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Effect of copper content and substrate bias on structure and mechanical properties of reactive sputtered CrCuN films

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ABSTRACT

The CrCuN films with various Cu contents were deposited under different substrate bias by DC magnetron sputtering. The influence of Cu content and substrate bias was examined with regard to the microstructure, morphology, and mechanical properties of these films. The CrCuN films containing low Cu content (3.4 at.%) present distinctive columnar growth. Their preferred orientations change from (1 1 1) (−50 V bias) to (2 0 0) (−200 V bias) and surface morphology changes from porous to granular structure with increasing bias. However, when the copper content is increased to 15 at.%, CrCuN films remain (2 0 0) preferred growth independent of bias, while the film maximum hardness is reduced from 32 GPa to 20 GPa because of excess soft metal.

1. Introduction

Nanocomposite films are composed of at least two separate phases with nanocrystallits and/or amorphous structure [1]. They have been developed greatly in recent years for their unique physical and functional properties [2–4]. At present, there are two groups of hard and superhard nanocomposites: (i) nc-MeN/hard phase and (ii) nc-MeN/soft phase [1]. Nanocomposite films based on hard/hard phases have attracted an overwhelming interest mainly focusing on the production, characterization and application [5–11] since Veprek et al. [12] found Ti–Si–N nanocomposite films could get ultrahardness of 80–105 GPa and high toughness.

However, a little attention has been paid to those coatings based on hard/soft phases [13–16]. Among this kind of nanocomposite films CrCuN is very interesting. On the one hand, CrN films are known to have high hardness, good corrosion resistance, high-temperature oxidation resistance and wear properties, and have become important technological materials in the fields of cutting and forming tools, bearing and machine parts, dies and moulds [17–19]. On the other hand, though many alloy elements have been added into CrN films for improved properties, such as Ag [20–22], Cu [23–25], W [26], Al [27,28], Si [29], Ti [30], Zr [31,32], etc., copper is an unusual element because copper and chromium are immiscible and cannot form intermetallic compounds according to equilibrium phase diagram. Therefore, the effect of the copper doping on microstructure and performance of CrN films deserves concerns. Myung et al. [33] thought the amount of metallic phase in a composite material depended on the grain size of hard phase and maximum value of mechanical properties of the composite material depended on the relative amount of metallic phase and the grain size of hard phase. Musil et al. prepared the CrCuN film with a high microhardness (HV = 35 GPa) and found the content of copper in the film strongly affected its structure and performance [25]. Superhard CrCuN film with about 40 GPa was obtained by Ezirmik et al. [24]. This further illuminates that nanocomposite films composed of hard nitride and soft metal could be hard or even superhard [1]. However, some experimental results also showed copper has little effect on the properties of CrN films, for example, Öztürk et al. found the slight difference between the hardness of CrN and CrCuN coatings (28 GPa and 27 GPa, respectively) and the addition of Cu did not change the tribological behavior of CrN coatings [23]. Therefore, a thorough study on CrCuN films needs to be done.

The purpose of the present study is to identify the influence of substrate bias on the structure of CrCuN films with different Cu contents deposited by DC reactive magnetron sputtering and

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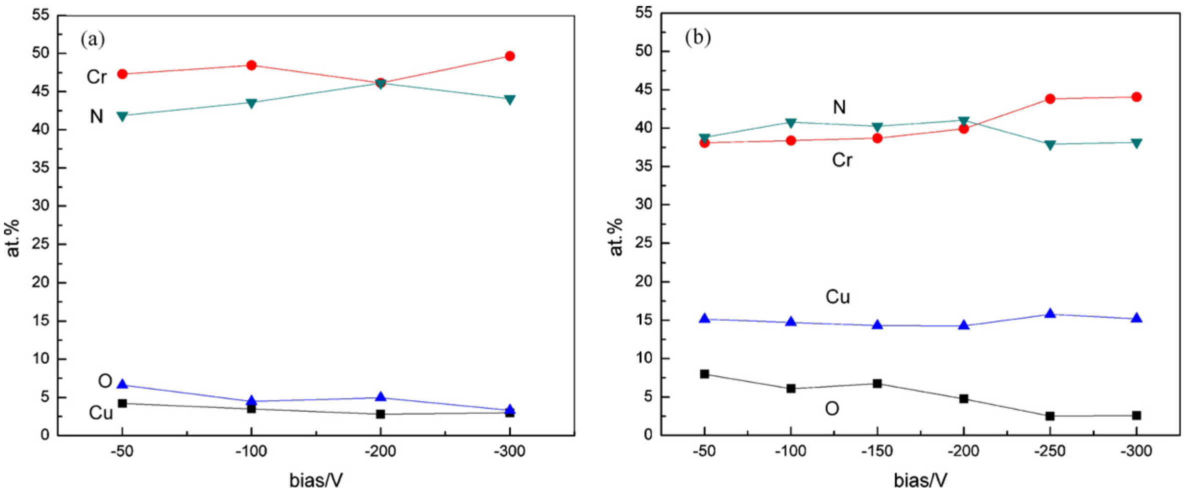

