Deposition and Characterization of Ceramic Thin Films and a New Experimental Approach to Evaluate the Mechanical Integrity of Film/Substrate Interfacial Layers

Yang Mu

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DEPOSITION AND CHARACTERIZATION OF CERAMIC THIN FILMS AND A NEW EXPERIMENTAL APPROACH TO EVALUATE THE MECHANICAL INTEGRITY OF FILM/SUBSTRATE INTERFACIAL LAYERS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Mechanical Engineering

by

Yang Mu

B.S., Beijing Institute of Technology, 2006

August 2015
This thesis is dedicated to my beloved grandmother
ACKNOWLEDGEMENTS

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ABSTRACT

Due to their corrosion resistance, high temperature stability, high strength, and high hardness, refractory ceramic thin films and coatings have been utilized for surface engineering of mechanical components and mechanical fabrication tools. Adhesion between ceramic thin films and coatings and the substrate is of critical concern for performance and life time of coated systems. In this dissertation, a custom designed and constructed ultra-high-vacuum (UHV) vapor phase deposition system was used for the preparation of ceramic thin films through low-pressure high-density plasma assisted physical vapor deposition (PVD) methods. Deposited thin films were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), instrumented nanoindentation, focus ion beam (FIB) scanning electron microscope (FIB SEM), and transmission electron microscope (TEM). The effective interfacial shear strength between TiN and CrN thin films and their substrates was evaluated through a substrate-tension method and a newly introduced experimental testing method involving FIB script-milling of film/substrate specimens into micro-pillars and instrumented compression testing performed on such micro-pillars. This micro-pillar testing protocol was further used to experimentally demonstrate, for the first time to our knowledge, a size effect in the shear strength in the configuration of confined shear plastic flow of ductile thin layers. This latter experiment furnishes new and fundamental data for micron scale plasticity theories.
CHAPTER 1
INTRODUCTION

1.1 Applications of Thin Films in Macro-Scale Devices

Thin films are widely used in surface engineering to improve the performance of the near-surface region by modifying the surface chemical and mechanical properties. For example, diamond-like carbon (DLC) coatings are an excellent candidate for application to automotive engines due to their low boundary friction, good wear resistance, and suitability to serve as a solid lubricant [1]. DLC also improves the tribological performance of die/metal-piece systems [2]. Highly hydrogenated DLC deposited by PACVD is a potential coating material for the ball bearings for aerospace craft because of its low friction and long wear time in both vacuum and in-air environments [3]. Thermal barrier coatings (TBCs) are considered as the candidate layer for aerospace sandwich panels [4]. A critical requirement for all these applications is high quality bonding between the coating and the substrate. Quantitative evaluation of the mechanical integrity of the interface region between coatings and substrates is therefore important.

1.2 Applications of Thin Films in Micro-Scale Devices and Microfabrication

The global microelectromechanical systems (MEMS) market has grown from its infancy in early 1980s [5] to be worth about ten billion U.S. dollars in 2011 [6]. So far, major categories of commercialized MEMS devices, including pressure sensors, accelerometers, gyroscopes, deflectable optical mirrors, have been fabricated from Si-based materials following protocols developed for integrated circuit processing industries [7]. Although metal-/alloy-based microsystems products are much rarer at present, their unique collection of physical properties enables construction of certain microdevices with either performance advantages over Si-based counterparts or no Si-based analogs at all. Piezoelectric Pb(Zr, Ti)O₃ (PZT) thin films have been vapor deposited directly onto 50μm thick Ti substrates [8]. Using the PZT/Ti materials
combination, MEMS scanner mirrors have been built with increased fracture resistance as compared to Si-based counterparts [9]. Free-standing microscale structures made of electrodeposited Co-Ni alloys have been demonstrated, with soft magnetic properties suitable for magnetic field actuation [10]. Micro grippers and other microscale actuators are enabled by the use of shape memory alloys in microsystems [11]. Wings for micro aerial vehicles were fabricated out of the Ti-6Al-4V alloy because of its mechanical properties [12]. The incorporation of metals/alloys into microsystems enables different device configurations/designs, and metal-based microsystem products hold promise technologically for improved performance or expanded functionality and commercially for additional applications and associated revenue streams.

In addition to microscale actuators and sensors, the continued trend towards miniaturization of electronic and medical devices demands efficient manufacturing of small metal-based parts, including miniaturized connector pins, sockets, screws, springs, etc [13]. To satisfy such demands, there are ongoing efforts focused on extending macroscale metal forming technologies down to the microscale [13,14]. Studies of micro bending [15], micro extrusion [16], and micro die upsetting [17] have all been conducted.

1.3 Thin Film Deposition Technologies

Over the last century, a variety of thin film deposition techniques have been developed with the development of vacuum technologies and plasma technologies. The general classification of deposition process was divided into four different groups: gaseous state processes, solution state processes, molten or semi-molten state processes, and solid state processes [18].
Physical vapor deposition (PVD) is one of the gaseous state processes that are used to deposit onto various substrates thin films of desired materials. One of the earliest vapor phase deposition experiments, dating back to the 19th century, is credited to Grove when he found metal deposition in a cathode glow discharge through the process later known as “sputtering deposition” [19]. Evaporation is the other main PVD method, which was discovered by Faraday in his experimentation dealing with fusing like metal wires, thereby evaporating thin films [20]. These two methods have been developed into two major PVD processes today: sputtering and evaporation. Both are now widely applied in laboratories and industrial productions [1,2,3,4]. However, thin films deposited through the evaporation method may not have the same stoichiometry as the starting material, when multicomponent sources are used. Sputtering of multicomponent targets usually results in deposited films with closely matching stoichiometries. Sputtering can also produce low impurity thin films with increased uniformity.

Sputtering deposition takes place in a vacuum environment, and is not a very simple process. To deposit the thin film successfully, effects of the film-growing environment and the vapor-phase fluxes need to be considered. Major factors involved with the thin film deposition process in a vacuum are: pressure of the vacuum system, mean free path (MFP) of the gas molecules, ratios between the partial pressures of reactive gases and the inert working gas, and the ratio between the materials flux arriving at the substrate surface and the reactive gas surface impingement flux [21]. According to kinetic theory [22]

$$\lambda = \frac{1}{2^{1/2} \pi d_0 n},$$  \hspace{1cm} (1.1)

Where $\lambda$ is the mean free length, $d_0$ is the molecular diameter and $n$ is the gas density. At room temperature,
\[
\lambda(cm) = \frac{0.005}{p(Torr)}.
\]  \hspace{1cm} (1.2)

Lower the pressure in the system would reduce the impurities left in the vacuum resulting in improve the purity of the thin film.

1.3.1 DC Sputtering

DC diode glow discharge is the simplest of the sputter deposition techniques. Figure 1.1 shows a scheme of DC diode sputtering. A high voltage DC power is applied to the sputtering target. Free electrons will be accelerated in the electric field generated between the sputtering target (cathode) and the substrate (anode). These electrons will collide with carrier gas atoms, which are usually Ar. Two basic reactions would happen depending on electron energy

\[
e + Ar \rightarrow Ar^* + e \rightarrow Ar + e + hf
\]

(1.3)
\[
e + Ar \rightarrow Ar^* + e + e
\]

(1.4)

Where \( h \) is the Planck constant, \( f \) is the frequency of the photon [23].

![Scheme of DC Sputtering](image)

Figure 1.1 Scheme of DC Sputtering [24]

Equation 1.3 shows that excitation transition of the Ar atom after collision with a low energy electron. During this transition, the emission energy will be accompanied by the
formation of a photon, which will cause the gas glow. The wavelength of the photon will be corresponded to the emission energy. Equation 1.4 shows ionization of the Ar atom after collision with a high energy electron. A secondary electron was generated in this collision. The positive Ar ions will be accelerated in the E-field to bombard the target. Target material atoms will be emitted from the surface and condense on the substrate surface to form the thin film. In this process, a secondary electron will be generated as well if the positive ions are energetic enough. Only when enough secondary electrons are emitted during the bombardment, the plasma would become self-sustaining. Since most secondary electrons are emitted from the target, high voltage between the target and substrate should be applied to create high energy ionized Ar.

Near the target surface, a dark zone will form due to the positive ion build up, where the applied target potential drops [21]. The thickness equals to the mean free path of secondary electrons. Therefore, the distance between two electrodes should be larger than this dark zone length to maintain a steady discharge. Increasing the sputtering pressure would help to sustain the plasma: according to Equation 1.2, the higher the pressure, the shorter the mean of path. Ions or electrons would have higher probabilities for collisions. But this increased sputtering pressure would significantly reduce the sputter deposition rate.

1.3.2 DC Magnetron Sputtering

In order to sustain the plasma and also maintain a good sputtering rate, dc magnetron sputtering would be introduced. The magnetic field applied near the cathode would confine the movement of the electrons to be near the target to sustain plasma. The important advantage of magnetron sputtering is that the operation pressure could be reduced and voltage applied to the cathode could be reduced as well.
1.3.3 Plasma Assisted Sputtering

The plasma generated by the DC glow discharge mainly depends on the voltage applied to the cathode, it is hard to exercise independent control of plasma parameters. For this reason, a separate plasma generator could be applied in addition to the DC glow discharge. With the help of the independently generated plasma, the sputtering rate will be enhanced, but also the re-sputtering rate will be increased.

1.3.4 Reactive Sputtering

Reactive sputtering is usually used to form compounds with a metal as one of its components. Metallic targets are sputtered in a mixture of a reactive gas and an inert gas, which is typically Ar. During the sputtering process, ions, radicals, and atoms of the reactive gas will bombard the substrate surface, and be condensed together with the sputtered target atoms onto the substrate to form the thin film. The most common compounds deposited through this method are oxides, carbides, nitrides, and mixtures such as oxycarbides and oxynitrides.

Unlike DC sputtering, the compound that forms on the substrate surface would be condensed on the target surface as well. Initially, with the introduction of the reactive gas into the deposition system, the deposition pressure in the system would remain as the initial introducing pressure, since the reactive gas would react with the sputtered atom and will be removed from the gas phase. The target will remain in metallic state in this stage. The formation of the compound on the target surface will lower the target sputtering rate. With increased introduction of the reactive gas into the system, the target surface will transition from the metallic state into the compound state, since rate of compound formation will exceed the target sputtering rate. A compound layer will thus form on the target surface. This transition will be accompanied by a sharp decrease of the deposition rate, and a sharp increase of the
system pressure [21]. Figure 1.2(a) illustrates typical DC reactive sputtering of Ti in an Ar/N\textsubscript{2} mixture to form TiN thin films, where the system total pressure changes because of the change in N\textsubscript{2} partial pressure. Figure 1.2(b) shows typical DC reactive sputtering of Cr in an Ar/N\textsubscript{2} mixture to form CrN thin films, where the system total pressure changes because of the change in N\textsubscript{2} partial pressure.

Figure 1.2 Working pressure in the vacuum plotted as the equivalent nitrogen flow: a) Ar/N\textsubscript{2} mixed gas with Ti target; b) Ar/N\textsubscript{2} mixed gas with Cr target

1.4 Thin Film Adhesion Tests

With the development of functional thin films and thin film deposition techniques, thin films are widely used in industrial products and academic laboratories [1,2,3,4]. Knowing the mechanical integrity of the interfacial region between thin films and their substrates becomes critical since it is the key to exploit other thin film properties and their applications. Over the past several decades, a lot of efforts were spent on measuring the interfacial bond strength. However, no direct measurement method was successfully developed [25].

Conventionally, pull and peel [26], three point bend [27], scratch test [25,28,29] were used to evaluate the interfacial adhesion. Though numerous adhesion measurement methods were established [30], no single technique is well accepted to everyone or applicable to all the
substrate–coatings combination system. Figure 1.3(a) shows a direct pull-off test. A normal force \( F \) is applied to a member glued to the coating. The interfacial separation stress of the coating could be calculated by measure the contact area \( A \) [25].

\[
\sigma = \frac{F}{A}
\]  

Figure 1.3 Typical adhesion test: a) Pull and peel test; b) Tape test; c) scratch test

Figure 1.3(b) shows an adhesive tape test. A force is applied to the adhesive member, and it could be applied with an angle to the coating. The difficulty of these types of techniques is that the adhesion between the member and coating needs to be stronger than the adhesion between coating and substrate, only then can it give an estimation of the interfacial strength. Figure 1.3(c) shows the scratch test. The indenter will slip into the film/coating with the increasing vertical load. The coating/film would be scratched away by the increased normal load when tangential sliding occurs. The critical normal load at which coating fracture/spallation occurs could be measured through this method. However, the configuration is usually too complicte to calculate the fundamental interfacial mechanical properties. New method like tension of ductile substrates [31], indentation [32], and laser spallation [33] are developed recently in addition to the pull and scratch tests.
In the laser spallation configuration, a high-fluence laser is travelling toward the film/substrate region. At the interface, the reflection of the laser-induced strain pulse will induce the tensile stress which would cause spallation of the coating. From the critical laser fluence, the interfacial tensile strength could be derived [33].

In the tension test configuration, brittle thin film was deposited onto a ductile substrate. After the tension load was applied, both the thin film and the substrate experienced the same strain. The strain will be elastic in the film and plastic in the substrate and induce cracks generated in the film, which is perpendicular to the tension load direction. When such transverse cracks occur, further tensile loading of the film occurs through shear of the film/substrate interfacial region. The transverse crack density in the film will grow until it reaches a plateau value, at which point the spacing between adjacent cracks will remain roughly constant without any further decrease as the substrate plastic strain grows beyond this point. Combine the initial tensile stress at which transverse crack forms in the film and the crack density at or after the plateau point, an effective interfacial shear strength could be derived [31].

1.5 Size Effect in Thin Film Interlayer

Size effects in plasticity have been documented through many experiments over the past two decades, including torsion of wires [34], bending of beams [35], and indentation by pyramidal [36], rectangle strip [37] and diamond wedge [38] indenters. Figure 1.4(a) shows that the hardness of single crystal Al increases dramatically as the Berkovich indenter diameter decreases. Size effects were also observed in uniaxial compression tests on cylindrical micro-pillars cut by focus ion beam (FIB) milling [39]. Figure 1.4(b) shows that the yield strength of Ni based micro-pillars decreases significantly as the pillar diameter increases.
Shear plastic flow in confined thin layers is also of significant interest since it is one of the typical cases studied in the development of strain gradient plasticity (SGP). According to SGP, size effects in shear flow of confined thin layers are associated with geometrically necessary dislocations (GNDs) generated when dislocations are blocked at the interfaces. Numerous models were used to analyze the mechanical reaction of confined thin films depending on their thickness [40,41,42,43,44], and they more or less predict similar behaviors. Figure 1.5(a) shows the shear stress trend by the change of the film thickness based on two theories. Figure 1.5(b) shows the comparison of two gradient theories.

Experimental attempts to measure shear plastic flow in confined thin layers was carried out by V. Tagraeli and N. Fleck [45]. Thin Al foils of different thicknesses were sandwiched in between and confined by Al2O3 ceramic layers. Shear loading of the thin Al layers was induced by tensile loading of Al2O3. However, this experiment yielded no conclusive results due to experimental difficulties.
Figure 1.5  a) Shear stress trend by the change of thin film thickness in two theoretical models [41]; b) An elasto-plastic thin film with thickness $h$ on an elastic substrate subjected to a biaxial tensile strain [43]

1.6 Outline of the Dissertation

Chapter 2 describes basic design of a low-pressure, high-density plasma assisted, hybrid, physical/chemical vapor deposition (PVD/CVD) system. An ultra-high vacuum (UHV) system was built up and an inductively coupled plasma (ICP) was used to generate a plasma independent of magnetron source operations. The preparation of ceramic titanium boride ($\text{TiB}_x$) films was presented in Chapter 3, together with its characterization and application. Meanwhile, how the settings of the ICP could significantly change the mechanical properties of the $\text{TiB}_x$ thin film was shown. Chapter 4 showed two methods of measuring the effective interfacial strength between ceramic thin films and substrates. Chapter 5 documents the experimentation which led to the first measurement of the dependence of shear flow stress on layer thickness in the geometry of confined shear flow of thin Cu films. Chapter 6 demonstrates the shear stress flow in two different geometries with the dependence of the interlayer thickness between two rigid bodies. Chapter 7 provides a brief result of the thesis.
1.7 References


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CHAPTER 2
DESIGN AND CONSTRUCTION OF A HIGH-DENSITY PLASMA ASSISTED ULTRA HIGH VACUUM (UHV) PHYSICAL VAPOR DEPOSITION (PVD) SYSTEM

As a part of work performed during this dissertation study, a previously existing plasma assisted vapor deposition system was modified and updated. The updated system enables the deposition chamber to be maintained under ultra-high vacuum (UHV) conditions at all times, with sample transfer from a load lock chamber to the deposition chamber occurring under high vacuum conditions. In what follows, details of system design and construction are given.

