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Deposition of hydrogen-free diamond-like carbon film by plasma enhanced chemical vapor deposition

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Hydrogen-free diamond-like carbon (DLC) films were deposited by the layer-by-layer technique using plasma enhanced chemical vapor deposition (PECVD), i.e., the alternative deposition of thin DLC layer and subsequent CF_4 plasma exposure on its surface. The hydrogen-free DLC could be grown on the Si wafer by repeated deposition of the 5 nm DLC layer and subsequent 200 s CF_4 plasma exposure on its surface. On the other hand, the conventional DLC deposited by PECVD contains 25 at. % hydrogen inside. The CF_4 plasma exposure on the thin DLC layer appears to etch weak C–C bonds and break hydrogen bonds, resulting in a widening optical band gap and increasing conductivity activation energy.
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The diamond-like carbon (DLC) film with no incorporated hydrogen has considerable interest, because of its high hardness and substitutional doping capability compared to its hydrogenated counterpart.[1–3] The DLC film deposited by plasma enhanced chemical vapor deposition (PECVD) has much hydrogen inside, typically higher than 20 at. %.[4] The incorporated hydrogen reduces film hardness. Hydrogen-free DLC film can be obtained by a filtered vacuum arc deposition or by ion beam deposition.[5,6] Mckenzie *et al.*, deposited hydrogen-free DLC with more than 85% sp^3 fraction by a filtered vacuum arc deposition.[7] However, large area uniform deposition is not easy when using this method.

In the present work, the layer-by-layer deposition method, i.e., the deposition of thin DLC layer and subsequent exposure of its surface to CF_4 plasma, was applied to deposit hydrogen-free DLC film.

We used a conventional PECVD system, in which rf power was applied to the substrate holder. $CH_4/H_2/He$ and CF_4/He were introduced for the deposition of the DLC layer and surface treatment, respectively. A glass plate and silicon wafer were used as the substrates for film deposition.

Table I depicts the layer-by-layer deposition conditions for the DLC films. The flow rates of He, H_2, and CH_4 were fixed at 50 sccm, 5 sccm, and 1 sccm, respectively, for DLC deposition and the flow rate of CF_4 was fixed at 30 sccm for the plasma treatment. The self-bias voltage was found to be -120 V at a fixed rf power of 100 W, and it depended strongly on the gas pressure and on the rf power used. The 100 s growth under the deposition mode shown in Table I resulted in 5 nm thick DLC layer. We have carried out 50 times repeated deposition and plasma exposure to obtain 200 nm thick DLC film which was used to measure FTIR (Fourier transform infrared) absorption. The stretching mode absorptions due to CH_n (n=1,2,3) were investigated and hydrogen content was calculated by using the absorption coefficients.[8] Interband optical absorption coefficients were measured using a Perkin-Elmer UV-VIS-IR spectrophotometer and the optical band gap was obtained using Tauc's plot.[9]

Figure 1 shows the FTIR transmittance spectra of the DLC films. The absorption peaks at 2870 cm^{-1}, 2925 cm^{-1}, and 2960 cm^{-1} corresponding, respectively, to sp^3 CH_3 (symmetrical), sp^3 CH_2 (asymmetrical) and sp^3 CH_3 (asymmetrical) modes,[10] appear in the FTIR spectrum for a conventional DLC film. The hydrogen content obtained from the absorption coefficient[8] for the conventional DLC film was 25 at. %. However, the hydrogen content for the DLC film deposited with 200 s CF_4 plasma exposure time was found to be less than 1 at. %. As can be seen from the figure, the CH_n vibration intensity disappears completely when the CF_4 plasma exposure time is 200 s. Therefore, we can deposit a hydrogen-free DLC film by PECVD using layer-by-layer deposition technique.

Figure 2 shows the optical band gap (E_g^{opt}) of the DLC film obtained from Tauc's plot. The optical band gap increases from 1.2 to 1.4 eV with increasing CF_4 plasma exposure time. The increase in the optical band gap appears to be due to the preferential etching of graphite phase in DLC by CF_4 plasma exposure.[11] The bonding and antibonding states of C–C sp^2 lie in the inner side of those for C–C sp^3 (Ref. 12). The removal of the sp^2 bonds, therefore, results in the widening band gap of the DLC.