Fig. 1. Chemical compositions of CrCuN films in function of bias voltage. (a) Low Cu content ($Cr_{0.95}Cu_{0.05}$ target) and (b) high Cu content ($Cr_{0.80}Cu_{0.20}$ target).

get a better understanding of nanocomposite films composed of hard/soft phases.

2. Experimental

CrCuN films were synthesized by DC magnetron sputtering in a balanced system. Two hot-pressed CrCu ($Cr_{0.80}Cu_{0.20}$, $Cr_{0.95}Cu_{0.05}$, at.%) targets with 80 mm diameter were used to get low and high Cu content films. Mirror polished AISI 304 stainless steel and monocrystalline silicon were used as substrates. The substrates were ultrasonically cleaned in alkaline liquor, acetone, ethanol and deionized water, for 20 min, respectively, and then dried with N_2 rapidly. Ar and N_2 flow rates were kept at 10 mL min^{-1} and 23 mL min^{-1}, respectively, controlled by separate mass flow controllers. The distance between the target and substrate was 60 mm. The target surface was pre-sputtered in pure Ar plasma for 5 min. And then CrCuN films were deposited under different substrate bias voltages of −50 V, −100 V, −150 V, −200 V, −250 V and −300 V. The total working pressure and power was 0.5 Pa, 150 W, respectively.

The film crystal structure was characterized using Cu-Kα radiation on a X-ray diffractometer (XRD) (Model Bruker D8 Discover) in a continuous scan mode at a step of 0.02° with the X-ray generator operated at 40 kV and 40 mA. X-ray photoelectron spectra (XPS) of CrCuN films were obtained by means of Kratos AXIS Ultra DLD. A FEI Sirion scanning electron microscope (SEM) was used to examine the film thickness and investigate the surface and cross-sectional morphology. The film thickness is kept about 4–5 μm by adjusting deposition time. The chemical compositions of the films were analyzed using an energy dispersive X-ray analysis (EDAX) attached to the SEM. Transmission electron microscope (TEM) was employed to investigate the local microstructure of the deposited films. The film hardness was evaluated using a microhardness tester (Model FM-700) under the exerted load of 0.098 N retained for 10 s. Each sample was tested for nine times and the hardness value was averaged.

3. Results and discussion

3.1. Chemical composition and phase structure of CrCuN films

The chemical compositions of CrCuN in function of bias voltage are demonstrated in Fig. 1. It is found that the Cu content almost does not change with bias, kept at 3.5 at.% for low Cu content films, 15 at.% for high Cu films, respectively. This is different from Musil et al.'s experiment results [25]. In his study, the Cu content in the CrCuN film decreases from 43 at.% to 0.2 at.% due to preferential resputtering of Cu when substrate bias reaches −700 V. And yet the stable Cu content in our study may be attributed to the low ionization of the DC magnetron sputtering related to the depositing machine.

