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High temperature brittle film adhesion measured from annealing-induced circular blisters

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ABSTRACT

Testing high temperature brittle film adhesion is necessary for understanding interfacial failure at elevated temperatures. However, current brittle film adhesion measurement methods are limited to room temperature. Experimental techniques to characterize high temperature brittle film adhesion are lacking, and temperature effects on brittle film adhesion remain poorly understood. Here, a simple, yet reliable method is developed to measure the adhesion of TiN films on Si substrates with native SiO_2 oxide layer from 300 °C to 500 °C, based on circular blisters induced by annealing. The circular blister size was proven to remain the same after cooling down to room temperature, based on *in situ* observations. Experimental results show that film adhesion energy gradually increases and then drops with annealing temperature. Thermally activated dislocation glide promotes easier nucleation of dislocations in Si substrate near the interface. This in turn increases dislocation shielding effects on the interfacial crack tip during its dynamic propagation, resulting in the initially increased adhesion with temperature. Plastic deformation of TiN film is not considered because the combination of the small grain size of less than 10 nm and the amorphous/nanocrystalline structure limits dislocation emission and grain sliding. Local phase film transformation from amorphous to nanocrystalline at the TiN/SiO_2 interface was demonstrated by high resolution transmission electron microscopy, causing adhesion reduction due to interfacial embrittlement and contact mismatch at 500 °C. In addition, the drop in adhesion induces circular blisters' transition from axisymmetric to non-axisymmetric.

1. Introduction

Brittle coatings are used to improve underlying substrates' mechanical and functional properties at elevated temperatures. Examples include protection coatings to prevent high temperature oxidation [1], diffusion barrier layer to inhibit interdiffusion between metal film and the substrate at high temperature [2], and thermal barrier coatings to improve operating temperature of turbine blades [3]. However, high temperature can induce coating compressive stress [1,4], increase interfacial roughness [5], or introduce chemical impurities [6], which promote interfacial delamination [7–9] and tremendously limit brittle coating applications at elevated temperatures. For reliable coating/substrate design, testing adhesion at elevated temperatures, along with understanding the factors affecting adhesion, are not only scientifically, but also practically necessary for engineering applications.

In the past decades, lots of methods have been proposed to determine brittle film adhesion qualitatively and quantitatively. Qualitative methods include pull off and peel tests, also known as tap tests [10]. To measure the adhesion energy quantitatively, five typical methods have been used, including scratch [11,12], four-point bending [13,14], stressed overlayers [15], hydrogen induced buckling [16,17] and nanoindentation [18,19] tests. These methods have been successfully used to study adhesion of brittle films at room temperature. However, measuring thin film adhesion at elevated temperatures has been challenging due to the testing difficulties, including sample preparation, accurate temperature measurements, controlling environment to prevent sample oxidation, and so on. As a result, only a few studies investigated the thin

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films' adhesion at elevated temperatures, but have been limited to temperatures below 130 °C using nanoindentation methods [20,21]. Adhesion of brittle films at elevated temperatures remains an unexplored area.

A large amount of work dealing with film adhesion at room temperature has suggested that many factors affect adhesion, including residual stress [22,23], film grain size [18,20,21], film/substrate interfacial structure and composition [24], and plastic energy dissipation in the film and/or the substrate [11,18,25–27]. Of particular note, all of these factors are inevitably affected by temperature. For example, temperature remarkably increases compressive stress in β-NiAl [1] and TiN [4] films on Si substrates due to the difference in thermal expansion coefficients. At elevated temperatures, thermally activated dislocation glide, grain boundary diffusion creep, and dislocation-based creep are more pronounced [28,29], contributing to an enhanced toughness, in particular near the brittle-to-ductile transition temperature [30]. Some studies have demonstrated that interdiffusion [31] and reactions between the film and the substrate, or adhesion layer at elevated temperature, can lead to the formation of new phases [24]. These studies imply that the high temperature film adhesion energy differs substantially from the room temperature values. Therefore, a new simple method to measure brittle film adhesion at elevated temperature is required.

If the film has a larger thermal expansion coefficient than the substrate, large compressive stress will arise with increasing temperature [1,4], inducing some interesting buckling morphology, including straight-sided blisters [9], circular blisters [32,33], and telephone cord buckles [8,15,34]. These buckling patterns with well-defined shapes have been utilized to evaluate mechanical parameters, such as the stress level [35] and adhesion energy [12,15,36,37] of brittle films at room temperature, by employing the elastic buckling model proposed by Hutchinson and Suo [38]. Similarly, buckling can also be used to characterize brittle film adhesion at high temperature and its dependence on temperature.

In this paper, we present a simple, but reliable method based on annealing-induced circular blisters' formation to determine the adhesion of TiN films on Si substrates with native SiO_2 oxide at high temperatures. Confocal laser scanning microscope (CLSM) was used to measure the circular blister dimensions (height and diameter). The dependence of film adhesion on temperature has been studied, and the corresponding mechanisms have been proposed.

