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The effect of substrate bias on the characteristics of CrN coatings deposited by DC-superimposed HiPIMS system

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Chromium nitride coatings were prepared by reactive DC-superimposed high-power-impulse magnetron sputtering (HiPIMS) system. The influence of substrate bias on the microstructure and mechanical properties of CrN coatings was investigated. XRD and cross-sectional SEM were utilized to characterize the film structures. Mechanical properties were characterized by nanoindentation and Vickers indentation test. The results revealed that the microstructure and mechanical properties of CrN coatings were affected by bias voltage. The CrN coatings exhibited dense and fine columnar grain structure with the hardness of about 18.7 GPa. The fracture toughness of CrN coatings was around 3.16 $\mathrm{MPa}\cdot\mathrm{m}^{1/2}$. However, further increase of the bias voltage from -250 V to -300 V led to the degradation of coating properties.

Keywords: HiPIMS; CrN coatings; substrate bias; microstructure; fracture toughness.

1. Introduction

Due to the outstanding hardness, toughness, wear and corrosion resistance,[1,2] chromium nitride (CrN) coatings have great applications in die molds, cutting tools, and engine parts. The hardness and wear resistance of the CrN hard coatings were

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reported, however there is still a lack of information about the relations among the microstructure, toughness and tribological behaviors. In general, the CrN coatings have high hardness to prevent plastic deformation. Toughness encompasses the energies required to both create the cracks and enable them to propagate until fracture. Therefore, coatings with good combination of hardness and toughness will have good performance. The substrate bias can be used to control the ion energy. Therefore, it is a parameter influencing the microstructure and properties of CrN coatings in physical vapor deposition.[3–5]

In this study, we explored the influence of substrate bias on the microstructure and mechanical properties of CrN coatings, and aimed at optimum deposition parameters for achieving good toughness and hardness of CrN coatings.

2. Experimental Details

2.1. *Samples preparation*

The schematic description of the deposition system was introduced in Ref. 6. The substrates were ultrasonically cleaned in acetone and ethanol, and installed 15 cm away from the target. The base pressure was 3.0×10^{-3} Pa. Prior to the deposition cycle, a 30-min argon etching process was applied to clean away surface oxides and improve the substrate surface activity. In the deposition cycle, a 300 nm metal Cr layer was deposited to improve CrN coatings' adhesion. The working pressure was 0.5 Pa. DC current was 3 A. Pulse voltage was 700 V with pulse width and repetition frequency of 200 μs and 50 Hz, respectively. The coatings deposited at different substrate biases, -50 to -300 V with an increase step of -50 V, were labeled as #1, #2, #3, #4, #5 and #6, respectively.

2.2. *Microstructures and mechanical characterizations*

The crystal structure of the coatings was characterized by X-ray diffractometer (XRD, Bruker D8 Advance X-Pert diffractometer) using Cu-K_α radiation in Bragg–Brentano mode. Cross-section microstructure of the coatings was characterized by high-resolution field emission scanning electron microscope (SEM, Hitachi S4800). The hardness and Young's modulus of the coatings were measured using MTS nanoindenter G200 tool equipped with a diamond Berkovich tip. The indentation depth was below 10% of the coatings' thickness to minimize the influence from substrates.

3. Results and Discussion

3.1. *The substrate current waveforms at different substrate biases*

The substrate voltage waveforms were presented as a form of high-frequency pulsed bias with the low-frequency induced voltage waveform as the envelope curve (see Fig. 1). The substrate current increased with the bias voltage. With the increase of

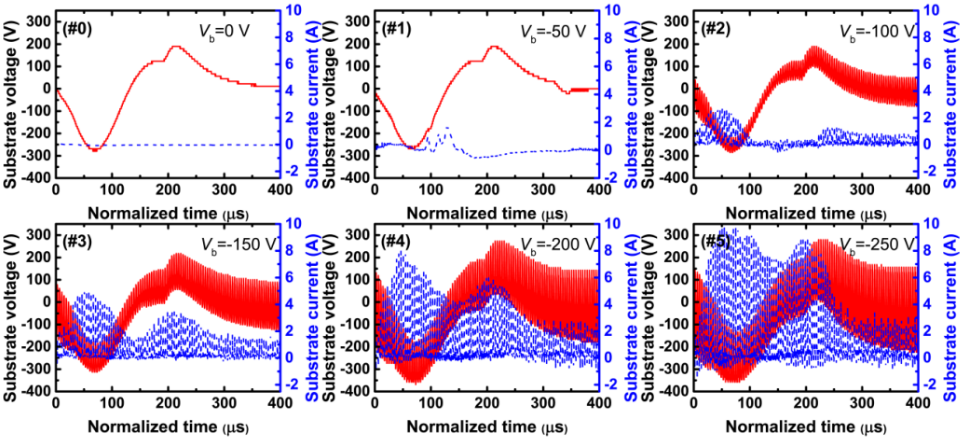
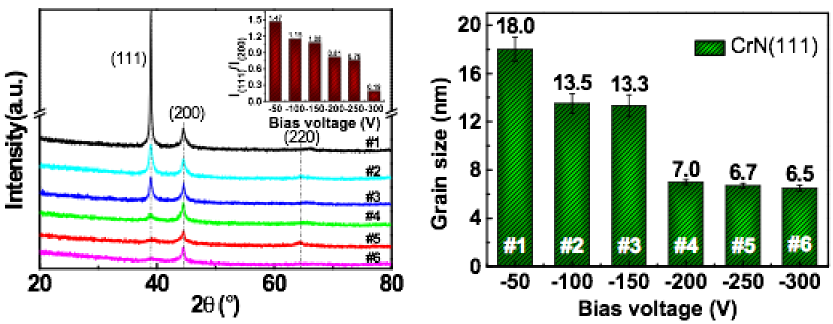


Fig. 1. (Color online) The substrate I–V curves and substrate powers under different substrate biases.



