, \quad \gamma = \sqrt{\frac{s}{\alpha}}, \quad \alpha = \frac{K}{\rho c}$$

Where Z_c and α are the characteristic impedance and the thermal diffusivity respectively. $\Gamma(0)$, is the ratio of the reflection coefficient at $z=0$ and is defined as follow:

$$\Gamma(0) = \frac{V^-(0)e^{\gamma z_{z=0}}}{V^+(0)e^{-\gamma z_{z=0}}} = \frac{Z_L - Z_c}{Z_L + Z_c} \quad (2-7)$$

The corresponding impedance at $z=-d$ is given by:

$$Z_{in}(-d) = Z_c \frac{Z_L + Z_c \tanh(\gamma d)}{Z_c + Z_L \tanh(\gamma d)} \quad (2-8)$$

where Z_L is the thermal impedance of the rear surface of the film. The thermal conductivity and thermal diffusivity of the film with thickness d can be represented by transmission characteristics γ and Z_c . The current source $Q(s)$ corresponds to the heat pulse which strikes the film surface. According to transmission-line, the voltage at $z=-d$ or the surface temperature of a film is described as:

$$V(-d) = Q(s)Z_{in}(-d) \quad (2-9)$$

$Z_{in}(-d)$ for a single layer film is given by equation (2-8). For N layer structure, this is equivalent to N component transmission-line and the input impedance can be obtained by repeating the equation (2-8) [27].

$V(-d)$ corresponds to the temperature excursion in the frequency domain, $T(z, s)$. Inverse Laplace transform can be used to obtain the temperature excursion $T(z, t)$ in the time domain from the temperature excursion $T(z, s)$ in the frequency domain (equation (2-9)).

$$T(-d, t) = \frac{1}{2\pi j} \int_{\xi-j\infty}^{\xi+j\infty} T(-d, s) e^{st} ds \quad (2-10)$$

Numerical approximation method (Stehfest method [28]) can be employed to calculate the equation (2-10). Stehfest method is given as:

$$f(t) = \frac{\ln 2}{t} \sum_{n=1}^N c_n F\left(\frac{n \ln 2}{t}\right) \quad (2-11)$$

$$c_n = (-1)^{n+N/2} \sum_{k=(n+1)/2}^{\min(n, N/2)} \frac{k^{N/2} (2k)!}{(N/2 - k)! k! (k-1)! (n-k)! (2k-n)!} \quad (2-12)$$

And $F(s)$ is the Laplace transform of $f(t)$.

A Gaussian pulse is used for pulse shape function. $Q(s)$ is the Laplace transform Gaussian pulse of the Nd:YAG laser. The time domain and the Laplace transform of the Gaussian pulse are given in the Table 2-1.

Table 2-1. Gaussian pulse shape time distribution function and Laplace transform

Pulse shape	$Q(t)$	$Q(s)$
Gaussian	$\frac{1}{c\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{t-b}{c}\right)^2\right]$	$\frac{1}{2} \left[1 + \operatorname{Erf}\left(\frac{b}{c} - \frac{cs}{2}\right)\right] \exp\left[-bs + \frac{c^2 s^2}{4}\right]$

Figure 2-3 shows a typical Gaussian pulse of Nd:YAG laser. After the curve fitting of the experimental data with the Gaussian profile, the fitted values of our Nd:YAG pulse are $b=2.48 \times 10^{-8}$ s, $c=4.73 \times 10^{-9}$ s.

Figure 2-3. Typical Gaussian pulse of Nd:YAG laser.

A captured signal is normalized and inverted to extract thermal properties of the films. In order to measure thermal properties, we fit the experimental thermal

response data to the analytical solution of the heat diffusion equation (equation (2-10)). The least square technique is used for curve fitting. This technique mathematically is expressed as:

$$F = \sum_{i=\text{measurement time}} (T_{i,\text{experimental}} - T_{i,\text{model}})^2 \quad (2-13)$$

where $T_{i,\text{experimental}}$ and $T_{i,\text{model}}$ are the data points of the experimental surface temperature and the data point of the modeled surface temperature respectively at time t_i . F is the sum of the square of the difference between the experimental data and the modeled data over the entire measurement time domain. The minimum of the function F can be obtained by changing the thermal properties of the film in the T_{model} . We used the Matlab software by utilizing their built-in functions for seeking the minimum point of F and obtain the curve fitted values.

2.1.2 Analytical solution for PPR applied to composite samples

2.1.2.1 Two-layer composite sample with thermal resistance

Transmission line theory can be used to obtain analytical solutions of heat conduction equation for the surface temperature of two and three-layer composite samples [27]. Figure 2-4 shows the schematic diagram of two and three-layer samples.

Figure 2-4. (a) Two-layer composite sample. (b) three-layer composite sample.

A two layer composite sample is equivalent to two section transmission-line. The interface between the gold film and the substrate can be modeled as a thermal resistance (R_{th}) in series with the two components in the transmission-line. The surface temperature excursion in frequency domain can be described by [27]:

$$T(s) = \frac{Q(s)}{e_1 \sqrt{s}} \left[\frac{\cosh(\eta_1 \sqrt{s}) + e_{21} \sinh(\eta_1 \sqrt{s}) + R_{th} e_2 \sqrt{s} \cosh(\eta_1 \sqrt{s})}{\sinh(\eta_1 \sqrt{s}) + e_{21} \cosh(\eta_1 \sqrt{s}) + R_{th} e_2 \sqrt{s} \sinh(\eta_1 \sqrt{s})} \right] \quad (2-14)$$

where $e_i = \sqrt{\rho_i c_i K_i}$, $e_{ij} = e_i / e_j$, $\eta_i = d_i / \sqrt{\alpha_i}$, $i = 1, 2$. ρ , c , K , α and d are the bulk density, specific heat, thermal conductivity, thermal diffusivity, and the thickness of each layer, respectively. The indices 1 and 2 stand for the gold film and the substrate respectively. R_{th} is the thermal resistance at the interface between the gold film and the substrate.

2.1.2.2 Three-layer composite sample

Three-layer sample equals a three section transmission-line. The surface temperature excursion in frequency domain when the boundary thermal resistance between layers is negligible, is given by [27]:

$$T(s) = \frac{Q(s)}{e_1 \sqrt{s}} \quad (2-15)$$

$$\left[\frac{(cosh \eta_2 \sqrt{s} + e_{32} sinh \eta_2 \sqrt{s}) cosh \eta_1 \sqrt{s} + (e_{31} cosh \eta_2 \sqrt{s} + e_{21} sinh \eta_2 \sqrt{s}) sinh \eta_1 \sqrt{s}}{(e_{31} cosh \eta_2 \sqrt{s} + e_{21} sinh \eta_2 \sqrt{s}) cosh \eta_1 \sqrt{s} + (cosh \eta_2 \sqrt{s} + e_{32} sinh \eta_2 \sqrt{s}) sinh \eta_1 \sqrt{s}} \right]$$

the surface temperature excursion in frequency domain with considering the thermal boundary resistance between the layers, is given by [29]:

$$T(s) = \frac{Q(s)}{e_1 \sqrt{s}} \quad (2-16)$$

$$\left[\frac{(cosh \eta_2 \sqrt{s} + e_{32} sinh \eta_2 \sqrt{s}) cosh \eta_1 \sqrt{s} + (e_{31} cosh \eta_2 \sqrt{s} + e_{21} sinh \eta_2 \sqrt{s}) sinh \eta_1 \sqrt{s} + R_1 cosh \eta_1 \sqrt{s} (e_3 \sqrt{s} cosh \eta_2 \sqrt{s} + e_2 \sqrt{s} sinh \eta_2 \sqrt{s}) + R_2 (e_3 \sqrt{s} cosh \eta_1 \sqrt{s} cosh \eta_2 \sqrt{s} + e_{31} e_2 \sqrt{s} sinh \eta_2 \sqrt{s}) sinh \eta_1 \sqrt{s} + R_1 R_2 e_3 e_2 s cosh \eta_1 \sqrt{s} sinh \eta_2 \sqrt{s}}{(e_{31} cosh \eta_2 \sqrt{s} + e_{21} sinh \eta_2 \sqrt{s}) cosh \eta_1 \sqrt{s} + (cosh \eta_2 \sqrt{s} + e_{32} sinh \eta_2 \sqrt{s}) sinh \eta_1 \sqrt{s} + R_1 sinh \eta_1 \sqrt{s} (e_3 \sqrt{s} cosh \eta_2 \sqrt{s} + e_2 \sqrt{s} sinh \eta_2 \sqrt{s}) + R_2 (e_3 \sqrt{s} sinh \eta_1 \sqrt{s} cosh \eta_2 \sqrt{s} + e_{31} e_2 \sqrt{s} cosh \eta_1 \sqrt{s}) sinh \eta_2 \sqrt{s} + R_1 R_2 e_3 e_2 s sinh \eta_1 \sqrt{s} sinh \eta_2 \sqrt{s}} \right]$$

where $e_i = \sqrt{\rho_i c_i K_i}$, $e_{ij} = e_i / e_j$, $\eta_i = d_i / \sqrt{\alpha_i}$, $i = 1, 2, 3$. ρ , c , K , α and d are the bulk density, specific heat, thermal conductivity, thermal diffusivity, and the thickness of each layer, respectively. The indices 1, 2 and 3 stand for the gold film, the film with unknown thermal conductivity, and the substrate respectively. R_1 is the thermal resistance between gold layer and film, and R_2 is the thermal resistance between the film and substrate.

2.1.3 Calibration

In order to calibrate the PPR technique, the three-layer model is applied to measure thermal conductivity of known thermal conductivity of 1 μm thick thermally grown SiO_2 film on Silicon substrate. The sample was evaporated with 5 nm titanium and 1 μm gold to enhance the heat absorption and obtain the thermorefectance response. Since the thermal resistance between the SiO_2 and the silicon (R_2) and between the SiO_2 and gold (R_1) is about two orders of

magnitude lower than the internal volume resistance ($d_{\text{SiO}_2}/K_{\text{int}}$) [30], equation (2-15) is used for curve fitting for the captured temperature profile. In the curve fitting process, three parameters –thermal conductivity of the gold and SiO_2 film and thermal diffusivity of SiO_2 film– were varied and least square optimization method was applied to minimize the difference between the normalized surface temperature profile and the three-layer model.

Figure 2-5 shows the normalized surface temperature profile and fitted curve using the three-layer model. The average thermal conductivity of gold is 273 ± 28 W/mK, about 86% of the bulk's value (317 W/mK). The size effect comes from the surface and grain boundary scattering which reduces the thermal conductivity of gold film. It was reported that the thermal conductivity of gold film is dependent on film thickness [31; 32]. The obtained thermal conductivity and diffusivity for SiO_2 film are 1.15 ± 0.19 W/mK and $(1.03 \times 10^{-6} \pm 2.4 \times 10^{-7})$ m^2/s , respectively. The result is consistent with the previous thermal conductivity measurement of SiO_2 film obtained by the 3ω technique [33]. In the curve fitting program, the bulk value of density 19300 kg/m^3 and specific heat 129 J/kgK are used, since these parameters do not change much with thickness [34]. The thermal properties of the silicon substrate are taken from the reference [35].

Figure 2-5. Transient surface temperature for Au/1 μm SiO₂/Si substrate.

2.2 3ω technique

Corbino [36; 37] in 1911 noticed that when a current at frequency ω runs through a resistor, in addition to a voltage across the resistor at frequency ω , the third-harmonic voltage (3ω) appears in the resistor. This effect is a consequence of the temperature dependence of resistivity. Later, it was found that the third-harmonic voltage has a practical application to measure the thermal properties of solids and liquids [38-40]. In this technique, a thin metal wire is used to heat the specimen indirectly and the same wire serves both as a heater and thermometer. The 3ω technique, was developed by Cahill and Pohl in 1987 [41] and now it is a familiar technique for thermal conductivity measurement on bulk and thin film. The method used is based on heat diffusion in a semi-infinite solid as shown in Figure 2-6. A thin electrically conductive wire is deposited on top of solid-state specimen whose thermal conductivity needs to be measured.

Figure 2-6. Schematic diagram of conductive wire deposited on top of solid for thermal conductivity measurement. This wire acts as a heater and thermometer.

In most thermal conductivity measurement techniques, heat is applied at a known rate and the temperature is monitored to deduct the thermal conductivity. In this method, the deposited wire acts as a heater and thermometer simultaneously when a sinusoidal current at frequency (ω) is running in the wire. The heater frequency is adjusted in such a way that the penetration depth of heat is smaller than the thickness of the solid. In this way heat diffusion equation in cylindrical coordinate can be used,

$$A \frac{\partial T(r, t)}{\partial t} = \frac{\alpha}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T(r, t)}{\partial r} \right) \quad (2-17)$$

where α is thermal diffusivity. In a sinusoidal heat source, equation (2-18) assumes to be a solution of equation (2-17):

$$T(r, t) = T_0 + \Delta T \exp(i2\omega t) \quad (2-18)$$

where ω is circular frequency, T_0 is constant temperature and independent of frequency and, ΔT is the temperature oscillation. The temperature oscillation depends on the several parameters such as the distance r from a wire, the geometry of the wire, the thermal conductivity of the substrate K_s , the boundary

condition and the penetration depth $\frac{1}{q} = \sqrt{\frac{\alpha}{2\omega}}$, where α is the thermal diffusivity.

The temperature oscillation decays with increasing distance from the heat source. The amplitude ΔT is given by Carslaw and Jaeger [42]:

$$\Delta T(r) = \frac{P}{\pi l K} \Psi_0(qr) = \frac{P}{\pi l K} \int_0^\infty \frac{\sin^2 u}{u^2} \frac{du}{(u^2 + iq^2 r^2)^{1/2}} \quad (2-19)$$

where P is the amplitude of power applied to the wire, l is the length of the wire, K is thermal conductivity of the underlying solid, Ψ_0 is the zero order modified Bessel function, $1/q$ as mentioned above is the thermal penetration depth, the depth that heat diffuses during one cycle of the AC power heating. In the limit where $|qr| \ll 1$, the temperature oscillation at the surface of the sample can be written as:

$$\Delta T = \frac{P}{\pi l K} \left\{ \frac{1}{2} \ln \left(\frac{\alpha}{r^2} \right) + \ln 2 - 0.5772 - \frac{1}{2} \ln(2\omega) - \frac{i\pi}{4} \right\} \quad (2-20)$$

The result has a real part (in-phase oscillation) and imaginary part (out-of-phase oscillation). The real part is dependent on heating frequency while the imaginary part is independent on it. Cahill et al. [41] experimentally showed that the thermal conductivity measurement based on in-phase is more reliable than that based on out-of-phase response. By measuring in-phase temperature oscillation in two frequencies, we are able to obtain the thermal conductivity of the underlying solid from following relation:

$$K = \frac{P}{2\pi l} \left(\frac{\ln(\omega_2/\omega_1)}{\Delta T_{\omega_1} - \Delta T_{\omega_2}} \right) \quad (2-21)$$

Unlike other photothermal measurement technique, knowledge of the thermal diffusivity of the materials is not needed. Thermal conductivity of underlying

surface can be determined by measuring temperature oscillation at the surface at two different frequencies.

