Research Article

Structure and Friction Behavior of $\text{CrN}_x/\text{a-C:H}$ Nanocomposite Films

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CrN and $\text{CrN}_x/\text{a-C:H}$ nanocomposite films were deposited on Si substrates by the magnetron sputtering technique. The structure, chemical state, and friction behavior of the $\text{CrN}_x/\text{a-C:H}$ films prepared at various CH_4 content were studied systematically. The CrN film shows strong (111) and (220) orientation, while the $\text{CrN}_x/\text{a-C:H}$ films consist of the nanocrystalline CrN_x or Cr particles embedded in an amorphous hydrocarbon (a-C:H) matrix and show weak diffraction peaks, which is in accordance with the XPS analysis results. The typical Raman D and G peaks are observed, indicating that the separated amorphous carbon or CN_x phase appears in the $\text{CrN}_x/\text{a-C:H}$ films. However, no chromium carbide was observed in all the as-deposited samples. From the SEM graphs, all the deposited films depicted a dense and compact microstructure with well-attached interface with the substrate. The average friction coefficient of the $\text{CrN}_x/\text{a-C:H}$ films largely decreased with increasing CH_4 content.

1. Introduction

Transition metal nitride films have found a wide technological use as hard, protective, and wear resistant coatings for cutting tools. Of transition metal nitrides, chromium nitride (CrN) films show a significantly higher adhesion to the substrate along with a high ductility, which is desirable for mechanical applications [1–5]. However, there are increasing numbers of applications where the mechanical and chemical properties of the binary nitrides are not sufficient. To further improve the tribological properties of CrN, alloying with another element to form a ternary hard coating has been explored [6–11]. Most frequently, a low friction coefficient is required, which helps to reduce friction losses and to increase load support capability. Nanocomposite coatings consisting of nanocrystalline ceramic or metal particles embedded in an amorphous hydrocarbon (a-C:H) matrix are able to combine high fracture toughness and wear resistance with a low coefficient [12, 13]. An example of these a-C:H based nanocomposite films is the TiC/a-C:H systems in which a correlation between coating mechanical properties and metal

concentration has been made by Meng and Gillispie [12] and Pei et al. [14, 15].

$\text{CrN}_x/\text{a-C:H}$ systems are, probably, similar to TiC/a-C:H systems, the most promising nitrides for protective coatings due to the formation of diamond-like structure, which can eventually decrease the friction coefficient. $\text{CrN}_x/\text{a-C:H}$ system is a relatively less studied coating but with promise to improve tribological behavior compared to CrN. However, the structure, chemical state, and friction behavior of the $\text{CrN}_x/\text{a-C:H}$ films were poorly studied systematically.

In this paper, we report the deposition and characterization of $\text{CrN}_x/\text{a-C:H}$ nanocomposite films using medium frequency magnetron sputtering system at various CH_4/N_2 ratios. The friction coefficient of the nanocomposite films was also observed in conjunction with the detailed examinations of the microstructures.

2. Experimental Process

The CrN and $\text{CrN}_x/\text{a-C:H}$ nanocomposite films were deposited on silicon (111) wafer using a medium frequency

TABLE 1: The deposition parameter and compositions of the as-deposited films.

Sample no.	Deposition conditions			
	N ₂ (sccm)	CH ₄ (sccm)	Ar (sccm)	CH ₄ content
C1	160	0	40	0
C2	140	20	40	10%
C3	120	40	40	20%
C4	100	60	40	30%
C5	80	80	40	40%
C6	60	100	40	50%

(20 kHz) magnetron sputtering technique. For the deposition system used in this study, a planar (280 mm × 80 mm × 8 mm) Cr target (99.8%) was mounted on the chamber wall.