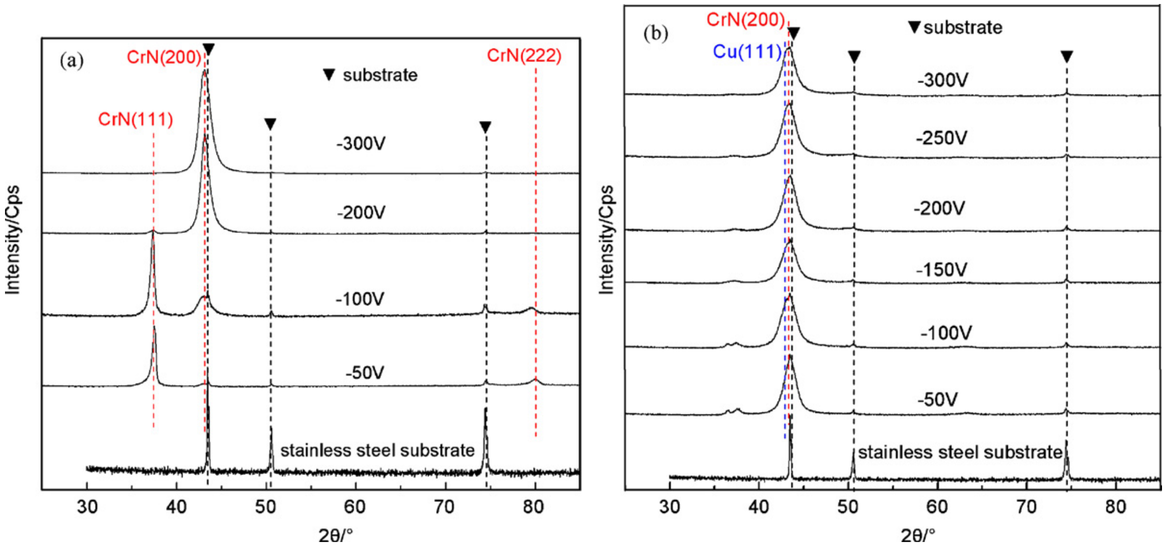

Fig. 2. XRD spectra of CrCuN films with different bias voltage. (a) Low Cu content ($Cr_{0.95}Cu_{0.05}$ target) and (b) high Cu content ($Cr_{0.80}Cu_{0.20}$ target).

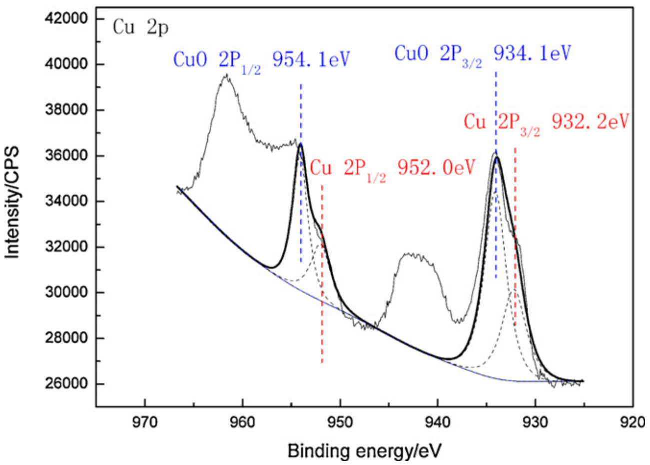

Fig. 3. XPS spectra of CrCuN films with low Cu content (about 3.4 at.%).

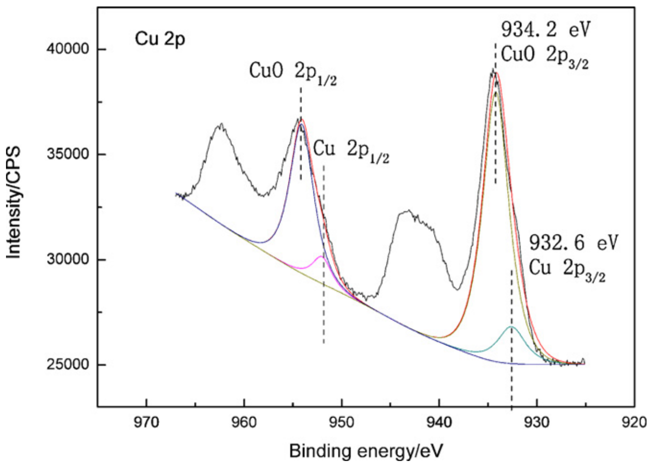

Fig. 5. XPS spectra of CrCuN films with high Cu content (about 15 at.%).

