Effect of heavy ion irradiation on self-supported diamond sheets


Abstract

The self-supported diamond sheets were deposited at various deposition pressure ($P_d$) using HFCVD technique. The sheets were characterized using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM). XRD shows the growth of cubic diamond. This is confirmed by Raman spectroscopy showing a sharp line at 1332 cm$^{-1}$ in all the sheets. The sheets deposited at low pressures show clean sharp facets. The sheets were irradiated with high energy Au and Ag ions of varying energy and dose. The energy range was 100–120 MeV and the dose varied between $1 \times 10^{12}$ and $3 \times 10^{13}$ ions. Raman spectra showed the reduction in the intensity of diamond line (1332 cm$^{-1}$) as well as non-diamond band at 1550 cm$^{-1}$ after irradiation. SEM images of irradiated sheets show a phase transformation on the surface of the crystal. A photoluminescence (PL) signal is observed after the irradiation of the sheets at 2.634 eV.

Keywords: Self-supported diamond sheets; Irradiation; Raman spectroscopy

1. Introduction

The irradiation of the thin films of CVD diamond with the heavy ions (Ag, Au, Ni, etc.) in the mega-electron-volt energy range is an important study, as the particle detectors based on this interesting material are becoming commercially viable. In principal, although the low-energy (10–100 keV) and high-energy (2–200 MeV) ion irradiation are similar phenomena, there are subtle differences, however. For instance, in the case of low energy irradiation, the modifications in the properties mainly take place due to the nuclear energy loss (elastic processes) $S_n$. In contrast, the electronic energy loss $S_e$ (inelastic processes) of a fast moving heavy ion in a high-energy domain is a dominant source of modification of the properties of the material. As we were interested in studying the effect of irradiation of different ions on the film, we selected Au and Ag ions. The energy of the ions was selected such that the ions will penetrate totally (using SRIM calculation). This will reduce the effect of nuclear energy loss and we will be able to study the effect with respect to the electronic energy loss for different ions.

A few reports already exist on the influence of irradiation on the properties of diamond. Hunn et al. [1] observed additional Raman peaks at 1450, 1490 and 1630 cm$^{-1}$ after C$^+$ irradiation. It is believed that the peaks at 1450 cm$^{-1}$ correspond to a vacancy related defect and the peak at 1630 cm$^{-1}$ has been tentatively assigned to a split interstitials. Walker et al. [2] conjectured that these defects might be responsible for the compensation of carriers in boron (2 MeV and dose $1 \times 10^{15}$ ions) doped diamond. Similar Raman peaks as reported above were also observed [3] upon the irradiation with He$^+$ of dose $7 \times 10^{16}$/cm$^2$. Irradiation of diamond with 350 keV Sb ions resulted in the creation of point defects [4]. It is also observed that the irradiation of a-C:H films generally leads to hydrogen release from the films [5,6]. Efforts are in progress to understand some of the above and other results of ion irradiation in the films.

In this paper, we report the effects of high-energy heavy ion (Ag$^+$ and Au$^+$ of energy ≥100 MeV) irradiation on CVD diamond films. The films were grown at different deposition pressures leading to a range of
samples with very high (no graphitic impurities) to poor (high graphite impurities) quality. A host of measurements (SEM, Raman, XRD and PL) were performed on the samples prior to and after the irradiation to understand the phenomena. Some of these results are reported here.

2. Experimental details

The deposition of the films were carried out in a hot filament chemical vapor deposition (HFCVD) apparatus; its details are discussed elsewhere [7]. Mirror polished p-type Si (100) wafers were used as substrate. The substrates were treated with 2 μm diamond powder and cleaned ultrasonically in an acetone bath. Prior to the deposition, the film substrates were dipped in HF followed by de-ionized water cleaning in order to remove the passive oxide layer of silicon. The precursor gases for diamond deposition were methane and hydrogen at the flow rates of 1.6 and 200 sccm. The substrate temperature was measured at the center of the substrate and held constant for all depositions at 880 °C. The films, for the present study, were deposited at pressures 20, 60 and 120 Torr.

Self supported diamond sheets were prepared by making a window of diameter 6–7 mm in the center [8]. The films were irradiated with 100 to 130 MeV Au+ and Ag+ and doses ranging from $1 \times 10^{12}$ to $3 \times 10^{13}$ ions using 15UD Pelletron at NSC, New Delhi. The vacuum in the irradiation chamber was better than $2 \times 10^{-6}$ Torr. The structural characterization of the samples was carried out using X-ray diffraction, Raman spectroscopy and SEM for the films before and after irradiation. Raman spectra were recorded using an Ar+ laser on a JOBIN YVONNE spectrometer.