The Si substrates were cleaned ultrasonically in acetone and deionized water and then dried under flowing gas. The sputtering chamber was evacuated to a pressure of 4.0×10^{-3} Pa with a turbomolecular pump before introducing sputtering gas. Then the Si substrates were sputtering-cleaned for 10 min at 1 Pa argon pressure with the substrate bias at -700 V. The 2-hour deposition process was carried out at a 40 sccm Ar flow rate and a 160 sccm N₂ and CH₄ mixture flow rate with a -100 V substrate bias. The power was kept about 1 kW. The substrate was positioned 50 mm away from the planar target. A series of CrN_x/a-C:H nanocomposite films with different Cr, C, and N ratios were prepared and the details were given in Table 1.

In this study, X-ray diffraction (XRD) was performed on Philips X'perts diffractometer at Cu-K α wavelength. To obtain the diffraction peak profiles of the thin films along the vertical direction, grazing angle X-ray diffraction (GAXAD) with a grazing angle of 1° was applied for phase identification and qualitative texture characterization. SEM (JSM-5600Lv) was utilized to observe the microstructure and measure the film thickness. Raman spectroscopy was done using a JOBIN-IVON LabRam HR800 with a laser wavelength of 633 nm (He-Ne-Laser). The XPS measurements of the films were performed on a Perkin-Elmer PHI-5702 multifunctional X-ray photoelectron spectroscopy, using Al-K α radiation (photon energy 1476.6 eV) as the excitation source. The XPS spectra were collected in a constant analyzer energy mode, at a chamber pressure of 10^{-8} Torr and pass energy of 29.4 eV, with 0.125 eV/step. The energy calibration of the XPS is always using the contaminating carbon from the absorbed carbonous materials and the pump oil evaporation to sample surface. However, CrN_x/a-C:H nanocomposite films cannot select contaminating C for energy calibration as the films contain carbon element. Therefore, we must adopt other means for energy calibrations. In this experiment, Au thin films about 2 nm thick were deposited on the tested surfaces for energy calibration of all the samples by thermal evaporation, and the binding energy of Au (Au 4f_{7/2} 84.00 eV) was used as the charge-up correction.

Friction tests were performed using a micro-tribometer (UMT-2MT, CETR Co., USA). Reciprocating friction tests were performed using a 3 mm steel ball loaded under 1 N,

reciprocated with a frequency of 100 rpm and amplitude of 5 mm, for up to 10 min. The tests were performed in ambient atmosphere with temperature of 18°C, humidity of 40%. The friction coefficient was determined by the average of continuously examined data.

3. Results and Discussions

Figure 1 shows the evolution on the XRD spectra of CrN and CrN_x/a-C:H films deposited under various CH₄ contents. According to the index, CrN, Cr₂N, and Cr peaks of principal diffraction in chart are compared with file PDF 76-2494, 35-0803, and 06-0694 (PCPDFWIN Version 2.3, JCPDS-ICDD (2002)). The films deposited without CH₄ show strong peaks corresponding to CrN (111) and (220) (with 37.60° and 63.51°) orientation and weak peaks corresponding to Cr₂N (111), (113), and Cr (110) (with 42.6° and 74.7° and 44.4°) (Figure 1 C1). This means that the film is mainly composed of CrN phase. Since the introduction of CH₄ in the reactive gas atmosphere, the intensity of CrN diffraction peaks reduce dramatically and become wider (Figure 1 C2). This spectrum makes much less well-defined diffraction peaks and makes interpretation difficult. There are broad peaks in the spectrum at approximately 37.5° and 44.0°. The former could correspond to Cr₂N (110) or CrN (111) and the latter is attributable to CrN (200) (with 43.7°), Cr₂N (111), and/or Cr (110). Further increasing the CH₄ content and reducing the N₂ content, the diffraction peaks of the films (Figure 1 C3–C6) are still very weak, but a diffraction of weak Cr (110) peak is detected. The large content carbon in the CrN_x/a-C:H films may denitrify the CrN to Cr, and finally the nanometer Cr grain embedded in amorphous hydrocarbon (a-C:H) matrix.

