Electrical and optical properties of diamond-like carbon films deposited by pulsed laser ablation

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ARTICLE INFO

ABSTRACT

Pulsed laser ablation of a graphite target was carried out by ArF excimer laser deposition at a laser wavelength of 193 nm and fluences of 10 and 20 J/cm^2 to produce diamond-like carbon (DLC) films. DLC films were deposited on silicon and quartz substrates under 1×10^{-6} Torr pressure at different temperatures from room temperature to 250 °C. The effect of temperature on the electrical and optical properties of the DLC films was studied. Laser Raman Spectroscopy (LRS) showed that the DLC band showed a slight increase to higher frequency with increasing film deposition temperature. Spectroscopic ellipsometry (SE) and ultraviolet–visible absorption spectroscopy showed that the optical band gap of the DLC films was 0.8–2 eV and decreased with increasing substrate temperature. These results were consistent with the electrical resistivity results, which gave values for the films in the range 1.0×10^4–2.8×10^5 Ω cm and which also decreased with deposition temperature. We conclude that at higher substrate deposition temperatures, DLC films show increasing graphitic characteristics yielding lower electrical resistivity and a smaller optical band gap.

1. Introduction

Diamond-like carbon (DLC) films are composed mainly of carbon atoms in an amorphous (non-crystalline) arrangement. The structure contains regions that are locally diamond-like and regions that are locally graphite-like in structure, but there is no long range order. Diamond has carbon arranged in a face-centred cubic (f.c.c.) structure with sp^3 hybridization. Graphite is the most abundant and stable allotrope of carbon found naturally, and is a hexagonal close-packed (h.c.p) crystal with the carbons in sp^2 hybridization. The differences in both structures and chemical bonds between sp^2 and sp^3 hybridized carbon produce the variation of the properties of DLC films. The ratio of sp^3:sp^2, therefore, indicates the specific property of each DLC film [1–5]. While much research effort has been focused on growing crystalline diamond films, they can usually only be deposited at high temperature (above ~700 °C), limiting the materials upon which diamond can be grown. In contrast, deposition of DLC films has been attracting a great deal of attention because of the low or room temperature deposition, smooth surface morphology and homogeneity of DLC films, which make them more useful than polycrystalline diamond films for many applications. For example, DLC films can be used as anti-reflective coatings on optics, cutting and abrasive wear tools, IR windows, computer hard disk coatings, bioresistant coatings for medical implants, watch cases and lenses, etc [2–7].

Therefore, nowadays, DLC film have been intensively studied and widely used in commercial applications due to their useful properties, which lie between those of diamond and those of graphite [6–9]. These films are relatively easy and economical to deposit. Moreover, the properties of DLC can be tailored to a specific application by adjusting these values during deposition.

Several DLC film deposition techniques, such as plasma-enhanced chemical vapor deposition (PECVD) [3,4,10], sputtering [11,12] and pulsed laser ablation (PLA) [2,5–9,13–21] are employed in fabricating DLC thin films. In principle, PLA is a favorable technique because of the advantage such an energetic process has in the production of high quality of DLC films with high proportion of sp^3 hybridized carbon bonds without hydrogen content [2,3,5–8,17,21]. The kinetic energy of carbon ions in the ablation plume and the substrate temperature are the main factors in controlling the properties of DLC films having the highest sp^3 content [5–8,17].

In this paper, the results of pulsed laser ablation of DLC films using an ArF excimer laser will be reported. The structural, electrical and optical properties of the DLC films have been investigated.

2. Experimental setup

In this work, all DLC films were deposited in a vacuum chamber which was evacuated by a rotary and a turbomolecular pump to a

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typical base pressure of 1×10^{-6} Torr. An ArF pulsed laser (wavelength 193 nm, 20 ns FWHM, 10 Hz repetition rate) was introduced into the chamber through an anti-reflection-coated convex focus lens and a quartz window. The laser, with fluences 10 and 20 J/cm^2, was focused onto a rotating high purity pyrolytic graphite (PG) disk, which was used as an ablation target. The laser spot size on the PG target surface was ~1.0×0.4 mm^2. The 'plume' of ejected material was emitted in a distribution centred along the surface normal of the target. Silicon and quartz wafers were used as substrates. A continuous wave (CW) CO_2 laser focused onto the back-side of a substrate was employed to heat the substrate controllably by adjustment of the CO_2 laser output power. DLC films were deposited for 15 min at various temperatures, such as room temperature, 150 °C and 250 °C.