2.2.1 The sensor

The method to measure temperature oscillation on the surface experimentally can be done by passing a current, $I(t)=I_0\cos(\omega t)$, on the deposited wire. The electrical power $P(t)=I^2R$ (Joule heating) fluctuates at 2ω . The fluctuation of electrical power causes temperature fluctuation in the wire at 2ω . Temperature fluctuation with 2ω results in fluctuating electrical resistance at 2ω . Therefore, the electrical resistance of the wire is,

$$R = R_0(1 + TCR \cdot \Delta T \cos(2\omega t)) \quad (2-22)$$

where TCR is the temperature coefficient of resistance of the wire. Thus, the voltage drop across the wire is given.

$$\begin{aligned} V = IR &= I_0 \cos(\omega t) R_0 (1 + TCR \Delta T \cos(2\omega t)) \\ &= I_0 R_0 \cos(\omega t) + \frac{1}{2} I_0 R_0 TCR \Delta T (\cos(3\omega t) + \cos(\omega t)) \end{aligned} \quad (2-23)$$

As shown in the above equation, the temperature oscillation on the surface can be obtained by measuring the third harmonic voltage ($V_{3\omega}$).

$$\Delta T = 2 \frac{dT}{dR} \frac{R_0}{V_0} V_{3\omega} = 2 \frac{V_{3\omega}}{TCR V_0} \quad (2-24)$$

By measuring the first and third harmonic voltage and the relative change of resistance of the wire versus temperature, the temperature oscillation can be obtained as a function of frequency. Now, if we combine the theoretical ΔT

(equation (2-21)) and experimental ΔT (equation (2-24)), the thermal conductivity of underlying solid can be given as follow.

$$K = \frac{V^3}{4\pi R^2 l} \left[\frac{TCR \ln \frac{\omega_2}{\omega_1}}{(V_{3\omega_1} - V_{3\omega_2})} \right] \quad (2-25)$$

where $V_{3\omega_1}$ and $V_{3\omega_2}$ are the in-phase third harmonic voltage at frequency f_1 and f_2 . Figure 2-7 shows the third harmonic voltage versus the frequency for 1 mm thick quartz slide. The obtained thermal conductivity for 1mm quartz is 1.43 W/mK. Thermal conductivity is determined by measuring third harmonic voltage at $f_1=700$ Hz and $f_2=1000$ Hz using equation (2-25).

Figure 2-7. Typical $V_{3\omega}$ versus frequency for 1mm thick quartz. The wire width and length are 10 μm and 1mm respectively.

Heating frequency selection is needed to have large penetration depth compared with wire width (2b), then, the line heat source approximation is valid and we can use the cylindrical heat diffusion equation (2-17). Also, because the sample is not infinite, the heating frequency should be adjusted large so that penetration

depth should be smaller than the thickness of underlying solid. In this way, a semi-infinite solid approximation can be used.

2.2.2 Thermal conductivity measurement of bulk and film

The 3ω technique was designed to measure the thermal conductivity of bulk solid and then Cahill extended the technique to measure thermal conductivity of thin film on substrate [43]. There are two ways to measure thermal conductivity of thin film on substrate. One is the slope method and another one is the differential method [44]. In both methods, heat conduction across the film is assumed one dimensional. To satisfy this assumption, several requirements have to be established as follow:

- Wire width should be larger compared to the film thickness, but should be smaller compared to the thermal penetration depth for line heat source approximation.
- Substrate's thermal conductivity should be higher than that of the thin film.
- Heating frequency should be adjusted in such a way that thermal penetration depth is much larger than the thickness of the film.

Figure 2-8 shows the cross section of the heat flow in the sample and geometry of the sample.

Figure 2-8. Heat flow for a low thermal conductivity film on high thermal conductivity substrate. In this case $K_f \ll K_s$ and $d_f \ll 2b$.

2.2.2.1 Slope method

Cahill and Pohl [41] showed a solution for equation (2-19) under an approximation for the condition that the penetration depth is much larger than the wire width ($q^{-1} \gg b$). Under this approximation, solution of the equation (2-19) is given as [45]:

$$\Delta T = \frac{P}{\pi l K} \left\{ \frac{1}{2} \ln \left(\frac{\alpha_{th}}{b^2} \right) + 0.923 - \frac{1}{2} \ln(2\omega) \right\} = \frac{P}{\pi l K} \left(-\frac{1}{2} \ln(2\omega) + const \right) \quad (2-26)$$

where b is the half of the wire width and $const$ is an expression independent of the frequency. In practice, we can obtain the temperature oscillation in a wide range of frequencies and then thermal conductivity of the solid can be calculated from the slope of the temperature oscillation versus frequency.

If the wire is deposited at the surface of the film on substrate, the experimental temperature oscillation at the surface, ΔT_{total} , has two components. One is from the substrate, ΔT_{Sub} , and the other is from the film, ΔT_{film} . When all the above requirements are established, the temperature drop across the film is independent on frequency. The temperature oscillation on the film/substrate ΔT_{total} is sum of the temperature oscillation of the substrate ΔT_{Sub} and

temperature oscillation of the film ΔT_{film} . Then, the temperature oscillation of the film is given by the following relation:

$$\Delta T_{film} = \Delta T_{total} - \Delta T_{Sub} \quad (2-27)$$

The temperature oscillation of the substrate is obtained from equation (2-26).

Then, the film thermal conductivity is calculated as

$$\Delta T_{film} = \frac{P d_f}{2lb K_{film}} \quad (2-28)$$

Where d_f and K_{film} are the thickness and thermal conductivity of the film, respectively.

2.2.2.2 Differential method

In the differential method, we need at least two samples to measure thermal conductivity of film. One sample is a film on substrate and the other is only the bare substrate (reference sample). ΔT_{total} and ΔT_{Sub} can be obtained from the first and second sample, respectively. Then, the thermal conductivity of film

$$K_{film} = \frac{d_f}{2lb} \cdot \frac{1}{((\Delta T/P)_{total} - (\Delta T/P)_{Sub})} \quad (2-29)$$

can be calculated from the following equation

The temperature oscillation is measured at the same power input by similar wire deposited on the film/substrate and reference sample. However, this method needs two sets of measurements; the film thermal conductivity measurement from equation (2-29) is insensitive to the substrate thermal conductivity.

Conductive samples such as solid and film on substrate must be also electrically insulated from the wire. In this case, the differential method is suitable to measure thermal conductivity of conductive film, because it is insensitive to the thermal conductivity of substrate and insulating layer.

2.2.3 Sample preparation

The first step in the sample preparation is the deposition of the gold wire on the surface of the samples. The gold wire is 1 mm long with various widths and the thickness around 150 nm and is fabricated with the lift-off process by spin coating and patterning by photoresist AZ5214E. A 5nm Ti layer is deposited between sample and gold wire to improve adhesion on the surface by electron beam evaporator. Then, the wire is released by lift off in acetone, methanol and DI water. The resistance of the gold wire is around 10-30 Ohm at room temperature. Scanning electron microscope (SEM) is used to measure the width and length of the wire. Figure 2-9 shows a SEM image of an array of gold wires with linewidth of 10 μm on the surface of the sample. After the gold wire deposition, the sample is placed in 28-pin package using thermal epoxy. Electrical connections to the gold wires have been made by commercial gold wirebonder as shown in Figure 2-9. Figure 2-10 shows a package sample ready for experiment.

Figure 2-9. SEM image of an array of gold wires on the surface of samples. The wire width and length are 10 μm and 1 mm, respectively. In this image electrical connection to a 10 μm wide wire was made using commercial gold wire bonder and gold wires.

Figure 2-10. Samples placed in 28-pin package and electrical connections are made by commercial gold wirebonder.

2.2.4 Experimental set-up, calibration and measurement

The sample packages were placed on the copper sample holder with thermal conducting epoxy in a closed cycle helium Cryostat (Janis CCS 150). The

thermal conductivity measurement can be done in vacuum. The pressure inside the Cryostat was adjusted around 10^{-6} torr and the temperature was controlled by commercial temperature controller (lakeshore 330) with accuracy 0.1 K during the measurement.

It is a big challenge to measure the third harmonic voltage accurately in 3ω technique. Figure 2-11 shows schematic diagram of the experimental set-up. The lock-in amplifier with output impedance $50\ \Omega$ is supplying a sinusoidal signal as the input to the device. The sample to be measured (R_h) is placed in one of the branches of Wheatstone bridge. In the other branches, there are three resistances R_1 , R_2 of fixed values and R_3 is a variable resistance.

Figure 2-11. Schematic circuit diagram of 3ω experimental setup. R_h is the resistance of the deposited gold wire on the sample. Sample is placed in the cryostat.

Cancellation of 1ω voltage can be done using the bridge connected to the differential input ($V_A - V_B$) of the lock-in amplifier. This can be done by adjusting the variable resistance R_3 in the bridge until the measured 1ω voltage by lock-in amplifier is minimum and in the range of 1 mV. The wire deposited

on the sample can act as a source of the third harmonic voltage and the third harmonic voltage across the wire is then measured by lock-in amplifier. The relation between the third harmonic voltage across the wire and measured third harmonic voltage by lock-in amplifier is given as follow:

$$V_{3\omega_{wire}} = \frac{R_h + R_1}{R_1} v_{3\omega}^{measured} \quad (2-30)$$

The temperature coefficient of resistance of wire is measured by temperature sensor located inside the Cryostat and temperature monitor with a resolution of 0.1 K. Thermal epoxy was applied to improve the contacts and we assume that the temperature at the top of the sample is same as the variation of temperature at the temperature controller. Figure 2-12 shows a typical resistance of the gold wire as a function of temperature to measure the TCR of the gold wire.

Figure 2-12. Resistance of deposited wire as a function of temperature to measure the TCR.

2.2.5 Calibration

Several calibrations were carried out. The first calibration is the thermal conductivity measurement of known thermal conductivity value of bulk samples. Figure 2-13 shows the fitted curve and the temperature oscillation of

the deposited gold wire on the quartz slide as a function of heating frequency.

The other measurements are listed in Table 2-2.

Figure 2-13. the fitted curve and the temperature oscillation of the in-phase component versus frequency for 1 mm thick quartz.

Table 2-2. Thermal conductivity of bulk materials measured with the 3ω technique at room temperature and compared with handbook values [35].

Thermal conductivity	Glass	Quartz	Si
Measured (W/mK)	1.1 ± 0.1	1.3 ± 0.10	148 ± 10
Handbook (W/mK)	1.1	1.4	152

Beside the thermal conductivity measurement of bulk samples, we measured the thermal conductivity of 210 nm thick sputtered SiO_2 thin film on silicon using the slope method. The obtained thermal conductivity of the film is 1.07 ± 0.11 W/mK and the result is consistent with the previous measurement [33]. Figure 2-14 shows the temperature oscillation of the in-phase component as a function of frequency for SiO_2 thin film on Si substrate. The thermal conductivity of SiO_2 thin film is calculated using equation (2-28).

Figure 2-14. Temperature oscillation versus heating frequency for 210 nm thick SiO₂ on Si substrate. Temperature oscillation of Si substrate is calculated based on the equation (2-26) with thermal conductivity of Si 148 W/mK.

2.2.6 Uncertainty of the measurement

There are several uncertainties and errors in the 3ω technique to measure thermal conductivity of bulk and film on substrate. For instance, for the case of a film on substrate, the calculated thermal conductivity is dependent on the width, length, resistance, and the temperature change with the resistance of the wire, the film thickness, the heating voltage (1ω) and 3ω voltage across the wire and the thermal conductivity of the substrate. These parameters cause the overall error and uncertainty in the thermal conductivity measurement of the film.

In order to calculate the uncertainty, we used a method presented by Kline and McClintock [46]. Based on this method, if the result, y , is a function of the independent variable ($x_1, x_2, \dots, x_n$), the uncertainty u_y is given by

$$u_y = \sqrt{\left(\frac{\partial y}{\partial x_1} u_1\right)^2 + \left(\frac{\partial y}{\partial x_2} u_2\right)^2 + \left(\frac{\partial y}{\partial x_3} u_3\right)^2 + \dots + \left(\frac{\partial y}{\partial x_n} u_n\right)^2} \quad (2-31)$$

where, $(u_1, u_2, \dots, u_n)$ are a corresponding uncertainties of the variable $(x_1, x_2, \dots, x_n)$. The variables with uncertainty in the thermal conductivity measurement of the film on substrate are the resistance (R), length (l), width ($2b$), and temperature change with the resistance (dT/dR) of the deposited wire on the film, the 1ω and 3ω voltage across the wire, the thickness of the film (d) and the thermal conductivity of the substrate (K_{sub}). All the uncertainties of the thermal conductivity measurements were calculated based on this method. Table 2-3 shows the uncertainty analysis and calculated error for thermal conductivity measurement of 210 nm thick sputtered SiO_2 thin film on silicon substrate. Thermal conductivity of the SiO_2 on Si is 1.07 ± 0.11 (W/mK) with about 10% uncertainty at room temperature.

Table 2-3. Uncertainty analysis for thermal conductivity measurement of 210 nm thick sputtered SiO_2 thin film on silicon substrate at room temperature.

Parameters	Nominal Value	$u_i (\pm)$
dT/dR	18.6 K/ Ω	0.3
b	6 μm	0.5
l	1 mm	0.005
K_{sub}	148 W/mK	10
d	210 nm	5
R	26.83 Ω	0.01
V_{ω}	0.629 V	0.001
$V_{3\omega}$	246 μV	5
K_{film}	1.07 (W/mK)	0.11

Chapter 3: Thermal Conductivity of TiAlN coatings

3.1 Introduction

In order to improve the performance and service life of cutting and forming tools, nitrides of binary metal alloy coatings are coated on them, resulting in a higher hardness and toughness. Today, there is a wide range of physical vapour deposition hard coatings for different applications [47; 48]. Ti-based hard coatings (e.g. TiN and TiAlN) are well known hard coatings in industry applications, typically deposited by PVD [49; 50]. TiAlN shows excellent mechanical properties, such as high hardness, oxidation resistance and excellent thermal stability, and the use of this coating has increased rapidly, in comparison to TiN [51-56]. Knowledge of the mechanical and physical properties is essential to improve the design of better coatings for industry applications. For example, microstructure, thermal properties, hardness,

toughness, and oxidation resistance are important requirements that always should be considered.

