Diamond-like carbon thin films for high-temperature applications prepared by filtered pulsed laser deposition

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Abstract

Diamond-like carbon thin films (DLC) with increased thermal stability were prepared by filtered pulsed laser deposition (F-PLD). The influence of different substrate temperatures on the growth and composition of DLC films was analysed using Raman spectroscopy and electron energy loss spectroscopy (EELS). The increase of substrate temperature leads to an increase in sp^2 carbon bond hybridisation and a decrease in the optical band gap. However, the deposited films show excellent thermal stability, with a slow transition from high sp^3 to low sp^3 content as a function of the substrate temperature. The importance of substrate temperature and the mechanical kinetic energy filter in relation to the mobility of the film-forming species from the highly ionised and energetic laser plume is discussed.
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1. Introduction

Since diamond-like carbon thin films (DLC) films were first deposited in 1971 [1], a large academic and industrial interest has developed due to their superior properties, which can vary widely from graphite- to diamond-like. Specific tailor-made films can be grown simply by optimising deposition parameters, resulting in a broad range of successful commercial applications e.g., magnetic data storage [2], coating of cutting tools [3], biocompatible materials for orthopaedic implants [4], cold-cathode electron emission [5], IR sensors and lenses [6].

Mechanical and tribological applications involving high temperatures, due to friction between moving parts, require DLC films with high thermal stability. It is well known that hydrogenated DLC films are less suitable, as hydrogen is released with raising temperature deteriorating the film properties (hardness). Therefore, several techniques were developed to achieve high-quality

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hydrogen-free DLC films, such as pulsed laser deposition (PLD), filtered cathodic vacuum arc (FCVA) and magnetron sputtering, [7,8]. However, when increasing the temperature of the substrate during PLD and FCVA deposition (100 °C for PLD and 200 °C for FCVA [9]) above a transition temperature, the films exhibit an abrupt change in their percentage of sp^3-bonded carbon and the related mechanical and electronic properties [9]. This transition temperature also serves as a measure of the thermal stability of films in high-temperature applications, such as the temperatures developed due to friction.

During PLD deposition, the bigger and heavier ablated clusters (droplets 1–2 μm in diameter), have a high sp^2-content and carry a higher kinetic energy, which can also lead to graphitisation of the deposited film [10]. To circumvent this problem, we introduced a mechanical separator to act as a filter, thus reducing the amount of graphitisation.

The DLC films grown using the filtered-PLD (F-PLD) method exhibit unique termal stability, with a high transition temperature ∼500 °C. The transition process itself is slow and gradual with increasing temperature, suggesting that the films retain their stability over a wide temperature range. We used Raman spectroscopy and EELS to characterise the atomic density and bonding of the films as a function of the substrate deposition temperature.

2. Experimental

F-PLD was used to deposit thin DLC films (∼120 nm). Fig. 1 shows a diagram of the experimental setup, with an inset photograph of the mechanical separator. The laser employed is a frequency tripled Nd:YAG laser (Quanta Ray PRO250) operating at 355 nm working in pulsed mode (10 Hz). The power density on the target surface was adjusted to 400 mJ/pulse using the focusing optics. The films were grown at a chamber base pressure of 1×10^{-3} Pa, and ablated at a constant number of laser pulses (4000) without the use of a buffer gas. The substrate deposition temperature, monitored using a thermocouple, was varied through resistive heating from 25 to 600 °C.
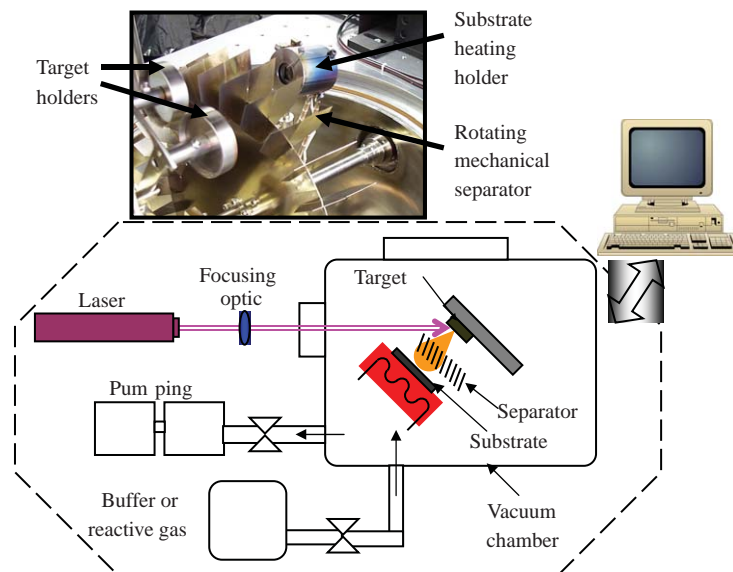