All deposited DLC films were analyzed using Laser Raman Spectroscopy (LRS) (Renishaw-2000), with an Ar ion laser excitation at $\lambda = 514$ nm and a power of 20 mW using a $50\times$ objective. A Woollam VASE Ellipsometer and Perkin Elmer Lambda Bio ultraviolet–visible (UV–VIS) spectrometer (1.0–5.0 eV photon energy) were used to analyze the optical properties of films. A four-point probe was used to determine the electrical properties of films.

3. Results and discussions

Raman spectra of DLC films on silicon substrates deposited at different temperatures and laser fluences are shown in Fig. 1. These spectra can be deconvoluted into two Gaussian peaks: a broad peak centred at approximately 1560 cm^{-1}, and an asymmetric shoulder at ~1360 cm^{-1}. These correspond to the G (graphitic) and D (disordered) peaks, respectively [1,2,7,12]. These spectra are consistent with the spectral characteristic seen from other DLC films [6,7,9,12,20]. The G-peak is attributed to the first-order scattering from zone-centre phonons of E_{2g_2} symmetry mode in single crystal graphite. The G mode is the relative motion of sp^2 hybridized carbon. It can occur from C=C sp^2 stretch vibrations of olefinic or conjugated carbon chains. The D peak is attributed to the disorder activated A_{1g} breathing motion of six-fold aromatic rings. The D mode is forbidden in perfect graphite [1,5,7]. The Raman frequency of the DLC peak showed a slight increase to higher frequency both with increasing temperature at constant laser fluences and with increasing laser fluences at constant temperature.

By fitting the Raman spectra the ratio of the intensities of the D and G peaks (I_D/I_G ratio) and the G-peak position have been evaluated because these parameters give information about the structural changes of sp^2 hybridized carbon domains [1,10,22]. For constant laser fluence, the G-peak position and I_D/I_G ratio increased with increasing substrate temperature, as shown in Fig. 2A and B,
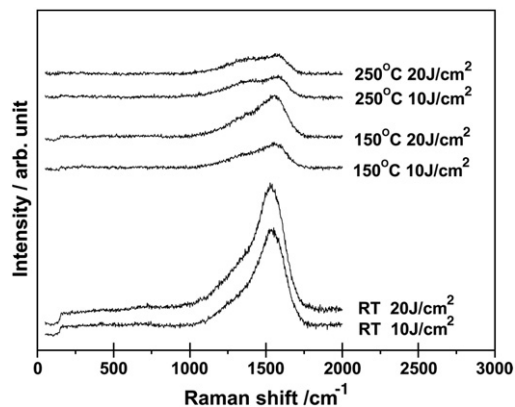

Fig. 1. Raman spectra (514 nm excitation) of DLC films deposited on silicon substrates at different temperatures and laser fluences. The spectra have been offset vertically for clarity.
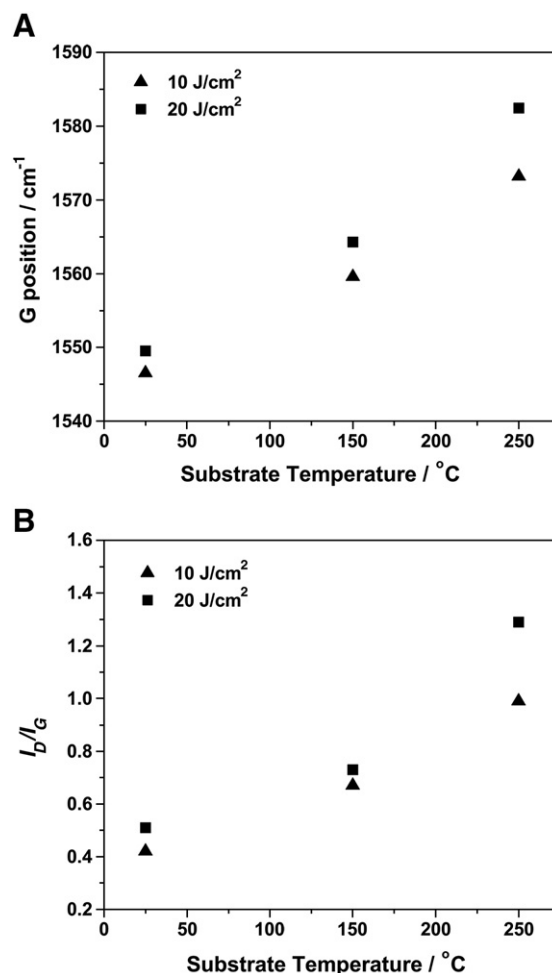