2.1 Vacuum System

The entire deposition system is equipped with two turbo molecular pumps, one cryogenic pump, one ion pump, two ion gauges (IG), one residual gas analyzer (RGA), a heatable sample stage, four balanced-magnetron sputtering guns, and three gate valves. The schematic layout of the deposition system is showed in Figure 2.1. The entire deposition system consists of two

Figure 2.1 Deposition system layout.
sections separated by a gate valve: a sample load lock section to load/unload samples and a deposition section maintained under UHV conditions at all times [1].

The load lock chamber is pumped by a turbo molecular pump (Pfeiffer, N₂ pumping speed 67liter/s) backed by a rotary mechanical pump (Pfeiffer, N₂ pumping speed 5m³/hr). Once a cleaned sample is loaded into the chamber, it usually takes about 6 hours to reach the target vacuum level of $\sim 1 \times 10^{-6}$ Torr. The deposition chamber is pumped by a combination of pumps: 1) a turbo molecular pump (Pfeiffer, N₂ pumping speed 260liter/s) backed by a rotary mechanical pump (Pfeiffer, N₂ pumping speed 6m³/hr), 2) a sputter ion pump (Gamma Vacuum, N₂ pumping speed 40-75liter/s), and 3) a cryogenic pump (Sumitomo, air pumping speed 1500liter/s). A RF quadrupole mass spectrometer (RGA, Stanford Research Systems) is used to measure the residual gas content in the deposition chamber, assess whether all pumps are under proper working conditions, and monitor gaseous impurities within the deposition system and possible system leakage. The entire deposition system is sealed with Conflat™ type Cu gaskets and Viton O-rings. In addition, all the gas lines are sealed with VCR™ type Ni gaskets.

The entire deposition system is fully sealed, together with the pumping system, RGA, and ion gauge. It is first pumped down by the turbo molecular pump, which is backed up by the connecting rotary mechanical pump [2]. This set up reduces the back-streaming of the mechanical pump oil. As soon as the pump system starts to work, heating tapes wrapped around the outside of the chamber shell help heat up the entire system. The chamber wall temperature reaches $\sim 100^\circ$C after an hour. As a result of this baking, gases previously trapped onto the inner walls of the chamber are gradually released. A 48-hour or longer baking process is needed to achieve an ideal base pressure of $3-5 \times 10^{-9}$ Torr, with the help of the cryogenic and ion pumps. Typical RGA graphs displayed in Figure 2.2(a), (b), (c) show the gaseous content left in the
chamber before, during, and after the baking process, and clearly indicate that the heating/baking process helps to accelerate gas desorption (mainly water) and achieve better ultimate base pressure. At base pressure, \( \text{O}_2, \text{H}_2\text{O}, \text{N}_2 \) the common residual gases are close to the background level of the RGA, with \( \text{H}_2 \) dominating the residual gas content after baking.

![Graph showing residual gas levels before and after baking.](image)

Figure 2.2  The gas left in chamber: a) Residual gas before the baking process; b) Residual gas after baking for 12 hours; c) residual gas after at least 48 hours baking process.

In addition to chamber enclosures, pumps, and RGA, more components are attached to the vacuum system, mainly the magnetron sputter guns, sputter deposition carrier gas lines, and dielectric plates for coupling an inductively coupled plasma (ICP) into the deposition chamber. Once these additional components are attached, the same baking procedure is applied, resulting in the same base pressure of \( 3\text{-}5 \times 10^{-9} \text{Torr} \) or less. Individual ultra-high-purity (99.999+%) gas bottles connect through UHV grade, totally isolated gas lines to separate, UHV compatible mass flow controllers (MKS, model#2179A), which are connected into a gas mixing manifold before
introduction into the deposition chamber. The two mostly commonly used gases for this dissertation work are Ar and N₂.

The manually operated gate valve between the turbo molecular pump and the deposition chamber is used to adjust the effective pumping speed and consequently the total pressure within the deposition chamber during the deposition process. The gate valve between the cryogenic pump and the deposition chamber is used to isolate the cryogenic pump from the input gas stream during the deposition process.

2.2 Sample Transfer Mechanism

A sample holder and sample transfer system, shown in Figure 2.3(a), are custom designed for thin film deposition onto two-inch diameter Si wafers with/without substrate heating. The round-shaped sample holder has a clearance hole in the center, into which cleaned Si wafers will be placed. For ease of Si wafer placement, the clearance hole has a crater rim with a diameter slightly larger than two-inch and a depth slightly larger than the thickness of typical Si wafers. A wafer is held in place by another stainless steel holding ring, with a clearance hole of one-inch diameter in the center. This holding ring is held onto the sample holder by screws. This design creates a cavity-like placement for the Si wafer, designed for a more even temperature distribution on the wafer in case it is heated up during deposition.

Three set screws and three L-shape openings are evenly distributed on the sidewall of the sample holder. This sample holder will be first loaded onto the load lock transfer piece (after the Si wafer is loaded), which has three evenly distributed arms. This transfer piece is connected to the stainless steel rod manipulator housed within the load lock chamber, and could move horizontally. On each arm, it has an “L-shape” opening, compatible with every set screw on the sample holder. With this “set screw-L shape” mechanism, the sample holder could be attached to
the transfer piece in the load lock, and transferred horizontally into the deposition chamber once the isolation gate valve opens.

![Diagram of sample transfer system and heating stage]

Figure 2.3  a) Scheme of sample transfer system; b) heating stage

In the deposition chamber, one stainless steel tube is placed in the center, with one end connected to a motorized stage and the other end connected to a stainless steel cylindrical transfer piece. The sample holder could be transferred onto the cylindrical transfer piece through the “set screw L-shape” mechanism. After the L-shape openings on sample holder get attached by the set screws on its sidewall, the holder will be loosened from the other stainless steel piece on the load lock transfer rod. The stainless steel tube could move up and down on the motorized stage and rotate at a pre-set speed. The sample holder now could be transferred down to the actual deposition chamber, equipped with balanced magnetron sputtering guns and ready for additional steps in the deposition process.

The cylindrical transfer piece and the sample holder combine to create a black-body cavity type box for the heater placed in its center, enabling more efficient and uniform heating of the Si wafer when heating is needed. By using the same transfer method in reverse, the sample could be transferred back into the load lock chamber after deposition is done.
2.3 Heating Stage

A BORALECTRIC™ heater (Momentive Performance) is used as the heating source in this vacuum system. Figure 2.3(b) shows the heating stage in detail. The heater is connected to the L-shaped Cu wire through a round-shaped quarter-inch thick ceramic plate (used for isolation and fixing the heater in position) by stainless steel screw, and isolated to this ceramic plate by wrapping another ceramic tube outside the screw. The two Cu wires, supplying the necessary electric current to heat up the Boralectric heater, go up to the stainless steel tube attached on the top of the cylindrical transfer piece, and go through the ceramic tube pre-installed in the stainless steel tube. This will keep the two Cu wires in position and separated from each other. On the other end of the two Cu wires are electric cables covered with glass fiber. These two cables will be connected to the ceramic-metal feed-through that provides the DC power from outside the vacuum system. This heater stage circuit will tremendously reduce the possibility of electrical shorts when bias voltages are applied to the sample holder while the sample heater is working.

2.4 Thin Film Deposition

Figure 2.4 shows a schematic of typical plasma assisted thin film deposition. Planar Cu induction coils are placed on the vacuum exterior side close to two parallel quartz windows on the deposition chamber. The two windows serve as the dielectric plates through which inductive coupling occurs between the external Cu coils and the ICP inside the deposition chamber [3]. Each Cu coil is connected to a 13.56 MHz RF power supply, through a commercial auto-tuning network. Four DC magnetron sputtering guns are placed with a 60-deg orientation to the inductively coupled plasma column. The electrically isolated sample holder is placed at the center of the deposition chamber, and could be rotated as a fixed rate or placed at a stationary position facing one or more sputter targets. An independently controlled bias voltage could be
applied to the sample to control the energy of ionic species hitting the substrate surface during deposition. By controlling the input power to the external induction coils, the plasmas density of the ICP column can be tuned independently, thus achieving separate control of the flux and energy of ionic species bombarding the substrate surface. Such control of gas phase ionic species makes the thin film deposition process more tunable. For refractory ceramic thin films, this increased deposition control enables deposition of fully dense films and some degree of control in the level of residual stress within the films.

Figure 2.4 Plasma assisted deposition layout

2.5 References


CHAPTER 3
LOW TEMPERATURE DEPOSITED TITANIUM BORIDE THIN FILMS
AND THEIR APPLICATION TO SURFACE ENGINEERING OF MICROSCALE MOLD INSERT

3.1 Introduction

Direct replication of microscale structures in metals by compression molding using microscale mold inserts is a promising technique for low-cost, high-throughput, fabrication of metal-based microdevices [1]. Extensive plastic flow during micromolding brings fresh metal-to-metal contact between the mold insert and the molded material. This contact can cause chemical reactions between the insert and the molded metal, leading to damage of molded parts and failure of the mold insert. Engineering the near-surface chemical and tribological properties of mold inserts is critical to alleviate such damage and improve insert life. Depositing suitable ceramic thin films conformally onto mold inserts with non-planar microscale features has been shown to be a feasible avenue for engineering surfaces of microscale mold inserts [2,3], and has led to demonstrations of compression micromolding of a wide range of metals and alloys, including Al [4], Cu [5], Ni [6], and NiTi [7].

Elemental Al and Al alloys possess good thermal conductivity and are relatively inexpensive. Microscale structures made of Al and Al alloys are of particular interest as building blocks for metal-based microchannel heat exchangers [8]. Although successful Al micromolding was demonstrated with mold inserts deposited with a conformal, amorphous hydrogenated carbon (a-C:H) based coating layer [4], the degradation of a-C:H films at medium temperatures of 300-500 °C [9,10] limits their long term stability and consequently life of a-C:H coated mold inserts. Thin films of titanium diboride (TiB$_2$) have been deposited by different vapor phase deposition techniques: chemical vapor deposition (CVD) at temperatures >900 °C from gaseous TiCl$_4$, BCl$_3$, and B$_2$H$_6$ precursors [11,12]; glow-discharge assisted CVD at 480-650 °C from
gaseous TiCl₄ and BCl₃ precursors [13]; inductively coupled plasma (ICP) assisted CVD at 250-400 °C from gaseous mixtures of TiCl₄, BCl₃, H₂, and Ar [14]; triode magnetron sputtering of TiB₂ targets at ~450°C [26]; unbalanced magnetron sputtering at 300 °C from stoichiometric TiB₂ targets [15]. Thin films of TiB₂ are known for high chemical stability, and show promise for Al dry machining applications [16,17].

In this paper, we report low temperature deposition of titanium boride (TiBₓ) thin films by balanced magnetron sputtering in Ar and ICP assisted balanced magnetron sputtering in Ar from stoichiometric TiB₂ targets. Chemical, morphological, structural, and mechanical characterizations of deposited TiBₓ films were carried out with X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and instrumented nanoindentation. TiBₓ thin films deposited at lower plasma densities via balanced magnetron sputtering were contrasted to those deposited at much higher plasma densities due to the ICP assist. The potential of applying TiBₓ thin films conformally deposited onto non-planar mold inserts to microscale compression molding of Al was explored. Fully dense TiBₓ thin films deposited conformally onto microscale Ta inserts are shown to withstand repeated contact with Al at molding temperatures of ~450 °C without delamination, and therefore of potential use for engineering insert surfaces for Al micromolding.

3.2 Experimental Procedures

Deposition of TiBₓ films was carried out in an ultra high vacuum physical/chemical vapor deposition (PVD/CVD) tool. This tool housed a 13.56 MHz ICP and four balanced magnetron sputtering sources. The ICP and the sputtering sources could be operated independently [18,19]. A schematic of the deposition chamber is shown in Figure 3.1, which had a base pressure of < 4×10⁻⁷ Pa. Cleaned substrates were first loaded into a load lock
Figure 3.1  A schematic representation of the deposition chamber. This top view shows four balanced magnetron sources with two facing elemental Cr targets and two facing TiB\textsubscript{2} targets, and two facing induction coils outside the chamber for ICP generation within.

chamber, separated from the deposition chamber with a gate valve. Evacuation of the load lock chamber proceeded until its pressure reached ~10\textsuperscript{-5} Pa, the substrate was then transferred into the deposition chamber. The four 75 mm diameter balanced magnetron sources faced the center of the deposition chamber. The substrate was placed in the chamber center, and rotated at ~12 rpm during deposition. Two facing stoichiometric TiB\textsubscript{2} (99.99\%) targets and two facing elemental Cr (99.99\%) targets were operated in the dc current-controlled mode. An Ar ICP was ignited within the deposition chamber by coupling through dielectric windows to external induction coils.

A series of TiB\textsubscript{x} thin films were deposited onto Si(100) wafers, 50mm in diameter, without additional heating. The Si(100) wafers were cleaned ultrasonically in methanol and blown dry before loading into the deposition system. The Ar flow was set at 20 sccm during the entire deposition process. The pumping conductance was adjusted to achieve total Ar pressures of 0.5-1.5 Pa. An electrical bias voltage of -50 V was applied to the substrate throughout the deposition process. Prior to deposition, the substrate surface was cleaned by ICP etching without
energizing the TiB$_2$ and Cr targets. The total input power to the ICP induction coils was 1000 W during etching, divided equally between the two coils.

After plasma etching, a Cr interlayer was immediately deposited onto the substrate by balanced magnetron sputtering of the two Cr targets without ICP assist. During Cr deposition, the two facing Cr targets were operated at 1.0 A. The deposition of a TiB$_x$ top layer commenced immediately after Cr interlayer deposition. Balanced magnetron sputtering of the two facing TiB$_2$ targets was conducted with and without ICP assist. During TiB$_x$ deposition, the two facing TiB$_2$ targets were operated at 0.5 A. With ICP assist, the total input power to the ICP induction coils was set at 1000 W, divided equally between the two coils. Without ICP assist, the total ICP input power was set to zero. Minor variations of deposition parameters were made, such as the total Ar pressure, the Cr interlayer thickness, or the TiB$_x$ layer thickness. Table 3.1 lists the deposition parameters for a number of TiB$_x$/Cr/Si(100) specimens, and illustrates such minor deposition parameter variations. It was found that such minor variations did not yield any significant difference in the resulting films.

The TiB$_2$ target power density was estimated from the total target power during sputtering together with an estimation of the area of the balanced magnetron race track on the target, and was determined to be ~100W/cm$^2$ with or without ICP assist. Previous measurements of plasma potential and ion current density within the ICP assisted CVD/PVD environment were performed using an electron emissive wire probe and a conventional planar Langmuir disk probe [20]. The densities of the low-pressure quasi-neutral plasmas were calculated from data on measured ion current densities [21]. The addition of the ICP raises the plasma density within the deposition chamber to ~10$^{11}$ cm$^{-3}$, at least one order of magnitude higher as compared to the case of balanced magnetron sputtering without ICP assist [20]. The plasma present near the substrate
Table 3.1  Conditions for deposition of a series of TiB$_2$/Cr/Si(100) specimens

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate bias (V)</th>
<th>Substrate etching</th>
<th>Cr interlayer</th>
<th>TiB$_2$ top layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ar pressure (Pa)</td>
<td>ICP input power (W)</td>
<td>Time (min)</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>1.33</td>
<td>1000</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.67</td>
<td>1000</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.67</td>
<td>1000</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.67</td>
<td>1000</td>
<td>5</td>
</tr>
</tbody>
</table>

surface during deposition causes a rise in substrate temperature, even without additional substrate heating. Previous substrate temperature measurements during deposition showed substrate temperatures of ~210 °C during etching, of ~140 °C during deposition without ICP assist, and of ~225 °C during ICP assisted balanced magnetron sputter deposition [20,22]. The TiB$_x$ deposition rates were respectively ~220nm/60min and ~360nm/60min with or without ICP assist, or ~0.6 Å/s to ~1.0 Å/s. The lower TiB$_x$ deposition rate with ICP assist is consistent with increasing ion bombardment of the growth surface during deposition.

Chemical characterization of as-deposited TiB$_x$/Cr/Si(100) specimens was carried out with XPS on a Kratos AXIS165 system, using a monochromatic Al Kα excitation source. All XPS spectra were collected after specimen surface sputter cleaning using a 5 kV Ar$^+$ ion gun operated at a total output current of 15 mA. The duration for cleaning was determined such that no perceptible change in XPS spectral features could be affected through further sputtering, and ranged from ~10 min to ~100 min. Chemical compositions were obtained from raw XPS spectra using Kratos supplied sensitivity factors.
The surface and cross-sectional morphology of as-deposited TiB_x/Cr/Si(100) specimens were examined on a FEI Quanta3D FEG electron column/focused Ga^+ ion beam column dual-beam instrument (FIB). Cross-sectional transmission electron microscopy (TEM) studies of TiB_x/Cr/Si(100) specimens were carried out on a JOEL JEM2011 microscope operated at 200 kV. Cross-sectional TEM specimens were prepared by FIB ion beam cutting followed by lift-out with an OmniProbe W probe installed within the FIB instrument, and thinned to electron transparency using 30 kV Ga^+ ion beams with successively decreasing currents. Additional SEM examinations were performed on a Hitachi S3600N microscope.