TABLE I. Layer-by-layer deposition conditions for the DLC films.

Condition	Deposition	CF_4 plasma exposure
rf power (W)	100	100
Pressure (mbar)	400	450
Flow rates (sccm)		
He	50	50
H_2	5	0
CH_4	1	0
CF_4	0	30
Sub. temp. (K)	300	300
Time (s)	100	0–200

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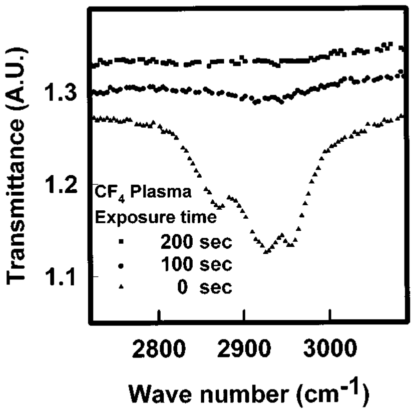

FIG. 1. Typical FTIR spectra for the deposited DLC films.

Figure 3 shows the temperature dependence of dark conductivity of the DLC films. The conductivity of the DLC shows an activated form and the activation energy increases from 0.25 to 0.55 eV with increasing CF_4 plasma exposure time up to 200 s. This means that the Fermi level moves toward the midgap after CF_4 plasma exposure because the optical band gap of hydrogen-free DLC is 1.4 eV. The conventional DLC shows a *p*-type behavior and the activation energy of conductivity is around 0.2 eV (Ref. 2). The newly developed DLC indicates a relatively high value (0.55 eV) of activation energy.

We deposited 200 nm thick DLC on the Si wafer to measure FTIR transmittance, which was nearly the maximum thickness we could grow in case of hydrogen-free films. The maximum thickness depended strongly on the substrate used because of the delamination of the film due to the stress build-up.

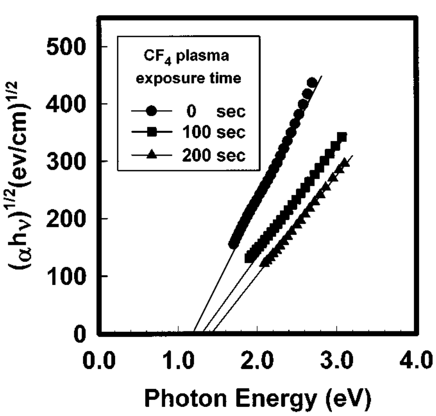

FIG. 2. Optical band gap of the deposited DLC films.

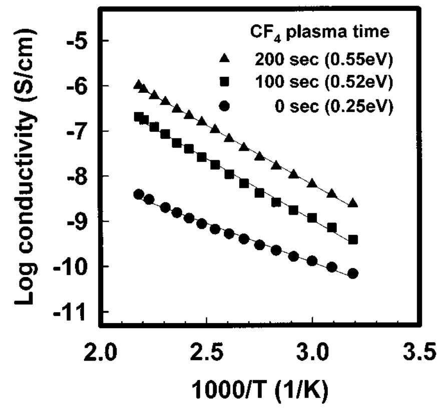

FIG. 3. Temperature dependence of conductivity for the deposited DLC films.

The CF_4 plasma exposure to thin DLC layer appears to etch some bonds and to relax the remaining network. The weak C–C and hydrogen atoms bonded to C atoms can be etched by F radicals. During this process the carbon atoms can be relaxed, resulting in hydrogen-free DLC. The Fermi level appears to move toward the midgap, because the material composition changes remarkably.

In summary, we have developed hydrogen-free DLC film by a PECVD using the layer-by-layer deposition technique. The conductivity activation energy increases from 0.25 to 0.55 eV and the optical band gap increases from 1.2 to 1.4 eV with increasing CF_4 plasma exposure time up to 200 s.

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