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Structure, morphology and nanoindentation behavior of multilayered TiN/TaN coatings

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Abstract

TiN/TaN coatings, consisting of alternating nanometer-scale TiN and TaN layers, were deposited using a magnetron sputtering system. The structure, morphology and hardness were assessed using X-ray diffraction, atomic force microscopy (AFM) and nanoindentation, respectively. The results showed that the TiN/TaN coatings exhibited good modulation periods and a sharp interface between TiN and TaN layers and had cubic structure. The hardness (H) and elastic modulus (E) of TiN and multilayered TiN/TaN films on Si substrate were evaluated by hardness-depth and elastic modulus-depth curves measured by a depth-sensing nanoindentation technique. And the yield strength was calculated using a relationship between the H, E and Y. The hardness characteristics of thin-film coated composites were predicted using the plastic-zone volume-law of mixture theory. The behavior of composite hardness is well predicted over the total indentation depth using the present analysis, even though there are large deviations between the analysis and the experimental results for TiN/TaN/Si systems.

Keywords: Multilayered TiN/TaN coatings; Structure; Nanoindentation behavior

1. Introduction

Multilayers with bilayer lengths on the nanometer-scale exhibit significant improvement in hardness, toughness, oxidation resistance and corrosion resistance as compared to single-layered coatings. Among them, transitional nitrides/nitrides have attracted much attention recently due to their substantial strength and hardness enhancements. Mutilayers consisting of very thin (2–10 nm) layers of nitride materials were deposited by magnetron sputtering have hardness in excess of 5000 kg/mm^2 [1]. This hardness is comparable to that of cubic-BN and is second only to diamond. Therefore, the potential for the development of new hard coatings for the machine industry (for example in cutting operation) is very large, using materials with good tribological properties as the individual layers of the multilayers. Up to now, most of the works have been done on the mechanism for nitride superlattice hardening. A variety of mechanisms have been used to explain the enhancement, including the effects of elastic anomalies, coherency strains and elastic modulus differences between the superlattice layers [2–4].

In recent years, nanoindentation technique has proven to be an appropriate method for evaluating the mechanical properties of hard thin films such as transitional nitrides/nitrides multilayers. The indentation response of a thin film on a substrate is a complex function of the elastic and plastic properties of both the film and the substrate. In order to measure 'film-only' properties, a commonly used rule of thumb is to limit the indentation depth to less than 10% of the film thickness [5]. However, this rule is not always unconditionally applicable in any case. At small indentation

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depth, the indentation size effect and surface roughness effect on the hardness become more significant and sometimes make this rule inapplicable. W.D. Nix reported a depth dependence of the hardness for 1.0 μm TiN film on silicon, which extended to a depth of indentation equal to 100 nm [6]. If the indentation depth exceeds a certain critical value, the composite hardness influenced by the substrate will be measured. The composite hardness presents more practically the mechanical property of film/substrate system under working condition than the film-only hardness dose. In this view, a reliable prediction of composite properties is of interests in practical application of film/substrate system. The variation of composite hardness with indentation depth has been predicted by various methods such as empirical approaches, the finite element techniques and geometrical modeling approaches as well [7–9]. Geometrical modeling approaches have been applied based on apportioning the contributions of the film and the substrate to the composite hardness through some idealization, such as load-bearing area-law of mixtures theory [10] and plastic-zone volume-law of mixture theory [11]. The former can be applied when the indentation cracking occurs within the film, so that the latter will be applied in our nanoindentation study.

Even though several coating studies have revealed that many nitride multilayers (TiAlN/VN [12], TiN/CrN [13] and TiN/Nb [14]) can outperform the single layered TiN in terms of hardness and wear resistance, little is known about the detailed nanoindentation characterization of the nitride multilayered coatings on the substrates, such as the effects of substrate on hardness and elastic modulus. The main purpose of this paper is to investigate the structure, morphology and nanoindentation behaviors of multilayered TiN/TaN film with particular reference to the effects of substrate on mechanical properties of film/substrate system, and establish correlations between nanoindentation properties of TiN/TaN film/silicon system and mechanical properties of both the film and substrate using the plastic-zone volume-law of mixtures theory.

2. Experimental

2.1. Thin film deposition

The polycrystalline TiN/TaN nanomultilayers were deposited using a magnetron sputtering system (JPG450, manufactured by Shenyang ZKY Technology Development Co., Ltd., China), which has three targets including one d.c. and two r.f. magnetron cathodes. The sputtering targets (diameter 6 cm) were pure Ti (99.9%) and Ta (99.9%), which were mounted on each of the r.f. cathodes. Ground and polished single-crystal silicon (111) wafers were use as substrate materials. The substrates were chemically cleaned in an ultrasonic agitator in acetone, absolute alcohol before being mounted in the vacuum chamber. The distance between the substrate holder and the target was 6 cm. For all coatings, the deposition sequence started with the growth of a thin (approximately 20 nm) Ti interlayer followed by a 200-nm-thick TiN layer. Both the Ti and the TiN layer were obtained with the substrates held stationary above the Ti target. After this, the substrate rotate to the position above Ta and Ti targets alternately and was held stationary for different times to obtain compositionally modulated structure. Modulation ratio was obtained though exact control of the stopping times in front of the Ti and Ta targets. Typically, TiN/TaN multilayers were deposited under a base pressure of 4×10^{-4} Pa and a total $Ar+N_2$ gas pressure of 5.0×10^{-1} Pa. The modulation ratio l_{TaN}/l_{TiN} was fixed at 2:1. The source power of Ti and Ta targets were 110 and 70 W, respectively. The total thickness of multilayers and TiN film was 1.3 μm, and all the substrates were resistively heated to 450 °C during deposition.

2.2. Structure, morphology characterization

The modulation periods of TiN/TaN multilayers were measured by the low-angle X-ray reflectivity method using Rigaku X-ray diffractometer (XRD) using Cu K_α radiation under condition of 40 kV and 30 mA. The coating crystallographic structures wear characterized by high-angle X-ray diffraction (XRD). An atomic force microscopy (AFM) was used to examine the surface morphologies of coatings.

2.3. Nanoindentation

The nanoindentation tests were performed using the Nanoindentater II with a Berkovich indenter tip from Nano Instruments Incorporated. The instrument was operated in the continuous stiffness mode (CMS) and the indentations were made using a constant nominal strain rate of 0.05 s^{-1}. Hardness and Yong's modulus was determined using the Oliver and Pharr analysis [5]. To obtain the composite hardness, nanoindentation tests were performed with an indentation depth more than 900 nm.

Hardness H means the resistance to local plastic deformation of materials, which has been conventionally obtained by measuring the projected contact area A:

$$H=\frac{P}{A} \tag{1}$$

where P is the load. Elastic modulus E can be obtained from the contact stiff, using the relation:

$$S=\beta\frac{2}{\sqrt{\pi}}E_r\sqrt{A} \tag{2}$$

$$\frac{1}{E_r}=\frac{1-\nu_i^2}{E_i}+\frac{1-\nu^2}{E} \tag{3}$$

where β is a constant that depends on the geometry of indenter and $\beta=1.034$ for a triangular indenter. E_r is the