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Magnetron Sputtered nc-TiN/a-SiN_x Nanocomposite Thin Films with High Hardness and High Toughness

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SUMMARY

Nanocomposite thin films comprise at least two constituent phases, for example, a dispersed nanocrystalline phase and a matrix. The matrix phase can be either amorphous or nanocrystalline. Nanocomposite thin films represent a new class of materials which exhibit improved mechanical, electronic, magnetic and optical properties owing to the size effect. Of all the exotic properties of the nanocomposite thin films, hardness and toughness are the most important ones for the applications in manufacturing industry. So far, researchers are focusing more on hardness. Some even reach 105 GPa by forming nc-TiN/a-Si₃N₄ (where nanocrystalline titanium (nc-TiN) embedded in amorphous silicon nitride matrix (a-Si₃N₄)) nanocomposite thin films using chemical vapor deposition (CVD) method. However, in most wear related applications, hardness is only one of many important properties, such as high hardness, toughness, good oxidation resistance, and so on.

This project focuses on the study of hardening and toughening mechanisms for nanocomposite thin films. The aim of this project is to **study the relationship between microstructure, hardness and toughness**, therefore to **obtain a thin film with high hardness and at the same time high toughness**. Reactive magnetron sputtering was used to prepare hard and superhard nc-TiN/a-Si_n nanocomposite thin films by co-sputtering Ti and Si₃N₄ targets in a gas mixture (argon and nitrogen). In order to improve the toughness of the as-prepared nanocomposite thin films, nickel was doped into the nc-TiN/a-SiN_x to obtain Ni-

toughened nc-TiN/a-SiN_x nanocomposite thin films by co-sputtering TiNi, Ti and Si₃N₄ targets. Co-sputtering of multi targets allows to tailor the microstructure by adjusting the deposition parameters, such as target power density, deposition temperature, substrate bias, and gas ratio. The as-deposited Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films possess high hardness and high toughness.

This project shows that superhard nc-TiN/a-SiN_x nanocomposite thin films are obtainable by reactive magnetron sputtering. Silicon content has a significant effect on film topography, microstructure and mechanical properties. With 14.9 at.% Si, the nc-TiN/a-SiN_x nanocomposite thin films possess an average hardness of 37 GPa. Refining grain size in the nanostructured thin films is the reason for the hardness increase. The toughness of the as-prepared nc-TiN/a-SiN_x nanocomposite thin films is improved by doping nickel. Doping from 0 to 40 at.% Ni in nc-TiN/a-SiN_x brings about an increase in toughness from 1.15 to 2.60 MPa m^{1/2} at an expense of hardness (dropped from 30 to 14 GPa). Ductile phase toughening through crack blunting and crack bridging is responsible for the toughness increase.

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SYMBOLS AND ABBREVIATIONS

Symbols

A	Contact area
$A(I)$	Area between loading and unloading curves
$A(II)$	Area under loading curve
D	Diagonal of Vickers indentation impression
D_w	Target power density
E	Elastic modulus
E_{eff}	Effective elastic modulus
E_f	Elastic modulus of film
E_i	Elastic modulus of indenter
E_r	Reduced elastic modulus
G	Shear modulus
G_c	Critical strain energy release rate
$G(r)$	Height-height correlation function
H	Hardness
H_p	Plastic hardness
H_U	Universal hardness
$I_m(hkl)$	Measured relative intensity of the reflection from (hkl) plane
$I_0(hkl)$	Standard relative intensity of the reflection from (hkl) plane
K	Stress intensity factor
K_{IC}	Fracture toughness
L	Original length of beam (or substrate)
L_{c1}	Lower critical load in scratch
L_{c2}	Higher critical load in scratch
P	Test indentation load
P_c	Load at fracture
P_g	Gas pressure
P_{max}	Peak indentation load
P_{N2}	Partial pressure of nitrogen
R	Radius of curvature

R_a	Roughness
R_1	Radius of silicon substrate before being coated
R_2	Radius of silicon substrate after being coated
S	Contact stiffness
T_{dep}	Deposition temperature
T_g	Gas temperature
T_{hkl}	Coefficient of texture
T_m	Melting point
T_{rm}	Room temperature
T_s	Substrate temperature
ΔU	Strain energy difference before and after cracking
U_{fr}^c	Energy dissipated during indentation chipping
U_{edge}	Energy of edge dislocation
U_k	Kinetic energy of ionized particles
U_{screw}	Energy of screw dislocation
$V_{boundary}$	Volume of grain boundary
$V_{crystal}$	Volume of crystalline
V_s	Substrate bias
Δa	Experiment error for lattice parameter
a	Half length of the diagonal of Vickers indentation impression Or length of the edge of cube corner indentation impression
a_{exp}	Experimental calculated lattice parameter
a_{true}	Lattice parameter true value
$\bar{b}$	Burgers' vector
b	Crack spacing
c	Crack length
d	Grain size
d_g	Diameter of gas molecule
d_{hkl}	Interplanar spacing
f_{gb}	Volume fraction of grain boundary
h	Indentation depth
h_c	Contact depth
h_{corr}	Corrected depth
h_f	Thickness of film on tensile substrate beam

h_{max}	Maximum indentation depth
h_{min}	Minimum indentation depth
h_s	Thickness of tensile substrate beam
$(h\ k\ l)$	Crystal plane indice
k	Boltzman constant
l_m	Mean free path
r	Crack tip radius
s	Span between two supporting positions
t'	Effective thickness
t_f	Thickness of film
t_s	Thickness of substrate
w	Width of the specimen
α	Smoothness quotient
α_f	Coefficient of thermal expansion of film
α_s	Coefficient of thermal expansion of substrate
β	Peak width at half maximum peak height
δ	Indenter geometry constant for fracture toughness calculation
δ_l	Indenter geometry constant for elastic calculation
δ_2	Indenter geometry constant for hardness calculation
δ_s	Geometrical parameter of specimen
ε	Indenter geometry constant for contact depth calculation
ε_f	Elastic strain of film
ε_s	Elastic strain of substrate
λ	X-ray wavelength
ν	Poisson's ratio
ν_f	Poisson's ratio of film
ν_i	Poisson's ratio of indenter
θ	Bragg angle
ρ	Crack density
σ	Residual stress
$\sigma_{applied}$	Applied stress
σ_c^f	Effective critical cracking stress
σ_g	Growth-induced stress
σ_m	Mismatch induced stress

σ_i	Tensile stress
σ_T	Thermal stress
σ_y	Yield stress
σ_y^s	Yield stress of the substrate
ω	Interface width
ξ	Lateral correlation length

Abbreviations

AES	Auger electron spectroscopy
AFM	Atomic force microscopy
CPR	Crack propagation resistance
CVD	Chemical vapor deposition
CTE	Coefficient of thermal expansion
DC	Direct current
DLC	Diamond like carbon
EDX	Energy dispersive X-ray analysis
FWHM	Full width at half maximum
GIXRD	Grazing incidence X-ray diffraction
HRTEM	High-resolution transmission electron microscopy
PD	Planar density
PVD	Physical vapor deposition
RBS	Rutherford back scattering spectroscopy
RF	Radio frequency
SAD	Selected area diffraction
SEM	Scanning electron microscopy
SZM	Structural zone model
TEM	Transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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CHAPTER 1 INTRODUCTION

1.1 Overview

Nanotechnology is one of the key technologies of the near future. Nanocomposite thin films comprise of at least two phases, the nanocrystalline and the matrix phase. The general characteristics of nanocomposite films are a host material with another material homogenously embedded in, with one (or both) of these materials having a characteristic length scale of 1-100 nm. There has been an increasing interest in the study of nanocomposite thin films owing to their promising properties. Switzerland embarked their national "nano science" program on January 1, 1996 [1], covering areas of nano-mechanics, nano-tools and nano-method, etc. In the field of wear protection, in machining application alone there are more than 40% of all cutting tools being coated by wear resistant films. However, the use of coolant is still inevitable in a lot of applications. Depending on the kind of machining, the recycling costs of these coolants amount to 10% - 40% of the total machining costs. For example, in Germany alone these costs approach one billion US dollars per year [2]. Wear resistant, hard films for high speed dry machining would allow the industry to increase the productivity of expensive automated machines and to save on the high costs presently needed for environmentally hazardous coolants. It is clear that the nanocomposite thin films are at the beginning of their development with a wide range of applications.

1.2 Objectives

Of all the exotic properties of the nanocomposite thin film, hardness and toughness are the most important ones in the field of manufacturing industry. By convention, hard materials usually refer to the materials with Vickers hardness greater than 20 GPa and superhard materials are those with Vickers hardness exceeding 40 GPa, while ultra-hard means the hardness exceeds 80 GPa. So far, researches are focusing more on hardness. Some even reach 105 GPa [3]. However, in most of the wear resistant applications, hardness is only one of the many properties, such as high hardness and toughness, good oxidation resistance, and so on. Thus, high hardness thin film in combination of high toughness needs to be studied.

1.3 Scope

In this project, I focus on the study of hardening and toughening mechanisms for nanocomposite thin films, emphasize the relationships between microstructure, hardness, and toughness. Nanocomposite thin films with high hardness and high toughness will be prepared with magnetron sputtering technique. The nanocomposite thin films possess of a multi-phases microstructure through "implanting" a nanocrystalline or a second or third phase of nano scale into the otherwise uniform and amorphous matrix. The nanocrystalline phase used is titanium nitride (nc-TiN) and the matrix is amorphous silicon nitride (a-SiN_x). In order to increase toughness, metallic Ni is selected as a toughening agent. The aim is a film with a good combination between high hardness and high toughness.

1.4 Organization of the thesis

Present status and development of nanocomposite thin films is presented in chapter 2. In this chapter, definition of nanocomposite thin films, microstructure design, preparation method, microstructure and mechanical property characterizations will be introduced and discussed in detail. The relationship between microstructure and mechanical properties will be illustrated. Project overview and experimental details will be described in chapter 3. The film deposition parameters, chemical composition and microstructure identification, and methodologies used for mechanical property characterization are discussed in detail. Chapter 4 presents results and discussions, where the film chemical composition, microstructure and mechanical properties of the resultant films are analyzed and summarized. The relationship among deposition parameters, chemical composition, microstructure and mechanical properties are dealt with systematically. Finally, the conclusions and recommendations are put in Chapters 5.

CHAPTER 2 CURRENT STATUS OF THE DEVELOPMENT OF NANOCOMPOSITE THIN FILMS

In this chapter, the present status of the research and technological development in the field of nanocomposite thin films will be reviewed. Discussed in details are coating design, preparation, chemical composition characterization and microstructure identification, followed by measurements of mechanical properties including hardness and toughness.

2.1. Introduction

Nanocomposite thin films comprise at least two phases, a nanocrystalline phase and a matrix phase, where the matrix can be either nanocrystalline or amorphous phase. The general characteristics of nanocomposite coating are a host material with another material homogeneously embedded in it, with one (or both) of these materials having a characteristic length scale of 1-100 nm as schematically illustrated in Fig. 2-1.

Fig. 2-1 Schematic diagram of nanocomposite coating microstructure, showing nanocrystalline phase embedded in matrix.

2.2. Deposition of Hard and Tough Thin Films

2.2.1. Design

In conventional bulk materials, refining grain size is one of the possibilities for hardness increase. The same is true for films or coatings. With a decrease in grain size, the multiplication and mobility of the dislocations are hindered, and the hardness of materials increases according to the ‘Hall–Petch’ relationship [4, 5]:

$$H(d) = H_0 + Kd^{-1/2} \quad (2-1)$$

This effect is especially prominent for grain size down to tens of nanometers. However, dislocation movement, which determines the hardness in conventional materials, has little effect when the grain size is less than approximately 10 nm. At this size scale, further reduction in grain size brings about a decrease in hardness (c.f. Fig. 2-2) because of grain boundary sliding [6]. Softening caused by grain boundary sliding is mainly attributed to large amount of defects in grain boundaries, which allow fast diffusion of atoms and vacancies under stress [7, 8].

Chapter 2 Current Status of the Development of Nanocomposite Thin Films

As such, further increase in hardness requires hindering of grain boundary sliding. This can be realized through proper microstructural design, i.e. by increasing the complexity and strength of grain boundaries [9]. Multiphase structures are expected to have interfaces with high cohesive strength, since different crystalline phases often exhibit different sliding systems and provide complex boundary to accommodate a coherent strain thus preventing formation of voids or flaws [10]. A variety of hard materials can be used in nanocomposite coating microstructural design. Fig. 2-3 shows potential hard materials.

Fig. 2-2 Hardness of material as a function of grain size. When grain size being greater than the optimum value, with decrease of grain size, hardness increases (Hall-Petch relationship). When grain size being less than the optimum value, with decrease of grain size, hardness decreases (anti-Hall-Petch relationship) [7]

Fig. 2-3 Hard materials for nanocomposite coatings in the bond triangle and changes in properties with the change in chemical bonding. They include (1) covalent bonding materials with high hardness and high temperature strength, (2) metallic bonding materials with good adhesion and toughness and (3) ionic bonding materials with good stability and inertness [11].

Apart from hardness, good mechanical properties also include high toughness. High toughness can be obtained in nanocomposite thin films through the nano size grain structure as well as deflection, meandering and termination of nanocracks [12]. Veprek proposed a design concept for novel superhard cerarnic/ceramic nanocomposite coatings with high toughness [13 -15]. In this design, multiphase structure is used to maximize the interface complexity and ternary or quaternary systems with strong tendency of segregating into binary compounds used to form sharp and strong interface in order to avoid grain boundary sliding [6]. The crystallite size is controlled to approximately 3-4 nm and the separation distance between crystallites maintained at less than 1 nm. Based on this design concept, Veprek and co-workers prepared nc-TiN/a-Si₃N₄/a-&nc-TiSi₂ [3], nc-TiN/a-Si₃N₄

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[16], nc-W₂N/a-Si₃N₄ [17], nc-VN/a-Si₃N₄ [18], nc-TiN/a-BN [19] and nc-TiN/a-BN/a-TiB₂ [20] superhard nanocomposite coatings by means of plasma CVD. In nc-TiN/a-Si₃N₄/a-nc-TiSi₂ nanocomposite coating system, TiN nanocrystals were imbedded in amorphous Si₃N₄ (existing in grain boundary). Also existing in grain boundaries were amorphous TiSi₂ and crystallite TiSi₂ (c.f. Fig. 2-4). An ultra high hardness (H_v exceeding 100 GPa [3]) was obtained for this system. In addition, the indentation test did not induce microcracks, indicating good toughness. The authors attributed the toughness enhancement to the lack of large stress concentration at the tip of the crack due to the nano scale of the crystals. In fact, the stress concentration factor at the tip can be estimated through [21]

$$\frac{\sigma_{tip}}{\sigma_{applied}} = 1 + 2\sqrt{\frac{c/2}{r}} \quad (2-2)$$

Where, c is crack length and r crack tip radius. For $c/2 = 1-2$ nm and $r = 0.2-0.3$ nm (one atomic bond length), the stress concentration factor is only 4-6 (according to eqn(2-2)): a very small number compared to 30-100 in conventional microstructure [3]. The crack propagation is also strongly hindered in the nanocomposite structure due to the absence of dislocation activity in crystallite of 3-6 nm in size. In this case, crack can only propagate along grain boundaries. When crack size approaches that of the crystallite, the crack has to undergo bending or branching. After that, only the component of the applied stress normal to the plane of the bent or branched crack may cause further propagation. Thus the stress that drives crack propagation decreases, resulting in a deceleration of crack propagation. In Veprék's design, two immiscible nitrides (nc-TiN and a-Si₃N₄) were used [13,22,23] to achieve thermal stability. This, however, may degrade

the cohesive strength of the interface between the crystal and boundary [24]. When local tensile stress at the crack tip is higher enough, unstable crack propagation eventually results [25].

Fig. 2-4 Schematic diagram of nanostructure of nc-TiN/a-Si₃N₄/a- & nc-TiSi₂ nanocomposite. TiN nanocrystals were imbedded in amorphous Si₃N₄ (existing in grain boundary). Also existing in grain boundaries were amorphous TiSi₂ and crystallite TiSi₂. TiN crystallite size is approximately 3-4 nm and the separation distance between crystallites is less than 1 nm [3].

In order to obtain superhardness, usually plastic deformation is strongly prohibited, and dislocation movement and grain boundary sliding are prevented, thus probably causing a loss in ductility. Today, more and more researchers realize that a certain degree of grain boundary sliding are necessary in order to improve toughness of nanocomposite coatings. Usually, to overcome the brittleness of ceramic bulk materials, a second ductile phase is incorporated to improve the toughness of the composite [26-28]. In recent years, the microstructure of these composites has been further refined by the addition of nanometer sized metal particles [29, 30].

Chapter 2 Current Status of the Development of Nanocomposite Thin Films

This should also apply to thin films and coatings. Musil and co-workers embedded crystalline nitrides in metallic Cu [31,32], Ni [33-35] and Y [36], etc. In these coatings, the crystallite size of the ceramic phase is normally controlled less than 10 nm, and the volume of the boundary is greater than that of hard phase [37]. The hardness of these coating systems varied from 35 GPa to approximately 60 GPa. The existence of metal matrix is expected to improve toughness by crack tip blunting and/or the increase of the work of plastic deformation. In such design, however, the metallic grain boundary thickness cannot be too thin: a very thin grain boundary renders the toughening mechanism ineffective because in the case of nano scale grains, dislocation movement is restricted [38]. Should this happen, the mechanical response of the ceramic/metal nanocomposite will be effectively similar to that of ceramic/ceramic nanocomposite. (That will defeat the purpose of incorporating the soft metallic phase), Another way of enhancing toughness is to allow grain boundary sliding to take place (rather than cracking) to release the accumulated strain. Voevodin et al. [38, 39] embedded hard nanocrystalline carbide of 10-20 nm in amorphous carbon (a-C) matrix. Crystallite size of this magnitude can restrict initial crack size and create a large volume of grain boundaries [40]. The thickness of amorphous boundary should be maintained above 2 nm to prevent interaction of atomic planes in the adjacent grains and to facilitate grain boundary sliding, but less than 10 nm to restrict path of a straight crack. As a result, nc-TiC/a-C and nc-WC/a-C nanocomposite thin films achieved a “scratch toughness [41]” 4-5 folds that of the nanocrystalline carbide alone, at expense of some hardness.

2.2.2.Synthesis

Different techniques are now available for preparation of nanocomposite thin films. The most promising methods are chemical vapor deposition (CVD) [42,43] and magnetron sputtering [44], although other methods, such as laser ablation, thermal evaporation, ion beam deposition and ion implantation are also used by various researchers [45]. High deposition rate and uniform deposition for complicated geometries are the advantages of CVD method compared with magnetron sputtering. However, the main concern for CVD method is that the precursor gases TiCl_4 , SiCl_4 , or SiH_4 may pose problems in production because of their corrosive nature and danger of fire hazard. Moreover, the incorporation of chloride in protective films may induce interface corrosion problems during exposure to elevated temperatures under working condition. For most applications, a low deposition temperature is required to prevent substrate distortion and loss of mechanical properties. This is difficult to realize in CVD process.

At present, significant effort is devoted to preparation of nanocomposite thin films using magnetron sputtering since this technology is a low-temperature and a far less dangerous method compared with CVD [46]. Also, it can easily scale up for industrial application. In magnetron sputtering, energetic ion bombardment is used to vaporize the source material, often referring to as the target. The deposition system is filled with a noble gas, often argon, to a total pressure of 0.01 to 0.1 mbar. A negative potential of some kV is applied to the target. Positive ions naturally occurring in the gas will therefore be accelerated towards the target. When they impinge on the target, they transfer their momentum to surface atoms

Chapter 2 Current Status of the Development of Nanocomposite Thin Films

of the target, and if the momentum in both direction and value is higher than the surface binding energy a target atom will be ejected, i.e. sputtered. This ejected flux of target atoms, which has a main direction, is then transported through the space towards the substrate. Depending on the gas pressure and the distance between substrate and target, the flux will be more or less scattered by the gas. The average distance an atom can travel before a collision is called the mean free path. The mean free path l_m can be estimated through [47,48]

$$l_m = \frac{kT_g}{\sqrt{2}\pi P_g d_g^2} \quad (2-3)$$

Where, k , Boltzman constant, T_g and P_g gas temperature and pressure, and d_g diameter of the gas molecule ($d_{Ar} = 0.364$ nm). During sputtering process, the film surface is ion bombarded, which can densify the growing film by enhancing the surface atom mobility. In addition, ion bombardment of the growing film can restrict the grain growth and permit the formation of nanocrystalline. The size and crystallographic orientation of grains can be controlled by the energy of bombarding ions. Kinetic energy of ionized particles can be estimated by [48-51]:

$$U_k \propto \frac{D_w V_s}{P_g^{1/2}} \quad (2-4)$$

Where, U_k , kinetic energy, D_w , target power density, V_s substrate bias and P_g gas pressure.

2.3. Physical Properties

2.3.1.Composition

Film characterization is an inevitable and vital step in ensuring high quality film for the intended application. Different characterization techniques can be used to identify nanocomposite thin films: X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Rutherford back scattering spectroscopy (RBS) and energy dispersive X-ray analysis (EDX) are powerful tools for characterizing the chemical composition [52], each with different penetration and accuracy, as illustrated in Table 2-1.

Table 2-1 Composition analysis methods [52]

Analysis Methods	Elemental Range	Detection Limits (at.%)	Spatial Resolution	Penetration
XPS	Li - U	0.1 - 1	100 μm	1.5 nm
AES	Li - U	0.5	10 nm	0.5 - 7.5 nm
RBS	Li - U	1.0	1 - 4 mm	2 - 30 nm
EDX	Be - U	0.1	0.5 - 2.0 μm	1 - 3 μm

2.3.2.Topography

Topography or surface morphology can be characterized using atomic force microscopy (AFM) and scanning electron microscopy (SEM). Topography or surface morphology of thin films can be affect by ion bombardment during the film growth and the post annealing or oxidation process. The effect of ion

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bombardment on film surface morphology has been investigated [53]. The study of the topography of thin film by AFM shows that the average roughness slightly decreases from about 1.6 nm to below 1.0 nm due to the applied ion bombardment. The effect of post annealing on surface morphology of amorphous carbon nitride films deposited by DC magnetron sputtering were studied, AFM result shows that thermal annealing can gradually change the surface structure to a uniform granular texture [54]. In studying annealing behavior of TiN/SiN_x, Diserens et al. [55] found that with increase in annealing temperature, the TiN/SiN, finely structured surface becomes smoother with the formation of a passive layer at 770 °C. Further increasing the temperature above 850 °C leads to significant increase in surface roughness, which finally leads to the formation of faceted grains at 940 °C.

2.3.3. Microstructure

Thin film microstructure information can be obtained by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), grazing incidence XRD (GIXRD), and selected area diffraction (SAD), etc.

2.3.3.1. Grainsue

The study of the grain size is especially important for nanocomposite thin films because of the magnitude involved. Precision control of grain size can be conducted using reactive magnetron sputtering, where the grain size can be

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controlled by basic process parameters including partial pressure of reactive gas (e.g. nitrogen for nitrides), substrate temperature, substrate bias and target power density which controlling content of alloying element. For transition metal nitride thin films prepared by reactive magnetron sputtering, partial pressure of nitrogen P_{N_2} has a significant effect on grain size. Take for an example, Ni-Cr-N thin film deposited at room temperature [34], the grain size d decreases with increase of partial pressure of nitrogen P_{N_2} (c.f. Fig. 2-5). Misina et al. [35] have investigated the effect of variation of substrate temperature on the grain size of TiN-Ni thin films. The size of both TiN and Ni grains increases sharply with increasing substrate temperature T_s in the range of 270-430 °C, as depicted in Fig. 2-6. They also have investigated the relationship between the variation of TiN grain size and substrate bias, V_s . The results are tabulated in Table 2-2. The TiN grain size generally increases with increase in substrate bias. The same trend was reported for Zr-Cu-N [56] and Cr-Cu-N [57] coatings system.

Fig. 2-5 Grain size and micro hardness of the Ni-Cr-N film deposited on 15 330 steel substrate as a function of partial pressure of nitrogen P_{N_2} . The grain size of (Cr,Ni)N continuously decreases from about 30 nm down to 2 nm with increasing partial pressure of nitrogen from zero to 0.3 Pa [34].

Fig. 2-6 Grain size of TiN and Ni as a function of substrate temperature. The size of both TiN and Ni grains increases with increasing substrate temperature in the range of 270-430 °C [35].

Table 2-2 Variation of the grain size of TiN with substrate bias, V_s [35]

Substrate Bias (V)	TiN Grain Size (nm)
-27	1.3
-100	3.8
-200	5.4

The concentration of the 'alloying element', such as the Cu concentration in TiN-Cu, Si concentration in nc-TiN/a-Si₃N₄, Si₃N₄ fraction in nc-TiB/a-Si₃N₄ and nc-

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W₂N/a-Si₃N₄ also have significant impact on the size of the crystallite in the coatings [12, 58, 59]. Veprek et al. [13, 60, 61] have investigated in detail the effect of silicon content on the grain size of nc-Me_nN (Me = Ti, V, W) in nc-Me_nN/a-Si₃N₄ nanocomposite thin films prepared by plasma CVD. They pointed out that the minimum crystallite size is expected at silicon content of 10-12 at.%. With silicon content increasing from zero to about 10-12 at.%, the grain size decreases, reaches a minimum and a further increases in silicon content results in increase in crystallite size (c.f. Fig. 2-7).

Fig. 2-7 Dependence of the crystallite size and lattice strain on the Si content in the nc-TiN/a-Si₃N₄ thin films. The minimum grain size 3.5 nm is obtained for Si content in the range of 10-12 at.% [61].

Similar results have been obtained by other researchers [62, 63] on both Ti-Si-N film system and other systems, e.g. effect of carbon on the phase structure of zirconia films. Surprisingly, superhard nc-(Ti_{1-x}Al_x)N/a-Si₃N₄ nanocomposite coatings are also thermally stable both in grain size and hardness up to a

temperature of 1200 °C (c.f. Fig. 2-8). Above 1200 °C, however, recrystallization takes place thus increasing in grain size and decreasing in hardness are observed.

Fig. 2-8 Example of annealing behavior of nc-(Ti_{1-x}Al_x)N/a-Si₃N₄ sample deposited on cemented carbide at a temperature of approximately 300 °C. The average crystallite size is approximately 3 nm after deposition. It is evident that this crystallite size does not show any significant increase up to a temperature of 1200°C, whereas the hardness shows a slight increase [23].