Instrumented nanoindentation of as-deposited TiB_x/Cr/Si(100) specimens was carried out on a MTS Nanoindentener XP System. A Berkovich diamond indenter was used. Calibration of the instrument load frame stiffness and the indenter tip area function were determined with a factory-supplied fused silica specimen. A range of calibration loads were applied, ranging from ~4x10^1 to ~4x10^4 µN, corresponding to an indenter contact depth (h_c) range from ~10 to 590 nm. Several indents were conducted at each load. Indentations on TiB_x/Cr/Si(100) specimens were carried out at multiple loads, ranging from ~160 to ~40960 µN, with multiple indents performed at each load. Values of the indentation modulus, E_{ind}=E/(1-v^2) where E and v are respectively the Young’s modulus and the Poisson’s ratio, and the hardness, H, were obtained from experimental load vs. displacement curves.

TiB_x thin films were deposited onto non-planar Ta mold inserts following deposition procedures outlined above, with ICP assist. These Ta inserts consisted of a series of parallel microscale rectangular protrusions, fabricated on the surface of a flat Ta coupon via micro electrical discharge machining (µEDM). As-machined Ta inserts were subjected to electrochemical polishing (ECP) to remove an altered surface layer due to the µEDM process.
Further details on fabrication of the Ta inserts were presented elsewhere [5]. Surfaces of Ta inserts were etched with an Ar ICP. An elemental Cr interlayer was deposited onto the Ta inserts immediately after the surface etch. Deposition of the TiB\textsubscript{x} top layer, typically with a duration of \(~75\) min, followed immediately after the Cr interlayer deposition with ICP assist.

3.3 Results and Discussion

Figure 3.2 shows typical XPS survey spectra collected from the top layers of TiB\textsubscript{x}/Cr/Si(100) specimens. Signals from Ti2s, Ti2p, Ti3s, Ti3p, B1s, and Ar2p levels are clearly visible. To remove oxygen surface contamination due to specimen handling in air, Ar\textsuperscript{+} ion sputter cleaning of the specimen surfaces was carried out in-situ the XPS analysis chamber. For the specimen deposited with ICP assist, Run 2 in Table 3.1, 25min of sputter cleaning removed all of the oxygen signature in the XPS survey spectrum, as shown in Figure 3.2(a), such that the O1s signal is at the background level. Figure 3.2(b) shows, in contrast, a clear O1s signal persisting in the XPS survey spectrum of the specimen deposited without ICP assist, Run 3 in Table 3.1, even after \(~100\)min of sputter cleaning. XPS data on this TiB\textsubscript{x} layer after prolonged sputter cleaning suggest that, in addition to surface contamination, oxygen was incorporated into the bulk of this TiB\textsubscript{x} layer. The overall compositions of the TiB\textsubscript{x} top layers shown in Figure 3.2(a) and 3.2(b) were determined as \(~\text{Ti}_{26}\text{B}_{74}\), exhibiting no significant difference whether ICP assist was employed during deposition. Thus XPS data show that the TiB\textsubscript{x} top layer is over-stoichiometric with respect to TiB\textsubscript{2}, with \(x\) close to 3.

Figure 3.3(a) shows the corresponding high-resolution Ti2p XPS spectra collected from two TiB\textsubscript{x} top layers, deposited with ICP assist (Run 2 in Table 3.1) and without ICP assist (Run 3 in Table 3.1). Measured Ti2p\textsuperscript{3/2} binding energies from the TiB\textsubscript{x} top layers are 454.6 eV, independent of whether the ICP assist was employed during deposition and consistent with
previous XPS studies on TiB$_2$, which showed Ti2p$^{3/2}$ binding energies in the range of 453.8-454.4 eV [23]. Figure 3.3(b) shows the corresponding high-resolution B1s XPS spectra. For the

Figure 3.2 XPS examination of TiB$_x$/Cr/Si(100) specimens: (a) an XPS survey spectrum of a TiB$_x$ top layer deposited with ICP assist; (b) an XPS survey spectrum of a TiB$_x$ top layer deposited without ICP assist.

Figure 3.3 High-resolution XPS studies of the TiB$_x$ top layers: (a) Ti2p spectra of the two TiB$_x$ top layers deposited with and without ICP assist; (b) O1s spectra of the two TiB$_x$ top layers deposited with or without ICP assist.

TiB$_x$ top layer deposited with ICP assist (Run 2 in Table 3.1), the only B1s binding energy peak observed is at 187.9 eV. For the TiB$_x$ top layer deposited without ICP assist (Run 3 in Table 3.1), the major B1s binding energy peak is also observed at 187.9 eV. However, a minor peak is
apparent at 193.2 eV. Previous XPS studies showed that the B1s binding energies for TiB₂ and B₂O₃ are at 187.3 eV and 193.1 eV, respectively [24]. Therefore the high-resolution XPS data shown in Figure 3.3 indicate that the dominant Ti and B atom bonding environments within the TiBₓ top layers are consistent with TiB₂ bonding. Data shown in Figure 3.3 are further consistent with the XPS survey spectra shown in Figure 3.2, and indicate that the oxygen content within the TiBₓ top layer deposited with ICP assist is insufficient to cause any additional binding energy signature. In contrast, the oxygen content within the TiBₓ top layer deposited without ICP assist is sufficiently high, even after Ar⁺ sputter cleaning of the surface, so as to causing a boron-oxygen binding energy signature consistent with bonding in B₂O₃.

Figure 3.4 shows surface morphologies of TiBₓ top layers, typical for depositions with and without ICP assist. Figure 3.4(a) shows that, with ICP assist (Run 1 in Table 3.1), the TiBₓ top layer surface appears completely dense. Figure 3.4(b) shows that, without ICP assist (Run 4 in Table 3.1), as-deposited TiBₓ top layer surface shows a nanoscale “cauliflower” type morphology, typical of films with pronounced columnar defects. Combining XPS data obtained with Ar⁺ ion sputter cleaning, shown in Figure 3.2, with surface morphology data, shown in

![Surface morphologies of TiBₓ/Cr/Si(100) specimens](image)

Figure 3.4 Surface morphologies of TiBₓ/Cr/Si(100) specimens: an SEM micrograph of the surface of a TiBₓ top layer deposited (a) without ICP assist, (b) with ICP assist.
Figure 3.4, it is suggested that the TiBₓ top layer deposited without ICP assist is under-dense with open nanoscale porosities, most likely at column boundaries, and that the TiBₓ top layer deposited with ICP assist is fully dense. The presence of open porosities in the former case led to oxygen incorporation into the bulk of the TiBₓ top layer after the specimen was exposed to air. The incorporated oxygen was not fully removed by Ar⁺ ion sputter cleaning because the porosities extended into the film bulk. The absence of such open nanoscale porosities when the TiBₓ top layer were deposited with ICP assist explains the absence of the boron-oxygen binding energy signature, shown in Figure 3.3.

One TiBₓ/Cr/Si(100) specimen deposited with ICP assist, Run 2 in Table 3.1, was characterized by TEM. Figure 3.5(a) shows a cross-sectional TEM bright-field (BF) image of this specimen. The image was taken with the electron beam direction parallel to the Si <110> zone axis orientation. Figure 3.5(a) illustrates the columnar structure of the interlayer and the top layer. Selected area diffraction patterns (SADPs) collected from the interlayer can be indexed to a cubic structure with a lattice parameter of a = 2.88 Å, consistent with the interlayer being elemental Cr. Figure 3.5(b) shows a typical SADP obtained from the TiBₓ top layer. The SADP exhibits polycrystalline diffraction rings, all of which can be indexed to a hexagonal crystal structure with lattice parameters of a=3.06 Å and c=3.22 Å. These lattice parameter values are consistent with those reported for the hexagonal TiB₂ phase with a = 3.03 Å and c = 3.23 Å [25], indicating that one crystalline phase exists within the TiBₓ top layer, i.e., hexagonal TiB₂. Figure 3.5(c) shows a typical cross-sectional high-resolution micrograph of the TiBₓ top layer, in which an aggregation of nanocrystalline columns in rough alignment with the direction of film growth is evident, consistent with the BF micrograph shown in Figure 3.5(a). Figure 3.5(c) and similar high-resolution micrographs also suggested the existence of some disorder at
boundaries between nanocrystalline columns. These observations are consistent with previous reports of titanium boride thin films deposited by unbalanced magnetron sputtering, in which a B-rich disordered layer exists in between nanocrystalline TiB$_2$ columns [15]. The existence of such B-rich disordered layers between TiB$_2$ nano-columns offers a plausible explanation for the overall film composition being more B rich as compared to TiB$_2$, as determined by XPS.

Figure 3.5 TEM examination of a TiB$_x$/Cr/Si(100) specimen deposited with ICP assist: (a) a cross-sectional BF image; (b) a SADP obtained from the TiB$_x$ top layer. The (hkl) assignments show the indexing of the polycrystalline rings to a single hexagonal crystal structure; (c) a high-resolution micrograph of the TiB$_x$ top layer. The approximate growth direction is indicated by the black arrow and an apparently disordered region in between two TiB$_2$ nano-columns is highlighted with white arrows.
Figure 3.6 shows results of instrumented nanoindentation on four TiBₓ/Cr/Si(100) specimens, Run 1, 2, 3, and 4 in Table 3.1. Figure 3.6(a) shows values of indentation modulus as a function of the indenter contact depth, measured from TiBₓ/Cr/Si(100) specimens deposited with and without ICP assist. As expected, the modulus value increases with decreasing contact depth, as the indenter penetrations are increasingly concentrated within the TiBₓ top layer. All specimens show modulus values from 300 to 400 GPa at contact depth below 50 nm. The large scatter in the data precludes clear differentiation between specimens. Figure 3.6(b) shows corresponding values of hardness measured as a function of the indenter contact depth. The hardness values again increase with decreasing contact depth. In contrast to the modulus data, measured hardness values show a clear distinction between TiBₓ top layers deposited with ICP assist (Runs 1 and 2 in Table 3.1) and without ICP assist (Runs 3 and 4 in Table 3.1). When TiBₓ deposition proceeded with ICP assist, measured hardness values increase to ~37 GPa before decreasing again with further decreasing contact depth, due to indenter tip rounding effects. When TiBₓ deposition occurred without ICP assist, measured hardness values stayed below 20
GPa. Indentation results presented in Figure 3.6 are consistent with the suggestion that TiB\textsubscript{x} layers deposited without ICP assist are under-dense with open nanoscale porosities at column boundaries. The increased Ar\textsuperscript{+} ion bombardment of the substrate surface during ICP assisted deposition, afforded by the increased plasma density, facilitated further densification of the TiB\textsubscript{x} layers and raising their hardness. Refractory ceramics, such as TiB\textsubscript{2}, are associated with strong bonding and reduced surface mobilities. The reduced surface mobility in turn leads to difficulty in film densification during vapor phase deposition, a difficulty often overcome by going to higher deposition temperatures [11,12,13,14,26]. It has been shown previously that full densification of TiN thin films can be affected by increased low energy ion bombardment during deposition, even at cryogenic temperatures [27]. The present observation of significant increase in TiB\textsubscript{x} hardness due to increased Ar\textsuperscript{+} ion bombardment during low temperature deposition is consistent with the previous work on TiN deposition.

Figure 3.7(a) shows an SEM overview of one microscale Ta mold insert, on which an elemental Cr interlayer and a TiB\textsubscript{x} top layer were deposited. The Ta insert consisted of an array of parallel rectangular microprotrusions, the width and height of which are \( \sim 150 \, \mu\text{m} \) and \( \sim 500 \, \mu\text{m} \), respectively. Figure 3.7(b) shows a magnified view of a typical rectangular protrusion. Micron scale undulations are observed to populate the entire protrusion surface. These undulations resulted from the \( \mu\text{EDM/ECP} \) processes. The deposited TiB\textsubscript{x}/Cr layers appear to conformally cover the entire insert surface. Figure 3.7(c) shows an SEM overview of one elemental Al plate, compression molded with the Ta insert shown in Figure 3.7(a) at \( \sim 450 \, ^\circ\text{C} \). Further details on the molding protocol were described elsewhere [4,5,6,7]. The molding process created a negative impression of the surface features on the insert, consisting of a parallel array of microscale rectangular trenches. A magnified view of a typical trench is shown in
Figure 3.7(d). The trench had near-vertical sidewalls and sharp sidewall-to-bottom transitions. The undulations on the trench bottom were a negative of those present on the top surface of the rectangular microprotrusions on the insert. The sidewall surfaces consisted of vertical marks, resulting from the insert sinking into and pulling out of the molded Al plate during the molding and demolding processes, respectively. The depth of the molded trenches was determined to be ~300 μm. Results presented in Figure 3.7 demonstrate that Ta inserts with conformally deposited TiBₓ/Cr layers can be used for microscale compression molding of Al, resulting in
creation of well-defined microscale features in Al plates in a parallel manner. Figure 3.8(a) shows an SEM overview of the same Ta insert after Al molding. The shape and surface morphology of the insert appeared to be well maintained and not altered by the molding process. Figure 3.8(b) shows a magnified view of a typical rectangular microprotrusion on the insert surface. It is apparent from Figure 3.8(b) that the molding and demolding processes led to material transfer from the molding Al plate to sidewall surfaces of the protrusion. Al transferred predominantly onto the protrusion sidewall surface, starting from just below the protrusion top surface to sidewall transition and ending at where contact between the molded Al and the insert ends. There is little Al transfer onto the protrusion top surface. Such observations are reasonable considering that plastic flow during molding occurs predominantly along the protrusion sidewall, with relatively little plastic flow occurring underneath the protrusion top surface [28].

Figure 3.9(a) shows an SEM micrograph of one rectangular microprotrusion on another Ta insert, onto which TiB$_x$/Cr layers were deposited. Figure 3.9(b) shows a FIB cross-section around the region of the protrusion top surface to sidewall transition. To protect the TiB$_x$/Cr
Examination of a Ta insert with TiBₓ/Cr deposition before and after Al molding: (a) an SEM micrograph of a typical rectangular protrusion on the Ta insert after TiBₓ/Cr deposition. The top and sidewall surfaces of the protrusion and the bottom surface of the trench in between protrusions are marked; (b) a FIB cross-section of the protrusion around the top-to-sidewall transition region. The Pt layer was deposited onto the protrusion to protect the specimen from ion beam damage during FIB cutting; (c) typical surface morphology of the insert sidewall surface after TiBₓ/Cr deposition; (d) typical surface morphology of the insert sidewall surface after Al molding at ~450 °C. Locations where intact titanium boride film faces the external environment and where transferred Al exists are marked.

layers, a Pt layer was deposited onto the specimen surface via ion beam catalyzed CVD from a Pt-containing gaseous metal-organic source within the FIB instrument prior to the commencement of Ga⁺ ion beam cutting. The FIB cross-section revealed the Ta substrate, the
elemental Cr interlayer with the lighter contrast, and the TiB\textsubscript{x} top layer with the darker contrast. Figure 3.9(b) demonstrates the conformal nature of the deposited TiB\textsubscript{x}/Cr layers. Additional examinations clearly showed that the TiB\textsubscript{x}/Cr conformal coverage extended to the entire Ta insert, including the protrusion top surfaces, all the sidewall surfaces, and the bottom surfaces. Figure 3.9(c) shows the typical morphology of the protrusion sidewall surface after TiB\textsubscript{x}/Cr deposition. The TiB\textsubscript{x} top layer covered the entire sidewall surface, including all the microscale undulations resulting from the \(\mu\) EDM/ECP processes. Figure 3.9(d) shows a magnified view of the insert sidewall surface, after three Al molding runs were executed at \(\sim 450 \, ^\circ\text{C}\). Figure 3.9(d) clearly shows that Al was transferred to the insert during the molding/demolding processes and that the TiB\textsubscript{x} top layer remained intact without delamination after Al molding, despite the Al transfer.

Past observations of TiB\textsubscript{2} coatings in sliding contact against Al in a rotating cylinder configuration have identified coating detachment from the TiB\textsubscript{2}/substrate interface as an additional degradation mechanism \cite{29}. Whether coating detachment from the Ta insert would occur in the present micromolding configuration cannot be deduced from previous macroscale observations. Results shown in Figure 3.9 suggest that conformal TiB\textsubscript{x}/Cr coatings deposited onto Ta mold inserts by ICP assisted balanced magnetron sputtering possess sufficient adhesion such that contact induced coating delamination does not occur during Al micromolding. Figure 3.9(d) also suggests that intimate contact between the transferred Al material and the insert with conformally deposited TiB\textsubscript{x}/Cr layers does not seem to occur uniformly. Al chips transferred onto the insert sidewall surfaces showed “flare up” around the edges, suggesting that adhesion between Al and the TiB\textsubscript{x} film is not strong. Such evidence is consistent with previous observations of macroscale Al transfer onto TiB\textsubscript{2} coated disks during pin-on-disk type sliding.
contact: Al transferred onto the TiB$_2$ surface during initial sliding was liberated and turned into loose debris during further sliding; the amount of Al transferred further depended on the roughness of the TiB$_2$ surface, with increased Al transfer onto rougher surfaces [16]. Present observations on Al transfer onto sidewall surfaces of Ta inserts with conformally deposited TiB$_x$/Cr layers also suggest that the micron scale surface undulations present on the Ta inserts due to the μEDM/ECP processes contribute to Al transfer. Further studies regarding the application of titanium boride thin films to insert surface engineering for Al micromolding applications remain to be conducted, especially on the influence of insert surface roughness and insert geometry on molding performance.

