Research Article

Incorporated W Roles on Microstructure and Properties of W-C:H Films by a Hybrid Linear Ion Beam Systems

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W-incorporated diamond-like carbon (W-C:H) films were fabricated by a hybrid beams system consisting of a DC magnetron sputtering and a linear ion source. The W concentration (1.08~31.74 at.%) in the film was controlled by varying the sputtering current. The cross-sectional topography, composition, and microstructure of the W-C:H films were investigated by SEM, XPS, TEM, and Raman spectroscopy. The mechanical and tribological properties of the films as a function of W concentration were evaluated by a stress-tester, nanoindentation, and ball-on-disk tribometer, respectively. The results showed that films mainly exhibited the feature of amorphous carbon when W concentration of the films was less than 4.38 at.%, where the incorporated W atoms would be bonded with C atoms and resulted in the formation of WC_{1-x} nanoparticles. The W-C:H film with 4.38 at.% W concentration showed a minimum value of residual compressive stress, a higher hardness, and better tribological properties. Beyond this W concentration range, both the residual stress and mechanical properties were deteriorated due to the growth of tungsten carbide nanoparticles in the carbon matrix.

1. Introduction

Diamond-like carbon film (DLC) is a metastable form of amorphous carbon with a certain dominant sp^3 bonding. Due to its unique properties such as high hardness, low friction coefficient, good chemical inertness, and the optical transparency in a wide range of VIS-IR, DLC film has been used as protective coatings in many industrial fields [1]. However, high residual stress is the major drawback of DLC films for its wider practical application [2–6]. Immense amounts of concrete research have shown that the incorporation of metal elements, such as Mo, Cu, Al, Cr, and W, is one of the good methods to decrease the internal stress of DLC films [7–12]. As one of the doped metal elements, W-incorporated DLC films (W-C:H) have been received considerable attention both in scientific research and industrial fields of carbon based materials [13–19]. The properties and structure of W-C:H films prepared by the process combining reactive magnetron sputtering with plasma source ion implantation were reported by Baba and coworkers [20]. Takeno et al.

[21] investigated the electrical properties and structure of W-C:H films prepared by radio frequency plasma enhanced chemical vapor deposition, and a resistive superconducting transition was discovered in their report. Wang et al. [22] reported a rapid increase and a gradual decrease in the residual stress of DLC films prepared by end-Hall-type ion gun with increasing W concentration. But considering the characterization complexity of carbon bonds caused by the incorporated W atoms and the easier controlled synthesis with a wide range of W concentration, the new deposition technique of hybrid ion beam system is demanded and the relationship between properties and structure of W-C:H films as a function of W concentration lacked study.

Ion beam sources have been widely used in the field of science and industry such as substrate cleaning, DLC film deposition and surface modification [20, 23–29]. Anode layer type linear ion source (ALIS) is a kind of closed drift type linear ion sources promoted by the plasma acceleration technology of the aerospace thruster [30]. As a large-area surface treatment technique, the ALIS is a gridded ion source

with simple electrode structure, which can provide a higher ion beam current density and readily be scaled to any desired length [30–34].

In this work, a hybrid ion beam deposition system consisting of a DC magnetron sputtering and an ALIS is employed to fabricate the W-C:H films, the used method focused on the W-C:H films with different W concentration, and the films were prepared by a unique hybrid ion beam system. The mechanical properties and structure of the films as a function of W concentration were studied. The results indicated that the DLC films with relatively low stress and high hardness could be achieved by doping a low concentration of W atoms.