Fig. 1. Schematic diagram and photograph of the chamber used for the F-PLD deposition of DLC films. The substrate temperature is controlled by resistive heating and monitored using a thermocouple. The mechanical separator is used to filter out large clusters of ablated graphite target, thus reducing the graphitisation of the deposited films.
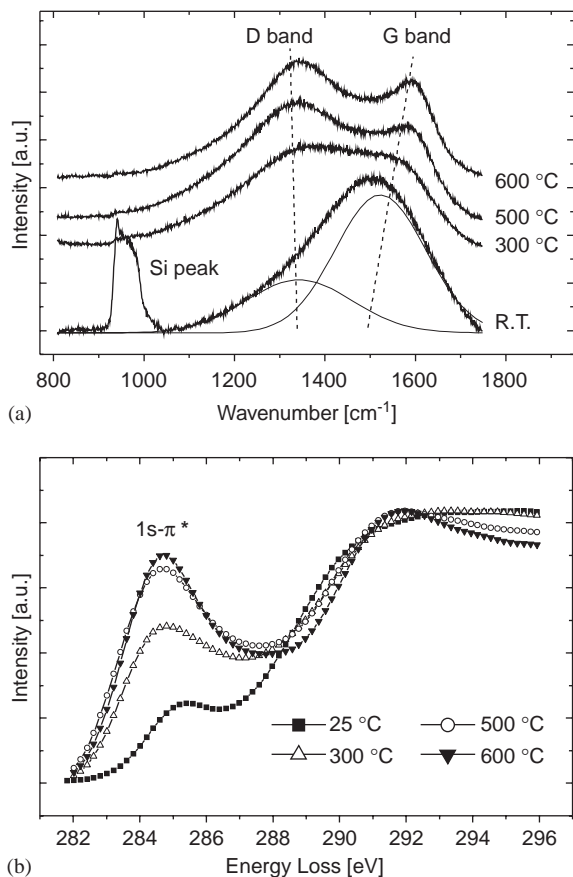
Fig. 2. Both (a) Raman and (b) carbon K-edge spectra of F-PLD deposited DLC films show increasing graphitisation with rising substrate temperature. As the temperature rises the ratio I_D/I_G is increased, G band is narrowed and its position shifted upward, indicative of higher structural order in sp^2 sites. K-edge EELS spectra are normalised on an area corresponding to the total number of carbon bonds. The size of the $1s-\pi^*$ peak shows an increased sp^2 content with the increase in substrate temperature.

Conventional micro-Raman spectroscopy of the deposited material was performed using a Jobin-Yvon system with the laser line at 632 nm from a HeNe laser in a backscattering geometry. After a linear background subtraction, the peaks in the Raman spectra (Fig. 2) were fitted using a linear combination of Gaussian–Lorentzian lineshapes (LabSpec V2.08 fi.DILOR). EEL spectra were acquired using a Gatan Imaging Filter (GIF) attached to a Philips CM20 TEM at an accelerat-

ing energy of 200 keV and collection semi-angle of 20 mrad.

3. Results

The sample deposited at room temperature, exhibits the D and G broad bands of amorphous carbon [11], centred on 1342 and 1523 cm^{-1} (Fig. 2a). The G mode is a bond-stretching vibration of a pair of sp^2 sites, and occurs irrespective of the sp^2 sites being arranged as olefinic chains or aromatic rings. The D mode is an $A1_g$ breathing vibration of a six-fold aromatic ring, previously only associated with disorder [8,12]. The ratio of the area under the D-band to that of the G-band (I_D/I_G) increases from <1 in the case of the room-temperature deposited sample to approximately six times the room temperature value when the deposition temperature is 500 °C.

Another significant feature clearly observed in the Raman spectra for the room temperature sample is the presence of a broad band (the quadrangle shaped peak) at $\sim960\,cm^{-1}$ (Fig. 2a), which reflects the second-order peak of the Si substrate [13]. As all the DLC films deposited for this study were of similar thickness (~120 nm) the intensity of the Si peak is an indirect signature of the optical transparency of the deposited film.

Next, DLC films were examined using EELS. The broad peak located in the low-loss region of the EELS spectra known as the low-loss plasmon, corresponds to excitations from valence electrons. From the plasmon energy the atomic density of the DLC films can be estimated using the "quasi-free" electron model [14]. The calculated atomic densities as a function of the substrate temperature are shown in Fig. 3a. The highest atomic density of 2.94 g/cm^{-3}, corresponding to the plasmon energy of 28.5 eV, is seen for the film grown at room temperature and it compares well with ta-C films grown by FCVA [15].

