

## Deposition and characterization of compositional gradient CrNx coatings prepared by arc ion plating

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Compositional gradient CrNx coatings were fabricated using arc ion plating in Ar/N<sub>2</sub> gaseous mixture by gradually increasing N<sub>2</sub> flux rate from 0 to 120 SCCM. The effect of negative substrate bias on the film microstructure and mechanical properties were systematically investigated with XRD, GDOES, and SEM. The results show that substrate bias has an important influence on film growth and microstructure of gradient CrNx coatings. The coatings mainly crystallized in the mixture of hexagonal Cr<sub>2</sub>N and fcc CrN phases. By increasing substrate bias, film microstructure evolved from an apparent columnar structure to an equiaxed one. With increasing substrate bias, deposition rate first increased, and then decreased. The maximum of deposition rate was 15 nm/min obtained at a bias of -50V.

Keywords: Chromium nitride (CrN), arc ion plating, functional gradient coating (FGC), substrate bias

### 1. Introduction

Increasing attention has been paid to chromium nitride (CrN) coatings due to its good properties, such as high hardness, good oxidation and wear resistance [1]. It also exhibits high ductility, excellent corrosion resistance and well environmental friendship. The CrN coating synthesized by physical vapor deposition (PVD) has been regarded as a good candidate for electroplating chromium coatings, which contain hazardous hexavalent chromium and bring in badly pollution in electroplating process. However, CrN coatings usually exhibit poor adhesion to metal substrates due to the abrupt change in materials properties (ceramic and metal materials) near the interface of a hard coating and a relatively soft metal substrate. The concept of functional gradient coating (FGC) was recently developed by introducing the structural and compositional changes gradually from the coating/substrate interface [2, 3]. As to Cr-N coatings, many efforts also have been devoted to CrNx coatings deposited with fixed N<sub>2</sub> flux ratio values [4-10]. As far as our best knowledge, there are few reports concentrating on compositional gradient CrNx coatings with N concentration continuously varying along depth direction.

In the current study, a gradient CrNx coating is designed as shown in Fig. 1. During deposition process, N<sub>2</sub> flux rate is increasing from 0 to 120sccm while film thickness builds up. Thus, the interface between coating and substrate is mental to metal, where a good adhesion is expected. The gradient CrNx coatings are fabricated using arc ion plating technique with N concentration continuously increasing along depth direction. The effect of substrate bias on the growth and microstructure of gradient CrNx coatings has been investigated.

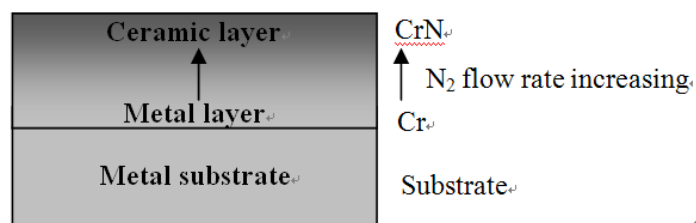


Fig. 1 Schematic view of CrNx coatings

## 2. Experimental

The gradient CrNx coatings were fabricated on AISI 304 steel and Si(100) wafer substrates using the arc ion plating technique. One Cr target with a purity of 99.99% was used in the arc ion plating system. A rotational substrate holder located at the center of the vacuum chamber which is well water-cooled. The distance between the Cr target and substrate holder was 350mm. Polished AISI 304 steel sheet (25mm×25mm×2mm) and Si(100) wafer (30mm×60mm×0.7mm) were selected as substrates. The substrates were ultrasonically cleaned in acetone, ethanol and de-ionized water sequentially for 15min. Then they were blown dry with N<sub>2</sub> and adhered vertically to the holder.

The chamber was evacuated to a base pressure less than  $6.0 \times 10^{-3}$  Pa using a rotate pump and a cryopump, and then was heated to and kept at a desired temperature by electrical resistance heating. Prior to deposition, the substrates were sputter-cleaned by Ar ions for 10 min with a bias of -600V in Ar atmosphere of 2.0Pa.

