Materials Characterization 118 (2016) 79–84

Contents lists available at ScienceDirect

Materials Characterization

journal homepage: www.elsevier.com/locate/matchar

Microstructure and superhardness effect of $CrAlN/SiO_2$ nanomultilayered film synthesized by reactive magnetron sputtering

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ARTICLE INFO

Article history:
Received 27 April 2016
Received in revised form 18 May 2016
Accepted 19 May 2016
Available online 21 May 2016

Keywords:
Multilayered coatings
Superhard
Epitaxial growth
Microstructural evolution
Strengthening mechanism
Magnetron sputtered coating

ABSTRACT

The $CrAlN/SiO_2$ nanomultilayered films with different SiO_2 layers thickness were synthesized by reactive magnetron sputtering. The effects of SiO_2 layer thickness on the microstructure and mechanical properties of $CrAlN/SiO_2$ nanomultilayered films were studied. The results reveal that, when SiO_2 layer thickness is less than 0.7 nm, originally amorphous SiO_2 layers can be forced to crystallize under the "template effect" of NaCl-structured CrAlN layers and grow epitaxially with them, resulting in the preservation of columnar growth structure and remarkable superhardness effect with the maximum value of hardness of 38.9 GPa. As the SiO_2 layer thickness exceeds 0.7 nm, however, SiO_2 layers transform back into amorphous state, which destructs the epitaxial structure between CrAlN and SiO_2 layers, leading to disappearance of columnar growth character and decrease of mechanical properties. The superhardness effect of $CrAlN/SiO_2$ nanomultilayered film can be attributed to the joint effects of modulus-difference and alternating-stress strengthening mechanisms.

1. Introduction

For many years, transition metal nitrides (TmNs) have been widely used as protective and wear resistant hard films for cutting and forming tools due to their superior mechanical and tribological properties [1,2]. Among these films, the CrAlN film is probably the most promising nitride for protective film, due to its more excellent oxidation resistance [3], higher hardness [4] and better tribological behavior [5,6], relative to the widely used TiAlN. For example, Yang et al. [7] reported that CrAlN film exhibited the satisfied oxidation resistance after thermal exposure for 10 h at 1050 °C in ambient air, whereas TiAlN film was already completely oxidized at 950 °C. Ding et al. [8] found CrAlN film deposited by lateral rotating cathode arc showed an evidently better corrosion resistance than TiAlN film prepared by the same technique. Our previous publication [9] also suggested that CrAlN film synthesized by reactive magnetron sputtering achieved the high hardness of 36.6 GPa together with excellent tribological resistance.

Nanomultilayered films, as new type of superhard film materials, have attracted the wide attention of researchers in the past decades [10,11]. These films are multi-laminate structures formed by depositing two or more kinds of materials alternatively at nanometer-scale thickness, which exhibit not only higher hardness compared with the single layer films due to superhardness effect, but also other properties, such as thermal stability, wear and corrosion resistance [12,13]. Especially, the TmN/oxide nanomultilayered structures, such as TiN/SiO_2 [14], $CrAlN/ZrO_2$ [15] and VN/AlON [16] nanomultilayered films, have been successfully synthesized by various techniques, which exhibit both high temperature oxidation resistance and sufficient hardness.

Furthermore, silicon dioxide (SiO_2) possesses high thermal and chemical stability [17,18] and is thus a good candidate as a component to be incorporated into the multilayer system. Inspired by these works, the novel $CrAlN/SiO_2$ nanomultilayered films are brought forward in this investigation. A series of $CrAlN/SiO_2$ nanomultilayered films with different SiO_2 layers thickness will be synthesized by reactive magnetron sputtering. The effects of SiO_2 layer thickness on the microstructure and mechanical properties of $CrAlN/SiO_2$ nanomultilayered films will be studied. Special attention will be paid to the microstructural conditions of $CrAlN/SiO_2$ nanomultilayered films when achieving superhardness effect.

