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Diamond & Related Materials 14 (2005) 1489 – 1493
DIAMOND AND RELATED MATERIALS
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Thermal stability of metal-doped diamond-like carbon fabricated by dual plasma deposition

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Received in revised form 11 March 2005; accepted 13 March 2005
Available online 12 May 2005

Abstract

Metal incorporation into amorphous diamond-like carbon films can provide superior properties as metal nano-clusters or nanocrystalline metallic carbides can be embedded in the carbon network. In this work, a filtered metal plasma cathodic arc technique is used to generate a metal plasma and acetylene is introduced to the metal plasma plume to deposit metal-containing DLC (Me-DLC) films and form nanocrystalline carbide phases in the amorphous carbon matrix. The films exhibit high thermal stability up to annealing temperatures of 500 °C as revealed by X-ray diffraction, transmission electron microscopy, and Raman spectroscopy. At treatment temperature over 500 °C, a large amount of hydrogen is lost from the Me-DLC films as shown by elastic recoil detection. Breakdown and structural collapse of the film at high temperature can be attributed to the breaking of C–H bonds. Consequently, the C–C networks become more graphite-like to facilitate the formation of volatile C–O and metal oxides phases.
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PACS: 81.05.Uw; 68.60.Dv; 68.55Jk; 52.77.Dq
Keywords: Diamond-like carbon; Metal doping; Thermal stability; Cathodic arc; Plasma deposition

1. Introduction

Diamond-like-carbon (DLC) which is a metastable form of amorphous carbon containing hybrid structures of sp^2 and sp^3 bonds has found many applications in biomedical engineering, protective coatings for magnetic storage disks, MEMS, cutting tools, anti-reflective coatings for IR windows, and field emission source for emitters due to its unique properties of high hardness, low friction, chemical inertness, and optical transparency, small electron affinity. However, there is a significant disadvantage of DLC film with regard to its low thermal stability especially at higher working temperature. Much research has been devoted to the study of the thermal stability of DLC as well as to correlate the materials' properties with changes in the hybrid structure of sp^2 and sp^3 bonds [1–3]. Much attention has also been paid to incorporate impurities into DLC films to enhance their properties and applications. For instance, nitrogen and phosphorus doped DLC have been shown to mitigate blood coagulation and cellular damage [4,5]. Other examples include fluorine, silicon and oxygen, metals, as well as transition metals introduction into DLC films to modify the internal stress, surface energy, friction coefficients [6], hardness and optical properties [7], as well as electrical conductivity [8,9]. It has been shown that DLC films comprising amorphous nanocomposites (silicon doping) can enhance the thermal properties [10,11] and Yang et al. [12] have observed a decrease in the film thickness of Si-doped DLC film upon high temperature annealing. Metal doping of DLC can create a two dimensional array of nanocrystalline metal clusters and metallic carbides within the amorphous carbon matrix. However, their thermal properties have not been extensively studied.

In this work, transition metals were added into DLC films using a filtered metal cathodic arc vacuum discharge technique in concert with the introduction of acetylene to

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doi:10.1016/j.diamond.2005.03.006

the metal plasma plume [13]. Fine metal carbide grains are found to be embedded inside the amorphous carbon cross-linked structures as revealed by Rutherford backscattering spectrometry (RBS), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), and laser Raman scattering. The thermal properties of the metal-doped DLC (Me-DLC) were investigated by subjecting the films to a series of annealing conditions (temperature) and compared to those measured from DLC films fabricated by conventional radio-frequency (RF) plasma-enhanced chemical vapor deposition (PECVD).