The deposition took place in an atmosphere of Ar (99.99% purity) and N<sub>2</sub> (99.99% purity) with a working pressure of 0.5Pa. The inlet flux rate of Ar gas was fixed at 40 SCCM. To obtain compositional gradient CrNx coating, the flux rate of N<sub>2</sub> varies from 0 to 120 SCCM (0, 20, 40, 60, 80, 100, 120 SCCM, every 20 min a shift). The total chamber pressure was controlled at 0.5Pa by a throat valve. During deposition, the rotational velocity of the substrate holder is fixed at 25rpm. A DC bias varying from 0V to -250V was applied to the substrates. The deposition parameters were summarized in Table 1.

Table 1 Deposition parameters for CrNx coatings by Arc ion plating

Base pressure	$6.0 \times 10^{-3}$ Pa
Working gas	$5 \times 10^{-1}$ Pa
Ar flow rate	40 SCCM
N <sub>2</sub> flux	0—20—40—60—80—100—120 SCCM, every 10 mins a shift
Arc current	55A
Deposition temperature	300°C
Deposition time	70 mins
Substrate bias	0V, -50V, -100V, -150V, -200V, -250V

The film structure was investigated using an X-ray diffractometer (XRD, BRUKER axs, D8) with Cu K radiation operated at 40 kV and 40 mA. The 2 scan range is from 20 to 80 at a 0.02 step size and a 0.2s dwell time. Film thickness was measured using a stylus (-STEP) instrument and a field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4800).

## 3. Results and discussions

### 3.1 Phase structure and depth profile of chemical composition

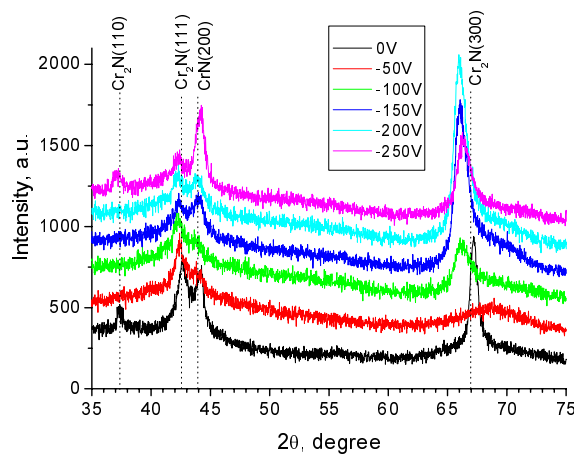


Fig. 2 XRD patterns of CrNx coatings deposited at 300C under various substrate biases

Fig.2 presents the XRD patterns of CrN<sub>x</sub> coatings deposited at 300C under various substrate biases. Some diffraction peaks occur at the position of 37.1, 42.5, 44.2 and 67.1, corresponding to Cr<sub>2</sub>N(110), Cr<sub>2</sub>N(111), CrN(200) and Cr<sub>2</sub>N(300) plane, respectively. We can conclude that the CrN<sub>x</sub> coatings deposited at 0V crystallize in the mixture of cubic rocksalt structure CrN and hexagonal Cr<sub>2</sub>N phases. When the bias increases to -50V, the CrN(200) and Cr<sub>2</sub>N(110) peaksweaken greatly, even vanish, meanwhile a broadening and weakening of Cr<sub>2</sub>N(300) peak is also observed, showing a preferred orientation along Cr<sub>2</sub>N(111) plane. It also can be deduced that the main content in the coating is Cr<sub>2</sub>N. In the XRD pattern of CrN<sub>x</sub> coatings deposited at -100V, Cr<sub>2</sub>N(300) peak occurs again, but the peak broadening and shift can be observed compared to the case of 0V. A little CrN(200) peak occurs again. As the bias increase further to -150V, the intensity of CrN(200) and Cr<sub>2</sub>N(300) peaks increases, especially the latter. The film shows a preferred orientation along Cr<sub>2</sub>N(300) plane. The film deposited at -200V exhibits a similar XRD pattern with that at -150V. When the bias increases to -250V, the intensity of CrN(200) peak continue to increases, whereas Cr<sub>2</sub>N(300) peak declines, indicating that the content of CrN phase in the films is increasing. Meanwhile, the Cr<sub>2</sub>N(110) peak appears again.