(a) (b)

Fig. 2. (Color online) (a) XRD spectra of the CrN coatings deposited at different bias voltages. (b) The averaged grain sizes.

bias voltage, current in pulse-on phase of nearly 10 A was obtained. However, only 2 A current was obtained from the DC magnetron discharge in pulse-off phase. Therefore, the high plasma density in high-power-impulse magnetron sputtering (HiPIMS) system makes it a convenient way to control the ion flux and ion energy by means of substrate bias. The influence of substrate bias on the microstructure and mechanical properties of the deposited coatings is studied in detail.

3.2. *Microstructures of the deposited chromium nitride coatings*

Figure 2(a) shows the XRD spectra of the coatings deposited on glass substrates at different bias voltages. The incident ions can gain more kinetic energy from the electrical field at higher bias voltage. Therefore, more adsorbates on the film growth interface have enough energy for moving to lower strain energy places.[7] As a result, the CrN coatings grew from the (111) orientation to (200) orientation at −200 V.

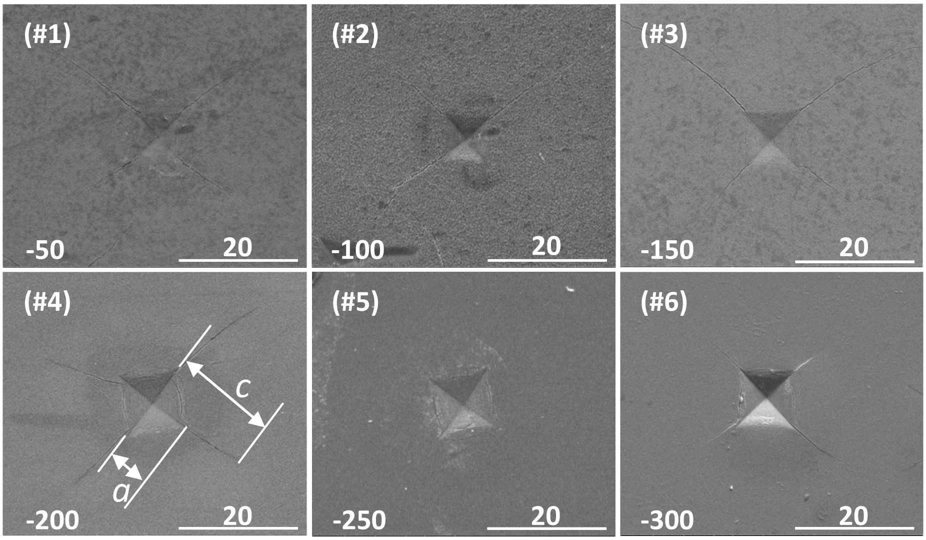


Fig. 3. Indentation images of CrN coatings deposited with different substrate bias voltages.

Figure 2(b) shows the averaged grain sizes of the (111) plane in the CrN coatings. It has a maximum of 18 nm at −50 V, and decreases with the increase of the substrate bias. The grain size holds at around 7 nm when the bias voltage is higher than −200 V.

3.3. *Mechanical properties of the deposited CrN coatings*

The nanoindenter hardness (H) and Young's modulus (E) of the deposited CrN coatings both increased dramatically with the substrate bias, and each reached the stable values of around 18.7 and 285 GPa at −250 V, respectively. However, higher substrate bias than −250 V did not result in higher hardness. Inversely, as the bias voltage was decreased from −250 to −300 V, the hardness declined a little.

Figure 3 presents SEM images of the Vickers indentation on the CrN coating samples. The cracks were formed in the indentation corners and expanded outwards. It could be found that the crack length c decreased with the increase of substrate bias. No cracks were observed in sample #5. However, the cracks reappeared in sample #6. It qualitatively indicates that the CrN coatings at −250 V have the best fracture toughness in the studied bias range. The calculated fracture toughness of the CrN coatings increased to a maximum of 3.16 $\mathrm{MPa \cdot m^{1/2}}$ at −250 V, and then declined to 2.78 $\mathrm{MPa \cdot m^{1/2}}$ at −300 V.

4. Summary

The microstructure and mechanical properties of DC-superimposed HiPIMS CrN coatings at different substrate biases were investigated in this work. With the increase of bias voltage, the preferential orientation changed from (111) to (200). The hardness of CrN coatings increased with the substrate bias to a maximum of 18.7 GPa at −250 V. High hardness and low elastic modulus ensure that the CrN coating had good toughness. The CrN coatings deposited at −250 V showed dense columnar microstructure, sufficient hardness, high fracture toughness and wear resistance. It could be concluded that energetic incident ions bombardment leaded to fined grains beneficial to the deposition of hard and tough CrN coatings. However, incident ions with too high energy at −300 V caused toughness reduce.

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