2.3.3.2. Lattice parameter

Although lattice parameter has been studied in detail, the peculiarities of lattice parameter changes require further efforts. Based on experience with TiN produced by magnetron sputtering, new hard compound films in the system Ti-Al-N, Ti-Zr-N, Ti-Al-Zr-N, Ti-Si-N and Ti-Al-V-N have been developed. Investigations show that all the compound coatings in this series crystallized into a face centered cubic

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(fcc) TiN lattice with reduced or enlarged lattice parameter depending on the amount and radius of the foreign atoms. For instance, the lattice parameter of Ti-Al-N cell is smaller than that of the TiN lattice, and the decrease aggravates with increase in aluminum content. Apparently some of the titanium atoms of the TiN lattice are replaced by aluminum atoms and substitutional solid solution of (Ti,Al)N comes into existence. Since aluminum atom is smaller (1.26 Å in radius [64]) than that of the titanium (1.47 Å in radius [64]), the (Ti,Al)N lattice decreases with increases in aluminum content [65]. For the nc-(Ti_{1-x}Al_x)N/a-Si₃N₄ system [66], there is an increase of the lattice parameter with increase of Ti content as show in Fig. 2-9. Rebouta et al. [67-69] have investigated the (Ti,Si)N ternary elements thin film prepared by reactive magnetron sputtering. XRD patterns with the 8-28 scan mode show that one of the phases is TiN. The other phase, it seems to be a cubic lattice structure, where the Si in this case occupies some of the Ti position. Other researchers also pointed out, with a silicon content of about 8-10 at.%, the crystalline phase reaches maximum lattice parameter, and then with the increase of silicon content, the lattice parameter decrease and Si₃N₄ come into being [61]. Such effects of the added alloying element can also be found in the Ti-Al-N system [70].

Fig. 2-9 Lattice parameter of TiAlSiN thin films vs. Ti content. With increase of Ti content, lattice parameter increases slightly. Notice, that the value of the lattice parameter with 30 at.% Ti is subjected to a large error because that sample is largely amorphous [66].

2.3.3.3. Structure

Mechanical properties are dictated by materials' structure. So it is important to investigate the structure. The microstructure of a single-phase film can be described by the so-called structural zone model (SZM) developed by Movchan et al. [71]. Three zones can be identified. In the first zone, where the homologue temperature T_s/T_m (where T_s is the substrate temperature and T_m the film melting point, all in K) < 0.3 , neither surface nor bulk diffusion is high enough. Adatoms will therefore have very low mobility on the surface, which results in a columnar structure with voids in the grain boundaries due to shadowing effects. In the second zone, $0.3 < T_s/T_m < 0.5$, the surface diffusion is high enough to give smooth and dense films. In the third zone where $T_s/T_m > 0.5$, bulk diffusion promotes growth of film with equiaxed grains. The model proposed by Movchan et

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al. has later been developed by Thornton [72, 73] through adding a third dimension, expressed in terms of the sputtering gas pressure (c.f. Fig. 2-10). The gas pressure determines the mean free path for all species, a high gas pressure relates to a low energy flux, as traveling species will lose energy through interactions with other species.

Fig. 2-10 Schematic diagram of dependence of film structure on substrate temperature and argon pressure: (1) at low argon pressure a broad zone 1- zone 2 transition zone consisting of densely packed fibrous grain was identified; (2) zone 2 columnar grains tended to be faceted at elevated temperatures, although facets were often replaced by smooth flat surfaces at high temperatures [72].

However, this model does not work when impurities or additives are incorporated in the film [74, 75]. Impurities or additives stop the grain growth and stimulate a re-nucleation of grain that results in the globular structure. For instance, in the Ti-Si-N thin film deposited by co-sputtering Ti and Si in nitrogen atmosphere, SEM observations show that the addition of silicon to TiN film transforms the (111)

oriented columnar structure into a dense finely grained structure [76], as shown in Fig. 2-11.

Fig. 2-11 SEM morphology of cross section of (a) TiN and (b) Ti-Si-N (12 at.% Si) films illustrating the influence of Si incorporation on the film morphology. The addition of Si changes the fracture morphology from a pronounced columnar microstructure to a dense, fine-grained structure for a Si content of 12 at.% [76].

To describe the microstructure of thin film with added element, Barna et al. [77-81] developed a two-phase microstructure model as shown in Fig. 2-12. Impurity or additive phase covering either the surface of individual islands or the grain boundaries in the polycrystalline structure can inhibit the grain boundary migration thus the processes developing the grain size and the restructuration texture are inhibited. By this way, decreased grain size and weak texture or even in random orientation can be achieved. This model has been successfully used in research. For example, the microstructure of the Zr-Cu-N nanocomposite thin films with low content (1.2 at.%) of Cu and high content (20 at.%) of Cu [56].

Fig. 2-12 Schematic diagram of main characteristics of structure zones considering the effect of impurities or additives on the microstructure. There are four typical microstructure zones. With increasing of additives, grain size decreases and random orientation can be obtained [77].

2.4. Mechanical Properties

2.4.1. Hardness Measurements

The materials handbook defines hardness as the resistance of materials to plastic deformation, usually by indentation. Hardness can be calculated through [10] :

$$H = \frac{P}{A} \quad (2-5)$$

Where, P is the test indentation load and A contact area. Microindentation and nanoindentation can be carried out to measure thin film hardness. Effect of the substrate on determination mechanical properties of films using indentation has been discussed in detail by Nix [82, 83]. It is widely accepted that when the indentation depth is less than one tenth of the thickness of the thin film, the effect of substrate on the film hardness can be neglected [84]. In microindentation, the tester applies the selected test loads from several hundred mN to about 10 N using dead weights. The indentations are typically made using a Vickers indenter which is a regular pyramid made of diamond with an angle of 136° between the opposite faces. The hardness value of thin film as thin as a few microns can be calculated using the test load and the contact area. Whereas in nanoindentation test, feature less than 100 nm across, thickness as thin as less than 5 nm, can be evaluated [52, 85]. In contrast to microindentation where the indentation force ranges from several hundred mN to about 10 N, nanoindentation only uses 100 μ N to a few mN. Nanoindentation can be carried out with a sharp indenter. The Berkovich indenter with an angle of 115° is useful when one wishes to probe properties at the smallest possible scale [86]. During the indentation, the indenter is forced into the surface at a selected rate and to a selected maximum force or a selected maximum indentation depth. A load-displacement curve is obtained and the depth of the indentation is measured to evaluate the actual contact area during indentation which yields the hardness and elastic properties. In this section, hardness measurements for thin films using indentation have been reviewed. These include Oliver-Pharr method, force indentation function method, and Joslin-Oliver method.

2.4.1.1.Olive-Pharr method

Today, the most widely used hardness measurement is that of Oliver-Pharr method [84]. This method assumes that there is always some downward elastic deflection or “sink-in” situation in the material surface upon indentation (c.f. Fig. 2-13).

Fig. 2-13 Schematic representation from a cross-section through an indentation, showing the maximum indentation depth h_{max} , contact depth h_c , minimum indentation depth h_{min} , and sink-in situation.

In this method, a small indentation is made with a Berkovich indenter, and displacement (or penetration depth) h , is continuously recorded during a complete cycle of loading and unloading and therefore a load-displacement curve is obtained as illustrated in Fig. 2-14. The contact depth h_c is estimated from the load-displacement curve through

$$h_c = h_{max} - \varepsilon \frac{P_{max}}{S} \tag{2-6}$$

Where, h_{max} maximum indentation depth, P_{max} peak indentation load, S contact stiffness and ε a constant which depends on the indenter geometry. Empirical

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studies have shown that $\epsilon = 0.75$ for a Berkovich indenter. The contact area A is estimated by evaluating an indenter shape function at the contact depth h_c :

$$A = f(h_c) \quad (2-7)$$

The shape function, $f(h_c)$, relates the cross-sectional area of the indenter to the distance h_c from its tip. For Berkovich indenter, the shape function is given by $f(h_c) = 24.56 h_c^2$. Once the contact area is determined from the load-displacement curve, the hardness H , and effective elastic modulus E_{eff} follow from:

$$H = \frac{P_{\text{max}}}{A} \quad (2-8)$$

and

$$E_{\text{eff}} = \frac{1}{\delta_1} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad (2-9)$$

Where, δ_1 is a constant which depends on the geometry of the indenter, and $\delta_1 = 1.034$ for the Berkovich one [84, 87].

Fig. 2-14 Load-displacement curves for Oliver-Pharr method, showing the maximum indentation depth $h_{\max}$, contact depth h_c and minimum indentation depth $h_{\min}$.

The Oliver-Pharr method of calculating contact area does not account for the "extra" area due to pile-up, and hence underestimates the contact area thus overestimates the hardness and effective elastic modulus [83]. However, if the thin film is harder than the substrate material, this method can be conveniently used to determine hardness with high precision. Because for hard film on soft substrate, there usually is the "sink-in" situation on the coating surface during indentation and very minimum pile-up.

2.4.1.2. Force indentation function method

Vickers indenter has been used in the force indentation function method. The universal hardness H_U is determined by both plastic and elastic components of the coating deformation, and can be calculated through [88]

$$H_U = \frac{1}{26.43} \frac{P_{\max}}{h_{\max}^2} \quad (2-10)$$

In addition to the universal hardness H_U , the plastic hardness H_p induced by plastic deformation can be estimated by [88]

$$H_p = \frac{1}{26.43} \frac{P_{\max}}{h_{\min}^2} \quad (2-11)$$

This method has been used by most of the material researchers to calculate the hardness of thin films. For superhard thin films, eqn(2-11) has been improved by using the contacted indentation depth h_c as [89,90]:

$$H_p = \frac{P_{\max}}{26.43h_c^2} \quad (2-12)$$

Where, h_c and $P_{\max}$ are defined in Fig. 2-14. However, this method does not work for very thin films. Because during the indentation process, the indentation load is quite high, the penetration depth will exceed one tenth of the film thickness easily. The substrate effect on film hardness cannot be avoided for very thin film.

2.4.1.3.Joslin-Oliver method

This method assumes that the material is elastically homogeneous and indenter modulus is known. In this method, the parameter P/S^2 is defined as a material characteristic property where P is the load and S the contact stiffness. Based on the classical definition of hardness, $H = P/A$, and the relationship developed by Sneddon, hardness can be evaluated through [82,83]

$$H = \frac{4}{\pi} \left(\frac{P}{S^2} \right) E_r^2 \delta_2^2 \quad (2-13)$$

$$\frac{1}{E_r} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu_f^2}{E_f} \quad (2-14)$$

Where, E_r the reduced modulus, δ_2 a constant that depends on the geometry of the indenter, E_i and E_f are the elastic modulus of the indenter and thin film,

respectively. ν_i and ν_f are the Poisson's ratio of the indenter and thin film. It is clearly seen that P/S^2 is directly proportional to hardness H , and inversely proportional to the square of the reduced modulus E_r . Thus the true contact pressure or hardness may be determined by measuring the load and contact stiffness, even when "pile up" occurs on the thin film surface. However this method is not so popular because of its assumption.

2.4.2. Toughness Measurements

In essence, toughness is the ability of a material to absorb energy during deformation up to fracture [10,91]. Fracture toughness is the ability of a material to resist the growth of a pre-existing crack. According to these definitions, toughness encompasses the energy required both to create the crack and to enable the crack to propagate till fracture, whereas fracture toughness takes only account of the energy required to facilitate the crack propagation to fracture. These are two different concepts and should not be confused and interchangeably used. For bulk materials and some thick films, fracture toughness is easily measured according to ASTM standards [92, 93]. However, for thin films, fracture toughness measurement remains difficult because of the thickness limitation [94]. As thin films are increasingly finding their way in engineering applications, thin film toughness assessment becomes imperative. Unlike the bulk materials, however, until now there is neither standard procedure nor commonly accepted methodology to follow. It is, however, good to note that increasing efforts have been made to address this tricky issue, and thus quite many test methods are proposed and used in various literatures.

The methodologies employed to measure toughness of for thin films fall into one of these methods: indentation, scratching and tensile tests, which are discussed in details below.

2.4.2.1. Indentation method

Perhaps, indentation is the most widely used tool in assessment of thin film toughness. Plastic deformation leads to stress relaxation in materials. The easier the stress relaxation proceeds, the larger plasticity is inherent in the material. Thus, comparing the plastic strain with the total strain in an indentation test directly gives a simple, rough but quick indication of how “tough” the material is. Plasticity is defined as the ratio of the plastic displacement over the total displacement in the load-displacement curve [95] (c.f. Fig. 2-15):

$$Plasticity = \frac{OA}{OB} \quad (2-15)$$

Where, OA is plastic deformation, OB total deformation. A superhard DLC film with hardness of 60 GPa has only 10% plasticity [96], whereas a “tough” nc-TiC/a-C film with a hardness of 32 GPa has 40% plasticity [39,41]. Hydrogen free amorphous carbon films with hardness of 30 GPa has a toughness of 50% to 60% in plasticity [97] depending on bias voltage during sputtering. Magnetron sputtered 1 μm thick $\text{Ti}_{1-x}\text{Al}_x\text{N}$ films with hardness 31 GPa obtained a plasticity of 32% [98].

Fig. 2-15 Schematic diagram of load-displacement curve obtained from nanoindentation. Plasticity is calculated by the ratio of OA/OB.

However, “plasticity” is not fracture toughness. To measure a film’s proper fracture toughness, Tsui et al. [99, 100] introduced a pre-crack into the film using focused ion beam milling. The crack opening force is generated by means of indentation sink-in effect. The sink-in effect provides a tensile stress on the film near the pre-crack tip and promotes the crack propagation. A Knoop indenter is used in order to induce a plane strain condition near the indenter. The location of the indenter and pre-crack is schematically shown in Fig. 2-16. The extent of the sink-in effect and tensile stress generated at the pre-crack are the largest at the center of the indentation and decrease along the elongated edges of the indentation. Thus, the crack tip opening distance and crack growth are different at different location along the pre-cracked trench. Under the plain strain condition, fracture toughness can be expressed as a function of crack tip blunting immediately before the catastrophic failure through the following equation:

$$K_{Ic} = \sqrt{m\Delta\sigma_y E} \quad (2-16)$$

Where, m is a dimensionless constant, approximately 2.0 for a plane strain condition [99, 101], σ_y the yield stress ($\sigma_y \approx H/3$ [10]), E the Young's modulus of the films, Δ the crack tip opening distance which is the amount of crack tip blunting before the catastrophic crack growth. The fracture toughness of NiP films with thickness of $9 \mu\text{m}$ deposited on aluminum substrate is thus determined as $15 \text{ MPa m}^{1/2}$ [100]. The uncertainties associated with this method come from the difficulty of making the pre-crack and measurement of the crack tip opening distance. In addition, for films on hard substrate, the sink-in effect may not be induced that would render the method ineffective.

Fig. 2-16 Schematic illustration of the orientation of the Knoop indentation relative to the pre-crack trench [99].

To avoid the difficulties in making the pre-crack, many researchers directly indent the films without a pre-crack. When the stress exceeds a critical value, a crack or

spallation will be generated. Failure of the film is manifested by the formation of a kink or plateau in the load-displacement curve or crack formation in the indent impression [102-104]. As a qualitative, crude and relative assessment, Holleck and Schulz [105] compare the crack length under the same load, and Kustas et al. [106] measures the “spall diameter” – the damage zone around the indenter. More quantitatively, length c of radial crack (c.f. Fig. 2-17) is related to the toughness (K_{IC}) through [107]:

$$K_{IC} = \delta \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (2-17)$$

Where, P applied indentation load, E and H are elastic modulus and hardness of the film, respectively. δ is an empirical constant which depends on the geometry of the indenter. For standard Vickers diamond pyramid indenter, value of δ is taken as 0.016 ± 0.004 [108] and 0.0319 [109, 110], respectively. The criterion for a well-defined crack is taken as $c \geq 2a$ [108], where a is the half of the diagonal length of the indent (c.f. Fig. 2-17). Both E and H can be determined from an indentation test at a much smaller load and analyzing of indentation load-displacement data [84]; crack length c can be obtained using SEM, thus implementation of the method seems straightforward [87].

Fig. 2-17 SEM observation of radial cracks at Vickers indentation. a , half of the diagonal length of the impression, c the crack length. A well-defined crack is taken as $c \geq 2a$.

However, the difficulty lies in the existence of cracking threshold, locating crack position and determining crack length. Although indentation can be realized with Vickers indenter, Berkovich indenter, or cube corner indenter [111, 112], there exists a cracking threshold below which indentation cracks cannot form. Existence of the cracking threshold causes severe restrictions on achievable spatial resolution. The occurrence of the indentation cracking depends on the condition of the indenter tip [113]. Harding et al. [114] found that indentation-cracking threshold could be significantly reduced by employing a sharper indenter (cube corner indenter compared to the Berkovich and Vickers indenters). The cube corner indenter induces more than three times the indentation volume as compared to that by the Berkovich indenter at the same load. Consequently, the crack formation is easier with the cube corner indenter thereby reducing the cracking threshold. For the cube corner indenter, the angle between the axis of symmetry and a face is 35.3° (as compared with 65.3° for the Berkovich indenter), and there are three cracks lying in directions parallel to the indentation diagonal (c.f. Fig.

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2-18). Cracks that are well defined and symmetrical around the cube corner indentation are used to calculate the toughness. Different researchers used different δ values: 0.0319 [109, 110], 0.040 [114] and 0.0535 [115]. Despite the inherited problems, due to its simplicity, the indentation method is widely used in toughness evaluation of thin films. To cite a few: sputter deposited DLC film (1.92 μm thick, 1.57 $\text{MPa m}^{1/2}$) [116], plasma sprayed Al₂O₃ (200-300 μm thick, containing 13% TiO₂, 4.5 $\text{MPa m}^{1/2}$) [117], atmospheric pressure CVD SiC (3 μm , 0.78 $\text{MPa m}^{1/2}$) [118], plasma enhanced CVD nc-TiN/SiN_x ($\sim 1.5 \mu\text{m}$, 1.3-2.4 $\text{MPa m}^{1/2}$) [119] and TiC_xN_y/SiCN (2.7-3.3 μm , $\sim 1 \text{ MPa m}^{1/2}$) [120].

Fig. 2-18 Schematic diagram of median-radial crack systems for cube corner indentation. a, length of the edge of impression. c, length of crack parallel to the indentation diagonal direction.

Some researchers suggest that the indentation load P , radial crack length c and toughness K_{IC} have the following relationship [121 - 123] :

$$\frac{P\chi_r}{c^{3/2}} = K_{IC} - 2\sigma(c/\pi)^{1/2} \quad (2-18)$$

Where, σ the residual stress at the film surface. For a Berkovich diamond indenter, $\chi_r = 0.016 (E/H)^{1/2}$. Since P , E , H , and c are all experimentally attainable from the indentation test, plotting $P\chi_r/c^{3/2}$ against $2(c/\pi)^{1/2}$ yields a straight line with K_{IC} as the interception with the ordinate axis and the residual stress as the slope. This method is developed for bulk materials, but has also been used to determine the toughness of an organic-inorganic hybrid coating of 3-20 μm in thickness on glass [123].

The methods described above require measurement of indentation-induced radial cracks, which is usually possible for relatively thick films (thickness being greater than microns). It could be difficult for thin and ultra-thin ($\leq 100 \text{ nm}$) films. In the case of thin films, indentation depth usually exceeds one tenth of the film thickness to generate radial cracks. As such, the elastic-plastic zone may already expand to the substrate [115, 124]. Furthermore, because of the shallow indentation depth required in the indentation technique, it is often difficult to precisely measure the radial crack length even under SEM [125], presume the indent can be located after transferring from the indenter to the SEM.

For thin films, a more reliable approach is the energy balance approach [125-130]: the energy difference before and after cracking is considered responsible for fracture of the film, and the energy release rate G_c , defined as the strain energy release per unit crack area, is calculated based on the energy difference. Once the energy release rate is obtained, toughness can be calculated from

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$K_{IC} = \sqrt{EG_c}$ (for plain stress condition mode I fracture), or

$K_{IC} = \sqrt{EG_c/(1-\nu^2)}$ (for plain strain condition mode I fracture).

As illustrated by Li et al. [125, 126], fracture of hard films under a load-controlled indentation measurement may be simplified into three stages (c.f. Fig. 2-19): (1) The first ring-like through-thickness crack forms around the indenter by high stress in the contact area; (2) Delamination and buckling occur around contact area at the film/substrate interface by high lateral pressure; (3) A second ring-like through-thickness crack forms and spalling is generated by high bending stresses at the edges of the buckled thin films.

Fig. 2-19 Schematic of the three stages during nanoindentation fracture in a film/substrate system: (1) first ring-like through-thickness crack formation, (2)

delamination and buckling and (3) second ring-like through-thickness crack formation and spalling [125].

The strain energy released in the first/second ring-like cracking and spalling can be calculated from the corresponding step in the load-displacement curve schematically shown in Fig. 2-20. OACD is the loading curve and DE is the unloading curve. Area under curve ABC represents the energy difference before and after the ring-like cracking, which is released as strain energy to create the ring-like through-thickness crack. The fracture toughness of the film is then written as

$$K_{IC} = \left(\frac{E_f}{(1 - \nu_f^2) 2\pi C_R} \frac{\Delta U}{t_f} \right)^{1/2} \quad (2-19)$$

Where, E_f and ν_f are Young's modulus and Poisson's ratio of the thin film, respectively. $2\pi C_R$ is crack length in the film plane, t_f film thickness, thus $2\pi C_R t_f$ is the crack area. ΔU is strain energy difference before and after film cracking. In this method, the cube corner indenter or the conical indenter are preferred because the through-thickness cracking of thin films can be accomplished at a low load, as demonstrated in a-C films (0.1 μm in thickness) [131], TiN/Ti(C,N)/TiC multilayers of total thickness of 8 μm [132], Ni/Al₂O₃ multilayers of 0.15 μm in thickness [133].

Fig. 2-20 Schematic diagram of a load-displacement curve, showing a step during the loading cycle and associated energy release (area ABC).

A somewhat similar approach was illustrated by Toonder and Malzbender et al. [128, 129] based on the chipping (c.f. Fig. 2-21) during indentation process. The energy release rate G_c during chipping under Berkovich indenter is expressed as:

$$G_c = \frac{U_{fr}^c}{3\pi t' C_d} \quad (2-20)$$

Where, C_d is the diameter of the delamination crack that initiated the chip, t' the effective film thickness, which accounts the fact that the crack does not propagate perpendicular to the film/substrate interface. t' equals to the film thickness t divided by $\sin(\theta)$, where θ is the average angle of the chipping edge. Number 3 in eqn(2-20) is related to the number of chips, under Berkovich indenter, there are usually three chips. U_{fr}^c is the energy dissipated during the chipping, which can be determined from analyzing the irreversibly dissipated energy (total energy minus the elastic energy), W_{irr} .

Fig. 2-21. SEM observation of indentation impression under Vickers indenter. Chipping is preceded by the growth of a delamination crack along the interface between the substrate and the coating. In the case of a Vickers indenter, four chips usually occur almost simultaneously.

Ignoring the thermal energy, after one indentation cycle the irreversibly dissipated energy W_{irr} comprises the energy dissipated due to the plastic deformation (U_{pl}) and the energy dissipated due to fracture or chipping (U_{fr}), or:

$$W_{irr} = U_{fr} + U_{pl} \quad (2-21)$$

W_{irr} can be determined through computing the area between the loading and unloading curve. By plotting W_{irr} vs. the indentation load, a curve can be obtained (c.f. Fig. 2-22). The onset of delamination changes the slope of the W_{irr} -P curve. Before chipping takes place, the total irreversibly dissipated energy comprises that for plastic deformation (U_{pl}) and delamination (U_{fr}^d). Upon chipping, U_{fr} comprises two components: the energy released in delamination, U_{fr}^d , and the energy released in chipping, U_{fr}^c , which is graphically attainable from the W_{irr} -P curve (c.f. Fig. 2-22). Plugging the energy released in chipping, U_{fr}^c back to eqn(2-

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20) gives rise to the critical strain energy release rate, which, in turn, yields films toughness through $K_{IC} = \sqrt{EG_c}$.

Fig. 2-22 Energy irreversibly dissipated during indentation, as a function of the peak load applied during the indentation. The onset of delamination changes the slope of the W_{irr} - P curve [128].

Possible errors come from energy determination, crack length measurement and crack area calculation due to irregularity in crack shape. TiAlSiN thin films with hardness of 29-32.5 GPa, thickness of 2 μm , have been measured this way and a toughness of 1.55-2.1 $\text{MPa m}^{1/2}$ is reported [134]. Malzbender and coworkers used the SiO_2 -filled methyltrimethoxysilane films (thickness of 2-4 μm) to compare the measurements of toughness by radial cracking method and the energy related chipping method [135]. The results differ from 0 to 22%.

2.4.2.2.Scratch method

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Scratch test is generally accepted as one of the simple methods in assessing adhesion strength of a film on its substrate by introducing a quantity of mechanical force or energy sufficient to detach the film from the substrate [136-138]. In the test process, a diamond tip is driven over a coated surface to produce a scratch. The load on the diamond tip is increased linearly to induce a shear force in the nearby film that is proportional to the applied load and transmitted through the bulk of the composite sample. As the mechanical properties of the film and the substrate are different, there is a discontinuity in the shear stress at the interface which, when sufficiently high, induces adhesive failure at a critical load. Generally, for hard thin films, microcracks appear in films during scratching before the final adhesion failure [139]. The minimum load at which the first crack occurs is termed the lower critical load L_{c1} and the load corresponding to the complete peeling off of the film from substrate is termed the higher critical load L_{c2} . Some researchers directly used the lower critical load to indicate cracking resistance [140, 141] or some even termed it “scratch toughness” [38, 41]. A magnetron sputtered $Ti_{1-x}Al_xN$ nanocomposite thin film (hardness 28.5 GPa, thickness 0.9 μm) reaches 70 N load without brittle failure at Rockwell diamond tip (200 μm in radius) is thus considered having good scratch toughness. In comparison, films of TiN (0.9 μm , $L_{c1} = 30-40$ N) and AlN (0.6 μm , at $L_{c1} = 20$ N) [98] are not so good in scratch toughness. Since residual stress affects critical load, multi-pass scratch test is proposed where the scratch is performed in the same scratch track several times with increasing load. Let the critical load L_c^i be the critical load after the i^{th} pass, as the difference between L_c^i and L_c^{i+n} ($n \geq 1$) becomes zero, the value of L_c^i is then taken as qualitative characterization of the “scratchtoughness” [142].

