2003

Structure and mechanical properties of Ti-Si-N coatings

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STRUCTURE AND MECHANICAL PROPERTIES
OF Ti-Si-N COATINGS

A Thesis
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirement for the degree of
Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

by
Xiaodong Zhang
B.S., Beijing University of Aeronautics and Astronautics, 2001
August 2003
Acknowledgements

The author gratefully acknowledges partial project support from Louisiana Board of Regents through contracts LEQSF(2000-03)-RD-B-03, LEQSF(2001-04)-RD-A-07, and the National Science Foundation through grant #DMI-0124441. The ion beam analysis work at the Argonne National Laboratory was supported by the DOE Office of Science, Basic Energy Sciences, under contract #W-31-109-ENG-38.

The author’s advisor, Dr. W. J. Meng, is especially acknowledged. Thanks for his smart ideas and technical support on the project. During the past two years, I’ve learned more than just strain gauges and super-strengthening through our collaboration. His scholastic expertise and advisory patience are both appreciated.

I would like to thank Dr. Glenn Sinclair and Dr. M. M. Khonsari for the thesis previewing.

Thanks to Ms. Dongmei Cao, Mr. Bo Shi and Ms. Wei Wang for the lab assistance and the life experience we’ve shared together. Thanks to Mr. Bao Feng for the lab tutoring in the early days.

I should also acknowledge all the help from our collaborators. They are Dr. Gary L. Doll and Mr. Ryan D. Evans from the Timken Company, Mr. Peter M. Baldo and Dr. Lynn E. Rehn from Argonne National Lab, Mr. Roland Tittsworth from Louisiana State University Center for Advanced Microstructures and Devices, and Dr. Jiechao Jiang from Louisiana State University Materials Characterization Center.
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Abstract

In order to better define conditions under which “super-strengthening” occurs in the Ti-Si-N system, we performed detailed experimental studies on how the structure and mechanical properties of Ti-Si-N coatings are influenced by the deposition temperature.

Different series of Ti-Si-N specimens were prepared in an inductively coupled plasma (ICP)-assisted reactive sputtering system at both low and high temperatures. Coating compositions were measured by Rutherford backscattering spectrometry (RBS) technique, surface roughness was examined on an atomic force microscope (AFM), coating thicknesses were obtained by performing cross-sectional scanning electron microscopy (SEM), and their structure examined with transmission electron microscopy (TEM). Vibrational frequency results from Raman spectroscopy were related to the residual stresses within the coating, which was measured by using a multi-beam optical sensing (MBOS) technique. The extent of phase separation within Ti-Si-N coatings is probed by combining X-ray absorption spectroscopy and TEM. The influence of the extent of phase separation on mechanical properties is probed by instrumented nanoindentation.

The nanocomposite structure and hardness of Ti-Si-N coatings were examined as a function of the coating deposition temperature. Models for hardness enhancements in the Ti-Si-N system are discussed in light of the present experimental results. Our experiments showed that the hardness of Ti-Si-N coatings was higher than that of B1-TiN, and that the deposition temperature significantly influences the nanoscale structure and mechanical properties of Ti-Si-N coatings.
Chapter 1. Introduction

Nanostructured ceramic materials have been intensely studied recently, due to their special mechanical\(^1\), tribological\(^2\), and functional properties\(^3\). In particular, they are used as protective coatings for engineering surfaces of macro- and micro-scale mechanical components. Various synthesis techniques, including vapor phase deposition\(^4\) and solid or liquid\(^5\) phase sintering, have been utilized to fabricate nanostructured ceramics. For synthesis of nanostructured ceramic coatings, vapor phase deposition is most commonly used.

1.1 Vapor Deposition of Ceramic Coatings

Ceramic materials usually have strong atomic bonds, therefore vapor deposition of dense ceramic coatings often requires high deposition temperatures, such as in conventional chemical vapor deposition (CVD). Oxide thin films deposited by CVD include SiO\(_2\)\(^6\), Al\(_2\)O\(_3\)\(^7\), transition metal oxide\(^8\), and mixed oxides such as aluminosilicate glasses\(^9\). Nitride thin films deposited by CVD include Si\(_3\)N\(_4\)\(^10\), BN\(^11\), AlN\(^12\), and transition metal nitrides\(^13\). Carbide thin films, such as TiC\(^14,15\) and WC\(^16\), have also been deposited by CVD.

Low-pressure plasma assisted Physical Vapor Deposition (PVD) techniques are also being widely used for synthesizing ceramic thin films, in which energetic ionic and neutral gas phase species bombard the surface and supply the activated species and provide the non-thermal energy needed for film growth. The technique of reactive sputtering in glow-discharged plasmas has been used to deposit TaN, TaC, and Ta\(_2\)O\(_5\)\(^17-19\), NbN\(^19\), and mixed transition metal nitrides\(^20\) as early as the 1960s. The successful application of reactive sputter deposited transition metal nitride and transition metal
carbide coatings to metal cutting tools \(^2_{1}\) has stimulated studies into the fundamental deposition parameters governing the structure of ceramic thin films. Binary transition metal carbide and nitride thin films such as TiC and TiN \(^2_{2}\), as well as metastable ternary nitrides such as TiAlN \(^2_{3}\), have been extensively studied.

**1.2 Composite Ceramics: Structure and Mechanical Properties**

High hardness and resistance against fracture are desired in surface engineering applications of nanostructured ceramic coatings. Multiphase composite materials can display higher hardness and toughness values as compared to single-phase materials \(^2_{4}\). For example, in single-phase TiN coatings, columnar grain boundaries can become the site for crack initiation \(^2_{5}\). However, fine and equiaxed grain structure in TiN could be achieved by periodically interrupting TiN growth through the introduction of nanolayers of a different material, which forces TiN to renucleate during growth \(^2_{6}\). Therefore, much research effort is focused on the synthesis, structure, and mechanical properties of composite ceramic coatings, including nanoscale multilayers and nanocomposite coatings.

Nanoscale multilayers belong to one type of engineered composite materials with nanoscale composition and structure modulation in one dimension and uniform distribution in the other two dimensions. Multilayered Au-Cu films was the first of this kind, when Dumond and Youtz in 1940 co-evaporated Cu and Au with modulated flux to form layered Au-Cu alloy films with a composition modulation wavelength of \(\sim 10\text{nm}\) \(^2_{7}\). Nanoscale multilayers are usually synthesized by repeating the deposition of two or more materials periodically onto the substrate. Tremendous interface area density, approximately \(10^6\text{mm}^2/\text{mm}^3\) \(^2_{8}\), has been reported for multilayers. This nanoscale
layering may produce very good adhesion, high hardness, and good wear resistance \(^{29, 30, 31, 32}\), and may be applied as interfacial bonding layers to promote adhesion and wear-resistant surface layers on cutting tools and many other rotating machineries.

Ceramic nanocomposite coatings, homogeneous over length scales of \(\mu \text{m}\) and larger, but structurally and compositionally modulated in three-dimensions on the nm length scale, constitute a favorable alternative to one-dimensionally composition/structure modulated multilayers for tribological applications. As compared to nanoscale multilayers, whose deposition requires precise flux modulation, and is difficult to implement on three-dimensional parts with complex surfaces, nanocomposite coatings rely on the nucleation and growth process itself to form the nanoscale structure/composition modulation, and are much more easily applied to parts with complex geometries.

Vapor phase deposited nanocomposite ceramic coatings have been extensively studied in the last five years. One notable family of nanocomposite ceramic coatings is metal-containing diamond-like carbon (DLC) coatings. DLC encompasses a wide range of amorphous carbon (a-C) and amorphous hydrogenated carbon (a-C:H) structures and possess some properties similar to that of diamond, e.g., relatively hard mechanically, inert chemically, and insulating electrically. Distinct from crystalline diamond, the amorphous structure of DLC makes it a good matrix for the incorporation of carbide-forming metals. By adding metals into the a-C or a-C:H matrix, metal-containing carbon (Me-C) and metal-containing hydrogenated carbon (Me-C:H) films are fabricated, including Ta-C:H \(^{33}\), Ti-C:H and W-C:H. For the Ti-C:H system, XRD and transmission electron microscopy (TEM) studies have revealed the presence of nm-sized crystalline
TiC clusters embedded within a-C and a-C:H matrices. Photoelectron spectroscopy evidence corroborated the presence of crystalline TiC nanoclusters within Ti-C:H. In the W-C:H system, TEM studies showed the presence of metastable cubic WC embedded within an a-C:H matrix. Similar XRD evidence of metastable cubic WC formation in W-C coatings has been observed in films deposited by magnetron sputtered assisted pulsed laser ablation.