Raman spectroscopy is widely used for the analysis of structural and phase disorder information in carbon and carbon related materials, at any wavelength, depending on several factors, such as disorder in bond length and in bond angle, clustering of the sp² phase, presence of sp² rings or chains, and sp²-to-sp³ ratio [16]. In order to investigate the bonded structure of carbon in the CrN_x/a-C:H films, we have studied the Raman spectra of the CrN_x/a-C:H films to distinguish different bonding types of carbon. Figure 2 shows the Raman spectra of the CrN and CrN_x/a-C:H films produced at various CH₄ contents. For the CrN films, no Raman peaks show in the wavenumber range of 1000–2000 cm⁻¹. For the films in sample C2 prepared at 10% CH₄ content, no obvious Raman peaks are shown in the wavenumber range of 1000–2000 cm⁻¹, and this reflects a much lower amount of graphite-like or diamond-like bonds in the films. However, the observable D peaks at ~1350 cm⁻¹ appeared in sample C3, with further increase of the CH₄ content to 30% (sample C4) in the reactive gas; the intensity of G peaks at 1580 cm⁻¹ are enhanced, indicating that the large content separated amorphous carbon phase appear in the films. By comparing Raman spectra of CrN_x/a-C:H films deposited at different CH₄ content, the structure of these films can be distinguished. The relative intensity of the D-band to the G-band becomes noticeable with the increase of

FIGURE 1: XRD spectra of CrN and CrN_x/a-C:H films. FIGURE 2: Raman spectra of CrN and CrN_x/a-C:H films.

CH₄ content. In a word, the “D” peak is mainly existent in Raman spectra when CH₄ flow rate is low (samples C2 and C3), consequently implying the presence of sp² rings. The “G” peak arises when the CH₄ content reaches around 30%, and the peak value is gradually enhanced with increasing the reaction gas discharge. At the same time, I_D/I_G decreases with increasing sp³ content. The sample C6 (50% CH₄ content) possessed the lowest I_D/I_G ratio, corresponding to the highest sp³ bond content. The conversion of sp² bonds to sp³ bonds of the films is further confirmed from XPS analysis, as discussed later.

XPS analysis of the deposited films was performed to further investigate the chemical bonding features of carbon and nitrogen sites in the deposited films. And the typical XPS spectra of C 1s and N 1s of the CrN and CrN_x/a-C:H films deposited at different CH₄ contents are shown in Figures 3 and 4.

The XPS C 1s peaks of the as-deposited films are shown in Figure 3. It can be seen that the C 1s spectra show an asymmetric and broad peak, and shift shifts towards higher binding energy with increase of CH₄ content from 0 to 50%. The asymmetric broad feature of the C 1s spectra indicates the existence of different type of bonds in the deposited films. The dashed lines in Figure 3 show the C 1s binding energy position of different binding state of carbon; the peaks at binding energy of 282.8 eV [16] reflect the binding states of carbon in chromium carbide. From the XPS C 1s peaks, it is found that the Cr atoms are not bonded obviously with C atoms in the CrN_x/a-C:H films. This result is also in accord with the XRD result without the observation of any

FIGURE 3: C 1s core level spectra of CrN and CrN_x/a-C:H films.

chromium carbide diffraction peaks. The binding energy at about 288 eV can be confidentially assigned to C–O species probably adsorbed on the surface of the samples, being the relative intensity very low. The C 1s spectra also could be fitted with three components at approximately 284.5, 285.5, and 286.5 eV, respectively. By comparing these peaks with referenced DLC films, the peaks at binding energy of 284.5 and 285.6 eV reflect the two binding states of sp² carbon and sp³ carbon atoms, respectively [17]. The peak centered at

FIGURE 4: N 1s core level spectra of CrN and $\text{CrN}_x/\text{a-C:H}$ films.