2. Experiment

Si (100) wafer of thickness $710 \pm 15 \mu\text{m}$ was used as the substrate material. A thin Si (100) wafer of thickness $250 \pm 5 \mu\text{m}$ was also used as substrate to accurately estimate the internal residual stress. The substrate was cleaned ultrasonically in acetone and dried in air before deposition. The W-C:H film was prepared on Si substrate by a hybrid ion beams deposition system consisting of a DC magnetron rectangular sputtering with a 100 mm (W) $\times$ 400 mm (L) W target (99.95%) and a 380 mm (L) anode layer type linear ion source (ALIS) [35]. The substrates were sputter-cleaned for 20 mins using Ar ions with a pulsed bias voltage of -100 V . The base pressure was evacuated to a vacuum of about $2 \times 10^{-5} \text{ Torr}$. During film deposition process, hydrocarbon gas (C_2H_2) was introduced into the linear ion source to obtain the hydrocarbon ions for DLC deposition. The Ar sputtering gas was supplied to the magnetron sputter for W sputtering. The concentration of tungsten in the films was controlled by varying the sputtering current from 0.9 to 1.5 A. The C_2H_2 flux and Ar flux were kept at 10 and 70 sccm, respectively, and the work pressure was kept at about $4.0 \times 10^{-3} \text{ Torr}$. Typical values of ALIS voltage and current were 1300 V and 0.2 A, respectively. A negative pulsed bias voltage of -100 V (350 KHz, $1.1 \mu\text{s}$) was applied to the substrate. The deposition time was 40 mins. For comparison, the pure DLC film was also prepared using ALIS and a negative substrate bias of -100 V .

The thickness of the deposited films was measured by surface profilometer (Alpha-Step IQ, USA). The cross-morphology of the deposited films was observed by a cross-section SEM (Hitachi S-4800). An X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250) with monochromated Al X-ray resource was used to characterize the chemical composition, atomic bonds, and microstructure of the films. High-resolution transmission electron microscopy (TEM, Tecnai F20), operated at 200 KeV with a point-to-point resolution of 0.24 nm, was used to clarify the microstructure. Raman spectroscopy (Renishaw inVia-reflex) equipped with a He-Ne laser of 532 nm exciting wavelength was used to measure the atomic bonds of the films at a detecting range from 600 to 2000 cm^{-1} .

The internal residual stress of the films was calculated using the Stoney equation, and the curvature of film/substrate composite was determined by a laser tester. Mechanical

properties were measured using the nanoindenter (MTS-G200) with the depth to 200 nm, and the hardness was chosen in a depth of around 1/10 of the coating thickness in order to avoid the contribution of Si substrate to the results. The tribological behaviors of the Si coated by the films were measured on a rotary ball-on-disk tribometer at room temperature with a relative humidity of about 50% under dry sliding conditions. All the tests were performed at 0.12 ms^{-1} sliding speed for a distance of 400 m and the applied load was 5 N.

3. Results and Discussion

Figures 1(a) and 1(b) showed the change of W concentration and average growth rate of the films as a function of the sputtering current, respectively. The W/C atomic ratio of the films was determined based on the atomic sensitivity factors and area ratio of the C 1s to W 4f peaks in XPS spectra of the films. The W concentration of the films increased from 1.08 to 31.74 at.% as the sputtering current increased from 0.9 to 1.5 A, as shown in Figure 1(a), while the growth rate of films decreased slightly from about 17 to 15 nm/min, as seen in Figure 1(b), which may be induced by antisputtering effect of W atoms with higher kinetic energy at 1.5 A sputtering current [36]. Noted that, less than the sputtering current of 0.9 A, it was difficult to extract the accurate amount of W concentration from the XPS spectra because of the serious W target pollution by the ionized carbon precursors. Beyond the case of 1.5 A, the deposited films showed a typical W metallic luster.

Figure 2 showed the cross-sectional SEM images of the films with different W concentrations. And the films in Figure 2 were marked by double-headed arrows. The images demonstrated similar smooth surface when W concentration was less than 4.38 at.% and exhibited the feature of the amorphous structure, which suggested that W-C:H films with W concentration less than 4.38 at.% kept amorphous features. However, when the W concentration increased to 31.74 at.%, the film became rough with emergence of nanoscale particulates in the carbon matrix, as illustrated in Figure 2(d), due to the formation of tungsten carbide phase.