Deposition of TiB$_x$/Cr thin films onto planar Si(100) and non-planar Ta substrates was carried out by balanced magnetron sputtering and ICP assisted balanced magnetron sputtering. Characterization of TiB$_x$ thin films suggested that increase in film densification occurred with increasing ion bombardment due to the ICP assist, despite the low-temperature deposition. The morphology of TiB$_x$ thin films deposited onto microscale non-flat Ta substrates was examined. The effectiveness of conformal TiB$_x$ thin films as reaction barriers for microscale compression molding of Al was studied by carrying out Al molding experiments at ~450 °C. The present results show that the TiB$_x$/Cr thin films can withstand repeated contact with Al at elevated temperatures in molding applications without delamination.

### 3.4 References


CHAPTER 4
TWO METHOD OF MEASURING INTERFACIAL SHEAR STRESS

4.1 Introduction

Agrawal and Raj performed uniaxial tensile testing of ductile metallic substrates on top of which brittle thin ceramic coatings are deposited. They pointed out that an evaluation of the limiting shear strength of the coating/substrate interfacial region can be achieved by examining cracks formed in the ceramic coating due to tensile deformation of the ductile substrate [1]. The same strain is experienced by the thin coating as the substrate is deformed, with the substrate strain being predominantly plastic and the coating strain being elastic. This strain leads to transverse cracking in the coating perpendicular to the direction of tensile loading. The density of such transverse cracks increases with increasing substrate plastic strain to a plateau value, beyond which further increase in substrate plastic strain does not cause additional decrease in crack spacing. An apparent failure stress in tension is derived for the coating [1],

\[ \hat{\sigma} = E \varepsilon_f , \] (4.1)

where \( E \) and \( \varepsilon_f \) are respectively the Young’s modulus of the coating and the strain at which transverse cracks in the coating develops. Combining this apparent failure stress with the saturation spacing of transverse cracks in the coating at large substrate strain, a limiting shear strength of the coating/substrate interfacial region is derived [1],

\[ \hat{\tau} = \frac{\pi \delta}{\hat{\lambda}} \hat{\sigma} , \] (4.2)

where \( \delta \) is the coating thickness and \( \hat{\lambda} \) is the saturation spacing between transverse cracks. Thus, a quantitative evaluation of this limiting interfacial shear strength can be achieved through measurement of the density of transverse cracks in the coating as a function of substrate tensile loading.
In this paper, two experimental attempts of assessing the limiting shear strength of coating/substrate interfacial regions have been described. The assessment through examination of transverse coating cracks induced by tensile substrate loading has been exemplified through experiments on TiN/Cr/steel and TiN/Ti/steel specimens. Failure of coating/substrate interfacial region induced by compression loading of micro pillars containing inclined interfaces has been illustrated through preliminary experiments conducted on TiN/Ti/Si specimens. This methodology is new and can yield a direct measure of the critical failure stress.

4.2 Experimental Procedures

An inductively coupled plasma (ICP) assisted chemical/physical vapor deposition (CVD/PVD) tool was used to deposit TiN coatings onto SAE1018 steel with three elemental Ti (99.95%) targets and one Cr (99.95%) in an Ar/N2 mixture. Steel substrates were machined into shapes of rectangular tensile bars. The tensile bars have gauge section cross-sectional dimensions of 6mm×4mm and a gauge length of 25mm [2]. They were mechanically polished to a smooth surface, cleaned in acetone and methanol, dried, and loaded into the deposition system. The substrates were rotated at ~12rpm during deposition. Deposition started with a plasma surface etch in a 13.56MHz Ar (99.999%) ICP with a total pressure of ~10mTorr. The total input power into the rf ICP was 1000W, and the substrate bias was -50V. Immediately following the substrate surface etch, an elemental Ti or Cr intermediate adhesion layer was deposited onto the steel substrate via balanced magnetron sputtering in Ar. After the Ti or Cr interlayer deposition, a TiN coating layer was deposited with ICP assist at a total input rf power of 1000W in an Ar/N2 mixture. The Ar/N2 gas input flow ratio was kept at slightly below the pressure hysteresis point, which signifies a change of Ti target surface condition from metallic to fully nitrided [3]. In so doing, nearly stoichiometric TiN deposition was achieved without a
significant decrease in the deposition rate. The total pressure during TiN deposition was below 11mTorr. No intentional substrate heating was applied. The substrate bias was kept at -50V throughout the Ti or Cr interlayer and the TiN top layer deposition. The third series of TiN coatings were deposited on 2 inch diameter, methanol, acetone cleaned silicon wafers. Immediately after same etching process, an elemental Ti interlayer, ~200nm in thickness, was deposited onto the substrate by sputtering the Ti targets in Ar with ICP assist. Deposition of TiN coating layers, ~5μm in thickness, occurred immediately after Ti interlayer deposition. An electrical bias voltage of -30V was applied to the substrate during TiN deposition.

As deposited TiN/Ti/Si(100) films were cut into small pieces and bonded with two similar size stainless steel sheet metal, then milled into micro pillars for displacement control compression test by NaNoindententer XP system[4].

Scanning electron microscopy was conducted on a Hitachi S3600N microscope and an FEI Quanta3D FEG system in a field emission electron beam/focused Ga\(^+\) ion beam (FIB) dual-beam configuration, with X-ray energy dispersive spectroscopy (EDS) capabilities. Both electron-induced secondary electron (SE) and ion-induced secondary electron (ISE) images can be acquired. Transmission electron microscopy (TEM) was carried out on a JEOL JEM2010 microscope operated at 200kV, again with EDS capabilities. X-ray diffraction (XRD) experiments were carried out on a PANalytical Empyrean system with a graphite mirror incidence beam monochromator, a 5-axes cradle sample stage, and a PIXcel3D photon counting detector.

Uniaxial tensile testing of bar specimens was carried out at room temperature on an MTS 858 system equipped with hydraulic grippes. Loading forces were measured with a MTS
661.19F-04 load cell. Strains in bar gauge sections were measured with an MTS 632.26F-20 extensometer.

4.3 Results and Discussion

Figure 4.1 shows a Ga\(^+\) FIB cross section into the surface of one typical TiN/Ti/steel specimen in the as-deposited state. Prior to FIB cutting, a Pt layer was deposited onto the specimen surface via Ga\(^+\) catalyzed deposition from a Pt-containing gaseous organometallic source to protect the coating surface. In the cross section, the steel substrate, the Ti interlayer, and the TiN top layer are clearly visible. The columnar structure of the TiN layer is also evident. Measurements of the thickness of the Ti or Cr interlayer and the TiN top layer were obtained from FIB cross sections such as that shown in Figure 4.1.

![FIB cross-section](image)

Figure 4.1 An SE image of a FIB cross-section of a typical TiN/Ti/steel specimen. The two small arrows denote the TiN/Ti and Ti/steel interfaces.

Two series of TiN coatings were deposited onto steel tensile bar specimens, both in the configuration of TiN/interlayer/steel. For the first specimen series, an elemental Cr interlayer was deposited onto steel, followed by the TiN top layer. The thicknesses of the interlayer and
the top layer were ~270nm and ~1.5μm, respectively, and kept nominally the same for all specimens in the series. For the second specimen series, an elemental Ti interlayer was deposited onto steel, followed by the TiN top layer. The thicknesses of the interlayer and the top layer were ~300nm and ~2.7μm, respectively, and kept nominally the same for all specimens in the series.

Figure 4.2(a) shows a plan-view SE image of one TiN/Cr/steel specimen, loaded in uniaxial tension to a total strain of 2.79%. The formation of long and straight cracks perpendicular to the tensile direction is evident in Figure 4.2(a). Figure 4.2(b) shows a plan-view SE image of one TiN/Ti/steel specimen, loaded to a total tensile strain of 4.06%. In addition to the long transverse cracks, secondary cracks oriented ~45° to the tensile direction are evident in Figure 4.2(b). These ~45° oriented cracks develop as the total tensile strain increases to 3% and above, and have been observed in previous in-situ observations by Chen et al. of transverse crack development in tensile loaded TiN/steel specimens [5]. These ~45° cracks are believed to be due
to substrate contraction perpendicular to the tensile direction after the transverse cracks have already formed, and are therefore not relevant to the determination of interfacial shear strength.

Figure 4.3 shows an SE image of a FIB cross section across a typical transverse crack in one TiN/Ti/steel specimen, loaded to a total tensile strain of 2.47%. The steel substrate, the Ti

interlayer, and the TiN coating layer are clearly visible in the cross section. Figure 4.3 indicates that the transverse crack goes through the entire TiN layer as well as the Ti interlayer, and stops at the Ti/steel interface. The mark on the cross sectional surface of the steel substrate, continuing from the transverse crack, is an artifact of the Ga⁺ irradiation from the top direction in the presence of the crack. In particular, Figure 4.3 shows that the transverse crack did not turn and extend into the TiN/Ti or Ti/steel interface.

From images such as those shown in Figure 4.2, the density of transverse cracks is assessed by counting the length of transverse cracks in an image area of ~190μm×160μm. Consistent with the previous discussion, only the transverse cracks were counted and the ~45° oriented cracks were not taken into account. For each value of total tensile strain, 3 to 7 separate
190μm×160μm image areas within the tensile gauge length were examined. The final density of transverse cracks is obtained by averaging the counting results from all image areas examined. Figure 4.4 shows values of transverse crack density, expressed as transverse crack length per unit area, versus the total true tensile strain of the steel substrate, $\varepsilon$. It was found that this crack counting scheme generates smoother data than counting number of transverse cracks per unit distance, although the two counting schemes generate data with similar trends. Together with the data points, Figure 4.4 shows results of least squares fitting of the transverse crack density data to the Boltzmann sigmoidal function,

$$N(\varepsilon) = D \left\{ 1 - \frac{1}{1 + \exp \left[ (\varepsilon - \varepsilon_f)/\Delta \varepsilon \right] } \right\}.$$  

In Equation 4.3, $N$ is the density of transverse cracks, $D$ is the saturation crack density, $\varepsilon_f$ is the fracture strain, and $\Delta \varepsilon$ is the sharpness of the sigmoidal curve. Table 4.1 shows the fitting results to both data sets. The values of adjusted $R^2$ of the Boltzmann fits to the two data sets for the TiN/Cr/steel and TiN/Ti/steel specimen series were respectively 0.97 and 0.98,
Table 4.1 Results of Boltzmann sigmoidal curve fit to experimentally measured transverse crack density in TiN coatings deposited onto steel substrates

<table>
<thead>
<tr>
<th>Specimen series</th>
<th>$\varepsilon_f$ (%)</th>
<th>$\Delta\varepsilon$ (%)</th>
<th>$D$ (mm/mm$^2$)</th>
<th>Adj. $R^2$</th>
<th>$\lambda$ (μm)</th>
<th>$\delta$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN/Cr/steel</td>
<td>2.2±0.1</td>
<td>0.4±0.1</td>
<td>79±3</td>
<td>0.97</td>
<td>12.7±0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TiN/Ti/steel</td>
<td>2.4±0.2</td>
<td>0.2±0.2</td>
<td>55±2</td>
<td>0.96</td>
<td>18.2±0.7</td>
<td>2.7</td>
</tr>
</tbody>
</table>

demonstrating similar and reasonable fit qualities. From the Boltzmann fits to the data obtained from the TiN/Cr/steel and TiN/Ti/steel specimen series, the values of $\varepsilon_f$ were determined to be 2.2±0.1% and 2.4±0.2%, respectively. The values of $\Delta\varepsilon$, which governs the sharpness of the sigmoidal curves, were similar, with $\Delta\varepsilon$ associated with the data for the TiN/Cr/steel specimen series being slightly larger. Reasonable agreement exists between the two $\varepsilon_f$ values obtained from two independently deposited series of TiN coatings. The mean value of presently determined $\varepsilon_f$, 2.3±0.2%, is in general agreement with in-situ observations of Chen et al.: they obtained $\varepsilon_f = 2.56\%$ from tensile loaded TiN/steel specimens made by hollow cathode discharge ion plating [5]. The apparent failure stress in tension for the present two series of TiN coatings is $E\varepsilon_f = 9.8±0.9$GPa, taking $\varepsilon_f = 2.3±0.2\%$ and $E = 427$GPa [6]. The saturation spacing between transverse cracks, $\lambda$, is the inverse of $D$. The values of $\lambda$ for the TiN/Cr/steel and TiN/Ti/steel specimen series are also shown in Table 4.1. It should be noted that ceramic coatings deposited with ion or plasma assist can contain significant level of intrinsic stresses [7], with the total residual stress within the coating often dominated by intrinsic stresses [8]. In the presence of a residual stress $\sigma_R$, Equation 4.1 is modified to [5]

$$\hat{\sigma} = E\varepsilon_f + \sigma_R.$$  \hspace{1cm} (4.4)
To obtain an estimate of the limiting interfacial shear strength, a measurement of the residual stress with the coating is thus necessary.

XRD experiments in different geometries were used to examine the structure of TiN coatings deposited and assess the level of residual stresses within them. Figure 4.5(a) shows a θ-2θ XRD pattern obtained from a typical specimen within the TiN/Cr/steel series. The Cr interlayer and the TiN top layer adopt preferred orientations of <110> and <111> parallel to the growth direction, respectively. Figure 4.5(a) also shows (110) and (200) reflections from the bcc

Figure 4.5 Characterization of TiN coatings deposited by ICP-assisted magnetron sputtering by X-ray diffraction: (a) a θ-2θ XRD pattern obtained from a typical TiN/Cr/steel specimen; (b) a glancing incidence XRD pattern obtained from the same TiN/Cr/steel specimen; (c) sin²ψ plot for TiN diffraction peaks from the TiN top layer.
α-phase of the steel substrate. Figure 4.5(b) shows a glancing incidence XRD pattern obtained from the same specimen. In the glancing incidence diffraction geometry, the X-ray incidence angle was fixed at \( \gamma = 5^\circ \) and the detector angle was scanned to obtain diffraction signals in the range of \( 20^\circ < 2\theta < 120^\circ \). The \( \Psi \) angle, the angle between the scattering vector \( \vec{k} \) and the sample surface normal \( \vec{n} \), is given by \( \Psi = \theta - \gamma \) [9]. A multitude of B1 TiN reflections are evident in Figure 4.5(b), together with several reflections from the α-phase of steel. The Cr(110) reflection is overwhelmed by the \( \alpha \) (110) reflection. Figure 4.5(c) shows a \( \sin^2 \Psi \) plot for the TiN top layer in the TiN/Cr/steel specimen. In Figure 4.5(c), values of B1 lattice constant \( a_{\text{TiN}} \) calculated from all TiN reflections shown in Figure 4.5(b) is plotted vs. \( \sin^2 \Psi \). A reasonable linear correlation is evident. Assuming an equal biaxial stress \( \sigma_R \) within the TiN layer, the \( \sin^2 \Psi \) plot is used to derive the residual stress within the coating [10]:

\[
a_{\phi} = \left[ \frac{1+v}{E} \sigma_R \right] a_o \sin^2 \Psi + \left[ 1 - \frac{2v}{E} \sigma_R \right] a_o. \tag{4.5}
\]

A linear least squares fit to the data shown in Figure 4.5(c) yields a slope of \(-0.0077\pm0.0011\)nm and an intercept of \(0.4275\pm0.0011\)nm, with an adjusted R\(^2\) of 0.78. The value of \( a_o \) was taken to be 0.424nm, the bulk lattice parameter of B1 TiN [11]. Values of \( E \) and \( v \) were taken respectively to be 427GPa and 0.194, corresponding to the Hashin and Shtrikman average for random polycrystalline aggregates of TiN [6,12]. From the fitted slope of the \( \sin^2 \Psi \) plot, Equation 4.5 yields \( \sigma_R = -6.5\pm0.9\)GPa, i.e., a compressive residual stress. The value of the \( \sin^2 \Psi \) intercept is then calculated to be 0.4265nm, consistent with the fitted intercept value of 0.4275nm. Taking \( E\varepsilon_f = 9.8\pm0.9\)GPa and \( \sigma_R = -6.5\pm0.9\)GPa, values of the limiting interfacial shear strength for the TiN/Cr/steel and TiN/Ti/steel specimen series are calculated from Equation
4.2 and 4.5 to be 1.2±0.7GPa and 1.5±0.8GPa, respectively. Due to the large errors in \( \hat{\tau} \) determination, the present results are unable to discern a significant difference in the limit shear strengths of TiN/Cr/steel and TiN/Ti/steel interfacial regions.