2. Experimental procedure

TiN films were deposited on 20 mm × 20 mm (111) Si substrates with native SiO_2 oxide using reactive RF-pulsed magnetron sputtering at 300 °C. The substrates were moved in front of the titanium target (99.99% pure) with a diameter of 76 mm. In order to weaken the interface, all substrates were not subjected to Ar plasma cleaning [39], thus, buckling was more likely to appear during film annealing. In the magnetron sputtering system used for film deposition, the base pressure was 2×10^{-3} Pa, the target power was 250 W, and the Ar working gas pressure was 0.3 Pa. Nitrogen gas flow during deposition was 0.9 cm^3/min, while argon flow was 30 cm^3/min. The nominal film thickness was about 600 nm, measured by CLSM (LEXTOLS4000, Olympus, Japan).

The change of the film surface topography with temperature was observed *in situ* by ultra-high temperature CLSM (VL2000DX-SVF17SP, Lasertec), which used infrared heating. The chamber was first pumped to 10^{-2} Pa, and then vented with Ar (≥99.99% pure) for 30 min before heating to prevent film oxidation. Due to larger thermal expansion coefficient of TiN film compared with the Si substrate [4], biaxial compressive stress in the film was generated during heating. Once the thermal stress approached the film critical debonding stress, circular crack formed at the TiN/SiO_2 interface, because the adhesion between the native SiO_2 oxide layer and Si substrate is much stronger than between the sputtered layer and SiO_2 [18,23,40,41]. The compressive stress would load the edge of the interface crack between the film and the substrate, causing the blister to spread, as seen in Fig. 1b–d. During annealing, the blister's diameter grew initially and then arrested, as seen in Fig. 1d–g. During cooling, the size of the blister remained the same due to the decrease in the biaxial compressive stress, i.e. the decrease in driving force for the blister propagation, as seen in Fig. 1g–i. Unfortunately, the ultra-high temperature CLSM (VL2000DX-SVF17SP, Lasertec) was unable to observe the three-dimensional topography, i.e. the height of the blisters. According to the previous *in situ* observations of the straight-sided blister growth [9], the height of the blister is related to its width, i.e. the height won't change if the width is kept the same. Therefore, the stabilized dimensions of the blisters at elevated temperature can be replaced by those at room temperature, and then the film adhesion at elevated temperature can be measured.

The original as-deposited sample was cut into smaller pieces, about 4 mm × 4 mm in size, and randomly divided into eight sets. Five sets of samples were placed into quartz tubes with 10^{-5} Pa pressure to prevent samples oxidation. Samples were annealed at various temperatures ranging from 300 °C to 500 °C, with a 50 °C interval, 5 °C/min heating rate and kept for 2 min at set temperature to stabilize the blisters morphology, and then naturally cooled in the furnace to room temperature. The blister topography of each sample after annealing was obtained at room temperature using CLSM (LEXTOLS4000, Olympus). More than 100 blisters were measured for each temperature to obtain average adhesion values.

X-ray diffraction (XRD) experiments were carried out in the $10°–90°$ 2θ range with Cu Kα radiation (TTRIII, Rigaku). The interfacial structure between the film and the substrate was observed in cross-section with high resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 FEI). Young's modulus and hardness of the films were measured by nanoindentation using Berkovich tip with an effective radius of 150 nm (TI900, Hysitron). The fracture toughness of annealed TiN films was measured by the indentation method [42], using a Vickers hardness tester (HV-1000, ALEC), with a load of 0.98 N.

3. Experimental results

3.1. Microstructure of TiN films at elevated temperature

Fig. 2 shows XRD patterns of TiN films on Si substrates in the as-deposited and annealed states obtained under the same XRD measurement conditions. An obvious increase in XRD intensity is observed in the film annealed at 500 °C compared to the as-deposited state, indicating higher degree of film crystallization with annealing [43,44]. Another observation is that no detectable film oxidation occurred during annealing, since only TiN diffraction reflections are present in the XRD patterns.

Fig. 3 shows interfacial HRTEM and the corresponding selected area electron diffraction (SAED) patterns. Fig. 3a reveals that the as-deposited TiN film consists of a purely amorphous layer, about 15 nm thick, followed by a layer with amorphous/nanocrystalline structure. The presence of thin amorphous layer near the interface is also observed in other sputter-deposited brittle films [45,46], which is attributed to rapid quenching of atoms as they arrive onto the substrate [47,48]. However, sputter deposition will heat the substrate, resulting in increased surface mobility of the film constituents, which favors the film growth with higher degree of crystallization further away from the interface [46,48]. No obvious crystallization of the amorphous layer is observed after 300 °C