It was shown that Al incorporation in TiN structure increases the oxidation resistance and hardness of the new TiAlN coatings. Knotek et al. [57] reported that the oxidation resistance of TiAlN coating is increased by the forming of a passive Al_2O_3 layer through diffusion of Al atoms to the coating surface, which protected the coating from further oxidation. Suzuki et al. [58; 59] studied the effect of the incorporation of Al atoms on hardness of TiN coating prepared by cathode arc and ion beam assisted techniques. By substitution of Al atom to Ti atom in the TiN structure, the lattice parameter of TiN gradually decreases with the amount of Al atoms, and thus the hardness of the coating is increased. However, when the Al content in the TiAlN coating is increased more than about 60 at.%, the phase transition occurs and the two-phase mixture (face-centered cubic (fcc) structure of TiN and hexagonal wurtzite structure of AlN) appears, the hardness of the coating is reduced. The phase transition in the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coating prepared by various techniques was investigated, and it was reported that the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings have a two-phase mixture consisting of fcc and wurtzite structural phases when the Al content is more than about 60 at.% ($x \sim 0.60$) [58-62].

Beside the protection requirement against wear and oxidation, thermal properties, and especially the thermal conductivity of hard coatings, plays an important role in their performance. For instance, materials with high thermal conductivity are required for electronic devices in order to dissipate heat and act

as a heat sink. Materials with low thermal conductivity are required for hard coatings in order to reduce the heat transported from the hot to cold sides and act as heat insulation. In high-speed machining, hot forging and casting, temperature at the tool-chip interface moves up, and this affects various tooling parameters (e.g. material softening [7], friction condition and tool deformation [6]) and coating formation and properties (e.g. oxidation rate, hardness and thermal conductivity). A lower thermal conductivity of the hard coating is desired as a barrier layer to delay the temperature rising on the tool substrate materials and redirects heat flow into the chip and to dissipate the heat from the chip. This effect helps to reduce heat transport to the metallic components and thereby protects the tools against thermal overload [9-11].

Up to now, many studies on Ti-based hard coatings have been focused on the mechanical and tribological properties, and only a few reports can be found in the literature about their thermal properties. Taylor et al. [63] measured the thermal conductivity of bulk TiN using flash diffusivity and radial heat flow diffusivity techniques in a wide temperature range. The obtained thermal conductivity of bulk TiN is 27 (W/mK) in the temperature from 200° C to 2000° C. Aivazov et al. [64] similarly showed that the thermal conductivity of TiN is independent in temperatures ranging from 77 to 1100 K. Martan et al. [65] studied the thermal conductivity of Ti-based hard coatings on high speed cutting stainless steel prepared by arc sputtering. Pulsed photothermal radiometry was used to measure thermal conductivity of the coatings. They reported that thermal conductivity of TiN and TiAlN (average Al/Ti atomic

ratio is 0.5) is 12 W/mK and 5.5 W/mK, respectively. Srinivasan et al. [66] measured thermal properties of TiAlN thin films on silicon substrate deposited with various N₂ flow rates using reactive DC magnetron sputtering. They reported an increase in thermal diffusivity and conductivity with increasing N₂ flow rates, and the measured values show that the thermal properties of the TiAlN films are much lower than the TiAlN bulk materials.

In order to reduce heat transport in TiN coating, Al is incorporated in the coating because of the following reasons:

- a) Microstructure of films, especially the grain size of the films has an important role to determine thermal properties such as thermal conductivity. Phonon transport represents heat transport in crystalline solids and phonon scattering determines the mean free path of phonon. Based on the kinetic theory, thermal conductivity of the materials is proportional to mean free path (MFP) of phonons, l , phonon velocity, v , and specific heat per unit volume, C , $K \sim Cvl$ [67]. Tuning heat capacity to change thermal conductivity is difficult because we need to modified dispersion relation [67]. The phonon velocity is proportional to elastic stiffness (related to chemical bonding, Y) and the mass density of atoms, M . $v = (Y/M)^{1/2}$. Changing v in a given sample is difficult as well. The efficient method to tune thermal transport in a given sample is mean free path of phonon. Defect and impurity atoms, which can be introduced in the form of dopant atoms or an alloy, in the lattice scatter phonon and reduce its mean free path and leads to lower thermal conductivity [68].
- b) TiN and TiAlN are the first and second generation hard coatings, respectively. TiAlN coating with different Al content can be fabricated easily by various method such as target material composition, plasma ionization setting and evaporation rate [69-71]. The microstructure of

TiAlN coating depends strongly on Al content, at low Al content the metallic nitride coatings would have cubic structure and at high Al content, hexagonal structure is observed in the coating. Kimura et al [72] studied the microstructure of TiAlN coatings with respect to variation in Al content. They reported that in $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coating, the columnar structure is disappeared and the grain size is decreased by increasing the Al content in the coating. This effect is consistent with our microstructure analysis of TiN and TiAlN coatings (see results and analysis section). Disappearing columnar structure and reducing grain size in TiAlN coating increase phonon scattering and results in decreasing mean free path of phonons. Consequently, in comparison to TiN, TiAlN has smaller grain size and lower thermal conductivity results in reducing thermal loading of the coated tools and more heat is dissipated via chip removal.

- c) Beside the effect of decreasing thermal conductivity of TiN with incorporation of Al, it was reported that the hardness and performance of the coatings is improved with the amount of Al atoms [73]. Oxidation resistance of the TiAlN coating is increase due to the formation of a promise Al_2O_3 layer through diffusion of Al atoms to the coating surface, which protected the coating from further oxidation [57] and tools coated by TiAlN show longer tool life at higher cutting speed [74].

The effect of how different Al content in TiN structures can influence the thermal conductivity of TiN coatings has not been addressed. Therefore, the purpose of this work is to investigate the thermal conductivity measurement of TiAlN coatings with different Al/Ti atomic ratios deposited on stainless steel. The thermal characterization was carried out by pulsed photothermal reflectance (PPR) technique at room temperature. The microstructure of the coatings was analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The variation of coatings' thermal conductivity with

different Al/Ti ratios will be discussed by focusing on the analysis of the microstructure.

3.2 Experiment

Ti-based hard coatings were deposited by a Platin π^{80} lateral rotating cathode arc (LARC) system in a pure nitrogen atmosphere. Figure 3-1 shows the schematic diagram of the LARC system. Jilek et al. [75] studied the advantage of LARC deposition over conventional arc deposition techniques by comparing the wear test of the tools coated by both systems. They showed that the tools deposited using the LARC technique has better wear resistance and a longer life-time compared to the tools deposited by the conventional arc deposition technique. There are two advantages of using the LARC system: first, uniform target erosion during the deposition because of the unique design of the cathodes; and the second advantage is the Virtual Shutter, which allows the target cleaning prior to coating deposition without contaminating the substrate surface. The specially designed, turnable magnetic field allows target evaporation to be directed away from the sample holder and substrates prior to deposition, as shown in Figure 3-1 (b). After the completion of the target cleaning process, without interruption of the plasma, the magnetic field guides the arc spot to face the samples holder and substrates for deposition. This unique design results in smooth surface and super adhesion strength of the coatings.

Figure 3-1 (a) Schematic diagram of the lateral rotating arc (LARC) deposition system. The deposition system comprises of two lateral rotating cathodes. One is elemental cathodes of Ti and another is Al or alloyed cathodes AlSi depending on coating requirements. (b) Target cleaning before deposition process without contaminating the substrates. In this stage 1) tube shutter is closed to protect the substrate from dust of the target cleaning. 2) Arc is burning towards the back and virtual shutter is on, (c) Smooth deposition with clean target. In this stage 1) Tube shutter is open. 2) Arc is burning towards the substrates and virtual shutter is off.

A series of TiAlN coatings, with a thickness around 3 μm , were deposited by a Platit π^{80} lateral rotating cathode arc (LARC) system. One Ti and one Al elemental cathode, which were laterally rotating during coating deposition, were used in this work. The atomic ratio of Al/Ti in the as-deposited coatings could be controlled by changing the DC current applied on the two cathodes (Ti and Al). I_{Al} and I_{Ti} were changed in opposite directions between 0 and 125 A with different current ratio of $I_{\text{Al}}/I_{\text{Ti}}$. Mirror-finished stainless steel AISI 304 (SS) coupons with a dimension of $2.5 \times 2.5 \text{ cm}^2$ and 1 mm thickness were used as coating substrates. The substrates were cleaned ultrasonically in a series of

alkaline solutions, washed in deionized water, dried by blowing nitrogen gas and then dried in an oven at 100° C. Then, the pre-cleaned substrates were placed on the carousel sample holder, which rotated continuously around the vertical axis at a speed of 12 rpm. The coating deposition was conducted in a flowing pure nitrogen atmosphere with a working pressure controlled at 1.5 Pa. During deposition, a negative DC bias of -70 V was applied to the substrates, and the substrate temperature was controlled at around 480° C. The thickness of the coatings was measured by using Tencor P10 surface profiler meter.

The coatings' composition was measured by energy dispersive analysis of X-rays (EDX), which is attached to a scanning electron microscope at 8 KeV and the INCA quantitative analysis software. The XRD measurements were performed on a Burker AXS D8 Advance X-ray diffractometer by using a Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$, 40 KV, 40 mA) under θ -2 θ scan mode in a 2θ range from 30° to 80°.

Sample preparation for cross-sectional transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) observations were performed using a focused ion beam (FIB) DA300 system from FEI. TEM images were taken on the cross-section microstructure of the coatings using a Tecnai X-TWIN system from FEI, working at 200 kV. The dark field STEM images were taken using a Fischione high angle annular dark field (HAADF) detector.

HRTEM image was used to identify the dislocation in the coating based on Fast Fourier transformation (FFT) and Geometric phase analysis (GPA). GPA is an

image-processing technique sensitive to small displacements of the lattice fringes in HRTEM images [76; 77]. FFT and GPA of high resolution micrographs were analyzed with the Digital Micrograph software (version 3.11.1 Gatan). Bragg filtered image is generated by applying spot mask to spots in the FFT of the HRTEM images. Afterwards, the FFT image was inverse Fourier filtered.

The coating's thermal conductivity was measured by PPR technique. In order to enhance the heat absorption, a 0.8 μm thick gold film was deposited on the surface of coatings.

3.3 Results and Analysis

Figure 3-2 shows the Al to Ti atomic ratio measured by EDX in the as-deposited TiAlN coatings as a function of the current ratio applied onto the Al and Ti cathodes. As expected that, the Al/Ti atomic ratio in the coatings increased monotonously with the increase of the current ratio $I_{\text{Al}}/I_{\text{Ti}}$. It was noted that for each coating sample, the Al/Ti atomic ratio is lower than the current ratio. This fact could be ascribed to the formation of an insulating AlN layer on Al cathode surface during coating deposition.

Figure 3-2. The Al/Ti atomic ratio in the as-deposited TiAlN coatings as a function of the current ratio applied onto the Al and Ti cathodes.

Figure 3-3 (a) and (b) show the XRD patterns of the as-deposited TiAlN coatings with different Al/Ti atomic ratio of 0.0 and 0.36. The coatings were crystallized into a rocksalt-type cubic structure [78]. The coatings show an evident (111) preferential orientation, with only the (111) diffraction peak (including its second order peak (222)) being clearly observed. The XRD pattern of TiAlN with Al/Ti atomic ratio of 1.60 and 2.5 are shown in Figure 3-3 (c) and (d). It indicates that the coatings show a two-phase mixture consisting of fcc and wurtzite crystalline phases. The XRD result of variation of the phases from the fcc structure to the two-phase mixture with increasing Al content in the TiAlN coatings is consistent with the result obtained from the coatings deposited using the dual-target magnetron sputtering [61] and the cathodic arc ion plating [60].

It was observed that the (111) diffraction peak shifted to a higher angle side, indicating a decrease of lattice parameters, gradually with an increase of the Al/Ti atomic ratio. The lattice decrease can be attributed to partial substitution

of Ti atoms with smaller Al atoms, resulting in a disordered fcc rocksalt-type structure. Suzuki et al. [59] also studied the microstructure of TiN and TiAlN using TEM observation and analyzing the diffraction patterns and they reported also that with addition of Al to the TiN structure, the lattice parameter of the TiN coating gradually decreases with the amount of Al atoms. Moreover, the intensity of the (111) peak decreased abruptly with the incorporation of Al into the coatings. This indicates that the Al incorporation results in a finer nanocrystalline structure or a decrease of the crystallinity of the coating.

Figure 3-3. The X-ray diffraction pattern of as-deposited TiN coating (a), as-deposited TiAlN coating at Al/Ti=0.36(b), as-deposited TiAlN coating at Al/Ti=1.60 (c), and as-deposited TiAlN coating at Al/Ti=2.5 (d).

Figure 3-4 (a) shows a cross-sectional TEM image of as-deposited TiN coating, and Figure 3-4 (b) shows a STEM image of as-deposited TiN coating on SS substrate and gives a good contrast of the grains. The TEM images reveal that the TiN coating consists of apparently fine and columnar grains that grow perpendicularly to the substrate surface. The average size of columnar grains is about 110 nm in width and about 500 nm in length. The grains at the base of the coating are smaller in size and the grains at the top of the coating are bigger and mainly oriented perpendicularly to the substrate surface.

Figure 3-5 (a) and (b) are a cross-sectional TEM image of as-deposited TiAlN coating and a STEM image of the as-deposited TiAlN coating on SS substrate. In this coating, the Al/Ti atomic ratio is about 0.36. The columnar grains which grow perpendicularly to the substrate are clearly observed in the TEM and STEM images. The average size of columnar grains is about 50 nm in width and about 400 nm in length. The grains at the base of the coating near the interface of the coating and substrate are smaller in size. Similar columnar structure has also been observed for TiN and TiAlN coatings on various substrates prepared by radiofrequency magnetron reactive sputtering and cathode arc technique [74; 79].