XPS provided the approach to analyze the chemical bonds of the deposited films by C 1s. Figure 3(a) displayed the XPS C 1s peaks of the pure DLC film and W-C:H films with different W concentrations. When the W concentration was less than 4.38 at.%, the C 1s spectra were divided into two peaks around 284.6 eV and 286.5 eV corresponding to the typical C-C/C-H and C-O/C=O binding energy, respectively [20, 37–39]. However, when the W concentration increased to 31.74 at.%, a shoulder peak with a lower binding energy of about 283.5 eV appeared, as shown in Figure 3(b). The peak at 283.1–283.6 eV is generally assigned to the W-C bonds [18, 20, 40], so it can be deduced that the tungsten carbide was formed in the films with a higher W concentration.

Figure 4 displayed the plan-view high-resolution TEM images and the corresponding SAED patterns of the pure DLC film and W-C:H films. Similar to the result of pure DLC, Figure 4(b) presented dense and smooth granular contrasts,

FIGURE 1: W concentration (a), growth rate and thickness (b) of the films as a function of sputtering current.

FIGURE 2: Cross-sectional SEM images of the pure DLC film (a); films with 1.08 at.% W (b), 4.38 at.% W (c), and 31.74 at.% W (d).

and the corresponding SAED patterns showed a broad and diffuse diffraction halo. It implied that the deposited films essentially formed a typical amorphous structure, and the W atoms were uniformly distributed and dissolved in the DLC matrix. But for the W-C:H film with 4.38 at.% W atoms (Figure 4(c)), a few nanoparticles with grain diameter about 5 nm were found in the film, and

more nanoparticles with similar grain diameter could be observed obviously in W-C:H film with 31.74 at.% W atoms (Figure 4(d)); the corresponding diffraction ring of SAED pattern in Figure 4(d) became much sharper than that in Figure 4(c), suggesting more carbide particles of high crystallinity existed in these films. Figure 4(d) revealed the clear lattice fringes of the nanoparticles

FIGURE 3: Typical C 1s high-resolution XPS spectra of the films with different W concentration (a), XPS spectra of the films with 31.74 at.% W (b).

FIGURE 4: Plan-view high-resolution TEM images and corresponding SAED pattern of the pure DLC film (a); films with 1.08 at.% W (b), 4.38 at.% W (c), and 31.74 at.% W (d).

FIGURE 5: Typical Raman spectrum (a) and G FWHM and position (b), I_D/I_G (c) of films with different W concentration.

(marked red circles) uniformly embedded in the DLC matrix, the sharp crystalline diffraction rings observed in Figure 4(d) indicated the existence of polycrystalline phases, which were identified to be the (111), (200), (220), (222), and (420) reflections of the cubic (FCC) WC_{1-x} structure. The TEM results indicated that the dissolved W atoms began to form WC_{1-x} phase in the DLC matrix when W concentration of the films was in the range of 1.08–4.38 at.%, and the films with higher W concentration were nanocomposite of WC_{1-x} particles embedded in the DLC matrix.

Raman is usually employed to characterize the atomic bonds of carbon films. Figure 5(a) displayed the Raman spectra of the W-C:H films at various W concentrations. Obviously, all samples presented a broad asymmetric Raman scattering band in the range of 1000–1700 cm^{-1} , which was essentially as the typical carbon bond feature in hydrogenated amorphous carbons films. Raman spectroscopy can be generally deconvoluted into two peaks: one named G-peak at

1580 cm^{-1} arising from E_{2g} symmetry stretching vibration mode caused by the sp^2 atom and the other named shoulder D-peak at around 1360 cm^{-1} caused by the zone edge of A_{1g} breathing mode [1]. The experimental spectrum was fitted using two Gaussian peaks after background correction. According to the fitted G-peak position, the intensity ratio of D-peak to G-peak (I_D/I_G), and the full width half maximum (FWHM) of the G-peak, the bonding structure of DLC films such as bond disorder, sp^2/sp^3 ratio can be derived qualitatively [41–43]. Figure 5(b) showed that when W concentration increased from 1.08 to 31.74 at.%, the G peak position shifted monotonically from 1544.6 cm^{-1} to 1554.9 cm^{-1} and the I_D/I_G ratio also increased from 1.32 to 1.57 as in Figure 5(c), implying a higher sp^2/sp^3 ratio in the W-C:H films with higher W concentration; however, the G-peak FWHM decreased from 175 cm^{-1} to 155 cm^{-1} ; it revealed that the degree of film structural disorder declined. But in comparison with the W-C:H films, the pure DLC film

FIGURE 6: Residual compressive stress as a function of W concentration.