Fig. 2. A plot of (A) the G-peak position versus the substrate temperature, and (B) the I_D/I_G ratio, both at 10 and 20 J/cm^2 laser fluences.

respectively. The observed behaviour that the G-peak shifts to higher energy, together with an increasing I_D/I_G ratio, is consistent with an increase in the size of the sp^2 domains. Therefore, the Raman spectra show that the DLC films exhibit increased graphitic character containing larger numbers of graphite clusters as the substrate temperature is increased. A similar behaviour was also observed for increasing laser fluences.

Raman spectra can used to obtain information on defects and the size of the graphite clusters to predict the optical band gap, E_g. It is well known that in amorphous carbon films the energy band gap is proportion to the graphite cluster size, while the I_D/I_G ratio is inversely proportion to the graphite cluster size [1,5,23]. Therefore, the relationship that I_D/I_G is inversely proportion to E_g, when a D peak is present, means that a decrease in the band gap will always be indicated by an increase in I_D/I_G. Therefore, the Raman spectra show decreasing energy band gap with increasing substrate temperature at constant laser fluences and increasing laser fluence at constant substrate temperature. This prediction is consistent with the spectroscopic ellipsometry (SE) results, as shown later in Fig. 4.

The optical properties of the DLC films on silicon, such as the refractive index (n), extinction coefficient (k) and E_g were examined by SE at a light angle incidence of 50°, 55°, 60°, 65°, and 70°. Fig. 3 shows an example of how n and k vary as a function of photon energy for one of our DLC films. The n and k values depended upon the deposition condition. In this work, n and k of deposited DLC films were found to be in the range 2.0–3.0 and 0–0.6, respectively. The value of k was found to increase with increasing photon energy. In SE measurements, when n and k values are obtained for each photon
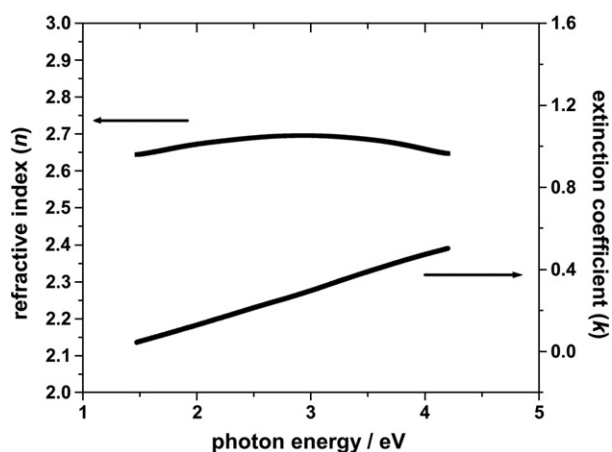
Fig. 3. Refractive index (n) and extinction coefficient (k) of a DLC film as a function of photon energy.

energy, E_g can be determined by extrapolating the plot of photon energy, E, with the quality $E\varepsilon_i^{1/2}$, where $\varepsilon_i = 2nk$. This is based on the relation: $\varepsilon_i(E) = B(E-E_g)^2/E^2$, where B is a constant [6,21].

UV–VIS spectroscopy was also used to determine E_g by optical transmission and absorption measurements of the DLC films deposited onto quartz. E_g can be obtained by using the Tauc relationship from calculation of the energy dependence on the optical absorption coefficient (α). This is based on the relation: $(\alpha h\nu)^{1/2} = B(E_g - h\nu)$, where B is the density of the localized state (Tauc gap constant) and $h\nu$ is the photon energy [5]. In a Tauc plot, $(\alpha h\nu)^{1/2}$ was plotted as a function of $h\nu$. E_g can be obtained from estimation of the intercept of the extrapolated linear fit with the Tauc plot curve.