A dislocation is identified as a defect in the lattice structure in which a few ions in a layer are missing [80]. During the deposition of film on a substrate with different crystalline lattice, the stress is created because of lattice mismatch between the film and the substrate. The stress involves in the formation of a dislocation in the film. The deposition process itself introduces stress components in the thin film, if the amount of this stress becomes higher than

the microscopic yield stress of the material, dislocations nucleate and glide inside the grains [81]. Another effect forms the dislocation in the material is irregularities at the grain boundaries. This effect can produce dislocations in the materials which propagate into the grain [80].

Figure 3-6 (a) and Figure 3-7 (a) show a HRTEM image of TiN and TiAlN coatings, respectively. In order to allow easy visualization of single dislocations, a GPA map was used. The GPA maps in Figure 3-6 (b) and Figure 3-7 (b) show the dislocation positions as hot-spots in the HRTEM images of TiN and TiAlN coatings, respectively. The comparison of the GPA maps reveals that the number of the dislocations seen in the TiAlN coating is much higher compared to the TiN coating. Figure 3-6 (c) shows the inverse FFT of one family of (200) planes in the region displayed by white box in Figure 3-6 (b). The dislocation can be clearly recognized as extra half planes, which are indicated with white circles.

Figure 3-4. (a) Cross-sectional TEM image of as-deposited TiN coating, (b) STEM image of as-deposited TiN coating on SS substrate.

Figure 3-5. (a) Cross-sectional TEM image of as-deposited TiAlN coating, (b) STEM image of as-deposited TiAlN coating on SS substrate. In this coating Al/Ti atomic ratio is 0.36.

Figure 3-6. (a) HRTEM image of TiN coating (b) GPA map of HRTEM image of TiN showing the position of dislocations (c) Inverse FFT of one family of (200) planes in the region displayed by white box in (b). The dislocation can be clearly recognized as extra half planes, which are indicated with white circles.

Figure 3-7. (a) HRTEM image of TiAlN coating with atomic ratio 0.36 (b) GPA map of HRTEM image showing the position of dislocations at the image as hot spots.

Figure 3-8 shows the normalized surface temperature excursion for Au/TiAlN/SS substrate. In order to obtain thermal conductivity and diffusivity of TiAlN coating, the temperature profile is fitted using a three-layer heat conduction model (equation (2-15)) to simulate heat transport in the Au/TiAlN/SS structure. Thermal boundary resistances between the layers is neglected in this model (the explanation is provided in Appendix A). In the curve-fitting process, three parameters—thermal conductivity of the gold film, TiAlN coating and thermal diffusivity of TiAlN coating—were varied and the least square optimization method was applied to minimize the difference between the normalized surface temperature profile and the three-layer model. The average thermal conductivity for gold film of 218 W/mK is obtained from curve fitting. Figure 3-9 shows the thermal conductivity of the TiAlN coatings as a function of the Al/Ti atomic ratio. The obtained thermal conductivity of pure TiN coating is around 11.9 W/mK. With the increase of Al incorporation, the thermal conductivity of the TiAlN coatings decreased rapidly and a minimum thermal conductivity of about 4.63 W/mK was obtained at the Al/Ti atomic ratio of around 0.72. When increasing Al content further, the thermal conductivity of these coatings slightly increased. Figure 3-10 shows the thermal diffusivity of the TiAlN coatings as a function of the Al/Ti atomic ratio. Being similar to the variation trend of thermal conductivity, the thermal diffusivity of the as-deposited TiAlN coatings decreases rapidly with the increase of Al incorporation in TiN structure. With increasing Al content further, the coatings' thermal diffusivity increased slightly. The error range is obtained by measuring at different locations on the sample and curve fitting.

Figure 3-8. Surface temperature excursion profile of the TiAlN, coated with 0.8 μm Gold. The Al/Ti atomic ratio is 0.36.

Figure 3-9. Thermal conductivity of the as-deposited TiAlN coatings as a function of Al/Ti atomic ratio.

Figure 3-10. Thermal diffusivity of the as-deposited TiAlN coatings as a function of Al/Ti atomic ratio.

3.4 Discussion

Based on the kinetic theory, thermal conductivity of the materials is proportional to mean free path (MFP) of phonons, phonon velocity, and specific heat per unit volume [82]. Phonons scatter by impurities, dislocations, defects, and boundaries in the crystal lattice, and phonon scattering determines the MFP of phonons. Impurity atoms, which can be introduced in the form of an alloy in the lattice, will shorten the MPF of phonons due to increasing phonon dispersion [83]. Lee et al. [84] studied the effect of alloying on reduction of thermal conductivity and reported that the thermal conductivity of bulk and thin film $\text{Si}_x\text{Ge}_{1-x}$ alloys are much lower than that of pure crystal Si and Ge.

XRD analysis and cross-sectional TEM observation showed that the microstructure of the coatings strongly depends on the Al content. TiN coating was crystallized into a rocksalt-type cubic (fcc) structure [61] and shows the strong (111) diffraction peak with preferential orientation growth. TiN has a

columnar structure as shown in Figure 3-4 (a) and (b), and this structure is very favorable to transfer heat in cross-plane direction. The columnar structure and large grain size are responsible for the high thermal conductivity. With incorporation of Al into the TiN structure, the intensity of (111) peak in TiAlN coatings reduces suddenly and the lattice parameters decreases. Previous studies have shown that Al incorporation in TiN results in a finer nanocrystalline structure and decreases lattice parameters [85; 86]. Also, it was reported that the formation of columnar structure in TiAlN coating is prevented by increasing Al content in the coating [87].

The reduction in thermal conductivity with Al addition, shown in Figure 3-9, can be explained by decreasing MFP of phonons due to local modification to lattice structure (disordering the fcc structure of TiN), reducing the grain size and increasing dislocation density in the coatings. Phonons need periodicity in the materials structure to propagate. Phonons are scattered, if they encounter any irregularities in the crystalline materials. As shown in the TEM images, with incorporation Al in TiN coating, the columnar grain diameter is decreased. When the grain diameters in the TiAlN coatings is decreased, the grain boundary and volume fraction of atoms locating in the grain boundaries are increased. The steps and ledges at the grain boundaries are an important source of dislocations in the materials. Therefore, dislocation density is increased in the coatings. These effects act to increase phonon scattering and reduce MFP of phonons, resulting in decreasing thermal conductivity of the coatings. The results show that when phonon scattering increases, thermal conductivity is

reduced for fine-grained TiAlN coatings. With the Al content increased further, the slight increase of thermal conductivity could result from the possible gradual separation of AlN, which is well-known for having a very high thermal conductivity (180 W/mK at 25 °C) [88].

3.5 Summary and Conclusion

In this chapter, we have studied the effect of the incorporation of the Al on the thermal conductivity and diffusivity of the TiAlN coatings prepared by a lateral rotating cathode arc (LARC) technique. To study the effect of the Al incorporation on the microstructure and thermal conductivity, a series of TiAlN coatings were deposited on stainless steel substrate in a pure nitrogen atmosphere. Microstructure of the coatings was analyzed by XRD and TEM observation.

XRD analysis and cross-sectional TEM observation reveal that TiN coating shows a clear columnar structure with a predominant (111) preferential orientation. With the incorporation of Al, the columnar structure of the coatings is weakened and the grain size of the coatings is decreased. Thermal conductivity and diffusivity of the as-deposited TiAlN coatings were measured at room temperature by using a PPR technique. The measured thermal conductivity of the pure TiN coating is around 11.9 W/mK. A significant decrease in thermal conductivity was found with increasing Al/Ti atomic ratio. The decrease in thermal conductivity of the TiAlN coatings is explained in terms of the increased phonon scattering due to the decrease in grain size of the coatings and increased dislocation density in the coatings. With the increasing

of Al content further, the coating shows a two-phase mixture consisting of fcc TiN and wurtzite AlN crystalline phases, and thermal conductivity increases slightly.

Chapter 4: Thermal conductivity of TiAlSiN coatings

4.1 Introduction

Currently, Ti-based coatings (e.g. TiN and TiAlN) represent state-of-the-art commercial PVD tool coatings based on their excellent physical and mechanical properties [62; 89; 90]. In the past few years, nanocomposite coatings, which are composed of a nanocrystalline hard material (e.g. TiN, TiAlN, or CrAlN) embedded in an amorphous matrix (e.g. Si₃N₄) with strong interfaces between the two phases, have attracted great attention all over the world due to their excellent properties, including enhanced toughness, super hardness (≥ 40 GPa), high oxidation resistance and temperature thermal stability, outstanding erosive and abrasive wear resistance, etc., over the commercial TiN and TiAlN coatings [91-95]. These nanocomposite coatings have been shown to be resistant to oxidation in air at temperatures over 800° C, and are thermodynamically stable. It has been reported that the oxidation

resistance of Ti-Al-Si-N coatings greatly improved with a few atomic percentages of Si, up to 1100° C in air, and TiAlSiN coated cermet cutting tools show better cutting performance than TiAlN-coated cermet cutting tools, particularly under high-speed machining conditions [94].

In addition to the protection requirements against wear and oxidation, thermal properties, particularly thermal conductivity, are also important factor to design of better coatings with enhanced performance. In some specific tool applications, e.g. high-speed machining, hot forging/casting, a lower thermal conductivity of the hard coatings is desired, which serves as a thermal barrier layer and can effectively delay the temperature rise on the tool substrate materials. Martan et al. [65] measured thermal conductivity of TiAlSiN deposited by arc sputtering on high speed cutting stainless steel using pulsed photothermal radiometry. They reported that thermal conductivity of TiAlSiN (average (Al+Si)/Ti atomic ratio is 0.9) is 1.6 W/mK. Fox-Rabinovich et al. [12] showed that a nano-multilayered AlTiN/Cu PVD coating performed better than an AlTiN coating in turning the hard-to-machine aerospace Ni-based Inconel 718 superalloy. They partially attributed the better cutting performance to the lower thermal conductivity of the nano-layered AlTiN/Cu coating. In the previous chapter, the thermal conductivity of a series of TiAlN coatings with a different Al/Ti atomic ratio was investigated using the PPR technique at room temperature. A significant decrease in thermal conductivity was found with increasing Al/Ti atomic ratio.

Nanocomposite coatings consists of two nanocrystalline phase or a single nanocrystalline embedded in an amorphous phase. Figure 4-1 shows the

diagram of a nanocomposite coating with a single crystalline phase embedded in amorphous phase. Nanocomposite coatings were identified as one of the promising coatings with high oxidation resistance, high hardness and toughness, and wear resistance [50]. Veprek et al [96; 97] reported that with addition of Si in TiN structure results nano-super hard nanocrystalline composite (nanocomposite) coatings. They showed that the Silicon is bound in stoichiometric Si_3N_4 (amorphous phase) in the coatings. The formation of a two-phase nanocomposite coating is caused by low solubility of Si in the lattice of B1-structured nitrides [98] and growing amorphous Si_3N_4 at temperatures below 1000 °C [99]. They also reported that with incorporation Si up to certain content in TiN structure, the hardness increases to a maximum value (50-70 GPa) and the average crystallinity size decreases to a minimum.

Furthermore, the addition of Si to TiN has been claimed to produce similar oxidation resistance to that observed for TiAlN coatings [100; 101]. Chang et al [102] studied the microstructure of TiAlSiN by varying the Si content and observed that the grain size of the coating is decreased from 8 nm to 4 nm corresponding to an increase in Si content from 1.2 at% to 4.4at%, respectively. Decrease in crystallinity size corresponds to increase the specific area of the interface between the TiAlN nanocrystals and the amorphous Si_3N_4 matrix, results in increasing phonon scattering and lowering thermal conductivity.

Figure 4-1. Diagram of nanocomposite coating with a single crystalline phase and an amorphous phase [97].

The objective of this chapter is to study the effect of adding Al and Si to TiN coatings and to investigate thermal properties of TiAlSiN nanocomposite coatings with different (Al+Si)/Ti atomic ratios. A series of TiAlSiN nanocomposite coatings were prepared by a cathode arc technique with a different (Al+Si)/Ti atomic ratio on stainless steel substrates, and a thermal conductivity measurement was carried out by PPR technique. The microstructure of the coatings was analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The behavior of the thermal conductivity of the TiAlSiN coatings with different (Al+Si)/Ti ratios will be discussed by focusing on the analysis of the microstructure.

4.2 Experiment

TiAlSiN nanocomposite coatings with a thickness of 2.2-2.6 μm were deposited by a LARC technique, which has been described in detail in a previous chapter. For deposition of the TiAlSiN nanocomposite coatings, one elemental Ti cathode and one Al+Si alloy cathode (with ~ 11 at.%Si) were used. These two cathodes were laterally rotating during the coating deposition. Mirror-finished

AISI 304 stainless steel (SS) coupons were used as substrates for coating deposition. Substrate cleaning process was explained in previous chapter. During the deposition, a negative bias of -70 V was applied to the substrate, and substrate temperature was controlled at 480° C. The coating deposition was conducted in a flowing pure nitrogen atmosphere with a working pressure controlled at 1.5 Pa. In order to control the composition of the as-deposited coatings, the direct current applied on the two cathodes, $I_{(Al+Si)}$ and I_{Ti} , was separately changed between 0 and 125 A with different current ratios, $I_{(Al+Si)}/I_{Ti}$.

The coatings' composition was measured by energy dispersive analysis of X-rays (EDX), which is attached to a scanning electron microscope at 8 KeV and the INCA quantitative analysis software. The Philips x-ray diffractometer in a θ -2 θ scan mode using CuK_{α} radiation (40kV, 30 mA) was used to analyze the coating crystalline structure. Thermal conductivity measurement on TiAlSiN nanocomposite coatings is done by using the PPR technique. In order to enhance the heat absorption, a 0.8 μ m thick gold film was deposited on the TiN and TiAlSiN films.

4.3 Results and analysis

Figure 4-2 shows the (Al+Si) to Ti atomic ratio measured by EDX analyses in the as-deposited TiAlSiN coating as a function of the current ratio applied onto the (Al+Si) and Ti cathodes. It is expected that the (Al+Si)/Ti atomic ratio in the coatings increased monotonously with the increase of the current ratio $I_{(Al+Si)}/I_{Ti}$.

Figure 4-2. (Al+Si) to Ti atomic ratio in the as-deposited TiAlSiN coatings as a function of the current ratio applied onto the Al+Si and Ti cathodes.

Figure 4-3 shows the XRD patterns of as-deposited coatings. All the coatings were crystallized into a rocksalt-type cubic (fcc) TiN structure. As no other nitride such as Si_3N_4 crystalline phase was detected from the XRD patterns, it can be inferred that the Si_3N_4 phase exists as an amorphous phase. The TiN coating shows a strong (111) preferred orientation, with only the (111) diffraction peak (including its second order peak (222)) being clearly observed. With Al and Si incorporated into the TiN, the diffraction peaks weakened and broadened. This could be due to an increase in amorphous content and diminution of grain size with the increase of Al and Si. Yu et al. [103] reported

that the XRD peak of TiAlSiN nanocomposite coatings were broadened and the grain size of the coatings was decreased with an increase of Si content.