2. Experimental details

The $CrAlN/SiO_2$ nanomultilayered films were fabricated on the silicon substrates by reactive magnetron sputtering system. The CrAlN layers were deposited from a $Cr_{50}Al_{50}$ alloy target (at.%, 99.99%) by DC mode and the power was set at 120 W. The SiO_2 layers were sputtered from SiO_2 target (99.99%) by RF mode and the power was set at 80 W. Both CrAl and SiO_2 targets were 75 mm in diameter. The base pressure

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http://dx.doi.org/10.1016/j.matchar.2016.05.016
1044-5803/

was pumped down to 5.0×10^{-4} Pa before deposition. The Ar and N_2 flow rates were 35 and 15 sccm, respectively, with the depositing pressure of 0.4 Pa and temperature of 300 °C. The configurations of CrAlN/SiO_2 nanomultilayered films were designed with CrAlN layers with a fixed thickness by depositing a CrAlN layer for 12 s along with variable SiO_2 layer thickness by depositing a SiO_2 layer for 4 s, 5 s, 6 s, 7 s, 8 s and 10 s. The monolithic CrAlN film was also fabricated for comparison. Based on the depositing rate derived from the monolithic CrAlN film, the thickness of a CrAlN layer was fixed at 6 nm for all the CrAlN/SiO_2 nanomultilayered films. The thickness of all films was about 2 μm.

The microstructures of CrAlN/SiO_2 nanomultilayered films were investigated by X-ray diffraction (XRD) using a Bruker D8 Advance with Cu K_a radiation, field emission scanning electron microscopy (FE-SEM) using a Philips Quanta FEG450, and field emission high-resolution transmission electron microscopy (HRTEM) using a Philips CM200-FEG. The XRD measurements were performed by a Bragg-Brentano (θ/2θ) scan mode with the operating parameters of 30 kV and 20 mA. The diffraction angles (2θ) ranges for low-angle and high-angle diffraction patterns were respectively scanned from 0.8° to 6.0° and from 30° to 80°. The hardness and elastic modulus were measured by a MTS G200 nanoindenter by using the Oliver and Pharr method [19]. 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

3.1. Microstructure of the CrAlN/SiO_2 nanomultilayered films

Fig. 1 shows the typical cross-sectional TEM images of CrAlN/SiO_2 nanomultilayered film with SiO_2 layer deposited for 7 s. From the low-magnification image of Fig. 1(a), it can be seen that the CrAlN/SiO_2 nanomultilayered film presents the compact structure, with the thickness of about 2.0 μm. It is worth noting that the crack within the film is attributed to the ion bombardment during the TEM specimen preparation. Fig. 1(b) exhibits that the CrAlN/SiO_2 nanomultilayered film is composed of columnar crystal structure with column width of tens of nanometers. Columnar crystal growth is a typical feature of monolithic CrAlN film prepared by vapor deposition [20], suggesting that the insertion of SiO_2 nanolayers with the proper thickness does not disturb the growth mode of CrAlN film. From the magnified Fig. 1(c), it is clear that, within the columnar crystals, the evident multilayered structure is formed with distinct interfaces. The thick layers with dark contrast and thin layers with bright contrast correspond to CrAlN and SiO_2, respectively.

The low-angle XRD patterns of the CrAlN/SiO_2 nanomultilayers with different SiO_2 layer thickness are shown in Fig. 2. The low-angle diffraction peaks are clearly observed for all the films, indicating that the periodic modulated structure with the distinct interfaces are formed within the CrAlN/SiO_2 nanomultilayered films. The modulation period of the nanomultilayered films can be calculated using the modified Bragg formula [21]. As the thickness of CrAlN layer is kept at 6.0 nm for all the nanomultilayered films, the thickness of SiO_2 layer can be evaluated, as indexed in Fig. 2, which will be verified by the subsequent HRTEM observations.

