High Temperature Oxidation Resistance and Electrical Properties of CrN/Cr Films Prepared by RF Magnetron Technology

Jia-Xin Zhang, Mei-Jie Zhang, Guang-Rui Gu, and Bao-Jia Wu

***Abstract*—In this work, CrN films were deposited on Si substrates with a Cr buffer layer (CrN/Cr films) by RF magnetron sputtering. The structure, surface morphology, chemical composition, high temperature oxidation resistance and resistivity were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and four-probe resist tester, respectively. The lattice constant of the CrN/Cr films with a (111) preferred orientation was estimated to be about 4.1336 Å. After high temperature heat treatment, the surface morphology of CrN/Cr films changed obviously, and the electrical properties of CrN/Cr films were improved. Our results can provide an important reference in the high temperature oxidation resistance research for CrN films.**

***Index Terms*—Rf magnetron sputtering, metal buffer layer, electrical properties, oxidation resistance.**

I. Introduction

Chromium nitride (CrN) coatings exhibit high hardness, good corrosion resistance, good wear resistance and low friction coefficient. They are widely used in cutting and forming tools, bearing and machine parts, dies and molds [1]-[7]. However, because of the occurrence of some new processes, such as high speed or dry machining, there are still industrial interests in protective coatings with further improved wear resistance, hardness and fracture toughness [8]-[11]. In such conditions, nanoscale multilayer coatings received much attention as they provide the flexibility to combine two materials with different structures and properties, which may bring to the new system not only the advantage owned by each constituent but also some characteristics superior than any component [12].

Many reports show that the preparation technology of high quality CrN films is still to be developed, and there are still some controversies about their characteristics. In addition, the research of metal/TiN multilayer films has made some progress [13], so the CrN/metal films need to be further studied [14]-[16]. Despite a significant number of works about the mechanical properties, hardness and wear resistance of multilayer coatings, there is still a lack of information about the high temperature oxidation resistance and electrical properties [17]-[19]. In this work, the CrN/Cr films were prepared by RF magnetron sputtering, followed by a systematic study by comparison method of the high temperature oxidation resistance and electrical properties.

II. Experimental Procedure

CrN/Cr films with good crystallinity were deposited on Si (100) substrates using a radio frequency (RF) magnetron sputtering system. A Cr target with 99.99% in purity was used and the substrate-to-target distance was kept at 60 mm. First, the Cr metal buffer layer was deposited on a Si (100) substrate by RF magnetron sputtering in an atmosphere of Ar gas. And then CrN films were sputtered on the Cr metal buffer layer, and the working gas was a mixture of Ar (99.99%) and N_2 (99.99%) and the total gas flow rate was maintained at 100 sccm. Prior to deposition, the chamber was evacuated to a base pressure of 5×10^{-5}Pa, and the Si substrate is always pre-sputtered by Ar for 10 min in order to remove the oxide and contaminant layer. During deposition, the sputtering power was 100 W, the ratio of N_2 flow over the total flow ($N_2/(N_2+Ar)$) was 50% and the substrate bias was 100 V. CrN films with a (111) preferred orientation at the best preparation condition were prepared. In the experiment, CrN films were annealed in air using a conventional furnace at 800℃ during 1 h.

The structure and chemical composition of coatings were investigated by X-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDX). The cross-section images of the multilayer coatings were observed by scanning electron microscopy. In order to get the information on the composition, molecular structure and valence states of the films, X-ray photoelectron spectroscopy (XPS) was measured. The resistivity of CrN films was measured by the four-probe method. The high temperature heat treatment of the sample was carried out in a high temperature sintering furnace.

III. Results and Discussion

A. Oxidation Resistance of CrN/Cr Films

The XRD patterns of CrN/Cr films are shown in Fig. 1. The as-deposited coatings present a cubic structure with an intense (111) diffraction peak and a weak (222) diffraction peak, whereas no other peaks from the coatings are observed.

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The CrN/Cr films have good crystallinity before annealing. However, the cubic CrN/Cr layer after annealing is still the preferred growth direction, but its diffraction peak obviously reduced and the crystal quality of the film also decreased. A Cr_2N-related diffraction peak and a number of chromium oxide diffraction peaks, such as Cr_2O_3, CrO_3 and CrO_2, appear on the surface of CrN/Cr film after high temperature heat treatment. During the high temperature heat treatment, the occurrence of Cr_2N phase shows that the decomposition of cubic CrN is combined with O to form an oxygen compound, and a Cr_2N phase with a high temperature thermostable structure is formed. According to XRD analysis, there is still no Cr-related information.

