

Growth of nanocrystalline diamond films by biased enhanced microwave plasma chemical vapor deposition: A different regime of growth

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Hard and smooth nanocrystalline diamond films are grown on mirror polished silicon substrates by biased enhanced growth (BEG) in microwave plasma chemical vapor deposition at lower temperatures. Hardness of the films varies with deposition condition and can be defined by the relative concentration of nanocrystalline diamond in the films, as measured by the Raman intensity ratio of the feature near 1150 cm^{-1} to the intensity of graphitic *G* band. The hardness of the films approaches the hardness of diamond at conditions giving maximum concentration of nanocrystalline diamond while still having a low amount of stress (1–2 GPa). A different regime of growth appears to exist in the films deposited by the BEG process that may, however, be a combination of surface and subsurface processes. © 2000 American Institute of Physics. [S0003-6951(00)05051-8]

In the growth of diamond by chemical vapor deposition (CVD) techniques, a high concentration of hydrogen is used. The growth of diamond is described to be taking place mostly via surface processes of addition and abstraction of radicals from the gas phase.^{1–4} Ions are not considered to be good for diamond growth as they enhance lattice disorders and also promote graphitic content in the deposit. On the other hand, in the growth of carbon films by hyperthermal species, ions with energy in the range 40–200 eV produce a high concentration of *sp*³ carbon in the films.^{5–8} In this case, the growth is dictated by a subplantation mechanism which relies on the shallow subsurface implantation of the carbon ions.⁵ Thus, the two routes of growth of carbon films are totally different, i.e., one relies on surface and the other on subsurface processes. Moreover, the deposits are predominantly crystalline and amorphous, respectively, in the two processes. We propose a moderate route in which films are deposited in a CVD diamond environment while continuously biasing the substrate to take advantage of both the processes in the growth. The CVD diamond condition results in high etching rates of the nondiamond carbon from the surface processes while continuous biasing takes advantage of subsurface phenomenon. Termed biased enhanced growth (BEG),⁹ this route can be considered as an extension of the bias enhanced nucleation of CVD diamond and results in the growth of hard and smooth nanocrystalline diamond (NCD).

The films were grown in a microwave plasma (MP) CVD system on mirror polished Si(100) substrates kept on the Mo holder that rests on a graphite susceptor. No diamond powder or any other *ex situ* treatment was performed prior to the depositions. Depositions were carried out for 1 h under continuous dc biasing to the substrate and, as mentioned before, termed the process as BEG.⁹ While the bias voltage was held constant throughout the deposition, bias current varied with time in the same fashion as commonly observed in bi-

ased enhanced nucleation in the growth of CVD diamond; the current increases after some incubation period followed by saturation at longer deposition time. The increase in the current is attributed to enhancement in electron emission from the surface as highly emissive diamond is deposited on silicon.¹⁰ Three sets of depositions were carried out at various substrate temperatures, methane concentrations in balance hydrogen, and biasing voltages. In every set of samples, only one of the above mentioned parameters was varied while keeping other parameters constant following the sequence described in Table I. The optimal condition of the varying parameter in a series giving maximum concentration of nanocrystalline diamond was picked up and kept constant in the next series and, in the end, deposition was carried out at all the optimized parameters for 1, 2, and 4 h. Structural characterizations of the films were carried out using Raman spectroscopy, x-ray diffraction (XRD), Auger electron spectroscopy (AES), and atomic force microscopy (AFM). Hardness of the films was measured by a nanoindenter (UMIS-2000) using a Berkovich diamond pyramid. The deposition rate is around 600–1800 nm/h and, in order to minimize the substrate effect on the hardness measurements, maximum loading force was not exceeded beyond 50 mN. Therefore, the indentation depth was kept within the critical depth (depending upon individual sample) beyond which there would be severe effect in the hardness measurement of the film from the substrate.¹¹

Figure 1 illustrates representative Raman spectra of the time series grown at optimized conditions for 1, 2, and 4 h. In general the spectra of other films show the same characteristics as reported elsewhere.^{9,12,13} However, the relative intensities of the main bands near 1150, 1350, 1500, and 1580 cm^{-1} vary with conditions. The band near 1150 cm^{-1} is assigned to the presence of the nanocrystalline phase of diamond.^{9,14–17} The Raman feature near 1500 cm^{-1} may be related to the disordered *sp*³ carbon in the films.¹⁸ The intensity of this band increases proportionally with the inten-

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TABLE I. Growth conditions (microwave power=1000 W, pressure=30 Torr).

