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The effect of annealing temperature on the structure of diamond-like carbon films by electrodeposition technique

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Diamond-like films have been prepared by electrodeposition in liquid phase. The films consist of a little amount of hydrogen, which can be removed by annealing at below 600 °C. The Raman signal of annealing films suggested: (1) the intensity ratio I_D/I_G increases which suggested that the crystallites grew in number and size with increasing temperature; (2) the D-line position changes from 1380 to 1346 cm^{-1}, and the G-line position from 1580 to 1604 cm^{-1} which indicated that partially tetrahedral bonds have been broken and have transformed to trigonal bonds, (3) the linewidths of the D and G-line decrease with the increasing annealing temperature. These results indicated that the primary bonding in the films changed gradually from sp^3-bonded to sp^2-bonded carbon with increasing annealing temperature, i.e., graphitization.

1. Introduction

Diamond-like carbon (DLC) films, used as a low-cost substitute for diamond, have attracted more and more attention for past decade. The chemical-vapor-deposition techniques need high deposition temperature that limited the application of the films. It has been desire target that DLC films can be deposited under low temperature and atmosphere. The liquid phase deposition techniques meet the need and have been applied for preparation of DLC films and relative carbon material following the attempting of Namba *et al.* [1–5]. Only Wang *et al.* [6] concluded that they obtained DLC films in methanol solution. However, up to now the thermal stability of the carbon films by liquid phase deposition have not reported. The thermal stability not only determines the films' application fields but also help understand the microstructure and properties of the films.

Some works on the annealing of amorphous carbon films has been reported. Nadler *et al.* [7] heated carbon films in vacuum and found the loss of hydrogen began at 500 °C and continued to temperature over 700 °C. With the increasing of substrates temperature from 30 to 200 to 450 °C, the carbon films' structure becomes nanocrystalline graphite-like ("glassy" carbon) phase [8]. Wu *et al.* [9] found no detectable loss of hydrogen when DLC films were rapidly annealed until 500 °C, whose Raman spectra similar to those of as-deposited films. No Raman signal was observed for annealing carbon films up to 400 °C except for the intensity photoluminescence [10]; further heating up to 500 °C, the signal of graphitic-like phase appeared at 1365 and 1605 cm^{-1}. Qing Zhang *et al.* [11] investigated the thermal stability of *a*-C:H films deposited by ECR-CVD method. They suggested that successive annealing cause the film transform from polymeric-like to graphitic-like structure. The transformation for the films annealed in O_2 gas occurs at lower temperatures (below 610 k) than for the films in vacuum (at least up to 670 k). These results indicated that the structural change of amorphous carbon films corresponds not only to the deposition condition but also to the annealing atmosphere.

In this letter the DLC films have been deposited on silicon substrates in methanol solution with electrodeposition method reported in literature [12]. Fourier transform infrared (FTIR) spectrophotometer and Micro-Raman spectroscopy have been used for characterizing the effects of annealing on microstructure and properties of DLC films at different temperatures.

2. Experiment

The experimental setup has been described earlier [12]. Analytical pure methanol was used as electroplating solution. A silicon sheet with a size of $25 \times 25 \times 1$ mm^3 was mounted on the negative electrode. Before deposition the substrates were cleaned by ultrasonic treatment in ethanol. The distance between the substrate and positive electrode (graphite) was 4 mm. The samples were deposited at room temperature at 50% duty cycle and 7 kHz with a pulse modulation source.

The sample was divided to several rectangles which subjected to heat treatment at a required temperature for 120 min (Ar gas flow, about 1 Torr) and then cooled down to room temperature. After each heating cycle the samples were characterized by Raman spectroscopy for the microstructure.

The Raman measurements were carried out by a Renishaw-1000 type confocal Raman spectrometer. The 514.5 nm line of an argon ion laser was focused to spots of about 1–2 μm in diameter, and the laser power is 5 mW on the samples. The instrument slit width is 25 μm. Monocrystalline silicon was used for calibration of the spectra. Commercial non-linear curve fitting software was used to deconvolute the curves. A Perkin-Elmer (L-710) Fourier transform infrared (FTIR) spectrophotometer was used to study the C—H stretching vibration of the samples. Transmission electron diffraction (TED) techniques were used to characterize the change of structure of film. The electric resistivity was measured by four-point probe meter.

