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SCANNING TUNNELING AND ELECTRONIC MICROSCOPY OF DIAMOND IRRADIATED BY HIGH ENERGY IONS

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1. INTRODUCTION

Utilization of ion tracks in solids has shown to be promising in future electronic applications[1]. Among potential applications the use of ion tracks in superhard semiconductors appears to be of interest for superdense nanosize electronic devices [2]. Recently it was predicted that tracks of heavy ions with energies of MeV/amu have relatively small lateral size in diamond [3], actually in the range of about a few nanometers. The tracks can be selectively doped with impurity atoms [4-5], and thus the doped ion tracks can reveal electronic properties. A model of ion tracks in super hard semiconductors has been proposed in [6]. In the schematic view of fig.1a the ion tracks are presented as rod-like macrodefects. According to this model the central core of a track consists of a significantly lower atom density compared with regular crystal matrix (in diamond this lack of density may have a value of up to 20%). Fig.1b shows this situation for a single track.

Ion tracks are specific defects of solids caused by high energy ion irradiation. The track formation mechanism and the parameters of the formed tracks are strongly controlled by the intensity of electronic stopping power of the fast ions in solids and by the characteristic properties of the irradiated substance.

The appearance of ion tracks has been unambiguously established in many insulating materials by different methods [7-8], including direct observation with high resolution electron microscopy [9]. The existence of ion tracks in superhard semiconductors has been shown by now only with indirect methods like luminescence or electron spin resonance (ESR)[10-11]. For further investigations it appears to be indispensable to prove the obtained data with direct methods. From this point of view the most interesting method is the scanning tunneling microscopy (STM). Firstly, the scanning tunneling microscopy gives opportunity to observe and investigate individual ion tracks on the irradiated surface with nm-scale resolution. Secondly, with this unique method it is possible to control individual ion tracks for potentiostatic measurements. In this presentation we report on the first results of the scanning tunneling microscopy from direct observation of ion tracks on diamond surface irradiated by high energy ions.

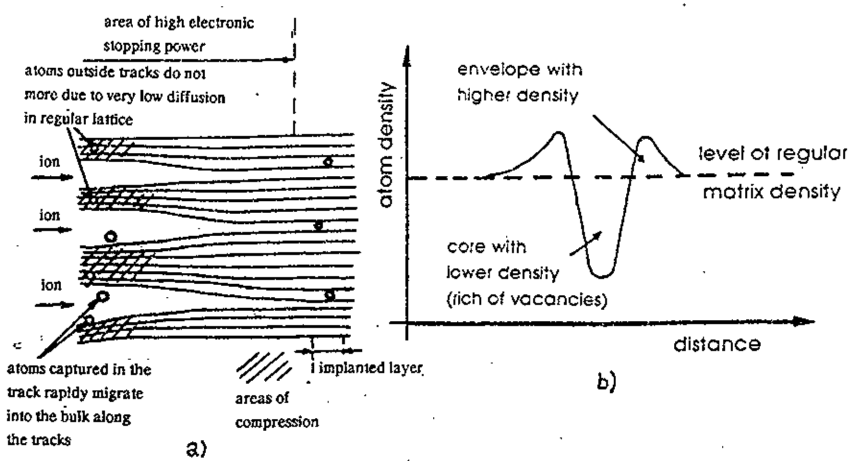


Fig. 1. a) scheme of tracks in solid matrix after irradiation by ions with energies over 1 MeV/amu;
b) suggested cross-section distribution of atom density inside the ion track.

2. EXPERIMENTAL

High pressure, high temperature synthetic boron doped diamonds were used for the investigations. The boron impurity in the crystals during growth from boron containing media was 0.5% of boron. This results in a specific resistance of about 3 Ω×cm. High energy irradiation of the samples by ^{84}Kr ions with an energy of 210 MeV and an ion fluence in the range of Ft=10^{12} ions/cm^2 was carried out exposing a [111] as-grown surface of a synthetic diamond crystal at the cyclotron U-400. The samples of natural diamonds were irradiated by ^{40}Ar (25 MeV) and ^{129}Xe (124 MeV) ions at the cyclotron U-300.