Growth parameter	Temperature (°C)	Biasing voltage (V)	Methane concentration (%)	Deposition time (h)
temperature	400–700	260	5	1
biasing voltage	600	200–320	5	1
methane concentration	600	200	2–6	1
deposition time	600	200	5	1–4

sity of NCD feature in the films as also observed by others.¹⁸ Other bands in the Raman spectra of our films near 1350 and 1580 cm^{-1} are popularly known as *D* and *G* bands, which are related to graphitic islands.¹⁴ However, the higher or equal intensities of the graphitic bands in Fig. 1 in the films compared to the intensity of the nanocrystalline diamond band do not represent a high amount of sp^2 carbon in those films. This is because of the well-known fact that the cross section of Raman scattering is 50–60 times higher for sp^2 -bonded carbon as compared to sp^3 -bonded carbon. The increase in the relative intensity of the NCD to the graphitic band may represent an increasing concentration of NCD in the films with deposition time. The results from other series are interpreted in the same terms, i.e., a higher relative intensity of the NCD feature the higher the concentration of NCD in the films. XRD patterns of the films, shown in Fig. 2, support this conjecture. The calculated interplanar spacing corresponding to the peaks at $2\theta \sim 44.05^\circ$, $75.25^\circ \pm 0.20^\circ$ in the XRD patterns of the films match closely with the interplanar *d* values of (111) and (220) planes of cubic diamond, respectively. It should be noted that the full width at half maximum of the diamond peaks in the films is, in general, high as compared to the CVD grown microcrystalline films. This is well correlated with the fact that diamond nanocrystallites¹⁵ are present in our films. As can be seen,

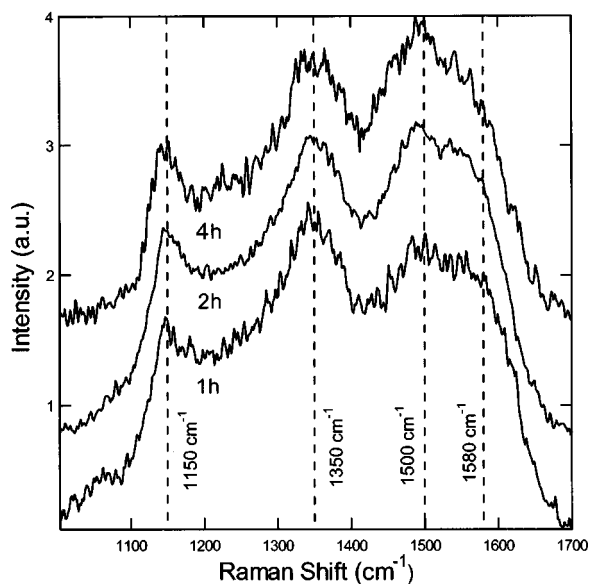


FIG. 1. Raman spectra of the films deposited at optimized condition for 1, 2, and 4 h.

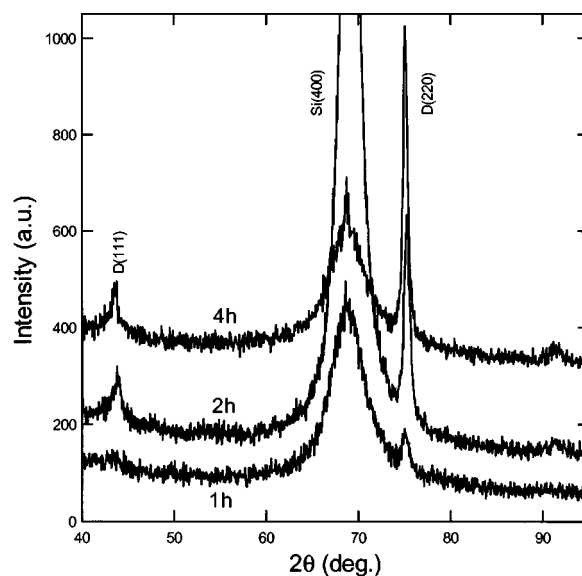


FIG. 2. XRD patterns of the films deposited at optimized condition for 1, 2, and 4 h.

the intensity of the peaks corresponding to the interplanar spacing of diamond (111) and (220) planes increases in the films with deposition time. AES of the films shown elsewhere indicated that the surface of NCD films consists dominantly with highly sp^3 carbon.⁹ The root mean square surface roughness, as measured by AFM in a $5 \times 5 \mu\text{m}^2$ area, varies in the range from 15 to 30 nm with deposition conditions.¹⁹ Stress in the films is compressive in nature and varies in the range of 1–2 GPa for the films grown at different time. Moreover, it should be mentioned here that the films are adhered strongly to the substrates and hence any thickness of the films can be grown irrespective of the amount of stress existing in them.¹³

The Raman intensity ratio of NCD (I_n) to graphitic *G* band (I_g) in the films and their hardness are plotted together in Figs. 3(a)–3(d) as a function of growth temperature, biasing voltage, methane concentration, and deposition time, respectively. As can be seen, the ratio I_n/I_g and hardness vary in the same fashion in all the films indicating that the relative concentration of NCD in the films may be responsible for the hardness of the films. However, if the relative concentration of NCD grains were solely responsible for the hardness, the latter would have been more in the case of the film grown at 400 °C compared to the film grown at 700 °C in temperature series [Fig. 3(a)]. The ratio, though very low in both cases, is higher in the former. This indicates that the hardness may be having contributions from cross-linked sp^2 structures as well.²⁰ However, more studies are needed to find the exact contributions from the concentration of NCD and cross-linked sp^2 structures in the films. It is interesting to note that the hardness in the films approaches the hardness of natural diamond at optimized conditions [Fig. 3(d)].