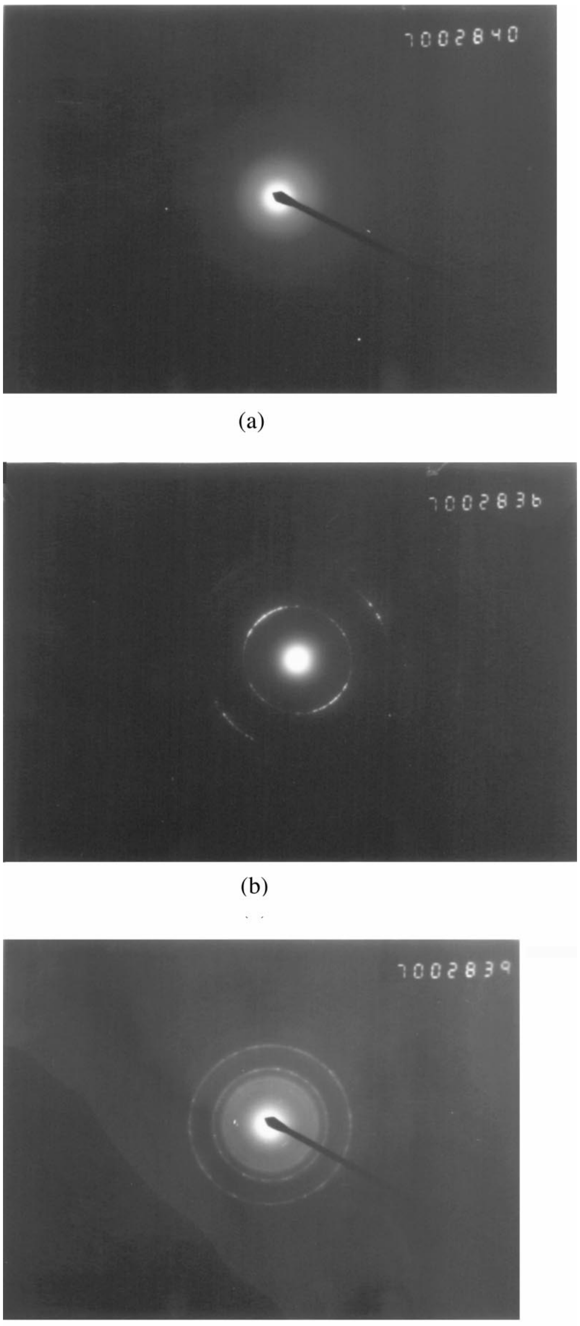
3. Results and discussion

The as-deposited films with pale color are transparent to infrared, and have high adhesive on Si substrates. The range of electric resistivity of samples is 10^7–10^8 Ω cm. Vicker's hardness (DLC/Si) is more than 1500. In addition, the films have good chemical inertness in various corrosive chemicals, such as strong acid, strong base and aromatic reagent.

3.1. TED and resistivity results

The films are grounded in a copper grid for viewing with transmission electron diffraction by etching Si substrates in HF: HNO_3 (1:9) solution. Fig. 1 illustrates the typical diffraction pattern of as-deposited and annealing films. Evidently the as-deposited film has a mainly amorphous phase with a diffuse halo (Fig. 1a), which agreed with the results of DLC films by CVD method. There is a drastic change in films annealed at 400 °C (Fig. 1b). Weak diffraction rings are seen by TED, corresponding interplane spacing distance of 0.206 and 0.120 nm. The values are very close to the spacing $d = 0.206$ and 0.126 nm of (111) and (220) crystalline graphite reflections, respectively. The other d values were not reliable due to the very weak signal.

Thermal stability of DLC films deposited by CVD showed that DLC could convert to nano-crystalline graphite at above 400 °C [10, 13] with high conductive ability. However, our films kept the same high resistivity (more than 10^7 Ω cm) at 500 °C, then the resistivity slightly decreased to 10^6 Ω cm at 600 °C. We inferred that the film is a mixture of amorphous carbon and very thin graphite particles. The crystallization degrees increased at 950 °C with clear and intensive diffraction rings by TED (Fig. 1c), which corresponded to structure of graphite-like. At the temperature, the resistivity of films sudden decreased to about 10^4–10^5 Ω cm. It indicated that the intensive graphitization has occurred at the annealing temperature.



(a)

(b)

(c)

Figure 1 The diffraction pattern of films: as-deposited (a), 400 °C (b) and 950 °C (c).