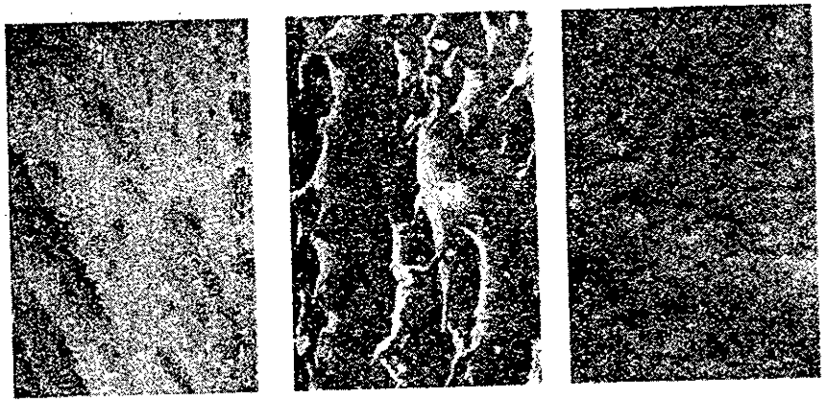
The samples have been investigated by the STM and SEM before and after irradiation with the high energy ions characterizing always the same macroscopic region of the surface. For the STM measurements no further treatment of the samples was necessary.

The SEM investigations were carried out with the use of scanning electronic microscope JSM-840. The resolution of this microscope is 40 Angstrem. The STM used for the investigations is a homebuild digitally controlled system equipped with a large scan option for imaging surface areas up to 22 µm x 22 µm [12,13]. The experiment is run at ambient pressure using mechanically prepared tips from thin Pt/Ir - wires. Atomic resolution of pyrolytic graphite (HOPG) was obtained probing the imaging conditions of the tips. Scan ranges from 1 nm x 1 nm up to 22 µm x 22 µm were used, registering only images reproducible for multiple scans of the same surface region. The bias voltage was about - 2.5 V at the sample and the tunneling current was 1.0 nA for all measurements. Imaging conditions for semiconductor surfaces investigated at ambient pressure have been tested with elemental and CVD-diamond films. The scanning speed used was in the range of about 500 nm/second to avoid charging effects at the surface. The evolution of the experiments included topographs as well as profiles and rms-roughness data of the surfaces.

3. RESULTS AND DISCUSSION

At the begining the amorphization of the semiconductor single crystals irradiated by different heavy ions was studied with the use of the back scattering technique (BST) [14-15]. The effect of low level amorphization of single crystals irradiated by the heavy ions with the high level of inelastic losses of energy was obtained. The same result was observed under the investigation of diamond single crystal, too[15]. For the understanding of this phenomenon we began the investigation of the diamond surface irradiated by different heavy ions.

The surface of diamond irradiated by ^{129}Xe and ^{40}Ar ions was investigated with the use of SEM technique. The energies of these ions are 124 MeV and 25 MeV. In fig.2 it is possible to see the surfaces of the natural diamond before (a) and after (b) irradiation by ^{129}Xe ions. The fluence was Ft= 5×10^{15} ion/cm^2. One can see that before the irradiation the diamond surface was a smooth one, but after the irradiation there are smooth and rough regions of the surface. The picture of the diamond surface after irradiation by ^{40}Ar ions differed in comparison with ^{129}Xe irradiation. It is clear from fig.2.c. In this case the ion fluence was Ft = 8×10^{15} ion/cm^2 and the structure of surface was totally amorphisized (the swelled type of the surface). In the case of ^{129}Xe ions the diamond conserved the crystaline structure, but in the case of ^{40}Ar ions the crystal was totaly amorphisized. This result was obtained with the use of BST [15]. Such differences may be connected with the evaporation of small diamond particles under the irradiation and then their condensation on the surface (see, for example [16]). The possibilities of thermal effects in ion tracks are discussed in ref. [17]. Another mechanism of inelastic sputtering of solids by ions was introduced in ref. [18].



a) b) c)

Fig.2. The SEM image of the the diamond surfaces before (a) and after irradiation by ^{124}Xe (b) (The ion fluence is Ft =5×10^{15} ion/cm^2) and ^{40}Ar (c) ions (The ion fluence is Ft = 8×10^{15} ion/cm^2).