Hoelm et al. [143] formulated an equation to related scratch test to proper fracture toughness. The model assumes that cracking in the microscratch test is a result of cracks being opened up on surface by the applied pressure at the bottom of the scratch groove. The coefficient of grooving friction can be calculated as the ratio of the tangential force (F) to normal force (P) (c.f. Fig. 2-23). The stress intensity solution for a mode I crack opening is thus given as

$$K_{IC} = \frac{2Pf_g}{R^2 \cot \theta} \left(\frac{a}{\pi}\right)^{1/2} \sin^{-1} \frac{R}{a} \quad (2-22)$$

Where P is the pressure opening the crack, R is the radius of the indenter cone into the groove, 2a is the total crack length, and f_g is the coefficient of grooving friction, which depends on the cone angle 2θ and can be obtained from the track width and the depth of penetration. However, this model is over-simplified and the actual state of forces in the groove ahead and right below the tip are much more complicated and have to be taken into account for better description of the process.

Fig. 2-23 Schematic diagram of the microscratch fracture toughness measurement with a pressure P opening a crack (2a) out of a groove width 2R [143].

More recently, Holmberg et al. [144] investigated the toughness of thin film through measuring of the tensile stress which induces the cohesion failure (i.e. generation of cracks in the film) through:

$$K_{IC} = \sigma_t \sqrt{b} f(c, b) \quad (2-23)$$

Where, σ_t is the tensile stress which induces the cracks in film during scratch obtained through a three-dimensional finite element modeling, c , crack length and b crack spacing, $f(c, b)$ a non-dimensional function dependent on crack length c and crack spacing b measured from the scratch track (c.f. Fig. 2-24). As $c \gg b$, eqn(2-23) reduces to $K_{IC} = \sigma_t \sqrt{b/2}$. Since the calculation of the tensile stress σ_t involves 3-D finite element modeling, and also a general $f(c, b)$ expression is not available, practical application of this method is difficult.

Fig. 2-24 Illustration of the scratch track and the cracks. The cracks observed are angular cracks at 1 mm, parallel cracks at 2.3 mm and angular cracks joining at 3 mm [144].

2.4.2.3. Tensile method

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For relatively thick free-standing films, fracture toughness can be directly measured using tensile method according to the ASTM standard E-399 [92] where the pre-crack is introduced easily by laser cutting, as in the case of diamond films with thickness of 150-200 μm [145]. The fracture toughness of the films is thus measured as 5-6 $\text{MPa m}^{1/2}$, comparable with those from indentation method.

For thin films, however, measurement without creating the pre-crack makes more sense because of the difficulties and uncertainties involved in making pre-cracks in micron or submicron thin films. Harry et al. [146-148] propose a micro-tensile method in which a flat rectangular substrate of dimensions L (length) $\times$ w (width) $\times$ h_s (thickness) coated with a film of thickness h_f is put under tension. In the tension process, the cracking of the film causes energy variations in the film/substrate system. For thin films ($h_f \ll h_s$) coated on flat substrate ($h_s \ll L$) with perfect adhesion (thus buckling of the film will not happen), the film/substrate system can be regarded as a thin composite beam. The toughness of the film is calculated based on energy balance when the cracking occurs.

$$\Delta U = \frac{(\sigma_c^f)^2 (h_f)^2}{E_f} \left\{ \pi f\left(\frac{E_f}{E_s}\right) + \frac{\sigma_c^f}{\sqrt{3}\sigma_y^s} \right\} \quad (2-24)$$

Where ΔU is the net energy change, $f\left(\frac{E_f}{E_s}\right)$ a function of the elastic modulus ratio and the values are tabulated in [149] for different modulus ratios, E_f and E_s are the Young's modulus for film and substrate, respectively. σ_y^s is the yield stress of the substrate. σ_c^f is the effective critical cracking stress which is experimentally determined. The critical strain energy release rate G_c for crack propagating through the film is:

$$G_c = \frac{\Delta U}{h_f} = \frac{(\sigma_c^f)^2 (h_f)}{E_f} \left\{ \pi f \left(\frac{E_f}{E_s} \right) + \frac{\sigma_c^f}{\sqrt{3} \sigma_y^s} \right\} \quad (2-25)$$

Fracture toughness (K_{IC}) of the film can be calculated through $K_{IC} = \sqrt{EG_c}$ once G_c is obtained. Harry et al. [146] deposited W and W-C solid solution (W(C)) films of thickness from 1.8 to 16 μm on stainless steel substrates and subjected the film/substrate composite beams under tension and measured the toughness of the W films as 1.0 to 2.5 $\text{MPa m}^{1/2}$ and that of the W(C) films as 0.2 to 1.0 $\text{MPa m}^{1/2}$. The major drawback of this method lies in its requirement of substrate properties. Toughness of film is in fact a property of the film itself, and should not vary with substrate.

2.5. Summary

Nanocomposite thin films usually comprise at least two phases. Owing to the size effect, nanocomposite thin films/coatings can obtain exotic properties among which toughness and hardness are the most important ones for the applications in manufacturing industry. Different design methods such as grain boundary strengthening, ductile phase toughening and grain boundary sliding are proposed and conducted to obtain nanocomposite coatings with combination of high hardness and high toughness. Nanocomposite thin films can be prepared with many methods among which magnetron sputtering is most popular. Compared with the CVD method, magnetron sputtering is far less dangerous and can be easily scaled up to industrial scale. The flexibility in alloying and thus composition control, low temperature processing, together with other advantages, outcast its

“line-of-sight” drawback and become widely accepted and used in industry. Microstructure of nanocomposite coatings plays an important role on hardness and toughness. Studies on lattice parameter, grain size, structure and morphology have been conducted. Relationship between hardness and microstructure has been investigated in detail by many researchers. Some even can obtain hardness of 105 GPa via optimum microstructure design. However, so far, the knowledge on toughening of nanocomposite hard and superhard thin films is still limited and more work on microstructure investigation of toughened nanocomposite thin film needs to be done. Testing process for hardness is a routine. Usually an indenter is impressed into the coating with certain load to induce an impression. Hardness can be calculated based on the indentation load, impression area and indenter shape function parameter. Among different analysis approaches, Oliver-Pharr method is most popular. Toughness measurement for thin films is difficult due to the small dimension in thickness. Until now, there is neither standard procedure nor standard methodology. As in qualitative or semi quantitative assessment, sometimes a quick plasticity measurement or a scratch adhesion test will suffice. But these test results should not be termed “toughness”. More elaborate quantitative measurements can be categorized into two main groups: the stress approach and the energy balance approach. The stress approach examines the stress state near the tip of the crack. Toughness is obtained through $K_C \propto \sigma_f \cdot \sqrt{a}$. Scratch in consideration of critical tensile stress, crack length and spacing, and indentation in consideration of the critical load and corresponding crack length, etc., fall into this category. Difficulties in these methods lie in the formation of the pre-crack, determination of the crack length, and the critical failure stress. These problems are not easily resolved due to the thickness dimension involved. The energy balance approach

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concentrates on the system's energy state before and after fracture of the film. This energy difference is considered consumed to increase new crack area. Toughness is thus obtained through the critical energy release rate G_c : $K_c = \sqrt{EG_c}$ (for plain stress mode I fracture), or $K_c = \sqrt{EG_c/(1-\nu^2)}$ (for plain strain mode I fracture), where G_c is related to the energy difference (ΔU) and crack area (ΔA) through $G_c \propto \Delta U/\Delta A$. Fallen under this category are indentation with chipping, tensile tests, and so on. Standardization of thin film toughness measurements seems necessary. Energy-based methodologies have clear advantages over stress-based approach.

CHAPTER 3 EXPERIMENT

3.1. Project Overview

Nanocomposite nc-TiN/a-SiN_x thin films can be obtained with hardness greater than 100 GPa [3]. However, for majority of applications the highest hardness is not the primary goal. More important is the appropriate combination of high hardness with toughness, and oxidation resistance etc. From the literature survey, it can be seen that nanocomposite thin films with high hardness and toughness are obtainable through optimal design of microstructure which can be tailored using reactive magnetron sputtering.

In this project, superhard nc-TiN/a-SiN_x nanocomposite thin films and Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films with high hardness in combination of high toughness will be prepared using reactive magnetron sputtering and thereafter characterized. Issues include chemical composition, topography or surface morphology, microstructure and mechanical properties. The schedule for preparation of superhard nc-TiN/a-SiN_x nanocomposite coatings and Ni-toughened nc-TiN/a-SiN_x nanocomposite coatings are listed in Fig. 3-1.

Fig. 3-1 Schedule for study of (1) superhard nc-TiN/a-SiN_x nanocomposite thin films and (2) Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films with high hardness in combination of high toughness. The highlight part is that will be conducted in this project.

3.2. Experimental Procedure

As dictated in the project overview section, hard and superhard nc-TiN/a-SiN_x nanocomposite thin films will be deposited using reactive magnetron sputtering. Then, Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films with high hardness in combination of high toughness will be prepared by doping metallic nickel into a-SiN_x matrix of the nc-TiN/a-SiN_x. Effects of deposition power density on chemical composition, surface morphology, microstructure, mechanical properties including residual stress, hardness and toughness, and oxidation resistance are to be studied.

3.2.1. Thin Film Preparation

3.2.1.1. Choice of film system

From the literature review, it is clear that the development of next generation hard and yet tough thin films should be based on appropriate design of multiphase nanocomposite material in which grain boundary sliding can be blocked to improve hardness, ductile phase deformation can be conducted to blunt crack tip and bridge cracks thus improve toughness. The obvious first choice of such a nc-/a- system that meets the above discussed criteria for achieving high hardness is straightforward: transition metal, such as Ti, forms stable, refractory and hard nitride TiN [150], which crystallize upon deposition even at relatively low temperatures of $\geq 100\text{ }^{\circ}\text{C}$ [151]. The TiN crystallites are in the rocksalt structure (Fm3m) with a lattice parameter of 0.42417 nm for the stoichiometric material.

The close packed structure, an fcc Ti sub lattice with N filling all octahedral sites, is due to relatively small size of the N atoms compared to Ti (0.074 vs. 0.147 nm (c.f. Table 3-1)). Silicon nitride (Si_3N_4), on the other hand, remains amorphous even at 1100 °C and it possesses of the desirable structural flexibility due to its fourfold coordination of silicon combined with the threefold coordination of nitrogen [15, 152]. In the Ti-Si-N systems, though several phases exist (c.f. Fig. 3-2), TiN and Si_3N_4 phases can be obtained by precision adjusting of the chemical composition. (Some properties of TiN and Si_3N_4 are tabulated in Table 3-2 and Table 3-3, respectively). TiN and Si_3N_4 are immiscible up to a relatively high temperature of 1000 °C [153]. Therefore, the nc-TiN/a- Si_3N_4 interface is expected to be sufficiently strong in order to avoid grain boundary sliding. So far, nc-TiN/a- Si_3N_4 nanocomposite thin films have been prepared with CVD method, and hardness even arrives at 105 GPa [3]. However, the toughness of the superhard nc-TiN/a- Si_3N_4 nanocomposite coatings needs to be improved. Doping metallic element is one of the most effective methods to improve ceramic toughness. For this, phase segregation (immiscibility) is needed for the formation of ductile metallic phase in the ceramic matrix. Ni is a prospected candidate: it does not form nitride with nitrogen and possesses of high oxidation resistance [64]. The precipitated metallic phase will blunt crack tip and bridge cracks during deformation. Therefore, hard and superhard nc-TiN/a- Si_3N_4 nanocomposite coatings expect to be toughened by doping Ni element.

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Table 3-1 Approximate atomic radius of nitrogen and selected elements [64]

Element	Atomic Number	Atomic Radius (nm)
N	7	0.074
Si	14	0.117
Ti	22	0.147
Ni	28	0.124
Al	13	0.126

Ion radius of Si^{4+} and Ti^{3+} are 0.041 and 0.075 nm, respectively [154].

Table 3-2 Properties of TiN and Si_3N_4 at room temperature (compiled with [64, 155-158])

Property	TiN	Si_3N_4
Structure	FCC (NaCl)	Tetragonal
Space group	Fm3m	P42212
Lattice parameter	0.42417 nm	a = 0.9245 nm c = 0.8482 nm
Color	Golden	Colorless if pure
Density	5.40 g/cm ³	3.19 g/cm ³
Melting point	2950 °C	1900 °C
Free energy (ΔG^0_{298})	-3.1×10^5 J/mol	-6.7×10^5 J/mol
Specific heat (C_p)	33.74 J/mol K	75.7-98.2 J/mol K
Thermal conductivity	19.2 Watt/m K	25-36 Watt/m K
Thermal expansion	9.35×10^{-6} /K	$2.8\text{-}3.2 \times 10^{-6}$ /K
Oxidation resistance	To 800 °C	To 1350 °C
Electrical resistivity	$20 \pm 10 \mu\Omega$ cm	$10^{14} \mu\Omega$ cm
Poisson's ratio	0.2-0.3	0.23-0.27
Young's modulus	250-600 GPa	260-330 GPa
Vickers hardness	18-21 GPa	16-18 GPa
Fracture toughness	2-3 MPa m ^{1/2}	5-7.5 MPa m ^{1/2}

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Table 3-3 Enthalpies and entropies of formation at 298 K for selected compounds [159, 160]

Compound	ΔH_f^0 (kJ/mol)	S^0 (J/mol K)
TiN	-338	30
TiO	-543	35
TiO ₂	-849	72
Ti ₂ O ₃	-1521	77
SiO ₂	-910	42
Si ₃ N ₄	-745	113

Fig. 3-2 Ti-Si-N phase diagram based on free energy data from Barin and Knacke [161, 162]. T = 700–1000 °C. The tie lines remain the same in the temperature range.

3.2.1.2. Sputtering system

E303A magnetron sputtering system as shown in Fig. 3-3 was conducted to deposit nanocomposite thin films. The system includes four 4-inch planar high performance water-cooled magnetrons and a heated rotatable substrate holder. The

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substrate-to-target distance was 100 mm to fully reactive between the working gas and sputtered target atoms. The substrate can be heated to a maximum temperature of 500 °C. Two 600 W RF generators and two 1 kW DC power supply can be automatically selected to individual targets. Also, the substrate holder can be earthed, floated or powered by a dedicated 600 W RF generator. This facilitates pre-sputter wafer cleaning and reverse bias sputter etching. The vacuum system is of high specification, with 800 1/s Cryogenic UHV vacuum and high performance rotary backing pump. Gas flow control is via mass flow control valves on three gas lines, with pressure control set point achieved by automatic close loop throttle valve control. Reactive sputtering is assisted by inert argon gas to avoid target poisoning and allow higher sputtering rate. The system is designed to coat multiple 2 to 4 inch wafers, and single 6 to 8 inch wafer one time. A load lock is fitted with an automatic wafer transfer arm. The dominant parameters during deposition are target power density, deposition temperature, substrate bias and gas ratio.

(a)

(b)

Fig. 3-3 Sputtering system used in this project (a) the outlook (b) the schematic structure of the main chamber. There are four individual targets in the chamber and co-sputtering can be conducted.

3.2.1.3. Deposition

3.2.1.3.1. nc-TiN/a-SiN_x

DC magnetron power was applied to Ti (99.99 %) target, while RF power was applied to Si₃N₄ (99.999%) target. Four-inch silicon (100) wafers were used as substrates. The substrates were cleaned using an ultrasonic bath (ethanol absolute 99%) for 15 minutes to remove the contamination, such as spots, oils, grease, dust, fingerprints, etc. The substrates were heated to 450 °C for 30 minutes prior to deposition. This process mainly removed water molecules, which were adsorbed on surface. The substrate holder rotated with 15 rpm during the deposition for uniformity. Deposition was performed at a substrate temperature of 450 °C for 2 hours to obtain film thickness of 0.6 μm. Base pressure for deposition was 1.33×10^{-5} Pa. During deposition, the gas (purity of N₂ are Ar are 99.9995 %) pressure

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was 0.67 Pa and gas flow rate was 30 sccm (standard cubic centimetre per minute). Film deposition parameters were listed in Table 3-4 according to which hard and superhard nc-TiN/a-SiN_x nanocomposite thin films were prepared.

Table 3-4 Experimental conditions for deposition of hard and superhard nc-TiN/a-SiN_x nanocomposite thin films

Sample Code		P1	P2	P3	P4	P5	P6	P7	P8
Deposition condition	Si ₃ N ₄ power density (W/cm ²)	1.1	2.2	3.3	4.4	5.5	6.6	6.6	7.7
	Power ratio of Ti to Si ₃ N ₄	5.00	2.50	1.67	1.25	1.00	0.67	0.33	0
	Gas ratio of N ₂ to Ar	1.0	1.0	1.0	1.0	1.0	0.5	0.5	0

In order to assess methodology of toughness measurement, 1.5 and 3 μm thick nc-TiN/a-SiN_x nanocomposite thin films were deposited on Si (100) and Ti6Al4V (hardness 3.5 GPa) substrate with 18 mm in length (L), 4 mm in width (w) and 150,300 or 550 μm in thickness (h_s) (c.f. Fig. 3-4). The alloy substrate surface has been carefully polished down to 1 μm diamond finish. Nanocomposite nc-TiN/a-SiN_x thin films were co-sputtered from Ti and Si₃N₄ targets in Ar/N₂ atmosphere using E303A magnetron sputtering system. The target power density on both Ti and Si₃N₄ targets was 5.9 W/cm², and gas flow rate for both Ar and N₂ was 15 sccm. The other deposition parameters (such as, gas pressure, substrate temperature, substrate rotation speed) were set up as the same with those for 0.6 μm thick nc-TiN/a-SiN_x nanocomposite thin films.

Fig. 3-4 Schematic diagram of the geometry of the Ti6Al4V beam substrate. L , w , and h_s are the length, width and thickness of the alloy substrate beam, respectively.

3.2.1.3.2. Ni-toughened nc-TiN/a-SiN_x

In order to obtain thin films with high hardness in combination of high toughness, Ni-toughened nc-TiN/a-SiN_x films were deposited by doping Ni into high hard nc-TiN/a-SiN_x. TiNi (atomic ratio of 50/50, 99.99%) target was used as the source of Ni. DC magnetron powers were applied to Ti and TiNi targets, while RF power was used on Si₃N₄ target. Four-inch silicon (100) wafers were used as substrate. The substrate treatment was the same as that for deposition of nc-TiN/a-SiN_x samples. Base pressure for deposition was 1.33×10^{-5} Pa. During deposition, the gas pressure was 0.67 Pa, gas flow rates for N₂ and Ar were 15 sccm, respectively. Deposition was performed at a substrate temperature of 450 °C for 2 hours to obtain films with thickness about 0.7 μm. Film deposition parameters were listed in Table 3-5 according to which Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films were prepared.

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Table 3-5 Experimental conditions for deposition of Ni-toughened nc-TiN/a-SiN, nanocomposite thin films

Sample Code		S1	S2	S3	S4	S5	S6	S7	S8
Deposition condition	Si ₃ N ₄ target power density (W/cm ²)	6.6							4.4
	TiNi target power density (W/cm ²)	0	0.2	0.7	1.1	1.4	1.6	2.2	4.4
	Target power ratio of TiNi/(TiNi+Ti)	0	0.04	0.12	0.20	0.25	0.30	0.40	1.00

3.2.2.Characterization

Sample characterization includes measurements of chemical composition, thickness, topography, microstructure, residual stress, hardness, toughness and oxidation resistance. These characterization techniques for the above items which being mostly used by the material researchers in researching and developing new materials were described in this section.

3.2.2.1.Composition

Chemical composition of as prepared thin films was determined by XPS analysis using a Kratos-Axis spectrometer with monochromatic Al K_α (1486.71 eV) X-ray radiation (15 kV and 10 mA) and hemispherical electron energy analyser. The base vacuum of the chamber was 2.67 × 10⁻⁷ Pa. The survey spectra in the range of 0-1100 eV were recorded in 1 eV step for each sample, followed by high-resolution

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spectra over different element peaks in 0.1 eV step, from which the detailed composition was calculated. The spectra were referenced to the C 1s line of 284.6 eV [163]. Curve fitting was performed after a Shirley background [164] subtraction by non-linear least square fitting using a mixed Gauss/Lorentz function, In the least square fitting analysis of Ti 2p spectra, the area ratio of the $2p_{3/2}$ to $2p_{1/2}$ envelope was kept constant at two with a constant energy difference of 5.8 eV. The parameters used in fitting the Ti 2p, Si 2p and Ni 2p spectra were listed in Table 3-6. Also listed were binding energy available in literatures. Sputter depth profiles of the films were obtained by recording the XPS spectra after sputtering with an accelerating voltage of 4 keV Ar ion beam. The bombardment was performed at an angle of incidence of 45° with respect to the surface normal. The sputter rate determined on a 30 nm thick SiO_2 sample was 3.0 nm/min. Half of the intensity of the oxygen plateau was taken as the measure of the oxide layer thickness.

Table 3-6 Literature values of Ti 2p, Si 2p,and Ni 2p line positions (eV BE)

Element	Ti 2p _{3/2}			Ref	Si 2p			Ref	Ni 2p			Ref
					Ni 2p _{1/2}	Satel. Peak	Ni 2p _{3/2}					
State	TiO ₂	TiN _x O _y	TiN		SiO ₂	Si ₃ N ₄	free -Si		Metallic Ni			
Position (eV)	458.0	456.5	455.0	[165]	103.4	101.9	99.6	[166]	870.7	859.3	852.8	[167]
	459.1 +/- 0.2	~ 457.0	455.2 +/- 0.2	[168]	103.6	101.6		[169]	870.7	859.6	853.0	*
	459.2	457.5	455.2	[170]	103 ~ 104		99.6	[171]				
	458.8	457.1	455.6	[172]	103.3	101.8	99.3	[173]				
	459.0	457.5 +/- 0.1	455.2	[174]	103.4	101.8	99.6	*				
	458.0	456.4	455.0	[175]								
	458.7	456.9	454.8	[176]								
	459.0	457.6	455.0	*								

* Present work

3.2.2.2.Thickness

Before deposition, a mark was made with a paintbrush on the surface of the substrate. After deposition, the mark was removed using acetone. A step was therefore obtained in the film. A contact mode surface profilometer (Dektak³ ST Surface Profiler) with a diamond stylus in 2.5 μm radius was used to measure the height of the step to determine the thickness of the film. The scanning distance was 1000 μm, scan speed in medium (12 seconds per scan), and data resolution in medium (4000 data points per scan). More than three readings were taken. The

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thickness obtained using this method has been confirmed with SEM cross-sectional observation.

3.2.2.3. Topography

Topography or surface morphology of the as-deposited film was characterized using AFM (Shimadzu SPM-9500J2). The measurement was conducted in ambient atmosphere in contact mode with a Si_3N_4 tip. The scan resolution is 256 pixels x 256 pixels, set point 2.000 V and scan rate 1.000 Hz. In order to quantitatively describe the surface morphology, the scaling theory [177, 178] was used to analyze the AFM roughness data. The height-height correlation function $G(r)$ was defined as [179]

$$G(r) \equiv \langle [h(x, y) - h(0, 0)]^2 \rangle \quad (3-1)$$

Thus the dynamic scaling hypothesis [180] suggests that:

$$G(r) = \begin{cases} r^{2\alpha} & \text{as } r \ll \xi; \\ 2w^2 & \text{as } r \gg \xi. \end{cases} \quad (3-2)$$

Where, the interface width (w) describes the vertical growth and the lateral correlation length (ξ) characterizes the lateral growth.

3.2.2.4. Microstructure

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The microstructure of the nanocomposite films was characterized using TEM (JEOL JEM 2010). The acceleration potential is 200 kV, camera constant changes from 1.5 to 2.5 nm x mm. An image analyzer was used to measure the crystalline size and amount from TEM micrographs. The size of the crystallite was measured from the TEM micrographs using the image analyzer by measuring two perpendicular dimensions of a crystallite. The average of these two-dimensional measurements was taken as the crystallite size. The amount of the crystalline phase, termed crystalline fraction, was estimated as the area ratio of the nanocrystalline phase to the total image area. For each sample, a large number (at least 10) of TEM micrographs were taken and the images analyzed for the average crystalline fraction. Though this method results in approximately 10% uncertainties due to contrast problem, it does give a first-degree approximation plus the visual advantage. The sample preparation procedures for TEM/HRTEM study were:

- (1) Prepare potassium bromide (KBr) tablets with diameter of 10 mm, thickness of 3 mm. The roughness (R_a) of the tablet is measured as 80 μm .
- (2) Deposit nc-TiN/a-SiN_x and Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films on different potassium bromide (KBr) tablets for 20 minutes for a thickness of the thin film of about 100 nm. The other deposition parameters keep the same with its counterpart which deposited on silicon wafer for 120 minutes.
- (3) The as-prepared nanocomposite thin films is floated off from the KBr tablets by dissolving the coated tablets in deionized water and then scoop the films out on copper grid.

- (4) Dry the films for two hours for TEM/HRTEM study.

To supplement the TEM results, XRD was used for microstructure and phase identification (Philips PW1830 with Cu tube anode ($\lambda = 0.15418$ nm) at 30 kV and 20 mA). The step size was 0.01° and step time 0.5 seconds. In order to reduce the interference from the substrate in case of thin films, GIXRD (Rigaku MAX 2000 with Cu K_α radiation) was conducted at scan rate of $2^\circ/\text{min}$, step size 0.032° and incident angle from 0.1° through 0.5° and 1.0° to 1.5° . Based on the XRD/GIXRD data, grain size, preferential orientation and lattice parameter were obtained.

Grain size

To estimate the grain size d , the well-known Scherrer formula [181] was used by measuring the full width at half-maximum (FWHM) of the XRD/GIXRD peak at the angle of interest:

$$d = C\lambda / \beta \cos \theta \quad (3-3)$$

Where, C is a constant ($C = 0.91$), d mean crystallite dimension normal to diffracting planes, λ is the X-ray wavelength, β in rad is the peak width at half-maximum peak height and θ is the Bragg angle. It should be noticed, Scherrer formula does not take the peak broadening induced by microstraining into account.

Preferential orientation

The degree of preferential orientation was quantitatively represented through a coefficient of texture T_{hkl} , defined as [182] :

$$T_{hkl} = \frac{I_m(hkl) / I_0(hkl)}{\frac{1}{n} \sum_1^n I_m(hkl) / I_0(hkl)} \quad (3-4)$$

Where, $I_m(hkl)$ is the measured relative intensity of the reflection from the (hkl) plane, $I_0(hkl)$ is that from the same plane in a standard reference sample and listed in Table 3-7 for TiN. n is the total number of reflection peaks from the coating. In present study, $n = 3$ since only three major peaks are selected (i.e., (111), (200) and (220) diffraction plane). For the extremely preferential orientation, $T_{hkl} = 3$. While for the random one, $T_{hkl} = 1$.