The average grain size of the TiAlSiN coatings was determined by Williamson-Hall method [104], $\beta\cos(\theta)=(0.94\lambda/\sigma)+4\epsilon\sin(\theta)$, where σ is the grain size, λ is the wavelength of the radiation (0.154 nm for CuK_α radiation), ϵ is the strain induced in the TiAlSiN coating due to crystal imperfection and distortion, θ and β are the position and full width of half-maximum (FWHM) of the coating diffraction peaks. $\beta\cos(\theta)$ was plotted with respect to $4\sin(\theta)$ for the diffraction peaks of TiAlSiN coatings. Strain and grain size are calculated from the slope and y-intercept of the fitted line, respectively. Figure 4-4 shows the average grain size of the TiAlSiN coatings as a function of (Al+Si)/Ti atomic ratio. The calculated grain size is in the range of 26-94 nm. Parlinska-Wojtan et al. [105] investigated the microstructure and growth of TiAlSiN coating on WC-CO substrate using TEM observation and reported that the grain size of the coating decreased approximately from 60 nm to 5 nm in width with the increasing Al+Si content from 10 to 50 at.% throughout the coating.

Figure 4-3. X-ray diffraction patterns of the as-deposited TiAlSiN coatings with different (Al+Si)/Ti atomic ratio.

Figure 4-4. Average grain size of the as-deposited TiAlSiN coatings as a function of the (Al+Si)/Ti atomic ratio.

Figure 4-5 shows a cross-sectional TEM image of as-deposited TiAlSiN nanocomposite coating with the corresponding selected area electron diffraction

(SAED) pattern, and Figure 4-6 shows a STEM image of as-deposited TiAlSiN coating and gives a good contrast of the grains. The TEM images reveal that the TiAlSiN coating consists of a weak columnar structure throughout the coating, which is the result of incorporating of Al and Si contents in TiN structure. The coating's grain size of approximately 20 nm in width is smaller than the grain size in TiN coating as shown in Figure 3-4 (a) and (b). The SAED pattern in Figure 4-5 shows spots and diffuse rings, which proves the nanocrystalline structure and amorphous character of the coatings [105].

The TEM images also show the formation of nanolayers in the coating with a periodicity of about 5 nm, as shown in Figure 4-7. Parlinska-Wojtan et al. [105] observed similar nanolayer in TiAlSiN nanocomposite coating deposited by arc plasma PVD technique. The formation of nanolayered arrangement is due to the deposition procedure. The LARC system for TiAlSiN deposition is equipped with Al+Si and Ti targets, and they are very close to each other, especially arranged on the same side of the cylindrical in the chamber, as shown in Figure 3-1. When the substrate on sample holder is rotating around a center and around its own axis, the sample distance from the targets with different composition is changing. Therefore, the layer deposited closer to the Al+Si and Ti targets are slightly richer in Al+Si and Ti, respectively, and there is no sharp transition between the layers. Sharp transition in chemical composition has not been observed by measuring the Ti, Al and Si contents in the nanolayers throughout the coatings using the EDX which is attached to the TEM.

Figure 4-7 shows the cross-sectional HRTEM image of the TiAlSiN nanocomposite coating and reveals the different microstructure with

incorporation of Al and Si in TiN structure. A weak columnar structure and crystalline grains embedded in a disordered matrix were observed. The amorphous phase of disordered matrix between the crystalline grains was observed as shown in the Fast Fourier transform (FFT) diagrams in Figure 4-7 (a) and (b). Yu et al. [103] studied the microstructure of TiAlSiN coatings and reported that with the increase of Si content in TiAlSiN coatings, the mixture of TiAlN nanocrystals in an amorphous Si_3N_4 matrix was formed. Christiansen et al. [106] observed a similar nanocomposite structure of nanocrystalline TiN embedded in an amorphous SiN_x matrix using HRTEM imaging for TiSiN coating.

Figure 4-5. Cross-sectional TEM image of as-deposited TiAlSiN coating and corresponding SAED pattern (inset) on SS substrate. In this coating the atomic ratio of (Al+Si)/Ti is 1.12.

Figure 4-6. STEM image of as-deposited TiAlSiN coating on SS substrate. In this coating (Al+Si)/Ti atomic ratio is 1.12.

Figure 4-7. Cross-sectional HRTEM image of as-deposited TiAlSiN coating on SS substrate and the corresponding FFT of the crystalline region (a) and amorphous region (b). The (Al+Si)/Ti atomic ratio in this coating is 1.12.

Figure 4-8 shows the normalized surface temperature profile for the Au/TiAlSiN/SS structure with two different atomic ratios of (Al+Si)/Ti. In order to obtain the thermal conductivity and diffusivity of TiAlSiN, the temperature profile is fitted by using a three-layer heat conduction model to simulate heat transport in the Au/TiAlSiN/SS structure. A Least Square optimization method is used to fit the experimental data to an analytical solution of heat diffusion for the three-layer model using three parameters, thermal conductivity of the gold film, TiAlSiN coating, and thermal diffusivity of TiAlSiN coating. The average thermal conductivity for the gold film of 228 W/mK was obtained from curve fitting.

Figure 4-9 shows the thermal conductivity of the as-deposited TiAlSiN coatings as a function of the (Al+Si)/Ti atomic ratio. Thermal conductivity of the pure TiN coating is 11.9 ± 1 W/mK, which is about half of the value reported by Taylor et al. [63] for bulk TiN material. It is observed that thermal conductivity of the TiAlSiN nanocomposite coatings decreases rapidly with increasing (Al+Si) incorporation. Figure 4-10 shows the thermal diffusivity of the TiAlSiN coatings as a function of the (Al+Si)/Ti atomic ratio. Thermal diffusivity of the pure TiN coating is $(2.7 \pm 0.3) \times 10^{-6}$ m²/s. Being similar to the variation trend of thermal conductivity, the thermal diffusivity of the as-deposited TiAlSiN coatings decreases drastically with the increase of (Al+Si) incorporation. The error range is obtained by measuring at different locations on the sample and curve fitting.

Figure 4-8. Surface temperature excursion profile of the TiAlSiN films, coated with 0.8 μm gold.

Figure 4-9. Thermal conductivity of the as-deposited TiAlSiN coating as a function of (Al+Si)/Ti atomic ratio.

Figure 4-10. Thermal diffusivity of the as-deposited TiAlSiN coating as a function of (Al+Si)/Ti atomic ratio.

4.4 Discussion

Microstructure of films, especially the grain size of the films, has an important role in determining thermal properties such as thermal conductivity. Phonon transport represents heat transport in crystalline solids, and the MFP of phonon is determined by phonon scattering. The effective method to tune thermal transport in a given sample is mean free path of phonon. Phonon is scattered by defect and impurity atoms, which can be introduced in the form of dopant atoms or an alloy in the lattice and results in reducing its MFP. The effective way to decrease thermal conductivity in the solids is alloying because this would reduce the phonon's MFP, and this leads to lower thermal conductivity [68].

Based on the XRD analysis and cross-sectional TEM observation, the microstructure of the TiAlSiN coatings strongly depends on the Al and Si contents. As discussed in a previous chapter, TiN coating shows the strong (111) diffraction peak (including its second order peak (222)) with preferential

orientation growth. TiN has a columnar structure as shown in Figure 3-4 (a) and (b), and this structure is very favorable to transfer heat in a cross-plane direction. The columnar structure and larger grain size are responsible for the high thermal conductivity. With incorporation of Al and Si into the TiN structure, the intensity of (111) peak in TiAlSiN coatings reduces suddenly and results in a finer nanocrystalline structure or a decrease of the crystallinity of the coating. With increasing Al+Si contents in the TiAlSiN coating, forming of the columnar structure reduces drastically and the fcc structure of TiN becomes distorted [5; 107].

The results show that thermal conductivity of TiN, which has a columnar structure, is 11.9 W/mK. However, with the incorporation of Al+Si, the columnar structure is disrupted, cubic structure of TiN distorted, and (111) preferred orientation is reduced; hence, thermal conductivity is decreased. When the grain size is comparable to the phonon's MFP, the event of phonon scattering increases and thermal conductivity decreases. Phonon scattering at the grain boundaries will reduce the coatings' thermal conductivity. In addition, the incorporation of Al atoms causes lattice distortion and consequently results in the formation of local strain fields, which in turn shortens the MFP of phonons and reduces thermal conductivity. It is noted that the effect of incorporation of Si in TiAlN films creates a nanocomposite structure that consists of nano-crystalline TiAlN surrounded by amorphous SiN_x [87; 108]. With further increases of Al and Si contents, the decrease of thermal conductivity could be attributed to the reduced grain size and formation of nanocomposite structure, which is consisted of crystalline nanograins

embedded in a disordered, lower thermal conductivity than TiAlN [45; 109], amorphous SiN_x matrix [110].

4.5 Summary and Conclusion

In this chapter, the effect of Al and Si incorporation on the thermal conductivity of the TiAlSiN coating prepared by a LARC technique was investigated. To study the effect, a series of TiAlSiN coatings were deposited on stainless steel substrate by a LARC technique in a pure nitrogen atmosphere. Thermal conductivity of the as-deposited TiAlSiN coatings at room temperature was measured by using a PPR technique. A significant decrease in thermal conductivity was found with increasing the (Al+Si)/Ti atomic ratio. The decrease in thermal conductivity of the TiAlSiN coatings could be attributed to the first, increased phonon scattering at the grain boundaries due to the decrease in grain size of the coatings and the second, formation of the nanocomposite structure, which consists of nano-crystalline TiAlN embedded in an amorphous SiN_x matrix.

Chapter 5: Thermal conductivity of [TiN/TiAlN]_n multilayer coatings

5.1 Introduction

Controlled deposition of the thin film allows producing multilayer materials with unique mechanical and physical properties. Knutsson et al. [78] reported that the hardness of TiAlN/TiN multilayer coatings was higher than the single layer and increases with decreasing multilayer period. It has been shown that multilayer TiN/TiAlN coatings are superior to single layer TiN and TiAlN coatings in many mechanical properties [62].

A lower thermal conductivity of the hard coating is required to improve performance of the tool substrate materials. Recently, it was reported that the nano-multilayered AlTiN/Cu coating has better cutting performance due to the lower thermal conductivity of nano-multilayered AlTiN/Cu than single layer AlTiN [12]. In the present work, we investigate the thermal conductivity of

TiN/TiAlN multilayer coatings, and demonstrate that it is lower than the thermal conductivity of TiN and TiAlN coatings. Moreover, it will be shown that the thermal conductivity depends on the coatings' microstructure and number of layers.

5.2 Experiment

[TiN/TiAlN]_n multilayer coatings (n is the number of bilayer) with a thickness about 1.2 μm were deposited onto a mirror-finished AISI 304 stainless steel (SS) substrate (with a dimension of $25 \times 25 \times 1 \text{ mm}^3$) using a LARC technique, which has been described in the third chapter. For deposition of the multi-layer coatings, one elemental Ti and Al cathodes were employed in this work. These two cathodes were laterally rotating during the coating deposition. During the deposition, a negative bias of -70 V was applied to the substrate, and the substrate temperature was controlled at 480° C. The coating deposition was conducted in a flowing pure nitrogen atmosphere with a working pressure controlled at 1.5 Pa. In order to control the composition of the as-deposited coatings, the direct current applied on the two cathodes, I_{Al} and I_{Ti} was fixed at 120 A and 50 A, respectively. For depositing the [TiAlN/TiN]_n multilayer coatings, the DC current applied on the Al cathode was turned on and off periodically. The total deposition time is fixed at 60 minutes, and the time to deposit each layer is $30/n$ minutes. We have prepared a series of five [TiN/TiAlN]_n multilayer coatings with the bilayer number n equal to 5, 10, 25, 50, and 100. The corresponding bilayer thickness ranges then from about 240 nm to 12 nm. Two TiN and TiAlN single layer coatings with thickness about 1.2 μm were deposited under identical conditions on the AISI 304 SS substrate

as well. The DC current of the Al cathode I_{Al} for TiN and TiAlN deposition was fixed at 0 and 120 A, respectively.

The chemical composition was measured by energy dispersive X-ray spectroscopy (EDX) analysis together with STEM imaging. Full quantification EDX analysis was performed using TEM Imaging and Analysis (TIA) software.

HRTEM imaging was used to identify the misfit dislocation between the layers in the multilayer coating based on Fast Fourier transformation (FFT) and Geometric phase analysis (GPA). FFT and GPA of the high resolution micrograph were analyzed with Digital Micrograph software (version 3.11.1 Gatan). Bragg filtered image is generated by applying a spot mask to spots in the FFT of the HRTEM image. Afterwards, the FFT image was inverse Fourier filtered.

In order to characterize the thermal conductivity of the coatings, the PPR method was used. First, a 1.0 μm layer of gold was deposited on the surface of the samples to enhance thermal absorption.

5.3 Results and analysis

Table 5-1 shows the EDX values of the Ti and Al content in the TiN and TiAlN layers in the multilayer coatings deposited with the LARC system with a bias voltage of -70 V at 480° C.

Table 5-1. Ti and Al content in the TiN and TiAlN layers in the multilayer coatings.

Layer	Ti content (at. %)	Al content (at %)
TiN	44.8 ±2.8	--
TiAlN	20.5 ±2.7	30.4 ±3.0

Figure 5-1 (a) shows the XRD patterns of the TiN and TiAlN singer layer coatings deposited on the SS substrate. The Al to Ti atomic ratio in the TiAlN coating is about 1.50. The diffraction peaks indicate that the TiN and TiAlN coatings were crystallized into a rocksalt-type cubic structure with the two strong Bragg peaks corresponding to the (111) plane (including the second order peak (222) for TiN), showing a preferential orientation growth along these orientations [111]. [111]. Note that with addition of Al in the TiN structure, the (111) diffraction peak shifts from 36.59° 2θ for TiN to 36.87° 2θ for TiAlN, indicating a decrease in lattice parameters from 0.425 nm for TiN to 0.422 nm for TiAlN. This can be explained by a substitution mechanism where the smaller Al atoms replace Ti atoms resulting in a disordered fcc rocksalt-type structure.

