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Applied Surface Science 115 (1997) 23–27

applied
surface science

Anomalous Auger electron spectroscopy results of chemical vapor deposited diamond (111) and (100) surfaces

Tarun Sharda ^a, D.S. Misra ^{a,*}, E.W. Seibt ^b, P. Selvam ^c^a Department of Physics, Indian Institute of Technology, Powai, Bombay 400 076, India^b Institut für Technische Physik, Forschungszentrum Karlsruhe, D-76021 Karlsruhe, Germany^c Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India

Received 15 August 1996; accepted 23 October 1996

Abstract

High resolution Auger electron spectroscopy was performed on (111) and (100) facets as well as on a microvoid of polycrystalline diamond films. Auger fine structure analyses of these facets indicate anomalous line shapes when electron beam was focused to about 0.2 μm diameter in contrast to the large area scans (beam size $\sim 10 \times 8 \mu\text{m}$) which exhibit a typical Auger pattern characteristic of diamond. This unusual behavior is discussed in terms of surface reconstruction which may occur due to Auger assisted desorption of hydrogen.

Diamond films have attracted considerable attention due to their unique characteristics. Recent upsurge in the growth of high quality polycrystalline diamond films originated in the development of chemical vapor deposition (CVD) techniques [1]. The mechanism of CVD diamond growth process [2–4], the surface characteristics and morphology [5,6] and the influence of hydrogen on various electrical [7], thermal [8] and structural properties [9] are some of the important issues being addressed presently. Raman spectroscopy, SEM [10], HREELS [11], TEM [12] and STM [6] studies have been carried out on (111) and (100) facets of these films. It is observed that (111) facets generally contain higher density of structural defects. In the present study, high resolution Auger electron spectroscopy

(HRAES) measurements were performed with an initial aim to investigate surface characteristics and environments of carbon atoms of different facets of the CVD diamond crystals. An inbuilt SEM in Auger spectrometer and a small size of the primary electron beam enabled us to select and analyze the (111) and (100) facets in details. Results of the above study along with AES depth profiles in the microvoids of the film, viz., non-diamond surface interface, are reported.

Diamond films were grown on Si (100) substrates by MPCVD technique using a gas mixture of 0.8 vol% methane in H_2 at a substrate temperature of 925°C and growth pressure of ≈ 40 Torr for 3 h. Details of the deposition parameters are reported elsewhere [4]. Films were systematically characterized by Raman spectroscopy, XRD, SEM and elastic recoil detection analysis (ERDA). A PHI multiprobe 600 (Perkin-Elmer) spectrometer equipped with SEM facility was used for HRAES measurements (e-beam: 10 keV, 200 nA, incident angle 51°; Ar^+ sputtering:

* Corresponding author. Fax: +91-22-5783480; e-mail: nirdesh@niharika.phy.iitb.ernet.in.

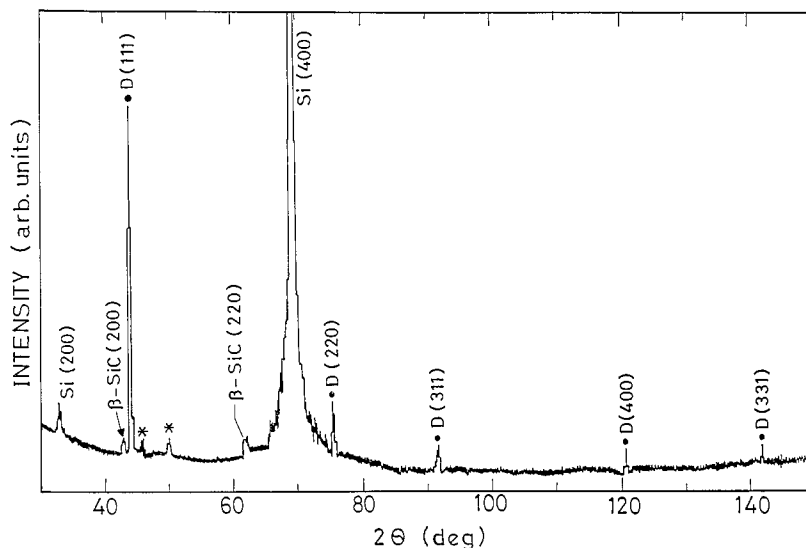


Fig. 1. XRD pattern of the diamond film. D denotes diamond and asterisk shows the peaks corresponding to other phases of SiC.