Different from metal-containing DLC coatings, another family of ceramic nanocomposite coatings is based on amorphous silicon nitride (a-Si:N). One typical example is the Ti-Si-N coating system, with Ti atoms incorporated into a-Si:N matrices. Based on chemical thermodynamics information of the Ti-Si-N system by Sambasivan and Petuskey, Veprek et al. synthesized Ti-Si-N coatings by radio-frequency (rf) plasma assisted CVD in a mixture of SiH₄, TiCl₄, H₂, and N₂ at 550 °C, and indicated that these coatings consisted of a mixture of nanocrystalline TiN and amorphous Si₃N₄. At a silicone content of ~8-9 at. %, the TiN crystal size reaches a minimum value of 3.0~3.5 nm, and the coating hardness was reported to reach a maximum ~ 50 GPa, as shown in Figure 1.1. This hardness value significantly exceeds the hardness of crystalline B1-TiN, as well as the linear rule-of-mixtures values in this two-phase system. The elastic modulus was also reported to exceed 500 GPa at this composition. This phenomenon of strength or hardness enhancement in composite materials systems, with strength/hardness significantly exceeding the linear rule-of-mixtures rules, is termed “super-strengthening”.

Veprek et al. have reported similar strengthening effects in the W-Si-N coating system, with coating hardness exceeding 50 GPa at Si compositions of 5-10 at. %.
figure 1.2, hardness anomalies were reported for the TiC/a-C:H system. Ceramic/metal nanocomposite coatings such as ZrN/Cu has also been reported to exhibit super-strengthening, with hardness exceeding 50GPa. 

Figure 1.1 Super-strengthening reported in the Ti-Si-N coating system [after Veprek, Reiprich, and Li, 1995].

Figure 1.2 Hardness anomaly reported in the TiC/a-C:H nanocomposite coating system [after Zehnder and Patscheider, 2000].
1.3 Super-strengthening

The super-strengthening effect was in-fact first observed in one-dimensional composition/structure modulated multilayer systems. For example, the strength or hardness enhancements of multilayers were observed in metal/metal systems such as Al/Cu\textsuperscript{45,46}, Ni/Pt and Pd/Pt\textsuperscript{47}, ceramic/ceramic system such as TiN/NbN\textsuperscript{48,49}, TiN/VN\textsuperscript{50}, TiC/TiN\textsuperscript{51} and metal/ceramic system such as Ta/TaN\textsuperscript{52}, Ti/TiC\textsuperscript{53}, Hf/HF-N and W/W-N\textsuperscript{54}, Ti/TiN\textsuperscript{55,56,57,58,59,60,61,62} and Al/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{63,64,65}. Some generalizations can be made from the experimental observations:

1. Super-strengthening in multilayers is usually observed when the composition modulation wavelength is on the nanometer scale;
2. The strength or hardness decreases as the modulation wavelength increases to a few hundred nm and above, in which case a linear rule-of-mixtures law applies;
3. Strength or hardness decreases again when the modulation wavelength approaches atomic dimensions.

Toward the strengthening mechanism in one-dimensionally composition/structure modulated structures, Koehler proposed that the strength enhancement is due to the repulsive dislocation image force at interfaces\textsuperscript{66}. Considering alternating layers of materials A and B with shear moduli $G_A$ and $G_B$ ($G_A > G_B$), the critical shear stress for a dislocation in B to operate is equal to the image force acting on the dislocation, and is given as:

$$\sigma_{cr} = \frac{R G_B \sin \theta}{8 \pi} \quad (1.3.1)$$
where \( R = (G_A - G_B)/(G_A + G_B) \), and \( \theta \) is the smallest angle between the interface and the glide plane in B. Based on a Peierls dislocation, Pacheco and Mura derived a different expression for the strength enhancement due to an A/B interface \(^{67}\),

\[
\sigma_{cr} = \frac{2 R G_B}{\pi^2} \quad (1.3.2).
\]

In deriving equation (1.3.2), the difference in \( G_A \) and \( G_B \) is assumed to be small. The total shear stress \( \sigma_B \) needed to produce plastic flow in B is

\[
\sigma_B = \sigma_{B\,\text{bulk}} + \sigma_{cr} \quad (1.3.3),
\]

where \( \sigma_{B\,\text{bulk}} \) is the shear stress needed to produce plastic flow in bulk B. The common feature of the Koehler-Lehoczky and Pacheco-Mura theories is the prediction that the A/B multilayer strength enhancement is proportional to the difference in shear moduli of A and B.

In terms of the super-strengthening mechanism in Ti-Si-N nanocomposite ceramic coatings, Veprek et al. \(^{68}\) proposed a model based on the three-dimensional nanostructure, as shown in Fig. 1.3, in which equiaxed nanocrystalline TiN was surrounded by a monolayer of a-Si:N. The nanoscale TiN crystals can confine the operation of Frank-Reed dislocation sources. Also, by assuming that the characteristic crack length within the ceramic nanocomposite coating is on the order of their nanometer structural length scale, the much-reduced characteristic crack length compared to conventional ceramics is suggested to lead to much higher critical stresses for crack propagation.

Further investigations on the Ti-Si-N ceramic nanocomposite coating system, stimulated by these earlier reports of super-strengthening, have yielded significant
variations of the hardness values. In the Ti-Si-N system, coating hardnees were reported in the range of ~ 40GPa$^{69}$, ~30GPa$^{70}$, ~50GPa$^{71}$, and 80-110GPa$^{72}$. At the present time, whether a dislocation or a crack based mechanism contributes dominantly to super-strengthening in ceramic nanocomposites has not been determined.

Figure 1.3 Suggested mechanism for high hardness of MeN/a-Si:N nanocomposite coatings [after Veprek, 1996].

1.4 Research Motivations and Objective

The varying structure and mechanical properties of Ti-Si-N coatings synthesized by different vapor deposition techniques reported in the literature show an incomplete understanding of the dominant mechanisms governing super-strengthening.

The deposition temperature of Ti-Si-N coatings is expected to significantly alter the surface diffusivities of atoms during film formation. Due to the spinodal decomposition nature of the TiN/a-Si:N phase separation, the deposition temperature may therefore influence the resulting structure of the Ti-Si-N coatings. In addition, surface bombardment by ionic species during PVD and plasma-assisted PVD/CVD may be different as compared to CVD and other thin film deposition processes, resulting in different film structures. Therefore the as-deposited coating structure needs to be related
to the specific deposition technique and deposition temperature. On the other hand, the mechanical properties measurements also need to be combined with detailed structural characterization for each set of Ti-Si-N specimens. To our knowledge, a detailed study on the deposition temperature dependence of the structure and mechanical properties of Ti-Si-N coatings has not been performed.

The objective of our research is to better define conditions under which super-strengthening could occur in the Ti-Si-N nanocomposite system. Detailed structure and mechanical properties information will be obtained experimentally, corresponding to the coating deposition conditions.
Chapter 2. Experimental Background and Procedures

This chapter contains brief introduction to experimental principles followed by reports of experimental procedures.

2.1 Deposition of Ti-Si-N Films

2.1.1 Thin Film Deposition Background and Experimental Setup

The deposition of thin films from the vapor phase can be classified into three general categories:

(1) Physical methods, including evaporation, magnetron sputtering, ion beam deposition, plasma enhanced physical vapor deposition (PE-PVD), electron beam assisted PVD (EB-PVD) and laser ablation, etc.

(2) Chemical methods, including chemical vapor deposition (CVD), and CVD with non-thermal energy input such as plasma, laser, and electron beam assist, etc.

(3) Hybrid methods, including reactive sputtering and glow discharge deposition, etc.

For the current study, ICP assisted hybrid PVD/CVD was employed to deposit Ti-Si-N films. This technique combines the magnetron sputtering process with plasma-induced chemical processes in the gas phase.

The deposition tool combines a 13.56 MHz ICP with four balanced magnetron cathodes. The cathodes are connected to negative DC voltage supplies, and work in the current-controlled mode. The two facing Ti (99.99%) cathodes were operated at the same current, as were the two facing Si (99.99%) cathodes. The substrate holder was negatively biased, facing each cathode as it continuously rotates. Ar and the reactive gas
N\textsubscript{2} were introduced as the medium for the plasma. Once the plasma is initiated, positive ions from the plasma strike the cathode surface. Neutral atoms and positive/negative ions from the cathode are removed by momentum transfer. Other particles, such as secondary ions, secondary electrons, and desorbed gases, are also emitted as a part of the sputtering process. Neutral atoms of Ti and Si, the predominant species sputtered from the cathodes, are transported across the plasma and react with nitrogen ionic and neutral species produced within the plasma at the surface of the substrate to form the tertiary Ti-Si-N coating.

Two schematics of our deposition tool are shown in Fig. 2.1 and Fig. 2.2, respectively. It consists of a specimen load lock pumped by a 170 l/s turbomolecular pump, a main deposition chamber separated from the load lock by a gate valve and a pumping / gas introduction chamber, to which a 1500 l/s cryogenic pump is attached through another gate valve. As shown in Fig. 2.2, the main deposition chamber is spherical in geometry and houses two facing induction coils together with the four balanced-magnetron sputter guns on the plane perpendicular to the specimen rotation axis. The induction coils are connected to 13.56MHz, 1.25kW generators through tuning networks. When energized, the induction coils ignite an ICP through dielectric windows, filling the entire deposition chamber. Such an ICP-assisted hybrid tool enables independent control of the plasma potential and the plasma density, which in turn controls the energy and flux\textsuperscript{74} of ionic species bombarding the substrate.

