

Available online at www.sciencedirect.com



Chemical Physics Letters 391 (2004) 56-59

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Spontaneous decrease of high surface electrical conductivity in diamond exposed to atmospheric air

Sławomir Kulesza *, Jaromir Patyk, Franciszek Rozpłoch

Zespół Fizyki Węgla, Instytut Fizyki, Uniwersytet Mikołaja Kopernika, Grudziądzka 5/7, 87-100 Toruń, Poland

Received 29 February 2004; in final form 21 April 2004 Available online 18 May 2004

Abstract

This Letter deals with spontaneous oxidizing of CVD diamonds exposed to room-temperature atmospheric air that is studied thanks to electrical measurements in a 2-point flat contact probe. Obtained results are explained in terms of the dipole model, which actually predicts accumulation of electrons in the oxidized films and hence should claim for its n-type conductivity. Unfortunately, the surface resistance is found to slightly increase under oxidizing. Generally, obtained data give evidence of usefulness of simple electrical measurements in studies of sorption-related processes in solids. © 2004 Elsevier B.V. All rights reserved.

Numerous experiments convince undoubtedly of the uniqueness of high surface electrical conductivity (HSEC) in hydrogenated diamonds considering especially those of CVD ones. It is commonly believed that there appears 100 nm thick accumulation layer in the subsurface region of hydrogen-passivated diamond structures that exhibits dominant p-type conductivity corresponding to holes with surface concentration of the order of 10^{13} cm⁻² and relatively low mobility of about $30-70 \text{ cm}^2/\text{V} \text{ s}$ [1,2]. Unfortunately, none of the HSEC generation mechanisms proposed so far has been found uncontroversial, although a number of works have concluded that hydrogen passivation onto the diamond's surface is necessary but not sufficient prerequisite to observe the HSEC and that physisorption of certain gaseous species must be also taken into consideration [3,4]. On that basis the so-called dipole model has been suggested [4], in which the subsurface diamond layer is penetrated by an electric field arising around adsorption-induced dipoles that makes possible accumulation of holes. Apart from that, the origin of the HSEC was independently derived from passivation of deep traps in diamond by hydrogen atoms [5], introduction of hydrogen-like shallow acceptor states [6],

etching of non-diamond carbon structures (i.e. graphitic and amorphic ones) by hydrogen plasma [7], or even creation a buried layer of acceptor traps [8].

Samples studied were hydrogenated diamond films grown from the mixture of hydrogen with small addition of propane–butane (not less than 96% vol. H₂) using commonly known hot-filament chemical vapor deposition method (HF-CVD) described in detail elsewhere [9]. The as-grown samples were mechanically cleaved to remove silicon substrates that results in free-standing, well-faceted 50–100 μ m thick diamond films, highquality of which was certainly confirmed by Raman spectroscopy together with scanning electron microscopy. In the course of storage under normal conditions, samples were permanently subjected to unintentional oxidizing caused by the oxygen being contained in the surrounding air. In the following, the very process is referred to as 'spontaneous oxidizing'.

Electrical characteristics were measured in a flat configuration using Keithley 6517 electrometer with a 2-point contact probe made from very thin platinum wire kept at a distance of approximately 3 mm. Let us note that evaporation of metallic contacts has been omitted and thereby both electrodes were pressed directly to the sample surface. Measurements were carried out either under normal conditions or in vacuum maintained by a standard rotational pump with a base

^{*}Corresponding author. Fax: +48-566225397.

E-mail address: colage@phys.uni.torun.pl (S. Kulesza).

^{0009-2614/\$ -} see front matter © 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.cplett.2004.04.075

pressure of 10^{-3} Torr. Temperature-dependent characteristics of surface resistance were recorded in vacuum maintaining rather slow heating rate of about 2 K/min from room temperature up to 600 K.

The dipole model relies on the different electronegativities of atoms at the diamond-adsorbate interfacial layer. According to the Pauling scale, carbon electronegativity amounts 2.5, while that of hydrogen is 2.1. This means the increased electron density distribution within the layer close to the crystal's surface. Therefore, given C-H bonds are to some extent ionic rather than purely covalent ones giving rise to the charge layer in which hydrogen atoms act as cations, whereas those of carbon are anions. Since the charge carriers are effectively separated by 0.11 nm, the dipole moments as high as 1.28×10^{-30} C m appear perpendicular to the diamond's surface that pre-induce subsurface hole accumulation region together with increase of the surface electrical conductivity. Moreover, recent electrical measurements [4] point out that the hole concentration in hydrogenated diamonds can be even raised due to physisorption of water molecules with relatively high dipole moment of 6.2×10^{-30} C m oriented parallel to that of C-H ones. In that manner effective dipole moment of the adsorptive coverage is composed of two parts, first of which is brought by stable hydrogen passivation, while the other one strongly depends on the number of water layers maintained by physical forces. This yields the surface hole concentration of 10^{13} cm⁻² [3] remaining, however, two orders of magnitude lower with respect to surface concentration of C atoms in diamond (slightly above 10^{15} cm⁻² depending on the crystal orientation).