6 keV, 2.2 A m^{-2} , incident angle 45° , sputter rate 10 nm min^{-1}). Multiplex and sputter depth profile techniques were used with Perkin-Elmer small-spot duoplasmatron Ar^+ source for quantitative analysis. The Auger transition signals used in the measurements were; C (KLL; 270 eV), Si (LMM; 91 eV), O (KLL; 510 eV) and N (KLL; 381 eV). While the survey scans were performed on an area of $\approx 8 \times 10^{-11} \text{ m}^2$ ($10 \times 8 \text{ }\mu\text{m}$), the spectra on (111) and (100) facets were recorded using a beam spot size of $\sim 0.2 \text{ }\mu\text{m}$. Depth profiles of the respective facets, viz., square and triangular as well as the microvoids were also studied.

Fig. 1 is XRD pattern of the film. The obtained interplanar spacings corresponding to (111), (220), (311) (400) and (331) planes match well with cubic diamond which indicate a high quality film. Micro-Raman spectrum (Fig. 2) of the film shows a narrow line corresponding to the natural diamond at 1332 cm^{-1} (FWHM $\approx 9.5 \text{ cm}^{-1}$). A broad Raman signal at 1500 cm^{-1} indicates the presence of non-diamond carbon. Since Raman scattering is ~ 50 times higher for non-diamond carbon [13], the impurity content of the film may be very small. Fig. 3a shows SEM image of the film and indicates that it is dominated by the (111) oriented grains. Fig. 3b and c respectively show the (111) and (100) surfaces selected for

HRAES studies. In Fig. 3d, a microvoid was identified and further studies were carried out to understand the interface profiles.

Fig. 4 illustrates the typical Auger line shapes of different parts of the film. For a comparison, the spectra of the natural diamond and graphite [14] are also included in the inset. In the survey mode, in which an area of $\approx 8 \times 10^{-11} \text{ m}^2$ ($10 \times 8 \text{ }\mu\text{m}$) was scanned, the line shape of the Auger spectra (Fig. 4a) of the film is characteristic of diamond. In our opinion, this represents few of the best films reported

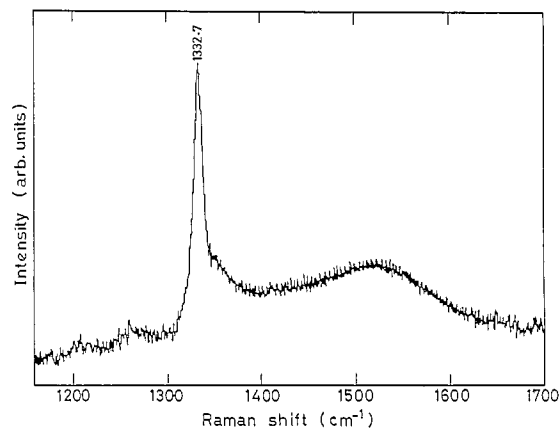


Fig. 2. Raman spectrum of the diamond film.

so far [15–17]. Four Auger transitions, viz., A_0 , A_1 , A_2 and A_3 are observed in the film. The positions of A_1 , A_2 and A_3 relative to A_0 , are shifted by 13, 27 and 33 eV, respectively. This compares very favorably with the results in natural diamond [14]. Auger spectra of the (111) and (100) facets (refer to Fig. 3b and c) of the same film were obtained by a beam spot size of $\sim 0.2 \mu\text{m}$ diameter and shown in Fig. 4b and c, respectively. In contrast to Fig. 4a, the line shapes of the latter is quite different and looks very much like graphite. The HRAES result on the microvoid (refer to Fig. 3d) of the film is shown in Fig. 4d. The line shape of the Auger spectrum in Fig. 4d is typical of SiC [18]. In agreement with Fig. 4d, the Auger depth profile (Fig. 5) of the microvoid indicates a non stoichiometric composition, $\text{Si}_x\text{C}_{1-x}$, with x varying with depth.

It is however, to be noted that such features were observed only when the electron beam was focused ($\sim 0.2 \mu\text{m}$ diameter). This indicates that a phase transformation either to graphite or a reconstruction of diamond surface may have taken place as a result

of the electron irradiation [19]. On the other hand, an interesting observation of the Auger fine structure analysis is the presence of characteristic plasmon features, viz., A_2 and A_3 in Fig. 4b and c, typical for diamond [14]. In addition, the half width of the main Auger peak (A_0) is nearly same ($\sim 6.5 \text{ eV}$) for all the spectra shown in Fig. 4a–c. Our conjecture is, therefore, that the Auger assisted desorption of surface hydrogen [19] may be taking place in the latter case because of an 3 orders increase in the electron current density. This in turn results in a surface reconstruction and hence may be a cause for the observed anomaly. Hydrogen depth profile of the film was obtained by ERDA and is illustrated in Fig. 6. The profile suggests that the CVD diamond films have hydrogen terminated surface. This observation is well supported by other techniques, such as HREELS, ESD, TPD and XPS [20–22].