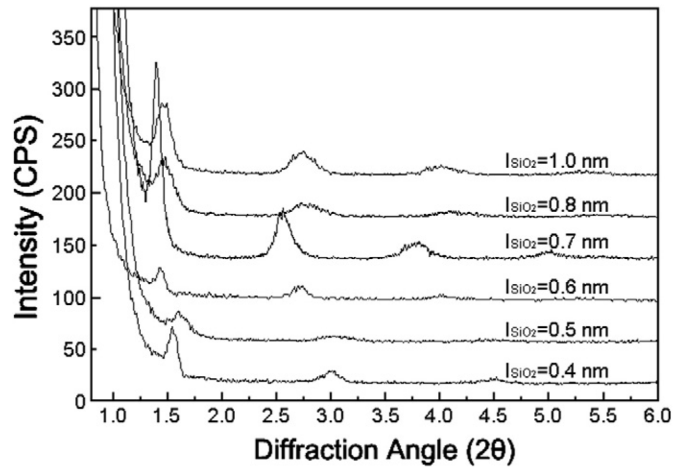

Fig. 2. Low-angle patterns of CrAlN/SiO_2 nanomultilayered films with different SiO_2 layer thickness.

The high-angle XRD patterns of monolithic CrAlN film and CrAlN/SiO_2 nanomultilayered films with different SiO_2 layer thickness are shown in Fig. 3. It can be seen that both monolithic CrAlN film and CrAlN/SiO_2 nanomultilayered films exhibit fcc (face-centered cubic) CrN phase with the (200) preferred orientation. No other phase except for Si substrate can be detected. Compared with the monolithic CrAlN film, the (200) peak intensity of CrAlN/SiO_2 nanomultilayered film reduces significantly, suggesting that the insertions of SiO_2 nanolayers decrease crystallinity of CrAlN film. In addition, when the SiO_2 layer thickness increases to 0.7 nm, the peak intensity of (200) plane of CrAlN/SiO_2 nanomultilayered film basically remains unchanged. As the SiO_2 layer thickness further rises to 0.8 nm or 1.0 nm, however, the peak intensity of (200) plane further decreases, indicating that thickening of SiO_2 layer leads to lower crystallization integrality.

Several reports revealed that, when the crystalline/amorphous nanomultilayered structure was formed, such as TiN/SiC [22], CrN/TiSiN [23] and ZrO_2/TiN [24] nanomultilayered films, with the initial increase of amorphous layer thickness, not only could amorphous layer be crystallized and grew epitaxially with crystal layer, but also newly deposited crystal layer could grow epitaxially on crystallized amorphous layer, leading to the "mutual promotion effect" of growth in nanomultilayered films and improvement of crystallinity [25].

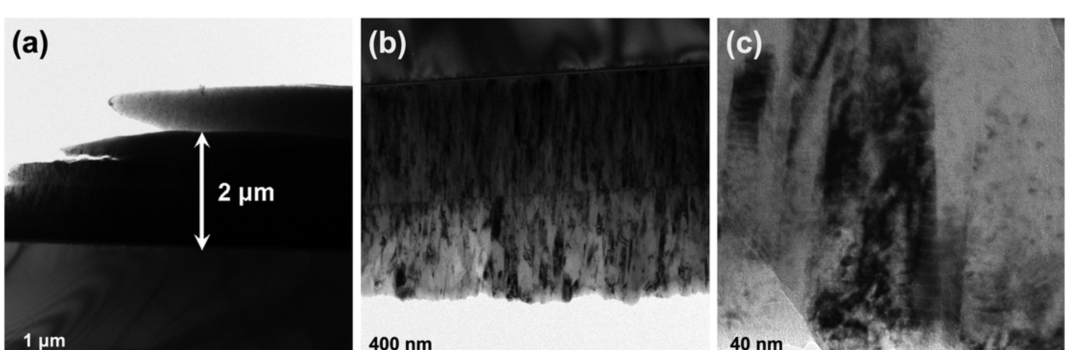

Fig. 1. Cross-sectional TEM images of CrAlN/SiO_2 nanomultilayered film with SiO_2 layer deposited for 7 s: (a) low-magnification, (b) medium-magnification and (c) high-magnification.