2. Experimental

The metal-doped DLC films were prepared on Si (100) substrate and the deposition setup and instrumental configuration have been reported elsewhere [14–16]. The base pressure was about 1×10^{-5} Torr and the samples were cleaned using RF argon plasma for 10 min at a bias of -1000 V. The metal plasma (molybdenum cathode for Mo plasma and tungsten cathode for W plasma) was generated in the metal vacuum arc plasma source using a pulse duration of about 300 μs, main arc current of 100 A, and repetition rate of 60 Hz. At the same time, acetylene gas was bled into the metal plasma plume to form a dual plasma. The plasma then diffused into the vacuum chamber through a 90° curved duct biased to +20 V in the presence of an external magnetic field that enhanced the plasma transport efficiency while removing macro-particles from the metal plasma. The plasma eventually impacted the samples which were held at about 15 cm from the exit of the curved duct. The metal cathodic arc source produces almost fully ionized metal plasmas. Theoretical and experimental investigations have been conducted to improve the metal arc ignition, plasma focusing, plasma transportation, as well as the output efficacy [17–19]. In this work, acetylene gas was bled into the vicinity of the metal plasma plume to generate the dual plasma consisting of both species. Due to electron oscillations in the duct [19], there was increased collision probability and carbon discharge efficiency along the duct when the dual plasma is transported by the electro-magnetic field formed around the biased duct. The thin films were synthesized using C_2H_2 flow rates of 5, 10 and 15 sccm and sample biases of -200 and -500 V.

Another set of samples was prepared using RF glow discharge of acetylene plasma using similar deposition parameters but without the metal cathodic arc. Several