FIGURE 7: The hardness and elastic modulus as a function of the W concentration.

exhibited a higher sp^2/sp^3 ratio and less structural disorder, which may be due to the change of plasma caused by the collision between the W atoms with high energy and the carbon atoms; other researchers also discovered structure evolution due to influence of ion energy [44–46].

Figure 6 showed that the residual compressive stress in the pure DLC films was about 1.7 GPa and arrived at 2.06 GPa in W-C:H film with 31.74 at.% W concentration; a minimum value about 1.485 GPa was obtained when the W concentration was 4.38 at.%, indicating that the residual compressive stress in the DLC films could be reduced in a proper range of W concentration. The decline of the film residual compressive stress could be explained by two stages. Firstly, at the lower W doping level, part of the W atoms was distributed in the DLC matrix without bonding with carbon atom, which provides the pivot location for the bond distortion and reduced the film compressive stress [9, 22]. Moreover, the other few W atoms formed the nanocrystallites and embedded in the carbon matrix, which could also relax

FIGURE 8: Friction coefficient (a) and average friction coefficient (b) in stable test condition of the films various W concentrations.

the stress by the diffusion and sliding of the grain boundary [11]. Since the W-C bond length was longer than that of the C-C bond; however, with further increasing the W concentration, more formation of W-C bond would induce the severe distortion of the atomic bond angles, which in turn increased the internal stress [9]. The present results agreed well with those reported by the others' work [17, 47].

Figure 7 depicted the hardness and elastic modulus as a function of the W concentration. It could be observed that, with more W atoms in the films, the hardness and elastic modulus of the films decreased from 18.5 GPa to 14.1 GPa and from 179.4 GPa to 161.5 GPa, respectively. Generally, the mechanical properties of DLC films mainly depend on the sp^3 carbon matrix [1], but the incorporation of W atoms and formation of nanoparticles in the DLC would break up the continuity of the carbon network, which would cause the decline of the hardness and elastic modulus. The similar phenomenon was also found in Cr-C:H and Ti-C:H films [48, 49].

The friction coefficient of the films with sliding distance evolution and coefficient in stable test condition were shown in Figure 8. It indicated that W-C:H films with W atoms less than 4.38 at.% had a lower friction coefficient compared with the pure DLC in the stable test condition. But when more W atoms were in the film, the friction coefficient of the film became larger than 0.3, exhibiting the feature of tungsten carbide in the DLC matrix. Similar to the Cr element as a strong carbide former candidate doped in DLC films, other phenomena were also discovered in Cr-C:H films with different Cr concentration [50], which could be attributed to the formed hard WC_{1-x} phase in the DLC matrix [24]. The tribological property related with the microstructure influenced by W concentration was in accord with the results analyzed by XPS, SEM, and TEM.

4. Conclusions

The W-C:H films were prepared by a DC reactive magnetron sputtering with W target (99.99%) in the Ar and C_2H_2 gas mixture. The concentration of tungsten in the films was varied from 1.08 at.% to 31.74 at.% by changing the sputtering current. The films mainly exhibited the feature of amorphous carbon when W concentration of the films was less than 4.38 at.%. The solubility of the W atoms in the DLC films was in the range of 1.08~4.38 at.%. W atoms would bond with C atoms, resulting in the formation of WC_{1-x} nanoparticles with the W concentration exceeding the solubility. The films with 4.38 at.% W concentration showed a minimum value residual compressive stress, a higher hardness value, and better tribological properties.

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