The XRD patterns of CrCuN with various bias and target are presented in Fig. 2. The CrCuN films containing low Cu content (Fig. 2a) are mainly composed of CrN (PDF76-2494), and the preferred orientation changes from CrN (1 1 1) in a low bias of −50 V to CrN (2 0 0) in a high bias of −200 V. The variation of preferred growth in CrCuN is similar to binary CrN films, perhaps due to very low Cu content. The increase of bombardment of nitrogen ion could be the main reason for change of preferred orientation. It would lead to a reduced Cr diffusion length, an enhanced surface island nucleation rate, and a lower chemical potential on the (2 0 0) surface, which favors preferred growth of (2 0 0) [34]. Furthermore, the increase of bias brings about left shift of CrN (2 0 0) peak, probably due to compression stress and the change of film composition.

In comparison with low Cu CrCuN films, the XRD patterns of CrCuN films containing high Cu content (Fig. 2b) are very different. First, the preferred orientations keep CrN (2 0 0) unrelated to bias, that is, in this case the bias effect on preference is not obvious. It seems that higher Cu content could facilitate (2 0 0) preferred growth. Second, the diffraction peaks generate broadening, probably indicating grain refining. Moreover, Cu peaks are observed in the films.

3.2. *Microstructure of CrCuN films*

Fig. 3 demonstrates the XPS analysis of CrCuN films with low Cu content under a substrate bias of −50 V, the C 1 s peak of adventitious hydrogen carbon (binding energy = 284.8 eV) is taken as a reference to calculate the binding energy. The peaks of Cu 2p correspond to Cu (932.2 eV) [35] and CuO (934.1 eV) [36]. It is clarified that a small quantity of Cu and CuO coexist in films. The TEM investigation of CrCuN films with low Cu content under −200 V is presented in Fig. 4. In the bright field image (Fig. 4a), columnar crystallites are obvious, in agreement of the results of selected area electron diffraction (Fig. 4b). Thus, no amorphous phases exist in films and no sharp peaks of Cu found in XRD patterns perhaps due to very low content of copper (3.4 at.%) which exceeds the limitation of XRD measurement.

The XPS analysis of high Cu content film deposited under −300 V is shown in Fig. 5. The peak of Cu 2p corresponds to Cu (932.6 eV) [37] and CuO (934.2 eV) [38]. And the film prepared under −200 V is further observed by TEM shown in Fig. 6. The bright field image (Fig. 6a) demonstrates that the film is composed of nanocrystal particles correspondence to the results of selected area electron diffraction (Fig. 6b). The TEM observation combined with the XPS