The present example of evaluating the limiting interfacial shear strength \( \hat{\tau} \) of TiN/Cr/steel and TiN/Ti/steel specimens through examination of transverse cracks in TiN during tensile loading of the steel substrate illustrates several issues with this technique. First, errors of \( \varepsilon_f \) and \( \sigma_R \) compound in the error for \( \hat{\tau} \), making the determination of \( \hat{\tau} \) less precise. Second, uncertainty exists in the choice of appropriate values of \( E \) and \( v \), as structures of most ceramic coatings are not completely characterized and are neither randomly oriented polycrystalline aggregates nor one single crystal domain as in epitaxial films. Third, Equation 4.5 was derived by assuming a simple sinusoidal interfacial shear stress profile [1], deviation from which would lead to a different multiplier in Equation 4.2 and therefore a different value for \( \hat{\tau} \). Uncertainties in values of \( E \) and \( v \) and the shear stress profile make the determination of \( \hat{\tau} \) less accurate. Last but importantly, this indirect estimate of the limiting shear strength of the coating/substrate interfacial region does not yield information on which part of the interfacial region plays the dominant role in strength determination. The relationship between structure and chemistry of the coating/substrate interfacial region and the interfacial strength is of paramount importance in design of coating/substrate interfaces. This relationship is not elucidated through this indirect estimate of \( \hat{\tau} \).

Figure 4.6(a) shows an SE image of a typical TiN/Ti/Si specimen. The TiN/Ti/Si assembly was tilted 45°, embedded in an epoxy matrix, and mechanically polished to the point that the coating/substrate interfacial region is clearly revealed on the polished surface. The specimen region shown in Figure 4.6(a) contains a top view of the polished surface as well as a
FIB-cut cross sectional view into the polished surface. The FIB cross section reveals the inclined TiN/Ti/Si interface region. The elemental Ti interlayer in between the Si substrate and the TiN coating is visible though its lighter contrast. Figure 4.6(b) shows a typical microscale cylindrical pillar defined by Ga\(^+\) FIB milling conducted perpendicular to the polished surface. The micro pillar contains the TiN/Ti/Si interface region at a 45° inclination with respect to the pillar axis.

Figure 4.6   Micro pillar fabrication by FIB milling: (a) an SE image of the FIB cross section of a TiN/Ti/Si specimen, tilted 45° and polished to reveal the interface region; (b) an SE image of a typical micropillar FIB cut from the 45° tilted TiN/Ti/Si specimen.

Figure 4.7 shows a typical measured raw load - displacement curve. For each pillar, the load increased approximately linearly with increasing indenter displacement at the beginning. Then the pillar failed abruptly when the load reached a breaking point, manifested in a large and abrupt displacement excursion: typically 4-5µm for a pillar diameter ~3 µm.

Figure 4.8 illustrate typical measurement scatter from multiple micro pillars, and indicate, within the experimental scatter, that there is not a significant dependence of the average interfacial shear stress at failure on the pillar diameter over the range of pillars tested. While
additional studies are needed to ascertain the exact nature of the compression induced interfacial failure, the average value of all data points shown in Figure 4.8, 1.0±0.1GPa, is curiously close

![Graph](image1.png)

**Figure 4.7** Compression testing of micro pillars containing inclined TiN/Ti/Si interfaces: a typical load-displacement curve obtained during compression testing of one 3μm diameter TiN/Ti/Si micro pillar containing a 45° inclined TiN/Ti/Si interface.

to the limiting interfacial shear strength determined through examination of transverse cracks induced by tensile loading in the TiN/Cr/steel and TiN/Ti/steel specimen series. The methodology of directly inducing interfacial failures by compression loading of micro pillars

![Graph](image2.png)

**Figure 4.8** Values of the average shear stress at failure by compression loading of TiN/Ti/Si micro pillars containing 45° inclined interfaces as a function of the pillar diameter.
containing inclined coating/substrate interfaces is new, can potentially yield an accurate measure of the critical failure stress, and deserves to be further explored.

4.4 References


CHAPTER 5
THICKNESS DEPENDENCE OF FLOW STRESS OF CU THIN FILMS IN CONSTRAINED SHEAR PLASTIC FLOW

5.1 Introduction

Size effects in plasticity have been documented through many experiments over the past two decades, including torsion of wires [1], indentation by pyramidal indenters [2], and bending of beams [3]. Shearing of a well-bonded metal layer sandwiched between two substrates which do not deform plastically has been one of the canonical cases studied in the development of strain gradient plasticity. In many respects, it captures in the simplest manner the essence of plastic strain gradients associated with geometrically necessary dislocations generated when plastic flow is blocked at the metal/substrate interfaces. Analytically, shear of confined layers is one of the simplest problems to solve, as illustrated in the following selection of theoretical papers on the subject [4, 5, 6, 7, 8]. Experimentation was performed previously in the configuration of shear loading of thin Al layers diffusion bonded between Al$_2$O$_3$ adherents [9]. The results of this experimentation, however, were inconclusive. Until now, experimental data for the confined shear problem have not been available to confront the theoretical predictions.

Shear plastic flow in confined thin layers, in addition to its scientific interest in furthering exploration of plasticity size effects, is of significant technological interest. Over the past two decades, vapor phase deposition of thin ceramic coatings has become an important means for engineering surfaces of mechanical components [10] and manufacturing tools [11]. Satisfactory adhesion of coatings to substrates is critical to the lifetime of coated systems and often the deciding factor for their implementation. To improve adhesion, interfacial adhesion layers are deposited between the ceramic coating and the substrate. Such interlayers often consist of elemental metals. When coated components are subjected to external load, shear strength of the interface region can become the limiting factor on how mechanical load is transmitted from the
substrate to the top coating [12]. Quantitative measurements of shear plastic flow in confined thin layers and correlation of such flow stress to their structure and composition are therefore important for engineering improved coating/adhesion-layer/substrate systems.

The dominant experimental means for determining yield strength of thin metal films at present is instrumented nanoindentation. However, mechanical property evaluation by indenting films on substrates encounters difficulties at small film thicknesses due to substrate influence [13]. A new experimental protocol for evaluating the mechanical integrity of interfaces between hard coatings and substrates was demonstrated recently [14]. Vapor phase deposited specimens in the configuration of coating/interlayer/substrate were fabricated via focused ion beam (FIB) into microscale cylindrical pillars. To make micro-pillars without significant taper, a FIB script program was employed [15] which enabled a lathe-like milling process with Ga+ ions. Specimens were oriented such that the coating/interlayer/substrate interface is inclined with respect to the pillar axis. Interfacial failures were then achieved through compression loading of the pillars in the axial direction [14]. When the coating and the substrate are both elastic-brittle materials, compression loading of pillars with inclined interfaces results in a predominantly shear loading on the interlayer. This test configuration therefore presents a suitable geometry for experimental evaluation of shear plastic flow of confined layers. We report here results of compression testing on CrN/Cu/Si(100) micro-pillars containing 45°-inclined interfaces.

5.2 Experimental Procedures

Deposition of CrN coatings was carried out in an ultra-high-vacuum vapor deposition tool, which housed a 13.56MHz inductively coupled plasma (ICP) and four balanced magnetron sputter guns [16]. All guns faced the center of the deposition chamber, with a base pressure of < 5×10⁻⁹Torr. Cleaned Si(100) substrates, 50.8mm in diameter, were placed into a load lock,
evacuated to $\leq 2 \times 10^{-6}$Torr, then transferred to a specimen holder placed at the center of the deposition chamber. No intentional substrate heating was applied during deposition. Three guns were fitted with pure Cr (99.95%) targets and one gun was fitted with pure Cu (99.95%). All guns operated in the dc current-controlled mode. The entire deposition sequence occurred in ~10mTorr of Ar (99.999%+). The Si substrate was first subjected to an Ar ICP etch for ~10min at a bias voltage of -50V, with a total of 1000W input into the ICP. Immediately after etching, an elemental Cu layer was deposited onto the Si substrate at a bias voltage of -50V by sputtering the Cu target in Ar ICP at a total input power of 1000W. Deposition of the CrN top coating layer, ~5μm in thickness, occurred immediately after Cu deposition at a bias voltage of -100V in an Ar/N$_2$ (99.999%+) ICP at the same total input power. During CrN deposition, the Ar/N$_2$ input flow rates were adjusted such that a nitrogen rich condition past the pressure hysteresis point was maintained. Five CrN/Cu/Si specimens were deposited, with nominally the same CrN layer thickness and varying Cu interlayer thickness t.

Structural characterization of the CrN/Cu/Si(100) films by X-ray diffraction (XRD) was carried out on a PANalytical Empyrean system with Cu Kα radiation, a graphite mirror incidence beam monochromator, 5-axes cradle sample stage, and a PIXcel3D photon counting detector.

Compositional analysis by X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos AXIS165 system with monochromatic Al Kα excitation. Prior to spectrum acquisition, specimen surfaces were etched with a 5kV 15mA Ar$^+$ ion beam for ~25min. Survey spectra obtained from typical Cu films showed that all observed spectral features can be assigned to various Cu core level transitions and Auger transitions.

Focused Ga$^+$ ion beam milling and specimen examination by electron- or ion- induced second electron (SE/ISE) imaging were carried out on an FEI Quanta3D FEG dual-beam...
instrument, which combines a field-emission electron source and a high-current Ga+ ion source and houses an X-ray energy dispersive spectroscopy (EDS) attachment. A Pt protection layer was deposited by Ga+ ion beam catalyzed Pt metal-organic gas source deposition onto the CrN top surface before the cross section was created by Ga+ ion milling perpendicular to the specimen top surface. The cross section was cut with Ga+ ion beams of successively reduced currents from 30nA to 1nA. CrN/Cu/Si(100) micro pillars were fabricated by ion lathe milling. Method was reported in details in earlier paper [14].

Compression loading of CrN/Cu/Si micro-pillars was carried out on a NanoIndenter XP system with a custom-made, ~10µm × ~10µm, flat-ended diamond punch. An increasing load was applied to the pillar top surface in the displacement-controlled mode, with raw indenter load L and total indenter displacement h monitored continuously. A constant loading time of 180sec to a preset h value was specified, and the loading was stopped when the specified h was reached, followed by load removal.

5.3 Results and Discussion

The top trace displayed in Figure 5.1 is a θ-2θ XRD pattern obtained from one Cu thin film, ~1180 nm in thickness, deposited on Si(100). All diffraction peaks, besides the Si(400) substrate peak, are indexed to an fcc pattern with a lattice parameter of 3.617Å, consistent with the deposit being elemental Cu. It is further evident that the deposited Cu film has a strong fiber texture, with a predominant orientation of Cu <111> parallel to the growth direction.

The middle trace in Figure 5.1 is a θ-2θ XRD pattern obtained from a CrN/Cu/Si(100) thin film, with CrN and Cu thickness of ~5500nm and ~1180nm, respectively. Cu diffraction peaks are overwhelmed by CrN peaks due to peak overlap. Besides the Si(400) substrate peak, all peaks are indexed to an fcc pattern with a lattice parameter of 4.18Å, close to the bulk
Figure 5.1  X-ray diffraction characterization: (top trace) θ-20 XRD pattern of a pure Cu film, (middle trace) θ-20 XRD pattern of a CrN/Cu/Si(100) film, (bottom trace) 2.5° glancing angle incidence diffraction pattern of the same CrN/Cu/Si(100) film.

B1-CrN lattice parameter of 4.149 Å and consistent with the top layer deposit being B1-CrN [17]. The XRD pattern also shows that the degree of texture within the CrN film is not as strong as the Cu film, with the CrN<111> and CrN<200> directions being the main crystallographic directions parallel to the growth direction. The bottom trace in Figure 5.1 shows a glancing incidence XRD pattern obtained from the same CrN/Cu/Si(100) film, with a fixed incidence angle of 2.5°. The shallow incidence angle leads to a longer X-ray interaction path within CrN, and consequently a higher number of more pronounced CrN diffraction peaks. Using the sin²ψ method [18] and taking the lattice parameter, Young’s modulus, and Poisson’s ratio of CrN to be respectively 4.149Å, 200GPa, and 0.2, residual stress within the CrN film was obtained from the glancing incidence data to be ~ 0.8GPa. Such a relatively low compressive residual stress level is beneficial for depositing CrN films of higher thicknesses.

Figure 5.2 shows a FIB cross-section of a typical CrN/Cu/Si(100) specimen. The Pt protection layer, the CrN layer, the Cu interlayer, and the Si substrate are clearly visible in the
cross-sectional SE image. The thickness of the Cu interlayer was measured from the cross section to be ~550nm, with an estimated error of ~5% based on results of repeat measurements on the same specimen. The cross section reveals a dense and columnar structure of the CrN top layer, typical of transition metal nitride films deposited with plasma or ion beam assist [19]. The inset of Figure 5.2 shows a tilted plan-view of the CrN top layer surface in its as-deposited state. The plan-view SE image shows surface roughness consistent with the columnar structure of the CrN top layer as well as the absence of any perceptible voids, indicative of a fully dense film.

Similar procedures were used to measure the Cu interlayer thickness values in all CrN/Cu/Si(100) specimens. Typical sizes of Cu grains were estimated by using the FIB cross section image, where channeling of primary Ga⁺ ions enhances contrast between neighboring grains with differing orientations. Lateral dimensions of Cu grains ranged from ~60nm to ~130nm with no obvious dependence on film thickness, as expected from low temperature depositions.

The top trace displayed in Figure 5.3 is a survey spectrum obtained from a typical Cu thin film. All observed spectral features can be assigned to various Cu core level transitions and Auger transitions. At the binding energies corresponding respectively to O1s and C1s levels,
Figure 5.3 XPS characterization: (top trace) a survey spectrum of one pure Cu film, (bottom trace) a survey spectrum from the CrN layer of one CrN/Cu/Si(100) specimen. 

~532eV and ~284eV, no signals were observed above background, indicating that oxygen and carbon contaminations within the Cu film were below the instrumental detection limit of ~1at.%. The bottom trace in Figure 5.3 is a survey spectrum obtained from the top layer of a typical CrN/Cu/Si specimen. All observed spectral features can be assigned to various Cr core level transitions and the N1s transition. Using factory supplied sensitivity factors, the N to Cr ratio was determined to be 49.3:50.7, indicating close to stoichiometric CrN. Again, no signals above background were observed at binding energies close to ~532eV and ~284eV, indicating little oxygen and carbon contamination within the deposited CrN. Combining results shown in Figures 5.1, 5.2, and 5.3, it is concluded that the deposited CrN/Cu/Si(100) specimens consist of a fully-dense polycrystalline B1-CrN top layer, a Si(100) substrate, and a polycrystalline Cu interlayer with oxygen and carbon contamination below 1at.%. The Cu interlayers have a strong fiber texture with Cu<111> //Si[100], and grain sizes of 60-130nm with no obvious dependence on thickness.

Figure 5.4 shows an array of 7 CrN/Cu/Si micro-pillars fabricated from one CrN/Cu/Si(100) specimen. All 7 micro-pillars have similar diameters D of ~4.6μm and the same interface inclination angle of 45° [14]. Micro-pillars were fabricated out of CrN/Cu/Si(100)
specimens with different t values. In all cases, the minimum distance between the CrN/Cu/Si interface and the pillar top surface was $\geq 2\mu m$, and the ratio $t/D$ was $<0.20$.

Figure 5.4 An ISE image of an array of CrN/Cu/Si(100) micro-pillars after FIB lathe-milling

Figure 5.5 shows a collection of raw L-h curves measured from five groups of micro-pillar specimens, with t values of $\sim 150\text{nm}$, $\sim 340\text{nm}$, $\sim 550\text{nm}$, $\sim 810\text{nm}$, and $\sim 1180\text{nm}$,

respectively. Within each specimen group, repeat measurements on 4 to 6 separate micro-pillars were conducted. Several features are evident. First, all L-h curves exhibit a rapid, approximately linear, increase in L with increasing h until a critical L value, $L_c$, is reached.

Figure 5.5 Raw L-h curves obtained from compression loading of CrN/Cu/Si(100) micro-pillars with 45°-inclined interfaces. Five groups of data were obtained from pillars with five t values.
Further increase in $h$ then occurs with little further increase in $L$. Second, the $L-h$ curves fall into five succinct groups, separated from each other according to the $t$ value. The smaller the $t$, the higher the $L_c$. Third, once $L_c$ is reached, further increase in $h$ does not continue without bound. An eventual catastrophic failure point was reached as $h$ continued to increase, manifested in large and discontinuous displacement excursions to $h$ values of several microns. The smaller the $t$ value, the earlier this catastrophic failure point is reached.

Figure 5.6 shows a sequence of events occurring at different stages of compression loading on one CrN/Cu/Si micro-pillar with a $t$ value of ~340nm. Figure 5.6(a) shows one micro-pillar after compression loading to $h$ ~400nm. It is evident from Figure 5.6(a) that a small but clear shear displacement of the top CrN portion occurred as a whole with respect to the bottom Si portion, along the original CrN/Cu/Si interface direction. Figure 5.6(b) shows another micro-pillar with the same $t$, with an $h$ value $>$4000nm. In this case, the catastrophic failure point was reached shortly after $h$ exceeded 400nm, with the next recorded $h$ $>$4000nm and well separated from a continuous group of progressively increasing $h$ values. Such data indicate a large and abrupt indenter displacement after reaching the failure point.