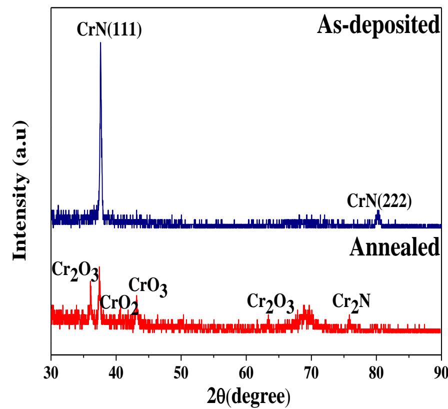


Fig. 1. XRD patterns of the as-deposited and annealed CrN/Cr film.

Fig. 2 shows the surface and cross-sectional SEM images of the CrN/Cr thin films. The as-deposited CrN/Cr films have very fine grains with typical pyramidal tetrahedron structures, and there is a significant growth consistency between the Cr and CrN layers, as shown in Fig. 2(a) and (b). This growth consistency was also reported in the literature on TiN/Ti multilayers [20]. The (100) plane of the cubic structure of the CrN crystal has the smallest surface energy density, and the cubic CrN had a (111) direction preferential growth influenced by three (100) planes during the deposition process, so the pyramidal tetrahedron structure is formed [21]. Fig. 2(b) shows the cross-section SEM diagram of the CrN/Cr films. It can be seen from the figure that there is no obvious boundary between the Cr and CrN layer, and shows a typical columnar growth structure.

The focal spot of the surface of the CrNr film and CrN/Cr films is shown in Fig. 2(c, d), respectively. Under the bombardment of high-energy particles, not only the growth defects will be formed between the grains on the surface of the film, but also a bombardment focal spot will be formed on the surface of the film[22], [23]. As shown in Fig. 2(c), the flake bombardment of the focal spot on the surface of the film leads to the discontinuous crystallization, which can affect the increase of the resistivity of the film.

As shown in Fig. 2(e), the surface structure of the annealed CrN/Cr thin film is completely destroyed and the pyramid structure disappears. The surface of the film is composed of grains with different sizes and different structures, and some grains are larger in size and have a sheet structure. XRD analysis shows that the surface structure of the CrN/Cr film is seriously damaged, which is attributed to the more surface defects and larger grain size. In addition, the clear outline of the tetrahedron structure also increases contact area with atmosphere, and the crystal structure of the CrN becomes more unstable at high temperature, so the cubic CrN phase decomposition and oxidation is accelerated. The grain size and structure have an obvious influence on the high temperature oxidation resistance of the film. Fig. 2(f) shows a cross-sectional SEM image of the CrN/Cr film after high temperature annealing. It can be seen that the surface failure of the film is seriously damaged and the columnar growth structure is deeply influenced.

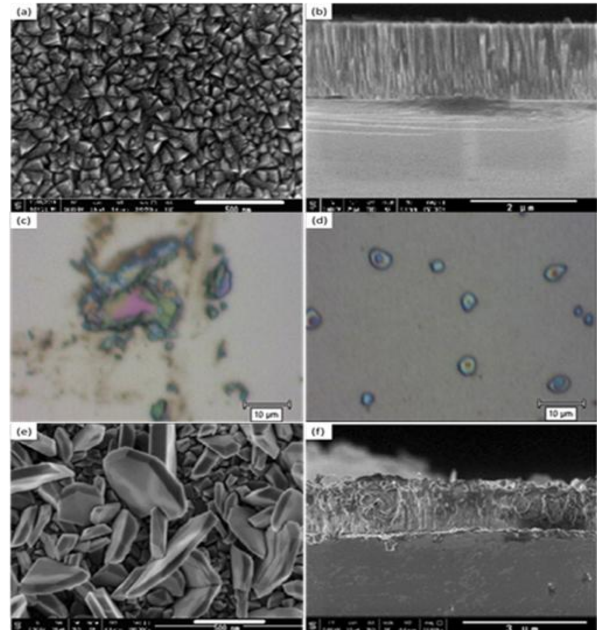


Fig. 2. Surface and cross section SEM images of CrN/Cr films: (a, b) as-deposited; (c, d) focal spot; (e, f) annealed.