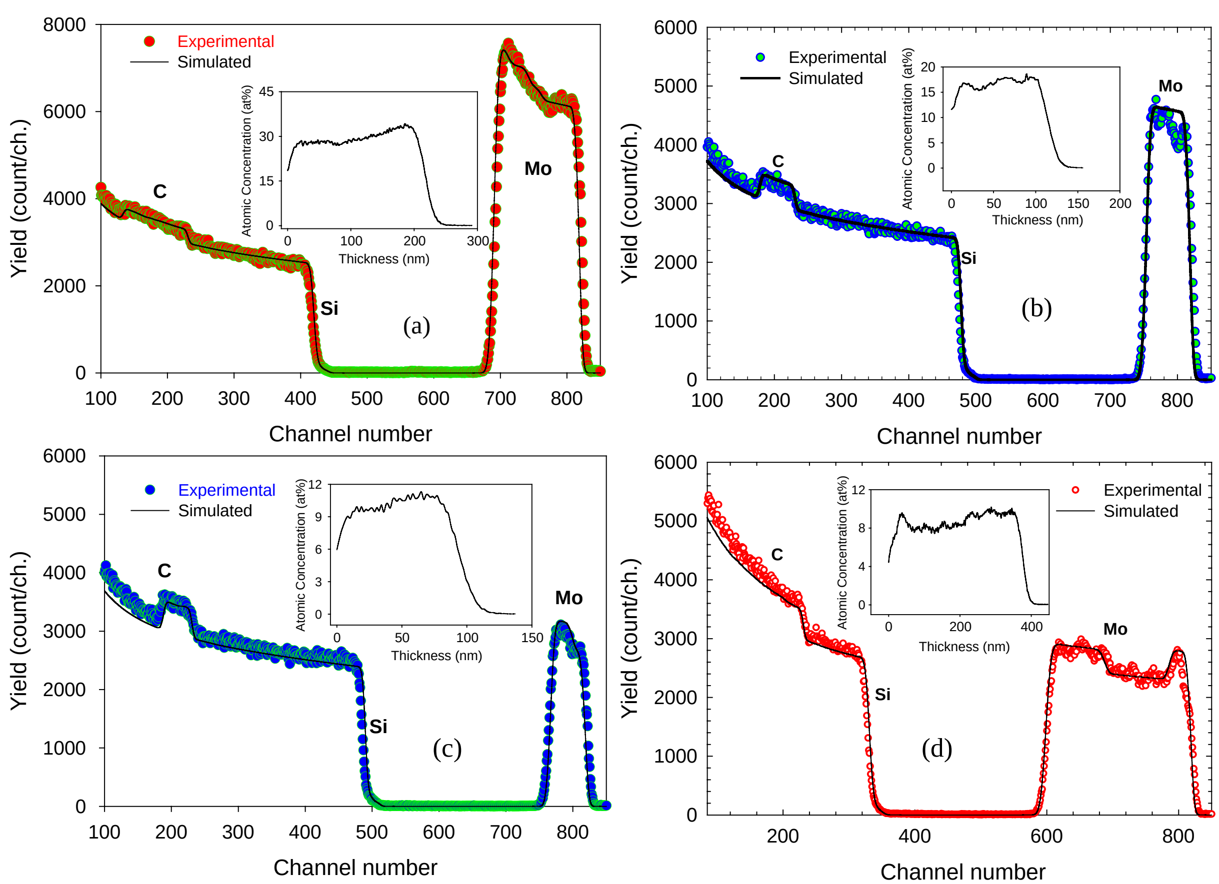

Fig. 1. RBS spectra of Mo-doped DLC with insets showing the in-depth atomic concentrations of the metal derived from the spectra: (a) -500 V substrate bias and 5 sccm C_2H_2 flow rate, (b) -200 V substrate bias and 5 sccm C_2H_2 flow rate, (c) -200 V substrate bias and 10 sccm C_2H_2 flow rate, and (d) -200 V substrate bias and 15 sccm C_2H_2 flow rate.

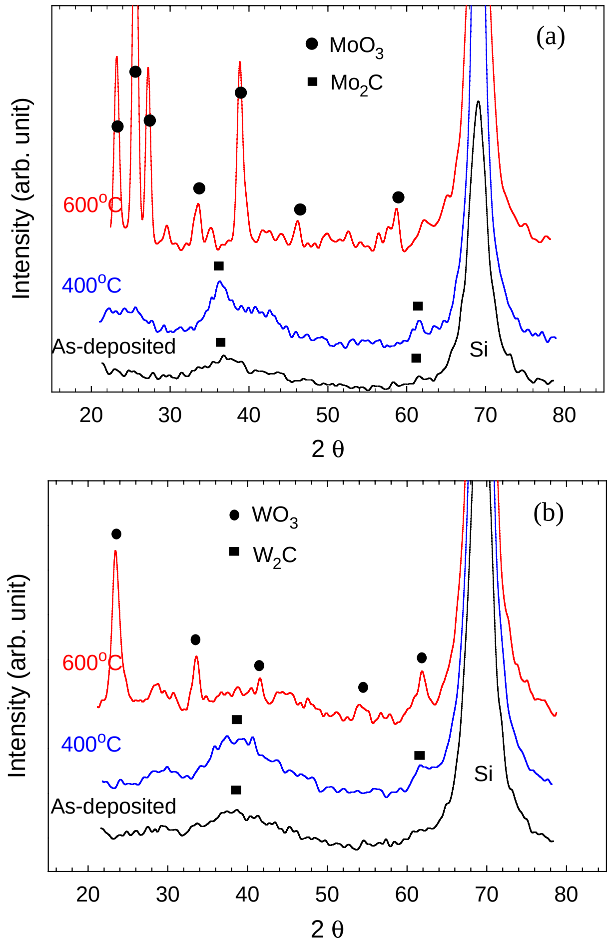

Fig. 2. XRD spectrum of metal-containing DLC after different temperature annealing: (a) Mo-doped and (b)W-doped.

analytical techniques were adopted to examine the microstructures and properties of the thin films. RBS using a 2 MeV $^4He^{++}$ beam and a backscattering angle of 170° and the simulation program SIMNRA version 5.0 were used to determine the composition while XRD using a Siemens D500/501 thin film diffractometer with a CuKα source and HR-TEM using JEOL-200CX were used to evaluate the film structures. In order to study the thermal properties of the films, the samples were subjected to a series of annealing conditions (temperature) in argon. The samples were further analyzed using argon laser Raman scattering excited by an Ar laser at 514.5 nm using a Jobin Yvon T64000 system and elastic recoil detection (ERD).