284.5 eV is also assigned to sp^2 bonding amorphous carbon phase and the surface contaminants [18]. The shifts of binding energy to higher values with CH_4 content increase have significantly been affected by the conversion of sp^2 site to sp^3 site C. This result is also in accordance with the result of the Raman analysis. The C 1s peaks are also deconvoluted to about 286.5 eV, which are assigned to bond of C–N [19]. This suggested that the carbon in the film might be bonded with the nitrogen and will be further discussed below.

The N 1s spectra of various CH_4 contents CrN and $\text{CrN}_x/\text{a-C:H}$ films are shown in Figure 4. For the sample C1 (Figure 4 C1), the binding energy at 396.2 eV was due to CrN and higher binding energy at 397.4 eV was identified with Cr_2N bond nitrogen (agreeing with the published binding energy values [20, 21]) with clear predominance of CrN phase in the film. These results mean that CrN and Cr_2N coexist in the sample C1 as the composition calculation result and XRD result. For the samples prepared at mixed CH_4 and N_2 gas atmosphere, the N 1s peak could be reconstructed by three peaks at 400.2 eV, 398.6 eV, and 396.2 eV. The binding energy of 398.6 eV and 400.2 eV is attributed to nitrogen atoms bonded sp^3C ($\text{sp}^3\text{C-N}$) and sp^2C ($\text{sp}^2\text{C-N}$) atoms [22], but the difference will not be discussed here. We consider these two binding energies as C–N bonding state. The binding energy of N 1s shifts towards higher value, and the peaks become more asymmetric and wider with a tail at high energy regions when the CH_4 content increases. It can be seen that the fraction of the Cr–N bond corresponding to the peaks at 396.2 eV decreases due to the shift of the N 1s binding energy to higher energy with increasing CH_4 content, which indicated that the peak at 396.2 eV becomes weaker and finally disappears in N 1s spectra for samples C5 and C6. This is corresponding to the denitridation of CrN to Cr in the relative higher CH_4 content atmosphere as the XRD results. The fraction of the peak of C–N bond increases with increase of CH_4 content, which suggests that the fraction of N bonded

to carbon atoms increases with the CH_4 content and became dominant at higher CH_4 content.

Figure 5 shows the fracture cross-sectional SEM micrographs of the CrN and $\text{CrN}_x/\text{a-C:H}$ films. As shown in figures, the deposited $\text{CrN}_x/\text{a-C:H}$ films possess a dense and compact microstructure with well-attached interface to the substrate. For the CrN film deposited at 0% CH_4 content, dense consecutive columnar grains with diameter of about 100 nm are observed (Figure 5(a)). The columnar structures are almost invisible in the cross-section layer of the film obtained at 10% CH_4 content so that the fractured cross-section looks nearly featureless (Figure 5(b)). The layers of the $\text{CrN}_x/\text{a-C:H}$ films fabricated at 30% and 50% CH_4 content are also without columnar structure (Figures 5(c) and 5(d)). Instead, some shallow dimples are observed on the fractured cross-sections, implying that plastic deformation occurred during the fracture of the film. These denser without super structure cross-section images of the $\text{CrN}_x/\text{a-C:H}$ films are corresponding to the poor crystallization as confirmed by the XRD results above.

Figure 6 shows the friction coefficients of the CrN and $\text{CrN}_x/\text{a-C:H}$ films sliding against a steel ball. The average friction coefficient of the films largely decrease from 0.825 to 0.45 with increasing CH_4 content. The decrease in friction coefficient with the increase of CH_4 content could be caused by the amorphous C:H or CN_x phase and the formation of tribochemical reaction in the wear process, which often takes place in many carbon-contained ceramics, for example, CN_x decomposed in the tribology process producing graphite tribolayer. These products of graphite are known to function as a self-lubricating layer. The formation of tribolayer would be more promoted with larger C content $\text{CrN}_x/\text{a-C:H}$ films. The increase of the self-lubricating layer resulted in the decrease of the friction coefficient in these film systems.

