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Microstructure and property of diamond-like carbon films with Al and Cr co-doping deposited using a hybrid beams system

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ABSTRACT

DLC films with weak carbide former Al and carbide former Cr co-doping (Al:Cr-DLC) were deposited by a hybrid beams system comprising an anode-layer linear ion beam source (LIS) and high power impulse magnetron sputtering using a gas mixture of C₂H₂ and Ar as the precursor. The doped Al and Cr contents were controlled via adjusting the C₂H₂ fraction in the gas mixture. The composition, microstructure, compressive stress, mechanical properties and tribological behaviors of the Al:Cr-DLC films were researched carefully using X-ray photoelectron spectroscopy, transmission electron microscopy, Raman spectroscopy, stress-tester, nanoindentation and ball-on-plate tribometer as function of the C₂H₂ fraction. The results show that the Al and Cr contents in the films increased continuously as the C₂H₂ fraction decreased. The doped Cr atoms preferred to bond with the carbon while the Al atoms mainly existed in metallic state. Structure modulation with alternate multilayer consisted of Al-poor DLC layer and Al-rich DLC layer was found in the films. Those periodic Al-rich DLC layers can effectively release the residual stress of the films. On the other hand, the formation of the carbide component due to Cr incorporation can help to increase the film hardness. Accordingly, the residual stress of the DLC films can be reduced without sacrificing the film hardness though co-doping Al and Cr atoms. Furthermore, it was found that the periodic Al-rich layer can greatly improve the elastic resilience of the DLC films and thus decreases the film friction coefficient and wear rate significantly. However, the existence of the carbide component would cause abrasive wear and thus deteriorate the wear performance of the films.

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1. Introduction

Metal-containing diamond-like carbon (Me-DLC) films have attracted a great deal of research attention owing to their excellent mechanical, tribological and biological properties [1–3]. Furthermore, comparing to pure DLC films, Me-DLC films exhibit relatively low internal stress and high adhesion strength [4–6]. So far, numerous Me-DLC with doping different metal atoms have been deposited using various techniques. It was reported that the doped metal atoms could create a two-dimensional array of nano-clusters within the DLC matrix or an atomic-scale composite dissolving in the DLC matrix, and the chemical state and existence form of the doped metal atoms would pronouncedly influence the properties of the DLC films [7,8]. For instance, when the weak carbide former atoms, like Al [5] and Ag [6], were incorporated into DLC, they tended to form ductile metal phases without bonding with C. These

soft metallic phases imbedded in the carbon matrix can effectively improved toughness and released internal stress via the plastic deformation. However, the soft and ductile metal phases would also cause the film hardness to decrease. On the other hand, the carbide formers, like Ti [4] and W [9], would bond with C and form hard carbide phase in the carbon matrix when they were doped into the DLC. The hard composite can significantly improve the hardness of the films. Nevertheless, the formation of Me–C bond length would increase the disorder degree of the carbon matrix and thus cause the residual stress to increase. In addition, the increase of the hardness would limit the plasticity and decrease the toughness of the films. It is very difficult to acquire a DLC films with a combination property of high hardness and toughness, and low internal stress via doping one kind of weak carbon former metal atoms or carbide former metal atoms. Nevertheless, the co-doping of carbide former and weak-carbide former metal atoms has been expected to be a good way for improving the DLC films [10,11].

In this paper, DLC films with the co-incorporation of the weak carbide former Al and carbide former Cr (Al:Cr-DLC) were deposited using a hybrid beams source comprising an anode-layer linear

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ion beam source (LIS) and high power impulse magnetron sputtering (HIPIMS) which can significantly increase the ionization rate and energy of the species for the growth films as compared to the DC magnetron sputtering (DCMS) [12]. The composition, microstructure, internal stress, mechanical properties and tribological behaviors of the films were studied as a function of the C_2H_2 fraction which was used to control the Al and Cr contents in the films. The relationships between the microstructure, internal stress, mechanical properties and tribological behaviors were discussed in detail.

2. Experimental details

Silicon (100) wafers of thickness at $525 \pm 15 \mu\text{m}$ were used as the substrates, which were cleaned ultrasonically in acetone, ethanol, and dried in air before being put into the vacuum chamber. The Al:Cr-DLC films were prepared by the hybrid beams system which consists of the LIS and the HIPIMS equipped with a AlCr (Al/Cr = 70/30 at.%) revolving target (purity 99.99%). Prior to deposition, the substrates were sputter-cleaned for 20 min using Ar ions by the LIS at a bias voltage of -300 V . The base pressure was evacuated to the vacuum of $3 \times 10^{-5} \text{ Pa}$. During depositing process, the pressure was kept at about 0.5 Pa , and the substrate holder rotation speed was set at 4 rpm. A gas mixture of C_2H_2 and Ar was introduced into the chamber as the gas precursor. The metal contents of Al and Cr in the films were controlled by varying the C_2H_2 fraction in the precursor gases and the total gas flux (Ar and C_2H_2) was kept at 100 sccm. Typical value of the LIS power was 1 kW (400 V and 2.5 A). For the HIPIMS unit, an average target power of 2 kW was maintained for all experiments. The target peak voltage was kept around 655 V. The pulse repetition frequency was 300 Hz and the pulse width was approximately $100 \mu\text{s}$ (3% duty cycle). A bias voltage of -100 V was applied to the substrate. The whole deposition process-time was 2 h.