3. Results and discussion

SEM studies show that the sheets grown at lower $P_d$ contain sharp faceted crystallites, whereas blunt spherical crystallites are seen in the sheets grown at higher $P_d$. The non-diamond impurities increase in the sheets grown at higher $P_d$, resulting in loss of sharpness of the facets. XRD measurements (not shown) on the sheets show the presence of single-phase cubic diamond. The SEM pictures of the films grown at different pressures are shown in Fig. 1. A sharp Raman line at 1332.5 cm$^{-1}$ is observed in all the sheets. A broad band corresponding to the non-diamond impurities also
Fig. 2. SEM pictures of the sheets after irradiation (a) and (b) 20 Torr sheet irradiated with Ag ions (c) and (d) 120 Torr sheet irradiated with Au ions with dose $10^{13}$ ions/cm², (e), (f) and (g) images 120 Torr sheet irradiated with Au ions with dose $3 \times 10^{13}$ ions/cm² (h) 60 Torr sheet irradiated with Au ions with dose $3 \times 10^{13}$ ions/cm².
appears at 1500 cm$^{-1}$ in the sheets. It is observed that the sheets grown at lower $P_d$ contain negligible non-diamond carbon, whereas the sheets grown at higher $P_d$ contain a significant amount of non-diamond carbon impurities. The color of sheets also changes progressively from white to yellowish brown as the non-diamond content increases. This is in agreement with the concentration of hydrogen H in the samples. H contents as estimated by ERDA are found to be 0.18, 0.24, 0.36 and 0.64 at.% in the sheets grown at 20 Torr, 40 Torr, 60 Torr and 80 Torr, respectively.

Fig. 2a–h show the SEM pictures of the diamond sheet irradiated using various ions with different energies. We find that the damage in the samples as a result of irradiation depends on the quality of the samples, type of the ions and the ion dose. Fig. 2a,b show the results following irradiation using 100 MeV Ag$^+$ with the dose $10^{13}$ on a diamond sheet deposited at 20 Torr. As stated earlier, the sample shows very clean and sharp facets. After irradiation with Ag$^+$, the damage to the diamond crystallite is evident. However, no phase transition is visible on the surface of the crystallites. The heavy ions appear to attack the vortex of the crystallites. On an enlarged image, the sides of the facets appear to develop the rough patches that may indicate formation of non-diamond impurities. Similarly the sheets deposited at 60 Torr again show little or no damage when irradiated with 100 MeV Ag$^+$ (Fig. 2c,d).

In contrast, the damage caused by Au$^+$ beam of same energy and same dose appears much higher. Fig. 2e,f show the damage on a diamond sheets irradiated with a gold beam of 100 MeV and dose $10^{13}$. The damage on the surface is much more substantial when the dose of the beam increases to $3 \times 10^{13}$. The surface of the diamond sheets evidently has melted and flown and the clear smaller crystallites underneath the surface can be clearly seen (Fig. 2g,h). The extent of the damage in case of $3 \times 10^{13}$ dose is not reported elsewhere.

The Raman spectra of the samples before and after the irradiation are shown in Fig. 3a–d. We can observe clearly from all the figures that the intensity of the Raman signal decreases after irradiation. This may be due to the increased absorption of the sample because of the generation of the defects in the diamond. Another subtle change is that the sharp line corresponding to Raman $E_{2g}$ mode at 1332 cm$^{-1}$ is transformed to a broad band with its maximum lying at 1300 cm$^{-1}$. This transformation is common to the samples. In addition, a
strong band at a Raman shift 700 cm\(^{-1}\) is evident (Fig. 3c,d) in the samples irradiated with Au\(^+\) with a dose \(3 \times 10^{13}\). This band is new and has not been commonly seen in CVD diamond. In case of natural diamond, this becomes visible when the samples are irradiated with C\(^+\) of energy 4 MeV. The band is not visible in the antistokes side and, therefore, is a PL band.

The above results show interesting features in the irradiated diamond samples. As reported earlier in natural diamond, we fail to see the peaks at Raman shift 1451, 1498 and 1634 cm\(^{-1}\) upon irradiation. The difference, however, could be due to the fact that in present case the irradiation is by heavy ions and thus the electronic energy loss processes play a much important role. The electronic energy loss is higher for Au than Ag ions. This may explain the appearance of the PL band at 700 cm\(^{-1}\). The PL band is visible only in Au\(^+\) irradiated samples. Also, it is evident only in the samples containing higher quantity of non-diamond carbon. It is likely that the irradiation with heavy ions result in creation of a defect 10–15 of carbon cluster resulting in this band. However, a more detailed study is required. The shift and broadening of the Raman \(E_{2g}\) mode suggests the conversion of crystalline diamond to possibly sp\(^3\) bonded amorphous network.

4. Conclusions

We have studied the influence of heavy ion irradiation on the self-supported diamond sheets. The ions used were Ag\(^+\) and Au\(^+\), respectively. The energy and the ions was 100 MeV and its dose varied from \(10^{13}\) to \(3 \times 10^{13}\). The damage caused by Au\(^+\) beam was much more than Ag\(^+\) beam. The diamond Raman line at 1332 cm\(^{-1}\) is transformed to a broad band with maximum lying at 1300 cm\(^{-1}\) signifying a phase transformation in the sp\(^3\) bonded diamond network. A new PL band centered at 700 cm\(^{-1}\) is observed in the samples irradiated with Au ions of dose \(3 \times 10^{13}\). No additional Raman peaks were observed at 1451, 1498 and 1634 cm\(^{-1}\) as reported earlier in the case of natural diamond.

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References