4. Conclusions

CrN and $\text{CrN}_x/\text{a-C:H}$ films were deposited on Si substrates by the magnetron sputtering technique. The composition of films can be controlled in large ranges through varying CH_4 content. The structure, chemical state, and friction behavior of the films were studied systematically. The CrN film showed strong (111) and (220) orientation with well crystallization. $\text{CrN}_x/\text{a-C:H}$ films are consisted of the nanocrystalline CrN_x or Cr particles embedded in an amorphous hydrocarbon (a-C:H) matrix with poor crystallization. The large content amorphous carbon or CN_x may prevent the CrN crystallization and denitrify the CrN_x to Cr. However, no chromium carbide diffraction peaks were observed in all the as-deposited samples. The $\text{sp}^3\text{-C}$ content in films increase with the CH_4 content increase, and the carbon in the films is bonded with the nitrogen in large CH_4 content. The deposited films depict a dense and compact microstructure with well-attached interface with the substrate. The $\text{CrN}_x/\text{a-C:H}$ films show smooth without super structure cross-section images corresponding to the poor crystallization. The average friction coefficient of the $\text{CrN}_x/\text{a-C:H}$ films largely decreased with an increase in C content. This behavior can be attributed

FIGURE 5: Cross-sectional SEM micrographs of CrN and CrN_x/a-C:H films. (a) Sample C1; (b) sample C2; (c) sample C4; (d) sample C6.

FIGURE 6: Friction coefficient of CrN_x/a-C:H films deposited in different CH₄ content.

to the tribochemical decomposition of a-C:H or CN_x in the tribology processes, which enables formation of graphite tribolayer, playing a role as self-lubricant. In addition, studies based on structure and friction behavior of CrN_x/a-C:H nanocomposite films, we will extend the research scope of such nanocomposite films are considered as potential protective surfaces on precise components or cutting tools in the future work.

Conflict of Interests

The authors declare that there is no conflict of interests including direct or indirect financial relations with any of the trademarks and companies mentioned in this paper.

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References

- [1] W. H. Zhang and J. H. Hsieh, "Tribological behavior of TiN and CrN coatings sliding against an epoxy molding compound," *Surface and Coatings Technology*, vol. 130, no. 2-3, pp. 240–247, 2000.
- [2] Y. Q. Fu, N. L. Loh, A. W. Batchelor, X. D. Zhu, K. W. Xu, and J. W. He, "Preparation and fretting wear behavior of ion-beam-enhanced-deposition CrN films," *Materials Science and Engineering A*, vol. 265, no. 1-2, pp. 224–232, 1999.
- [3] J. W. Seok, N. M. Jadeed, and R. Y. Lin, "Sputter-deposited nanocrystalline Cr and CrN coatings on steels," *Surface and Coatings Technology*, vol. 138, no. 1, pp. 14–22, 2001.
- [4] B. Tang, X. D. Zhu, N. S. Hu, and J. W. He, "Study on the structure and tribological properties of CrN coating by IBED," *Surface and Coatings Technology*, vol. 131, no. 1-3, pp. 391–394, 2000.