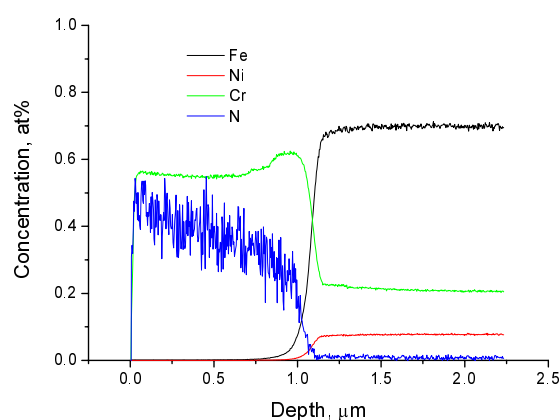


Fig. 3 GDOES depth profile of CrN<sub>x</sub> coatings deposited on 316L stainless steel at a bias of -50V

Fig. 3 shows the typical depth profile of CrN<sub>x</sub> coatings deposited on 316L stainless steel at a bias of -50V. It is obvious proof for the compositional gradient CrN<sub>x</sub> coatings deposited in this study.

### 3.2 Film morphology

Fig. 4(a) and (b) present surface morphology of the CrN<sub>x</sub> coatings deposited at a bias of 0V and -250V. There are some macroparticles on film surface, which is the characteristic feature of arc ion plated coatings. It can be observed in Fig. 4(b) that the macroparticles become fewer with increasing substrate bias. Similar phenomena were identified in the deposition of TiN, TiO<sub>2</sub> and AlN coatings by applying a pulsed negative substrate bias [11-13]. This macroparticle-filtrationeffect is related to the hybrid mechanism of ion bombardment and electrical repulsion induced by negative substrate bias. In addition, as the bias voltage increases the film surface is much denser and smoother within macroparticle-free zone.

SEM images presented in Fig. 4(c) and (d) show fractured cross-section of CrN<sub>x</sub> coatings deposited at various substrate biases. Loose and pronounced columnar microstructure with some pinholes is observed in the coatings deposited at 0V, as shown in Fig. 4(c). The interface between metal and ceramic zones can also be clearly characterized in Fig. 4(d). When the bias voltage increases, the pronounced columnar structure is almost invisible so that the fractured cross-section looks nearly featureless except for some torn lips. An obvious evolution from columnar to highly dense microstructure is observed, indicating grain refinement in the CrN<sub>x</sub> coatings. These phenomena of microstructure densification and evolution are ascribed to high ionization rate in arc ion plating process, and ion bombardment enhanced by applied substrate bias.