2.1.2 Deposition of Ti-Si-N specimen at low and high temperatures

Double-side polished, two-inch diameter Si(100) wafers were used as substrates. They were ultrasonically cleaned in acetone followed by methanol, before been loaded
into the vacuum system. Prior to coating deposition, the Si substrate surface was etched in an Ar (99.999%) ICP for 10 min at a constant bias voltage of –100V. Immediately after etching, Ti-Si-N layers were deposited in a gas mixture of Ar/N₂ (99.999%/99.999%), with the substrates rotating continuously in the center of the deposition zone. During Ti-Si-N deposition, the Si substrate was subjected to a constant bias voltage of –50 V, the ratio of Ar/N₂ gas input flow rates was fixed at 10.0/1.2, and the total pressure was kept at ~1.8 mTorr. Ti and Si compositions within the coating were adjusted by varying the Ti and Si cathode currents in the range of 0.0 – 1.0A and 0.0 – 0.3A, respectively. The total ICP input power during the entire deposition process was fixed at 1000W.

Figure 2.1 Schematic of the ICP assisted hybrid CVD/PVD tool: deposition tool layout.
Figure 2.2 Schematic of the ICP assisted hybrid CVD/PVD tool: deposition chamber layout.

Three series of Ti-Si-N specimens were deposited. For the first and second specimen series, no intentional substrate cooling or heating was applied, and substrate temperature measurements, by attaching type-K thermocouples to sacrificial substrates, showed that the deposition temperature was ~250°C. As compared to the first series of specimens, the second series of Ti-Si-N samples underwent longer deposition time and have broader composition coverage. For the third specimen series, Si(100) substrates were fitted into a Ta holder, and radiatively heated by a dc powered flat boron nitride coated graphite heater mounted on the backside of the holder, with a ~0.25 inch gap between the heater and the Si substrate. The Si substrate temperature was monitored by attaching respectively two type-K thermocouples to the center of a sacrificial substrate and the Ta holder. Prior to deposition, the temperature at the center of the Si substrate was monitored in addition by an Ircon infrared pyrometer. With 45V supplied to the heater, the Ta holder temperature was measured at ~475°C. At steady state, the Si substrate temperature readings from the thermocouple and the pyrometer corroborate each other, and give ~650°C at the center of the substrate. An additional temperature
Table 2.1.2 Deposition parameters for Ti-Si-N specimens.

<table>
<thead>
<tr>
<th>Series</th>
<th>Sample</th>
<th>Ti cathode current (A)</th>
<th>Si cathode current (A)</th>
<th>Ti/Si ratio</th>
<th>Deposition Time (Min)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
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<td>W10001</td>
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<td>3.333333</td>
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<td></td>
</tr>
<tr>
<td></td>
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<td>3.571429</td>
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increase of ~50°C was observed during Si substrate etching due to plasma heating. The heater voltage was fixed at 45V during the deposition of the third series of Ti-Si-N
specimens, with the deposition temperature estimated to be ~700 °C. Deposition parameters for the second and third specimen series were identical except for the deposition temperature. Table 2.1.2 lists the deposition parameters for all the Ti-Si-N specimens prepared. A silicon nitride/Si(100) specimen was prepared at ~250°C, and a hetero-epitaxial B1-TiN/Si(111) specimen was also synthesized to compare with the Ti-Si-N coatings.

It is worthwhile to note that the structure and mechanical properties are mainly to be compared between the second and third series of Ti-Si-N specimens, since they cover similar composition and thickness ranges. Unless specifically pointed out, experimental data on film structure and properties in this thesis are collected from the second series of Ti-Si-N specimens deposited at ~250°C and the third series of specimens prepared at ~700°C.

2.2 Composition and Thickness Measurement

Coating composition was measured by Rutherford backscattering spectroscopy (RBS) using a 1.6MeV He$^+$ ion beam and a surface barrier detector at 135° to the beam direction. The specimens were tilted toward the detector, 10° off the normal to the beam. Further details on the principles of RBS have been presented elsewhere. Thickness of Ti-Si-N coatings was measured by cross-sectional scanning electron microscopy (SEM) and cross-sectional TEM.

2.3 Substrate Curvature measurement and Raman Spectroscopy

Compressive stress usually occurs in magnetron sputtered thin films due to energetic ion bombardment of the film surface during deposition. It has been shown that high compressive stresses may influence hardness measurements. In addition, these
stresses furnish a driving force for cracking of coating and delamination of coating from the substrate\textsuperscript{79}. The measurement of residual stresses within as-deposited Ti-Si-N specimens is therefore relevant.

The total residual stress $\sigma_i$ in a thin film at room temperature consists of thermally-induced stress $\sigma_{th}$ and intrinsic stress $\sigma_i$. The thermal component is due to the thermal expansion mismatch between the substrate and the film, and can be calculated by:

$$\sigma_{th} = E_f (\alpha_f - \alpha_s) (T_d - T)$$ \hspace{1cm} (2.3.1),

where $E_f$ is the film Young’s Modulus, $\alpha_f$ and $\alpha_s$ are respectively the thermal expansion coefficient of the film and the substrate, $T_d$ is the deposition temperature, and $T$ is the room temperature. The intrinsic stress $\sigma_i$ is directly related to the film structure, and therefore ion bombardment during deposition as well as nucleation and growth processes\textsuperscript{80}.

The residual stress measurement techniques can be divided in two main classes\textsuperscript{81}:

(1) those based on the curvature or deflection of the substrate, the so-called deflection technique; and

(2) those based on direct measurement of the elastic strains in thin films using X-ray diffraction techniques.

In our experiment, the total residual stress within the Ti-Si-N specimens as-deposited at $\sim 250^\circ$C was measured by monitoring substrate curvature before and after deposition at room temperature. The measurement schematic and the actual setup are shown in Fig. 2.3 and Fig. 2.4, respectively. A linear array of parallel laser beams generated from a single 658nm AlGaInP diode laser beam passing through a multi-pass
optical etalon was directed at the Ti-Si-N/Si specimens in normal incidence. The reflected beams were detected by a CCD array. Further details on this multi beam optical sensing (MBOS) setup were reported elsewhere\textsuperscript{82}.

Figure 2.3 Schematics of the MBOS setup for wafer curvature measurement.

![Figure 2.3 Schematics of the MBOS setup for wafer curvature measurement.](image)

Figure 2.4 Inside configuration of the MBOS instrument.

![Figure 2.4 Inside configuration of the MBOS instrument.](image)

The Si substrate curvature $K$ is related to the relative change in reflected spot spacing, $\Delta D/D_0$, by
\[ K = -\frac{\cos \theta}{2L} \left( \frac{\Delta D}{D_0} \right) \] (2.3.2),

where \( L \) and \( D_0 \) are the optical path length and initial reflected spot spacing from an optically flat surface, respectively. The optical path length \( L \) was calibrated to be \( \sim1.17 \text{m} \) by placing an optical mirror with a known radius of curvature of \( 4.0 \text{m} \) at the specimen position. The total average residual stress \( \sigma_r \) within the coating was related to the substrate curvature change \( \Delta K \) before and after deposition via the Stoney’s Equation,

\[
\sigma_r = \frac{1}{6} \frac{E}{1-\nu} \frac{t_s^2}{t_f} \Delta K \] (2.3.3),

where \( E/(1-\nu) \) is the biaxial modulus of the Si(100) substrate, and \( t_s \) and \( t_f \) are the thicknesses of the substrate and coating, respectively. A negative \( \Delta K \) denotes increasing substrate convexity on the coating side, and signals compressive stress within the coating.

Raman Spectroscopy has been used to study vibrational characteristics of solids. When the sample is irradiated by an intense laser beam with frequency \( \nu_0 \), the Raman scattered light beam is observed with frequencies of \( \nu_0 + \nu_m \) or \( \nu_0 - \nu_m \), where \( \nu_m \) is the relevant vibrational frequency. Due to the shift of vibrational frequencies with respect to atomic volume, as expressed by the Gruneisen parameter \(^{83} \), the vibrational frequencies of crystals are expected to shift when mechanical strain is introduced into the crystal. Therefore, if the crystalline phase inside the Ti-Si-N coatings is under a compressive stress, we would expect a shift in the vibrational frequency.

Raman scattering measurements were performed on Ti-Si-N specimens deposited at \( \sim250 \text{ °C} \). Scattering signals from as-deposited coatings were collected from a Jobin-Yvon LabRam Micro-Raman instrument with a 20 mW 633 nm HeNe laser radiation
source. Filters were used to attenuate the incident beam such that spectra were obtained with 2 mW of incident laser power with the laser beam focused to a spot several µm in size. To avoid effects of laser heating, spectra were acquired repeatedly until a steady state condition was observed. All spectra reported were acquired under steady state conditions.

2.4 High-resolution TEM and Selected Area Diffraction

The atomic structure of Ti-Si-N films was further probed by performing high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED).