A hydrogen terminated surface of diamond will be of (1×1) pattern. Hence, the Auger peak shape is characteristic of the diamond. The irradiation of (111) and (100) surfaces with higher electron beam



Fig. 3. SEM of the diamond film showing surface morphologies; (a) survey mode; (b) (111) facet; (c) (100) facet; (d) microvoid on which AES studies were performed.

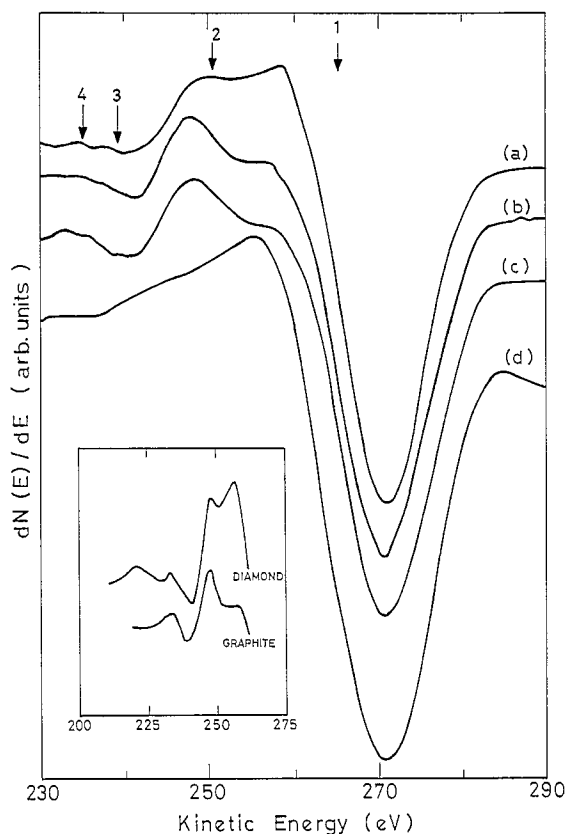


Fig. 4. Auger line shapes corresponding to Fig. 3, (a) survey mode (b) (111) facet (c) (100) facet (d) microvoid present on the sample. Arrows 1, 2, 3 and 4 correspond to Auger peak A_0 , A_1 , A_2 and A_3 respectively. Inset shows line shapes of the natural diamond and graphite taken from Ref. [14].

current density may result in a reconstruction to (2×1) pattern due to desorption of surface hydrogen via modified Knotek–Feibelman mechanism result-

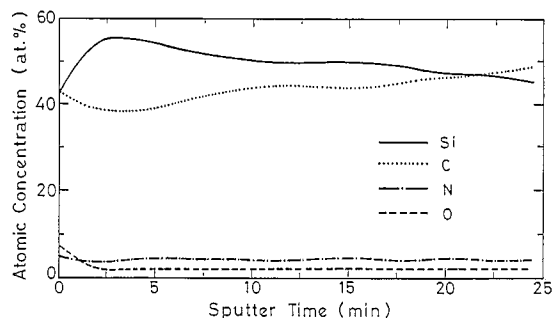


Fig. 5. Auger depth profile of the microvoid located on the surface of diamond film.

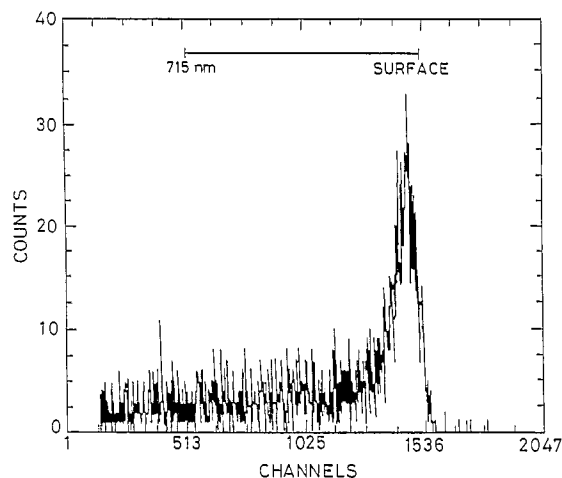


Fig. 6. Hydrogen recoil spectrum of the diamond film.

ing in π -bonded structures on the surface [19]. In this process, hydrogen desorption occurs due to ionization of $1s$ electron of the surface carbon atom (which is terminated with the same hydrogen) followed by a KV_1V_1 Auger transition which leaves the two-hole final state behind. Subsequently the dangling bonds on diamond surface may reconstruct as alternate seven membered and five membered rings resulting in π orbitals at surface as proposed by Pandey [23]. A similar reconstruction at the surface of our films may explain the observed anomaly of the Auger spectra in (111) and (100) oriented grains.