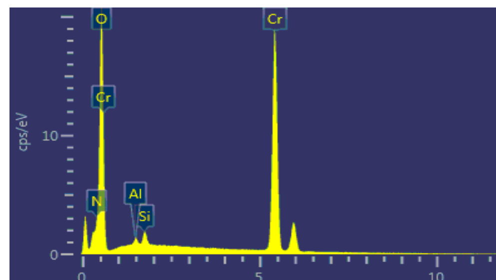


Fig. 3. EDX spectrum of CrN/Cr films annealed at high temperature.

Fig. 3 shows the EDX spectrum after annealing at high temperature. EDX analysis results are shown in Table I. The results show that the CrN/Cr film has a significant decrease in the content of N and a significant increase in the content of O element after annealing, and the ratio of the decrease and the increase of the CrN/Cr film is larger, which also proves that the O element is adsorbed on the surface of the film and Cr-N bond is more damaging. The Al element is derived from the impurities at the time of measurement.

Fig. 4 shows the XPS spectrum of the Cr, N, and O elements of the CrN/Cr film after annealing. As shown in Fig. 4(a), after the high temperature annealing, there are the three distinct peaks of $Cr2p^{1/2}$, $Cr2p^{3/2}$ and O1s located at 585.06 eV, 575.66 eV and 532.28 eV [26], respectively. The selected area N1s peak inserted in Fig. 4(a) shows the

intensity of the peaks after annealing is significantly reduced, which also indicates that a large part of the N element diffuses into the film at high temperature annealing. Fig. 4(b) shows the single XPS spectrum of $Cr2p^{3/2}$ of the CrN/Cr film, the results show that the Cr-related compounds in the annealing process have changed significantly. The information about the metal Cr does not appear in the XPS spectrum, which again shows that the metal Cr has been completely transformed at 800℃ high temperature.

TABLE I: EDX ANALYSIS RESULTS OF THE ANNEALED CRN/CR FILMS

Element	Apparent concentration	Wt.%	At.%
N	9.64	0.40	8.04
O	47.17	27.43	51.35
Cr	53.21	66.91	36.14
Si	2.08	1.22	2.53
Al	0.49	0.04	0.76

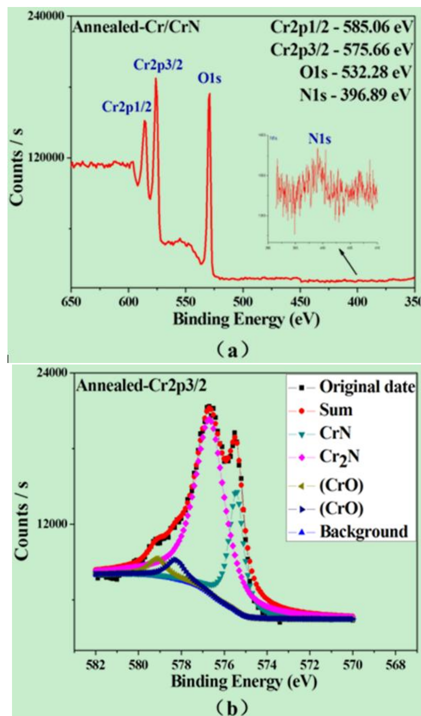


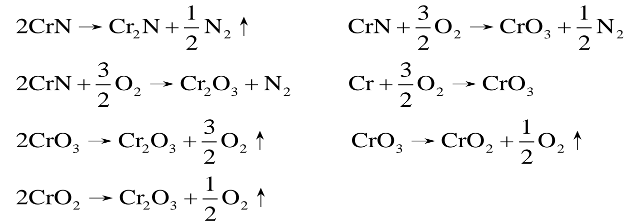
Fig. 4. XPS spectrum of the CrN/Cr films after annealing. (a) CrN/Cr; (b) $Cr2p^{3/2}$.

As shown in Table II, the cubic CrN of the film surface gradually decomposed and changed to Cr_2N and CrO after high temperature heat treatment. In addition, we found that the total (CrO) content of CrN/Cr films was relatively high after annealing. It was also known that the CrN/Cr film surface was highly damaged from XRD and SEM analysis, which can accelerate the oxidation of CrN/Cr thin films. The oxidized form of the film surface: on the one hand, the diffusion of O elements from the air into the interior of the film, destroying the chemical bonds between Cr and N, and recombining with Cr-bonds to form various chromium oxide [24]-[26]; On the other hand, CrO_3 decomposes into CrO_2 which is easily converted to more stable Cr_2O_3 at high temperatures, and CrO_3 also undergoes a transition to Cr_2O_3 [27]. Some literature reports show that chromium oxide has similar Gibbs free energy, so that different oxides can simultaneously exist in the samples [28].