TEM is a powerful tool for the study of material structures. As electrons transmit through the specimens, different operation modes such as bright field (BF) or dark field (DF) imaging, electron diffraction, and high-resolution, are possible depending on the electron lens settings and the use of apertures. Further details on the principles of TEM are presented elsewhere.

2.4.1 TEM Sample Preparation

Electron scattering and imaging within a TEM requires that the sample has to be thin enough such that the electron beam could transmit through without too much attenuation. There has to be a thin and uniform area on the Ti-Si-N/Si specimen that is under direct illumination of the electron beam. The specimen can be examined in either plan-view or cross-section.

Mechanical grinding, precision polishing, and ion milling were used to thin down the specimen. The main procedure for the preparation of a cross-sectional Ti-Si-N/Si sample includes the following:
(1) Cut two slices of as-deposited Ti-Si-N/Si sample with about identical size and with the width of ~0.5mm;

(2) Clean them thoroughly in acetone and then in methanol;

(3) Glue the two sample slices face-to-face on the coating side with the M-bond 610 adhesive;

(4) On a diamond cutting wheel, cut a thin and uniform piece from the glued sample with about 0.8mm in thickness;

(5) Using the Gatan model 623 Disc Grinder, precisely grind one cross-section side of the sample until a flat and roughly smooth plane is reached;

(6) Mount the grinded side onto a Mo ring with M-bond 610 adhesive, allow 20 minutes to cure, and precisely grind the other side until the total sample thickness reaches 80~100µm and surface roughness is below 10µm;

(7) Polishing the plane of interest on a Gatan model 656 Dimple Grinder, until the small area under the dimpler is transparent to visible light, in which case the thin area thickness is about 10~30µm;

(8) Mount the specimen gently into a Gatan model 691 precision ion-milling machine, and let the 4kV Ar⁺ ion guns sputtering both sides of the specimen until perforation.

For the preparation of a plane-view Ti-Si-N/Si sample, only the Si substrate side is polished, until the film and substrate total thickness reaches ~60 µm, followed by dimple grinding the same side to a thickness of < 20 µm. Then the Si substrate side is ion-milled by 4kV Ar⁺ ion until perforation, followed by brief ion milling from both sides prior to examination to remove possible contamination due to re-deposition.
2.4.2 TEM and SAED Operations

Cross-sectional and plane-view TEM examinations of as-deposited Ti-Si-N coatings were performed using a JEOL JEM2010 instrument operated at 200 kV.

If the diffracted electron beam from the specimen is blocked on the back focal plane by the objective aperture, the primary beam passes through the aperture and creates the sample image on the image plane of the objective lens, and the image is further enlarged by the intermediate and projector lens. The final image obtained in this way is called a “bright-field” image.

If the diffracted beam, instead of the primary beam, passes through the objective aperture and forms the image, the obtained image is a “dark-field” image. Dark-field images can usually be acquired by translating the objective aperture or tilting the primary beam to a certain angle\(^{85}\).

At high magnification, all intermediate lenses are strongly excited and there are four image inversions. The magnification is increased as the strength of the intermediate lens rises. In the electron diffraction mode, the objective lens forms the first intermediate image of the specimen. A selected area aperture sits in the plane of the first intermediate image, and allows a particular part of the specimen to be selected for electron diffraction. The selected-area diffraction patterns (SADPs) were formed on the objective lens back focal plane, in which all the parallel rays from the specimen in a certain direction are focused on a point in the diffraction pattern.

Camera constant calibration for SADP patterns was accomplished by examining zone-axis single-crystal diffraction patterns from the Si substrate at the same camera length setting.
2.5 X-ray Absorption Near Edge Structure (XANES) Spectroscopy

2.5.1 Theoretical Background of X-ray Absorption Spectroscopy

The Ti-Si-N coatings structure has been studied by TEM and electron diffraction, which are sensitive to the long-range atomic order in crystals or nanocrystals. The X-ray absorption near edge structure (XANES) spectroscopy, on the other hand, provides short-range atomic order information in the film, such as the immediate bonding environment surrounding Ti and Si atoms. Because XANES is sensitive to only the atomic short-range order, it can be applied equally well to crystalline and amorphous solids.

Any material can absorb X-ray to some extent. When an X-ray beam passes through a solid, the intensities of the incoming and outgoing X-ray follow the following relationship:

\[ I = I_0 \exp(-\mu x) \]  \hspace{1cm} (2.5.1),

where \( I \) and \( I_0 \) are respectively the transmitted and incident X-ray intensities, \( x \) is the thickness of the sample, and \( \mu \) is the linear absorption coefficient of the sample. The linear absorption coefficient depends on the atomic species within the material, as well as on the energy of the incident X-ray beam. When the incident photon energy reaches or exceeds the electron binding energies, photoabsorption occurs which results in the release of a photoelectron from the core level. This process greatly changes the absorption coefficient, and an absorption edge appears on the \( \mu \)-\( E \) diagram. The outgoing spherical wave of the photoelectron will be backscattered by the neighboring atoms. The backscattered wave interferes with the outgoing wave, making the probability of photon absorption change, which results in a change in the measured absorption coefficient. Therefore, different atomic bonding environments such as the type and number of
neighboring atoms, bond length, and bond angle, make the oscillations on the μ-E curve to be different. As a result, beyond the absorption edge, the oscillations on the μ-E curve depend sensitively on the atomic short-range order. Because absorption edges corresponding to different atoms occur at different energies, X-ray absorption spectroscopy can yield atom-specific short-range order information within a solid.

XANES spectroscopy covers the μ-E spectra region between the absorption edge and a few hundred eV beyond. The physics of XANES is based on many complicated effects, such as multiple scattering, many-body interactions, and distortion of the excited state wave function by Coulomb and band structure, and has been treated elsewhere.

Although a first principles approach to XANES is rather complex, the application of XANES spectral features as “fingerprints” can be easily carried out for the identification of particular structures and chemical species. By comparing XANES spectra of the material investigated with those of a series of reference samples, which are chosen to provide a step-wise change in a certain structure or electronic parameter, bonding information related to the first few coordination sphere can be obtained from the observed spectral features.

### 2.5.2 XANES Measurement on the Ti-Si-N Samples

The electron synchrotron provides a high intensity/high stability X-ray source, which helps the acquisition of XANES spectra with high resolution and high signal-to-noise ratio. In our experiments, XANES spectroscopy was performed on the Double Crystal Monochromator (DCM) beam line of the synchrotron facility at the Louisiana State University Center for Advanced Microstructures and Devices (LSU CAMD).
For the first series of Ti-Si-N samples deposited at ~250°C, both Ti and Si K-edge spectra were collected using the Total Electron Yield (TEY) technique at ambient temperature. The total electron current from the specimen was measured with a Lytle detector biased at +45V in a chamber with flowing He gas. The incident photon intensity was monitored with a He-filled ionization chamber. Photon energy selection was provided by a Ge(220) and an InSb(111) DCM at the Ti and Si K-edge, respectively. XANES measurements consisted of step scans in different energy regions relative to the edge position, ~4970eV, and ~ 1840eV for Ti and Si K-edge, respectively. A typical Si K-edge scan consisted of 0.55, 0.15, and 0.35 eV steps in the regions 1810-1835, 1835-1855, and 1855-1900 eV, respectively. A typical Ti K-edge scan consisted of 1.05, 0.35, and 0.65 eV steps in the regions 4930-4955, 4955-5010, and 5010-5100 eV, respectively. The integration time of 1sec/step was used. Up to six spectra were consecutively acquired from each specimen and averaged.

Ti K-edge spectra were recorded in the fluorescence mode for the second and third series of Ti-Si-N specimen. Photon energy selection was provided by a Ge(220) DCM mounted on a micro-stepper. The incident photon intensity was still monitored with the He-filled ionization chamber. An eight-channel Ge detector with energy discrimination was used to collect eight fluorescence spectra simultaneously for each specimen. The Ti K-edge scan consisted of approximately 1.2, 0.3 and 0.6 eV steps in the regions 4900-4954, 4954-4982, 4982-5400 eV, respectively. The integration time of 1sec/step was used. The eight fluorescence channel spectra were averaged.

The averaged XANES spectra were normalized to unit edge height by fitting the pre-edge and post-edge regions respectively with a first-degree polynomial and a third-
degree polynomial using the WinXAS97 analysis package. Spectra from the Ti-Si-N specimens deposited at both temperatures were compared to that of the a-Si:N/Si(100) specimen at the Si K-edge and that of the TiN/Si(100) specimen at the Ti K-edge.

2.6 Mechanical Properties of Ti-Si-N Coatings

Mechanical properties of the Ti-Si-N coatings, in terms of hardness and elastic modulus, are characterized by instrumented nanoindentation. This technique employs high-resolution instrumentation to continuously control and monitor the loads and displacements of a diamond pyramidal indenter as it is driven into and withdrawn from a material.

For the measurement of thin film mechanical properties, it is generally required to precisely detect the submicron scale displacement and submilli-Newton scale force. The nanoindentation technique makes these detections possible, by utilizing either a piezo-electric or an electrostatic actuator to apply the force and a sensor for measuring the indenter displacements. The residual indents on the submicron scale could also be imaged, by mounting the indenter onto a scanning probe microscope and performing scans after each indentation.

