Microstructural evolution, mechanical properties and strengthening mechanism of TiN/Ni nanocomposite film

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ABSTRACT

A series of TiN/Ni nanocomposite films with different Ni content were synthesized by reactive magnetron sputtering. The microstructural evolution, mechanical properties and strengthening mechanism of TiN/Ni nanocomposite film were studied. When Ni:Ti ratio is less than 1:24, the small amount of Ni can be dissolved in the TiN matrix, leading to the slight decrease of the hardness and elastic modulus. When Ni:Ti ratio rises to 4:21, Ni inclines to separate from TiN due to the thermodynamic incompatibility as an interfacial phase and grow coherently with adjacent TiN crystallites. As a result, the TiN/Ni film was remarkably strengthened with the maximal hardness and elastic modulus of 33.3 GPa and 373 GPa. As Ni:Ti ratio further increases to 5:20, Ni interface transforms into amorphous state, leading to the destruction of the epitaxial growth structure and the rapid decrease of hardness and elastic modulus. The strengthening effect of TiN/Ni nanocomposite film can be attributed to the coherent interface between Ni interfacial layers and TiN crystallites.

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1. Introduction

As superhard film materials, nanocomposite films have been widely investigated in the past decades for use as wear-resistant coatings on tools and mechanical components [1–3]. Such films are composed of nanocrystallites ($\leq$10 nm) of transition metal nitrides, carbides, or borides encapsulated by a covalent interfacial layer, which can be classified in two categories according to the type of interfacial layer. The first class is nanocomposite films with interfacial layer of compound (e.g., Si_3N_4, BN or CN_x). Among these nanocomposites, the pseudobinary TiSiN (TiN/Si_3N_4) is a representative film due to strong surface segregation of TiN and Si_3N_4 phases, which has been investigated by many groups [4–7]. The second type is nanocomposite films consisting of interfacial layer used by metal that does not form stable nitrides (e.g., Ni, Cu or Y). Musil and his coworkers have performed wide studies on this type of nanocomposites [8–11] and reported the obvious "superhardness effect" in these nanocomposite systems.

Currently, the nanostructure and strengthening mechanism of the nanocomposite films have been widely explained by nc-TmN/a-Si_3N_4 model proposed by Veprek et al., in 1995 [12], in which equiaxed TmN (transition metal nitride) nanocrystallites (nc-TmN) were encapsulated in an amorphous Si_3N_4 (a-Si_3N_4) interface. However, this model is in dispute due to lack of direct experimental evidence. Our recent publication on TiSiN and TiAlSiN nanocomposite films found that [13], when TiSiN and TiAlSiN nanocomposite films were strengthened with a proper Si content, Si_3N_4 interfacial phase could not only be crystallized between adjacent TiN and TiAlN nanocrystallites, but also coordinate the misorientations between Ti(Al)N nanocrystallites and grow coherently with them, which suggested that TiSiN and TiAlSiN nanocomposite films could not be strengthened by nc-TmN/a-Si_3N_4 model, but coherent-interface mechanism. However, whether the coherent-interface strengthening mechanism can apply to the nanocomposite film with interfacial layer of metal deserves further investigation.

The TiN/Ni film is regarded as a typical nanocomposite film with an interfacial phase of Ni metal [14]. In this investigation, TiN/Ni nanocomposite films with different Ni contents were synthesized

by reactive magnetron sputtering. The dependence of microstructure and mechanical properties for the TiN/Ni nanocomposite film on Ni content would be studied. Special attention would be paid to the interfacial morphology through high resolution transmission electron microscopy (HRTEM) observations when TiN/Ni nanocomposite film was strengthened, which was expected to clarify the strengthening mechanism of TiN/Ni nanocomposite film.

2. Experimental

The TiN/Ni nanocomposite films were fabricated on the silicon substrates by reactive magnetron sputtering system. The TiN/Ni films were sputtered from TiNi compound targets (99.99%) with 75 mm in diameter by RF mode and the power was set at 300 W. The TiNi compound targets with different Ni content were prepared by respectively cutting the pure Ti (at.%, 99.99%) and Ni targets (at.%, 99.99%) into 25 pieces and then replacing different piece of Ti with the same piece of Ni. Adopting this method, TiNi targets with different Ti:Ni volume or area ratios, including 24:1, 23:2, 22:3, 21:4 and 20:5 were prepared. The base pressure was pumped down to 5.0×10^{-4} Pa before deposition. The Ar and N_2 flow rates were 38 and 5 sccm respectively. The working pressure was 0.4 Pa and substrate was heated up to 300 °C during deposition. To improve homogeneity of films, the substrate was rotated at a speed of 10 r/min. The thickness of all the TiN/Ni films was about 2 μm.

The microstructures of TiN/Ni nanocomposite films were characterized by XRD using a Bruker D8 Advance with Cu K_a radiation and field emission HRTEM using a FEI Tecnai G2 F30 at an accelerating voltage of 300 kV. The grain sizes of the films were estimated by Scherrer formula [15]:

$$D = \frac{0.9\lambda}{B \cos\theta} \qquad (1)$$

where D is the grain size, λ is the wavelength of Cu K_α, B is the full width of half maximum (FWHM) of the measured peak and θ is the typical diffraction peak position. The preparation procedures of cross-section specimen for HRTEM observation are as follows. The films with substrate were cut into two pieces and adhered face to face, which subsequently cut at the joint position to make a slice. The slices were thinned by mechanical polishing followed by argon ion milling. The composition was characterized by an energy dispersive spectroscopy (EDS) accessory equipped in a Philips Quanta FEG450 scanning electron microscopy (SEM). The hardness and elastic modulus were measured by a Agilent G200 nanoindenter by using the Oliver and Pharr method [16]. The measurements were performed by using a Berkovich diamond tip with a load of 5 mN. The indentation depth was less than 1/10th of the film thickness to minimize the effect of substrate on the measurements. Each hardness or elastic modulus value was an average of at least 16 measurements.