In agreement, Figure 5.6(b) shows the diamond punch impacted the top of the bottom Si portion of the micro-pillar, causing a part of it to fracture. Examination of the part of the pillar not damaged by the indenter impact shows clear evidence that pillar failure was a result of continued shear displacement of the top CrN portion as a whole with respect to the bottom Si portion, along the original CrN/Cu/Si interface direction. The shear displacement occurred with the bottom Si and top CrN portions undeformed. In Figure 5.6(b), Cu is present on the top Si surface as well as the bottom CrN surface, both exposed as the result of the extensive shear displacement. The presence of Cu on the two surfaces was confirmed by spot mode EDS. Clear
sliding marks are evident on the exposed top Si surface. Results shown in Figures 5.5 and 5.6, combined, show unequivocal evidence of the occurrence of shear plastic flow within the Cu interlayer. Similar results, both in terms of the L-h curves and the image features, have been observed at all five t values.

![ISE images of micro-pillars at different stages during compression loading](image)

Figure 5.6 ISE images of micro-pillars at different stages during compression loading: (a) one pillar after the compression load was removed after a total indenter displacement of 400nm was reached, (b) one pillar after a total indenter displacement of >4000nm. The Cu interlayer thickness was ~340nm.

The raw L_c values were therefore converted to nominal shear flow stresses, \( \tau \), for the Cu interlayers. With the Cu interlayer at a 45° inclination, \( \tau = \sigma/2 \), where \( \sigma \) is L_c divided by the right cross-sectional area of the pillar, i.e., \( \sigma \) is the critical compression stress. Figure 5.7 shows values of \( \tau \) plotted as a function of t. Each data point in Figure 5.7 represents an independent test on a separate pillar. The data points, 4 to 6 at each t value, fall on top of each other in Figure 5.7. For the data group with the largest scatter, at t ~1180nm, the average value and standard deviation for \( \tau \) was measured as 0.41±0.01GPa. This measured flow stress value of 410MPa is close to a previously reported room temperature flow stress for nanocrystalline Cu [20]. As t decreases, the value of \( \tau \) increases to ~0.80GPa at t = ~150nm. The measured \( \tau \) increase lies
significantly outside the range of data scatter, showing a clear dependence of $\tau$ on $t$ in confined shear plastic flow. To our knowledge, this is the first time such dependence has been measured unequivocally. Separate measurements showed that the critical compression stress did not exhibit a strong dependence on the pillar diameter. For a given Cu interlayer thickness, the difference in the critical compression stress was measured to be $<10\%$ as the pillar diameter varied between $\sim 5\mu m$ to $\sim 2\mu m$.

Figure 5.7 Values of the nominal shear flow stress of Cu interlayers as a function of the interlayer thickness.

Ideal shear strength of single crystal Si has been reported to be $\sim 7$ GPa [21]. The hardness of CrN has been measured to be $>20$ GPa [12]. Given that $\sigma$ values presently measured were $<2$ GPa, the fact that both Si and CrN remained undeformed during compression loading is expected. Direct comparison between data presented in Figure 5.7 and non-local plasticity theories are complicated by several factors. One is that the Cu interlayers presently studied are polycrystalline with small grain sizes. Even though the predominance of Cu grains are oriented with the $\{111\}$ slip plane parallel to the shear direction, the presence of numerous grain boundaries within the shear plane presents a more complicated situation as compared to previous simulations [4-8]. Another is that, instead of a perfectly flat interface, the CrN/Cu interface
contains sub-micron scale roughness resulting from the columnar structure of the CrN top layer. The presence of such roughness is manifested in the sliding marks shown in Figure 5.6(b), when the shear plastic flow is occurring close to the CrN/Cu interface. Experimental efforts to better control such complications, e.g., by controlling the grain size of the metal interlayer, are ongoing.

In summary, compression loading of CrN/Cu/Si(100) micro-pillars containing inclined interfaces yielded unequivocal evidence of shear plastic flow within polycrystalline Cu thin films confined between undeforming single crystal Si(100) and polycrystalline CrN. A clear and significant dependence of the shear flow stress on Cu layer thickness was demonstrated. The present results give a new and independent measure of the size effects in confined shear plastic flow. It is hoped that the presently described shear test will just be the beginning of experimental efforts to generate more data on this fundamental problem.

5.4 References


CHAPTER 6
MICRO-PILLAR MEASUREMENT OF PLASTICITY IN CONFINED CU THIN FILMS

6.1 Introduction

In the last two decades, the dominant experimental means for affecting plastic flow in small volumes, including in thin metal films, has been instrumented micro- and nano-indentation. A methodology for extracting hardness values from experimentally obtained load-displacement curves has been established and well accepted [1]. In particular, a principal avenue through which length scale dependent plasticity effects are demonstrated experimentally has been through the indentation size effect [2]. However, for measuring plastic flow in thin films, substrate influence complicates the determination of the mechanical flow strength using indentation [3, 4].

We recently demonstrated a new experimental protocol for evaluating the mechanical integrity of interfaces between hard coatings and substrates [5]. Vapor deposited specimens in the configuration of coating/interlayer/substrate were fabricated via scripted focused ion beam (FIB) milling into microscale cylindrical pillars, with interfaces at a pre-determined inclination angle with respect to the pillar axis. Axial compression loading of the pillars then resulted in interfacial failures, providing a quantitative measurement of the critical failure stress [5]. When the coating and the substrate are both elastic-brittle materials, such as CrN and Si, and the interlayer is a metal, such as Cu, axial compression of micro-pillars with inclined interfaces results in a combination of compressive and shear stress acting on the interlayer. Furthermore, with well bonded interfaces, extensive plastic shearing of thin polycrystalline Cu interlayers was observed, together with a significant dependence of the shear flow stress on the Cu thickness [6].

Shearing of a metal layer bonded between two non-deforming substrates is the iconic example that illustrates the connection between gradients of plastic strain and enhanced flow
strength. Due to its analytical simplicity, the confined shear problem has been widely considered as an example in the development of continuum strain gradient plasticity (SGP) and discrete dislocation plasticity (DDP) theories [7,8,9,10,11]. Normal compression of a finite width metal layer bonded between rigid platens has also been considered as an application of SGP theories [12]. Normal compression of a metal thin film bonded to platens was suggested as a useful loading geometry for measuring the material length parameter underlying the size effect, especially if companion shear data are available [12]. The micro-pillar experimental technique described in [5] and [6] creates such a possibility of conducting normal compression and shear tests on the same metal thin film.

In this paper, we report results of axial compression testing on CrN/Cu/Si(100) micro-pillars, with interfaces either perpendicular to the pillar axial direction or at a 45° inclination. Compression testing of the micro-pillars has been performed on an instrumented nanoindenter with a flat punch at different pillar diameters, \( D \), Cu interlayer thicknesses, \( h \), and over a range of indenter displacements, \( d \).

### 6.2 Deposition and Structural Characterization of Polycrystalline CrN and Cu Thin Films

Cu and CrN thin films were vapor phase deposited onto 50mm diameter Si(001) wafers in an ultra-high-vacuum (UHV) deposition tool in a load-locked configuration. The deposition chamber housed a 13.56MHz inductively coupled plasma (ICP). Four balanced magnetron sputter sources, accepting 75mm diameter sputter targets, faced the center of the deposition chamber. The base pressure of the deposition chamber was \( \sim 3 \times 10^{-9} \)Torr [13,14,15]. Cleaned Si(001) substrates were evacuated to \( \leq 3 \times 10^{-7} \)Torr in the load lock and then transferred to a holder placed at the center of the UHV deposition chamber. One elemental Cu (99.99%) target and three elemental Cr targets (99.95%) were used, all operated in the dc current-controlled
Deposition of Cu thin films occurred in ~10mTorr of pure Ar (99.999%+). Deposition of CrN thin films occurred in ~10mTorr of Ar/N\textsubscript{2} (99.999%+/99.999%+) mixture. Prior to deposition, Si substrates were subjected to an Ar ICP etch for ~5min at a bias voltage of -50V. All depositions occurred without intentional substrate heating.

A series of single-layer Cu thin films were deposited onto Si(001) substrates. Cu deposition occurred with the sputter source operated at 1.0A, and with an Ar ICP assist at a total ICP input power of 1000W. A substrate bias of -50V was applied during deposition. The Cu film thickness was controlled through the deposition time. Another series of bilayer CrN/Cu thin films were deposited onto Si(001) substrates. Cu interlayers were first deposited onto Si(001) in pure Ar with ICP assist, followed immediately by deposition of CrN top layers in an Ar/N\textsubscript{2} mixture, also with ICP assist at a total ICP input power of 1000W. During CrN deposition, a substrate bias of -100V was applied. To ensure CrN deposition at close to stoichiometry, the input N\textsubscript{2} flow was kept above the pressure hysteresis point.

Morphological characterization of the Cu/Si(001) and CrN/Cu/Si(001) specimens was carried out by scanning electron microscopy (SEM) on a FEI Quanta3D FEG focused ion beam (FIB) instrument with an X-ray energy dispersive spectroscopy (EDS) attachment. The FIB instrument combines a field-emission electron source and a high-current Ga\textsuperscript{+} ion source, and enables scanning images taken in either the electron-induced secondary electron (SE) mode or the ion-induced secondary electron (ISE) mode.

Typical results of morphological observation from CrN/Cu/Si(001) specimens are illustrated in Figure 6.1. Figure 6.1(a) shows an SE image of a cross section perpendicular to the original specimen surface, created by Ga\textsuperscript{+} ion milling. A Pt protection layer was laid on top of the specimen surface prior to ion milling by Ga\textsuperscript{+} catalyzed deposition from an organometallic Pt
precursor. Figure 6.1(a) shows in sequence the Pt protection layer, the CrN top layer, the Cu interlayer, and the Si substrate. The thicknesses of the CrN and Cu layers were measured respectively to be ~5.5µm and ~810nm, with typical scatter of ±5% based on repeat measurements. Figure 6.1(b) shows a plan-view SE image of the as-deposited CrN top surface, with surface roughness typical of vapor deposited polycrystalline columnar refractory ceramics. Both the cross section and the plan-view images indicate that the CrN top layer is fully dense.

![FIB examination of a typical CrN/Cu/Si specimen: (a) A cross sectional SE image; (b) a 52° tilted plan-view SE image.](image)

Compositional characterization of the Cu/Si(100) and CrN/Cu/Si(001) specimens was carried out by X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS165 spectrometer with monochromatic Al Kα excitation. Composition quantification was obtained from raw XPS spectra using factory supplied sensitivity factors. Prior to XPS spectra collection, the specimen surface was sputter cleaned with an Ar⁺ ion beam for ~20min, with the Ar⁺ ion beam set at 4kV and 15mA.

Figure 6.2 shows XPS survey spectra collected from top layers of a typical Cu/Si specimen and a typical CrN/Cu/Si specimen. The Cu spectrum shows peaks consistent with
Cu3p, Cu3s, and Cu2p emissions. Signal at the O1s and C1s positions, at binding energies of 532eV and 284eV, is not above the noise level. The CrN spectrum shows peaks consistent with Cr3p, Cr3s, Cr2p, Cr2s, and N1s emissions. Signal at the O1s and C1s positions is also not above the noise level. The Cr:N ratio is determined to be 51:49. XPS data thus show that the Cu layers consist of elemental Cu, and that the CrN layers consist of Cr and N at close to the stoichiometric ratio. The O and C impurity levels in both Cu and CrN layers are below the XPS detection limit of ~1at.\%.

![XPS survey spectra](image)

**Figure 6.2** XPS survey spectra collected from top layers of a typical Cu/Si specimen and a typical CrN/Cu/Si specimen. In both cases, the oxygen impurity level is at or below the XPS detection limit of ~1 at.\%.

Structural characterization of Cu and CrN thin films was carried out by X-ray diffraction (XRD) on a PANalytical Empyrean system. Diffraction patterns were obtained using CuKα radiation with specimens mounted on a χ-φ-x-y-z stage. Diffraction patterns in the glancing incidence geometry, the symmetric θ-2θ geometry, and the ω-rocking curve geometry are
obtained with an incident beam graphite mirror and a Pixel3D detector. X-ray pole figure data were obtained with an incident beam double-cross slit and a scintillation detector.

Results of XRD characterization of the structure of CrN layers in CrN/Cu/Si(001) specimens are illustrated by data shown in Figure 6.3. The glancing incidence XRD pattern, shown in Figure 6.3(a), collected from one typical CrN/Cu/Si(001) specimen at an beam incidence angle $\gamma=2.5^\circ$, shows diffraction peaks only from the CrN top layer. All diffraction peaks can be indexed to a cubic structure with lattice parameter $a = 4.18\AA$, close to the bulk B1-CrN lattice parameter of 4.15Å [16]. The $\theta$-2$\theta$ XRD pattern, shown in Figure 6.3(b) and collected from the same specimen, shows the Si(004) diffraction peak from the Si substrate and

![Figure 6.3 XRD examination of a typical CrN/Cu/Si(001) specimen: (a) glancing incidence ($\gamma=2.5^\circ$) diffraction pattern; (b) $\theta$-2$\theta$ diffraction pattern; (c) $\sin^2\Psi$ analysis of the glancing incidence data shown in (a)
one minor Cu(220) diffraction peak from the Cu interlayer in addition to all diffraction peaks indexed to B1-CrN, with \( a = 4.18\text{Å} \). Taken together, glancing incidence and \( \theta-2\theta \) XRD data are consistent with the CrN film having the B1-NaCl structure, being polycrystalline, and with preferential alignment of CrN<111> and CrN<200> along Si[001], the growth direction.

The level of residual stress within the CrN top layer was estimated from analysis of the glancing incidence XRD data shown in Figure 6.3(a). When the X-ray incidence angle was fixed at \( \gamma = 2.5^\circ \) and the detector was scanned to obtain diffraction signals in the range of \( 20^\circ < 2\theta < 120^\circ \), the angle between the scattering vector \( \vec{k} \) and the specimen surface normal \( \vec{n}, \Psi \), is given by \( \Psi = \theta - \gamma \) [17]. The CrN lattice parameter, \( a_{\text{CrN}} \), was calculated from the multitude of B1-CrN diffraction peaks shown in Figure 6.3(a), and plotted versus \( \sin^2 \Psi \) in Figure 6.3(c). Assuming an equal biaxial residual stress \( \sigma_R \) existing within the CrN layer, the variation of \( a_{\text{CrN}} \) as the \( \Psi \) angle varies relates in the following way to \( \sigma_R \) [17,18]:

\[
a_{\psi} = \left[ \frac{1+\nu}{E} \sigma_R \right] a_o \sin^2 \Psi + \left[ 1 - \frac{2\nu}{E} \sigma_R \right] a_o.
\]  

In Equation 6.1, \( E \) and \( \nu \) are respectively the Young’s modulus and Poisson’s ratio of the CrN layer, and \( a_o \) is the bulk lattice parameter of CrN. A linear least squares fit to the data shown in Figure 6.3(c) yielded a slope of -0.022±0.017Å and an intercept of 4.187±0.007 Å. The negative slope of the \( \sin^2 \Psi \) plot indicates that the residual stress within CrN is compressive. Independent of the values of \( E \) and \( \nu \), the fact that the slope uncertainty is comparable to the slope itself indicate that the level of residual stress is moderate. Values of \( E \) for CrN reported in the literature vary widely from ~200GPa to above 400GPa [19,20]. Taking \( a_o \) to be 4.15 Å, \( \nu \) to be 0.2 [21], and \( E \) to be 400GPa [22], the fitted slope of the \( \sin^2 \Psi \) plot yields \( \sigma_R = -1.8\pm1.4\text{GPa} \). It is noted that, since \( E = 400\text{GPa} \) is a high value for CrN, this \( \sigma_R \) value represents an upper bond.
estimate (e.g., taking $E = 300\text{GPa}$ would result in a $\sigma_R$ value of $-1.3\pm1.0\text{GPa}$). Both the magnitude and the large uncertainty associated with the $\sigma_R$ value again indicate that the level of compressive residual stress within the CrN layer is moderate. A moderate residual stress level within CrN makes it easier to deposit thick CrN top layers, e.g., that shown in Figure 6.1(a). Diffraction data similar to those shown in Figure 6.3 were obtained from other CrN/Cu/Si(001) specimens.

Results of XRD characterization of the structure of Cu/Si(001) specimens are illustrated by data shown in Figure 6.4. The glancing incidence XRD pattern, shown in Figure 6.4(a), collected at an beam incidence angle $\gamma=2.5^\circ$ from one Cu/Si(001) specimen with Cu thickness of ~1180nm, shows diffraction peaks which can all be indexed to an fcc structure with lattice parameter $a$ of 3.617Å, close to the bulk fcc-Cu lattice parameter of 3.615Å [23]. The $\theta$-20 XRD pattern, shown in Figure 6.4(b) and collected from the same specimen, shows the Si(004) diffraction peak from the Si substrate and only fcc-Cu (111) and (222) diffraction peaks. The glancing incidence and $\theta$-20 XRD data are consistent with the Cu film having the fcc structure, being polycrystalline, and with strong preferential alignment of Cu<111> along Si[001].