STM-images of non-irradiated and irradiated by ^{84}Kr surfaces are presented in fig.3. Fig.3a shows a surface of 3820 A x 2319 A before treatment with the ion beam, the maximum height being 10.7 nm. The characteristic step shapes are shown on the flat surface, having a rms roughness of 0.2 nm. Fig.3b gives an example of the surface morphology after the irradiation. The scan range is 580 nm x 580 nm and the maximum height is 5.5 nm. It is clearly seen that the ion irradiation results in a strong roughening of the surface (rms values up to 9 nm). The irradiated surfaces appeared to have a lower conductivity compared to the untreated surfaces as probed by slightly different tunneling

conditions. The lowering of conductivity is due to implantation effects.

The profile of a characteristic region in fig.3b, that is given in fig.4, proves that the roughness of the surface is actually caused by individual pits. The density of pits covering the irradiated surface equals roughly the irradiation fluence (Ft≅10^{12}ion/cm^2). From this fact it is deducted that the pits are results of the ion impact onto the surface. The observed diameters of the pits start at about 3 nm rising locally to about 20 nm. From the diameter distribution of the pits and theoretical proposal of the ion track sizes we conclude that the 3 nm pits are caused by single ions, while greater pits are representing multiple ion impact at the same position on the surface. An interesting peculiarity of the track manifestation on the irradiated diamond surface has been observed. This is a very inhomogeneous areal distribution of the surface roughening. From fig.5 one can see that the swelling of the surface does not appear throughout the irradiated areas but forms some kind of cell structure where the swelled zones occur intermittently with relatively smooth zones. The boundary between these two types of zones may be very sharp. It covers an area of 125 nm x 125 nm and the maximum height is 1.1 nm. The observed inhomogeneous distribution of ion tracks cannot be explained by inhomogenity of ion irradiation since the irradiation has been carried out with a scanned ion beam. Moreover a plastic film which was irradiated simultaniously with the diamond samples as a reference sample showed quite uniform distribution of ion tracks. A possible reason for the inhomogenity resulting from the ion beam exposure that was found in the STM investigations is an inherent distribution of the local specific resistivity across the surface. To understand this the mechanism of track production by heavy ion bombardment should be mentioned. The ion track can be formed in a solid matrix by two mechanisms: thermal peak and coulomb explosion [19].

The thermal peak mechanism is effective in substances possessing thermal conductivity low enough to prevent rapid dissipation of the energy deposited along the ion path via electronic stopping. An estimation made in accordance with the model of the work in ref. [20] gives very low efficiency of the thermal mechanism in diamond because of its very high thermal conductivity.

The coulomb explosion mechanism appears to be much more effective in superhard semiconductors. Diamond being a very good insulator is able to keep electrically charged species in the crystal for a relatively long time. This time is believed to be long enough to allow the ionized atoms appearing during electronic stopping of fast ions to be pushed apart.

Obviously this mechanism of track production is inhibited in crystals of increased electrical conductivity promoting neutralization of the charged ions. Thus one can propose that the inhomogenity of the ion track distribution in synthetic diamond is based on spatial inhomogenity of the electrical conductivity and hence inhomogenity of the boron concentration. Such a submicron scale inhomogeneous distribution of boron in diamond might be understood quite easily due to the effect of morphological unsteadiness of the layer growth and anisotropy of boron incorporation by [111]- and [100]- pyramides during the growth process. Another reason for such phenomenon (inhomogenity of pit distribution on the surface) is connected with the limits of STM method.

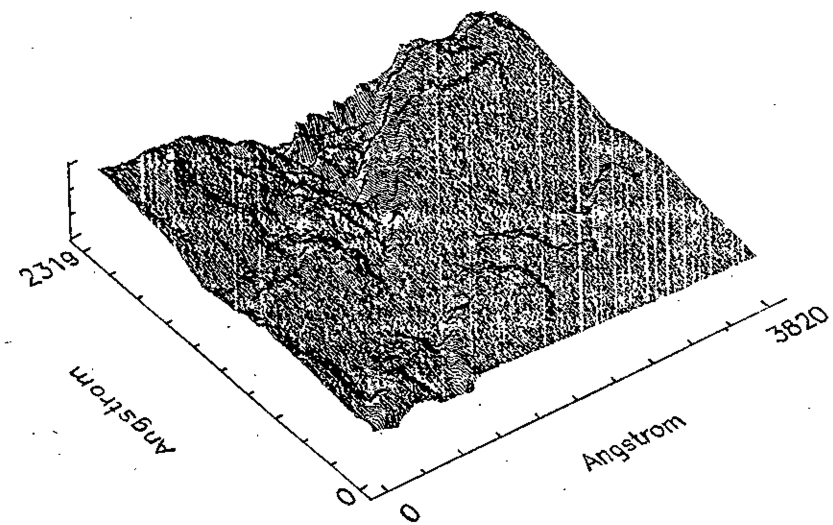


Fig. 3. a) surface of boron doped synthetic diamond before irradiation, the scanning area is 3820 A x 2319 A, height is 10.7 nm.