Table 3-7 Relative intensity of XRD peaks in a standard reference TiN sample (JCPDS 38-1420)

Peaks	(111)	(200)	(220)
Relative intensity	72	100	45

Lattice parameter

Lattice parameter of the solid solution for cubic structure was calculated according to peak positions or the distance between the crystal planes through [183] :

$$a_{\text{exp}} = d_{hkl} \sqrt{h^2 + k^2 + l^2} = f(\theta) \quad (3-5)$$

$$a_{\text{exp}} = a_{\text{true}} + \Delta a = a_{\text{true}} + C\Phi(\theta) \quad (3-6)$$

$$\Phi(\theta) = \frac{\cos^2 \theta}{2} \left(\frac{1}{\sin \theta} + \frac{1}{\theta} \right) \quad (3-7)$$

Chapter 3 Experiment

Where, a_{exp} is the experimentally calculated lattice parameter, a_{true} is the true value, Δa is the experiment error, d_{hkl} is the interplanar spacing and (hkl) are the crystal plane indices. C is a constant, θ is Bragg angle, and Δa to be 0 when $\Phi(\theta)$ to be 0. Therefore plotting a_{exp} against $\Phi(\theta)$ and extrapolating to $\Phi(\theta) = 0$ gives rise to the true lattice parameter.

3.2.2.5. Residual stress

Residual stress was measured using a Tencor FLX-2908 laser system by testing the curvature changes of silicon substrate before and after film deposition. At least five measurements were performed for each sample at different orientation of silicon wafer. The residual stress σ can be calculated through Stony equation:

$$\sigma = \frac{Et_s^2}{(1 - \nu)6Rt_f} \quad (3-8)$$

Where $E/(1-\nu)$ is the biaxial elastic modulus of the substrate, t_s and t_f are thickness of the substrate and film, respectively. R is the substrate radius of curvature, which is calculated through:

$$R = \frac{1}{\left(\frac{1}{R_2} - \frac{1}{R_1}\right)} = \frac{R_1 R_2}{(R_1 - R_2)} \quad (3-9)$$

Where, R_1 and R_2 are the radius of silicon substrate before and after film deposition.

3.2.2.6.Hardness

Hardness was evaluated using a Nano IITM with a Berkovich indenter. The indentation depth was set less than one tenth of the film thickness to avoid substrate effect. At least five indentations were made for each sample. The results were an average of these readings from Oliver-Pharr method.

3.2.2.7.Toughness

3.2.2.7.1.Indentation method

Micro hardness tester (DMH-1) was used to obtain well-defined radial cracks for coatings on silicon wafer substrate. To ensure measurable crack length, the indentation was conducted at load of 10.00, 5.00, 3.00, 2.00, 1.00, 0.50 and 0.25 N, respectively. For each load, at least five readings were obtained. In order to reduce substrate effect on thin film toughness, Nano IITM with Berkovich indenter was also used to characterize these samples. The indentation was performed at the depth of 1300, 1000, 700, 400 and 200 nm, respectively. For each depth, at least five readings were obtained. Only samples with well-defined radial cracks were used to calculate thin film toughness.

3.2.2.7.2.Scratch method

Scratch test was conducted using Shimadzu SST-101 scan scratch tester: The X-Y table of the scratch tester was moved in the X-direction, and also moved side-ways (in the Y-direction) to generate a 'scanning scratch' effect and thus greatly

increase the coverage of each scratch (c.f. Fig. 3-5). At the same time, an increasing normal load was applied continuously to the surface of the film through a diamond indenter of 15 μm in radius until total failure of the film. A scratch speed of 2 $\mu\text{m/s}$ and scanning amplitude of 50 μm were used. At least three tests were performed on each sample.

Fig. 3-5 Schematic diagram of scan scratch test used in this project. The X-Y table of the scratch tester moves in the X-direction, and also moves side-ways (in the Y-direction) to generate a ‘scanning scratch’ effect and thus greatly increase the coverage of each scratch.

3.2.2.7.3. Two-step uniaxial tensile method

The two-step uniaxial tensile test was performed using Instron 5569 system at room temperature. In order to tension substrate with different thickness to certain elongation, two kinds of load cells (the load cell capacities are 500 and 100 N, respectively, with errors less than $\pm 0.5\%$). In a test, the load was continuously increased, and the load-extension data were recorded. Testing was done with either tension-extension mode or tension-profile mode. The tension-extension mode was

conducted to determine the elastic range of the substrate and critical thickness ratio of film to substrate. The extension rate was set as 0.05 mm/min and testing was interrupted at different extension levels. While the tension-profile mode was used to determine film toughness, the extension rate for both first and second step was fixed at 0.05 mm/min and the recover rate was set at 0.005 mm/min. Film cracking can be identified by the loss of linearity of the load-extension curve.

3.2.2.8.Oxidation resistance

To study films oxidation resistance, oxidation was performed using Elite Furnace (BRF14/5-2416) at 450 °C, 550 °C, 625 °C, 700 °C, 750 °C, 800 °C, 850 °C and 900 °C to 1000 °C in static hot air. After a 10 min heating ramp, the temperature was kept constant for 15 min. After the specimen was oxidized for the pre-determined time, the specimen was cooled down to a temperature around 300 °C within 20 min, then drawn from the furnace and left until room temperature thereafter for oxidation resistance study using XPS, AFM and GIXRD.

CHAPTER 4 RESULTS AND DISCUSSIONS

4.1. Physical Properties of nc-TiN/a-SiN_x

The as prepared nc-TiN/a-SiN_x nanocomposite thin films are studied using different characterization techniques, such as XPS, AFM, XRD/GIXRD, TEM/HRTEM, scratch, microindentation and nanoindentation tests. The results and discussions are presented in this chapter.

4.1.1. Composition

The nc-TiN/a-SiN_x nanocomposite thin films are etched with Ar ion beam for 15 min before composition measurement. The chemical compositions obtained from XPS are listed in Table 4-1, in which the atomic concentration of Si, Ti and N are used to describe the samples. The results show that N contents for all samples are about 50 ± 5 at.%, while Si and Ti contents vary greatly with the experimental conditions, mainly Si₃N₄ target power density.

Table 4-1 Chemical composition characteristics of hard and superhard nc-TiN/a-SiN_x nanocomposite thin films

Sample Code	XPS Chemical Composition (at.%)		
	Si	Ti	N
P1	1.7	50.4	47.9
P2	5.2	43.1	51.7
P3	7.2	38.1	54.7
P4	11.3	35.1	53.6
P5	14.9	29.4	55.7
P6	23.6	21.4	55.0
P7	32.5	15.7	51.8
P8	52.7	0	47.3

4.1.1.1.Quantitative compositional analysis

Fig. 4-1 shows a detailed XPS survey scan spectrum with indexed peaks. XPS survey scan spectrum with binding energy from 0 to 1100 eV is recorded. The dominant signals are from C, O, N, Si and Ti. The oxygen and carbon contamination exist because the film is exposed to air (ambient laboratory) and the XPS spectrum is obtained before the film surface being etched.

Fig. 4-1 XPS survey scan of nc-TiN/a-SiN_x nanocomposite thin film with 23.6 at.% Si (Sample P6). The dominant signals are from C, O, N, Si, and Ti.

Fig. 4-2 shows one of the typical XPS depth profiles of the nc-TiN/a-SiN_x nanocomposite thin film. There is an inevitable oxygen contamination in the top most layer of the film, It is possible that the reaction with residual gases in the spectrometer chamber or the ionic transport via impurities in the Ar gas causes this residual oxygen content in films. Though oxygen exists as deep as 75 nm and carbon at approximately 25 nm, their concentrations are very low, which are expected to render a very insignificant effect on the film's mechanical properties such as nanoindentation hardness. (Should there be any influence on hardness owing to the existence of oxides, the effect would be such that the measurements would underestimate the hardness because both Ti and Si oxides have low hardness: 16 GPa for DC magnetron sputtered TiO_x [184], approximately 10 GPa in the case of reactive cathodic vacuum arc deposited TiO₂ [185] and 8 GPa in the case of pulsed magnetron sputtered SiO₂ [186], etc.). Silicon content remains almost constant. Whereas nitrogen and titanium contents slightly increase in the first 10 nm and then remain at constant values. From the depth profile (c.f. Fig.

4-2), the oxygen and carbon concentrations are too low in comparison with Ti, Si and N, and thus ignored in composition computation.

Fig. 4-2 XPS depth profile of nc-TiN/a-SiN_x nanocomposite thin film with 14.9 at.% Si (Sample P5). Silicon content remains almost constant. Whereas nitrogen and titanium contents slightly increase in the first 10 nm and then remain at constant values.

Fig. 4-3 shows the XPS spectra of Ti 2p and Si 2p as a function of silicon content. It has been documented that the shoulders observed on the high binding-energy side of the Ti 2p_{3/2} and Ti 2p_{1/2} component peaks are inherent characteristic features of stoichiometric TiN [187, 188]. This stoichiometric TiN characteristic feature has been observed in our nc-TiN/a-SiN_x nanocomposite thin films (c.f. Fig. 4-3 (a)). Fig. 4-3 (b) shows the Si 2p peak intensity increases significantly with the increase in silicon content.

(a)

Fig. 4-3 Stacks of (a) Ti 2p and (b) Si 2p XPS core level spectra for nc-TiN/a-SiN_x nanocomposite thin films with different Si content after removing of surface layer.

In order to obtain more detailed information on the chemical composition, the acquired XPS core level spectrum of Ti 2p and Si 2p for the nc-TiN/a-SiN_x nanocomposite thin film with 23.6 at.% Si (Sample P6) after 15 min Ar ion beam etching were deconvoluted. Curve fitting was performed after a Shirley background subtraction by non-linear least square fitting using a mixed

Gauss/Lorentz function. The parameters used in the fitting procedure are listed in Table 3-6. Fig. 4-4 shows the XPS core line fit for Ti 2p spectra. There are three main components of Ti-N, Ti-O and Ti-X (combination of TiN_x , TiN_xO_y and satellite peak), and no unbound Ti metallic bonds can be detected. The peak at 455.0 eV is attributed to Ti-N bond or TiN. The peak at 459.0 eV is related to Ti-O or TiO_2 . The peak at 457.6 eV is contributed from Ti-X. From Fig. 4-4, it can be seen that the main contribution comes from TiN and Ti-X, and nearly no TiO_2 . This is due to the high base vacuum ($\times 10^{-5}$ Pa) before films deposition. Another reason is that before XPS narrow scan and core line fit, a 15 min Ar ion beam etching was conducted to remove the surface oxide due to expose in air (ambient laboratory).

Fig. 4-4 Ti 2p deconvolution of nc-TiN/a-SiN_x nanocomposite thin film with 23.6 at.% Si (Sample P6). There are three main components of Ti-N, Ti-O and Ti-X (combination of TiN_x , TiN_xO_y and satellite peak). The peak at 455.0 eV is attributed to Ti-N bond. The peak at 459.0 eV is related to Ti-O bond. The peak at 457.6 eV is contributed from Ti-X.

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Fig. 4-5 shows the quantitative deconvolution results of Ti 2p spectra of nc-TiN/a-SiN_x nanocomposite thin films with different silicon content. The relative atomic ratios of Ti in TiN, TiO₂ and TiX are calculated. Ti-O remains a low concentration for all the films. Ti-X peak component increases and TiN component decreases significantly with increases in silicon content. There is a gradual shift of Ti 2p peak to higher binding energy and Ti-X component increases significantly with increases of silicon content. The reason can be partly attributed to the increase of non-stoichiometric component, and another reason could be due to the silicon involvement into titanium structures.

Fig. 4-5 Changes of the different Ti 2p components of nc-TiN/a-SiN_x nanocomposite thin films with different Si content after deconvolution. Ti-O remains a low concentration for all the films. Ti-X peak component increases and TiN component decreases significantly with increase in Si content.

Fig. 4-6 shows the Si 2p core level spectrum of nc-TiN/a-SiN_x nanocomposite thin film with 23.6 at.% Si (Sample P6). Three chemically distinct components are

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found in Si 2p core level photoelectron spectrum. The peak corresponding to 101.8 eV is attributed to Si-N bond of stoichiometric Si_3N_4 . Another weak component at about 103.4 eV corresponds to Si-O bond. Traces of Si peak (at 99.6 eV) can be detected, belong to free silicon. The existence of free Si is often observed to exist in nc-TiN/a-SiN_x thin films synthesized by magnetron sputtering [189]. The Ti-Si bonding energy is at 98.8 eV, too close to that of elemental Si, thus difficult to eliminate the possibility of existence of TiSi, in the system. However, one thing is for sure: its amount is minute even if there is. Take TiSi as an example, from thermodynamics, the formation of Si_3N_4 is much more favored compared with formation of TiSi, since the formation energy for Si_3N_4 (-665.4 kJ/mol) is much more negative than that for TiSi (-132.2 kJ/mol) [190].

Fig. 4-6 Si 2p deconvolution of nc-TiN/a-SiN_x nanocomposite thin film with 23.6 at.% Si (Sample P6). The peak corresponding to 101.8 eV is attributed to Si-N bond of stoichiometric Si_3N_4 . Another weak component at about 103.4 eV corresponds to Si-O bond. Traces of Si peak at 99.6 eV can be detected, belong to free silicon.

Fig. 4-7 shows the quantitative deconvolution results of Si 2p spectra of nc-TiN/a-SiN_x nanocomposite thin films with different silicon content. Most of silicon element exists as Si-N bond, although Si-O as well as traces of Si-Si and Si-Ti bonds can be occasionally observed.

Fig. 4-7 Change of the different Si 2p components of nc-TiN/a-SiN_x nanocomposite thin films with different Si content after deconvolution. Most of Si element exists as Si-N bond.

4.1.1.2. Effect of deposition conditions

Fig. 4-8 shows the relationship between silicon content and Si₃N₄ target power density (from 1.1 to 5.5 W/cm²) for the nc-TiN/a-SiN_x nanocomposite thin films (Sample P1 to P5) deposited at 450 °C with a constant Ti target power density of 5.5 W/cm². It is obvious that with increases of Si₃N₄ target power density from 1.1

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to 5.5 W/cm^2 , the silicon content in the as-prepared nanocomposite thin films increase linearly from 1.7 at.% to 14.9 at.%.

Fig. 4-8 Si content changing linearly with Si_3N_4 target power density. With increase of Si_3N_4 target power density from 1.1 to 5.5 W/cm^2 , the Si content in the as-prepared thin films increases linearly from 1.7 at.% to 14.9 at.%.

Fig. 4-9 shows the relationship between silicon content and deposition target power ratio of Ti to Si_3N_4 for the nc-TiN/a- SiN_x nanocomposite thin films (Sample P1 to P8) deposited at 450°C . With increase in target power ratio of Ti to Si_3N_4 from 0 to 1.5, the silicon content in the as-deposited nc-TiN/a- SiN_x nanocomposite thin films decreases significantly from 52.7 at.% to 7.2 at.%, and then tails off.

Fig. 4-9 Si content changing with target power ratio of Ti to Si₃N₄ target. With increase in target power ratio from 0 to 1.5, the Si content in the as-deposited nc-TiN/a-SiN_x thin films decreases significantly from 52.7 at.% to 7.2 at.%, with further increase in power ratio, the trend does not sound scientific.

4.1.2.Topography

To evaluate the effect of target power density of Si₃N₄ on surface morphology, Si₃N₄ target power density is changed from 1.1 to 5.5 W/cm² while Ti target power density is kept constant at 5.5 W/cm². Topography characteristics of the as-prepared nanocomposite thin films are tabulated in Table 4-2.

Table 4-2 Topography characteristics of hard and superhard nc-TiN/a-SiN_x nanocomposite thin films

Sample Code	Roughness	Interface Width	Lateral Correlation Length
	R _a (nm)	ω (nm)	ξ (nm)
P1	5.8	7.3	28.0
P2	2.5	3.4	13.8
P3	1.5	1.8	12.8
P4	0.9	1.0	9.6
P5	0.7	1.0	9.4

Fig. 4-10 shows the AFM images (300 nm x 300 nm) of the nc-TiN/a-SiN_x nanocomposite thin films with different Si₃N₄ target power densities. With increasing Si₃N₄ target power density, the roughness gradually decreases. Numeric treatment of the images gives rise to the height-height correlation function G(r). Fig. 4-11 plots G(r) as a function of r for sample represented by Fig. 4-10 (e), i.e., 5.5 W/cm² Si₃N₄ target power density. As predicted by eqn(3-2), when r is small, G(r) has a power law dependence on distance r. At “distant” locations (as r is large), G(r) is nearly constant. Fitting the curve to eqn(3-2) gives the lateral correlation length ξ = 9.4 nm, the interface width ω = 1.0 nm and the smoothness exponent α = 0.854. The oscillation is due to the insufficient sampling size [179]. Similar treatment of other samples listed in Table 4-2 results different parameters ω, ξ, and α as a function of Si₃N₄ target power density. Plotting these values gives rise to Fig. 4-12 and Fig. 4-13.

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(a)

(b)

(c)

Fig. 4-10 AFM topography of the nc-TiN/a-SiN_x nanocomposite thin films with increasing Si₃N₄ target power density (in W/cm²): (a) 1.1 (b) 2.2 (c) 3.3 (d) 4.4 (e) 5.5 with roughness (R_a, nm) 5.8, 2.5, 1.5, 0.9 and 0.7, respectively.

Fig. 4-11 Height-height correlation function $G(r)$ for the nc-TiN/a-SiN_x nanocomposite thin film with Si₃N₄ target power density of 5.5 W/cm² (c.f. Fig. 4-10 e). The oscillation is due to the insufficient sampling size.

Fig. 4-12 Interface width ω and lateral correlation length ξ vary with Si₃N₄ target power density. With increase in Si₃N₄ target power density, both interface width and lateral correlation length decrease.

Fig. 4-13 Surface smoothness quotient α and roughness R_a vary with target power density. With increase in Si_3N_4 target power density, surface roughness R_a decreases, while the smoothness quotient α increases.

The morphology of the growing surfaces is determined by the competition of vertical build-up and lateral diffusion (c.f. Fig. 4-14). The vertical build-up is caused by the random angle incident of the arriving atoms (due to the uniform rotation of the substrate), and the growth produces columnar film structure. The lateral growth depends on surface diffusion which is largely determined by kinetic energy of the arriving ions. This is clearly seen from the trends of ω and ξ in Fig. 4-12. As Si_3N_4 target power density increases from 1.1 to 5.5 W/cm^2 the interface width ω decreases from ~ 7 to ~ 1 nm (c.f. Fig. 4-12), indicating that the film becomes smoother (recall that ω is the root mean square of the vertical fluctuation), which is more directly observable in terms of increasing smoothness quotient (α) or decreasing roughness (R_a) in Fig. 4-13. As target power density increases, ξ decreases from ~ 28 to ~ 10 nm. Since ξ depicts the distance within which the “height” values (i.e., roughness) are correlated, larger ξ means the

surface topography is correlated in a wider area. This is seen as larger “humps” as in Fig. 4-10 (a) for film deposited at lower power density (1.1 W/cm^2). The growth kinetic is controlled by the mobility of the impinging atoms on the surface before they condense and become entrapped in the film. This mobility can be enhanced by inputting energy to the system such as increasing deposition temperature or supplying impact energy through ion bombardment. At low target power density, ions have low mobility thus would be more likely to “stick” at where it arrives: the surface diffusion is slow, the chances of erasing the peaks and filling up the “valleys” are small, thus increasing a much rougher surface. In the same token, small ξ indicates the surface topography is correlated only in a small area, as seen in Fig. 4-10 progressively from (b) through (e) as target power density increases. As Si_3N_4 target power density increases, the kinetic energy obtained by each Si or SiN_x (as well as amount) increases, which transforms into faster lateral diffusion and smoothens out the roughness at locations farther away, making the “hump” more localized and smaller, giving rise to a smaller value of ξ and greater values of α [191, 192].

Fig. 4-14 Schematic diagram of the competition of vertical build-up and lateral diffusion determines the morphology of the growing surfaces [193].

4.1.3. Microstructure

The effect of sputtering power density of Si₃N₄ target on microstructure includes effects on crystal phase, grain size and distribution, preferential orientation, and lattice parameter are evaluated. Microstructure characteristics of the as-prepared nanocomposite thin films are tabulated in Table 4-3.

Table 4-3 Microstructure characteristics of hard and superhard nc-TiN/a-SiN_x nanocomposite thin films

Sample Code		P1	P2	P3	P4	P5	P6	P7	P8
Crystallite	Fraction (%)	3.6	6.7	7.3	7.1	10.8	1.1	0	0
	Size (nm)	7.2	8.2	7.5	5.8	6.0	3.2	0	0
Coefficient of Texture T _{hkl}	(111)	2.84	0.01	0.62	--	0.00	--	--	--
	(200)	0.02	1.34	1.79	--	0.13	--	--	--
	(220)	0.14	1.64	0.60	--	2.87	--	--	--
Lattice parameter	a _{TiN} (nm)	0.42350	0.43788	0.42994	--	0.44408	--	--	--

4.1.3.1. Crystal phase and amorphous matrix

Fig. 4-15 shows the bright field HRTEM morphological appearance of nc-TiN/a-SiN_x nanocomposite thin film with 11.3 at.% Si (Sample P4). Crystallites are embedded in matrix. The grain size is about 6 nm. Analysis of the selected area diffraction (SAD) pattern shows that these crystallites are polycrystalline TiN. No crystalline TiSi₃ and Si₃N₄ are found. In general, TiN crystallographic planes of (111), (200) and (220) exhibit the more distinct rings than other diffraction rings (c.f. Fig. 4-16). Proof of the crystallites being TiN also comes from the XRD analysis (Fig. 4-17). The substrate on which film was deposited is silicon wafer (100), and the peak at about 69° in Fig. 4-17 belongs to silicon (400) diffraction.

Fig. 4-15 HRTEM bright field micrograph of nc-TiN/a-SiN_x nanocomposite thin film with 11.3 at.% Si (Sample P4) showing the crystalline in size of 6 nm embedded in matrix.

Fig. 4-16 SAD pattern of nc-TiN/a-SiN_x nanocomposite thin film with 11.3 at.% Si (Sample P4) showing the crystalline TiN. (1 1 1), (2 0 0) and (2 2 0) crystallographic planes exhibit the more distinct rings than other diffraction rings.

Fig. 4-17 XRD pattern of nc-TiN/a-SiN_x nanocomposite thin film with 11.3 at.% Si (Sample P4). Formation of crystallite TiN is confirmed.

Analysis of the SAD pattern (where there is no crystallite) gives rise, on the other hand, to a diffuse pattern typical of an amorphous phase (c.f. Fig. 4-18). Together

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with the XPS analysis (c.f. §4.1.1), where silicon is mostly in Si-N bond, the results confirm that the amorphous phase is amorphous silicon nitride (a-SiN_x). Usually, the TiN deposited at such condition is in crystalline phase. Silicon nitride, however, stays amorphous even at 1100 °C [15, 76]. These results are in agreement with the idea of spontaneous formation of such nanostructure due to spinodal decomposition which occurs during deposition [23].

Fig. 4-18 SAD pattern (where there is no crystallite) of nc-TiN/ a-SiN_x nanocomposite thin film with 11.3 at.% Si (Sample P4) showing a diffuse pattern typical of an amorphous phase.

Fig. 4-19 shows an empiric model for the phase formation in Ti-Si-N coating system, including formation of nanocrystalline titanium nitride (nc-TiN) and amorphous silicon nitride matrix (a-SiN_x). The deposition conditions for Ti-Si-N coating system are: deposition temperature at 450 °C, total deposition power densities of (Ti + Si_3N_4) targets greater than 6.6 W/cm^2 . In such deposition condition, the mobility of the species at the growing Ti-Si-N surface can be enhanced by the high deposition temperature and the ion bombardment effect

which is due to the high deposition target power density. This enhancement in mobility is high enough to assure the nanocrystals/amorphous phase segregation, forming the nc-TiN/a-SiN_x nanocomposite.

Fig. 4-19 Empiric model for phase formation in Ti-Si-N coating system: formation of nanocrystalline titanium nitride (nc-TiN) and amorphous silicon nitride matrix (a-SiN_x) [194].

4.1.3.2. Grain size and distribution

Usually, XRD results are used to calculate grain size with Scherrer formula [181] or Williamson-Hall plot analysis [195] owing to the convenient sample preparation comparing with that of TEM sample. However, grain size calculated based on XRD results can be affected by some factors, such as residual stress and texture. Thus, bright field TEM morphological appearance of the nc-TiN/a-SiN_x

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nanocomposite thin film is used to determine the grain size and crystallite fraction. Typical bright field TEM micro photos and the corresponding SAD patterns of nc-TiN/a-SiN_x thin films with different silicon content are presented in Fig. 4-20 (with high magnification) and Fig. 4-21 (with low magnification). Grain size and crystallite fraction obtained based on the high magnification photos are consistent with those on the low magnification ones.

(a)

(b)

Fig. 4-20 Bright field TEM images (high magnification) and corresponding SAD patterns of nc-TiN/a-SiN_x nanocomposite thin films with different Si content: (a) 5.2 at.% (b) 14.9 at.% and (c) 52.7 at.%. With increase of Si content, grain size decreases.

Fig. 4-21 Bright field TEM images (low magnification) of nc-TiN/a-SiN_x nanocomposite thin films with different Si content: (a) 5.2 at.% (b) 14.9 at.% and (c) 52.7 at.%. With increase in Si content, grain size decreases.

Fig. 4-22 shows the nc-TiN grain size change as a function of silicon content. The grain size of the nc-TiN basically decreases with increase in silicon content. With reference to the deposition condition, actually, the Ti target power density does not vary (5.5 W/cm²) while Si₃N₄ target power density from 1.1 to 5.5 W/cm² (Sample P1 through P5) with N₂ to Ar gas ratio as unity. Though the presence of a large amount of N₂ may result in Ti target poisoning to a certain degree (by forming TiN on Ti target surface) that would contribute to some lessening of the Ti ion partial pressure, this effect would be the same for Sample P1 to P5 since they have the same Ti target power density and the same N₂ flow rate. However, the increasing of Si₃N₄ target power inevitably increases the silicon ion's mobility and partial pressure while reducing the titanium ion's partial pressure, giving rise to more probability of forming SiN_x than TiN crystals. By the same token, the growth of TiN nanocrystals is hindered, resulting in a decrease in the crystallite size. The nc-

TiN/a-SiN_x nanocomposite thin films with Si₃N₄ target power density of 6.6 and 7.7 W/cm² (Sample P6 through P8) and Ti target power density of 4.4 W/cm² down to zero, the titanium ions do not have enough mobility or energy to form nc-TiN, thus the films deposited are basically amorphous.

Fig. 4-22 TiN crystallite size vs. Si content based on the TEM image observation. With increase of Si content from 1.7 at.% to 52.7 at.%, TiN crystallite size decrease from about 8 nm to zero.