Figure 5-1 (b) shows the XRD patterns of the [TiN/TiAlN]_n multilayer coatings deposited on SS with different bilayer number of 5, 10, 25, 50 and 100. The XRD pattern shows a fcc structure of the coatings with two peaks at (111) and

(200) corresponding to the TiN (111) and (200) planes, indicating a light texture growth along this orientation.

Figure 5-1. X-ray diffraction pattern of the as-deposited (a) TiN and TiAlN single layer coatings and (b) $[\text{TiN}/\text{TiAlN}]_n$ multilayer coatings with different bilayer number n .

A TEM cross-sectional image of an as deposited $[\text{TiN}/\text{TiAlN}]_{100}$ multilayer is shown in Figure 5-2. The periodic dark and bright layers in the TEM images are the TiN and TiAlN layers, respectively. Because of the lower scattering factor of Al, the TiAlN layers appear slightly brighter than the TiN layers [112]. The image displays the polycrystalline layers with columnar grains that grew through the multilayer cross section with around 50 nm wide columns.

Figure 5-2. Cross sectional TEM images of $[\text{TiN}/\text{TiAlN}]_{100}$ multilayer deposited on AISI 304 substrate by the LARC system.

Figure 5-3 (a) shows a HRTEM image of the $[\text{TiN}/\text{TiAlN}]_{100}$ multilayer coating along the $\langle 110 \rangle$ zone axis and the corresponding FFT in the inset. A magnified and IFFT filtered image of the region indicated by the white square in Figure 5-3 (a) is shown in Figure 5-3 (b). The FFT pattern reveals the fcc crystalline structure of the multilayer coating. GPA analysis was also carried out on the region indicated by dashed lines in Figure 5-3 (b) as shown in Figure 5-3 (c). The corresponding IFFT image of one family of planes is presented in Figure 5-3 (d). The dislocation can be clearly recognized as extra half planes which are indicated by "T" symbols. The misfit dislocations are shown along the interface in both the GPA map and IFFT image. The misfit dislocations form because of the lattice mismatch between the TiN and TiAlN layer and the Al content in the TiAlN layer. Suzuki et al. [59] reported that the lattice mismatch between the

TiN and TiAlN (with Al/Ti atomic ratio of 1) coatings deposited by the cathode arc technique is about 1.4%.

Figure 5-4 (a) and (b) show a cross sectional STEM of as deposited $[\text{TiN}/\text{TiAlN}]_5$ and $[\text{TiN}/\text{TiAlN}]_{100}$ multilayer coatings, respectively. It can be observed that the columnar grain size reduces in width and in length by increasing the number of layers.

Figure 5-3. (a) High resolution TEM image of a $[\text{TiN}/\text{TiAlN}]_{100}$ multilayer coating along the $\langle 110 \rangle$ direction. The corresponding FFT is shown in the upper right inset showing the fcc structure. (b) Magnified and inverse FFT of the region indicated by solid lines in (a) showing the atomic arrangement along the interface. (c) GPA map of the region indicated by the black dashed lines in (b) showing the position of the misfit dislocations at the interface as hot spots. (d) Inverse FFT of one family of planes to show the existence of dislocations indicated as extra half planes. Dislocations are shown by "T" symbols.

Figure 5-4. (a) and (b) a cross sectional STEM image of $[\text{TiN}/\text{TiAlN}]_5$ and $[\text{TiN}/\text{TiAlN}]_{100}$ multilayer coatings on SS substrate, respectively.

Figure 5-5 displays the thermal conductivity of as deposited $[\text{TiN}/\text{TiAlN}]_n$ multilayer coatings as a function of the bilayer number. The thermal conductivity of TiN and TiAlN single layer coatings are shown in the graph as well. It is observed that the thermal conductivity of TiN decreases rapidly with incorporation of Al in the TiN structure. The obtained thermal conductivity of the $[\text{TiN}/\text{TiAlN}]_5$ multilayer coating is 4.92 W/mK and the thermal conductivity decreases to 3.25 W/mK for the coating with bilayer number of 100. The thermal diffusivities of the TiN and TiAlN single layers and $[\text{TiN}/\text{TiAlN}]_n$ multilayer coatings as a function of the bilayer number are shown in Figure 5-6. A similar behavior is observed for the thermal diffusivity, i.e., it decreases with increasing bilayer number.

Figure 5-5. Thermal conductivities of the as-deposited TiN, TiAlN single layers and $[\text{TiN}/\text{TiAlN}]_n$ multilayer coatings with different bilayer n .

Figure 5-6. Thermal diffusivities of the as-deposited TiN, TiAlN single layers and $[\text{TiN}/\text{TiAlN}]_n$ multilayer coatings with different bilayer number n .

5.4 Discussion

Phonons scatter by impurities, dislocations, defects, and boundaries in the crystal lattice and phonon scattering determines the MFP. Impurity atoms, which can be introduced in the form of an alloy, in the lattice will change the acoustic impedance $Z = \rho v$, where ρ is the density and v is the speed of sound (note that the speed of sound depends on the elastic stiffness of the chemical

bond). When the incident phonon meets a change in the acoustic impedance, it will scatter and this leads to a lower thermal conductivity.

The effective thermal conductivity of multilayer coatings is determined by the thermal conductivity of each layer and the thermal boundary resistance between the layers. Defects such as misfit dislocations are formed between the layers when there is a mismatch between the lattice constants of the layers. Phonons are scattered by defects in interfaces between the layers, resulting in a reduced thermal conductivity. It was reported that the thermal conductivity of a multilayer film can be smaller than that of their alloys and decreases with increasing number of layers [84; 113].

The XRD analysis shows that the microstructure of the TiN, TiAlN and [TiN/TiAlN]_n multilayer coatings strongly depends on the Al content and number of bilayer n , respectively. TiN shows a strong (111) diffraction peak with preferential orientation growth. TiN has a columnar structure and this structure and large grain size are responsible for the high thermal conductivity (see Figure 3-4). The (111) diffraction peak is weakened in TiAlN and multilayer coatings, such that the preferential orientation growth reduces in these coatings.

HRTEM observation and GPA were applied to examine the quality of the interfaces between the layers. Misfit dislocations are formed in the interfaces between the TiN and TiAlN layers because of strain energy due to lattice-mismatched multilayer growth [114; 115]. By increasing the number of layers, the misfit dislocation density increases in the multilayer coating and phonon

scattering increases at the interfaces of layers, resulting in a reduced thermal conductivity. The STEM observation of the two multilayer coatings with bilayer numbers of 5 and 100 confirmed that the columnar structure growth and grain size decrease with increasing number of layers. The multilayer deposition prevents the formation of the columns and results in a finer nanocrystalline structure. The phonon scattering increases in grain boundaries, and thus the MFP reduces, which results in a decreasing thermal conductivity of multilayer coatings. When increasing the bilayer number in the $[\text{TiN}/\text{TiAlN}]_n$ multilayer coatings, the decrease in thermal conductivity can be attributed to disruption of the columnar structure, and the increased phonon scattering at the interfaces of layers and grain boundaries.

5.5 Summary and Conclusion

A series of $[\text{TiN}/\text{TiAlN}]_n$ multilayer and a single layer TiN and TiAlN coatings were deposited on a stainless steel AISI 304 substrate by a lateral rotating cathode technique. The PPR technique was used to measure the cross-plane thermal conductivity of the coatings at room temperature. The obtained thermal conductivity for single layer TiN and TiAlN shows that the incorporation of Al in the TiN structure reduces the thermal conductivity significantly. XRD analysis and TEM observation reveals that the preferential orientation growth along the (111) direction reduces in the coatings and that the grain size decreases with increasing the bilayer number. The HRTEM images and GPA maps of multilayer coatings show extensive defects at the interfaces between the TiN and TiAlN layers because of strain energy due to lattice-mismatched multilayer growth. The decrease in grain size and increase in misfit dislocation

density in the multilayer coating are responsible for reducing heat transport in the coatings with increasing bilayer number.

Chapter 6: Thermal conductivity of Pt-doped n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposite

6.1 Introduction

The ever-increasing energy demand and the global environment concerns have created a significant interest in exploiting novel energy materials against waste, pollution and global warming. With the capability to transform a temperature difference into electricity, and vice-versa, thermoelectric (TE) materials are potential candidates for waste heat recovery [16] and solid-state cooling [116] in a silent, reliable manner that is environmentally benign. Thermoelectric devices have a simple configuration, and there are no moving parts or greenhouse gases, as shown in Figure 6-1. The devices are formed of two types of semiconductor, n-type and p-type, which are connected in a series. Electrons and holes carry the current in the n-type and p-type, respectively. As illustrated in Figure 6-1 (a), the refrigeration is possible if voltage is used to run the current across a p-n junction. The hot electrons in n-type and hot holes in p-type

flow away from the cold side to the other side, which results in cooling (Peltier effect) [117; 118]. A temperature as low as 160 K can be reached by this method [116].

If one side is heated and the other side is cooled, the temperature gradient is thereby produced, as shown in Figure 6-1 (b). Electron/hole pairs are created at the hot side and absorb heat in the process. A voltage potential (the Seebeck voltage) is generated by the temperature gradient between the hot and cold sides of the TE materials. The voltage potential is proportional to the temperature gradient; this proportionality is defined as Seebeck coefficient [118]. This effect is the basic operation of thermocouples used to measure temperature as well.

Figure 6-1. Schematic of the thermoelectric heat engines. (a) Peltier effect, cooling and heating by running the current across a TE junction. (b) Seebeck effect, electrical current is generated by applying temperature gradient on TE materials.

Despite the advantages of using TE devices, the major problem with TE devices is poor efficiency, and this problem limits the usage of the TE devices so far. The efficiency of a TE material is governed by the dimensionless ZT , where T is the temperature and Z depends on material's thermal and electrical transport properties. Materials with low thermal conductivity and high electrical

conductivity have enhanced thermoelectricity [18]. High electrical conductivity and low thermal conductivity are desired to decrease Joule heating and sustain large temperature differences, respectively. The efficiency of TE devices, ZT , which is called thermoelectric figure of merit, is given as

$$ZT = \frac{S^2 \sigma}{K} T \quad (6-1)$$

where S , σ and T are the Seebeck coefficient, electrical conductivity and absolute temperature, respectively, and K is the thermal conductivity, which is composed from electronic carriers (K_e) and lattice vibration (K_L) contributions. Therefore, material selection is an important step to have highly efficient thermoelectric energy conversion. Materials with $ZT > 3$ can compete with conventional refrigerators and generators. Since 1950, the room temperature ZT of bulk semiconductor increased slightly from around 0.6 to 1 as shown in Figure 6-2. Increasing ZT is challenging due to the fact that the three parameters, S , K and σ , are interdependent, and changing one of them alters the others. Increase in ZT due to a decrease in thermal conductivity can be achieved by alloying and using the semiconductors of high atomic weight. $\text{Si}_x\text{Ge}_{1-x}$ alloy for high temperature TE material (power generation) is a good example to have lower thermal conductivity due to the alloying effect while maintaining good electrical conductivity [84]. Another way to decrease thermal conductivity without changing S and σ very much in bulk materials is to use semiconductors of high atomic weight such as Bi_2Te_3 and its alloys with Sb and Sn for room temperature and below (refrigeration) [19]. High atomic weight decreases speed of sound and thereby reduces thermal conductivity in the materials.

Figure 6-2. Thermoelectric figure of merit at room temperature versus year [19]. In 1950, the thermoelectric properties of Bi_2Te_3 and its alloys with Sn and Sb were discovered. Bulk material with $ZT_{300\text{K}} > 1$ has not been discovered. Nano-structured thin film superlattice of $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ with period 2.5-25 nm have $ZT_{300\text{K}} \sim 2.4$ and $\text{PbSeTe}/\text{PbTe}$ quantum dot superlattices have $ZT_{300\text{K}} \sim 1.6$.

However, the strong interdependence of the electronic transport properties (S , σ and K_e) has limited a ZT to about unity for commercial devices for a long time. Currently, the best commercially available TE materials for room temperature applications are still bismuth telluride-based intermetallic semiconductor materials, typically p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ and n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, although established as TE candidate more than 50 years ago [117]. Over the past two decades, nanostructures, such as superlattice thin films [119; 120], nanowires [121], and nanograins [122-125] have been introduced to enhance the TE property. At this stage, their major contribution was believed to be a significant reduction in K_L through the phonon scattering at the grain boundaries. Very recently, nano-engineering has been further extended to heterostructured nanocomposite materials. Typically, theoretical calculations [126; 127] have revealed that the metallic nanoinclusions, as secondary phase embedded in the semiconductor matrix, can introduce an energy-dependent carrier scattering

effect, where the band bending at the metal/semiconductor interface can scatter low-energy (cold) carriers to enhance the Seebeck coefficient without losing much in electrical conductivity. Such an energy-filtering effect can realize the simultaneous improvement in the power factor ($\text{PF} = S^2\sigma$) along with the suppressed thermal conductivity, thus promising to achieve higher ZT. This has been successfully demonstrated in $\text{Bi}/\text{Bi}_2\text{Te}_3$ [128] and $\text{Bi}_2\text{Te}_3/\text{Bi}_2\text{S}_3$ [129] nanocomposites, $\text{Pt}/\text{Sb}_2\text{Te}_3$ [130] and $\text{Ag}_x\text{Te}_y/\text{Sb}_2\text{Te}_3$ [131] dropcast films, $\text{PbTe}/\text{Bi}_2\text{Te}_3$ barbell nanowires [132], etc. based on various wet-chemical synthesis methods.

Physical vapour deposition techniques, such as pulsed laser deposition (PLD) [133; 134], sputtering [135; 136] and thermal evaporation [137], cater for dense and textured thin films with coherent grain boundaries, ensuring the excellent electrical conduction comparable to bulk single crystals [134]. In addition, they facilitate the Micro-Electro-Mechanical-system (MEMS) processing for on-chip devices [138]. On the other side, the power factor improvement was still a great challenge in the Bi_2Te_3 -based n -type polycrystalline materials due to their strong anisotropic dependence on texture [139; 140]. In this study, for the first time, we report the preparation of n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ textured thin films with Pt nanoinclusions via a one-step PLD method. Platinum was selected to dope $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ thin films because of the following reasons:

- a) Platinum and gold are highly unreactive metal, have stable electrical properties and they do not oxidize at any temperature [141]. XPS surface analysis confirms that the Pt species in the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ matrix are free from oxidization. The metals oxidize at any temperature (such as Cu, Cr, Al, Ag and

etc...) and do not have stable electrical properties are not promising choice for doping [141].

b) As illustrated above, the low thermal conductivity of thermoelectric film is desired to have high performance. Thermal conductivity of Pt (71.6 W/mK) is lower than Au (318 W/mK) [141]. Therefore, Pt is better choice for doping instead of Au.

c) The metals with high reflectivity are not suitable candidate for PLD method; because the laser pulse even in high energy is not able to vaporize them. For instance, reflectivity of Pt and Al at 248 nm wavelength is about 37% and 93%, respectively [142]. Therefore, Pt with low reflectivity at 248 nm is better selection for pulse laser deposition method.

d) Reflectivity of Au and Pt at 248 nm is about the same [142]. First, the film was prepared by using Au stripe to fabricate Au nanoinclusions, but the Au content was not detected by EDX analyses. This is due to the low absorption coefficient of gold, which is smaller than the absorption coefficient of Pt, at 248 nm wavelength (the absorption coefficient, ψ , is related to the excitation coefficient, κ , by the equation, $\psi=4\pi\kappa/\lambda$, where λ is the wavelength of the incident beam) [142].