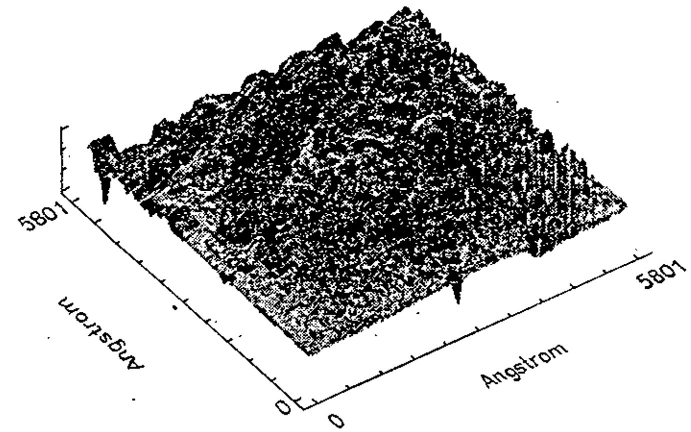


Fig.3. b) surface area of boron doped synthetic diamond after irradiation by heavy ions, 580 nm x 580 nm, height is 5.5 nm.

From this we can conclude, that for a homogeneous structering with heavy ions insulating (not boron doped) diamond surfaces should be exposed. This does not restrict the application of these structures for building electronic devices, as the ion tracks are doped after preparation, leaving the rest of the surface insulating allowing for higher threshold voltages.

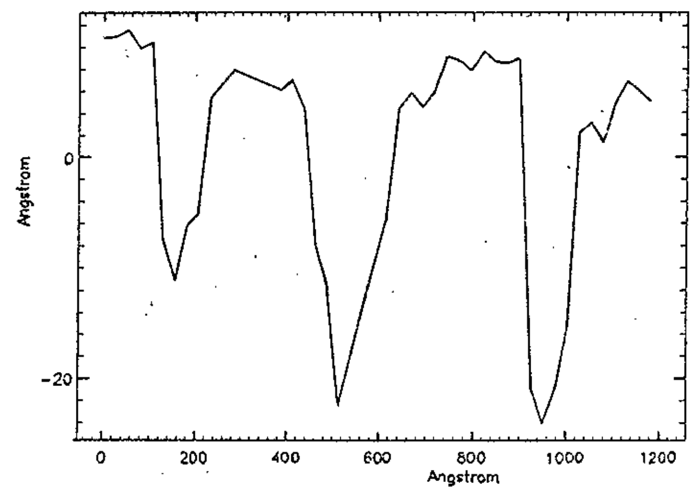


Fig. 4. Characteristic profile showing individual ion tracks.

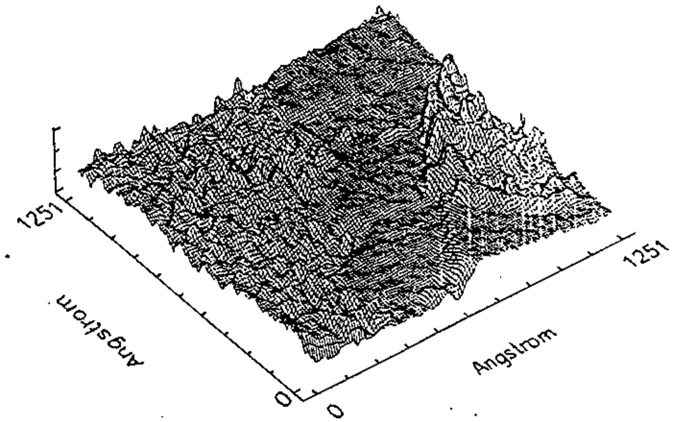


Fig. 5. Irradiated region of the diamond surface showing cell structure of damaged and non damaged area, 125nm x 125nm, height is 1.1 nm.