Fig. 4-23 shows the relationship between crystallite fraction and silicon content. Increase of silicon composition comes from the increase in silicon nitride target power density. At higher sputtering power density of Si₃N₄, more ionic nitrogen should be available for the formation of TiN crystallites from more complete ionization of reactive N₂ gas and certain degree of dissociation from the Si₃N₄ compound. Also, higher target power density effectively exerts stronger ion bombardment on the growing film thus supply more nucleus for formation of crystalline TiN. In addition, more kinetic energy can enhance segregation and formation of TiN. Though this effect applies equally on SiN_x matrix, it does not

show up since it is amorphous. As a result, the nc-TiN crystallite fraction increases with silicon content. The drastic dip in nc-TiN crystallite fraction from 23.6 at.% Si actually comes from the reduction in Ti target power density to 4.4, 2.2 W/cm² and zero, very little or no nc-TiN is formed.

Fig. 4-23 TiN crystallite fraction vs. Si content based on the TEM image observation. With increase of Si content from 1.7 at.% to 14.9 at.%, TiN crystallite fraction increase from 4 % to 11%. Further increase in Si content to 52.7 at.%, nearly no TiN crystallite phase.

It should be pointed out that for the TEM samples, deposition time is only 20 min, while that for those deposited on silicon wafers is 120 min. Therefore, the average grain size measured based on TEM micro photos might be slightly smaller than those 120min ones due to grain growth.

4.1.3.3.Preferentialorientation

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Fig. 4-24 reveals that Si_3N_4 target power density has a significant effect on the orientation of the TiN crystallites. The degree of preferential orientation can be quantitatively represented using coefficient of texture, T_{hkl} , through eqn(3-4). The calculated coefficient of texture is tabulated in Table 4-3 and plotted in Fig. 4-25. At low Si_3N_4 target power density level, the nc-TiN is mainly oriented in the [111] direction (the open squares in Fig. 4-25). Increasing the Si_3N_4 sputtering target power density level, the preferential orientation changes from [111] to [200] (the solid circles) and [220] (the open circles). Further increase of the target power density aligned the nc-TiN crystallites mainly in the [220] direction. At very high Si_3N_4 target power density, the crystallites predominantly orient along [220] direction.

Fig. 4-24 XRD patterns of the nc-TiN/a-SiN_x nanocomposite thin films with different Si₃N₄ target power density. Revealing a significant effect of Si₃N₄ target power density on the orientation of the nc-TiN crystallites.

Fig. 4-25 Coefficient of texture of nc-TiN crystallites changing with Si₃N₄ target power density. With increase in Si₃N₄ power density, the preferential orientation changes from [111] to [200] (the solid circles) and [220] (the open circles). Further increase of the target power density aligned the nc-TiN crystallites mainly in the [220] direction. At very high Si₃N₄ target power density, the crystallites predominantly orient along [220] direction.

The orientation and the evolution of the growing film depend basically on the effective total energy: the rule of the lowest energy. This is also true in the case of preferential growth orientation of TiN thin films [196]. The most prominent competition energies are surface energy [197] and strain energy [198]. The surface energy of a plane can be calculated using the sublimation energy and the number of free bonds per surface area. For TiN the surface energy for the (111), (200) and (220) are 400, 230 and 260 J/m², respectively. Sublimation energy is 6.5×10^{-19} J/atom [155, 197]. The (200) plane is the plane of the lowest surface energy in the TiN crystal (which has the NaCl-type structure [199,200]). Thus, as the surface energy is the main driving force, the TiN crystallites will orient on (200) plane (or

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[200] growth direction). At the very beginning of the deposition, it should be a surface energy controlled process because the strain energy has not kicked in yet, thus (200) crystallographic plane should predominantly parallel to the substrate surface. Since the total strain energy is proportional to the layer thickness and depends on the mean elastic moduli acting in the (hkl) plane parallel to the interface, competition from strain energy kicks in as the film grows. For pure TiN, the strain energy is minimized when the (111) plane is parallel to the interface [155]. In our experiment, even though the crystallite is not pure TiN but (Ti,Si)N solid solution, at low Si₃N₄ target power density, the amount of Si atoms in the TiN lattice is very limited (less than 2 at.% in the whole film at 1.1 W/cm² as revealed by XPS), thus the strain energy of the (111) plane dominants. As a result, the (111) texture is resulted. As deposition power density increases, the ions obtain greater kinetic energy and even high enough to force into the empty space in the TiN lattice and form interstitial solid solution, as manifested in the lattice parameter increase (c.f. Table 4-3). Meanwhile, simple calculation reveals that for fcc structure (c.f. Fig. 4-26), (111) plane has the highest planar density (PD) [10] (defined as number of atoms per unit area in the plane): $0.29/r^2$ where r is the radius of the atom forming fcc lattice. Thus squeezing into (111) plane is more difficult (would cause more increase in total system energy). For (200), $PD = 0.25/r^2$, and for (220), $PD = 0.18/r^2$. Therefore, it is more probable for the arriving ions to insert into (200) or (220) planes resulting in the least increase in the total system energy (less strain energy generated because the atoms or ions do not have to squeeze as hard). Consequently, since (220) plane has the lowest planar density, at high deposition power density, the preferential orientation becomes [220] direction.

Fig. 4-26 Schematic diagram of fcc structure. (111) plane has the highest planar density: $0.29/r^2$ where r is the radius of the atom forming fcc lattice. For (200), $PD = 0.25/r^2$, and for (220), $PD = 0.18/r^2$.

4.1.3.4. Lattice parameter

During co-sputtering of Ti and Si_3N_4 targets in Ar and N_2 atmosphere, aside from forming amorphous SiN_x in the matrix, silicon also enters into TiN crystallites as solid solute which can affect the nc-TiN lattice parameter. The calculated lattice parameter are listed in Table 4-3 and plotted in Fig. 4-27 as a function of Si_3N_4 target power density. With increase of Si_3N_4 target power density, the lattice parameter increases from 0.42350 to 0.44408 nm. It is interesting to note that the measured TiN lattice parameter of 0.42350 nm at the lowest Si_3N_4 target power density (1.1 W/cm^2) is smaller than that of the database value of 0.42417 nm (c.f. Table 3-2), all other values are larger than this value. At 1.1 W/cm^2 target power density level, there is reason to believe the silicon ions for this deposition had very low kinetic energy thus very low mobility. In such a case, silicon forms

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substitutional solid solution with TiN [69], i.e., (Ti,Si)N. Since the ionic radius of Si^{4+} (0.041 nm) is only about half of that of Ti^{3+} (0.075 nm) (c.f. Table 3-1), substitution of titanium with silicon results in reduction in lattice parameter. Thereafter, the Si_3N_4 target power density is increased to 2.2, 3.3 and 5.5 W/cm^2 , silicon ion would have obtained much more kinetic energy thus formed interstitial solid solution (c.f. Fig. 4-28) [154]. Therefore, an increase in lattice parameter is observed.

Fig. 4-27 Calculated lattice parameter as a function of Si_3N_4 target power density. With increase of Si_3N_4 target power density from 1.1 to 5.5 W/cm^2 , lattice parameter increases from 0.42350 to 0.44408 nm.

Fig. 4-28 Schematic diagram of microstructure of (Ti,Si)N solid solution, where Si in the interstitial position of TiN lattice.

4.1.4. Summary

The effect of Si_3N_4 target power density (and/or target power ratio of Ti to Si_3N_4) on chemical composition, topography and microstructure of the nc-TiN/a- SiN_x nanocomposite thin films can be summarized as follows:

- (1) Nanocrystalline TiN has been imbedded in amorphous silicon nitride matrix to form nc-TiN/a- SiN_x nanocomposite thin films via co-sputtering of Ti and Si_3N_4 targets in argon and nitrogen atmosphere.
- (2) As the sputtering power density increase, the resultant coating surface becomes smoother. The surface topography is quantitatively described through surface scaling with the parameters of interface width (ω) and the lateral correlation length (ξ). The effect of the target power density is readily understood via atomic mobility.

- (3) At a Ti target power density of approximately 5.5 W/cm^2 , the Ti to Si_3N_4 target power ratio should be greater than unity in order for nc-TiN to form in amorphous SiN_x matrix. Deviating from this condition, TiN crystallites will not form and Ti will dissolve in amorphous SiN_x .
- (4) Detailed XPS studies reveal that Ti forms stoichiometric TiN plus a very small amount of Ti-O bonding, element Si and/or Ti-Si bonding. The amorphous SiN_x is mainly stoichiometric Si_3N_4 .
- (5) Aside from forming a- SiN_x in the matrix, Si atoms also imbed into TiN for (Ti,Si)N solid solution crystallites. At low target power density, the solid solution is substitutional. With increase of power density, the amount of silicon dissolved in the TiN crystallite increases, and in the meantime, the interstitial components increase which is manifested in the increase in the TiN lattice parameter.
- (6) The crystallites have a preferential orientation varying with the deposition target power density. As conveniently described by the coefficient of texture, the degree of preferential orientation along [111] direction decreases and finally tails off with increase of Si_3N_4 target power density. At the same time, the crystallites orient along [200] and [220] direction and eventually [220] direction dominants, as Si_3N_4 target power density increases from 1.1 to 5.5 W/cm^2 .

4.2. Mechanical Properties of nc-TiN/a- SiN_x

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The effect of sputtering power density of Si_3N_4 target on mechanical properties, such as residual stress, Young's modulus, hardness and adhesion strength are summarized in Table 4-4.

Table 4-4 Mechanical characteristics of hard and superhard nc-TiN/a- SiN_x nanocomposite thin films

Sample Code		P1	P2	P3	P4	P5	P6	P7	P8
Residual stress	σ (MPa)	-4.2	-5.6	-40.2	-82.0	-150.0	--	-67.5	-52.5
Hardness	H (GPa)	7.6	16.6	20.7	25.8	36.8	16.4	15.5	15.0
Young's modulus	E (GPa)	196	209	222	276	324	211	185	184
Critical load (mN)	L_{C1}	200	300	250	225	175	50	50	50
	L_{C2}	350	375	450	375	325	200	225	250

4.2.1. Residual Stress

The residual stress data obtained from eqn(3-8) is plotted in Fig. 4-29 as a function of Si_3N_4 target power density. With increase of Si_3N_4 target power density, the residual stress increases from nearly 0 to about -0.15 GPa. The minus sign

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indicates the stress is in the compressive state. This is a very small residual stress for magnetron sputtering deposited thin films.

Fig. 4-29 Relationship of residual stress with Si_3N_4 target power densities. With increasing Si_3N_4 target power density, the residual stress increases from nearly 0 to about -0.15 GPa.

Assuming that the stress resulted from pure change of temperature is zero (as a result of slow cooling from deposition temperature to room temperature), the residual stress (σ) in magnetron sputtered films is structure-related and results from the following three aspects (c.f. eqn(4-1)): thermal stress (σ_T), growth-induced stress (σ_g) and structural mismatch-induced stress (σ_m):

$$\sigma = \sigma_T + \sigma_g + \sigma_m \quad (4-1)$$

The thermal stress (σ_T) is an extrinsic stress resulted from the difference in coefficient of thermal expansion (CTE). The latter two stresses (growth-induced stress (σ_g) and structure mismatch-induced stress (σ_m)) constitute the intrinsic stress [201,202]. In our nc-TiN/a-SiN_x nanocomposite thin films, since the matrix

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is amorphous, basically no effort is needed in structure “matching” between nc-TiN and the a-SiN_x matrix therefore $\sigma_m \sim 0$. Thus in our system, the residual stress (σ) mainly comes from the thermal stress (σ_T) and the growth-induced stress (σ_g) which is analyzed in details below.

(1) Thermal stress (σ_T)

The thermal stresses originate from the fact that the CTE is different between the thin film and the substrate. Hence the shrinkage of the film differs from that of the substrate during post deposition cooling. The stress in the film measured at room temperature T_{rm} (usually 25 °C) can be calculated using the following equation [203,204]:

$$\sigma_T = \frac{E_f}{1-\nu_f} \int_{T_{dep}}^{T_{rm}} (\alpha_s(T) - \alpha_f(T)) \cdot dT \quad (4-2)$$

Where, T_{dep} and T_{rm} represent the deposition temperature and room temperature, respectively. E_f and ν_f are the elastic modulus and the Poisson’s ratio of the film. $\alpha_f(T)$ and $\alpha_s(T)$ are CTE of the thin film and substrate, respectively. Though normally CTE varies with temperature, for a rough estimation, if we do not take the temperature effect into account, we may use the CTE data from literatures (listed in Table 4-5) to estimate the thermal stresses. Our XPS analysis shows there is no trace of Ti-Si, even if there is some, the amount is quit small. So we do not consider the TiSi phase effect during the residual stress analysis. Using XPS composition results (c.f. Table 4-1) and assuming only TiN and Si₃N₄ (for simplicity of estimating fraction of a-SiN_x) exists in the film, TiN fraction is estimated. Based on the rule of mixtures between TiN and Si₃N₄, CTE values of

the nc-TiN/a-SiN_x nanocomposite thin films are calculated and put in Table 4-6. Also tabulated in Table 4-6 are the thermal stresses calculated using eqn(4-2). Note that these values positive, i.e., a tensile stress is generated in the film due to thermal mismatch between the film and the substrate. That is easily understood since the CTE of the film is greater than that of the substrate. Upon cooling, the shrinkage in the film would be more than that in the substrate. Since the film is not delaminated, the film must then be “stretched” (thus tensile stress) to satisfy the continuity between the film and the substrate.

Table 4-5 Material constants used for calculation of thermal stress σ_T

Constant	Notation	Value	Ref.
CTE (Si substrate)	α_{Si}	$2.6 \times 10^{-6} /K$	[205]
CTE (TiN)	α_{TiN}	$9.4 \times 10^{-6} /K$	[206]
CTE (Si ₃ N ₄)	$\alpha_{Si_3N_4}$	$2.5 \times 10^{-6} /K$	[206]
Poisson’s ratio (for all films)	ν_f	0.25	[207]

Table 4-6 Calculated CTE and thermal stress σ_T

Sample Code	Si ₃ N ₄ Power Density (W/cm ²)	TiN (%)	CTE ($\times 10^{-6} /K$)	E (GPa)	σ_T (GPa)
P1	1.1	98.86	9.3	196	0.75
P2	2.2	96.17	9.1	209	0.78
P3	3.3	94.07	9.0	222	0.80
P4	4.4	90.33	8.7	276	0.95
P5	5.5	85.56	8.4	324	1.05

(2) Growth-induced stress (σ_g)

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The stress resulting from the growth of sputtered thin film depends on substrate temperature, gas pressure and bias voltage, i.e. the kinetic energy of the ions. In magnetron sputtering, the kinetic energy of the ions is of the order of 100 eV [201, 208], sufficient to create defects in the growing layer. Increasing the bombardment leads to an increase in stress [202]. In general, as the sputtering power density increase, the kinetic energy of the impinging ions increases, which results in the increase in the strain of the film [209]. Within a certain sputtering power range, this can be best understood by relating the deposition ion energy (U_k) with the target power density (D_w) together with substrate bias (V_s) and gas pressure (P_g) through eqn(2-4) :

$$U_k \propto \frac{D_w V_s}{P_g^{1/2}} \quad (2-4)$$

Therefore, this energetic ion generates stress in both amorphous matrix and nanocrystalline phase. In amorphous matrix, the energetic ionic bombardment induces atomic distortion or displacement of atoms from their equilibrium (stress-free) location. In crystalline phase, this energetic ion generates lattice distortion in terms of substitutional or interstitial solid solution (c.f. Table 4-3) resulting increase of lattice parameter of the nc-TiN from 0.42350 nm to 0.44408 nm. The total growth-induced stress (σ_g) can be seen from the difference of the total residual stress (σ) and the thermal stress (σ_T). From eqn(4-1),

$$\sigma_g = \sigma - \sigma_T \quad (4-3)$$

Since the total residual stress (σ) (neglecting structural mismatch-induced stress σ_m) is from nearly zero to -0.15 GPa, and the thermal stresses (σ_T) are about 1 GPa (c.f. Table 4-4), the growth-induced stress (σ_g) is therefore about -1 GPa. These

two components of the residual stresses are opposite in sign thus mostly cancel out each other, resulting in an almost stress-free thin film.

4.2.2.Hardness

4.2.2.1.Nanoindentation

Fig. 4-30 shows one typical nanoindentation load-displacement profile of nc-TiN/a-SiN_x nanocomposite thin film with 14.9 at.% Si (Sample P5). The film thickness is 600 nm. The film roughness (R_a) in 300 nm x 300 nm areas is about 0.8 nm (less than 1% of the film thickness), which is identified using AFM. The maximum load during indentation is 1.14 mN and the maximum indentation depth is 50 nm (less than one tenth of the film thickness). The hardness and Young's modulus analyzed using Oliver-Pharr method are 36.8 GPa and 324 GPa, respectively.

Fig. 4-30 Nanoindentation load-displacement profile of nc-TiN/a-SiN_x nanocomposite thin film with 14.9 at.% Si (Sample P5). Nanoindentation depth is

less than one tenth of the films thickness so as to avoid effect of substrate on film hardness.

4.2.2.2. Effect of indentation depth

Nanoindentation with different indentation depth were performed on nc-TiN/a-SiN_x nanocomposite thin film with 11.3 at.% Si (Sample P4, with 600 nm in thickness) to study the effect of indentation depth on film hardness. Fig. 4-31 shows the measured hardness as a function of indentation depth. When indentation depth within one tenth of film thickness, the average measured hardness nearly keeps constant which represents the intrinsic hardness. The measured intrinsic hardness of nc-TiN/a-SiN_x nanocomposite thin film with 11.3 at.% Si is 25.8 GPa. Under lower indentation depth, such as 25 nm, the deviation from the average value is much larger than that under high indentation depth such as 50 nm. This is due to the fact that small indentation depth is apt to be significantly affected by surface roughness compared with that under high indentation depth. When indentation depth exceeds one tenth of film thickness, with further increase in depth, the measured hardness decreases linearly. This is due to that the elastic-plastic deformation field in the film just below the indenter is not confined to the film itself, but a long-range field that extends into the silicon substrate. The effect of silicon substrate on film hardness is inevitable. The silicon (100) wafer substrate has much lower hardness (9.8 GPa) than that (25.8 GPa) of nc-TiN/a-SiN_x nanocomposite thin film with 11.3 at.% Si (Sample P4). Therefore, with increase in indentation depth, the measured hardness decreases.

Fig. 4-31 Hardness as a function of indentation depth. When indentation depth is less than one tenth of the coating thickness, the hardness nearly keeps constant value about 25.8 GPa. With increase of indentation depth, the measured hardness decreases due to the effect of Si substrate (hardness 9.8GPa).

4.2.2.3. Effect of residual stress

Fig. 4-32 shows the relationship among hardness, residual stresses and silicon content for nc-TiN/a-SiN_x nanocomposite thin films. Veprek [15] pointed out that the intrinsic hardness values for film are those with residual stress less than 1 GPa. Under that condition, the residual stress will not contribute to the measured hardness value. Since all the as-prepared nc-TiN/a-SiN_x nanocomposite thin films with residual stress far less than 1 GPa, the enhancement of the hardness in these nanocomposite films is not due to the residual stress.

Fig. 4-32 Relationship among hardness, residual stress and Si content for nc-TiN/a-SiN_x nanocomposite thin films. There is no impact on the film hardness from the residual stress.

4.2.2.4.Effect of grain size and crystallite fraction

Plotting nanoindentation hardness against nc-TiN crystallite size gives rise to Fig. 4-33. This clearly demonstrates: (a) as crystallite size decreases (going from right to left on X-axis), film hardness increases drastically (Hall-Petch relationship); (b) the maximum (37 GPa) is approximately 6 nm crystallite size; (c) further decreases in crystallite size bring about a decrease in hardness (the anti-Hall-Petch effect); and (d) the hardness tails off to the hardness of an amorphous phase as crystallite size diminishes. This result matches extremely well with Schiotz’s theoretical prediction [7].

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Fig. 4-33 Nano indentation hardness vs. nc-TiN crystallite size in the nc-TiN/a-SiN_x nanocomposite thin films: both Hall-Petch and anti-Hall-Petch phenomena are observed.

Fig. 4-34 displays the relationship between film hardness together with crystallite fraction as a function of silicon content. The film hardness increases significantly to about 37 GPa at about 14.9 at.% Si, corresponding to the maximum crystallite fraction about 11 %. Further increase in silicon brings about drastic decrease in hardness to about 15 GPa which is a common value reported for Si₃N₄ thin film, this again, corresponds to the reduction in crystallite fraction. In order to simplify the calculation, assuming crystallite is in ball-shape with diameter of d and the grain boundary is the near out-layer (thickness Δd) of the crystallite, then the volume of grain boundary V_{boundary} can be roughly estimated using

$$V_{\text{boundary}} = \frac{V_{\text{crystal}}}{\frac{4}{3}\pi\left(\frac{d}{2}\right)^3} \cdot \left[\frac{4}{3}\pi\left(\frac{d}{2} + \Delta d\right)^3 - \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 \right] \quad (4-4)$$

Taking the first two terms of the Taylor expansion, eqn(4-4) is simplified to

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$$V_{boundary} \approx \frac{V_{crystal}}{\frac{4}{3}\pi\left(\frac{d}{2}\right)^3} \cdot 4\pi\left(\frac{d}{2}\right)^2 (\Delta d) = 6 \frac{V_{crystal}}{d} \quad (4-5)$$

Where, $V_{crystal}$ is the volume of crystalline. From eqn(4-5) it can be seen that the grain boundary volume is proportional to crystalline volume and reversely to grain size. With increase in silicon content to about 14.9 at.%, the grain size decreases to about 5 nm (c.f. Fig. 4-22) while crystalline fraction (represented in area ratio in this case) increase to 11% (c.f. Fig. 4-23). Therefore, the grain boundary volume should be increase significantly. Thus, there is more grain boundary to effectively hinder dislocation propagation, which is contributed to the hardness increase. With further increase in silicon content, the crystallite fraction (represented in area ratio in this case) decreases to less than 1%, and at the same time, grain size decrease to 3 nm. Grain boundary strengthening is weakened. The grain boundary sliding is the more active, which contribute to the hardness decreases.

Fig. 4-34 Hardness varying with nc-TiN crystallite fraction and Si content. The film hardness increases significantly to about 37 GPa at about 14.9 at.% Si, corresponding to the maximum crystallite fraction about 11 %. Further increase in

Si brings about drastic decrease in hardness to about 15 GPa which is a common value reported for Si₃N₄ film, this again, corresponds to the reduction in crystallite fraction.

4.2.2.5. Relationship between hardness and Young's modulus

Fig. 4-35 shows the relationship between hardness and Young's modulus for a number of nc-TiN/a-SiN_x nanocomposite thin films with different silicon content. The experiment data show an approximately linear increase of the Young's modulus with the hardness. The Young's modulus varies by a factor of 5.45 showing a proportionality $E = [122 \pm 8] + [5.45 \pm 0.37] \times H$. It is generally accepted that hardness of bulk material scales with the energy of dislocation because the plastic deformation of crystalline materials is due to dislocation activity, and the energy of a dislocation is proportional to the shear modulus through [210]

$$U_{screw} = G \bar{b}^2 \quad (4-6)$$

$$U_{edge} = G \frac{\bar{b}^2}{1 - \nu} \quad (4-7)$$

Where, U_{screw} and U_{edge} are energy of screw dislocation and edge dislocation, respectively. $\bar{b}$ is Burgers' vector. G is the shear modulus which is related to Young's modulus E . Therefore, it is not surprised such correlation between the indentation hardness H and the Young's modulus E can be found for the hard and superhard nc-TiN/a-SiN_x nanocomposite thin films.

Fig. 4-35 Correlation between indentation hardness and Young’s modulus for nc-TiN/a-SiN_x nanocomposite thin films.

Fig. 4-36 shows H^3/E^2 as a function of thin film hardness. The ratio of H^3/E^2 is regarded by Tsui et al. [211] as an important criterion of the resistance against plastic deformation for hard materials and emphasized by Musil [212] as an important criterion of mechanical properties for hard nanocomposite thin film. Measured values of hardness H and Young’s modulus E enables the ratio H^3/E^2 can be calculated, which gives information on the resistance of materials to plastic deformation. The higher the ratio of H^3/E^2 , the higher the resistance to plastic deformation. From Fig. 4-36, it can be seen clearly that the resistance to plastic deformation increases with increase of film hardness.

Fig. 4-36 H^3/E^2 as a function of hardness. The resistance to plastic deformation increases with the increase of film hardness.

4.2.3. Toughness Measurement and Assessment of Methodology

As reviewed and pointed out in section §2.4.2, presently there is neither standard procedure nor commonly accepted methodologies to follow for measuring toughness of thin films. To assess methodologies, several testing methods including indentation, scratching, and tension are carried out to measure toughness of nc-TiN/a-SiN_x nanocomposite thin films.

4.2.3.1. Indentation

4.2.3.1.1. Microindentation

Substrate effect

During indentation process, below the indenter contact point there is a tensile stress. When the tensile stress exceeds the critical cracking stress of the coating, a

median sub-surface crack initiates. The initiated sub-surface crack becomes unstable over time and expands towards the film when the load is removed. Usually, under microindentation condition, the indentation depth exceeds one tenth of the film thickness and thus the elastic-plastic zone may expand to the substrate. Therefore, substrate properties have impact on the crack behavior. For titanium alloy substrate, due to its high ductility (reduction in area during tensile is greater than 20%), plastic deformation in the alloy substrate just below the indenter edge will reduce stress concentration in the thin films. Thus, the crack will initiate and propagate inside the indentation impression rather than along the indenter edge direction. The cracks are in the form of palm shape (c.f. Fig. 4-37 (a)). On the contrary, for the silicon substrate, due to its brittleness (toughness $0.90 \text{ MPa m}^{1/2}$ [213]), there is higher stress concentration in the thin films just below the indenter edge. Thus, the crack in the thin films will propagate along the indenter edge direction to release the strain energy (c.f. Fig. 4-37 (b)). Due to the absence of well-defined radial crack, the toughness of hard coating deposited on ductile substrate cannot be valuated using microindentation method through eqn(2-17):

$$K_{IC} = \delta \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (2-17)$$

This limits the application of microindentation method to hard coatings deposited on brittle substrate system which can initiate well-defined ($c \geq 2a$) radial cracks.

Fig. 4-37 Indentation impression of hard nc-TiN/a-SiN_x nanocomposite thin films (hardness 7.6 GPa, thickness 3 μm) on (a) ductile substrate Ti6Al4V and (b) brittle substrate Si wafer under Vickers indenter. Indent hard coating on ductile substrate can induce palm shape cracks which can not be used to calculate coating toughness, while indenting hard coating on brittle substrate can induce well-defined ($c \geq 2a$) radial cracks which can be used to calculate coating toughness.