The thicknesses of the deposited films were measured by a cross-section SEM (Nova nanoSEM 430, FEI) measuring scale, and the film thicknesses are ranging from $2.5 \mu\text{m}$ to $3 \mu\text{m}$. An X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi) with Al (mono) $K\alpha$ ($h\nu = 1486.6 \text{ eV}$) was used to characterize the chemical composition and chemical bonds of the deposited films. The XPS energy step size was 0.05 eV for the high-resolution spectrums. Before commencing the measurement, Ar^+ ion beam was used to etch the sample surface for 5 min to remove contaminants. The contents of the elements in the films were calculated according to the atomic sensitivity factors and the relative area ratios of the peaks in XPS spectra of the films. And the hydrogen concentration in the films was neglected due to the lack of signal intensity in the current XPS detection measurement. High-resolution transmission electron microscopy of the films was performed on FEI Tecnai G2 F20S-Twin microscope with a 200 kV acceleration voltage. The TEM specimen were prepared by mechanical polishing and precision ion polishing system (Gatan PIPS691). The carbon atomic bond details of the films were characterized using Raman spectroscopy with incident light from a Ar^+ laser at a wavelength of 514.5 nm .

Mechanical properties were measured by the nano-indentation technique with a indentation depth about 1/10th of the film thickness to minimize the substrate contribution. Six replicate indentations were made for each sample. The tribological behaviors of the films was measured using a ball-on-plate tribometer (Center for Tribology UMT-3) at room temperature with the humidity of 50% under dry sliding condition. A steel ball (GCr15, HRC60) with a diameter of 6 mm was used as the friction counter body. All the tests were performed at 20 mm/s sliding velocity for a sliding time of 1200 s and the applied load was 3 N. The length of the wear track was 5 mm and the reciprocating frequency was 2 Hz. After tests,

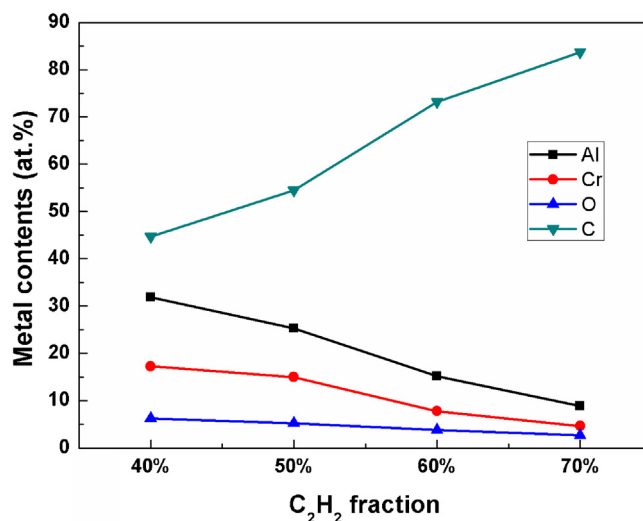


Fig. 1. Al, Cr, C and O contents of Al:Cr-DLC films as a function of the C_2H_2 fraction in the gas mixture.

the wear track profiles were measured by the surface profilometer. And the wear rates were evaluated as volume per sliding distance per load.

3. Results and discussion

The evolution of the Al, Cr, C and O contents in the Al:Cr-DLC films is presented in Fig. 1 as a function of the C_2H_2 fraction. It can be seen that as the C_2H_2 fraction increased, both the Al and Cr contents decreased continuously from 31.8 at.% to 8.9 at.% and from 17.2 at.% to 4.7 at.%, respectively, while the C content increased from 44.7 at.% to 83.7 at.%, indicating that we can control the doped Al and Cr contents of the films via adjusting the C_2H_2 fraction in gas mixture. The ratios of Cr and Al in the films were kept at around 0.54, higher than that in the target (Cr/Al = 30/70 at.%) we used. This phenomenon might be due to the higher sputtering rate of Cr than that of Al. A small amount of oxygen (not higher than 5 at.%) was found in the films. The existence of oxygen can be mainly attributed to the residual oxygen in the chamber due to the relatively high base pressure.

High resolution XPS spectra for the Al2p, Cr2p, and C1s regions of the films are plotted in Fig. 2(a)–(c), respectively. It can be seen that the intensities of the Al2p and Cr2p peaks increased with decreasing C_2H_2 fraction, indicating that the Al and Cr contents increased. The Al2p spectra could be deconvoluted into two peaks: a major peak around 73 eV and a weak peak around 75 eV, corresponding to Al in the metallic state and Al in oxide state, respectively. This result indicates that aluminum did not bond with carbon to form carbide, which can also be illustrated by the C1s spectra. Normally, aluminum carbide has a binding energy at 281.5 eV and aluminum oxycarbide has a binding energy at 282.5 eV [13,14]. However, both of them were not observed in the C1s spectra of the films, as shown in Fig. 2(c). The Cr2p spectra reveal a symmetrical sharp peak centered at $\sim 574 \text{ eV}$, as expected for the $2p_{3/2}$ state of the metallic Cr. A small peak at $\sim 575 \text{ eV}$ deconvoluted from the major peak could be assigned to Cr–O bonds. However, there is no significant difference between the Cr2p peaks in those Al:Cr-DLC films. Previous paper indicated that the Cr2p peak could not be used effectively to differentiate the chemical bonds between metallic Cr and Cr carbide [7]. Nevertheless, the C1s spectrum can be used to determine the existence of the carbide. The C 1s spectra of the films could be fitted with three peaks. The peak at the relatively lower binding energy of about 283 eV could be assigned to Cr–C bonding and the

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