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Fabrication and characterization of nanolayered single element nitride coating

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ABSTRACT

Tantalum nitride (TaN) and Hafnium nitride (HfN) coatings were deposited through magnetron sputtering at various Ar/N_2 inlet gas ratios and RF input power control, respectively. The nitrogen contents of the single layer nitride coatings decreased with the Ar/N_2 ratio and increased with the input powers. TaN coating could be fabricated with crystalline structure, c-TaN, with a preferred orientation (200), while the amorphous feature TaN, a-TaN, was deposited with low Ar/N_2 ratio and excess N content. For HfN, the similar HfN crystalline features with a preferred orientation (111) were observed for all conditions. The c-TaN and a-TaN layers were alternately stacked into nano-multilayer. The HfN multilayer was deposited with layers generated at 150 and 125 W. The c-TaN film exhibited superior mechanical strength, whereas the a-TaN coating had a better corrosion resistance. Combining crystalline and amorphous TaN layers to form a multilayer improved the mechanical behavior. The HfN films, both in single-layer and multi-layer form, exhibited columnar structure feature under various sputtering input powers. Although the multilayer feature for HfN coating by various power input modulation did not exhibit significant improvement for hardness, the scratch resistance was elevated.

1. Introduction

For mechanical tool components which have to suffer thermo-mechanical shocks, the transition metal nitrides, such as TiN, TaN, and CrN, are widely used as protective coatings due to their well abrasion and heat resistances [1–4]. Tantalum nitride and Hafnium nitride films having specific mechanical properties are potential candidates for protective coating against harsh environments [5]. Both of them have been employed to form multilayer assemblies, such as HfN/Si_3N_4, HfN/VN and Ta/TaN [6–8]. The multilayer, as a composite coating, combines various characteristics from its stacking single layers [9–12]. In Staia's work, wear resistance has been enhanced by HfN and TiCN multilayer configuration [10]. Chen and coworkers have studied the mechanical properties of TaN/CN_x multilayer system [12]. The hardness and Young's modulus can increase from 20 and 165 GPa to 31 and 294 GPa, respectively, with the addition of CN_x into the multilayer coating. In recent years, some studies indicate that one element film with different sputtering conditions, such as nitrogen flow ratio and substrate bias, forms various microstructure and exhibits different properties [13,14]. TaN coatings can be deposited with crystalline and amorphous structure by adjusting the gas flow ratio [13]. Analogously, Aron and Grill have pointed out that the composition, friction coefficient, hardness and adhesion of the HfN films are related with the nitrogen content in $Ar + N_2$ atmosphere [15,16]. The TaN layers with different microstructure features are further stacked to develop multilayer coatings [17]. The promoted strength and mechanical properties of this nanoscale single element nitride crystalline/amorphous multilayers are attributed to the interface and heterostructural feature between crystalline and amorphous layers. However, the corrosion resistance of TaN crystalline/amorphous multilayers has not been reported yet. The case for depositing identical element nitride multilayer with alternating structures is challenging and is not widely investigated. Using one and single element target to manufacture a multilayer coating, not only the cost but also the complexity of sputtering process can be reduced.

In this study, single and multilayer TaN and HfN coatings were deposited by reactive magnetron sputtering technique. In order to fabricate single element nitride coating with various microstructures, the Ar/N_2 gas inlet ratio and the input power are set as the controlling parameters for TaN and HfN, respectively. The multilayer is then deposited by sequential stacking of layers with different microstructure features. The phase, microstructure, hardness, scratch and the corrosion resistance of the coatings are analyzed and discussed.

2. Experimental procedures

The nitride coatings of interest were grown on AISI 420 steel sheet substrate and Si (111) wafer for various analyses. All the substrates were cleaned by an ultrasonic agitator with acetone and followed D.I. water before deposition. The single layer and multilayer coatings were

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fabricated by radio frequency (RF) magnetron reactive sputtering. The high purity Ta (99.995%) and Hf (99.999%) targets both with 2 in. and 6 mm in diameter and thickness, respectively, were applied as deposition sources. The chamber was evacuated down to 3.2×10^{-6} Pa. The substrates were kept at 350 °C during deposition. The working distance from target to substrate was controlled at 100 mm. Pre-sputtering was performed with pure Ar for 5 min. The working pressure was about 5.7×10^{-3} Pa under a total gas flow ($Ar + N_2$) of 20 sccm. In this study, interlayers of Ta and Hf thin films were firstly deposited on the substrates for TaN and HfN coatings, respectively, in order to promote the adhesion. The interlayer was manufactured under 100 W input power for 10 min.

For TaN single layer coatings, the Ar/N_2 flow ratio was controlled at 18/2 and 12/8 sccm/sccm to form two kinds of TaN layers, namely crystalline c-TaN and amorphous a-TaN layers, respectively. By alternatively sequential stacking of c-TaN and a-TaN, the TaN multilayer was then fabricated. For HfN single layer coatings, the gas flow ratio of Ar/N_2 was fixed at 19/1 and the RF input power was controlled at 75 W, 125 W and 150 W. The HfN multilayer was deposited by alternatively sequential stacking of 150 W and 125 W films. Both for TaN and HfN multilayer films, each stacking layer was controlled at 10 nm in thickness. The overall coating thickness for TaN and HfN samples were around 1 μm and 0.95 μm, respectively. The sputtering conditions for TaN and HfN were designated in Tables 1 and 2, respectively.