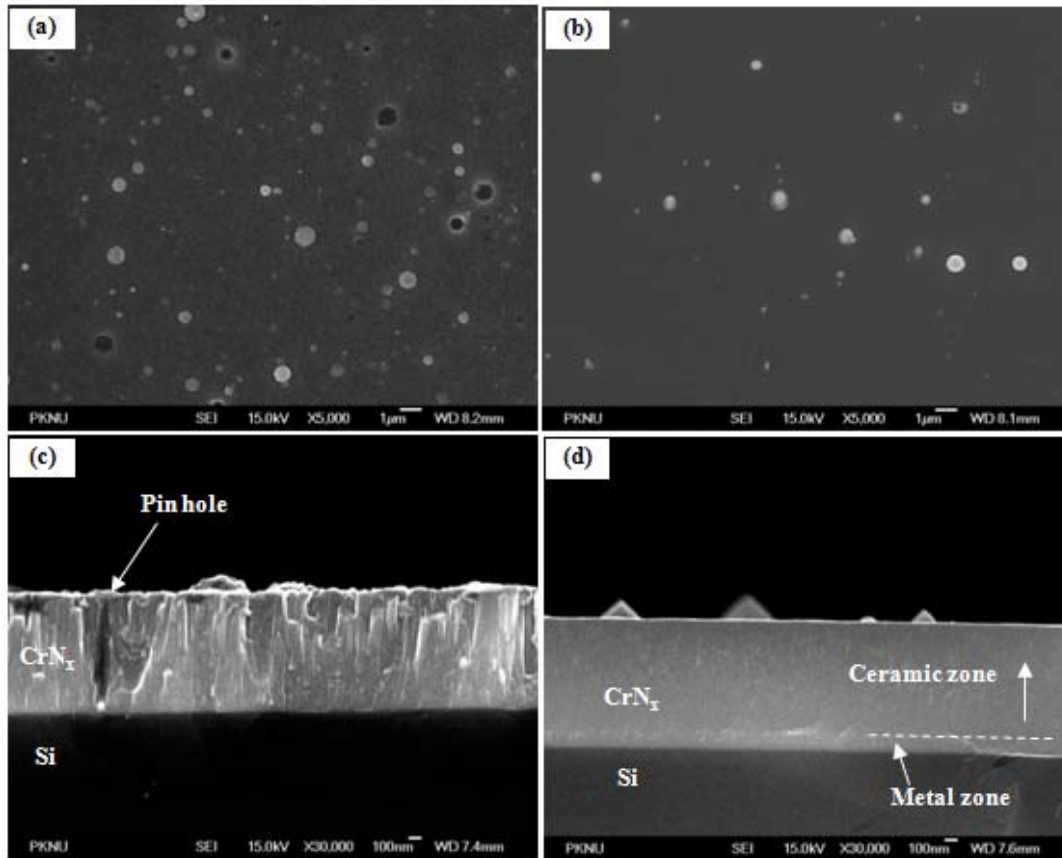


Fig.4 Surface ((a) 0V, (b) -250V) and cross-sectional ((c) 0V, (d) -50V) SEM images of CrNx coatings on Si(100) wafer.

### 3.3 Deposition rate

Fig. 5 shows the dependence of deposition rate of the CrNx coatings as a function of substrate bias. The film thickness was obtained by measuring cross section of CrNx coatings in FE-SEM images, as shown in Fig. 4. At least 3 measurements at different positions were performed on each sample, and then the average value was recorded. With increasing substrate bias, deposition rate of CrNx coatings increases first and then decreases. A maximum value of about 15nm/min is observed at a bias of -50V. When the bias increases further, deposition rate begins to decrease. The decline trend becomes apparent when the bias increases up to -100V.

Negative substrate bias can accelerate deposited ions and increase the ion energy of bombardment, resulting in an increase of nucleation density and consequently an improvement in deposition rate. This phenomenon is usually called "accelerated deposition effect". However, a higher substrate bias can cause excessively strong ion bombardment and etch the forming film to thin, which is called "sputtering effect". At a lower bias, the former effect is prominent; as a result, deposition rate is increasing. In the case of higher biases, the sputtering effect is dominant, resulting in a decrease of deposition rate. This explains the tendency of deposition rate versus substrate bias presented in this work.

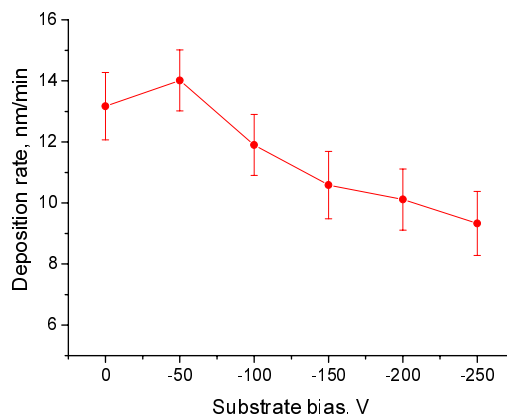


Fig. 5 The dependence of deposition rate of CrNx coatings as a function of substrate bias

#### 4. Conclusion

Compositional gradient CrNx coatings were fabricated using arc ion plating in Ar/N<sub>2</sub> gaseous mixture by gradually increasing N<sub>2</sub> flux rate. The coatings mainly crystallized in the mixture of hexagonal Cr<sub>2</sub>N and fcc rocket-salt CrN phases. By increasing substrate bias, film microstructure evolved from an apparent columnar structure to an equiaxed one. With increasing substrate bias, deposition rate first increased, and then decreased. The maximum of deposition rate was 15 nm/min obtained at a bias of -50V.

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