3.2. IR spectra

It is well known that the stretching (and the bending) C—H vibrations is rather sensitive to their environment, since IR absorption spectroscopy was particularly well suited as a probe of the different C—H configuration. The IR absorption spectra relating to C—H bond stretching vibration at the region of 2800–3100 cm^{-1} was presented in Fig. 2. There were three obvious bands could be observed in as-deposited films (Fig. 2a). The intensive bands at 2857 and 2923 cm^{-1} corresponded to the stretching vibration of $C(sp^3)$-H_3 group. Another weak band at 2962 cm^{-1} can be assigned to the stretching vibration of $C(sp^3)$-H_2 group. However, the aromatic character corresponding to sp^2-CH stretching vibration around 2966–3050 cm^{-1} was very weak [13–15]. The analysis showed that hydrogen bond mainly to sp^3 C—H in as-deposited films. Using the average value of 1.3×10^{21} cm^{-2} for the inverse cross section

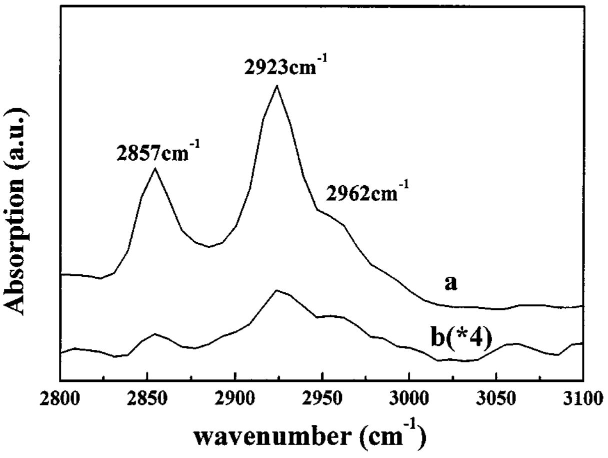


Figure 2 The IR spectra of as-deposited film (a) and annealing at 400 °C (b).

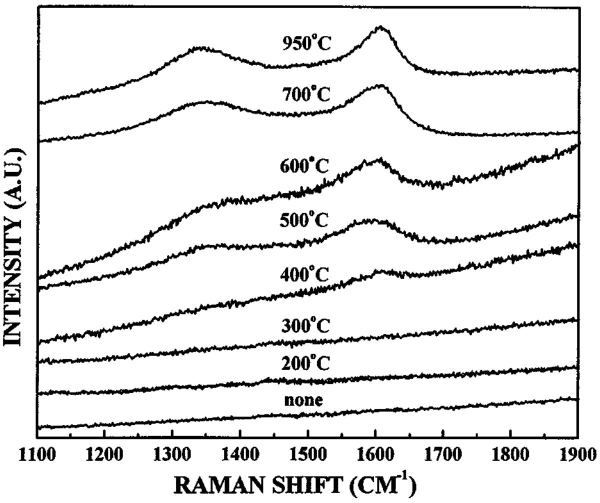


Figure 3 The Raman spectra of films with different annealing temperature.

of the C—H mode [16], the concentration of hydrogen bonded to carbon is estimated to be about 20 at % from the integrated areas of C—H stretching modes.

Annealing causes a significant change in the intensity of C—H stretching bands which practically reduced to nearly disappear at 400 °C (Fig. 2b). The spectrum has been amplified for four times. The intensity sharply decreased. A new band appeared at 3055 cm^{-1}. The showed that a large content of hydrogen had been removed and the sp^2-CH stretch vibration increased at annealing 400 °C. The instrument can not detect the C—H bands above 600 °C.

It is known that the heat treatment of amorphous carbon films leads to the evolution of hydrogen and causes a structural change. Bonded hydrogen is released generally at the temperature range from 400 to 600 °C, then the tetrahedral sp^3 transform gradually into trigonal sp^2 structure [13–15]. When the sp^2 carbon becomes dominant, the amorphous carbon changes into a structure with the increasing graphitic phase or long-range order. The properties of films therefore can be dominated by graphite. From the IR spectra, the hydrogen in our films could be completely removed by annealing lower 600 °C, the fraction of sp^2 carbon gradually increased. Comparing to the results of TED, we inferred that the film was still a sp^3 carbon structure with small sp^2 carbon cluster distributed in its until 600 °C. Gonzalez-Hernandez *et al.* [17] suggested that once most of the hydrogen has been driven out, crystallization into the graphite phase took place. Reyes-Mena *et al.* [10] also concluded that the sudden increasing in the conductivity in films can be understand in term of dehydrogenation followed by the nucleation and growth of conductive graphite particles. In our film, the diffraction intensity of graphite-like phase and the conductivity increased with the increasing temperature, which indicated that the fraction of sp^2 carbon cluster (graphite phase) increased.