Fig. 4 shows E_g values in range of 0.8–2.0 eV (measured by SE and UV–VIS spectroscopy) for DLC films deposited at different temperatures and laser fluences. These results are similar to those from laser-deposited DLC films in other reports [5,6,8,9,13,21,24]. The trends in E_g from UV–VIS were found to be the as those from SE. It was found that E_g decreases with increasing substrate temperature for the same laser fluence. At the same temperature, E_g at 10 J/cm^2 laser fluence was higher than E_g at 20 J/cm^2 of laser fluences. Therefore, these SE results confirm the E_g prediction by Raman, and are consistent with the structure change seen in the DLC films. This means that DLC films deposited at high temperature and laser fluence lead to graphitization of the films [2,7,17].

The resistivity values of all the DLC films were obtained by four-point probe measurement. The resistivity was calculated from: $\rho =$
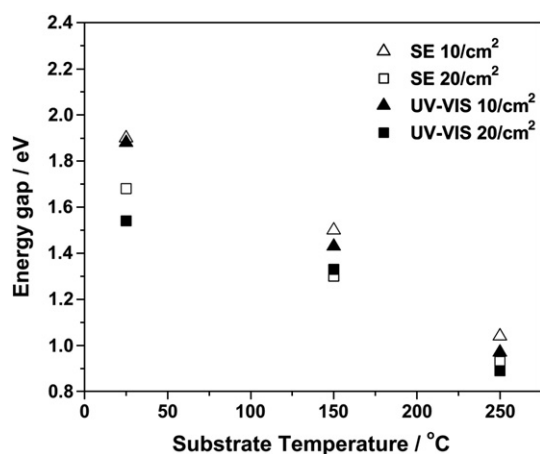

Fig. 4. Tauc energy gap of DLC films deposited on silicon and quartz substrates at difference temperatures and laser fluences.
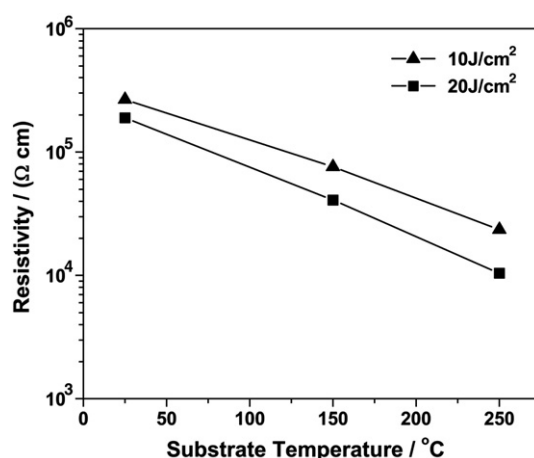

Fig. 5. Resistivity of DLC films deposited at difference temperatures and laser fluences.

$(\pi/\ln 2) \times (V/I) \times d$, where ρ is the resistivity of the films (Ω cm), V is the measured voltage (V), I is the source current (A.), and d is the film thickness (cm). The resistivity results of DLC films were found to be in the range 1.0×10^4–2.8×10^5 Ω cm, as shown in Fig. 5. These results are consistent with those from laser-deposited DLC films in other reports [17,20]. The resistivity was found to decrease with increasing substrate temperature at constant laser fluences. For the same temperature, the resistivity at 10 J/cm^2 is higher than that at 20 J/cm^2 laser fluence. These resistivity trends are consistent with the findings from both the structural and optical results: the conclusion being that the films contain more graphite with sp^2 hybridization with increasing substrate temperature and laser fluence.

4. Conclusions

DLC films have been deposited by ArF pulsed laser ablation of graphite at room temperature, 150 °C and 250 °C. The optical band gap was found to be in the range of 0.8–2.0 eV. The resistivity of DLC films was found to be in the range of 1.0×10^4–2.8×10^5 Ω cm. The properties of the DLC depend upon both the substrate temperature and laser fluences. However, at higher substrate temperature, the Raman D-band showed a slight increase to higher frequency, whilst the optical band gap and resistivity decreased. These findings are consistent with an increase in graphitic character of the films with increasing deposition temperature.

Acknowledgements

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