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Microstructural characterization and strengthening mechanism of AlN/Y nanocomposite and nanomultilayered films

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ABSTRACT

The AlN/Y nanocomposite and nanomultilayered films with different Y contents were fabricated by the magnetron sputtering technique. The microstructures and mechanical properties of the AlN/Y nanocomposite and nanomultilayered films were characterized and measured, respectively. The AlN/Y nanocomposite film is composed of equiaxed AlN nanocrystallites encapsulated by the Y interfaces. When the Y:Al ratio is 2:23, Y interfaces can exist as the crystallized state and keep the epitaxial growth with the adjacent AlN nanocrystallites. Accordingly, the crystallization degree and mechanical properties are improved. The AlN/Y nanomultilayered film consists of the evident multilayered structure with distinct interfaces. When the Y-layer thickness is no more than 0.7 nm, Y layers are inclined to grow epitaxially with the adjacent AlN layers, leading to the improvement of crystallization degrees and mechanical properties. The interfacial evolutions and mechanical properties variations between AlN/Y nanocomposite and nanomultilayered films have the common feature as the Y content grows. It has been experimentally and theoretically verified that the AlN/Y nanocomposite and nanomultilayered films have the same coherent-interface strengthening mechanism.

1. Introduction

As the new type of superhard film materials, the nanocomposite and nanomultilayered films have attracted great attention in the field of material surface engineering during the past decades [1–3]. These films have been successfully used as the protective coatings due to their high hardness, good oxidation, and wear resistance for increasing the lifetime of the tools, moulds, and other devices.

The nanocomposite films are characterized as the composite structure with the nanocrystallized matrix (nc-matrix) surrounded by the interface. According to the different materials of the interfaces, the nanocomposite films can be divided into two categories: the nc-matrix/compound and nc-matrix/metal. As for the nc-matrix/compound nanocomposite films, the TiSiN (TiN/Si_3N_4) is a representative film due to the strong thermodynamic incompatibility between TiN and Si_3N_4. Veprek and other researchers have carried out the wide investigations on this nanocomposite film and high hardness has been achieved [4–7]. For the nc-matrix/metal nanocomposite films, such as ZrN/Y [8], AlN/Cu [9], and ZrN/Ni [10] nanocomposite films, Musil and his coworkers have done the extensive studies on these films, and the strenghtening effect has been found in some film systems [8–11].

The nanomultilayered films was firstly theoretically proposed by Koehler [12] in 1970, and the strenghtening effect was experimentally verified in the Au-Ni and Cu-Pd superlattice thin films by Yang et al., in 1977 [13]. The nanomultilayered films can be classified into two types: crystalline/amorphous systems, such as $CrAlN/SiO_2$ [14], TiN/SiC [15], VN/AlON [16], and crystalline/crystalline systems, such as $CrAlN/ZrO_2$ [17], VC/TiN [18], AlN/CrN [19]. It is believed that under the critical individual modulation-layer thickness, the modulation layers can form the coherent interface, leading to the strenghtening effect of the nanomultilayered films.

It has been widely accepted that the nanocomposite and nanomultilayered films can present the strenghtening effect under the particular structure and composition. For the strenghtening mechanism of nanomultilayered films, the strenghtening effect can be universally attributed to the coherent interface between the

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modulation layers, which can block the movement of dislocations [20,21]. With regard to the nanocomposite films, however, the strenghtening mechanism is still in dispute.

The nc-TiN/a-Si_3N_4 strengthening model believes that the TiSiN nanocomposite film consists of TiN nanocrystallites encapsulated by the amorphous Si_3N_4 interfacial phase. The average size of TiN nanocrystallites is too small (5–10 nm) for dislocation activities. The grain-boundary sliding becomes the main deformation mechanism, which requires more energy and, therefore, leads to high hardness [22,23]. However, some research groups brought forward different opinions on this mechanism. Hultman et al. reported that the Si_3N_4 layer could be crystalline based on their ab initio calculations [24]. Kong et al. reported that TiN crystals were formed to the fibrous or columnar structure, rather than equiaxed nanocrystallites, divided by the crystallized Si_3N_4 interface [25]. Our recent research also found that when the TiNiN nanocomposite films were strengthened, the Ni interfacial phase could be crystallized between adjacent TiN nanocrystallites [26].

In order to illustrate the difference and relationship within the strenghtening mechanisms between the nanocomposite and nanomultilayered films, the AlN/Y nanocomposite and nanomultilayered films with different Y contents are fabricated by reactive magnetron sputtering in this study. The influences of Y contents on the microstructures and mechanical properties of the AlN/Y nanocomposite and nanomultilayered films are investigated, respectively. Special attention would be paid to the interfacial microstructural evolutions of the AlN/Y nanocomposite and nanomultilayered films with the increase of Y content, which is expected to clarify the essential relation between their strenghtening mechanisms.