Fig. 4-38 shows the micrographs of indentation impression under different indentation load for nc-TiN/a-SiN_x nanocomposite thin films (hardness 7.6 GPa, thickness 3 μm) on brittle silicon substrates. Under high indentation load, such as 10.00 N, the well-defined ($c \geq 2a$) radial cracks can be generated and the characterization of such crack is quit easy due to the high spacial resolution of the

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corresponding SEM image. For example, even under low magnification of 420 times, the cracks are well defined (c.f. Fig. 4-38 (a)). While, under low indentation load, such as 0.25 N, it is not easy to induce well-defined radial cracks due to the cracking threshold under which crack cannot be initiated. In addition, even if there is cracking occurs in the coating surface, it is difficult to locate and observe the crack using SEM even under high magnification of 5,000 times (c.f. Fig. 4-38 (c)). In order to obtain well-defined cracks under Vickers indenter, high indentation load should be applied to. However, the effect of substrate on film toughness under high indentation load is significant compared with that under low indentation load.

Fig. 4-38 Micrographs of microindentation impression of nc-TiN/a-SiN_x nanocomposite thin films on silicon substrate. Indentations were conducted using Vickers indenter under load of (a) 10.00 N, (b) 1.00 N and (c) 0.25 N. High indentation load results in well-defined cracks ($c \geq 2a$) and thereafter high spacial resolution SEM micrograph. The measured toughness, however, affected significantly by the substrate due to the deep indentation depth under high load.

In order to study the calculated toughness changing with indentation depth, microindentation was conducted on nc-TiN/a-SiN_x nanocomposite thin films (with hardness of 7.6 GPa, thickness of 3 μm) under indentation load of 10.00, 5.00, 3.00, 2.00, 1.00, 0.50 and 0.25 N. Toughness under different indentation load were calculated through eqn(2-17):

$$K_{IC} = \delta \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (2-17)$$

Indentation depth h for Vickers indenter was calculated through [88]

$$h = \frac{D}{2\sqrt{2} \tan 68^\circ} = \frac{1}{7} D \quad (4-8)$$

Where, D is the diagonal of the indentation impression. Fig. 4-39 shows the plot of as-calculated toughness value against indentation depth. It can be seen clearly that the as-calculated toughness values based on the microindentation data are affected significantly by indentation depth. The calculated toughness increases dramatically from 1.25 to 1.90 MPa m^{1/2} with decrease indentation depth from 7 to 1 μm. This is due to the fact that the elastic-plastic zone below indenter tip has expanded to silicon substrate and the substrate effect has come into play. The calculated toughness compounds that both of the thin film and the silicon substrate. Since toughness of silicon substrate is 0.90 MPa m^{1/2} [213] which is below the as-calculated toughness of the coatinghubstrate system. Under smaller indentation depth, the contribution from the silicon substrate is smaller. Thus, the calculated toughness value (1.90 MPa m^{1/2}) under lower indentation depth (about 1 μm) is greater than that (1.25 MPa m^{1/2}) under higher indentation depth (about 7 μm). To deduce the film toughness from the substrate-effected data, K_{IC} values are plotted and then the curve is extrapolated to the depth of about one tenth of the film thickness to obtain a film toughness of about 2.00 MPa m^{1/2}.

Fig. 4-39 Relationship between calculated toughness and indentation depth. With increase in indentation depth, the as-calculated toughness decreases, which indicates that the effect came from silicon substrate on calculated toughness is strengthened.

Repeatability

To investigate the repeatability of microindentation method in determining thin film toughness, microindentation under different indentation load were conducted on 600 nm thick nc-TiN/a-SiN_x nanocomposite coatings with different silicon content. The well-defined ($c \geq 2a$) cracks generated by microindentation were used to calculate the thin films toughness through eqn(2-17). In order to obtain well-defined radial crack ($c \geq 2a$) and to focus and observe conveniently under SEM, indentation load of 10.00, 5.00, 2.00 and 1.00N were used. The sample information and calculated toughness values are tabulated in

Table 4-7 and plotted in Fig. 4-40. The extrapolated toughness value in

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Table 4-7 were obtained by plotting the calculated toughness value and then extrapolating the curve to depth of about one tenth of the film thickness.

Table 4-7 Toughness of nc-TiN/a-SiN_x nanocomposite thin films with different Si content under different indentation load

Sample Code	Indentation Load (N)				Extrapolated Toughness Value (MPa m ^{1/2})
	10.00	5.00	2.00	1.00	
	Calculated Toughness Value (MPa m ^{1/2})				
P1	1.13	1.40	1.18	1.53	1.31
P2	0.75	0.96	0.82	0.92	0.86
P3	1.20	1.40	1.89	2.00	1.62
P4	0.81	0.89	1.11	1.46	1.07
P5	0.75	0.73	0.72	0.94	0.78
P6	0.86	0.83	1.13	1.16	0.99
P7	0.95	0.80	0.99	1.15	0.97
P8	0.88	1.04	0.87	1.23	1.00

Fig. 4-40 shows the calculated toughness of nc-TiN/a-SiN_x thin films with different silicon content under different indentation load. All the curves obtained under different load, such as 10.00, 5.00, 2.00 and 1.00 N, confirm that nc-TiN/a-SiN_x nanocomposite thin film with 7.2 at.% Si (Sample P3) possesses of the highest toughness. In addition, all the curves plotted show consistent trend, which indicates the microindentation method has high repeatability and can be used as a fairly reliable representation of toughness for thin films. However, it should be pointed out that the measured toughness is affected by the silicon substrate under such high indentation load due to the small thickness (0.6 μm) of the coatings.

Fig. 4-40 Toughness (under different test load: 10.00, 5.00, 2.00 and 1 .00 N) of nc-TiN/a-SiN_x nanocomposite thin films with different Si content. From the four curves plotted, it can be concluded that microindentation is a reasonable method for thin film toughness measurement with high consistency and repeatability.

It is worth pointing out that, in this section, we assess the toughness measurement methodology. The drop of toughness for nc-TiN/a-SiN_x with 5.2 at.% Si is not due to the test method. This trend has also been observed for other testing approaches, such as scratch, nanoindentation (c.f. Fig. 4-43 and Fig. 4-48). The mechanism that toughness of nc-TiN/a-SiN_x nanocomposite thin film varies with silicon content needs further study.

4.2.3.1.2. Nanoindentation

In order to reduce substrate effect on thin film toughness measured, lower indentation load is desired for smaller indentation depth. In contrast to

microindentation where the indentation force ranges from a few hundred mN to about 10N, nanoindentation only uses 100μN to several mN.

Fig. 4-41 shows the nanoindentation impression (under Berkovich indenter) of nc-TiN/a-SiN_x nanocomposite thin film with hardness of 7.6 GPa, thickness of 3 μm on silicon substrate. In order to acquire well-defined cracks and easily locate and observe through SEM, indentation load at 450 mN is used, which results in 1.3 μm indentation depth. Due to the deposition of carbons on the surface of the sample results from cracking of hydrocarbon vapor in the residual gas in SEM chamber, the indentation impression is blur even the indentation depth achieve as deep as 1.3 μm. Thus, calculated toughness using nanoindentation data can be significantly affected due to the lack of accurate measurement of crack length. This gives rise to a problem in accurately determining crack length for toughness measurement using nanoindentation method, though the substrate effect on film toughness can be reduced. In addition, locating the nanoindentation impression is not an easy job.

Fig. 4-41 SEM observation of nanoindentation impression under Berkovich indenter of 3 μm thick nc-TiN/a-SiN_x nanocomposite thin film on Si substrate with indentation depth of 1.3 μm

Fig. 4-42 shows one typical nanoindentation load-displacement curve, based on which, plasticity is calculated as a qualitative, crude and relative assessment of thin film toughness. In order to get rid of the substrate effect on film toughness, indentation depth which less than one tenth of thin film thickness should be used. The calculation proceeds according to illustration in §2.4.2.1:

$$Plasticity = \frac{OA}{OB} \quad (2-15)$$

The “plasticity” shows the ability of the material to change its shape when fracture is absent. Therefore, it cannot characterize directly the fracture toughness K_{IC} . In addition, since toughness is related to material ability of absorbing energy during deformation, perhaps it is more reasonable to use the ratio of absorbed energy to total energy to calculate the plasticity (c.f. Fig. 4-42):

$$Plasticity = \frac{A(I)}{A(I) + A(II)} \quad (4-9)$$

Where, $A(I)$ the area between loading and unloading curve, which represents the absorbed energy. $A(I)+A(II)$ the area under the loading curve, which represents the total energy applied during deformation.

Fig. 4-42 A typical nanoindentation load-displacement curve, which can be used to plasticity analyze.

The calculated plasticity using eqn(2-15) and (4-9) are plotted in Fig. 4-43. From the resultant plots in Fig. 4-43, it can be seen that both values show the consistent trends for all the tested nc-TiN/a-SiN_x nanocomposite thin films. The nc-TiN/a-SiN_x thin film with 7.2 at.% Si (Sample P3) showing highest plasticity indicates best toughness, which is agreed with that from scratch results (c.f. Fig. 4-48) and microindentation results (c.f. Fig. 4-40). While, nc-TiN/a-SiN_x thin film with 14.9 at.% Si (Sample P5) shows the poorest toughness.

Fig. 4-43 Plasticity (calculated using ratio of plastic deformation to total deformation and ratio of absorbed energy to total energy) of nc-TiN/a-SiNx nanocomposite thin films with different Si content. Sample P3 shows the highest plasticity. In addition, both values present the consistent trend.

It can be seen from Fig. 4-43 that the plasticity obtained simply as the ratio of indentation depth has almost identical result from that obtained as the ratio of the energy involved. From the definition of toughness, it is more reasonable to use the ratio of absorbed energy to the total energy. However, since the plasticity calculated using these two values has the same scale and the same trend, using the ratio of leftover displacement to the total displacement is much preferred as a rough measure of toughness due to its simplicity.

4.2.3.2.Scratch

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In scratch test, the critical loads L_{c1} and L_{c2} can be determined through the combination of optical observation (c.f. Fig. 4-44) and the sudden kink in friction (expressed in terms of voltage ratio in Fig. 4-45) [142,214]. The complete peeling off of the film from substrate is represented by a big sudden change in friction.

Fig. 4-44 Optical observation with (a) low magnification (b) high magnification of the film surface after scanning scratch, showing the cracking occurs and total peeling off of coating from substrate.

Fig. 4-45 One example of scratch test showing lower critical load L_{c1} under which the cracking occurs in coating, and higher critical load L_{c2} under which coating total peeling off from substrate

Fig. 4-44 shows the optical observations of scan scratch track on nc-TiN/a-SiN_x nanocomposite thin film surface at both low and high magnification. Below the lower critical load L_{c1} , the thin film is scratched by the scratch tip, associated with the plastic flow of materials. At and after the lower critical load L_{c1} , cracks were observed. The schematic diagram of scratch damage mechanism for the nc-TiN/a-SiN_x nanocomposite thin film is shown in Fig. 4-46. Before the lower critical load L_{c1} , if a film has good toughness, scratch associated with the plastic flow of materials is responsible for the damage of film (Fig. 4-46 (a)). If a film has a poor toughness, cracking could occur during the scan scratch process, associated with cracks and debris (Fig. 4-46 (b)). When the load increases up to the higher critical load L_{c2} , delamination or buckling will occur, which induces totally peel off of films from substrate (Fig. 4-46 (c)).

Fig. 4-46 Schematic diagram of scan scratch damage mechanism of the nc-TiN/a-SiN_x nanocomposite thin film: (a) scan scratch associated with the plastic flow of materials (b) crack formation in film at the lower critical load L_{c1} and (c) total peeling off of coating from substrate at the higher critical load L_{c2} .

Fig. 4-47 shows the scratch toughness which represented by lower critical load L_{c1} varying with silicon content in nc-TiN/a-SiN_x nanocomposite thin films. The scratch toughness is characterized using lower critical load L_{c1} obtained from the scratch test. The highest scratch toughness can achieve approximately 300 mN for nc-TiN/a-SiN_x nanocomposite films with 5.2 at.% Si. However, the critical load is not “fracture toughness” (and, of course, the unit is wrong for fracture toughness!). What the lower critical load represents is a load bearing capacity, or crack

initiation load. May be it can be treated as some sort of “crack initiation resistance”: the higher the L_{c1} , the more difficult it is to initiate a crack in the film. However, initiation of a crack does not necessarily result in fracture in the film; what also important is how long the film can hold and withstand further loading before a catastrophic fracture occurs. Thus, the film toughness should be proportional to both the lower critical load L_{c1} and the load difference ($L_{c2} - L_{c1}$) between the higher and the lower critical load. The product of these two terms is termed “scratch crack propagation resistance”, or CPR_s :

$$CPR_s = L_{c1} (L_{c2} - L_{c1}) \quad (4-10)$$

The parameter CPR_s , can be used as quick qualitative indication of the film toughness or used in a quality control process for tough film.

Fig. 4-47 Scratch toughness represented by lower critical load L_{c1} for nc-TiN/a-SiN_x nanocomposite thin films with different Si content. Sample P2 shows the best toughness property.

As a first-degree approximation, the parameter "scratch crack propagation resistance" (or CPR_s) is used to qualitative estimate the film toughness. The film toughness represented by CPR, for nc-TiN/a-SiN_x nanocomposite thin films with different silicon content has been shown in Fig. 4-48. High L_{c1} value means that the film has high ability of resisting cracking. Whereas high L_{c2} value means that the film is more durable, i.e., even if the cracking occurs, the film is not damaged totally. From the viewpoint of machining application, the nc-TiN/a-SiN_x nanocomposite thin film prepared with silicon content of 7.2 at.% is preferred for its good comprehensive mechanical properties. This film has high crack initiation resistance (with $L_{c1} = 250$ mN) and high adhesion strength (with $L_{c2} = 450$ mN). At the same time, the film has a high hardness of about 20 GPa. While the nc-TiN/a-SiN_x nanocomposite thin film with silicon content of 5.2 at.%, shows poor mechanical properties, the crack propagation resistance (CPR_s) is the lowest (c.f. Fig. 4-48). The ability of resisting to crack for this film (with 5.2 at.% Si) is not too low ($L_{c1} = 300$ mN). However, if the cracking occurs, the film will be damaged totally in a short time due to its lower adhesion strength ($L_{c2} = 375$ mN).

Fig. 4-48 Toughness (denoted by crack propagation resistance) of nc-TiN/a-SiN_x nanocomposite thin films with different Si content. Sample P3 shows the best toughness property.

4.2.3.3. The two-step tensile method

4.2.3.3.1. Assumptions

A two-step uniaxial tensile method to characterize toughness of thin hard films has been proposed. In this method, the film/substrate system is subjected to uniaxial tensile stress until the thin film fractures while the substrate is still elastic. After the load is removed to allow complete elastic recovery, this system is subjected to a second loading to the previous extension. The toughness of the thin film is then derived from the energy difference between the two subsequent load-extension curves. The onset of film fracture is manifested by the generation of a kink and loss of linearity in the load-extension curve (c.f. Fig. 4-49). The crack initiation and propagation patterns are examined using SEM. In order to simplify the toughness calculation, the following assumptions are made:

- (1) The film adheres perfectly to the substrate during loading and unloading thus there is no interfacial cracking (i.e., no adhesion failure).
- (2) The elasticity of the substrate material is good enough for it to remain elastic while cracking occurs in the film. Therefore, no plastic deformation of the substrate to affect the film toughness calculation.
- (3) The aspect ratio of substrate length to thickness is large enough to warrant a plain stress condition during test.

The cracking of the thin film layer causes energy variations in the film/substrate system. The net energy change ΔU can be determined from an energy balance in the system. Under the assumption of no adhesion failure, the energy difference ΔU before and after the crack generation is the area difference $S_{OABCEO} - S_{ODEO}$ (c.f. Fig. 4-49).

$$\Delta U = \int_{OABCEO} P_1(x) dx - \int_{ODEO} P_2(x) dx \quad (4-11)$$

Where P is load in Newton, x is extension in millimeter (thus $P(x)dx$ directly gives rise to energy), and subscript 1 or 2 denotes the loading sequence (step 1 or step 2). This is the energy used to create the parallel through-thickness cracks. The energy release rate G_c is defined as the strain energy release per unit crack area [125,215]:

$$G_c = \frac{1}{2} \left(\frac{1}{w\rho L f(\theta)} \right) \left(\frac{dU}{dC} \right) \quad (4-12)$$

Where, ρ is the crack density defined as number of cracks per unit length (crack/ μm) that is obtainable from the corresponding SEM photographs, w is the substrate width, L the substrate length, thus $w\rho L$ is the total crack length in the film plane, $f(\theta)$ is a dimensionless factor dependent on crack orientation ($f(\theta) \geq 1$). For cracks perpendicular to the film/substrate interface, $f(\theta) = 1$. For thin film, the through-thickness cracks propagate instantaneously and the cracking is a single event, i.e. $dU/dC = \Delta U/h_f$ [126], thus eqn(4-12) can be rewritten as:

$$G_c = \frac{1}{2} \left(\frac{1}{w\rho L} \right) \left(\frac{\Delta U}{h_f} \right) \quad (4-13)$$

Where, h_f is the film thickness, $2w_p L h_f$ is the total crack area, ΔU is the strain energy difference before and after cracking. Since the cracking in the film under tensile condition is predominantly Mode I fracture, and because of the plain stress condition, the critical stress intensity factor K_{IC} [216] therefore can be borrowed to approximate the critical toughness of the thin film:

$$K_{IC} = \sqrt{EG_c} = \left[\left(\frac{E}{2w\rho L} \right) \left(\frac{\Delta U}{h_f} \right) \right]^{1/2} \quad (4-14)$$

Where, E is the Young's modulus of the thin film.

Fig. 4-49 Schematic diagram of load-extension curve under the two-step uniaxial tensile test with extension-control. The first step loading is along OABC; the second step loading is along OD. The energy different is the area in OABCDO.

4.2.3.3.2. Testing

Breaking the film without yielding its substrate does limit the choice of substrate materials. In this study, Ti6Al4V was used as the substrate material because of its

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well-known elasticity. Fig. 4-50 shows the load-extension curve in the tension-extension mode for uncoated Ti6Al4V substrate. The linear relationship between load and extension indicates that the substrate remains elastic up to 1.4 % strain (extension 0.24 mm).

Fig. 4-50 Load-extension curve in tensile-extension mode for uncoated Ti6Al4V substrate, showing range of the elastic deformation

In addition to the substrate mechanical property requirement, substrate thickness, thin films thickness, and residual stress in thin films must be kept in certain range. For thinner substrate coated with high residual stress thin films, the substrate/coating system will be curved or bended after deposition. This will induce buckling (under compressive residual stress) or cracking (under tensile residual stress) during straightening the coatinghubstrate system before conducting tensile test. For thick substrate, if the coating thickness too low, the load cell cannot tell the cracking occur during tensile test.

To study the buckling phenomenon for thin substrate coated by thin film with high residual stress, samples from Prof. Veprek's research group were characterized. 6.1-6.2 μm thick nc-TiN/a-Si₃N₄ thin films with 7-10 at.% Si were deposited by reactive sputtering on 300 μm thick Ti6Al4V alloy substrate. Compressive residual stress in the thin film is about 5 GPa. Fig. 4-51 (a) presents a Ti6Al4V substrate (thickness of 300 μm) before and after coating with nc-TiN/a-SiN_x nanocomposite thin film. After coating, the sample was bent due to the high compressive residual stress (5 GPa) in the thin film. Fig. 4-51 (b) shows SEM observation of the coating/substrate system after clamping in the tensile test configuration. The coating is buckled due to high compressive stress during the process of straightening the substrate. This shows that effective application of the two-step method for toughness measurement needs thicker substrate or film with minimized residual stress. Taking the machine sensitivity into consideration, thinner substrate with minimized residual stress is preferred.

(a)

(b)

Fig. 4-51 (a) Ti6Al4V substrate showing arch shape due to being coated with high-compressive-residual-stress (5 GPa) thin film; (b) buckling of coating after clamping in the testing configuration, which due to the high compressive stress in the thin film.

Fig. 4-52 shows the effect of substrate thickness on the test sensitivity as 1.5 μm thick film is deposited on substrate of different thickness (150, 300 and 550 μm) giving rise to a film/substrate “thickness ratio” of 1.0%, 0.5% and 0.3%. At the beginning of the loading, there is a deflection owing to the compressive stress in the film and stress due to clamping. With further increase of the load, the load-extension curves become linear until a loss of linearity, which indicates the cracking of the thin film (c.f. Fig. 4-52 b, c). The sensitivity of the load cell to the thickness ratio of thin film to substrate is different. In this study, when the thickness ratio is 0.3% (Fig. 4-52 curve a), no kink is observed in the load-extension curve since the substrate is too thick for the effect of the thin film to show up. As the thickness ratio is increased (or substrate thickness is reduced) to 0.5%, a kink is discernable (Fig. 4-52 curve b). When the thickness ratio increases

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to 1.0% (Fig. 4-52 curve c) the kink becomes profound. This can be easily seen from analysis of the load distribution between the film and the substrate: $F = F_f + F_s$, where F is the load and subscript f stands for film and s for substrate. The size of the kink thus depends on the share of the load on the film. In other words, Kink size $\propto F_f/F_s$. Since the load on the film and that on the substrate are $F_f = \varepsilon_f w E_f h_f$ and $F_s = \varepsilon_s w E_s h_s$, where w and h are the width and the thickness respectively, assuming negligible plastic deformation before fracture in the film, we have $\varepsilon_f = \varepsilon_s = \varepsilon$, where ε is the elastic strain.

Therefore, $\frac{F_f}{F_s} = \frac{E_f h_f}{E_s h_s}$, that is, the size of the kink depends on both modulus and thickness of both film and substrate. In the experiment above, the same film and substrate were used, i.e., E_f and E_s are the same, the size of the kink thus depended only on the ratio of the thickness ratio. For different film of the same thickness, the greater is the modulus ratio, the larger the kink size.

Fig. 4-52 Load-extension curves in tensile-extension mode for nc-TiN/a-SiN_x thin film deposited on different thickness substrate: 150, 300 and 550 μm (Sample

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information refer to §3.2.1.3.1). When the thickness ratio is 0.3%, no kink is observed (curve a). The thickness ratio is increased to 0.5%, a kink is discernable (curve b). When the thickness ratio increases to 1.0% the kink becomes profound (curve c).

Fig. 4-53 illustrates the load-extension curve of the two-step tensile test performed in tension-profile mode, based on which the energy difference ΔU is calculated. During the first loading, the total energy absorbed by coating/substrate system is 3.84×10^{-2} J. The energy absorbed during the second loading is 3.71×10^{-2} J, thus the energy difference is 0.13×10^{-2} J. Clearly, the difference in absorbed energy comes from the film cracks initiation and propagation.

Fig. 4-53 Load-extension curve obtained with two-step uniaxial tensile test in the tension-profile mode for thin film/substrate system (Sample information refer to §3.2.1.3.1), showing energy difference during cracking is about 0.13×10^{-2} J.

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Fig. 4-54 depicts the parallel cracks observed on film surface after the second loading in the tension-profile mode, and the crack density measured is about 0.1 cracks per micron. Some transversal extension delamination perpendicular to the extension plane with a width of $\sim 50 \mu\text{m}$ can also be observed. This behaviour can be understood by taking into account of the release of the stored elastic energy in thin film. The compressive stress in the films and the stored elastic energy are the two driving forces for buckling of the film layer. The stored elastic energy is mainly transformed into the surface energy of the newly created surfaces. Plugging the energy difference $\Delta U = 0.13 \times 10^{-2} \text{ J}$, crack density $\rho = 0.1 \text{ crack}/\mu\text{m}$, $w = 4 \text{ mm}$, $L = 18 \text{ mm}$, $h_f = 3 \mu\text{m}$, and $E = 222.5 \text{ GPa}$ into eqn(4-14) gives rise to the toughness of the nc-TiN/a-SiN_x thin film as $2.60 \text{ MPa m}^{1/2}$.

Fig. 4-54 also shows the debonding of coating from substrate. Debonding of the thin film affects the measured toughness. However, the way of the influence depends on when the debonding occurs: if the film delaminates from the substrate in the first tensile step, less force is needed to extend the coating/substrate system to the same extension, a lower first-step curve results, resulting in underestimation of ΔU if the delamination occurs during the second tensile step, a lower second-step curve results, giving rise to an overestimation of ΔU thus the calculated toughness will be higher. Our observation shows that in this experiment debonding occurred after the film cracking had reached certain crack density or basically during the second loading. Thus some degree of overestimation is expected.

Fig. 4-54 Parallel cracks observed in the nc-TiN/a-SiN_x thin film after the second step tensile in the tension-profile mode, showing a crack density of 0.1 crack/μm. Also, presenting some debonding tracks on the coating.

The two-step tensile method can be used to quantitatively determine thin film toughness though there are two drawbacks. The biggest draw back of this method is in the elasticity requirement of the substrate: the substrate has to remain elastic while the coated film is undergoing fracture. For ceramic thin films (hard nitride, oxide, as well as superhard nanocomposite thin films), this is not a problem. The second draw back or important requirement is the perfect adhesion between the film and the substrate. That can usually be achieved through proper deposition parametric study or inclusion of interfacial bond layer. The biggest advantage of the method lies in its independence from substrate properties (except requiring that the substrate be much more elastic than the film), the ease and speed in experimentation. The principle of the method, data treatment and sample preparations are simple. Uniform distributions of stress on the thin film surface provide good information on the flaw distribution. In addition, the tensile test covers more area, the property as characterized is more representative of the material intrinsic property compared with the indentation or bending method.

4.2.4. Summary

The effect of Si_3N_4 target power density (and/or target power ratio of Ti to Si_3N_4) on mechanical properties, such as residual stress, hardness and toughness, of the nc-TiN/a- SiN_x nanocomposite thin films can be summarized as follow:

- (1) The residual stress resulted from sputtering deposition of nc-TiN/a- SiN_x nanocomposite thin films comprise mainly of the growth-induced stresses and the thermal stress. The growth-induced stress increases with sputtering target power density, but only reaches about -1 GPa even at the highest target power density used. The growth-induced stress is opposite in sign and roughly equal in quantity to the thermal stress induced by difference in coefficient of thermal expansion between the film and the silicon wafer substrate. As a result, the magnetron sputtered nc-TiN/a- SiN_x nanocomposite thin films becomes almost stress-free.
- (2) Hardness was measured using nanoindentation with depth less than one tenth of film thickness. The indentation data was analyzed using Oliver-Pharr method. The enhancement in hardness is not due to the low residual stress (less than -1 GPa) but due to the microstructure. The relationship between the nc-TiN/a- SiN_x nanocomposite thin film hardness and the crystallite size of nc-TiN matches the Hall-Petch relationship at larger crystallite size and anti-Hall-Petch relationship as the crystallite size becomes very small (below 6 nm in this study). The relationship between

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hardness and Young's modulus is agreed with that obtained from the other nanocomposite thin film system.