The above results give us an interesting insight into the growth of NCD by BEG process in MPCVD and indicate towards a different regime of growth than the growth of CVD diamond or diamond-like carbon/*ta*-C explained in terms of surfaces and subsurface processes, respectively. The hypothesis of a different growth mechanism is based, first, from the results of an increase in the relative concentration of

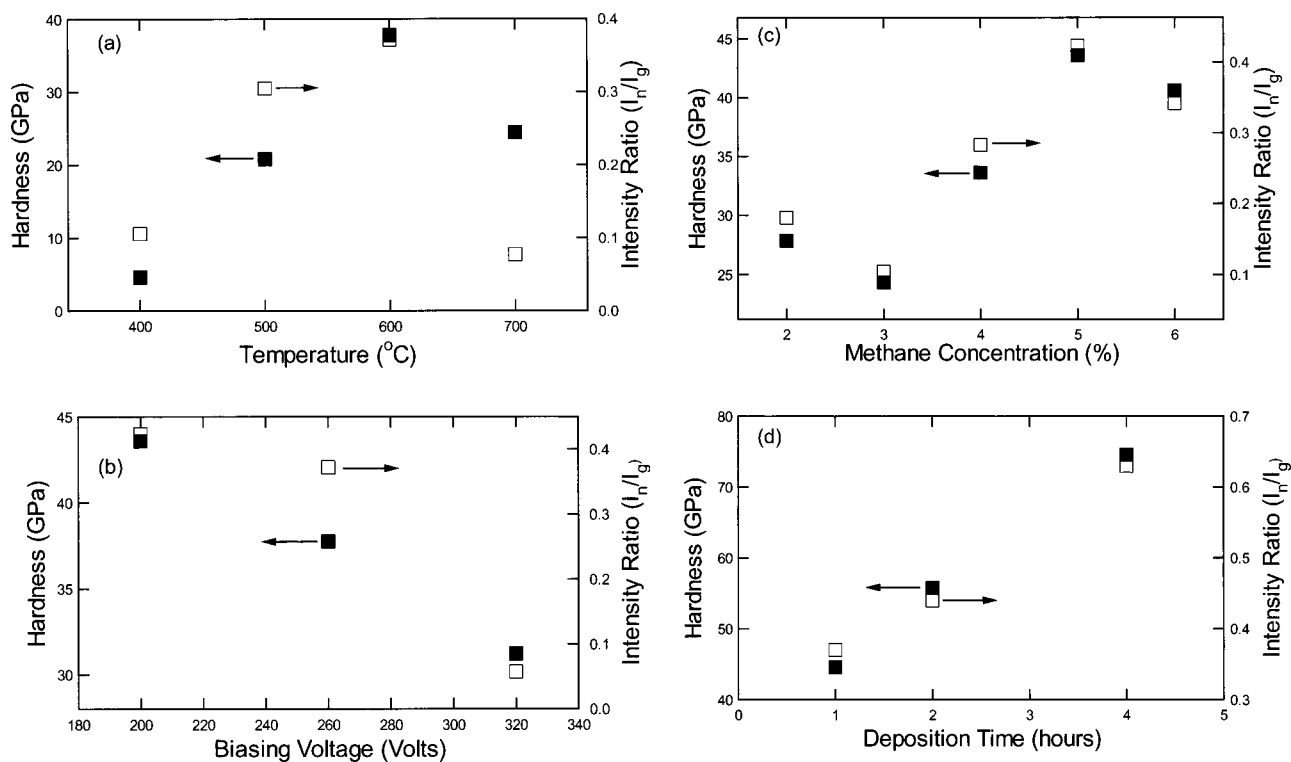


FIG. 3. Plot of hardness and Raman intensity ratio of NCD (I_n) to graphitic G band (I_g) of the films as a function of: (a) temperature, (b) biasing voltage, (c) methane concentration, and (d) deposition time. Hardness data presented in the graph is averaged from a few sets of five indents on the samples.

NCD with an increase in gas-phase methane concentration. Whereas it is a well-known fact that concentration of sp^2 carbon increases with methane concentration in the growth of CVD diamond. Second, the trends observed in our films in the hardness and amount of stress¹⁹ (not shown here) with different growth conditions do not follow the same trend as commonly observed in the growth explained using subplantation mechanism.^{6,21}

Therefore, we conclude a different regime of growth prevails in the films deposited by BEG process. It may, however, be a combination of surface processes, typical of CVD diamond and subplantation process, typical for growth by energetic species. The BEG process takes advantage from the shallow subsurface implantation to obtain smooth NCD films whereas the CVD diamond conditions help in etching out the graphitic carbon from the surfaces. It is supported by the fact that the biasing conditions used in the present work are not far from the energy required for subplantation⁹ and, apart from having a high concentration of NCD, the surfaces of the films are also shown to be consisting of highly sp^3 carbon.⁹

In conclusion, nanocrystalline diamond films were grown at various conditions by BEG in MPCVD with the hardness of the films approaching the hardness of natural diamond at a condition giving the maximum concentration of nanocrystalline diamond. A different regime of growth is realized in the films deposited by the BEG process, which may be a combination of the subplantation process, typical for growth by energetic species and surface processes, typical of CVD diamond.

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