The concentrations of sp^2 and sp^3 bonded carbon atoms can be estimated by comparing the integrated intensity of the π^* peak associated with electron transitions from the core to unoccupied states in the π^* band (Fig. 2b). The highest content of sp^3-bonded carbon was measured for samples
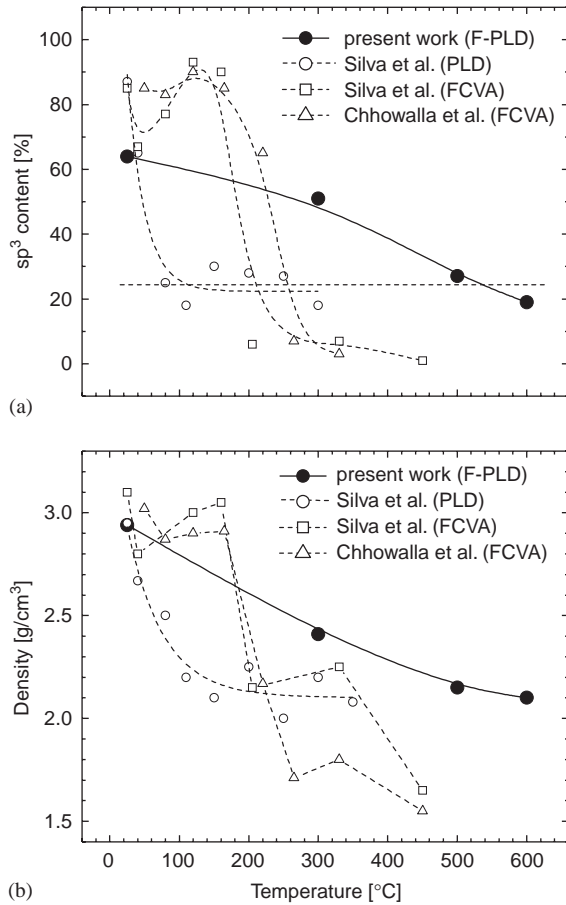
Fig. 3. Dependence of (a) the sp^3 content and (b) the atomic density as a function of the substrate temperature. The results are compared with other authors [9,16] and prove that DLC films prepared by F-PLD have a high thermal stability and show a much more gradual transition from high sp^3 to low sp^3 concentrations.

prepared at room temperature (64%). The concentration of sp^3-bonded carbon decreases with increasing substrate temperature (Fig. 3b). For substrate temperatures above 600 °C the films are almost graphite-like in nature (sp$^2 \sim 81\%$).

Results presented in Fig. 3 show a significant improvement in the thermal stability of DLC films. Silva et al. [9] observed transition temperatures of 100 and 200 °C for samples prepared using PLD and FCVA, respectively. In their study, the concentration of sp^3-bonded carbon remains on a constant low level at 25–30% (even less for the FCVA prepared samples <10%) for temperatures beyond the transition temperature. In comparision with other autors [9,16] the transition process reported here from high sp^3- to low sp^3-bonded carbon films is slow and gradual with increasing temperature (Fig. 3a). It is not until a deposition temperature of 500 °C that the sp^3 concentration falls below 30%.

These results support the importance of surface energy and kinetic energy of incident particles in the ordering of sp^2 states in a-C thin film. Many authors explain their results based on the subplantation theory [9,16–18] and found that if the substrate temperature is increased above a certain threshold value, which gives the carbon ions the necessary mobility across the surface, a more sp^2 dominant structure is formed.

A possible explanation for the higher transition temperature has been proposed by Chhowalla et al. [16]. They observed a rise in the transition temperature with decreasing ion energy (for ion energy 90 eV the transition temperature was between 200 and 240 °C) and it is concluded that the deposition temperature is more significant when it is a substantial fraction of the energy associated with the film forming species. Therefore, the kinetic energy of the vapour-phase particles is one of the most critical factors in deposition. The interaction of the incident laser light with the graphite target leads to the formation of an isothermally expanding plasma consisting of electrons, atoms, ions and clusters. With increasing laser fluence, smaller cluster sizes and higher ion densities can be achieved, as the fragmentation of clusters to smaller sizes can take place if they absorb sufficient energy. In our experiments the laser fluence of 12.7 J/cm^2, gave rise to an sp^3 fraction of 64% at room temperature. Koivusaari et al. [18] have also shown that better quality DLC films are deposited for higher laser fluence.

In terms of kinetic energy our F-PLD has one significant feature: a mechanical separator (Fig. 1) which is a fast rotating fan (6000 rpm) used to filter out macro-droplets and clusters. This separator plays a crucial role in achieving higher thermal stability of DLC films. Thus, the higher thermal

stability of DLC films was obtained by mechanical filtering, which was used to obtain incident particles with low energies ($<10\,eV$ for PLD) and very low clustering.

4. Conclusion

In conclusion, the F-PLD technique was used to deposit DLC films at varied substrate temperatures. It was observed that the DLC films prepared at room temperature exhibited the widest optical gap. The films also showed excellent thermal stability, with a slow transition from high sp^3 to low sp^3 content as a function of substrate deposition temperature. This stability is highly desirable for industrial purposes extending a family of DLC applications withstanding high temperature and harsh environments. It is believed that the slow transition process is a result of the high laser fluence used and consequently the substantially suppressed clustering by the mechanical filtering of the plasma plume.

Acknowledgement

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