- (3) Toughness measurement and assessment evaluation results confirm that microindentation is a convenient and repeatable technique used to characterize toughness of hard thin film deposited on brittle substrate. At high indentation load, well-defined ($c \geq 2a$) radial crack lengths generated are clear and can be easily used to calculate toughness. However, substrate effect may come into play and affect the actual values of thin film toughness. At lower indentation load, substrate effect on thin film toughness measurement can be reduced. However, there comes other difficulties including generating well-defined ($c \geq 2a$) radial crack, locating the crack, focusing of crack under electron microscopy and measuring the crack length. Nanoindentation test can be conducted to characterize thin film toughness both quantitatively and qualitatively. In quantitative determination of thin film toughness, the substrate effect can be significantly reduced, however, difficulties come from locating the indentation impression and measuring crack length. In qualitative characterization, plasticity can present consistent trends for series samples. However, plasticity is not "toughness". Scratch test data can be used indirectly to qualitatively characterize thin film toughness. Crack propagation resistance parameter has been proposed. However, these parameters are not termed "toughness". Two-step tensile test can be conducted to measure the toughness of the thin films in case of satisfying the assumptions.

- (4) Toughness of as prepared nc-TiN/a-SiN_x nanocomposite thin films (Sample P1 to P8) has been measured using microindentation method due to its convenience. To deduce the film toughness from the substrate-effected data, K_{IC} values are plotted and then the curve is extrapolated to the depth of about one tenth of the film thickness to obtain the film toughness. The results show that nc-TiN/a-SiN_x nanocomposite thin film with 7.2 at.% Si has the highest toughness value of 1.62 MPa m^{1/2}, while the thin film with 14.9 at.% Si has the poorest toughness (0.78 MPa m^{1/2}).

4.3. Toughening of nc-TiN/a-SiN_x

Irie et al. [217] proposed doping metallic nickel into hard and superhard TiN coatings by cathodic arc ion plating to improve toughness. TiN and Ni were selected for the high hardness phase and high toughness phase, respectively. In this study, in order to increase toughness of hard and superhard nc-TiN/a-SiN_x nanocomposite thin films, metallic nickel was doped into the Ti-Si-N coating system by co-sputtering of Ti, TiNi and Si₃N₄ targets in Ar/N₂ atmosphere. The effects of target power ratio of TiNi/(TiNi+Ti) on chemical composition, topography, microstructure and mechanical properties have been studied. The experimental conditions for all these samples have been described in Table 3-5. The as-prepared Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films were studied using different characterization techniques, such as XPS, AFM, XRD/GIXRD, TEM/HRTEM, scratch, microindentation and nanoindentation. The results and discussions are presented in this section.

4.3.1.Composition

All the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films are etched with Ar ion beam for 15 min before composition measurement. The chemical compositions obtained from XPS are listed in Table 4-8, in which the atomic concentration of Ni, Ti, Si and N are used to describe the samples. The results show titanium content for all samples is about 30 ± 5 at.%. Ni content for all samples varies greatly from zero to 38.8 at.% with the different experimental conditions, mainly target power ratio of TiNi/(TiNi+Ti).

Table 4-8 Chemical composition characteristics of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films

Sample Code			S1	S2	S3	S4	S5	S6	S7	S8
Deposition condition	Si ₃ N ₄ power density (W/cm ²)		6.6							4.4
	TiNi power density (W/cm ²)		0	0.2	0.7	1.1	1.4	1.6	2.2	4.4
	Power ratio of TiNi/(TiNi+Ti)		0	0.04	0.12	0.20	0.25	0.30	0.40	1.00
XPS Chem. Com.	Ni	(at.%)	0	2.1	4.3	6.3	13.0	16.4	19.0	38.8
	Ti		35.7	37.2	33.2	29.3	26.2	26.6	27.4	26.8
	Si		12.5	10.6	14.0	15.3	17.0	14.1	11.5	4.7
	N		51.8	50.1	48.5	49.1	43.8	42.9	42.1	29.7

4.3.1.1.Quantitative compositional analysis

Fig. 4-55 shows one detailed XPS survey scan spectrum with indexed peaks. XPS survey scan spectra with binding energy from 0 to 1100 eV is recorded. The dominant signals are from C, O, Ni, Ti, Si and N. The oxygen and carbon contaminations existed because of the film exposing to air (ambient laboratory) and the XPS spectrum obtained before thin film surface being etched by Ar ion beam.

Fig. 4-55 XPS survey scan of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film. The main signals come from C, O, N, Si, Ni and Ti.

Fig. 4-56 shows one typical XPS depth profile of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 4.3 at.% Ni (Sample S3). There is an inevitable oxygen and carbon contamination layer on film surface, which are expected to render an insignificant effect on the film's mechanical properties such as nanoindentation hardness. Ni and Si contents increase at the beginning and then remain almost constant, whereas Ti and N contents increase dramatically at the beginning and then increase slightly afterwards.

Fig. 4-56 XPS depth profile of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 4.3 at.% Ni (Sample S3).

Fig. 4-57 shows the Ni 2p core level spectrum. The peaks at the binding energy value of 853.0 eV and 870.7 eV are confirmed to be 2p_{3/2} and 2p_{1/2} of metallic nickel, respectively. The peak at 859.6 eV is the satellite peak probably due to the consequence of sputter-damaged crystallites [171]. There exists no nickel nitride, as has been reported by Ref. [217, 218] that nickel would not react with N₂ because formation of nickel nitride is thermodynamically much more unfavourable than formation of TiN.

Fig. 4-57 Ni 2p core level spectrum. The peaks at the binding energy value of 853.0 and 870.7 eV are confirmed to be $2p_{3/2}$ and $2p_{1/2}$ of metallic Ni, respectively. The peak at 859.6 eV is the satellite peak probably due to the consequence of sputter-damaged crystallites.

4.3.1.2. Effect of deposition conditions

Fig. 4-58 shows the relationship between chemical composition and target power ratio of $\text{TiNi}/(\text{TiNi}+\text{Ti})$ for the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films (Sample S1 to S8) deposited at 450 °C. It is obvious that Ni content in the as-prepared thin films increases linearly from 0 to 39 at.% with increase of $\text{TiNi}/(\text{TiNi}+\text{Ti})$ from zero to unit, while N content decreases linearly from 52 at.% to 30 at.%. Ti content decreases from about 35 at.% to 26 at.% with increase of $\text{TiNi}/(\text{TiNi}+\text{Ti})$ from zero to 0.25, with further increase in target power ratio, Ti content keeps constant at about 26 at.%. For Si content, with increase in target power ratio from zero to 2.5, silicon content increases from 12 at.% to 17 at.%, with further increase of $\text{TiNi}/(\text{TiNi}+\text{Ti})$ to unit, silicon content decreases to 5 at.%.

Fig. 4-58 Content changing with target power ratio of TiNi/(TiNi+Ti). With increase of TiNi/(TiNi+Ti) from zero to unit, Ni content increases linearly from zero to about 39 at.%.

4.3.2.Topography

The effect of sputtering target power ratio of TiNi/(TiNi+Ti) on surface topography is evaluated using AFM. Film topography characteristics are listed in Table 4-9.

Table 4-9 Topography characteristics of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films

Sample Code			S1	S2	S3	S4	S5	S6	S7	S8
Topography	Roughness (nm)	R _a	6.3	6.1	5.4	4.2	3.8	2.5	1.6	--
	Interface width (nm)	ω	8.0	7.4	6.6	6.4	3.9	3.2	1.3	--
	Lateral correlation length (nm)	ξ	14.6	13.9	11.3	10.5	9.8	9.4	--	--

Fig. 4-59 shows the AFM images ($1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$) of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films prepared with different target power ratio of TiNi/(TiNi+Ti). With increase of target power ratio, the roughness gradually decreases. Numeric treatment of the images gives rise to the height-height correlation function $G(r)$ as described through eqn(3-1).

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(c)

(d)

(e)

Fig. 4-59 AFM topography of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films with increasing power ratio of TiNi/(TiNi+Ti): (a) 0 (b) 0.04 (c) 0.12 (d) 0.20 (e) 0.25 (f) 0.30 and (g) 0.40, with roughness (R_a, nm) 6.3, 6.1, 5.4, 4.2, 3.8, 2.5 and 1.6, respectively.

Fig. 4-60 plots $G(r)$ as a function of r for the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films (Sample S1 to S7) represented by Fig. 4-59. The oscillation is due to the insufficient sampling size [179]. As predicted by eqn(3-2), when r is small, $G(r)$ has a power law dependence on distance r . At “distant”

locations (i.e., r is quite large), $G(r)$ is nearly a constant. Fitting the curves using eqn(3-2) gives the interface width ω and lateral correlation length ξ . Plotting these values gives rise to Fig. 4-61. The competition of vertical build-up and lateral diffusion determines the morphology of the growing surfaces. The vertical build-up is caused by the random angle incident of the arriving atoms (due to the uniform rotation of the substrate), and the growth produces columnar film structure. The lateral growth depends on surface diffusion which is largely determined by kinetic energy of the arriving ions. This is clearly seen from the trends of ω and ξ in Fig. 4-61. As target power ratio of TiNi/(TiNi+Ti) increases from 0 to 0.3 the interface width ω decreases from ~ 8 to ~ 3 nm (c.f. Fig. 4-61), indicating that the film becomes smoother (recall that ω is the root mean square of the vertical fluctuation). As target power ratio of TiNi/(TiNi+Ti) increasing, ξ decreases from ~ 15 to ~ 9 nm. Since ξ depicts the distance within which the “height” values (i.e., roughness) are correlated, smaller ξ means the surface topography is correlated in a narrow area.

The growth kinetics is controlled by the mobility of the impinging atoms on the surface before they condense and become entrapped in the film. This mobility can be enhanced by inputting energy to the system such as increasing deposition temperature or supplying impact energy through ion bombardment. The preferential sputtering of a compound target by ion bombardment is well known [219]. Since titanium and nickel have different melting point (1660 and 1453 °C [220]), Ni is apt to be sputtered. In addition, the presence of a large amount of N_2 can result to a certain degree of Ti target poisoning (by forming TiN on Ti target) that would contribute to lessening of the Ti ion partial pressure. Preferential

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sputtering and target poisoning are the reasons for ion bombardment effect strengthening with increase of TiNi target power though the (TiNi-tTi) total power kept at constant for the Ni-toughened nc-TiN/a-SiN_x thin films (Sample S1 to S7). Thus, at low target power ratio of TiNi/(TiNi+Ti), ions have low mobility thus would be more likely to “stick” at where it arrives: the surface diffusion is slow, and the chances of erasing the peaks and filling up the “valleys” are small, thus increasing a much rougher surface. In the same token, small ξ indicates the surface topography is correlated only in a small area. As target power ratio of TiNi/(TiNi+Ti) increases, the kinetic energy obtained by each Ni and/or TiN (as well as amount) increases, which transforms into faster lateral diffusion and smoothens out the roughness at locations farther away, making the “hump” more localized and smaller, giving rise smaller value of ξ and ω [191, 192].

Fig. 4-60 Height-height correlation $G(r)$ for the thin films with different TiNi/(TiNi+Ti) power ratio. The oscillation is due to the insufficient sampling size.

Fig. 4-61 Interface width ω and lateral correlation length ξ vary with target power ratio of TiNi/(TiNi+Ti). As target power ratio of TiNi/(TiNi+Ti) increases from 0 to 0.3, ω decreases from ~8 to ~3 nm and ξ decreases from ~15 to ~9 nm.

4.3.3.Microstructure

The effect of sputtering target power ratio of TiNi/(TiNi+Ti) on microstructure, such as crystalline phase, grain size, preferential orientation and lattice parameter are tabulated in Table 4-10.

Table 4-10 Microstructure characteristics of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films

Sample Code			S1	S2	S3	S4	S5	S6	S7	S8
Microstructure	Grain size (nm)	d	3.9	8.8	11.8	7.8	4.6	4.4	3.2	3.2
	Latt. Param. (nm)	a _{TiN}	0.418	0.419	0.416	0.417	0.41	0.41	0.42	0.43
	Coefficient of Texture	T ₁₁₁	89	59	78	01	603	135	25	237
		T ₂₀₀	1.20	0.61	0.36	0.54	1.06	0.58	1.01	0.90
		T ₂₂₀	1.05	1.54	1.67	1.62	0.97	1.62	1.22	1.25
			0.76	0.84	0.97	0.86	0.97	0.80	0.77	0.85

4.3.3.1. Crystal phase and amorphous matrix

Fig. 4-62 shows the bright field HRTEM morphological appearance of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 2.1 at.% Ni (Sample S2). Crystallites are embedded in matrix. The grain size is about 8 nm. Analysis of the SAD patterns shows that these crystallites are polycrystalline TiN. No crystalline Ni, TiSi and Si₃N₄ are found (c.f. Fig. 4-63). In general, (1 1 1), (200) and (220) TiN crystallographic planes exhibit the more distinct rings than other diffraction rings. Proof of the crystallites being TiN also comes from the analysis of the GIXRD pattern (c.f. Fig. 4-64).

Fig. 4-62 HRTEM bright field micrograph of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 2.1 at.% Ni (Sample S2) showing the crystallite in size of 8 nm.

Fig. 4-63 SAD pattern of the crystallite with pattern index, showing the crystalline TiN phase.

(a)

(b)

Fig. 4-64 GIXRD patterns of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films with (a) 2.1 at.% Ni (Sample S2) and (b) 19.0 at.% Ni (Sample S7). Showing the existence of crystalline TiN.

Fig. 4-64 confirms the existence of crystalline TiN. In addition, no peaks from crystalline metallic Ni and Si₃N₄ can be identified in the GIXRD patterns. SAD analysis of the matrix (where there is no crystallite) gives rise to a diffuse pattern typical of an amorphous phase. Together with the XPS analysis in §4.1.1, where nickel is in the Ni-Ni bond and silicon is mostly in Si-N bond, the results verify that the amorphous matrix comprises of amorphous metallic Ni and amorphous silicon nitride (a-SiN_x).

4.3.3.2. Grain size and distribution

Grain size calculated using Scherrer formula was listed in Table 4-10 and plotted in Fig. 4-65. In small amount of Ni, such as less than 4.3 at.%Ni, with increase of target power ratio of TiNi/(TiNi+Ti), in other words, with increase of Ni content, the nc-TiN crystallite size increases. Which may due to the reason that small quantity of metallic nickel can decrease the formation energy of TiN and excite the crystallite growth. When Ni content greater than 4.3 at.%, with the increase of target power ratio TiNi/(TiNi+Ti), as surface mobility is enough, the segregated Si and Ni can be sufficient to nucleate and develop the SiN_x phase and metallic Ni phase respectively, which form a layer on the growth surface, covering the TiN nano crystallites and limiting their growth. From the analysis of peak widths in the

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GIXRD patterns a grain size decrease from ~12 nm to ~3 nm (c.f. Fig. 4-65) is also evident, which is consistent with Si and Ni segregation.

Fig. 4-65 Change of grain size with target power ratio of TiNi/(TiNi+Ti).

The grain size change with changes in target power ratio of TiNi/(TiNi+Ti) is also confirmed with the TEM micrograph observation (c.f. Fig, 4-66). It should point out that the grain size in TEM sample is smaller than those from XRD analysis. Because the deposition time for the TEM samples are about 20 min, while the XRD ones are about 2 hours.

Fig. 4-66 TEM micrographs of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films with different power ratio of TiNi/(TiNi+Ti): (a) 0.04, (b) 0.20 and (c) 0.40. Showing a reduction in grain size.

4.3.3.3.Preferential orientation

The peak orientation can be observed directly from Fig. 4-67. The degrees of the preferential orientation denoted by coefficient of texture calculated through eqn(3-4) are listed in Table 4-10 and plotted in Fig. 4-68. The coefficient of texture T_{hkl}

for (111), (200) and (200) are closed to unit, indicating a random orientation. That means addition of Ni results in deterioration in preferential orientation. In the synthesis of nc-TiN/a-SiN_x nanocomposite thin films a competitive growth has been put forward to explain the development of TiN (220) preferential orientation (c.f. §4.1.3.3). Taking into consideration of the effect of metallic Ni addition, it is reasonable to deduce that the segregated additives Ni inhibit the growth of TiN crystals to stimulate spore of other TiN nuclei. Consequently the competitive growth is suppressed, resulting in weak texture. This agrees with the effect of soft metal additives (Cu, Ag, etc.) on weakening of texture reported in Ref. [221,222].

Fig. 4-67 GIXRD patterns of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films (Sample S1 to S8) with different target power ratio of TiNi/(TiNi+Ti), showing random orientation.

Fig. 4-68 Calculated coefficient of texture of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films (Sample S1 to S8) with different target power ratio of TiNi/(TiNi+Ti). The coefficient of texture T_{hkl} for (111), (200) and (200) are closed to 1, which indicates a random orientation.

4.3.3.4.Lattice parameter

Table 4-10 lists the lattice parameter measurements of the nc-TiN crystallites calculated using the GIXRD patterns shown in Fig. 4-67. At Ni = 0 (without doping of Ni), the lattice parameter of nc-TiN is 0.41889 nm. However, pure TiN crystals should have a lattice constant of 0.42417 nm (JCPDS 38-1420). This is because the nc-TiN embedded in a-SiN_x already forms solid solution with Si to become nc-(Ti,Si)N. Since Si⁴⁺ has a radius of 0.041 nm, only about half of that of Ti³⁺ (0.075 nm) [154], substitution of Ti with Si results in reduction in lattice parameter [69]. With increase of TiNi/(TiNi+Ti) from zero to 0.3, the lattice parameter decreases from 0.41889 to 0.41135 nm. With further increase of TiNi/(TiNi+Ti) to unit, the lattice parameter increases to 0.43237 nm. When target

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power ratio of TiNi/(TiNi+Ti) is less than 0.3, the measured TiN lattice parameter is smaller than that of the database value of 0.42417 nm (JCPDS 38-1420). The ionic radius of Ni³⁺ (0.056 nm [223]) is less than that of Ti³⁺ (0.075 nm [154]), thus the reason of further reduction of the (Ti,Si)N lattice parameter is clear: Ni enters nanocrystalline (Ti,Si)N by substituting Ti, thus forming nc-(Ti,Si,Ni)N. When target power ratio of TiNi/(TiNi+Ti) becomes greater than 0.3, nc-(Ti,Si,Ni)N becomes saturated with Ni thus further increase in Ni forces it to enter in the interstitial position. This results an abrupt increase in lattice parameter.

Fig. 4-69 Calculated lattice parameter as a function of target power ratio of TiNi/(TiNi+Ti). With increase of TiNi/(TiNi+Ti) from zero to 0.3, the lattice parameter decreases from 0.41887 nm to 0.41135 nm. Further increase in TiNi/(TiNi+Ti), the lattice parameter increases to 0.43237 nm.

4.3.4.Mechanical Properties

The effect of sputtering target power ratio of TiNi/(TiNi+Ti) on mechanical properties, such as residual stress, Young’s modulus, hardness and toughness are tabulated in Table 4- 11.

Table 4-11 Mechanical characteristics of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films

Sample Code			S1	S2	S3	S4	S5	S6	S7	S8
Mechanical properties	Residual stress (MPa)	σ	-407	-566	-1355	-1122	-661	-33	230	320
	Hardness (GPa)	H	28.4	32.6	28.3	28.5	20.2	19.5	18.8	14.4
	Young’s modulus (GPa)	E	295	296	298	278	265	267	226	250
	Toughness (MPa m ^{1/2})	K _{IC}	1.15	1.21	1.36	1.23	1.73	1.95	2.25	2.60
	Adhesion (mN)	L _{c2}	587	618	628	627	821	882	785	717

4.3.4.1.Residualstress

Fig. 4-70 shows the measured residual stress of the Ni-toughened nc-TiN/a-SiN_x thin films as a function of target power ratio of TiNi/(TiNi+Ti). With increase of TiNi/(TiNi+Ti) target power ratio from zero to 0.12, the residual stress increases from -400 to -1300 MPa. With further increase of TiNi/(TiNi+Ti) target power ratio to 0.30, the residual stress decreases to near zero. The minus sign indicates the stresses are in compressive state. With increase of TiNi/(TiNi+Ti) target power

ratio from 0.30 to 1.00, the residual stress changes from compressive to tensile state with value of 300 MPa. The compressive residual stress increases from -407 to -1355 MPa is possibly due to the ion bombardment. However, the decrease with further increase in Ni needs to be studied further.

Fig. 4-70 Relationship of residual stress with target power ratio of TiNi/(TiNi+Ti).

4.3.4.2. Hardness

Fig. 4-71 displays the relationship between hardness and Ni content, including a typical nanoindentation load-depth profile. The measured hardness of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films increases from 28 to 33 GPa with Ni content increased from 0 to about 2.1 at.%. A further increase in Ni content brings a decrease in hardness to 14 GPa. When the Ni content is less than 2.1 at.%, the growth of amorphous metallic Ni is inhibited by the shortage of Ni atoms. The nickel atoms disperse in the TiN lattice and result in lattice distortion (c.f. Fig. 4-69). Since lattice distortion can stop the dislocation propagation, an increase in measured hardness is expected, mainly due to the solution hardening.

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Further increase in Ni results in more lattice distortion thus solution hardening effect should be enhanced. However, increase of nickel composition comes from the increase in target power ratio of TiNi/(TiNi+Ti), which can improve the mobility of sputtered Ni adatoms. Thus Ni adatoms conglomerate to form network phase, together with a-SiN_x phase to block the growth of TiN crystals. When the TiN grain size decreases below a certain limit, the fraction of grain boundary (Ni + Si₃N₄) increases rapidly and the hardness would decrease due to the grain boundary sliding. That should account for the hardness decreases with further increase in Ni content.

Fig. 4-71 Hardness varying with Ni content in the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films. With increase of Ni content, hardness decreases due to grain boundary sliding.

4.3.4.3. Toughness

Toughness of the Ni-toughened nc-TiN/a-SiN_x thin films was studied using microindentation method, since the microindentation method can achieve highly consistent results. In order to deduce the film toughness from the substrate effected data, K_{IC} values are plotted and then the curve is extrapolated to the depth of one tenth of the film thickness (Details refer to §4.2.3.1.1). Fig. 4-72 shows the toughness of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films as a function of Ni content. Compared with the high hardness nc-TiN/a-SiN_x nanocomposite thin film (Sample S1) where there is no Ni, the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films (Sample S2 to S8) show an increased toughness. With increase of Ni content, the film toughness increases. With increase in nickel content in the as-prepared thin films, the main mechanisms responsible for toughness enhancement are (c.f. Fig. 4-73): (1) Relaxation of the strain field around the crack tip through ductile phase (metallic nickel) deformation or crack blunting, whereby the work for plastic deformation is increased. (2) Ni adatoms can form network phase surrounding the TiN crystals. Bridging of cracks by ligaments of the ductile metallic nickel phase behind the advancing crack tip, whereby the work for plastic deformation is also increased [224,225].

Fig. 4-72 Toughness as a function of Ni content. With increase of Ni content, the film toughness increases. Indicating a significant effect of ductile metallic Ni on enhancement of film toughness.

Fig. 4-73 Schematic diagram of ductile phase toughening mechanism through (1) ductile phase deformation or crack blunting, and (2) crack bridging.

4.3.5. Oxidation Resistance

4.3.5.1. Oxidation variation with depth

Chemical state of Ti, Si and Ni

Fig. 4-74 shows XPS depth profiles of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 2.1 at.% Ni (Sample S2) oxidized at 850 °C. Roughly judging from the oxygen and nitrogen concentration, the profiles in Fig. 4-74 can be divided into five regions. Detailed analysis of the chemical state of Ti (c.f. Fig. 4-75) gives rise to composition evolution from TiO₂ to TiN_xO_y to TiN as entering into the oxidation layer. Fig. 4-75 (a) plots Ti 2p core level spectra in the binding energy range from 452 to 468 eV for all the five regions. Sampling for Region I is at the surface, for Region II~V in the middle of each region. Fig. 4-75 (b) is the quantitative deconvolution result of relative concentration of Ti in TiO₂, TiN_xO_y and TiN.

In Fig. 4-75 (a), Ti 2p peaks of the oxidized film consist of three doubles: Ti 2p_{3/2} at 459.0, 457.6, 455.0 eV, and Ti 2p_{1/2} at (459.0+5.8), (457.6+5.8), (455.0+5.8) eV. The pair at 459.0 and (459.0+5.8) eV is assigned to TiO₂; the pair at 457.6 and (457.6+5.8) eV is ascribed to oxynitride TiN_xO_y, the pair at 455.0 and (455.0+5.8) eV is for TiN (c.f. Table 3-6). From Fig. 4-75 (a), it is obvious that deep inside the coating (Region V), the main composition is still TiN (the nanocrystalline TiN in the nanocomposite thin film); moving more toward the surface (c.f. Fig. 4-74), regions IV and III, the amount of TiN decreases while TiN_xO_y increases. At the same time, TiO₂ appears. As the oxidation degree becomes even more severe (Region II and I), both TiN_xO_y and TiN decrease to give way to formation of more

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and more TiO_2 . At the surface, TiN and TiN_xO_y completely disappear while TiO_2 prevails (c.f. Fig. 4-75 (b)).

As seen also from Fig. 4-74, nitrogen content drastically drop from its bulk composition of about 50 at.% in Region V to less than 2 at.% in the oxidation layer (Region II and I). This is in agreement with earlier analysis of the evolution of the compounds as depth varies in the oxide layer. Since the total amount of N is low and it is responsible for TiN , TiN_xO_y , and Si_3N_4 (to be discussed later), it is reasonable to assume that x in TiN_xO_y is very small while y is large (oxygen content is greater than 65 at.% in Region II). From the shape of the oxygen and nitrogen profiles, it is obvious that during the oxidation process, oxygen diffuses inward and nitrogen diffuses outward. It is interesting to note that nickel diffuses towards the surface from the depth and builds up close to the surface (the drop of the relative amount at the surface comes from the calculation involving surface adsorbed C). It is believed that the surface enrichment of Ni will benefit the oxidation resistance of the film.

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Fig. 4-74 XPS depth profile of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 2.1 at.% Ni (Sample S2) oxidized at 850 °C in hot air for 15 min. A sharp oxide/nitride interface exists and a nickel on the top layer of the oxidized coating is observed. Five regions can be distinguished in this area from the surface to the non-oxidized material core according to the chemical state of Ti and Si.

(a)

(b)

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Fig. 4-75 (a) Ti 2p core level XPS spectra evolution, a shift of the Ti 2p_{3/2} signal toward higher binding energies indicates the formation of a TiO₂ layer on top of the oxidized coating. (b) Change of the different Ti 2p components in different regions (from Region I through II, III and IV to V).