Thermal conductivity of the films was measured by 3ω technique, and it is found that the thermal conductivity decreases with an increasing Pt dopant amount in the films.

6.2 Experiment

$\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ -based thin films with high c-axis texture were prepared on fused silica substrates at 350° C in 20 Pa (150 mTorr) argon pressure by using a KrF excimer laser (Lambda Physik Compex, $\lambda = 248$ nm) under 3 Hz repetition with $\sim 1.2 \text{ J/cm}^2$ laser energy density for each pulse. In order to prepare nanocomposite thin film with Pt nanoinclusions, a commercially available $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ tablet target was partially covered by a 0.1 mm thin platinum stripe (99.99%, Goodfellow) along the diameter. As illustrated in the inset of Figure 6-3, the rotation of the target setup during deposition ensured alternate deposition of both materials. Instead of using a pre-mixed composite target, our method can mostly avoid the simultaneous deposition and inter-reaction of Pt and Bi-Te-Se materials in a mixed plume. In addition, a variable amount of Pt nanoinclusions could be achieved by changing the width of the platinum stripe (1–3 mm). The thickness of each thin film was measured by a surface profiler (Alpha-Step IQ), while the Pt amount was detected by electron probe micro-analyzer (EPMA) equipped on a JEOL JXA-8530F Field emission microprobe. The thickness, Pt content and the nominal composition of each thin film are listed in Table 6-1.

Table 6-1. Thickness, Pt content and nominal composition of the thin films.

Sample	Thickness (nm)	Pt content (wt%)	Composition
N ₀	253	0	$\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$
N ₁	247	0.62	$\text{Pt}_{0.025}/\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$
N ₂	254	1.13	$\text{Pt}_{0.046}/\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$
N ₃	251	1.46	$\text{Pt}_{0.060}/\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$

The crystal structures of the thin films were characterized by X-ray diffraction (XRD) in a Bruker D8 Advance diffractometer with a $\text{Cu } K_\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Surface analysis of the thin films was performed by an X-ray photoelectron spectroscopy (XPS) using Theta Probe XPS (Thermo Fisher Scientific) equipped with an aluminum anode (15 kV, 100W, $h\nu = 1,486.6 \text{ eV}$). Cross-sectional transmission electron microscopy (TEM) images, selected-area electron diffraction (SAED) patterns and compositional analysis were taken using a JEOL 2100F at 200 kV equipped with Oxford X-ray energy dispersive spectroscopy (EDX) detector. The in-plane electrical conductivity and Seebeck coefficient of the thin films were measured by an Ulvac ZEM-3 using the standard steady-state method. The thermal conductivity of the thin films was measured by the differential method in 3ω technique; the detail was explained in chapter two. In order to fabricate a reference sample and an insulator layer between the gold wire and conductive TE films, 600 nm thick SiO_2 film was deposited by sputtering method on the bare substrate and TE films/substrate, respectively. Then a gold wire with 1 mm length, 40 μm width and 150 nm thickness, used as the heater and thermometer, was fabricated by using a lift-off technique on the SiO_2 layer. Ti layer with 5 nm thickness was used as an adhesion layer between gold wire and SiO_2 film.

6.3 Results and discussion

Figure 6-3 shows the XRD patterns of the as-prepared thin films, all of which can be clearly indexed to the well-crystallized rhombohedral structure (R-3m) of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ as previously reported [128]. In contrast with the powder XRD pattern, remarkably enhanced (00 l) peaks, as well as the very weak peak of

(015) at $2\theta \sim 28^\circ$, can be observed in the thin film patterns, which indicates their strong c -axis texture perpendicular to the substrate. For the thin films with Pt nanoinclusions, no diffraction peaks related to platinum metal phase can be detected in their XRD patterns, which is mostly because of the tiny amount of the Pt nanoinclusions in the matrix phase (<1.5 wt%, as detected by EPMA and listed in Table 6-1).

Figure 6-3. XRD patterns of the as-prepared thin films as compared with the powder XRD pattern. Inset is the schematic illustration of the nanocomposite thin film preparation by PLD method.

Pt species in the nanocomposite thin films can be detected by XPS surface analysis. Figure 6-4 (a) shows the XPS fine scan of Pt 4f in thin film N2. The binding energy of Pt doublets are located at 74.74 eV and 71.25 eV for Pt 4f

(5/2) and (7/2), respectively, with the spin energy separation about 3.49 eV. These values are characteristic for metallic platinum [143], showing that the Pt species in the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ matrix are free from oxidization or forming telluride compounds. In Figure 6-4 (b), the low-magnification cross-sectional TEM image shows a uniform thin film with columned structure perpendicular to the substrate surface. The high-magnification image in Figure 6-4 (c) reveals that the column structure corresponds to a well-crystallized $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ matrix phase with their layered lattice parallel to the substrate. The column edges are mostly composed of the grain boundaries of matrix phase with the presence of a great amount of stacking faults and structural defects [134]. The SAED pattern in Figure 6-4 (e), taken from the squared area in Figure 6-4 (c), clearly indicates a $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ single crystal pattern with *c*-axis perpendicular to the substrate. This is very consistent with the *c*-axis texture in the XRD pattern, and the same as the reported Bi_2Te_3 -based thin films [134; 135]. Besides the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ matrix phase, some dark contrast regions at the matrix phase boundaries, about 5~10 nm in width and 10~20 nm in length, can also be observed in Figure 6-4 (c). These regions can be clearly identified as Pt nanoinclusions based on the EDX line scan analysis. In addition, some of the Pt nanoinclusions are crystallized, as indicated by the well-ordered lattice in the circled area in Figure 6-4 (c), as well as its corresponding fast Fourier transform (FFT) pattern in Figure 6-4 (d).

Figure 6-4. (a) XPS Pt 4f scan, (b) low- and (c) high-magnification TEM images of the thin film N2, and (d) FFT and (e) SAED patterns of the circled and squared area in (c), respectively.

Under our TEM-EDX analysis, Pt nanoinclusions are located only at the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ grain boundaries but not inside the matrix grains. This may originate from the thin film growth mechanism of the Bi_2Te_3 -based thin films as well as our method to introduce Pt nanoinclusions with platinum. Based on physical vapor deposition techniques [135], Bi_2Te_3 -based materials have the strong tendency to stack along the c -axis during the deposition process, and leave the high-energy dangling bonds of ab -directions at lateral grain boundaries. This is usually followed by an intensive growth along ab -directions on a hot substrate surface [134], which can be regarded as a ripening process. In

our PLD fabrication of nanocomposite thin films, the laser ablation takes place alternately on the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ target and on the platinum stripe; thus, the mixing of and the reaction between Pt and Bi-Te-Se are largely suppressed. When the successive laser-ablated Pt atoms reach the growing thin film surface, the high-energy sites at $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ matrix phase grain boundaries are highly favorable in order to reduce the system energy. Since the Pt content in the sample is quite low, and most of the *c*-plane surfaces for matrix grains are not contaminated, the texture growth for the later $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ layers is unaffected. In the thin film ripening process, however, the grain growth of the matrix phase (along *ab*-directions) may be slightly interrupted at the site of Pt nanoinclusions, thus leaving the site as part of the matrix grain boundaries. Figure 6-5 shows measured temperature oscillation at room temperature of the gold wire as a function of the heating frequency for $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, $\text{Pt}_{0.025}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ and reference samples. Thermal conductivity of the TE films is calculated using equation (2-29). Measured cross-plane thermal conductivity of the TE films shown in Figure 6-6 at room temperature indicates that the thermal conductivity of TE film decreases with an increasing amount of Pt. The grain boundaries are increased by introducing Pt nanoinclusions with size and distribution in a few to hundreds nanometer scale. Phonons with mean free paths matched with the grain size and Pt nanoinclusion size are scattered effectively [144]. As shown in Figure 6-4 (b) and (c), the grains and Pt nanoinclusions with different sizes are responsible for scattering phonons with a variety of wavelengths. This scattering mechanism reduces lattice thermal

conductivity over the wide range of mean free paths of phonons in the thin films.

Figure 6-5. Measured temperature oscillation, ΔT , at room temperature of the gold wire as a function of the frequency for $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, $\text{Pt}_{0.025}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ and reference sample. Reference sample is 600nm thick SiO_2 on substrate. $\Delta T_{TE \text{ film}}$ is the temperature drop through the thickness of the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ and $\text{Pt}_{0.025}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ films.

Figure 6-6. Measured cross-plane thermal conductivity as a function of Pt content for the pure and nanocomposite thin films by the differential method in the 3ω technique.

In order to estimate the in-plane ZT values of these textured thin films, the in-plane thermal conductivity $K_{//}$ values were derived by the approximation based on the measured $K_{\perp}$, the Wiedemann-Franz law (with the Lorentz number $L =$

$2.0 \times 10^{-8} \text{ V}^2\text{K}^{-2}$ [124; 145]) and the assumption that the anisotropic factors of these textured thin films are the same as single crystals ($K_{//,e}/K_{\perp,e}= 4.3$ and $K_{//,L}/K_{\perp,L}=1.6$ [146]). The approximated calculation details can be found elsewhere [147]. As shown in Table 6-2, the estimated in-plane thermal conductivity of the thin films decreases from 1.162 W/mK for the pure phase thin film to as low as 0.86 W/mK by the addition of Pt nanoinclusions.

Table 6-2. Electrical conductivity, Seebeck coefficient, in-plane thermal conductivity $K_{//}$ and figure of merit of the thin films.

Sample	$\sigma_{\text{in-plane}}$ $\times 10^4 \text{ S/m}$	Seebeck $\times 10^{-6} \text{ V/K}$	$K_{//}$ W/mK	Temperature K	ZT
N0	6.655	209.375	1.162	303.05	0.760
N1	6.875	215.631	0.979	303.54	0.991
N2	7.152	221.601	0.909	303.38	1.171
N3	7.555	203.931	0.860	303.59	1.108

As a result, the estimated in-plane ZT of our textured nanocomposite thin films reaches 1.17 at room temperature, which corresponds to a more than 50% enhancement. In fact, the in-plane thermal conductivity of our nanocomposite thin films could be even lower than those shown in Table 6-2. Since the Pt nanoinclusions are mostly located at the grain boundaries between ab -planes, scattering of the in-plane phonons (transferring along ab -directions) would be more efficient than that of the cross-plane phonons. Therefore, an even greater gain for the in-plane ZT value can be expected. This is largely due to the great increase in carrier concentration as well as the simultaneous reduction in lattice thermal conductivity, based on the introduction of nanocomposite structure into the textured thin films.

6.4 Summary and conclusion

Textured n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ thin films with Pt nanoinclusions are successfully prepared via pulsed laser deposition. The TEM observation reveals that the Pt nanoinclusions are embedded at the grain boundaries of the semiconductor matrix. Thermal conductivity of samples is measured by the 3ω technique. By introducing Pt nanoinclusions, electrical conductivity of the nanocomposite thin film can be greatly improved due to increased carrier concentration, while the thermal conductivity is reduced. The reduction in thermal conductivity can be attributed to increased phonon scattering with a variety of wavelengths due to increased grain boundaries by introducing Pt nanoinclusions with different sizes and distribution in a few to hundreds nanometer scale. The increase of ZT values for thin films resulted from a significantly decreased lattice thermal conductivity arising from the scattering of Pt nanoinclusions and grain boundaries.

Chapter 7: Conclusions and Recommendations for Future Research

7.1 Conclusions

The objective of this work was to understand and examine the role of nanostructure in low dimension materials as a way of tuning thermal conductivity. In this work, room temperature thermal conductivities of Ti-based hard coating such as TiN, TiAlN, TiAlSiN and [TiN/TiAlN]_n multilayer coatings and Pt-doped n-type Bi₂Te_{2.7}Se_{0.3} nanocomposite were measured. Pulsed photothermal reflectance (PPR) and 3 ω techniques were applied to measure thermal conductivity of Ti-based hard coatings and n-type Bi₂Te_{2.7}Se_{0.3} nanocomposite, respectively.

Firstly, the TiAlN coatings with different atomic percentages of Ti and Al were deposited on stainless steel substrate (SS) to understand the effect of different material compositions on the thermal conductivity of the coatings. A series of

TiAlN coatings with different Al/Ti atomic ratio from 0 to 2.5 were deposited in a flowing pure nitrogen atmosphere. The result shows that the thermal conductivity and diffusivity of the coatings decrease rapidly with incorporation of Al in the TiN structure. The as-deposited TiAlN coatings showed a minimum thermal conductivity of about 4.5 W/mK at around Al/Ti=0.72. With the increase of Al content further, coating shows a two-phase mixture consisting of fcc TiN and wurtzite AlN crystalline phases, and thermal conductivity increases slightly.

In order to understand the effect of Al and Si contents and different material composition on thermal properties of nanocomposite TiAlSiN hard coating, a series of TiAlSiN coatings with different (Al+Si)/Ti atomic ratios from 0 to 1.59 were deposited on SS substrate. The result shows that the thermal conductivity and diffusivity of the coatings decrease rapidly with increasing Al and Si incorporation. The decrease in grain size and formation of nanocomposite structure, which consisted of crystalline nanograins embedded in a disordered, amorphous SiN_x matrix, are responsible for increasing phonon scattering and reducing the heat transported in the coatings.