4. SUMMARY

The morphology of synthetic and natural diamond surfaces irradiated by high energy ions has been characterized by the use of scanning electronic and tunneling microscopy. The evaluation of topographs, profiles and rms-data of the irradiated and non irradiated surfaces has revealed the possibility of producing single ion tracks in the diamond. This is a basic need for structering synthetic diamond films to be used in nanoscale electronic devices with high mechanical and thermal stability. Boron doped diamond proved to have an inhomogeneous distribution of ion bombardment pits, obviously due to an inhomogeneous doping with boron. For homogeneous structering with heavy ions insulating diamond samples should be used.

The mechanism of pit formation in superhard semiconductors like diamond will be studied in more detail in future.

REFERENCES

1. A.M.Zaitsev. Material Science and Engeniering B11, p.179-190, 1992.
2. A.M.Zaitsev, A.A.Melnikov, V.S.Varichenko, V.F.Stelmakh, W.R.Fahrner, B.Burchard, D.Fink, E.H. te Kaat. Workshop VIKSI, Hahn-Meitner-Institute, Berlin (1992).
3. A.Yu.Didyk, V.S.Varichenko, A.M.Zaitsev, V.I.Kuznetsov, V.A.Skuratov, V.F.Stelmakh, V.D.Shestakov. JINR Commun. R14-86-411, Dubna (1986).
4. D.Fink, L.T.Chadderton, S.A.Cruz, W.R.Fahrner, V.Hnatowicz, E.H.te Kaat, A.A.Melnikov, V.S.Varichenko, A.M.Zaitsev. 2nd Int. Symp. on "Swift Heavy Ions in Matter", May 19-22 (1992), Bernsheim, Germany.
5. A.F.Burenkov, V.S.Varichenko, A.M.Zaitsev, F.F.Komarov, G.G.Konoplyanic, A.A.Melnikov, V.F.Stelmakh, V.V.Tkachev. Phys. Stat. Sol.(a) 115, p.427-435 (1989).
6. V.S.Varichenko, A.M.Zaitsev, A.A.Melnikov, V.F.Stelmakh. Sverhtverdye Materialy 1, p.3-8 (1989) (in Russian).
7. F.Thibaudau, J.Coustry, E.Balanzat, S.Bouffard. Phys.Rev.Lett. 67, p.1582-1585 (1991).
8. D.Albrecht, P.Armbruster, R.Spohr, M.Roth, K.Schaupert, H.Stuhrmann. Appl.Phys. A37, p.36-46 (1985).
9. J.M.Constantini, F.Ravel, F.Brisard, M.Caput, C.Cluzean. Nucl. Instrum. Meth. Phys. Res. B80/81, p.1249-1254 (1993).
10. A.R.Filipp, V.V.Tkachev, V.S.Varichenko, A.M.Zaitsev, A.R.Chelyadinskii, Yu.A.Kluev. Diamond and Related Materials, 1, p.791 (1989).
11. D.P.Erchak, V.G.Efimov, A.M.Zaitsev, V.F.Stelmakh, N.M.Penina, V.S.Varichenko, V.P.Tolstukh. Nucl.Instrum.Meth.Phys.Res.B69, p.443-451 (1992).
12. Th.Fries, C.Becker, M.Bohmer, K.Wandelt. Frenius J.Anal.Chem. 341, p.193 (1991).
13. Th.Fries. Thesis, University of Bonn (1993).
14. S.A.Karamyan, Yu.Ts.Oganessian, V.N.Bugrov. Nucl. Instr.& Meth. B43, p.153 (1989).
15. A.Yu.Didyk, A.M.Zaitsev, S.A.Karamian. JINR Rapid Commun. No.4[37]-89, p.44-49 (1989).
16. A.Yu.Didyk. JINR Commun., R14-94-333, Dubna, 13 p. (1994).
17. A.A.Davydov, A.I.Kalinichenko. Voprosu Atomnoi Nauki i Tecniki 3[36], p.27-29 (1985) (In Russian).

18. I.A.Baranov, Yu.V.Martynenko, S.O.Tsepelevich and Yu.N.Yavlinskii. Usp.Fiz.Nauk, v.156, p.477-511 (1988) (In Russian).
19. R.L.Fleicher, P.B.Price, R.M.Walker. In.: Nuclear Tracks in Solids, University of California Press, Berkely (1975).
20. L.E.Seiberling, J.E.Griftith, T.A.Tombrello. Rad.Eff.52, p.201-210 (1980).

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