2. Experimental

2.1. Film deposition

The AlN/Y nanocomposite and nanomultilayered films were fabricated on the silicon substrates by a JGP-450 magnetron-sputtering system. The AlN/Y nanocomposite films were sputtered from AlY compound targets (weight percent, wt.%, 99.99%) with 75 mm in diameter by the radio-frequency (RF) mode, and the power was set at 300 W. The AlY-compound targets with different Y content were prepared by, respectively, cutting the pure Al (atomic percent, at.%, 99.99%) and Y targets (at.%, 99.99%) into 25 pieces and then replacing different pieces of Al with the same piece of Y. Using this method, AlY targets with different Y:Al volume or area ratios, including 1:24, 2:23, 3:22, 4:21, and 5:20 were prepared.

The AlN/Y nanomultilayered films were deposited from a Al-metal target (wt.%, 99.99%) by DC mode (120 W) and a Y metal target (wt.%, 99.99%) by a RF mode (60 W). Both Al and Y targets were 75 mm in diameter. The individual modulation-layer thickness of the multilayered film was obtained by controlling the staying time of substrates in front of each target. The configuration of AlN/Y nanomultilayered films was designed with a fixed AlN layer thickness (18 s) and variable Y layer thickness (3 s, 5 s, 7 s, 9 s, and 11 s).

The Si substrates were ultrasonically cleaned in acetone and alcohol before being mounted on a rotatable substrate holder in the vacuum chamber. The distance between the substrate and target was 50 mm. 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 monolithic AlN film was also fabricated for comparison. The thickness of all the films was about 2 μm.

2.2. Microstructural characterization

The microstructures of the AlN/Y nanocomposite and nanomultilayered films were characterized by X-ray diffraction (XRD) using a Bruker D8 Advance with Cu K_α radiation ($\lambda = 0.15406$ nm), field-emission high-resolution transmission electron microscopy (HRTEM) using a Tecnai G2 F30 at an accelerating voltage of 300 kV. 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.

2.3. Mechanical tests

The mechanical properties (hardness and elastic modulus) of the AlN/Y nanocomposite and nanomultilayered films were measured by an Agilent G200 NANO Indenter by using the Oliver and Pharr method [27]. The measurements were performed by using a Berkovich diamond tip with a depth of about 150 nm. The indentation depth was less than 1/10th of the whole film thickness so as to minimize the impact of substrate on the measurements. The final hardness and elastic modulus values of each sample were the average of 16 measurements.

3. Results

3.1. AlN/Y nanocomposite films

3.1.1. Microstructures

The typical cross-sectional TEM images of the AlN/Y nanocomposite film with the Y:Al ratio of 2:23 are presented in Fig. 1. From the low-magnification image of Fig. 1(a), it can be seen that the AlN/Y film shows the dense and compact structure. From the magnified images of Fig. 1(b) and (c), the AlN/Y film is composed of many equiaxed nanocrystallites with an average size of 4 nm–8 nm. Between the nanocrystallites, there exist the interfaces with the dark contrast.

Due to the high chemical stability of Y, it cannot combine with N element to form compound phase during the synthesis of film. Owing to the low Y content, the nanocrystallite and interface phases are deduced to be AlN and Y, respectively. Since the Y and AlN have no solid solubility, the Y inclines to surround the AlN nanocrystallites as the interface phase. As a result, the nanocomposite structure can be created within the AlN/Y film. The similar phenomenon can be observed in ZrN/Y [8], AlN/Cu [9] and TiN/Ni [26] nanocomposite films.

The XRD patterns of AlN/Y films with different Y contents are shown in Fig. 2. It can be seen that the only diffraction peak located at 33.2° can be observed, which refers to (100) crystal planes of the hcp (hexagonal close packed) structured AlN phase, suggesting the AlN/Y films exhibit hcp AlN phase with the (100) preferred growth orientation. No diffraction peak from Y is detected in the patterns, which can be attributed to the low content of Y.

When the Y:Al ratio is 1:24, the (100) diffraction peak can hardly be observed, suggesting that the crystallization degree is low. With an initial increase of the Y content, the intensity of AlN (100) diffraction peak increases and reaches to the maximum value with the Y:Al ratio of 2:23, suggesting that the crystallization degree improves with the proper addition of Y element. As the Y content further enhances, the intensity of AlN (100) diffraction peak gradually decreases, suggesting that the crystallization degree of the AlN/Y film renewedly deteriorates.

Since the AlN/Y film with the Y:Al ratio of 2:23 exhibits the highest crystallization degree, the cross-sectional microstructures