3.3. Raman spectra

The carbon has two crystalline forms: graphite is consisted of sp^2-bonded carbon and diamond is a sp^3-bonded carbon structure. Amorphous carbon films, however, consist of a mixture of these two types bond at least. The property and microstructure of amorphous carbon films mainly depend on the ratio of sp^2/sp^3. Raman spectroscopy is very sensitive to change in translational symmetry and used for the study of disorder and crystallite formation in thin carbon films. Fig. 3 showed the Raman spectra of the samples heat treated at different temperature. At low annealing temperature (below 400 °C), no Raman signal except for PL can be observed, which indicated that the carbon atoms have mainly the sp^3 coordination [18, 19]. This agreed with the result of IR. Raman signal appeared in the range of 1000 to 2000 cm^{-1} as annealing at 400 °C. The signal consisted of two bands whose maximum intensities are located at approximately 1380 and 1583 cm^{-1}. The low frequency line has been denoted by D and its origin related to structure disorder in the graphitic-like phase, whereas the high-frequency line, the G line, corresponds to the zone center phonon dispersion in crystalline graphite [20, 21]. The intensity of D and G lines gradually increased and the PL decreased with increasing temperature. A significant change in the peak shape occurs between 500–600 °C. In order to quantitative analysis the evolution of Raman spectra, commercial non-linear curve fitting software was used to deconvolute the spectra. The results are showed in Fig. 4. And the temperature dependence of the fitting parameters, relative integrated intensity, line position, and full width at half-maximum (FWHM) will be discussed separately.

3.3.1. The relative integrated intensity ratio I_D/I_G

As shown in Fig. 4, the intensity ratio increases with the temperature. At low annealing temperature (below 400 °C), no Raman signal except for PL can be observed. The rise of the I_D/I_G ratio with annealing temperature is consistent with a model that predicts a growth in number and/or size of crystallites. The ratio is roughly proportional to the ratio of momentum nonconserving-to-conserving phonons which

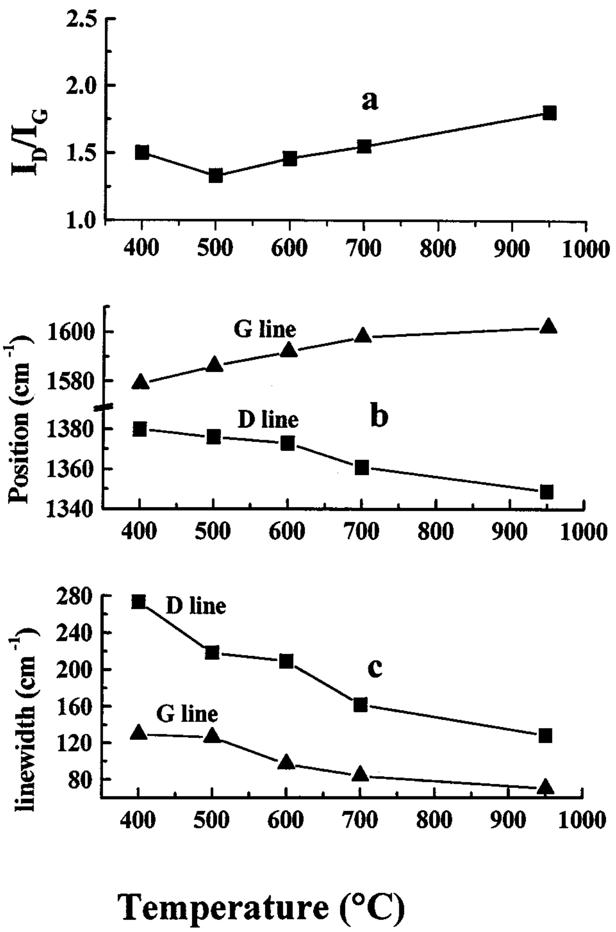


Figure 4 The deconvoluted results of Raman spectra.

contribute to the Raman spectrum. At low annealing temperature, very small crystallites are likely to exist in carbon films, but due to their small size and number, they are only weakly coupled to the incoming laser beam and contribute no to Raman spectra. When the annealing temperature increase, the crystallites grow in number and size, and thus they begin to contribute to the Raman spectra, causing the I_D/I_G ratio to increase.

We measured the electron diffraction of films and found that the Raman signal could be observed as soon as the crystalline structure could be detected in film by TED method. The as-deposited films only revealed an amorphous DLC structure (Fig. 1a), which kept no change until 400 °C, Raman signal wasn't observed in this temperature range. When the diffraction rings could be detected (Fig.1b) the Raman signal could been observed, too. During annealing process, the crystallites were growing in number /or size, and thus cause the Raman signal change. These indicated that crystallites in number /or size influenced the observation of Raman signal.