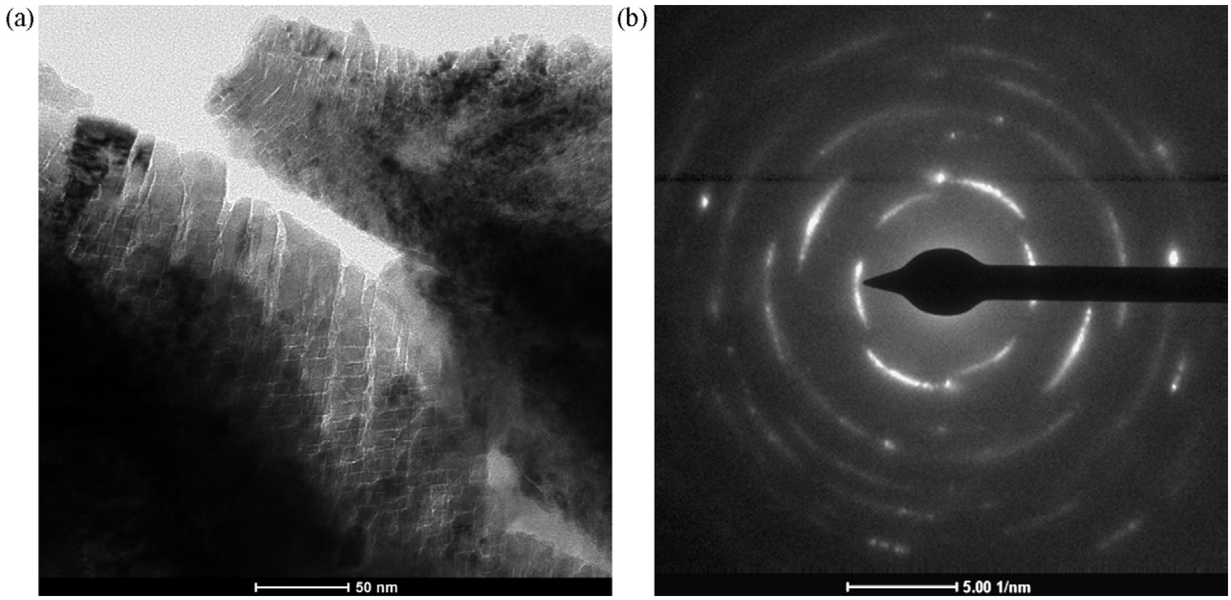

Fig. 4. Bright field TEM image (a) and SEAD pattern (b) of the CrCuN film with low Cu content (about 3.4 at.%).

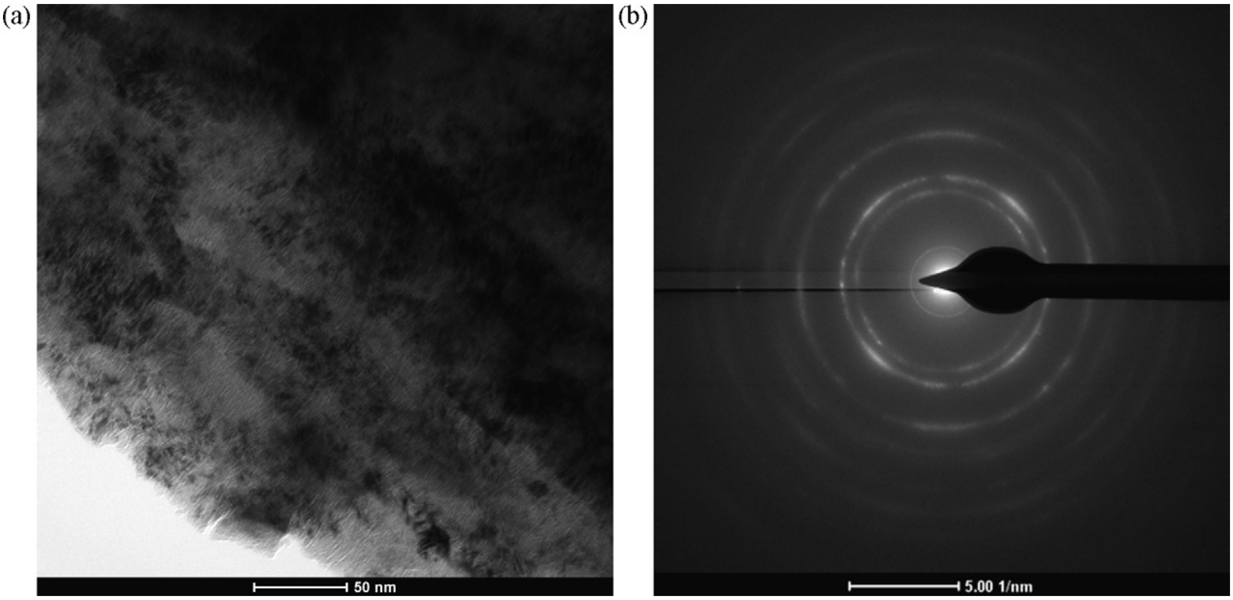

Fig. 6. Bright field TEM image (a) and SEAD pattern (b) of the CrCuN film with high Cu content (about 15 at.%).