$[\text{TiN}/\text{TiAlN}]_n$ multilayer coatings with bilayer number n equal to 5, 10, 20, 50, and 100 were deposited on SS substrate. The purpose of using this method was to understand the effect of increasing interfaces in the coating to reduce the heat transported. The obtained thermal conductivity and diffusivity decrease with the increase in the bilayer number, and coating shows the lowest thermal conductivity of 3.25 W/mK for coating with bilayer number of 100. The microstructure analysis of multilayer coatings shows a high defect and misfit

dislocation density between the TiN and TiAlN layers and a decrease in grain size of the coating with an increase in the bilayer number as well. With an increase in the number of bilayer in the $[\text{TiN/TiAlN}]_n$ multilayer coatings, the decrease in thermal conductivity can be attributed to the increased phonon scattering at the interfaces between the layers and grain boundaries.

By taking into consideration of all the results, we have successfully realized that the thermal properties of Ti-based hard coatings strongly depend on the microstructure and composition of the coatings. In order to have optimum performance for high-speed machining, by considering the lower thermal conductivity and higher hardness (coating's hardness is provided in appendix B), the suggested composition of Al/Ti and (Al+Si)/Ti atomic ratio for TiAlN and TiAlSiN coatings are at the range of around 0.7 and 0.60, respectively. For multilayer coating, the bilayer number 100 is suitable for high-speed machining because of enhanced hardness and low thermal conductivity. In total, our thermal properties' investigation was performed to explore and optimize the coating composition and layer structure to achieve the enhanced room temperature coatings performance for high-speed machining.

Textured *n*-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ thin films with Pt nanoinclusions were prepared via pulsed laser deposition. Our investigation of the thin film's thermal conductivity indicates that the thermal conductivity is dependent on Pt content. The microstructure analysis shows that the Pt nanoinclusions with different size and distribution in a few to hundreds nanometer scale are embedded at the grain boundaries of the semiconductor matrix. Electrical conductivity of the nanocomposite thin film is improved by introducing Pt nanoinclusions due to

increased carrier concentration while the thermal conductivity is reduced. The reduction in thermal conductivity can be attributed to increased phonon scattering due to increased grain boundaries by introducing the Pt nanoinclusions. The increase of ZT values for thin films resulted from a significantly decreased lattice thermal conductivity, arising from the scattering grain boundaries.

7.2 Recommendations for future research

Despite our investigation on tuning thermal properties of Ti-based hard coating for high speed machining and Pt-doped *n*-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ thin film for thermoelectric device application, some interesting topics for further work are highly recommended.

- For high temperature and high-speed machining applications, thermal properties of hard coatings are most important. In this study, room temperature thermal conductivity of Ti-based hard coatings was measured by the pulsed photothermal reflectance technique. Investigation of the coating's thermal conductivity at high temperature is recommended to study the thermal conductivity variation with temperature. This would help to understand the phonon scattering in the coatings at high temperature and optimize the coating composition and layer structure to achieve the best possible high temperature coating performance.
- For the coatings, a study has been carried out for cross-plane thermal conductivity. TiN coating has a columnar structure and according to

microstructure analysis, the formation of columns in TiN coating is disrupted by incorporation of Al and Si contents. However, in-plane thermal conductivity has not been carried out for the coatings. Thus, a study is needed to characterize the in-plane thermal conductivity by 3ω and transient thermal grating techniques to realize the effect of Al and Si contents on in-plane thermal conductivity.

- To understand the effect of different deposition techniques on thermal properties and microstructure of the Ti-based hard coatings, the coatings can be deposited by another method such as sputtering technique. Ti-based hard coating (such as nanocomposite and multilayer) with different microstructure can be fabricated and dependence of thermal properties with microstructure can be studied as well.
- Currently for room temperature applications, bismuth telluride-based intermetallic semiconductor, typically n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, and p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, with enhanced figure of merit (ZT) are the best candidates for thermoelectric materials [117]. Our investigation showed that the Pt doping in n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ film decreases lattice thermal conductivity and increases its figure of merit. However, doping Pt in p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ thermoelectric film and the effect of the doping on lattice thermal conductivity and figure of merit is another interesting area of study.

Author's Publications

Journal papers:

- 1) Ting Sun, **M. K. Samani**, N. Khosravian, Q. Liu, Q. Yan, B. K. Tay, C. L. Gan, H. H. Hng, Enhanced thermoelectric properties of n-type Bi₂Te_{2.7}Se_{0.3} thin films through the introduction of Pt nanoinclusions by pulsed laser deposition, submitted to *Nano Energy*.
- 2) **M. K. Samani**, et al. Thermal conductivity of titanium nitride/titanium aluminum nitride multilayer coatings deposited by lateral rotating cathode arc, submitted to *Surface and Coating Technology* (under review).
- 3) N Khosravian, **M.K. Samani**, G.C. Loh, G.C.K. Chen, D. Baillargeat, B.K. Tay, Effects of a grain boundary loop on the thermal conductivity of graphene: A molecular dynamics study, *Computational Materials Science* (2013) 79, 132-135
- 4) S. Fan, L.Y. Lim, Y.Y. Tay, S.S. Pramana, X. Rui, **M.K. Samani**, Q. Yan, B.K. Tay, Rapid fabrication of a novel Sn–Ge alloy: structure–property relationship and its enhanced lithium storage properties, *Journal of Materials Chemistry A* (2013) 1 (46), 14577-14585
- 5) **M. K. Samani**, X. Z. Ding, S. Amini, N. Khosravian, J. Y. Cheong, G. C. K. Chen, B. K. Tay, Thermal conductivity of TiAlSiN Coatings deposited by lateral rotating cathode arc, *Thin Solid Film* (2013) 537, 108-112.
- 6) N. Khosravian, **M. K. Samani**, G. C. Loh, G. C. K. Chen, D Baillargeat, BK Tay. Molecular dynamic simulation of diamond/silicon interfacial thermal conductance, *Journal of Applied Physics* (2013) 113 (2).
- 7) **M. K. Samani**, N. Khosravian, G. C. K. Chen, M. Shakerzadeh, D. Baillargeat, B. K. Tay. Thermal Conductivity of Individual Multiwalled Carbon Nanotubes. (2012), *International Journal of Thermal Science*, 62, 40-43.
- 8) M. Shakerzadeh, **M.K. Samani**, N. Khosravian, E.H.T. Teo, M. Bosman, B.K. Tay. Thermal conductivity of nanocrystalline carbon films studied by pulsed photothermal reflectance. *Carbon* (2011), volume 50, issue 3, 1428–1431.
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- 10) Xing-Zhao Ding, **M. K. Samani**, George Chen. (2010). Thermal Conductivity of PVD TiAlN Films using Pulsed Photothermal Reflectance. *Applied Physics A - Materials Science & Processing*, (2010) 101: 573–577.
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Conference:

- 1) **M. K. Samani**, L. Loisel, X. Z. Ding, N. Khosravian, G Chen, B. K. Tay, Engineering the Thermal Properties of CrAlSiN PVD Hard Coatings for Machine Tool Applications, E-MRS 2014 Spring Meeting, France.
- 2) L. Loisel, B. Lebental, **M. K. Samani**, C. W. Tan, C. S. Cojocaru, D. Baillargeat, B. K. Tay, Nanosecond-laser-induced graphitization and amorphization of thin nano-crystalline graphite films, E-MRS 2014 Spring Meeting, France.
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- 9) **M. K. Samani**, George Chen, N. Khosravian. (2009, November). Temperature-dependent Thermal Conductivity of Multi-walled Carbon Nanotubes. Paper presented at 10th annual Conference on Laser Ablation (COLA), Singapore.
- 10) Xing-Zhao Ding, **M. K. Samani**, George Chen. (2009, November). Thermal Conductivity of PVD TiAlN Films using Pulsed Photothermal Reflectance Technique. Paper presented at 10th annual Conference on Laser Ablation (COLA), Singapore.

Appendix A

Thermal boundary resistances of TiN coating

A discontinuity in temperature between the layers is caused by thermal boundary resistance when the adhesion between neighboring layers is poor. The heat diffusion into underlying layers is slowed down by the thermal boundary resistance. The thermal boundary resistance is small when film adheres well to the neighboring layers. In a two-layer model, thin film, sandwiched between the gold film and the substrate, is part of the thermal resistance, R_{th} . R_{th} is expressed as $R_{th}(d)=d_{film}/K_{in}(d)+R_{12}$, where $d_{film}/K_{in}(d)$ is the internal volume resistance, d is the thickness of the film, K_{in} is the thermal conductivity of the film and R_{12} is the thermal boundary resistances between the layers. Since this thermal resistor is linearly proportional to the film thickness, the volume resistance becomes large for thicker films. Thus for thicker films which are well adhered to the neighboring layers, the interface thermal resistance is relatively small (as compared to the volume resistance) and can be neglected. Conversely, if the thickness of the film is rather small or the adhesion is poor, we can expect the interface thermal resistance to become significant hence cannot be neglected.

In order to measure thermal boundary resistances ($R_{12}=R_1+R_2$) of TiN coating (thermal boundary resistances between the gold film and the TiN coating, R_1 , and between the TiN coating and substrate, R_2), the two-layer heat conduction model in the PPR technique was used [20; 25]. In this method, the thin TiN coating is modeled as a thermal resistance between gold film and SS substrate.

The TiN coatings with different thickness from 43 nm to 168 nm were deposited on stainless steel AISI 304 (SS) by the LARC system in a pure nitrogen atmosphere. During deposition, a negative DC bias of -70 V was applied to the substrates, and the substrate temperature was controlled at around 480° C. Then, a 0.8 μm thick gold film was deposited on the TiN coatings to enhance the heat absorption for the photothermal reflection measurement.

Figure A.1 shows the normalized surface temperature profile for the Au/TiN/SS structure. In order to obtain the thermal resistance (R_{th}), the temperature profile is fitted by using a two-layer heat conduction model to simulate heat transport in the Au/TiN/SS structure. A Least Square optimization method is used to fit the experimental data to an analytical solution of heat diffusion for the two-layer model using two parameters, thermal conductivity of the gold film, and thermal resistance (R_{th}). The average thermal conductivity for the gold film of 230 W/mK was obtained from curve fitting.

Figure A. 1 Surface temperature excursion profile of 43 nm TiN coating on SS substrate, coated with 0.8 μm gold.

Figure A.2 shows the thermal resistance as a function of the TiN coating thickness. It is observed that the thermal resistance increases with increasing the TiN coating thickness. Thermal boundary resistances (R_{12}) is determined by extrapolating to zero TiN coating thickness. The obtained thermal boundary resistances is $(2.86 \pm 0.24) \times 10^{-8} \text{ m}^2 \text{ K/W}$.

Figure A. 2 Thermal resistance for the TiN coatings.

Figure A.3 (a) and (b) show TEM and HRTEM images of the interface between the TiN and SS substrate, respectively. The SS substrate was directly coated with a TiN layer. The quality of the interface between the TiN and SS substrate is clearly observed in the images. The negative DC bias applied to the substrate increases the incidence energy of Ti ion during the deposition on SS substrate and improves the adhesion between the TiN coating and the substrate. Similar conditions were applied to deposit TiAlN and TiAlSiN coatings on SS substrates and improve the adhesion between the coatings and substrates as well. Vaz et al. [148] studied the addition of Al and Si in adhesion behaviour of TiN coating on high-speed steel by scratch test and reported that the addition of Al and Si in TiN structure improves the adhesion behavior of TiN coating. So,

we expect that the thermal boundary resistances (R_{12}) for TiAlN and TiAlSiN coatings is lower than the TiN coating.

Figure A. 3 (a) TEM image of the interface between the TiN and SS substrate; (b) HRTEM image of the interface between the TiN and SS substrate.

For TiN coating, the obtained thermal boundary resistances is in the range of $10^{-8} \text{ m}^2\text{K/W}$. Therefore, the thermal boundary resistances between the layers can be neglected. This is because the volume resistance (d/K_{int}) is in the range of $10^{-7} \text{ m}^2\text{K/W}$ (chapter 3-5), whereas the thermal boundary resistances (R_1 and R_2) are more than one order of magnitude lower. The volume resistance for TiAlN and TiAlSiN coatings is much higher than the thermal boundary resistances (R_{12}) for these coatings, because the thermal conductivity of these

coatings is lower than TiN coatings. Thus, for Ti-based hard coatings, a three-layer model (equation (2-15)) can be used for curve fitting and thermal contact resistance between the interfacial layers is neglected.

Appendix B

Nanotest 550 nanoindenter (Micro Material Ltd, UK) equipped with a Berkovich diamond indenter (a three-sided pyramid) was used to measure microhardness of the coatings. The Oliver and Pharr method was used to calculate the hardness. In order to avoid the substrate effect, maximum indentation depth was set at less than one tenth of the coating thickness. Hardness measurements were calibrated using a fused silica standard sample with the hardness around 8.8 GPa. The average hardness and standard deviation for each coating are shown in the figures.

B.1 Hardness of the TiAlN coatings

Figure B-1 shows the hardness of the TiAlN coatings measured by nanoindentation as a function of the Al/Ti atomic ratio in the coatings. It was found that in the lower range of Al content, the hardness of the coatings increased gradually with increasing Al content in the coatings, and a maximum hardness of about 35.8 GPa was obtained at Al/Ti=0.72. This increase in hardness is due to the solid solution hardening effect [149]. When the Al/Ti atomic ratio is increased further, hardness of the coatings dropped rapidly. With higher Al content, the softer h-AlN appears in the structure and reduces the coating hardness [59].

Figure B. 1 Hardness of the as-deposited TiAlN coatings as a function of the (Al/Ti) atomic ratio.

B.2 Hardness of the TiAlSiN coatings

Figure B-2 shows the hardness of the TiAlSiN coatings measured by nanoindentation as a function of the (Al+Si)/Ti atomic ratio in the coatings. It was found that in the lower range of Al+Si content, the coatings' hardness gradually increased with increasing (Al+Si)/Ti atomic ratio, and a maximum hardness of about 39 GPa was obtained at (Al+Si)/Ti=0.6. For more detail and description of the hardness, the reader is referred to reference [150].

Figure B. 2 Hardness of the as-deposited TiAlSiN coatings as a function of the (Al+Si)/Ti atomic ratio.

B.3 Hardness of the multilayer $[\text{TiN}/\text{TiAlN}]_n$ coatings

Figure B-3 shows the hardness of single layer TiN coating and the $[\text{TiN}/\text{TiAlN}]_n$ multilayer coatings measured by nanoindentation as a function of the bilayer number (n). It was found that the multilayer coatings show higher hardness than the single layer TiN coating. The maximum hardness of about 34.8 GPa was obtained for multilayer coating with bilayer number of 100. For more detail and description of the hardness, the reader is referred to reference [78].

Figure B. 3. Hardness of the as-deposited $[\text{TiN}/\text{TiAlN}]_n$ multilayer coatings as a function of the bilayer number (n).

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