3. Results and discussion

Fig. 1 shows the RBS spectra of the molybdenum-containing DLC films prepared on silicon substrate prepared under different substrate biases and C_2H_2 flow rates. One can note that the metal in-depth distribution is relatively uniform as illustrated in the insets of Fig. 1. When the bias voltage is increased, both the metal concentration and amorphous carbon film thickness increase due to the higher formation and incorporation rate relative to sputtering loss. Our results also show that a higher C_2H_2 flow rate leads to more particle collisions between metal and C_2H_2 as well as species of C_2H_2 and denser C_2H_2 plasma, and as a result, there is a smaller metal content in the deposited films.

The microstructure of the as-deposited and annealed DLC films doped with molybdenum and tungsten was evaluated using XRD and the results are shown in Fig. 2. The broad diffraction peak at around 38° is attributed to the small grain size of metallic carbides or carbide clusters embedded in the DLC film. When the film undergoes annealing, the diffraction peak becomes sharper suggesting that the carbide clusters agglomerate to larger clusters. On the other hand, the carbide signals disappear and only the metal oxide signals can be detected by XRD when it is annealed at 600 °C. It is believed that oxygen in the ambient reacts with the carbon atoms and metal to form oxides. Carbon oxides are volatile and only the metal oxides remain on the surface.

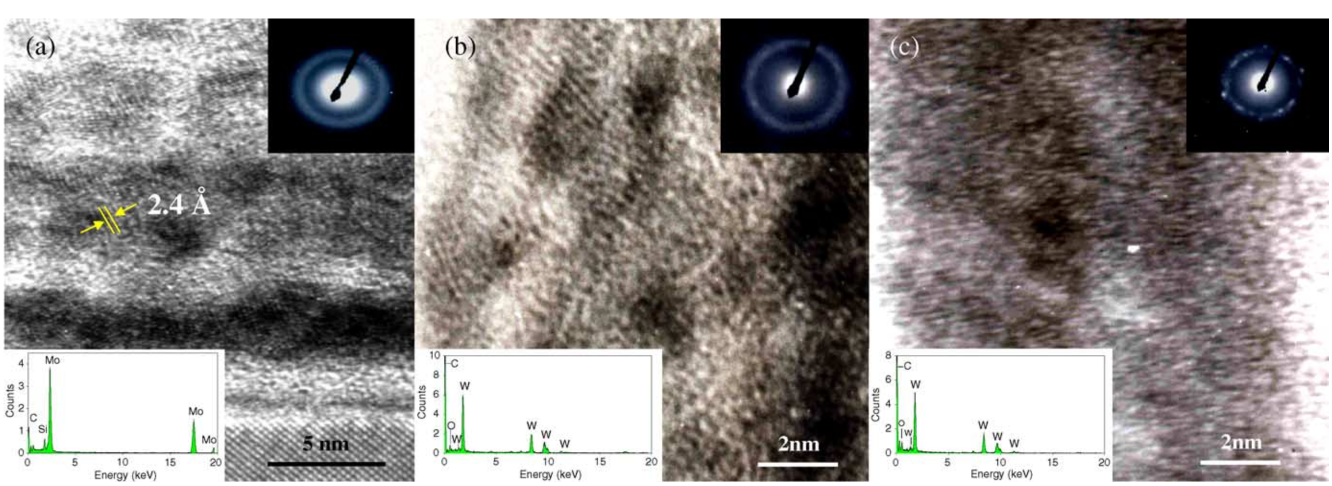

Fig. 3. HR-TEM micrographs of metal-containing DLC with the insets showing the SAD patterns and EDS spectrum: (a) As-deposited Mo-DLC, (b) As-deposited W-DLC, and (c) 400 °C annealed W-containing DLC.