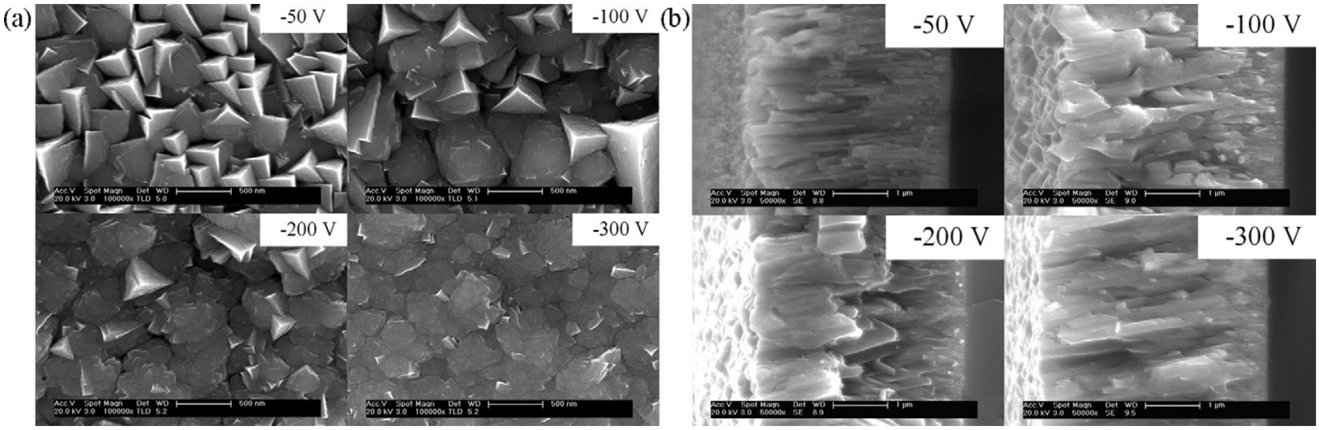

Fig. 7. SEM images of CrCuN films with low Cu contents under different bias. (a) Surface images and (b) cross-sectional images.

results substantiates that no amorphous phase exists in CrCuN films regardless of Cu content.

SEM images of CrCuN films with low Cu content are given in Fig. 7. As negative bias voltages increase, surface morphology of CrCuN films changes from irregular shape with angular structure (porous structure) for −50 V to globular structure (dense structure) for −200 V (Fig. 7a), which is corresponding to variation of preferred orientation from CrN (1 1 1) (−50 V) to CrN (2 0 0) (−200 V) (Fig. 2a). Furthermore, the film under a bias of −300 V appears many fine globular grains, showing dense structure. Cross-sectional profiles demonstrate that CrCuN films grow as a typical columnar way under different bias (Fig. 7b).

Fig. 8 shows morphology of CrCuN films containing high Cu content. From their surface images (Fig. 8a), the films demonstrate ‘plane’ grains in accordance with (2 0 0) orientation (Fig. 2b), which is a little distinctive of (2 0 0) grain shape of low Cu content films (Fig. 7a) because of the effect of high Cu content. And an increase in bias could refine grains until difficult to distinguish grains for −300 V. From cross-sectional morphology (Fig. 8b), the grain boundary become vague and the films form a nearly feature-

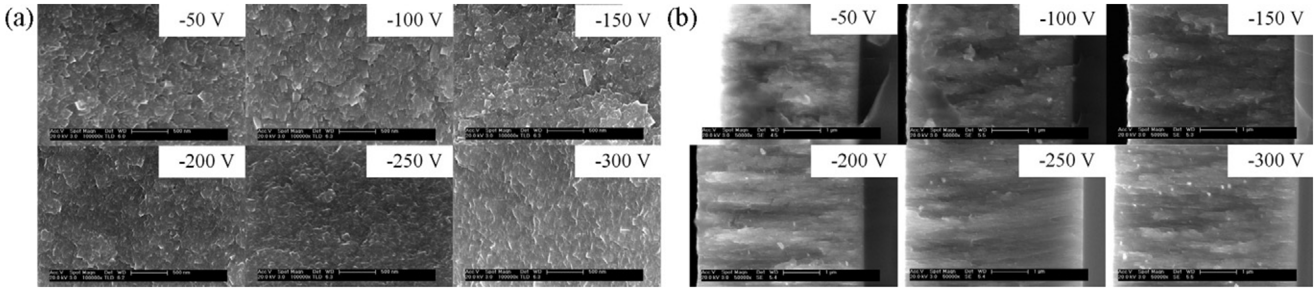

Fig. 8. SEM images of CrCuN films with high Cu contents under different bias. (a) Surface images and (b) cross-sectional images.