The texture in Cu films was shown in more detail by background corrected Cu(111) pole figure data shown in Figure 6.4(c), collected from three different Cu films deposited on Si(001), with total film thickness values of ~150nm, ~550nm, and ~1180nm. In all cases, the Cu(111) diffraction intensity peaks along the growth direction and drops to <10% of the peak intensity at directions deviating from the growth direction for >5°. Furthermore, the pole figure data clearly show in-plane rotational symmetry of the Cu(111) diffraction intensity, at all film thicknesses probed. The pole figure data are further corroborated by Cu(111) $\omega$-rocking curve data shown in Figure 6.4(d). Measured rocking curve width decreases monotonically from 4.4° at the Cu film
thickness of ~150nm to 3.0° at ~550nm and to 2.4° at ~1180nm. Taken together, X-ray diffraction data shown in Figure 6.4 indicate that the Cu films are fcc in structure and have almost perfect fiber texture with Cu<111> along Si[001] to within a few degrees. The Cu films are polycrystalline with random in-plane orientation.

Figure 6.4  XRD examination of a typical Cu/Si(001) specimen with a cu film thickness of ~1180nm: (a) glancing incidence (γ=2.5°) diffraction pattern; (b) θ-2θ diffraction pattern; (c) background corrected Cu(111) pole figures from three polycrystalline Cu layers on Si(001), the Cu film thickness values are indicated on top of the pole figures; (d) Cu<111> rocking curves from three polycrystalline Cu layers on Si(001), the Cu film thickness values are indicated on top of the curve

Grain structure of CrN and Cu thin films was further characterized by transmission electron microscopy (TEM), carried out on a JEOL JEM2011 microscope operated at 200kV. Cross-sectional TEM specimens were made from sputter deposited thin films by Ga⁺ ion sectioning into rectangular sections, lift-out using an in-situ OmniProbe, gluing by Ga⁺ catalyzed Pt deposition onto a TEM grid, followed by Ga⁺ ion thinning at 30kV and 5kV. Final specimen
thinning/cleaning was performed on a Gatan PIPS II ion polishing system using an \( \text{Ar}^+ \) ion beam at 500eV or less. Further details regarding \( \text{Ga}^+ \) ion beam sectioning and TEM specimen lift-out have been described elsewhere [24]. Additional TEM specimens were made without the final \( \text{Ar}^+ \) ion thinning/cleaning step. With respect to characterizing the grain structure, no significant difference was found between specimens with or without the final low energy \( \text{Ar}^+ \) thinning/cleaning step.

A cross-sectional TEM bright-field (BF) image, shown in Figure 6.5(a), was obtained from the CrN/Cu/Si(001) specimen whose morphology was shown in Figure 6.1. The specimen was oriented with the Si substrate in the [110] zone axis direction. Both CrN and Cu layers are polycrystalline. Both CrN/Cu and Cu/Si interfaces appear clean, without indication of extensive interdiffusion and reaction. For this specimen, the Cu interlayer thickness was measured from Figure 6.5(a) to be ~810nm, which was consistent with the value measured by FIB cross sectioning in Figure 6.1(a). Figure 6.5(b) shows selected area diffraction patterns (SADPs) obtained respectively from the CrN top layer, the Cu interlayer, and the Si substrate areas. The SADP from Si shows the Si[110] zone axis diffraction pattern. The SADPs from Cu and CrN are consistent with the structure of Cu being fcc and that of CrN being B1-NaCl. Figure 6.6 shows a typical TEM bright-field/dark-field (BF/DF) image pair of the CrN top layer near the CrN/Cu interface. The CrN layer has a pronounced columnar structure, with columns with widths ~50nm and large length/width ratios. The columnar structure of CrN shown in cross sectional TEM is consistent with the rough surface morphology observed in Figure 6.1. The CrN layer appears fully dense, without indication of inter-columnar voids. Figure 6.7 shows a typical TEM BF/DF image pair of the Cu interlayer near the Cu/Si interface. The Cu layer consists of a random mixture of columnar and near equi-axed grains. The presence of nano-twins within the columnar
Figure 6.5  Cross sectional TEM examination of a typical CrN/Cu/Si(001) specimen: (a) A cross sectional BF image across the entire Cu interlayer. The CrN/Cu and Cu/Si interfaces are indicated by white arrows;  (b) typical SAED patterns collected from the (left to right) CrN, Cu and Si layer.

Figure 6.6  Cross sectional TEM examination of the CrN top layer: (a) A BF image, (b) A DF image. White arrows indicate the location of the CrN/Cu interface
Cu grains are visible in the BF image, with twin spacing <100nm. Similar image features were observed from Cu films at different thicknesses. Additional DF imaging shows Cu grains ranging from ~20nm to ~100nm in widths, and with morphologies ranging from near equi-axed grains to columnar grains with large length/width ratios. Similar grain structures were observed from all Cu films, with thicknesses ranging from ~150nm to ~1180nm.

Figure 6.7 Cross sectional TEM examination of the Cu interlayer: (a) A BF image, (b) A DF image. White arrows indicate the location of the Cu/Si interface.

6.3 Instrumented Indentation of Polycrystalline Cu and CrN Films

Instrumented indentation was carried out at room temperature on a Nanoindenter XP system, using a three-sided pyramidal Berkovich diamond indenter. The indenter’s Young’s modulus and Poisson’s ratio are 1170GPa and 0.07, respectively. The machine compliance and the projected indenter tip area as a function of the indenter contact depth was calibrated using a factory supplied fused silica standard following the Oliver-Pharr method [1]. The Young’s modulus and Poisson’s ratio for the fused silica standard were taken respectively to be 72GPa and 0.18, independent of the indenter contact depth. The calibration covered a contact depth range from 40nm to 2100nm. Raw indentation loading and unloading curves were obtained in the load-controlled mode using a constant loading and unloading time of 15sec, with a 30sec
load hold at the maximum load, $L_{\text{max}}$. Multiple load vs. indenter displacement, $L$-$d$, curves were obtained at one $d_{\text{max}}$ value, and $d_{\text{max}}$ was varied to obtain a complete set of indentation data.

Figure 6.8 displays indentation results obtained from a Cu/Si(001) specimen, with a Cu film thickness of ~1180nm. Figure 6.8(a) shows values of measured indentation modulus, $E_{\text{ind}} = E/(1-\nu^2)$, as a function of the indenter contact depth. Error bars for the modulus value are derived from repeat $L$-$d$ curves at the same $d_{\text{max}}$ value. In the absence of an independent measurement on the Poisson’s ratio, only $E_{\text{ind}}$ can be obtained from the elastic unloading portion of the indentation curve. Figure 6.8(a) shows that $E_{\text{ind}}$ increase slightly from ~150GPa at large contact depths to ~170GPa at contact depths between 200nm to 350nm.

The elastic stiffness constants for fcc Cu are respectively $C_{11} = 168.4$GPa, $C_{12} = 121.4$GPa, and $C_{44} = 75.4$GPa [25], and those for diamond-cubic Si are respectively $C_{11} = 165.6$GPa, $C_{12} = 63.9$GPa, and $C_{44} = 79.5$GPa [26]. The elastic compliance constants for Cu are respectively $S_{11} = 14.99(\text{TPa})^{-1}$, $S_{12} = -6.28(\text{TPa})^{-1}$, and $S_{44} = 13.26(\text{TPa})^{-1}$, and those for Si are respectively $S_{11} = 7.69(\text{TPa})^{-1}$, $S_{12} = -2.14(\text{TPa})^{-1}$, and $S_{44} = 12.58(\text{TPa})^{-1}$ [26]. Young’s
modulus in the <001> and <111> directions of cubic crystals are obtained from the compliance constants as [27],

\[
E_{100} = \{s_{11}\}^{-1}, \quad \text{(6.1)}
\]

\[
E_{111} = \left\{s_{11} - \frac{2}{3} \left[ s_{11} - s_{12} - \frac{1}{2} s_{44} \right] \right\}^{-1}. \quad \text{(6.2)}
\]

For Cu, \(E_{100}\) and \(E_{111}\) are respectively 67GPa and 191GPa. For Si, \(E_{100}\) and \(E_{111}\) are respectively 130GPa and 188GPa. Furthermore, Poisson’s ratio in the <hkl> direction of cubic crystals are given by [28]

\[
\nu_{hkl} = \frac{1}{2} - \frac{E_{hkl}}{2(C_{11} + 2C_{12})}. \quad \text{(6.3)}
\]

For Cu, \(\nu_{100}\) and \(\nu_{111}\) are respectively 0.42 and 0.27. For Si, \(\nu_{100}\) and \(\nu_{111}\) are respectively 0.28 and 0.18. In the <001> and <111> directions, the Cu indentation modulus takes on respectively values of 81GPa and 206GPa and the Si indentation modulus takes on respectively values of 141GPa and 194GPa. Based on the XRD results shown in Figure 6.4, the relevant indentation moduli for indentation on the present Cu/Si(001) specimens should respectively be \(E_{\text{ind}}(111) = 206\)GPa for the Cu film and \(E_{\text{ind}}(001) = 141\)GPa for the Si substrate, i.e., the Cu/Si specimen goes from an elastically stiffer film to an elastically more compliant substrate. Thus the data shown in Figure 6.8(a) is trend-wise consistent with what is expected based on the predominant fiber texture of the Cu films, with Cu<111>//Si[001]. Measured \(E_{\text{ind}}\) value is close to \(E_{\text{ind}}\) for the Si substrate at large contact depths.

Figure 6.8(b) shows values of measured hardness as a function of the indenter contact depth. Error bars for the hardness value are derived from repeat \(L-d\) curves at the same \(d_{\text{max}}\) value. Measured hardness values decrease from above 4GPa at large contact depths to ~3GPa at contact depths between 200nm to 350nm. The indentation hardness of Si at room temperature is
~10GPa, limited by a pressure-induced phase transformation [29]. The Cu/Si specimen goes from a softer film to a harder substrate. Thus the observed decrease in hardness with decreasing contact depth is again qualitatively consistent with expectation. Caution should be exercised in taking the measured hardness value of ~3GPa at small contact depths as an “intrinsic” hardness of the Cu film, for it is influenced by two extra factors: one being the effect of a harder Si substrate and the other being the expected presence of an indentation size effect. Both effects tend to elevate measured hardness values. For these reasons, indentations on Cu/Si specimens with smaller Cu film thicknesses were not performed.

Figure 6.9 displays indentation results obtained from a 6.2μm thick polycrystalline CrN film deposited on Si(001), over a range of indenter contact depth from ~1400nm to ~370nm. Figure 6.9(a) shows that the indentation modulus increases monotonically with decreasing indenter contact depth, to ~275GPa at the smallest contact depth of ~370nm. The observed trend is consistent with the expectation for an elastically stiffer film on an elastically more compliance substrate, where measured indentation modulus decreases monotonically with increasing indenter contact depth [30]. A simple extrapolation of the data shown in Figure 6.9(a) suggests that the indentation modulus of the present CrN film is ~300GPa. Figure 6.9(b) shows that measured hardness values in the same contact depth range exhibit only a modest change, from ~16GPa to ~18GPa. Noting that values of indenter contact depth normalized to the CrN film thickness range from 0.06 to 0.23, a simple average of all hardness values shown in Figure 6.9(b) yield a hardness value of ~17GPa, a value believed to be representative of the presently deposited CrN films.

Values of Young’s modulus for CrN as reported in the literature vary widely, from 190GPa to above 400GPa [22,20]. Moduli of sputter deposited CrN films are often reported to
Figure 6.9  Instrumented indentation of a CrN/Si(001) specimen with a CrN thickness of ~6.2μm: (a) indentation modulus vs. contact depth, (b) hardness vs. contact depth. The indentation modulus be between 200GPa and 250GPa, well below 400GPa [21]. A CrN indentation modulus of ~300GPa is consistent with previous reported Young’s modulus values of 270-300GPa on sputter deposited CrN films [31,32]. A wide range of CrN hardness values have been reported in the literature, from 10GPa to above 30GPa [33]. Hardness of CrN was also reported to depend strongly on the level of residual stress [34]. The presently measured hardness for CrN of ~17GPa is consistent with the moderate level of residual compressive stress existing within the CrN layer, obtained from estimates based on glancing incidence XRD measurements data shown in Figure 6.3.

6.4  Micro-Pillar Preparation and Compression Test

Two groups of CrN/Cu/Si micro-pillar specimens were made after cutting each as-deposited wafer into smaller sized pieces. Thin stainless steel sheets of matching sizes were prepared. One micro-pillar group was made by gluing a steel-wafer-steel sandwich assembly, mounting the assembly into epoxy with a fixture which maintained the wafer at a 45° inclination to the epoxy top surface, and polishing the epoxy top surface with SiC abrasives and a final 1μm diamond suspension to expose the CrN/Cu/Si interfaces [5,6]. The other micro-pillar group was made by directly mounting small Si wafer pieces onto a flat platen, keeping the exposed CrN
surface parallel to the platen surface. Scripted Ga⁺ milling was used to fabricate micro-pillars perpendicular to the polished surface or the Si wafer surface for cases where interfaces were 45° inclined or perpendicular to the pillar axis. An array of micro-pillars was fabricated for each specimen group. Additional details of the FIB milling process were reported previously [5,6]. The milling process yielded right circular cylindrical pillars with smooth sidewalls and no obvious taper (see e.g., images shown in Figure 6.10). In each micro-pillar group, pillars of different diameters were fabricated for one particular Cu interlayer thickness. Table 6.1 summarizes the combinations of pillar diameters and film thicknesses fabricated and tested.

Table 6.1 A summary of CrN/Cu/Si(100) micro-pillars fabricated and compression tested, with different pillar diameters, \( D \), Cu film thicknesses, \( h \), and interface inclinations.

<table>
<thead>
<tr>
<th>Cu interlayer thickness (nm)</th>
<th>CrN/Cu/Si(100) micro-pillar diameter (( \mu m ))</th>
<th>Interface inclination = 45°</th>
<th>Interface inclination = 0°</th>
</tr>
</thead>
<tbody>
<tr>
<td>~150</td>
<td>~4.8</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>~340</td>
<td>~4.8</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>~550</td>
<td>~2.8, ~4.0, ~4.9</td>
<td>~5.0</td>
<td></td>
</tr>
<tr>
<td>~810</td>
<td>~4.6</td>
<td>~5.0</td>
<td></td>
</tr>
<tr>
<td>~1180</td>
<td>~4.9</td>
<td>~3.0, ~3.9, ~5.0</td>
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Compression loading of CrN/Cu/Si micro-pillars was carried out on a NanoIndenter XP with a custom-made, ~10\( \mu m \times ~10\mu m \), flat-ended diamond punch. An increasing load was applied to the pillar top surface in displacement-control, with raw indenter load \( L \) and total indenter displacement \( d \) monitored continuously. A preset constant loading time was applied to the micro-pillar group with 45° inclined interfaces. A constant loading rate of 10nm/s was
applied to the micro-pillar group with interfaces perpendicular to the pillar axis. A preset \( d \) value was specified, and the loading was stopped when the specified \( d \) was reached, followed by load removal. No obvious changes in \( L-d \) curves were observed if loading time or rate were changed. In what follows, raw \( L-d \) curves are presented without correcting for system stiffness contributions.

Figure 6.10  Examples of the two groups of CrN/Cu/Si micro-pillars following plastic deformation of the Cu interlayer: (a) with the Cu layer inclined at 45° to the compression axis; (b) with the Cu layer perpendicular to the compression axis. In (b), a vertical FIB cut has been made following the deformation to reveal the interfaces and the barreled shape of the material squeezed out at the edge of the layer. Thicknesses of the Cu interlayers in (a) and (b) are ~340nm and ~1180nm, respectively.

Figure 6.11(a) shows a typical raw \( L-d \) curve obtained from compressing a CrN/Cu/Si micro-pillar with interfaces at a 45° inclination with respect to the pillar axis. The pillar diameter \( D \) is ~5μm, and the Cu interlayer thickness \( h \) is ~550nm. A region of steep increase in \( L \) vs. increasing \( d \), marked A in Figure 6.11(a), is followed by a load plateau region, marked B in
Figure 6.11(a), in which $d$ increases at little change in $L$. As $d$ increases further, an abrupt and large displacement excursion is observed, marked C in Figure 6.11(a).

![Figure 6.11 and 6.12](image)

**Figure 6.11** (a) A typical raw load-displacement curve obtained from compression testing of one CrN/Cu/Si micro-pillar with 45° inclined interfaces; (b) Raw load-displacement curves for three pillar diameter, D with Cu thickness $h = \sim 550$nm.