The formation of nanocrystalline carbides in the amorphous carbon matrix is observed in our HR-TEM micrographs and the insets displaying the selected-area diffraction (SAD) pattern and energy dispersive X-ray spectrometry (EDS) spectrum are depicted in Fig. 3. For the Mo-doped sample, the EDS and SAD results show the existence of elemental molybdenum and a polycrystalline pattern in the film, respectively. The arrows in Fig. 3a indicate that a spacing of 0.24 nm for the molybdenum carbide structure. The carbide structure exhibits irregular grains which are dispersed and enclosed by amorphous carbon phases. For the W-doped samples, larger grains can be observed after the sample has been annealed at 400 °C and the results are consistent with the narrowing of the diffraction peaks in the XRD spectra.

The pure DLC films (prepared by RF glow discharge deposition) and metal-containing DLC films (fabricated by metal cathodic arc deposition with acetylene introduction) were examined using laser Raman scattering to further compare their structures and properties after annealing. Raman scattering is a useful technique to determine the structures and chemical bonding of disordered carbon. DLC films consist of a hybrid structure of sp^2 and sp^3 showing a D band (disorder) and G band (graphite) at around 1350 and 1580 cm^{-1}, respectively, in the Raman spectrum [20]. Changes in the structures or chemical states of the DLC result in shifts in the G band and the ratio of the intensity of the D band I_D to that of G band I_G. Fig. 4 summarizes the results of the G peak shift and the ratios of I_D to I_G calculated from the pure DLC and metal-containing DLC samples annealed at different temperatures. Shifting of the G-peak position shifts to higher wave numbers and increase of the I_D/I_G ratio with increasing annealing temperature indicate increasing size and number of the graphitic sp^2 clusters. The pure DLC film does not show the carbon signal in the Raman spectrum after annealing at over 400 °C but on the other hand, the Me-DLC films still show the carbon signal after annealing up to 500 °C. The Mo-doped DLC exhibits a stable value of I_D/I_G ratio throughout a wide range of annealing temperatures. It can be deduced that the pure DLC film gradually graphitizes and oxidizes at high temperature. Tallant et al. [2] have found that in pure DLC films, sp^3 begins to convert to sp^2 at around 200–300 °C and completely at around 450 °C, and our results are similar. A relative constant ratio of I_D/I_G observed from the metal-containing DLC films indicate a slower rate of graphitization and higher thermal stability.

Heating of hydrogenated DLC films may result in the loss of hydrogen and CH_x species. A previous study on ion beam irradiation of DLC films showed the breaking of C–C and C–H bonds and oxidation of the film via the formation of C–O bonds [21]. Irradiation of nitrogen-doped DLC films resulted in a decrease in the C–H bonds and an increase in the C–C and C–N bonds in the absence of