The composition analyses were determined with an electron probe microanalyzer (FE-EPMA, JAX-8800, JOEL, Japan). The cross-sectional images and the phase identifications were carried out through field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan) and X-ray diffractometer (XRD, Ultima IV, Rigaku, Japan). The X-ray was generated by a Cu target with a Cu Kα monochromatic radiation. The hardness and Young's modulus of the coatings were measured by nano-indentation (TriboIndenter, TI 900, Hysitron, USA). The scratch test was performed with a microscratch tester (Scratch Tester, J&L Tech, Korea) with progressive loading from 0 to 50 N. The Tafel curves are measured by electrochemical workstation (Jiehan-5000, Jiehan, Taiwan) in a 3.5 M NaCl solution. The scanning ranges from −0.5 V to +0.5 V according to the open circuit potential, and the scanning rate is 0.001 V/s.

3. Results and discussion

3.1. TaN film

3.1.1. Microstructure

The compositions of TaN single layer coatings are listed in Table 1. The Ar/N_2 ratios in manufacture process exhibited a strong influence on composition of the TaN coatings. The nitrogen content was increased as the Ar/N_2 ratios decreased. Because of the higher gas flow of N_2, the Ar^+ ion intensity and energy in the plasma were lowered down. A lower Ta content down to 39.3 at.% in the coating was expected.

X-ray diffraction patterns of TaN coatings prepared with various Ar/N_2 ratios are shown in Fig. 1. The TaN single layers fabricated with Ar/N_2 gas flow ratios exhibited obviously disparate microstructures. The c-TaN film generated under $Ar/N_2 = 18/2$, exhibited a well-crystallized microstructure which was realized from the strong TaN peaks and a preferred orientation (200) in the diffraction pattern. The a-TaN film fabricated at $Ar/N_2 = 12/8$ exhibited no characteristic peaks and showed an amorphous structure owing to the excessive nitrogen. The detailed microstructures analysis, such as TEM images and selected area electron diffraction (SAED), revealed amorphous and crystalline layers in a previous work [17]. Besides, for the cross-sectional images of TaN single layer coatings, columnar crystalline structure and smooth image for c-TaN and a-TaN also could be obtained in the work.

Table 1
The deposition condition and composition of various TaN coatings.

Coating designation	Gas flow (sccm) $Ar:N_2$	Chemical composition (at.%)	
		Ta	N
Multilayer	–	–	–
c-TaN	18:2	47.8 ± 2.9	52.2 ± 2.9
a-TaN	12:8	39.3 ± 0.8	60.7 ± 0.8

Input power of Ta for all coatings is fixed at 100 W and overall coating thickness was set at around 1 μm.

Table 2
The deposition condition and composition of various HfN coatings.

Coating designation	RF input power (W)	Chemical composition (at.%)	
		Hf	N
Multilayer	150/125	–	–
HfN	150	69.5 ± 0.8	30.5 ± 1.0
	125	62.2 ± 0.3	37.7 ± 0.3
	75	45.7 ± 0.7	54.3 ± 0.6

Gas flow ratio of Ar/N_2 was fixed at 19/1 and overall coating thickness for all HfN samples was set around 0.95 μm.

3.1.2. Corrosion behavior of TaN coatings

The corrosion behavior of TaN various coatings is investigated using potentiodynamic polarization. The corrosion potential (E_{corr}) and the corrosion current density (I_{corr}) of the TaN coatings were shown in the Tafel polarization plot in Fig. 2. The corrosion current density (I_{corr}) can be calculated by Stern and Geary Eq. [18]:

$$Rp = \frac{\Delta E}{\Delta I} = \frac{\beta a \cdot \beta c}{2.3 Icorr(\beta a + \beta c)}$$

where I_{corr} is corrosion rate, $\beta\alpha$ and βc are tafel slope of anode and cathode curves, ΔI and ΔE are change of current and polarization potential, respectively, and Rp is the polarization resistance. The a-TaN had highest Rp and lowest I_{corr} around 43.6×10^3 (Ω/cm^2) and 8.5×10^{-7} (A/cm^2), respectively, as listed in Table. 3. The better corrosion resistance of a-TaN was attributed to the amorphous microstructure which suppressed the corrosion attack. The columnar structure of c-TaN, on the other hand, provided paths for propagation of chemical attack along the grain boundaries and a poorer corrosion resistance was resulted.

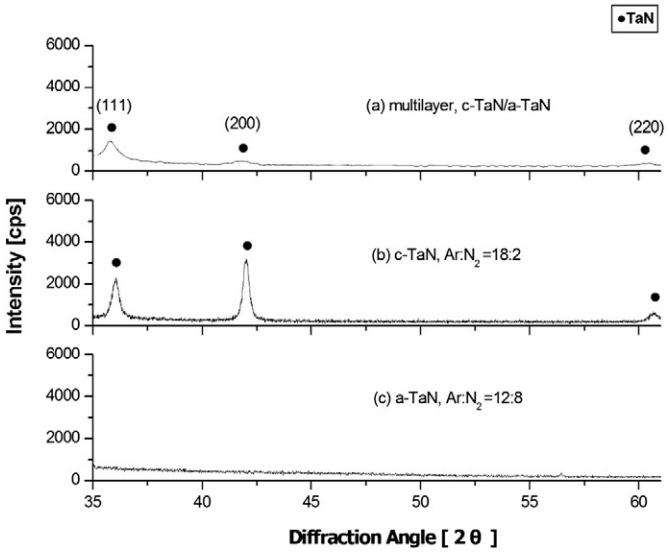

Fig. 1. X-ray diffraction patterns of TaN coatings prepared with various Ar/N_2 ratio.