- [5] C. Gautier and J. Machet, "Study of the growth mechanisms of chromium nitride films deposited by vacuum ARC evaporation," *Thin Solid Films*, vol. 295, no. 1-2, pp. 43–52, 1997.
- [6] J. H. Park, W. S. Chung, Y.-R. Cho, and K. H. Kim, "Synthesis and mechanical properties of Cr-Si-N coatings deposited by a hybrid system of arc ion plating and sputtering techniques," *Surface and Coatings Technology*, vol. 188-189, pp. 425–430, 2004.
- [7] M. Uchida, N. NihirA, A. Mitsuo, K. Toyoda, K. Kubota, and T. Aizawa, "Friction and wear properties of CrAlN and CrVN films deposited by cathodic arc ion plating method," *Surface and Coatings Technology*, vol. 177-178, pp. 627–630, 2004.
- [8] J. Almer, M. Oden, and G. Hakansson, "Microstructure, stress and mechanical properties of arc-evaporated Cr-C-N coatings," *Thin Solid Films*, vol. 385, no. 1-2, pp. 190–197, 2001.
- [9] P. Hones, R. Sanjines, and F. Levy, "Sputter deposited chromium nitride based ternary compounds for hard coatings," *Thin Solid Films*, vol. 332, no. 1-2, pp. 240–246, 1998.
- [10] K. H. Lee, C. H. Park, Y. S. Yoon, and J. J. Lee, "Structure and properties of $(\text{Ti}_{1-x}\text{Cr}_x)\text{N}$ coatings produced by the ion-plating method," *Thin Solid Films*, vol. 385, no. 1-2, pp. 167–173, 2001.
- [11] S. H. Yao and Y. L. Su, "The tribological potential of CrN and Cr(C,N) deposited by multi-arc PVD process," *Wear*, vol. 212, no. 1, pp. 85–94, 1997.
- [12] W. J. Meng and B. A. Gillispie, "Mechanical properties of Ti-containing and W-containing diamond-like carbon coatings," *Journal of Applied Physics*, vol. 84, no. 8, pp. 4314–4321, 1998.
- [13] Y. Pauleau and F. Thiery, "Deposition and characterization of nanostructured metal/carbon composite films," *Surface and Coatings Technology*, vol. 180-181, pp. 313–322, 2004.
- [14] Y. T. Pei, D. Galvan, J. T. M. de Hosson, and A. Cavaleiro, "Nanostructured TiC/a-C coatings for low friction and wear resistant applications," *Surface and Coatings Technology*, vol. 198, no. 1-3, pp. 44–50, 2005.
- [15] Y. T. Pei, D. Galvan, and J. T. M. de Hosson, "Nanostructure and properties of TiC/a-C:H composite coatings," *Acta Materialia*, vol. 53, no. 17, pp. 4505–4521, 2005.
- [16] Z. Lin, F. Wang, D. Gao, D. Ba, and C. Liu, "Frictional and optical properties of diamond-like-carbon coatings on polycarbonate," *Plasma Science and Technology*, vol. 15, no. 7, p. 690, 2013.
- [17] L. Ramqvist, K. Hamrin, G. Johansson, A. Fahlman, and C. Nordling, "Charge transfer in transition metal carbides and related compounds studied by ESCA," *Journal of Physics and Chemistry of Solids*, vol. 30, no. 7, pp. 1835–1847, 1969.
- [18] S. Trusso, C. Vasi, and F. Neri, " CN_x thin films grown by pulsed laser deposition: raman, infrared and X-ray photoelectron spectroscopy study," *Thin Solid Films*, vol. 355-356, pp. 219–222, 1999.
- [19] D. Das, K. H. Chen, S. Chattopadhyay, and L. C. Chen, "Spectroscopic studies of nitrogenated amorphous carbon films prepared by ion beam sputtering," *Journal of Applied Physics*, vol. 91, no. 8, p. 4944, 2002.
- [20] L. Cunha, M. Andritschky, L. Rebouta, and K. Pischow, "Corrosion of CrN and TiAlN coatings in chloride-containing atmospheres," *Surface and Coatings Technology*, vol. 116–119, pp. 1152–1160, 1999.
- [21] Q. G. Zhou, X. D. Bai, X. W. Chen, D. Q. Peng, Y. H. Ling, and D. R. Wang, "Corrosion resistance of duplex and gradient CrN_x coated H13 steel," *Applied Surface Science*, vol. 211, no. 1-4, pp. 293–299, 2003.
- [22] J. Hao, T. Xu, and W. Liu, "Effect of deposition pressure on microstructure and properties of hydrogenated carbon nitride films prepared by DC-RF-PECVD," *Journal of Non-Crystalline Solids*, vol. 351, no. 49–51, pp. 3671–3676, 2005.