2.6.1 Mechanics Background of Indentation

During the loading-unloading process of indentation, the material surface profile changes conforming to the shape of the indenter. As shown in Fig 2.5, both elastic and plastic deformation occurs when the material is under indenter loading. At the indenter position, contact depth, \( h_c \), equals to the total indentation depth, \( h \), minus the specimen surface displacement, \( h_s \). As the indenter is withdrawn and load removed, the elastic
deformation is completely recovered and only the plastic indent remains. The depth of the plastic indent is \( h_f \), and \( a \) is the radius of the contact circle.

![Diagram of surface profile during contact with an indenter.]

Figure 2.5 Change of surface profile during contact with an indenter.

One can effectively separate the elastic and plastic response through the analysis of a complete loading-unloading cycle. Fig 2.6 shows a typical experimental load-displacement curve, in which \( h_{\text{max}} \) is the maximum depth, \( h_f \) is the final depth, and \( S \) is obtained from the upper portion of the unloading curve, \( S = dP/dh \). \( S \) is known as the contact stiffness.

![Diagram of load-displacement curve.]

Figure 2.6 A typical instrumented nanoindentation load-displacement curve.
Hardness $H$ is defined as the contact pressure under the applied load:

$$H = \frac{P}{A} \quad (2.6.1),$$

where $P$ is the applied load and $A$ is the projected contact area. To obtain the elastic modulus from the load-displacement relationship, one has to consider the deformation of both the material and the non-rigid indenter:

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad (2.6.2),$$

where $E_r$ is called the reduced modulus, $E$ and $\nu$ are respectively Young’s modulus and Poisson’s ratio of the specimen, and $E_i$ and $\nu_i$ are respectively those of the indenter. For a diamond indenter, $E_i = 1141$ GPa and $\nu_i = 0.0792$. Contact Stiffness is

$$S = \frac{dP}{dh} = \frac{2\beta}{\sqrt{\pi}} E_r \sqrt{A} \quad (2.6.3),$$

where $\beta$ is a constant depending on the indenter geometry, for example, $\beta = 1.034$ for a three sided pyramidal Berkovich tip. Oliver and Pharr established a numerical method to derive the contact area $A$ from the analysis of indentation load-displacement data, rather than direct imaging of the indent. They start by fitting the unloading curve to the power-law relation

$$P = B(h - h_f)^m \quad (2.6.4),$$

where $B$ is a constant, $h_f$ is the final depth, and $m$ is a fitting index empirically determined. From (2.6.3) and (2.6.4), the contact stiffness is established by differentiating (2.6.4) and evaluating the result at the maximum contact depth:
Practically, only the upper portion of the unloading data, for example from, 95% to 65%, is fitted to obtain the contact stiffness.

At this point we still need to determine the contact depth $h_c$ and the projected contact area $A$. For a specified indenter, $h_c$ is calculated from $h$, $P_{\text{max}}$ and $S$:

$$h_c = h - \varepsilon \frac{P}{S}$$

(2.6.6),

in which $\varepsilon$ is an indenter geometry constant, and $\varepsilon = 0.75$ for a Berkovich indenter. In order to evaluate $A$, an empirical relationship between $A$ and the $h_c$ has to be established, i.e., $A = f(h_c)$. This is known as the shape function of the indenter tip, which is usually experimentally calibrated before performing any measurements. Calibration consists of making indents into a solid with known elastic modulus, usually fused silica, and extracting the area function from the experimentally determined contact stiffness. Once the projected contact area and contact stiffness are known, material hardness and elastic modulus can be calculated from (2.6.1), (2.6.2), and (2.6.3).

2.6.2 Calibration of Area Function and Load Frame Compliance

Instrumented nanoindentation was carried out on a Hysitron Triboscope interfaced to a Digital Instrument Dimension 3100 atomic force microscope (AFM). AFM images were also taken at the same site where indentations were made. Two types of three-sided pyramidal diamond indenters were used for indentation and image acquisition. An ideal Berkovich indenter, with an equivalent cone angle of 70.32 degrees, has an area function
An ideal cube corner indenter, with an equivalent cone angle of 42.28 degrees, has an area function

\[ A(h_c) = 24.5h_c^2 \quad (2.6.7). \]

Because of the much-increased sharpness of the cube corner tip, it can be used for shallower indents while inducing plastic deformation in the indented material. Both Berkovich and cube corner diamond indenters have been used in our experiments.

The area function for perfect indenter tips needs to be modified for a real indenter with finite rounding at the tip. Also since the load frame deforms together with the sample and the indenter, the compliance of both the load frame and the specimen has to be considered:

\[ C = C_f + C_s \quad (2.6.9), \]

where \( C_f \) is the load frame compliance, \( C_s \) is the specimen compliance, and \( C \) is the total compliance. \( C \) was obtained directly from the load-displacement data. Contact depth \( h_c \) can be calculated from (2.6.6), and an estimation of the contact area \( A \) will be obtained from (2.6.7) or (2.6.8). \( C_s \) is the inverse of stiffness \( S \) for elastic contact. Taking (2.6.3) and applying \( \beta = 1 \) for circular contact,

\[ C_s = \frac{1}{S} = \frac{\sqrt{\pi}}{2E_r} \frac{1}{\sqrt{A}} \quad (2.6.10). \]

By assuming \( E_r \) is independent of the contact depth, we can plot \( C \) as a function of \( A^{1/2} \) at different loads. The intercept of the straight line with \( C \) axis gives the machine compliance \( C_f \). From (2.6.9) and (2.6.10), we get
\[ A = \frac{\pi}{4} \frac{1}{E_r^2} \frac{1}{(C - C_f)^2} \]  \hspace{1cm} (2.6.11).

Using pairs of \((A, h_c)\) over a range of depth, we can fit \(A\) vs. \(h_c\) to an expression following Oliver and Pharr,

\[ A(h_c) = ch_c^2 + c_1h_c^4 + c_2h_c^2 + c_3h_c^4 + c_4h_c^8 + c_5h_c^{16} \]  \hspace{1cm} (2.6.12),

where \(c\) is a geometric constant \((c = 24.5\) for the Berkovich indenter and 2.598 for the cube corner indenter), and \(c_1\) to \(c_5\) are the fitting parameters to be determined.

In our experiments, the instrument load frame compliance and indenter tip area function were calibrated with a vendor supplied fused silica specimen assuming a contact-depth \((h_c)\) independent elastic modulus. The calibration load range was 100 - 13000 \(\mu\)N for Berkovich indenters, corresponding to an indenter contact depth range of 8 < \(h_c\) < 220 nm. The calibration load range was 30 – 1000 \(\mu\)N for cube corner indenters, corresponding to a contact depth range of 6 < \(h_c\) < 150 nm. A set of indentation load-displacement curves obtained on the fused silica calibration specimen using the cube corner tip is shown in Figure 2.7.

2.6.3 Measurement of Hardness and Elastic Modulus of Ti-Si-N specimens

Indentation measurements on as-deposited Ti-Si-N/Si specimens were carried out on both a Berkovich and a cube corner diamond indenter at multiple loads ranging from 13000 to 100 \(\mu\)N, with multiple indents performed at each load. The Oliver/Pharr analysis procedure was followed to extract values of the indentation modulus, \(E_{ind} = E/(1-\nu^2)\), where \(E\) and \(\nu\) are respectively the Young’s modulus and Poisson’s ratio, and the hardness, \(H\), from the experimental load vs. displacement curves. Results taken at
contact depths less than 10% of the total coating thickness were averaged to obtain the modulus and hardness values, excluding indents made at very low loads where the contact became elastic, causing an apparent hardness drop. Coating surface profiles were examined in the contact AFM mode with the Berkovich indenter tip, and the average roughness of the as-deposited coatings was determined to be approximately 2nm, independent of the Si composition.

Figure 2.7 Indentation load-displacement curves obtained on fused silica using a cube corner tip.
Chapter 3. Results and Discussion

3.1 Experimental Results on Ti-Si-N Specimens Deposited at 250°C

3.1.1 Coating Surface Roughness, Composition and Thickness

Figure 3.1.1 shows a contact AFM image of the as-deposited surface of a Ti-Si-N coating, deposited at ~250°C with a Si composition of 19.2 at. %. The surface morphology shown is representative of the entire series of Ti-Si-N coatings deposited at 250°C. Additional AFM imaging showed that the average roughness ($R_a$) of the as-deposited coatings was ~2 nm, independent of the Si composition.

![AFM Image](image)

Figure 3.1.1 A contact AFM image of the as-deposited surface of a Ti-Si-N coating with a Si composition of 19.2 at. %. The vertical scale on the 4 µm × 4 µm scan is 20 nm.