3. Results and discussion

Considering the difference in sputtering rates of Ti and Ni, the constituents of all TiN/Ni nanocomposite films synthesized by magnetron sputtering are characterized by EDS. The compositions (atom%) from TiNi targets with Ti:Ni ratios of 24:1, 23:2, 22:3, 21:4 and 20:5 are respectively $Ti_{49.16}Ni_{2.05}N_{48.79}$, $Ti_{47.42}Ni_{4.19}N_{48.39}$, $Ti_{46.59}Ni_{6.33}N_{47.08}$, $Ti_{44.96}Ni_{8.72}N_{46.32}$ and $Ti_{43.32}Ni_{10.59}N_{46.09}$, suggesting the Ti:Ni ratios of TiN/Ni films are basically consistent with those of TiNi targets. The XRD patterns of TiN film and TiN/Ni nanocomposite films with different Ni content are shown in Fig. 1. It can be seen that all the films are only composed of fcc (face-centered cubic) structured TiN phase with the (200) preferred
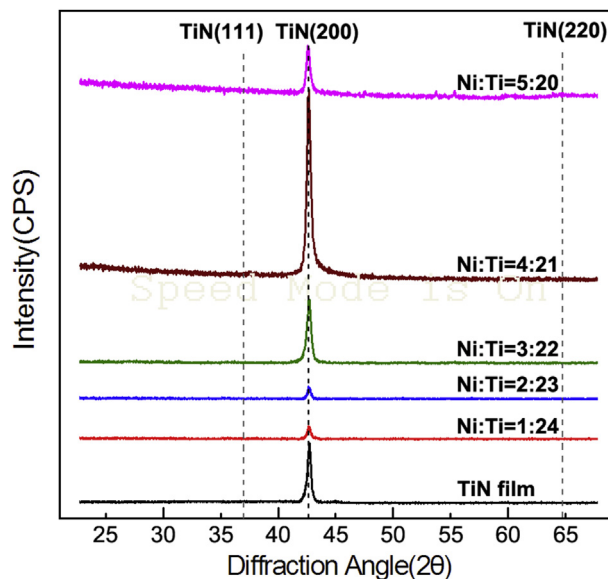

Fig. 1. XRD patterns of TiN film TiN/Ni nanocomposite films with different Ni content.

orientation, while no Ni phase is detected. Musil ever attributed the absence of metal interface phase in XRD patterns to the amorphous characteristic [8,9]. Actually, it can also be explained by the low content of interface phase. From the XRD patterns, with an initial addition of Ni (Ni:Ti = 1:24 or 2:23), the intensity of TiN (200) diffraction peak decreases, suggesting that the addition of Ni deteriorates crystallinity of film. As the Ni:Ti ratio rises from 2:23 to 4:21, the intensity of TiN (200) diffraction peak remarkably increases, indicating the improvement of the film crystallinity. When the Ni:Ti ratio further increases to 5:20, the TiN (200) peak intensity renewedly descends, which is close to that of TiN film, implying that excessive Ni content can lead to the deterioration of film crystallinity.

The influence of Ni content on crystallinity throws doubt upon the nc-TmN/a-Me (a-Me means amorphous metal used for interfacial phase) model. If Ni phase exists as amorphous state, the increase of Ni:Ti ratio from 1:24 to 4:21 only leads to thickening of amorphous Ni interface, which cannot improve the crystallinity of film, but lower it due to the increasing impeditive effect on TiN growth. Therefore, whether Ni interfacial phase is amorphous deserves to be further deliberated.

From the Scherrer formula [15], the grain sizes of TiN film and TiN/Ni nanocomposite films with Ti:Ni ratios of 24:1, 23:2, 22:3, 21:4 and 20:5 are estimated as 29 nm, 23 nm, 20 nm, 17 nm, 15 nm and 8 nm, respectively, indicating that the grain size basically decreases with increase of Ni content. Reasonably, according to the effects of Ni content on crystallinity and grain size of TiN/Ni film, it can be deduced that, low content of Ni disturbs the growth of TiN phase, resulting in the initial decrease of film crystallinity and grain size. With the increase of Ni:Ti ratio, due to the thermodynamic incompatibility of TiN and Ni [14], Ni can interrupt and divide the TiN columnar grain into equiaxed TiN nanocrystallites, which eventually encapsulates TiN nanocrystallites as an interfacial phase, resulting in the continual decrease of grain size. When Ni:Ti ratio increases to 4:21, interfacial phase of Ni reaches to a proper thickness. Under such circumstances, Ni interface is incline to grow coherently with adjacent TiN nanocrystallites in order to lower interfacial energy [17,18], leading to the improvement of film crystallinity. In our previous investigation on TiSiN and TiAlSiN nanocomposite films [13], when Si_3N_4 interfacial phase reaches to a proper thickness, it can be crystallized under the template effect of