The development of the I_D/I_G ratio in carbon as a function of temperature is known. According to Tuinstra and Koening [22] the increase in particle size is related to the decrease in the intensity ratio I_D/I_G however, our data showed an increasing I_D/I_G ratio that agreed with a previous report [20]. This may be interpreted as a partial conservation of the $q = 0$ selection rule. Momentum conservation is only observed in large crystals; thus, at enough high annealing temperature we should begin to see a decrease in the I_D/I_G ratio, however, heated treatments at temperatures higher than 950 °C degrade the films, making the measurements unreliable. These implied that the size of sp^2 cluster was not enough large and decrease the I_D/I_G ratio until 950 °C. All graphitization didn't take place at the temperature.

Also, the I_D/I_G ratio can be used to get a quantitative estimation of the sp^2 cluster size (the sp^2 correlation length L_a). Tuinstra and Koenigis found a linear correlation between I_D/I_G and $1/L_a$, with larger values of I_D/I_G corresponding to small values of L_a. The largest I_D/I_G ratio in their work is 1.1 and corresponds to an L_a of about 3.5 nm. The I_D/I_G ratios, observed in our work were, however, all higher than 1.1, the maximum value observed in the microcrystalline graphite studies. The linear relationship between I_D/I_G and the inverse of the microcrystalline size, $1/L_a$, may no longer hold for these Raman results.

3.3.2. D- and G-line position

As shown in Fig. 4, the G-line position changed from 1580 to 1604 cm^{-1}, and D-line from 1380 to 1346 cm^{-1} with increasing temperature. In a theoretical study of the Raman spectroscopy for amorphous carbon, Beeman *et al.* [23] suggested that increasing the amount of sp^3-bonded atomic sites in amorphous carbon results in a downshift of the G-band position. Richter [24] also found that frequency shifts in the G band are caused by changes in the force constants associated with changes in the sp^3-bonding fraction. So the position of G-line in the Raman spectra is correlated to (at least) two film properties—the sp^2/sp^3 ratio [25] and the film stress [26]. The G-line position shifted to high frequency with the increasing annealing temperature. It means that the sp^2 bonding fraction increase, i.e., partial tetrahedral bonds have been broken and have transformed to trigonal bonds. The position and intensity shifts of D and G lines are the most sensitive indication that the films are changing from ones with bond-angle disorder to ones containing threefold-coordinated crystallites, i.e., the graphitization of the films. The D-line position shifted to low frequency and grew from a shoulder into single peak, which also suggested that the bond-angle disorder decreased.

3.3.3. D and G linewidth

With the increasing of annealing temperature (above 600 °C), the decrease in linewidth of D and G lines (Fig. 4c) indicated the removal of bond-angle disorder and the increasing dominance of crystallites. The linewidth was very large at low temperature because of the bond-angle disorder. The line then narrowed as the disorder was removed by annealing and as crystallites became more dominant. The D-line width was considerably larger than that of G-line. This was partially because, for low intensities, it was more difficult to judge the width of a wide line than a narrow one.

For hydrogenated amorphous carbon films, the most conspicuous trend is that toward narrower line width and increased D line intensity with decreasing optical gap and a corresponding increase in the fraction of sp^2 coordinated carbon in the film. From the analyses above, the sp^2 coordinated carbon became gradually dominant with the increasing annealing temperature and caused the properties of films could be controlled by sp^2 carbon phase (graphite phase) such as high conductive ability.

Summarizing these results, it may be inferred that the DLC films initially were primarily sp^3 C amorphous in which very small sp^2 carbon cluster may embedded. The film is still stability until 600 °C. With the increasing temperature, tetrahedral bonds gradually transformed to trigonal bonds. Intensive graphitization occurred at above 950 °C.

4. Conclusion

Diamond-like films have been prepared by liquid phase electrochemical method. The films consist of a little amount of hydrogen, which bonded mainly to sp^3 C—H and could be completely removed by annealing lower 600 °C. The film was still stability and the fraction of sp^3 carbon was dominant until 600 °C. The Raman signal of annealing films have been investigated: (1) the intensity ratio I_D/I_G increased; (2) the G-line position shifted from 1580 to 1604 cm^{-1} and the D-line position changed from 1380 to 1346 cm^{-1} and become a single peak; (3) the linewidth of the D and G-line decreased with the increasing annealing temperature. These results indicated that the primary bonding in the films changed gradually from sp^3-bonded carbon to sp^2-bonded carbon as annealing proceeds.

Acknowledgements

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