Figure 3.1.2 shows the average composition of the Ti-Si-N coatings deposited at ~250°C, as measured by RBS, as a function of the ratio of Ti cathode current to Si cathode current. As the Ti atom flux increases relative to the Si atom flux during deposition, the Ti composition increases monotonically from below 1 at. % to ~40 at. %, the Si composition decreases monotonically from ~40 at. % to ~8 at. %, the Ar composition decreases from ~4 at. % to below 1 at. %, and the N composition changes...
only slightly from ~56 at. % to ~52 at. %. At low Ti compositions, the N composition is close to that of Si₃N₄, 57 at. %. As the Ti atom flux increases, Si atoms within the coating are replaced by Ti atoms, while the N fraction stays relatively constant. Thickness for the present series of Ti-Si-N coatings ranged from 160 to 410 nm, based on the cross-sectional SEM and TEM measurements. A typical cross-sectional SEM image of the Ti-Si-N/Si specimen is shown in Figure 3.1.3.

Figure 3.1.2 Composition of Ti-Si-N coatings deposited at ~250°C as a function of the ratio of Ti cathode current to Si cathode current during deposition.

3.1.2 Structural Information by TEM and XANES

Figure 3.1.4 shows a cross-sectional TEM bright-field (BF) micrograph of a Ti-Si-N specimen deposited at ~250°C with 6.3 at. % Ti. A uniform coating layer is seen on the Si(100) substrate.

Figure 3.1.5 shows a cross-sectional HR-TEM micrograph of the same specimen, clearly showing that the entire coating structure is amorphous, with all Ti atoms dissolved within the a-Si:N matrix.
Figures 3.1.6 and 3.1.7 show cross-sectional HR-TEM images of two Ti-Si-N specimens deposited at ~250°C with 12 at. % and 15 at. % Ti, respectively. While the entire coating structure at 12 at. % Ti appears amorphous, lattice fringes are clearly visible from certain areas of the Ti-Si-N coating with 15 at. % Ti, showing crystalline domains less than 3nm in size. The corresponding SADP shown in Figure 3.1.8, obtained from the 15 at. % Ti specimen and taken from the regions that included the Si substrate, shows clearly the presence of diffraction rings in addition to the Si(100) spot pattern and the characteristic amorphous halo from the a-Si:N matrix. The diffraction rings can be indexed to a cubic structure with lattice parameters close to that of B1-TiN, and indicate that the nanocrystalline precipitates are TiN grains. It should be noted that the continuous diffraction rings shown in Figure 3.1.8 indicate that there is no preferential orientation of the TiN nanocrystals in this specimen. Figures 3.1.6 and 3.1.7 show that the dissolution limit for Ti atoms in the a-Si:N matrix lies between 12 and 15 at. %; precipitation of nanocrystalline TiN occurs beyond 15 at. % Ti.

Figure 3.1.3 Cross-sectional SEM examination of a Ti-Si-N specimen deposited at ~250°C with 15 at. % Ti.
Figure 3.1.4 Cross-sectional TEM examination of a Ti-Si-N specimen deposited at ~250°C with 6.3 at. % Ti: BF micrograph.

Figure 3.1.5 Cross-sectional TEM examination of a Ti-Si-N specimen deposited at ~250°C with 6.3 at. % Ti: HRTEM micrograph.
Figure 3.1.6 Cross-sectional TEM examination of Ti-Si-N specimens deposited at ~250°C: HRTEM micrograph of a Ti-Si-N coating with 12 at. % Ti.

Figure 3.1.7 Cross-sectional TEM examination of Ti-Si-N specimens deposited at ~250°C: HRTEM micrograph of a Ti-Si-N coating with 15 at. % Ti.

Figure 3.1.8 Cross-sectional TEM examination of Ti-Si-N specimens deposited at ~250°C: corresponding SADP of the Ti-Si-N coating with 15 at. % Ti.
Figures 3.1.9 (a) and 3.1.9 (b) show SADPs obtained from a Ti-Si-N specimen deposited at ~250°C with 17.5 at. % Ti in plan-view and in cross-section, respectively. Figures 3.1.9 (a) shows that the in-plane orientation of the TiN nanocrystals is random, while Figures 3.1.9 (b) shows that a strong TiN<100> texture in the growth direction develops, with TiN(100) in parallel with Si(200). Figure 3.1.9 (c) shows the corresponding cross-sectional dark-field (DF) TEM micrograph, which clearly shows evidence for nanocolumnar TiN growth, with the TiN column height in the growth direction greatly exceeding the in-plane column width.

Figure 3.1.9 TEM examination of a Ti-Si-N specimen deposited at ~250°C with 17.5 at. % Ti: (a) plan-view SADP, (b) cross-sectional SADP, (c) cross-sectional DF micrograph.
Figure 3.1.10 (a) shows normalized Ti K-edge XANES spectra of a number of Ti-Si-N coatings from the first series of samples deposited at ~250°C. The Ti K-edge spectrum of the B1-TiN/Si(111) specimen is shown in Figure 3.1.10 (a) for comparison. At all Si compositions, the post-edge XANES oscillations exhibit a one-to-one correspondence with those of the B1-TiN specimen, indicating that the short-range order surrounding the Ti atoms within the Ti-Si-N coatings is predominantly B1-TiN like. The normalized Si K-edge XANES spectra of the same set of Ti-Si-N coatings are shown in Figure 3.1.10 (b). The Si K-edge spectrum of the a-Si:N/Si(100) specimen is also shown for comparison. Figure 3.1.10 (b) shows that, at all Si compositions, the overall spectral shape of the Ti-Si-N coating spectrum is similar to that of a-Si:N. The a-Si:N spectral shape is relatively featureless, with a pronounced white line peaking around 1846 eV and one additional broad peak around 1860 eV, consistent with an amorphous structure. The Ti-Si-N coating spectra exhibit appreciable differences in the pre-edge region as compared to that of the a-Si:N specimen. The transition threshold begins at ~ 1838 eV for the Ti-Si-N coatings, as compared to ~ 1841 eV for the a-Si:N specimen. The difference becomes more pronounced as the overall Si composition decreases. As the Si composition decreases, the peak of the white line also shifts from 1845.3 to 1846.6 eV. Figure 3.1.10 (c) shows two Si K-edge XANES spectra taken from an identical Ti-Si-N specimen with 7.0 at. % Si. The two spectra were taken with the InSb(111) DCM fully tuned and 50% detuned, respectively. The close agreement between the two spectra indicates that possible distortion of the Si K-edge spectral features due to the presence of higher order harmonics is not significant in the present set of data.
Figure 3.1.10 XANES spectra: (a) Ti K-edge spectra of a number of specimens from the first series of Ti-Si-N coatings deposited at ~250°C and from B1-TiN (b) Si K-edge spectra from the same set of Ti-Si-N coatings and from a-Si:N; (c) tuned (dot) and 50 % detuned (line) Si K-edge spectra of a Ti-Si-N coating with 7.0 at. % Si.
The overall spectral similarity of the Si K-edge XANES from the Ti-Si-N coatings to that from a-Si:N suggests that Si atoms incorporate into the Ti-Si-N coatings in an a-Si:N-like environment. This spectral similarity supports the lack of significant Si incorporation into the B1-TiN phase. It is, however, believed that the spectral differences in the edge and white-line regions between the Ti-Si-N coatings and the a-Si:N specimen are suggestive of some Ti atoms being present within the first few coordination shells of Si, in addition to Si and N atoms. Without significant Si substitution into B1-TiN, proximity of Si and Ti atoms can arise by either Ti atom dissolution within the a-Si:N phase or preferential Ti – Si bonding across TiN/a-Si:N interfaces. In the latter case, with decreasing Si composition, the fraction of such bonds is expected to increase because the surface to volume ratio of the a-Si:N phase increases. This is consistent with the observed gradual changes seen in the Si K-edge XANES spectra as the overall Si composition decreases.

Figure 3.1.11 shows the Ti K-edge XANES spectra collected from the second series of Ti-Si-N specimens deposited at ~250°C. The influence of TiN precipitation on the spectra shape is evident. At 12 at. % of Ti or below, the XANES spectra is relatively featureless, except for a broad peak around 5.0 keV immediately after the edge. This suggests that all Ti atoms are dissolved within a-Si:N. A double peak feature appears around 5.0 keV at 15 at. % of Ti, and becomes better defined with the increase of Ti composition. Post-edge oscillations also present at higher Ti composition. These post-edge oscillations show an one-to-one correspondence with those of the B1-TiN XANES spectrum and suggests the appearance of crystalline TiN after the dissolution limit is reached.
Figure 3.1.11 Normalized Ti K-edge XANES spectra of the second series of Ti-Si-N specimens deposited at ~250°C as a function of the Ti composition.

From data collected on Ti-Si-N coatings deposited at ~250°C, a few conclusions can be drawn. The Si K-edge XANES spectra suggest that there is no significant Si incorporation into the B1-TiN phase, and that the short range order surrounding Si atoms is a-Si:N like. The combination of XANES with HR-TEM shows that the Ti dissolution limit within the a-Si:N is between 12-15 at. %. The Ti K-edge XANES spectra show that the short-range order surrounding Ti atoms is B1-TiN like beyond the Ti dissolution limit, in agreement with the TEM evidence. Taken together, the TEM images and XANES spectra demonstrate that, beyond the Ti dissolution limit, these Ti-Si-N coatings consists of a nm-scale mixture of a B1-TiN phase and an a-Si:N phase, i.e., they are TiN/a-Si:N nanocomposites.