Fig. 4-76 (a) plots Si 2p core level spectra in different region of the oxide layer. Si 2p spectrum has three possible states (c.f. Table 3-6): 99.6 eV for atomic silicon (Si⁰); 101.8 eV corresponds to Si-N bond (stoichiometric Si₃N₄); 103.4 eV for Si-O bond (stoichiometric SiO₂). Some authors reported Si-Ti bonding at 98.8 eV or existence of titanium silicide [169]. This experiment does not observe any Si-Ti bonding. Fig. 4-76 (b) is the quantitative deconvolution result of relative concentration of Si in SiO₂, Si₃N₄, and Si⁰.

Going from deep in the film outward to the surface of the oxide layer (from Region V down to Region I in Fig. 4-76 (a)), it is worth noting: (1) The amorphous silicon nitride matrix is actually prominently a-Si₃N₄ with a very small amount of free silicon (< 10 at.% of all silicon in the film, see Fig. 4-76 (b)); The existence of free Si is due to deficit in nitrogen source compared with Si source during deposition process. (2) Moving toward the surface, the amount of the free silicon decreases to zero, the amount of Si in the state of Si₃N₄ drops from about 80 at.% to 15 at.% while Si in SiO₂ increases from about 10 at.% to 85 at.%. In other words, the free silicon and some of the Si₃N₄ become oxidized into SiO₂.

TiN films start to oxidized at a temperature level of 550 °C [226], while Si₃N₄ is more oxidation resistant than TiN as reported by Gogotsi and Porz [227,228]. In

fact, this is also noticed by comparing surface oxidation state of Ti and Si from this experiment: at the surface, TiN is completely oxidized into TiO_2 (c.f. Region I in Fig. 4-75 (b)); while also at the surface of the same sample, there is still about 15 at.% Si in the form of Si_3N_4 free from oxidation (c.f. Region I in Fig. 4-76 (b)).

Fig. 4-76 (a) Si 2p core level XPS spectra, a shift of Si 2p signal towards higher binding energy indicates the formation of a SiO_2 layer on top of the oxidized

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coating. (b) Change of the different Si 2p components in different regions (from Region I through II, III and IV to V).

Fig. 4-77 shows Ni 2p core level spectra. Metallic nickel (Ni^0) has a binding energy value of 853.0 eV ($2p_{3/2}$) and 870.7 eV ($2p_{1/2}$) (c.f. Table 3-6). The peak at 859.6 eV is the satellite peak probably due to the consequence of sputter-damaged crystallites [171]. A few points are worth noticing in Fig. 4-77: (1) There is no peak shift for Ni 2p, which indicates that the Ni does not react with oxygen at 850 °C. (2) From deep in the film towards the surface, Ni peak intensities increase from Region V to Region I, indicating Ni diffusion towards sample surface, as also illustrated in Fig. 4-74.

Fig. 4-77 Ni 2p core level XPS spectra evolution in different regions (from Region I through II, III and IV to V). Metallic nickel is confirmed and the decreasing of peaks intensity from outer layer to inner layer indicates existing of Ni enrichment in the outer layer.

Fig. 4-78 shows XPS depth profile of nc-TiN/a-SiN_x nanocomposite thin film oxidized at 850 °C for 15 min. The oxidation treatment for this sample is the same as that for the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film. The thickness of the oxide layer is about 420 nm, compared with that (~315 nm, c.f. Fig. 4-74) for Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films, it can be concludes that Ni addition can improve the oxidation resistance of the nc-TiN/a-SiN_x nanocomposite thin films.

Fig. 4-78 XPS depth profile of the nc-TiN/a-SiN_x nanocomposite thin film (without Ni) oxidized at 850 °C in hot air for 15 min.

Phase identification

Fig. 4-79 shows the GIXRD patterns with different incident angle for Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 2.1 at.% Ni (Sample S2) oxidized at 550 °C for 15 min. No XRD peaks are observed for crystalline Si₃N₄,

SiO₂ and Ni. Since XPS analysis indicated existence of Si₃N₄ and SiO₂ (c.f. Fig. 4-76 (b)), thus these phases must be in amorphous state. XPS results indicated existence of metallic Ni (c.f. Fig. 4-77) from surface to the in-depth place of the film; this is also evident from Fig. 4-79: as incident angle increases to 1.5°, no crystalline peaks of Ni are observed. At the low incident angle (such as 0.1°), the presence of well-crystallized TiO₂ (rutile) and TiN are observed. With increase in the incident angle, the intensity of TiO₂ peaks decreases while the intensity of TiN peaks increases, indicating reduction in oxidation with depth. (X-ray penetration depth increases as incidence increases). This agree well with the XPS analysis (c.f. Fig. 4-75 (b)).

Fig. 4-79 GIXRD patterns with different incident angle (from 0.1° through 0.5 and 1.0 to 1.5°) for Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 2.1 at.% Ni (Sample S2) oxidized at 550 °C in hot air for 15min. On the surface (under low incident angle 0.1°) most are crystallite TiO₂. Inner the coating (under high incident angle 1.5°), most are crystalline TiN.

43.5.2.Oxidation variation with temperature

Chemical composition

Fig. 4-80 shows the surface composition of the thin films oxidized at 450-1000 °C. With increase of oxidation temperature, oxygen content increases slightly, silicon decreases slightly, and titanium remains constant, while nitrogen decreases sharply. At 450 °C nitrogen is about 25 at.%. A hundred degree increase to 550 °C brings about a significantly decrease to 7 at.%. Further increase of temperature to 625 °C, N decreases to < 4 at.%. The significant decrease in N comes from the oxidation of Ti from TiN and the oxidation of Si from Si₃N₄. These reactions deplete N through formation of N₂ (see details in §4.3.5.3). The fact that nitrogen still persists in the surface layer indicates that Si₃N₄ still exists even at 1000 °C. Also note from Fig. 4-80, as the oxidation temperature increases from 450 to 900 °C, surface nickel increases from 1 at.% to 9 at.%; i.e., higher temperature promotes outward diffusion of nickel. Further increase to 1000 °C, however, surface nickel drastically decreases to 3 at.% (reason is still unclear).

Fig. 4-80 Change of Ti, Ni, Si, N and O species in the thin film surface with elevated oxidation temperature. With increase of oxidation temperature, oxygen content in surface area increases slightly and titanium remains constant, while a decrease in nitrogen amounts is observed. The gradual enrichment in nickel and deficient in silicon with elevated oxidation temperature to 900 °C is observed.

Phase identification

Fig. 4-81 shows the GIXRD patterns of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 2.1 at.% Ni (Sample S2) oxidized at elevated temperature from 550 °C through 625, 700, 750 and 850 to 950 °C. Since an incident angle of 0.5 is low enough to observe both TiN and TiO₂ peaks (c.f. Fig. 4-79), 0.5° is chosen for all the samples in Fig. 4-81. As temperature increases, slowly the intensity TiO₂ peaks increase and that of TiN peaks decreases. At 850 °C and above, the number and intensity of TiO₂ peaks increase significantly, signaling the total collapse of the film's oxidation resistance.

Based on the GIXRD analysis for the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 2.1 at.% Ni (Sample S2) oxidized at 950 °C, taken $2\theta = 42.528$, 74.176 and 77.824° , respectively, the calculated lattice parameter of TiN is 0.4247 nm, which agrees with the standard value of TiN ($a_{\text{JCPDF}} = 0.42417$ nm) very well (as stipulated by [55], an error of 0.0005 nm can be considered as perfect match). This indicates that there is no interstitial or substitutional solid solution existing after oxidation. In addition, the Ni-toughened nc-TiN/a-SiN_x is stress-free after oxidation even though transformation of Si₃N₄ into SiO₂ leads to a 96% molar

volume increase. It is understandable that the high temperature involved facilitated effective atomic diffusion that neutralized possible generation of internal stresses.

Fig. 4-81 GIXRD patterns of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 2.1 at.% Ni (Sample S2) oxidized at temperature from 550°C through 625, 700, 750 and 850 to 950 °C in static hot air for 15min. Formation of crystallized TiO₂ on the surface is observed.

Topography

Fig. 4-82 shows the roughness change of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film with 2.1 at.% Ni (Sample S2) oxidized at 450, 550, 625, 750, 850 and 950 to 1000 °C. With increases of oxidation temperature from 450 to 850 °C, the roughness increases slightly from ~1 to ~4 nm. However, with further increases to 1000 °C, the roughness increases drastically to ~41 nm. The metallic nickel is known for its anti-oxidation properties and its presence as a passive layer to maintain the stability of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin

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film at low oxidation temperature by hindering migration of oxygen atoms. Above a threshold temperature, in this case, 850 °C (depends on nickel content), the barrier effect of metallic nickel can no longer prevent oxygen diffusion. Consequently, rutile nucleation and growth occur, which induces a strong roughening of the surface that, in turn, allows penetration of oxygen atoms further into the film to fuel an acceleration of the oxidation process.

Fig. 4-82 Surface roughness change with elevated oxidation temperature. With increases of oxidation temperature from 450 to 850 °C, the roughness increases slightly from ~1 to ~4 nm. Further increases to 1000 °C, the roughness increases dramatically to ~41 nm.

4.3.5.3.Discussions

The experiment suggests that the oxidation of the Ni-toughened nitride is mainly a diffusional process; nickel atoms diffuse outward and oxygen ions diffuse inward (c.f. Fig. 4-74). Oxidation proceeds by a progressive replacement of nitrogen with

diffused oxygen. The oxidation of titanium nitride to rutile or titanium dioxide (TiO_2) starts at 450 °C according to:

This mechanism is in agreement with the general theory for the oxidation of nitride, which considers that the process is controlled by anionic diffusion [229 - 233]. The oxidation of silicon nitride to stoichiometric SiO_2 starts at ~450 °C according to this reaction:

This oxidation is the result of the inward diffusion of oxygen through the oxide layer [234,235]. Five regions can be distinguished in the oxidized layer (c.f. Fig. 4-74) consisting of the following six components: TiO_2 , TiN_xO_y , TiN , SiO_2 , Si_3N_4 and Ni (c.f. Fig. 4-75, Fig. 4-76, and Fig. 4-77). The TiO_2 and TiN are crystalline phases while Si_3N_4 , SiO_2 are amorphous phases (c.f. Fig. 4-79). Following XPS depth profile (Fig. 4-74) and GIXRD result at different incident angles (Fig. 4-79) of the oxidized film, a schematic representation of the phase distribution in the oxidized layer is proposed in Fig. 4-83, where white cycles represent crystalline TiO_2 , gray cycles crystalline TiN_xO_y , black cycles crystalline TiN , small solid cycle metallic Ni , and the background is amorphous Si_3N_4 with amorphous SiO_2 .

From top to the core of the film, or from left to the right in Fig. 4-83, Region I is composed of mainly crystalline TiO_2 , amorphous SiO_2 and metallic Ni in the amorphous matrix of Si_3N_4 ; In Region II the extent of oxidation is lessened (less

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amount TiO_2 and lots of TiN_xO_y); In Region III, more TiN presents while TiN_xO_y reduces; In Region IV, even less TiN crystalline is oxidized (reduced amount of TiO_2 and TiN_xO_y); In Region V, though there are still TiN_xO_y , basically no TiO_2 exists. The presence of a Ni-rich zone at the top of the oxide layer effectively blocked the inward diffusion of O. This is similar to the oxidation resistance behavior of TiAlN, where a strong aluminum migration to the surface to form a passive layer - in that case, alumina - to protect the TiAlN coating [236]. As oxidation temperature increases, the oxidation process becomes faster, presumably by the increase of the diffusivity of O_2 and N_2 . Combining the components information at the oxide area from XPS (c.f. Fig. 4-80), GIXRD (c.f. Fig. 4-81) and the topographical information from AFM observations (c.f. Fig. 4-82) allow us to assume there is a threshold temperature (depends on the nickel content), in this case 850°C , below which the Ni-toughened nc-TiN/a-SiN_x forms a stable nickel rich layer, the number of diffusion paths (grain-boundaries, defects) would considerably decrease leading to the passivation regime, limiting oxygen diffusion thus increase the oxidation resistance. Above the threshold temperature, the barrier effect of metallic nickel can no longer prevent oxygen diffusion. Consequently, oxide thickness increases significantly, the rutile nucleation and growth along random direction occur, and roughness of the surface increases drastically.

Fig. 4-83 Proposed microstructural model for the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film after oxidation. Five regions can be distinguished from surface to core material.

4.3.6.Summary

The effect of target power ratio of TiNi/(TiNi+Ti) on chemical composition, topography, microstructure, mechanical properties and oxidation resistance of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films can be summarized as follow:

- (1) The Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film can be prepared by co-sputtering of Ti, TiNi and Si₃N₄ targets in Ar/N₂ atmosphere. XPS analysis shows that Ni is in the metallic state without reaction with N₂. Together with TEM and GIXRD results, it can be concluded that metallic nickel is in amorphous state.
- (2) As target power ratio of TiNi/(TiNi+Ti) increase from 0 to 0.3, interface width decreases from ~8 nm to ~3 nm and lateral correlation length

decreases from ~15 nm to ~9 nm, which confirm that increasing the target power ratio of TiNi/(TiNi+Ti) results in smoother coating surface.

- (3) The coefficient of texture for (111), (200) and (220) crystal plane of nc-TiN in the Ni-toughened nc-TiN/a-SiN_x nanocomposite are closed to unit, which indicates that the addition of Ni resulting in a random orientation of nc-TiN.
- (4) Results from nc-TiN lattice calculation show that at low target power ratio, the solid solution is substitutional with nickel taking the place of titanium. With further increase of target power ratio the interstitial components increase due to high-energy ion bombardment.
- (5) The residual stress of Ni-toughened nc-TiN/a-SiN_x thin films increases from -400 to -1300 MPa with increase of TiNi/(TiNi+Ti) target power ratio from zero to 0.12. Further increase of TiNi/(TiNi+Ti) target power ratio to unit, the residual stress decreases and changes from compressive to tensile state with value of 300 MPa.
- (6) The hardness of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films keeps constant with little increase of Ni content, which is due to the solid solution hardening. Further increase in Ni content, hardness decreases which due to the grain boundary sliding.
- (7) Toughness of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films increases with increase of Ni content. Doping from 0 to 40 at.% Ni in nc-TiN/a-SiN_x brings about an increase in toughness from 1.15 to 2.60 MPa m^{1/2} at some expense of hardness (dropped from 30 to 14 GPa). Ductile phase toughening through crack blunting and crack bridging is responsible for the toughness increase.

- (8) The oxidation of Ni-toughened nc-TiN/a-SiN_x thin film is mainly a diffusional process; nickel atoms diffuse outward and oxygen ions diffuse inward. Oxidation proceeds by a progressive replacement of nitrogen with diffused oxygen.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATION

5.1. Conclusions

Hard and superhard nc-TiN/a-SiN_x nanocomposite thin films and Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films have been prepared using magnetron sputtering. The relationship between target power ratio (such as Ti to Si₃N₄, and/or TiNi to (TiNi+Ti) and physical properties (chemical composition, surface topography, and microstructure, etc.), mechanical properties (residual stress, hardness and toughness), have been studied systematically. **The most important results of this work are these on measurement of the fracture toughness and toughening of the hard and superhard nc-TiN/a-SiN_x nanocomposite thin films.** Conclusions are drawn in the following aspects:

1. Physical properties of nc-TiN/a-SiN_x

Nanocrystalline TiN has been imbedded in amorphous silicon nitride matrix to form nc-TiN/a-SiN_x nanocomposite thin films via co-sputtering of Ti and Si₃N₄ targets in argon and nitrogen atmosphere, As increase of Si₃N₄ power density, the resultant film surface becomes smoother. At a Ti target power density of approximately 5.5 W/cm², the Ti to Si₃N₄ target power ratio should be greater than

unity in order for nc-TiN to form in amorphous SiN_x matrix. Deviating from this condition, TiN crystallites will not form and Ti will dissolve in amorphous SiN_x . Detailed XPS studies reveal that Ti forms stoichiometric TiN plus a very small amount of Ti-O bonding, element Si and/or Ti-Si bonding. The amorphous SiN_x is mainly stoichiometric Si_3N_4 . Aside from forming a- SiN_x in the matrix, Si atoms also imbed into TiN for (Ti,Si)N solid solution crystallites. At low target power density, the solid solution is substitutional. With increase of power density, the amount of silicon dissolved in the TiN crystallite increases, and in the meantime, the interstitial components increase which is manifested in the increase in the TiN lattice parameter. The crystallites have a preferential orientation varying with the deposition target power density. As conveniently described by the coefficient of texture, the degree of preferential orientation along [111] direction decreases and finally tails off with increase of Si_3N_4 target power density. At the same time, the crystallites orient along [200] and [220] direction and eventually [220] direction dominants, as Si_3N_4 target power density increases from 1.1 to 5.5 W/cm^2 .

2. Mechanical properties of nc-TiN/a- SiN_x

The residual stress resulted from sputtering deposition of nc-TiN/a- SiN_x nanocomposite thin films comprise mainly of the growth-induced stresses and the thermal stress. The growth-induced stress increases with sputtering target power density, but only reaches about -1 GPa even at the highest target power density used. The growth-induced stress is opposite in sign and roughly equal in quantity to the thermal stress induced by difference in coefficient of thermal expansion between the film and the silicon wafer substrate. As a result, the magnetron

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sputtered nc-TiN/a-SiN_x nanocomposite thin films becomes almost stress-free. Hardness was measured using nanoindentation with depth less than one tenth of film thickness. The indentation data was analyzed using Oliver-Pharr method. The enhancement in hardness is not due to the low residual stress (less than -1 GPa) but due to the microstructure. The relationship between the nc-TiN/a-SiN_x nanocomposite thin film hardness and the crystallite size of nc-TiN matches the Hall-Petch relationship at larger crystallite size and anti-Hall-Petch relationship as the crystallite size becomes very small (below 6 nm in this study). The relationship between hardness and Young's modulus is agreed with that obtained from the other nanocomposite thin film system. Toughness measurement and assessment evaluation results confirm that microindentation is a convenient and repeatable technique used to characterize toughness of hard thin film deposited on brittle substrate. At high indentation load, well-defined ($c \geq 2a$) radial crack lengths generated are clear and can be easily used to calculate toughness. However, substrate effect may come into play and affect the actual values of thin film toughness. At lower indentation load, substrate effect on thin film toughness measurement can be reduced. However, there comes other difficulties including generating well-defined ($c \geq 2a$) radial crack, locating the crack, focusing of crack under electron microscopy and measuring the crack length. Nanoindentation test can be conducted to characterize thin film toughness both quantitatively and qualitatively. In quantitative determination of thin film toughness, the substrate effect can be significantly reduced, however, difficulties come from locating the indentation impression and measuring crack length. In qualitative characterization, plasticity can present consistent trends for series samples. However, plasticity is not "toughness". Scratch test data can be used indirectly to qualitatively

characterize thin film toughness. Crack propagation resistance parameter has been proposed. However, these parameters are not termed “toughness”. Two-step tensile test can be conducted to measure the toughness of the thin films in case of satisfying the assumptions. Toughness of as prepared nc-TiN/a-SiN_x nanocomposite thin films (Sample P1 to P8) has been measured using microindentation method due to its convenience. To deduce the film toughness from the substrate-effected data, K_{IC} values are plotted and then the curve is extrapolated to the depth of about one tenth of the film thickness to obtain the film toughness. The results show that nc-TiN/a-SiN_x nanocomposite thin film with 7.2 at.% Si has the highest toughness value of 1.62 MPa m^{1/2}, while the thin film with 14.9 at.% Si has the poorest toughness (0.78 MPa m^{1/2}).

3. Toughening of nc-TiN/a-SiN_x

The Ni-toughened nc-TiN/a-SiN_x nanocomposite thin film can be prepared by co-sputtering of Ti, TiNi and Si₃N₄ targets in Ar/N₂ atmosphere. XPS analysis shows that Ni is in the metallic state without reaction with N₂. Together with TEM and GIXRD results, it can be concluded that metallic nickel is in amorphous state. As target power ratio of TiNi/(TiNi+Ti) increase from 0 to 0.3, interface width *w* decreases from ~8 nm to ~3 nm and lateral correlation length decreases from ~15 nm to ~9 nm, which confirm that increasing the target power ratio of TiNi/(TiNi+Ti) results in smoother coating surface. The coefficient of texture for (111), (200) and (220) crystal plane of nc-TiN in the Ni-toughened nc-TiN/a-SiN_x nanocomposite are closed to unit, which indicates that the addition of Ni resulting in a random orientation of nc-TiN. Results from nc-TiN lattice calculation show

that at low target power ratio, the solid solution is substitutional with nickel take the place of titanium. With further increase of target power ratio the interstitial components increase due to high-energy ion bombardment. The residual stress of Ni-toughened nc-TiN/a-SiN_x thin films increases from -400 to -1300 MPa with increase of TiNi/(TiNi+Ti) target power ratio from zero to 0.12. Further increase of TiNi/(TiNi+Ti) target power ratio to unit, the residual stress decreases and changes from compressive to tensile state with value of 300 MPa. The hardness of Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films keeps constant with little increase of Ni content, which is due to the solid solution hardening. Further increase in Ni content, hardness decreases which due to the grain boundary sliding. Toughness of the Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films increases with increase of Ni content. Doping from 0 to 40 at.% Ni in nc-TiN/a-SiN_x, brings about an increase in toughness from 1.15 to 2.60 MPa m^{1/2} at some expense of hardness (dropped from 30 to 14 GPa). Ductile phase toughening through crack blunting and crack bridging is responsible for the toughness increase. The oxidation of Ni-toughened nc-TiN/a-SiN_x thin film is mainly a diffusional process; nickel atoms diffuse outward and oxygen ions diffuse inward. Oxidation proceeds by a progressive replacement of nitrogen with diffused oxygen.

5.2. Recommendations

This project has successfully prepared hard and superhard nc-TiN/a-SiN_x nanocomposite thin films and Ni-toughened nc-TiN/a-SiN_x nanocomposite thin films using magnetron sputtering. The relationships among deposition parameters (such as target power density), chemical composition and microstructure, as well

as mechanical properties (hardness, toughness, et al.) of the as-prepared nanocomposite thin films have been investigated systematically. From the schedule of this project, and experiment results obtained so far, it can be concluded that the following directions are very important and future work should focus on these areas.

1. Further study on hard and superhard nc-TiN/a-SiN_x nanocomposite thin films

Hardness of nc-TiN/a-SiN_x nanocomposite thin film has been studied in details, however, the toughness of nc-TiN/a-SiN_x is need further study, such as the mechanism that toughness of the nc-TiN/a-SiN_x varies with silicon content.

2. Toughening of hard and superhard nc-TiN/a-SiN_x nanocomposite thin films

From this project, it is obviously that toughening of hard and superhard nc-TiN/a-SiN_x nanocomposite thin film is an interesting topic. Several issues need considering:

- (1) Designing of microstructure

It is well known that multiphase systems display many similarities with composite materials and often display higher hardness and toughness values than single-phase materials. Different phases exhibit different sliding systems and provide complex boundary to accommodate a coherent strain thus preventing formation of voids or flaws. Accordingly, superhard nanocomposite films with high toughness can be obtained through optimized design of multicomponent and multiphase structure. To prevent the grain boundary sliding and crack growth, a well-defined interface of high cohesive strength is needed. This microstructure can be obtained from

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those compounds showing a wide miscibility in the solid state but a certain chemical affinity to each other to form high-strength grain boundaries. In addition to Ni, Cu and Al are the candidates for this selection.

- (2) Investigating on relationship among deposition parameters, microstructure and mechanical properties

The expected microstructure and improved mechanical properties can be obtained using magnetron sputtering process by selecting suitable deposition parameters, which include target power density, deposition temperature, bias voltage, gas ratio of argon to nitrogen. The effects of alloying element (such as Al, Cu) and deposition parameters (such as gas ratio, substrate bias) on morphology and microstructure of Ti-M-Si-N ($M = \text{Al, Cu}$) thin films need to be studied systematically in the future.

- (3) Studying on toughening mechanisms

Toughening mechanisms, such as transformation toughening, toughening by whisker bridging, residual stress toughening, metallic phase toughening, and microcracks phase toughening have been well established in ceramics with microcrystalline structure. The applicability of these toughening mechanisms in hard nanocomposite thin film is the most fundamental issue. Research on nanocomposite toughening can be performed to yield more information about the toughening mechanism for hard and superhard nanocomposite thin films.

3. Toughness measurement of thin films

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Fracture toughness of bulk materials is a topic of classical measurement, but that of thin films, especially hard and superhard thin films, is a totally different game owing to the specimen dimensions (especially for thickness) and lack of convincing test procedure. As thin films and coatings are increasingly finding their way in engineering applications, the toughness assessment for thin films and/or coatings becomes more and more imperative. For engineering applications, it is of vital importance that the toughness of a thin film or coating be evaluated with a convincing method and procedure. Unfortunately it is still not the case yet. This calls for more attention in this area of the thin film studies. There are several issues need to be considered for further study.

(1) Developing new method for thin films toughness measurement

Based on the existing knowledge of thin film toughness measurement, new method should be explored. So far, there are two quantitative methods to characterize thin film toughness, one is stress approach, and the other is energy balance approach. The stress approach examines the stress state near the tip of the crack. Substrate effect on crack formation due to the coating thickness limitation, and spacial resolution on crack observation due to small indentation impression cannot be avoided. Thus, the stress approach cannot handle such issues. The development of new testing approach for thin films should be based on the energy balance approach which considering the energy changing before and after thin film cracking.

In the energy approach, there are two key points. One is the crack area (ΔA) Initiated, and the other is energy difference (ΔA) which initiate the crack. So far,

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indentation, tensile, and buckling can be conducted to induce films cracking and crack area can be determined conveniently using optical or electron microscopy. While, the determination of energy difference is a little difficult. Further study should be focused on introducing and analyzing the energy difference.

(2) Further studying on two-step tensile method

So far, we have proposed two-step tensile method to characterize thin films toughness. This method is simple in principle and easy to carry out. To fully understand this method, more work need to be done to study factors which affect the toughness measurement of thin films, such as extension rate, elongation length, and different substrate materials.

To satisfy the requirement of characterizing interfacial fracture toughness, two-step tensile method needs to be improved. The key point is to discern interfacial adhesion energy from the total energy change during coating cracking and debonding from the substrate. To predict failure rates and provide a description of the failure, Weibull distribution, which is often used to characterize fracture strength, can be made use of. To test the applicability of a new method, the method should be used for a variety of coatings. Aside from usual industrial coatings, such as TiN, TiAlN, CrN, DLC, Si₃N₄, biological coatings such as hydroxyapatite (HA) can also be put into test. As a matter of fact, one of my follow Ph.D students on biological coating studies is working on this aspect.

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