Alternatively, the presence of sp^2 bonded carbon shown by micro-Raman could also explain the above results if most of it existed at the surface. The Auger spectra obtained in large area scan mode in our samples (Fig. 4a), on the other hand, prove that amount of sp^2 bonded carbon on the surface of the films is very small. Only other possibility, then, is the presence of local sp^2 bonded carbon inhomogeneities exactly at the same location where the electron beam was focused. However, because similar results were obtained on many other films grown by MPCVD as well as hot filament CVD, such a possibility may be considered remote.

In conclusion, anomalous HRAES results are obtained on (111) and (100) facets of the diamond films grown by MPCVD. The results are explained on the basis of the surface reconstruction by KF-mechanism.

Acknowledgements

We acknowledge Dr. D.K. Avasthi and Mr. D. Kabiraj from NSC, New Delhi for ERDA measurements and Dr. H.D. Bist and Mr. S. Bhargava from IIT, Kanpur for Raman spectroscopy studies for the present work. We also acknowledge gratefully the financial assistance provided by the Board of Research in Nuclear Sciences, Department of Atomic Energy, Government of India for the above work.

References

- [1] P.K. Bachmann and H. Lydtin, in: *Diamond and Diamond-like Films and Coatings*, eds. R.E. Clausing, L.L. Horton, J.C. Angus and P. Koidl (Plenum Press, New York, 1991) p. 839.
- [2] S.J. Harris, *Appl. Phys. Lett.* 56 (1990) 2298.
- [3] W. Banholzer, *Surf. Coat. Technol.* 53 (1992) 1.
- [4] T. Sharda, D.S. Misra, D.K. Avasthi and G.K. Mehta, *Solid State Commun.* 98 (1996) 879.
- [5] K. Kobashi, K. Nishimura, Y. Kawate and T. Horiuchi, *Phys. Rev. B* 38 (1988) 4067.
- [6] Th. Frauenheim, U. Stephan, P. Blaudeck, D. Porezag, H.G. Busmann, W.Z. Edling and S. Lauer, *Phys. Rev. B* 48 (1993) 18189.
- [7] K. Baba, Y. Aikawa and N. Shohata, *J. Appl. Phys.* 69 (1991) 7313.
- [8] M.I. Landstrass and K.V. Ravi, *Appl. Phys. Lett.* 55 (1989) 1391.
- [9] T. Sharda, D.S. Misra and D.K. Avasthi, *Vacuum*, in press.
- [10] S.A. Stuart, S. Praver and P.S. Weiser, *Appl. Phys. Lett.* 62 (1993) 1227.
- [11] T. Aizawa, T. Ando, M. Kamo and Y. Sato, *Phys. Rev. B* 48 (1993) 18348.
- [12] W. Zhu, C.A. Randall, A.R. Badzian and R. Messier, *J. Vac. Sci. Technol. A* 7 (1989) 2315.
- [13] N. Wada and S.A. Solin, *Physica B* 105 (1981) 353.
- [14] P.G. Lurie and J.M. Wilson, *Surf. Sci.* 65 (1977) 476.
- [15] J.A. Martin, L. Vazquez, P. Bernard, F. Comin and S. Ferrer, *Appl. Phys. Lett.* 57 (1990) 1742.
- [16] B.R. Stoner, G.H.M. Ma, S.D. Wolter and J.T. Glass, *Phys. Rev. B* 45 (1992) 11067.
- [17] S.Y. Choi, C.J. Zhang and G.S. Lee, *Thin Solid Films* 206 (1991) 204.
- [18] A.J.V. Bommel, J.E. Crombeen and A.V. Tooren, *Surf. Sci.* 48 (1975) 463.
- [19] B.B. Pate, *Surf. Sci.* 165 (1986) 83.
- [20] S.T. Lee and G. Apai, *Phys. Rev. B* 48 (1993) 2680.
- [21] J. Wu, R. Cao, X. Yang, P. Pianetta and I. Lindau, *J. Vac. Sci. Technol. A* 11 (1993) 1048.
- [22] A.V. Hamza, G.D. Kubiak and R.H. Stulen, *Surf. Sci.* 237 (1990) 35.
- [23] K.C. Pandey, *Phys. Rev. B* 25 (1982) 141.