3.1.3 Residual Stress and Raman Scattering Measurement Results

Figure 3.1.12 shows the variation of the total residual stress at room temperature, obtained from curvature measurements according to the Stoney’s equation, within the Ti-Si-N coatings deposited at ~250°C as a function of the Ti composition. A constant
compressive stress of $\sim -1\text{GPa}$ is observed at Ti compositions below the Ti dissolution limit. As the TiN nanocrystals precipitate out of the a-Si:N matrix, the residual stress increases monotonically with increasing Ti composition, to $\sim -4\text{GPa}$.

![Figure 3.1.12](image)

Figure 3.1.12 Total average residual stress within Ti-Si-N coatings deposited at $\sim 250^\circ\text{C}$, measured by a substrate curvature method, as a function of the Ti composition.

Figure 3.1.13 shows a series of Raman spectra obtained from Ti-Si-N specimens deposited at $\sim 250^\circ\text{C}$. At Ti compositions below 12 at. %, where all Ti atoms are dissolved within the a-Si:N matrix, the Raman spectra exhibit a strong peak near $520\text{cm}^{-1}$ originating from the Si zone center mode. The bank-like feature from 900 to $1000\text{cm}^{-1}$ also originates from the second-order spectrum of Si. Below 12 at. % Ti, the Ti-Si-N coatings are optically transparent, allowing Raman spectral features of the Si substrate to be measured in reflection. The Si second-order feature and the zone center peak diminish in intensity as nanocrystalline TiN precipitation initiates at 15 at. % Ti, showing only remnants at 17.5 at. % Ti, where $<100>$ textured nanocolumnar TiN develops, and completely disappear at higher Ti compositions. As the Ti-Si-N coatings rapidly become
optically opaque after nanocrystalline TiN precipitation, a broad band around 550 cm\(^{-1}\) emerges, the center of which appears to shift with increasing Ti composition. This broad Raman feature was previously reported for TiN coatings and was attributed to defect-induced Raman scattering, considering that the perfect B1-TiN crystalline lattice is centrosymmetric and first-order Raman inactive. The observation of this Raman feature for the present series of Ti-Si-N specimens indicates the presence of point defects within the nanocolumnar TiN grains.

![Raman spectra](image)

Figure 3.1.13 Raman spectra from Ti-Si-N coatings deposited at \(\sim 250^\circ\text{C}\), as a function of the Ti composition.

Figure 3.1.14 shows the center position of the defect-induced TiN Raman band as a function of the average stress within the Ti-Si-N coating measured by substrate curvature, where an approximately linear correlation is evident. A linear least-squares fit to the data shown in Figure 3.1.14 yields the functional dependence of the TiN Raman peak position \(E\) on the average residual stress \(\sigma\),

\[
E(\sigma) = (551 \pm 1) \text{ (cm}^{-1}\text{)} - (6.4 \pm 0.4) \text{ (cm}^{-1}/\text{GPa}) \sigma(\text{GPa}) \quad (3.1.1).
\]
The magnitude of this Raman mode dependence on stress is comparable to previously observed stress dependencies in other ceramic materials \(^9\), and lends indirect support to the residual stress measurements.

![Graph showing the center position of the defect-induced TiN Raman band as a function of the coating average stress.](image)

Figure 3.1.14 Center position of the defect-induced TiN Raman band as a function of the coating average stress.

### 3.1.4 Mechanical Properties

Figures 3.1.15 and 3.1.16 show, respectively, the indentation modulus and the hardness of Ti-Si-N coatings deposited at ~250°C measured by instrumented nanoindentation with a Berkovich indenter as a function of the Si composition. Measured indentation moduli do not exceed 300GPa over the entire composition range. Similar to the trend observed for the residual stress, the measured hardness stays approximately constant at ~20GPa in the Si composition range corresponding to total dissolution of Ti atoms within the a-Si:N matrix (42 to 26 at. % Si), and increases significantly as the volume fraction of nanocolumnar TiN grains increases. Over the entire composition range, the hardness remains at ~37GPa or below. Although the measured hardness exceeds that of B1-TiN (22-24 GPa), it is not observed to reach 50 GPa or above\(^9\).
Figure 3.1.15 Nanoindentation of Ti-Si-N specimens deposited at ~250°C: indentation modulus as a function of the Si composition.

Figure 3.1.16 Nanoindentation of Ti-Si-N specimens deposited at ~250°C: hardness as a function of the Si composition.
3.2 Experimental Results on the Ti-Si-N Specimens Deposited at 700°C

3.2.1 Coating Composition and Thickness

The composition of the Ti-Si-N coatings deposited at 700°C is measured by RBS. The thicknesses of some of the samples were obtained from cross-sectional TEM. The results are listed in Table 3.2.1.

Table 3.2.1 Composition and thickness of high temperature Ti-Si-N coatings.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Ti Composition (at. %)</th>
<th>Si Composition (at. %)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTSN 0201</td>
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<td>38.5</td>
<td>-</td>
</tr>
<tr>
<td>HTSN 0301</td>
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<td>34.5</td>
<td>155</td>
</tr>
<tr>
<td>HTSN 0401</td>
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<td>30.5</td>
<td>163</td>
</tr>
<tr>
<td>HTSN 1003</td>
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<td>250</td>
</tr>
<tr>
<td>HTSN 2001</td>
<td>50</td>
<td>0.0</td>
<td>313</td>
</tr>
</tbody>
</table>

3.2.2 Structural Information by TEM and XANES

Figure 3.2.1 shows a cross-sectional HR-TEM micrograph of a Ti-Si-N coating deposited at ~700°C with 6 at. % Ti, which clearly indicates that the entire coating is amorphous in structure. The inset in Figure 3.2.1 shows the corresponding SADP, with only diffuse halos present, consistent with the high-resolution imaging.

Figure 3.2.2 shows a cross-sectional HRTEM micrograph of a Ti-Si-N coating deposited at ~700°C with 11.5 at. % Ti. The presence of lattice fringes, arranged in the form of nanocolumns, 2nm or less in width and more than 20nm in height in the growth direction, is clearly evident. The corresponding SADP is shown in Figure 3.2.3, and shows the presence of crystalline diffraction signatures in addition to the Si (100) spot pattern and the characteristic amorphous halo from the a-Si:N matrix. In contrast to low temperature deposition, this SADP shows that a strong TiN<100> texture develops along the growth direction immediately after the Ti dissolution limit within a-Si:N is reached.
This finding is consistent with the expectation of higher surface mobility at the higher deposition temperature.

Figure 3.2.1 Cross-sectional TEM examination of Ti-Si-N specimens deposited at \(~700^\circ\text{C}\): HRTEM micrograph of a Ti-Si-N coating with 6 at. % Ti.

Figure 3.2.2 Cross-sectional TEM examination of Ti-Si-N specimens deposited at \(~700^\circ\text{C}\): HRTEM micrograph of a Ti-Si-N coating with 11.5 at. % Ti.
Figure 3.2.3 Cross-sectional TEM examination of Ti-Si-N specimens deposited at ~700°C: corresponding SADP of the Ti-Si-N coating with 11.5 at. % Ti.

Figure 3.2.4 shows a cross-section HRTEM micrograph of a Ti-Si-N coating deposited at ~700°C with 32 at. % Ti and illustrates that the nanocolumnar TiN structure persists to higher Ti compositions. TiN forms pronounced nanocolumns, with ~5nm in-plane size and column height well in excess of 20nm. The pronounced TiN<100> texture in the growth direction is also evident in the corresponding SADP in the inset.

Figure 3.2.4 A cross-sectional HRTEM micrograph of a Ti-Si-N specimen deposited at ~700°C with 32 at. % Ti, the corresponding SADP is shown in the inset.
The precipitation of nanocrystalline B1-TiN is confirmed by the Ti K-edge XANES spectra, shown in Figure 3.2.5, obtained from Ti-Si-N coatings deposited at ~700°C. At 6 at. % Ti or below, where all Ti atoms are dissolved within the a-Si:N matrix, the Ti K-edge XANES spectra exhibit a broad peak around 5.0 keV, and remain relatively featureless at higher photon energies. At 11.5 at. % Ti, a double-peak structure and a more pronounced dip appear at ~5.0 keV and ~5.1 keV, respectively. These spectral features sharpen further with increasing Ti composition, and exhibit a one-to-one correspondence with spectral features of a nearly pure TiN coating deposited at the same temperature. Combining evidence from HRTEM and Ti K-edge XANES, the effect of increasing the deposition temperature from ~250°C to ~700°C is to decrease the Ti dissolution limit within the a-Si:N matrix to below 11.5 at. % Ti. Additional cross-sectional TEM examinations showed that the TiN coating deposited at ~700°C again possesses a columnar structure, with a TiN column width of ~30nm or higher.