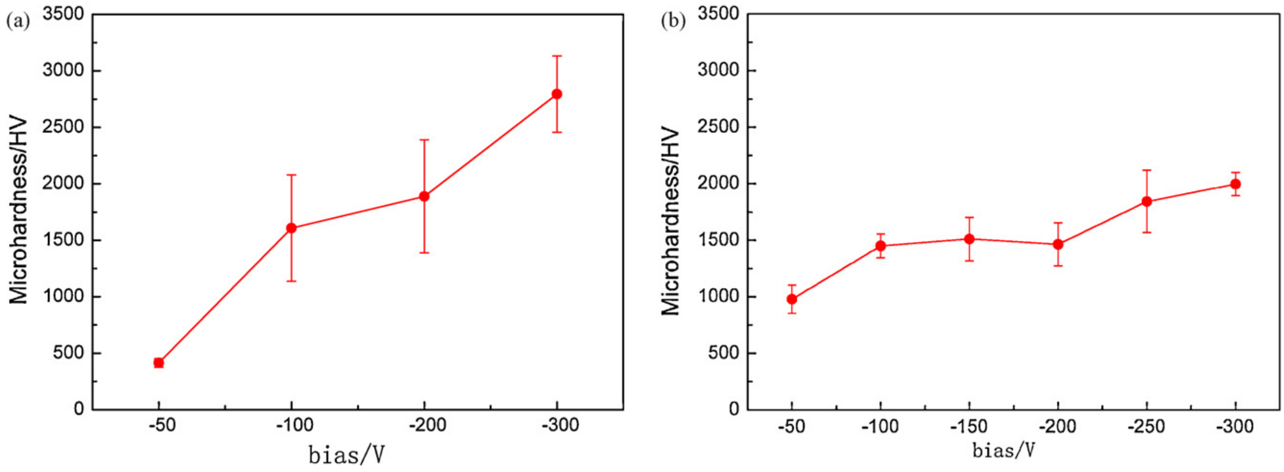

Fig. 9. The relationship between the substrate bias and hardness of CrCuN films. (a) Low Cu content ($Cr_{0.95}Cu_{0.05}$ target) and (b) high Cu content ($Cr_{0.80}Cu_{0.20}$ target).

less structure. From Figs. 7 and 8, high bias can get dense structure, because the increase of bias voltage induces improved energy of impinging atoms/ions, enhancing their mobility and leading to film densification.

Comparing with the morphology of CrCuN with various Cu content under the same bias, a dramatic change in structure (from coarse to fine, from columnar to nearly featureless, from globular to 'plane') is primarily attributed to soft metal of Cu. Here Cu is highly mobile because of its immiscibility in CrN films and thus able to disrupt the columnar grain growth during deposition and hence control the size and shape of grains. These results have been found in previous researches [23,33,39].

3.3. Hardness of CrCuN films

The relationship between the bias and hardness of CrCuN films is shown in Fig. 9. As bias increases, both low and high Cu films improve their hardness due to the dense structure and compressive stress as a result of bias effecting. Under the same substrate bias, with increasing copper content the films have finer structure (Figs. 7a and 8a), but the film hardness is greatly reduced. This is mainly due to the decrease in the interface energy between the grains with increasing of the soft metal at the grain boundaries.

4. Conclusion

The CrCuN films with low and high Cu content have been prepared by DC reactive magnetron sputtering under different bias. In low Cu content films, with increasing bias the columnar structure still occurs and the preferred orientation changes from (1 1 1) to (2 0 0). The dense structure and compressive stress due to high bias results in increasing hardness; in high Cu content films, the typical columnar structure almost vanishes. With increasing bias the preferred orientation keeps (2 0 0) and grains get finer leading to improved hardness. In addition, under the same substrate bias conditions the increased Cu content can refine structure and change grain shape, but still reduce hardness because of too much soft metal.

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