TABLE II: XPS ANALYSIS RESULTS OF CRN FILMS ON CR METAL BUFFER AFTER ANNEALING

Binding energy(eV)	FWHM	Area	Area Percent	Compound
575.43	0.8	11200	22.85%	CrN
576.67	1.65	33540	68.42%	Cr2N
578.26	1	2240	4.57%	(CrO)
579.13	1	2040	4.16%	(CrO)

Through the above research and analysis, the transformation of the CrN/Cr films at high temperatures can be described by the following reactions:



$$2CrN \rightarrow Cr_2N + \frac{1}{2}N_2\uparrow \qquad CrN + \frac{3}{2}O_2 \rightarrow CrO_3 + \frac{1}{2}N_2$$

$$2CrN + \frac{3}{2}O_2 \rightarrow Cr_2O_3 + N_2 \qquad Cr + \frac{3}{2}O_2 \rightarrow CrO_3$$

$$2CrO_3 \rightarrow Cr_2O_3 + \frac{3}{2}O_2\uparrow \qquad CrO_3 \rightarrow CrO_2 + \frac{1}{2}O_2\uparrow$$

$$2CrO_2 \rightarrow Cr_2O_3 + \frac{1}{2}O_2\uparrow$$

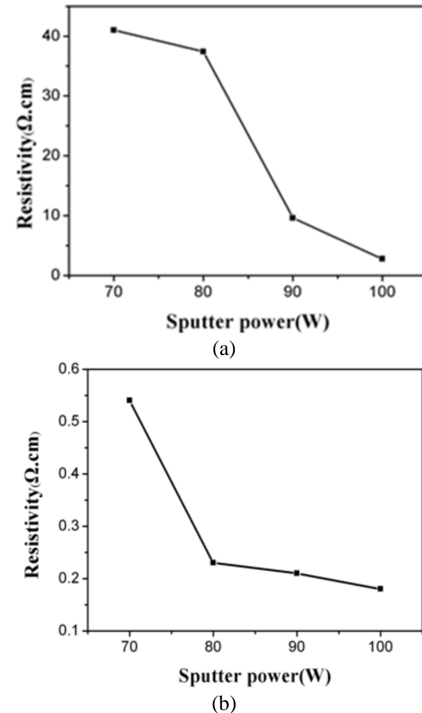


Fig. 5. The resistivity of (a) CrN and (b) CrN/Cr films deposited at different power.

B. Electrical Properties of CrN/Cr Films

The resistivity in the CrN films and CrN/Cr films decrease to a minimum as the power increases from 70 W to 100 W (solid data points in Fig. 5(a) and Fig. 5(b)), this is consistent with the crystallinity of the film obtained with XRD analysis. The CrN films have a relatively low resistivity under the best deposition conditions. Compared with CrN films, the resistivity of CrN/Cr films is obviously decreased with one or two orders of magnitude difference. The main reason is that the impact of Cr metal buffer layer makes the cubic CrN crystal positive tetrahedral structure is clear and has a larger grain size, and more grain boundaries, which led to the film resistivity is small [29]. In addition, due to the existence of Cr buffer layer, the focal spot size decrease, the carrier concentration of the films increases,

thus the roughness and scattering effect decrease, which further reduces the resistivity.

IV. Conclusions

CrN films were deposited on a Cr metal buffer layer by RF magnetron sputtering technique. The electrical characteristics and high temperature oxidation resistance of CrN/Cr films were analyzed systematically. The main factors affecting the oxidation resistance and thermal stability of the film are: (1) the influence of the crystal structure on the surface. The clear pyramid structure reduces the thermal stability of the films at high temperature, and further promotes the oxidation degree of the films. (2) The presence of Cr_2N phase leads to the increase of the thermal stability of the film and the further oxidation of the film, and the formation of the Cr_2O_3 phase at high temperature also prevents the further oxidation of the film. There are two main factors affecting the resistivity of

CrN film: (1) the influence of the crystal quality of the film. As the crystalline quality of the film increases, the mobility of the carrier in the film increases and then the resistivity of the film decreases. (2) The influence of the film size and surface defects. The resistivity is reduced because that the number of grain boundaries are increased by the coarser grain size and surface defects making.

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