Figure 3.2.5 Normalized Ti K-edge XANES spectra of Ti-Si-N specimens deposited at ~700°C as a function of the Ti composition.
3.2.3 Mechanical Behavior

The mechanical behavior of a Ti-Si-N coating with 32 at. % Ti deposited at ~700°C is illustrated in Figure 3.2.6. The load-displacement curve was obtained using a Berkovich diamond indenter. The indentation modulus and hardness of the Ti-Si-N coating are determined to be (369±40) GPa and (60±13) GPa, respectively. The apparent extent of plastic deformation induced by indentation with the Berkovich indenter in the Ti-Si-N coating is very small, as evidenced by the nearly overlapping loading and unloading curves. While a contact pressure under load is obtained from analyzing the initial portion of the unloading curve, assigning this contact pressure as the specimen hardness may be questioned, since little plasticity is involved. We have therefore carried out additional nanoindentation measurements with a cube corner indenter.

Figure 3.2.6 A load – displacement curve obtained with a Berkovich indenter on a Ti-Si-N specimen with 32 at. % Ti deposited at ~700°C.

Figure 3.2.7 shows load-displacement curves obtained with one cube corner indenter on three specimens, the Ti-Si-N coating with 32 at. % Ti deposited at ~700°C, a Ti-Si-N coating with 30.5 at. % Ti deposited at ~250°C, and the TiN standard specimen.
In contrast to load-displacement curves obtained with a Berkovich indenter, the cube corner indenter clearly induces significant plasticity in all three specimens. Judging from the maximum indenter penetration depth shown in Figure 3.2.7, both Ti-Si-N specimens are harder than the TiN standard specimen. At approximately the same composition, the hardness of the Ti-Si-N specimen deposited at ~700°C is higher than that of the one deposited at ~250°C. This conclusion is confirmed by additional indentation measurements at varying loads, as shown in Figure 3.2.8.

![Load-displacement curves obtained with a cube corner indenter on three specimens: a Ti-Si-N coating with 32 at. % Ti deposited at ~700°C, a Ti-Si-N coating with 30.5 at. % Ti deposited at ~250°C, and a TiN standard specimen.](image)

Analysis of the indentation data obtained with the cube corner indenter at contact depths of 15-30nm using the Oliver/Pharr method yielded hardness values for the Ti-Si-N specimens deposited at ~700°C and ~250°C of 40.3±2.5 GPa and 31.5±1.9 GPa, respectively. In comparison, the hardness of the TiN standard specimen is determined to be 22.2±0.2 GPa, in agreement with previous measurements. The significant plasticity induced by indentation with the cube corner tip at shallow depths makes hardness
determination in these thin films more reliable as compared to indentation with the more blunt Berkovich indenter, where an error in indenter area function determination at small depths may result in a large error in the contact pressure/hardness measurement. We believe that this is the case for the data shown in Figure 3.2.6, and that the contact pressure of ~60GPa is overestimated.

Figure 3.2.8 Nanoindentation load – displacement curves obtained with a cube corner indenter on two specimens under varying loads: a Ti-Si-N coating with 32 at. % Ti deposited at ~700°C and a Ti-Si-N coating with 30.5 at. % Ti deposited at ~250°C.

Several conclusions can be drawn from the present set of indentation data. First, the hardness values of both Ti-Si-N specimens are higher than that of the TiN standard specimen, ~22GPa. Second, the Ti-Si-N specimen deposited at the higher temperature of ~700°C shows higher hardness as compared to the specimen deposited at the lower temperature of ~250°C. Third, hardness values approaching or exceeding 50GPa have not been found within the three series of Ti-Si-N specimens studied to date.

While the present results confirm that Ti-Si-N specimens deposited at ~700°C can be significantly higher than that of TiN, the morphology of the present series of Ti-Si-N coatings, nanocolumnar TiN grains along the growth direction interdispersed within an a-
Si:N matrix, is different than that previously reported by Veprek et al., who deposited equiaxed nanocrystalline TiN grains separated by an a-Si:N matrix\textsuperscript{100,101}. Thus the particular morphology of equiaxed nanocrystalline TiN grains surrounded by a very thin layer of a-Si:N suggested by Veprek et al, cannot be the only reason for the super-strengthening effect in the Ti-Si-N system.

A complete separation of B1-TiN and a-Si:N phases within the nanocomposite implies little dissolution of Si and Ti atoms within the TiN and a-Si:N phases, respectively. Our results show that few Si atoms are incorporated into the TiN crystals\textsuperscript{99}, although there’s some Ti dissolution into the a-Si:N phase. HRTEM images indicate that the internal TiN/a-Si:N interfaces are atomically sharp, with no significant difference between the interface thicknesses of the low and high temperature deposited coatings (see Figure 3.2.4 and ref. 99). Assuming stoichiometry in the TiN phase, the decrease in the Ti atom dissolution limit within the a-Si:N matrix at the higher deposition temperature of \(\sim 700^\circ C\) therefore implies a steeper composition gradient across TiN/a-Si:N interfaces, i.e., a sharper interphase interface. An increase in hardness with increasing interfacial sharpness is reminiscent of hardness data in one-dimensional composition modulated multilayers, where lower hardness is generally observed when interfaces become more diffuse\textsuperscript{102}. In analogy to hardness enhancements in ceramic/ceramic multilayers, which is believed to be due to dislocation barriers presented by the internal interfaces, we suggest that the super-strengthening observed in the present Ti-Si-N coatings may likewise be related to limitations on dislocation propagation due to the presence of internal, albeit irregular and three-dimensional, TiN/a-Si:N interfaces. Further investigations along these lines are in progress.
4.1 Structure and Mechanical Properties of Ti-Si-N Coatings

We have performed a detailed experimental study on the structure and mechanical properties of Ti-Si-N coatings deposited at both low and high temperatures.

Structural characterizations by high resolution transmission electron microscopy and X-ray absorption near edge structure spectroscopy have shown that Ti-Si-N coatings are two-phase nanocomposites with nano-columnar TiN crystals embedded within the amorphous Si:N matrixes. XANES spectra also proved that the short-range order surrounding the Ti atoms is predominantly B1-TiN like at composition beyond the dissolution limit in a-Si:N, and Si atoms incorporate into the Ti-Si-N coatings in an a-Si:N like environment. While few Si atoms are dissolved into the TiN phase, the dissolution limit of Ti into a-Si:N is determined to be between 12 and 15 at. Ti % at ~250 °C. Increasing the deposition temperature to ~700 °C decreases the dissolution limit to between 6 and 11.5 at. Ti %, and closer to 6 at. %.

HR-TEM images also showed that the internal TiN/a-Si:N boundaries are atomically sharp, independent of the deposition temperature. Therefore, with a decrease on the Ti dissolution limit within a-Si:N, increasing the deposition temperature increases the composition gradient across the phase boundary. The degree of phase separation of TiN/a-Si:N goes to more completion upon an increase of deposition temperature from ~250 °C to ~700 °C.

A hardness enhancement (~40GPa) in the Ti-Si-N coating with 32 at. % Ti deposited at ~700 °C has been observed, in contrast to the hardness values ~32GPa for the coating deposited at ~250 °C with a similar composition. Thus a sharper interface is
suggested to influence super-strengthening in the Ti-Si-N system. In analogy to the Koehler’s mechanism for the strength enhancement in one-dimensional nano-multilayer, one possible explanation for the observed super-strengthening in Ti-Si-N system is due to the 3-dimensional internal TiN/a-Si:N interface working as barriers against dislocation motion.

4.2 Suggestions for Future Work

At the deposition temperature of ~700 °C, the Ti-Si-N coatings will have an increased surface atom mobility as compared to those prepared at ~250 °C. Rather than in the range of 6 to 11.5 at. Ti%, the dissolution limit of Ti within a-Si:N at this temperature could be more precisely determined, by reducing the Ti/Si cathode current ratio step between adjacent Ti-Si-N samples near the dissolution limit. In addition, the fracture toughness of the specimens with hardness enhancement may need to be tested.

For the Ti-Si-N specimens deposited at high temperature, a systematic residual stress/hardness/modulus variation as a function of composition is currently missing. Detailed stress monitoring and mechanical properties characterization remain to be performed towards this end.

Percolation of a-Si:N has been suggested to play an important role in determining the mechanical properties of TiN/a-Si:N nanocomposites\textsuperscript{103}. For three dimensional site percolation, the percolation threshold ranges from 20% to 40%\textsuperscript{104}. In the present series of Ti-Si-N coatings, the nanocrystalline TiN grains grow in a columnar-like fashion along the growth direction. Covering the entire Ti composition range, from pure a-Si:N to almost pure TiN, the present Ti-Si-N coatings deposited at ~250 °C did not show any
mechanical properties anomaly near the percolation threshold. Whether this is still the case for the high temperature deposited Ti-Si-N coatings awaits clarification.
Bibliography


76. Some XANES data from the first series of specimens deposited at ~250°C are referred to when describing the bonding environment of both Ti and Si atoms in Ti-Si-N coatings.


81. F. Vaz et al., Residual stress states in sputtered Ti<sub>1-x</sub>Si<sub>x</sub>N<sub>y</sub> films, Thin Solid Films 402, 195 (2002).


Vita

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