Figure 6.12 shows typical morphologies associated with compression of CrN/Cu/Si micro-pillars with interfaces at a 45° inclination to the axial direction. Figures 6.12(a), 6.12(b), and 6.12(c) correspond to the three load stages marked A, B, C in Figure 6.11(a). In stages A and B, no deformation of the CrN and Si sections is observed. Figure 6.12(a) shows that little or no deformation of the Cu interlayer occurred in the region where $L$ increases sharply with increasing $d$. Figure 6.12(b) shows that the load plateau is indeed associated with shear plastic flow within the Cu interlayer, leading to a small but clear rigid shift of the CrN top pillar portion with respect to the Si bottom. The load plateau covers a wide range of $d$ values, extending to $d > 600$nm. Figure 6.12(c) shows that the final abrupt and large displacement excursion, shown in Figure 6.11, is associated with a catastrophic shear translation of the CrN top pillar portion, leading to impact of the diamond indenter on the top of Si bottom portion of the pillar. The sliding marks on the Cu surface, clearly evident in Figure 6.12(c), again offer evidence that extensive shear plastic flow occurred within the Cu interlayer confined between elastic-brittle
CrN and Si. Based on data and morphological observations shown in Figures 6.11 and 6.12, the average plastic shear flow stress of the Cu interlayer, $\bar{\tau}$, was calculated from the plateau load value, $L$. The average compression stress applied to the pillar is $\bar{\sigma} = L/(\pi D^2/4)$, and the average shear stress in the Cu interlayer is $\bar{\tau} = \bar{\sigma}/2$.

Figure 6.12 Morphology of compression tested CrN/Cu/Si micro-pillars with 45° inclined interfaces: (a), (b), and (c) correspond to stages A, B, and C in the L-d curve displayed in Figure 6.11(a)

Figure 6.13 summarizes the results of shear testing on Cu interlayers, obtained from compression loading of CrN/Cu/Si micro-pillars with varying Cu interlayer thickness $h$ and pillar diameter $D$. For $h = 550$nm, Figure 6.13(a) shows that the value of $\bar{\tau}$ has little dependence on $D$. On the other hand, data shown in Figure 6.13(b), obtained from pillars with $D = \sim5\mu$m, clearly demonstrate that the Cu interlayer thickness $h$ has a significant influence on $\bar{\tau}$, which changes by a factor of two over the $h$ range of 150nm - 1180nm. Each data point shown in Figure 6.13 represents an independent test on a separate micro-pillar, and it is apparent from Figure 6.13 that the scatter in measured $\bar{\tau}$ values is relatively low. Figure 6.13 shows a clear dependence of the shear flow stress of the Cu interlayer on its thickness, and a significant size effect.

Figure 6.14(a) shows a typical raw $L$-$d$ curve obtained from compressing a CrN/Cu/Si micro-pillar with interfaces perpendicular to the pillar axis. The pillar diameter $D$ is $\sim5\mu$m, and
Figure 6.13  Shear flow stress measured from compression testing of CrN/Cu/Si micro-pillars with 45° inclined interfaces: (a) average shear flow stress vs. pillar diameter, (b) average shear flow stress versus Cu interlayer thickness $h$. The dash line in (b) shows output from the SGP model.

the Cu interlayer thickness $h$ is ~1180nm. A region of steep increase in $L$ vs. increasing $d$ is again followed by a load plateau region, marked A in Figure 6.14(a), in which $d$ increases as $L$ remains approximately a constant. As $d$ increases further, the $L$-$d$ curve transitions from the load plateau to a region with further steep increase in load, marked B and C in Figure 6.14(a). Finally, an abrupt and large displacement excursion is observed, marked D in Figure 6.14(a).

Figure 6.14  (a) A typical raw load-displacement curve obtained from compression testing of one CrN/Cu/Si micro-pillar with interfaces perpendicular to the pillar axis; (b) Raw load-displacement curves for three pillar diameter, D with Cu thickness $h$ = ~1180nm
Figure 6.15 shows typical morphologies associated with compression of CrN/Cu/Si micro-pillars with interfaces normal to the pillar axis. Figures 6.15(a), 6.15(b), 6.15(c), and 6.15(d) correspond to the four load stages marked A, B, C, and D in Figure 6.14(a). In stages A, B, and C, no deformation of the CrN and Si sections of the pillar is observed. Figure 6.15(a) shows that the load plateau is indeed associated with plastic flow within the Cu interlayer, as it is squeezed out at the layer perimeter. Figure 6.14 shows that the load plateau covers a reasonably wide range of $d$, from ~300nm to ~550nm, indicating that a significant reduction in the Cu thickness occurred within the plateau region. As the load plateau transitions to another steep load increase, Figures 6.15(b) and 6.15(c) show that significant additional amounts of Cu has been squeezed out at the layer perimeter. The sliding marks on the Cu surface, clearly evident in Figure 6.15(b), again offer clear evidence that plasticity occurred within the Cu interlayer confined between elastic-brittle CrN and Si due to compression loading. Figure 6.15(d) shows that the final abrupt and large displacement excursion in this case is associated with fracture of the Si bottom portion of the micro-pillar. While we do not presently understand the reason for the transition from the load plateau to a further increasing load in compression of CrN/Cu/Si micro-pillars with normal interfaces, $L-d$ data and morphological observations shown in Figures 6.14 and 6.15 again suggest that we can evaluate the average plastic compression flow stress of the Cu interlayer, $\bar{\sigma}$, from the plateau load value, $L$, through $\bar{\sigma} = L/(\pi D^2 / 4)$.

Figure 6.16 summarizes the results of compression testing on Cu interlayers, obtained from compression loading of CrN/Cu/Si micro-pillars with varying Cu interlayer thickness $h$ and pillar diameter $D$. For $h = 1180$nm, Figure 6.16(a) shows that the value of $\bar{\sigma}$ depends significantly on $D$. Even though an $\bar{\sigma}$ increase with increasing $D$ is expected from conventional plasticity theory [35], the observed dependence of $\bar{\sigma}$ on $D$ is stronger than what is expected.
Figure 6.15 Morphology of compression tested CrN/Cu/Si micro-pillars with perpendicular interfaces: (a), (b), (c), and (d) correspond to stages A, B, C, and D in the L-d curve displayed in Figure 6.14.

without a material size effect. At a fixed $D$ of $\sim 5\mu m$, Figure 6.16(b) shows that $\sigma$ exhibits an even stronger dependence on $h$, increasing by a factor of two as the Cu interlayer thickness decreases from 1180nm to 550nm. Each data point shown in Figure 6.16 again represents an independent test on a separate micro-pillar, and relatively low scatter in measured $\sigma$ values is again apparent. Figure 6.16 shows clear dependencies of the compression flow stress of the Cu interlayer on its thickness and the pillar diameter, again exhibiting significant size effects.
Figure 6.16  Compression flow stress measured from compression testing of CrN/Cu/Si micro-pillars with normal interfaces: (a) average compression flow stress vs. \( D \) for a Cu interlayer thickness \( h \) of 1180nm, (b) average compression flow stress vs. \( h \) at a fixed pillar diameter \( D \) of \( \sim 5 \mu m \). The dash line shows output from the SGP model.

Through data shown in Figures 6.10 – 6.16, we demonstrated that the micro-pillar protocol shown in this paper is an effective means for obtaining quantitative measurements on plasticity of thin metal layers confined between elastic-brittle solids. This protocol further allows quantitative evaluation of the plastic response of confined thin metal layers in simple yet significantly different deformation geometries. Furthermore, the measured dependence of flow stress on Cu film thickness is significantly different depending on whether deformation occurs in pure shear or normal compression, illustrating that manifestations of mechanical size effects depend significantly on the deformation geometry in the same material. The present data set, taken together, offers a good test case for non-local plasticity theories.

6.5  The Material Length Parameter and Trends Predicted by Strain Gradient Plasticity

The purpose of this section is to illustrate that the experimental trends shown in Figures 6.13 and 6.16 are qualitatively captured by predictions of an elementary SGP model with one consistent set of material parameters. Subsequent efforts will be made to obtain more accurate agreement with the experimental results. Indeed, in part, the value of the present set of
experimental data is that it can serve as a test case for the further development of SGP and DDP—theories which are not yet sufficiently reliable for applications purposes.

A simple small strain deformation theory of SGP [7,12] will be employed here, which has three material parameters: a reference flow stress, $\sigma_y$, a strain hardening exponent, $N$, and a material length parameter, $l$. The uniaxial tensile stress-strain relation is assumed to follow the power law: $\sigma = \sigma_y \varepsilon^N$. An effective plastic strain is defined as $E_p = \sqrt{2e_{ij} e_{ij}^p / 3 + l^2 2e_{ijk} e_{ijk}^p / 3}$, which combines the conventional effective plastic strain with an analogous term formed from the plastic strain gradients and the material length parameter. Elastic strains are neglected, and the work density under proportional straining is $U(E_p) = [\sigma_y / (N + 1)]E_p^{N+1}$. In the deformation theory, this work density is identified with the strain energy density of the solid. It reproduces $\sigma = \sigma_y \varepsilon^N$ in uniaxial tension. The energy in the layer is $\Phi = \int_V U(E_p) dV$ where $V$ is the layer volume. At a prescribed average shear strain across the layer in the shear case, or at a prescribed uniform normal relative displacement of the interfaces in the normal compression case, the desired strain distribution minimizes $\Phi$ among all admissible distributions. Admissibility requires that the plastic strains vanish at the interfaces with the adjoining segments of the pillar, modeling the blocked dislocation motion.

The raw $L-d$ curves, shown in Figures 6.11(b) and 6.14(b), indicate that within the flat plateau region there is relatively little strain hardening. Thus, the predictions which follow will be based on the limit $N \to 0$, such that the solid is rigid-perfectly plastic and characterized by the tensile yield stress $\sigma_y$ and material length parameter $l$. The computations for the normal compression case have been carried using a method similar to that detailed in References [12], but for the present axisymmetric geometry rather than plane strain. Predictions from the model
are presented in dimensionless form in Figure 6.17, covering the parameter variations of the experiments discussed in Section 6.4. The strong dependence on $h/l$ in each part of Figure 6.17 highlights the influence of the material length parameter. The predictions asymptote to those for a conventional rigid-perfectly plastic solid when $h/l > 5$. The predicted response of an elastic-perfectly plastic solid without strain gradient effects, i.e., the limit as $l/h \to 0$, is also included in Figure 6.17 for comparison.

To make a direct comparison with the experimental results shown in Figures 6.13 and 6.16, it is necessary to assign values to $\sigma_Y$ and $l$. We have not made independent measurements of tensile yield stress of Cu thin films, but several papers on this subject exist in the literature [36]. Reported $\sigma_Y$ values are in the range of 0.3 to 0.4 GPa for Cu thin films of thicknesses around 1 μm or larger. In the following simulations, we take $\sigma_Y = 0.35$ GPa. Then, based on the SGP results shown in Figure 6.17(a), we choose $l$ to reproduce the experimentally measured average shear flow stress, $\bar{\tau} = 0.70$ GPa, in Figure 6.13(a) for Cu layers with $h=550$ nm, yielding an $l$ value of 647 nm. It is interesting to note that previous tensile testing of supported Cu thin
films [37] and bulge testing of free-standing Cu thin films [38] with surface passivation yielded respectively \( l \) values of \( \sim 0.6\mu m \) and \( \sim 0.35\mu m \), largely consistent with the present fitted \( l \) value.

The SGP model predictions, computed with the single parameter set of \( \sigma_y = 0.35GPa \) and \( l=647nm \), are plotted in dimensional form as dashed lines in Figures 6.13(b), 6.16(a), and(b). As evident from these figures, while the predictions of the simple SGP theory capture the general trend in each of the three comparisons, they overestimate the strength enhancement for the thinner layers. In addition, the theory predicts a stronger increase in \( \bar{\sigma} \) with pillar diameter than what is observed in the experimental data. As noted above, the present SGP model is the simplest theory one could choose. One obvious limitation which is likely to be important is the fact that the model is isotropic and thereby ignores plastic anisotropy associated with the dominant \(<111>\) fiber texture of the Cu grains. More accurate predictions may require a single crystal representation of the polycrystalline layer. This and other possibilities are left for the future. We also note that the present set of polycrystalline Cu interlayers, at any thickness studied, contain numerous grain boundaries which can serve as dislocation sources. In addition, all Cu interlayers were deformed to large plastic strains as a result of the loading applied. The present data should serve as a challenge for both continuum and DDP theories.

6.6 Concluding Remarks

A new experimental protocol has been described for testing plasticity of thin metal films confined between and bonded to non-deforming, elastic-brittle materials in a micro-pillar geometry. Experimental results for plastic flow of sputtered Cu thin films in both confined shear and normal compression have been obtained from CrN/Cu/Si micro-pillars. These results have been compared to a simple strain gradient plasticity model for a perfectly plastic solid characterized by an unconstrained tensile yield stress \( \sigma_y = 0.35GPa \), which was identified using

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data for free standing films from the literature, and a material length parameter $\ell = 647\, nm$, which was chosen to fit the present shear data for Cu film with a thickness of $550\, nm$. The Cu film thicknesses tested ($550-1180\, nm$) encompass the material length parameter, and the testing results reveal a factor of two increase of the effective shear strength of the thinnest film relative to the thickest film. Furthermore, the effective shear strength of the thickest confined Cu film ($1180\, nm$) is already twice that expected for the Cu shear strength under unconfined conditions, i.e., $0.4\, GPa$ compared with $\sigma_y / \sqrt{3} = 0.2\, GPa$. Thus, the experimental data obtained for the thinnest Cu films ($550\, nm$) for both the shear test and the normal compression test reveals an elevation of the effective strength of the Cu by a factor of four above the value expected for thicker films—a significant size effect. The simple SGP model captures the essential trends of Cu film deformation in both confined shear and normal compression geometries, but improvements in quantitative agreement with experimental data will require further modeling efforts.

Until now, plasticity in metal thin films has been experimentally probed by instrumented nanoindentation and tensile testing of either free-standing metal films or metal films supported on polymeric substrates. While substrate effects complicate indentation testing of thin films on substrates, the experimental complexity associated with tensile testing of free-standing or supported thin films curtails its wide usage. In comparison, the present experimental results illustrate that extensive plastic deformation can be induced within thin metal films by using the micro-pillar protocol described in this letter, and that this protocol allows quantitative plasticity data to be obtained from the same metal film under significantly different deformation geometries. The new experimental results presented in this letter offer independent test cases for confronting new developments in SGP—the wide range of parameters capable of being
represented in such data sets is believed to be valuable for further experimental calibration and validation of non-local plasticity theories.

In addition to the scientific interest in understanding micro- and nano-scale mechanical behavior of materials, plastic flow in confined thin metal layers is also of significant interest to surface engineering technologies. Vapor phase deposition of thin ceramic coatings has become an important means for engineering surfaces of mechanical components \([39,40]\) and manufacturing tools \([41,42]\). Satisfactory adhesion of coatings to substrates is critical to the lifetime of coated systems. To improve adhesion between ceramic coatings and substrates, thin metallic interlayers are often deposited between the coating and the substrate. When coated components are subjected to external contact, this adhesion interlayer is put under combinations of compression and shear. How such thin interlayers deform plastically has a significant bearing on the mechanical response of the coating/interlayer/substrate system as a whole. Data presented here represent, to our knowledge, the first set of quantitative data on how thickness and deformation geometry of thin metal interlayers influence their plastic behavior under stress conditions relevant to interlayer performance. It is hoped that further investigations along the lines outlined in this letter will advance the fundamental understanding on how to effectively engineer coating/substrate interfaces for wide ranging applications of coated mechanical components and manufacturing tools.

### 6.7 References


CHAPTER 7
SUMMARY

This dissertation focuses on design and construction of a plasma assisted PVD system, deposition and characterization of refractory ceramic thin films, and macro and micro scale mechanical testing of the integrity of film/substrate interfacial layers.

An inductively coupled plasma (ICP) was used to assist vapor phase deposition in either physical or chemical vapor deposition (PVD/CVD). An existing system was redesigned into a completely ultra-high vacuum (UHV) system, with a load-lock chamber attached to the deposition chambers to maintain UHV conditions in the deposition chamber at all times.

TiB$_2$ thin films deposited on microscale Ta inserts by low temperature ICP assisted PVD showed good potential for Al and Al-based alloy molding. TiB$_2$ coated Ta inserts had no coating delamination after multiple Al molding and demolding runs.

A new experimental protocol for evaluating the mechanical integrity of film/substrate interfacial layers was demonstrated, and showed good potential for quantitative evaluation of film/substrate interfacial strength. In contrast to existing testing protocols, the present method combines microscale fabrication by FIB milling and instrumented micro/nano mechanical testing, and significantly decreases the experimental error associated with quantitative evaluation of the mechanical properties of interfaces.

With the same experimental testing protocol, shear flow stress in thin Cu layers confined between two elastic-brittle bodies in different geometries were measured and, for the first time to our knowledge, shown to possess a significant dependence on its thickness. This first experimental observation of a size effect in confined shear plastic flow offered new and fundamental data for micron scale plasticity theories.
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Yang Mu was born in 1984, in Hubei Province, People’s Republic of China. He studied in Materials Science and Engineering department in Beijing Institute of Technology, China, from 2002 to 2006, and obtained Bachelor’s degree in Materials Science and Engineering. He became a graduate student in Louisiana State University in Mechanical Engineering department started at 2007. Currently, he is a philosophy of doctorial candidate major in Mechanical Engineering. His research interest is focused on vacuum technology, thin films preparation and characterization, and micro/nano scale mechanical response of materials.