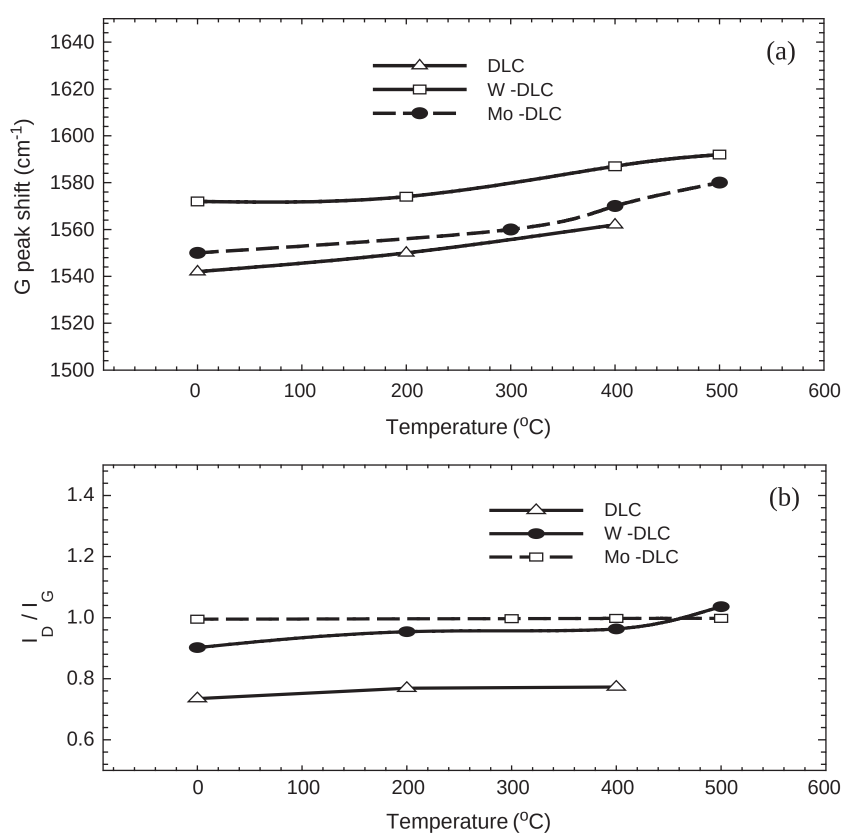

Fig. 4. Variation of the G peak shift and the ratio of I_D/I_G calculated from pure DLC and Me-DLC as a function of annealing temperature.

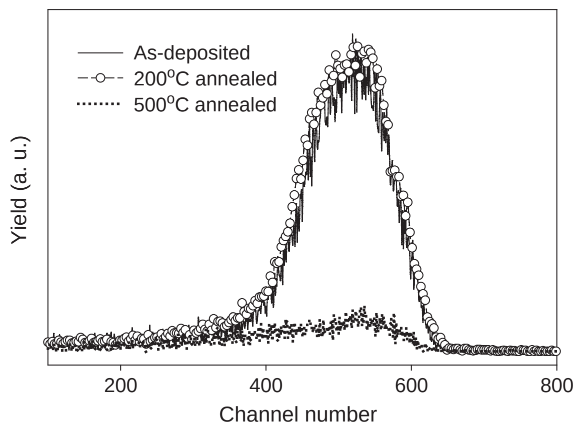

Fig. 5. Relative hydrogen contents in W-DLC for different annealing temperatures.

materials loss. Fig. 5 displays the relative hydrogen content in the W-doped DLC after different temperature annealing as determined by ERD. There is very little hydrogen loss from the film if the annealing temperature is below 200 °C. However, a significant amount of hydrogen leaves the film when the anneal temperature is around 500 °C. Thus, the thermal instability of the DLC film can be associated with the loss of hydrogen that causes a collapse in the carbon matrix. The modified DLC films can withstand a higher temperature due to the formation of new bonds. Our XRD and TEM results provide the clue that the carbide phases are relatively thermally stable and continue to coalesce into larger grains at below 500 °C. The Raman scattering results of our samples show that thermal activation can induce the changes of the DLC structures and cause full relaxation of the pure DLC films at above 400 °C. The metals incorporated into the carbon matrix to some extent not only can reduce and retard the relaxation rate of the film under thermal activation but also can tolerate higher annealing temperature without serious graphitization and structural collapse.

4. Conclusion

A metal cathodic arc was ignited in the presence of acetylene to generate dual plasma to prepare metal containing DLC films. The metal content and film thickness can be controlled by varying the process windows. XRD and TEM results indicate that nano-cluster metallic carbides are embedded in the carbon networks. In addition, the metal-containing DLC films exhibit a higher thermal stability when compared to pure DLC films and the incorporated metals retard the loss of hydrogen and relaxation rate of the carbon networks under annealing.

Acknowledgements

The authors acknowledge Prof. S. P. Wong and Dr. W. Y. Cheung for RBS measurements and Mrs. M. L. Ruan for HR-TEM analysis. The work was supported by Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grant (CERG) #CityU 1120/04E.

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