In contrast, electronegativity of oxygen amounts 3.4 and hence it is considerably to expect that chemisorption of oxygen atoms in diamond should give rise to electric field within subsurface layer making possible accumulation of electrons. However, electron concentrations in wide-bandgap semiconductors are extremely low even in doped crystals so that adsorption of oxygen will lead solely to depletion of holes together with continuous decrease of electrical surface conductivity. As seen, the dipole model accounts well for observed restorable changes in the HSEC caused by sorption of H₂O molecules [4], permanent vanishing of the HSEC in strongly oxidized environments, and at last explains, why the HSEC cannot be observed whatsoever in hydrogenated, undoped crystals of silicon and germanium [10]. In such a case both elements exhibit equal electronegativity of 1.8 and hence their atoms once passivated by hydrogen can act as cations preventing accumulation of holes.

In Fig. 1 current–voltage characteristics of CVD diamond sample at normal conditions are shown that correspond to the as-grown diamond sample subjected for 90 min to plasma hydrogenation at substrate temperature 800 K under pressure of 30 Torr (solid circles) and Fig. 1. Current–voltage characteristics measured on nominally undoped CVD diamond surface under normal conditions (room temperature, atmospheric pressure) subjected for 90 min to hydrogen plasma treatment at substrate temperature 800 K and hydrogen pressure 30 Torr (closed circles) prior to exposure for 7 days to room-temperature atmospheric air (open circles). The plasma treatment is believed to remove non-diamond contaminations and to make the hydrogen passivation layer so that the diamond films closely resemble those in an as-grown state.

subsequently exposed for 7 days to room-temperature atmospheric air (open circles). Presented plots are consistent with the dipole model mentioned previously as to the fact that hydrogenation itself cannot induce surface conductivity in diamond of substantial amounts and that adsorption of gas species from atmospheric air results in pronounced increase of the conductivity within approximately four orders of magnitude. Moreover, the dominant charge transfer mechanisms can be established using the space-charge-limited current (SCLC) theory [11]. Indeed, I(V) curve of the as-hydrogenated sample presented in a log-log scale clearly exhibits two regimes of the current flow. The first one corresponds to ohmic conduction of thermally excited charge carriers in the range from 0 up to about 20 V, where straight line with the slope of 1 is evident. In turn, straight line with the slope of 2 extends over 20 V that defines charge carrier injection regime. Assuming given path geometry with cross-section area $S = 10^{-8}$ cm² and length L = 0.3 cm together with hole mobility $\mu_p = 50 \text{ cm}^2/\text{V} \text{ s}$ such a threshold voltage value yields relatively low hole concentration within accumulation layer of the order of 7.5×10^{15} cm³. With respect to that, I(V) curve of the air-exposed sample gives approximately four orders of magnitude higher hole concentration that, furthermore, remains ohmic in the whole range studied. This implies concentration of holes excited thermally being higher to those of injected ones.

Fig. 2 shows a plot of surface resistance of CVD diamond samples at normal conditions as a function of their prolonged exposure to room-temperature atmospheric air. As seen, the resistance slightly tends to



 10^{-2}



Fig. 2. Plot of the surface resistance variations against the storage time under normal conditions of the CVD diamond samples reflecting thereby the effect of spontaneous oxidizing. To the points straight line has been fitted with the slope of approximately $(10 \pm 6) \times 10^3 \ \Omega^3/$ month; let us note the logarithmic scale on the ordinate axis. Each of the surface resistance value corresponds to a mean one calculated for the given set of samples made and stored under identical conditions.

increase with elapsed exposure time. Such an effect has not been realized before that onto as-hydrogenated diamond surface brought in contact with the air the two concurrent processes are started simultaneously, namely physisorption of water molecules and chemisorption of oxygen atoms. The former is a short-term process that results in rapid hole accumulation and hence is responsible for the initial HSEC generation, whereas the latter is a rather slow process of degradation of the hydrogen passivation that in contrast accounts for hole depletion followed by long-term deterioration of the HSEC. Linear regression gives the decrease rate of the surface resistance of approximately $(10 \pm 6) \text{ k}\Omega/\text{month}$, which in a given current path geometry is equivalent to surface resistivity variations of about (0.3 ± 0.2) m Ω cm/ month. Actually, exponential function should be far advantageous here, but due to substantial scattering of the points in Fig. 2 appropriate fitting procedure could not be completed. The scattering is associated largely with current path length variations depending in fixed probe geometry on a film roughness.

Apart from the long-term HSEC deterioration discussed previously, the detrimental effect of the oxygen implies changes within the adsorbate coverage structure that can be investigated using electrical measurements as well. To this end, temperature-dependent characteristics of surface resistance of as-grown CVD diamonds spontaneously oxidized by room-temperature atmospheric air for, respectively: 3, 33 and 57 months, were collected and drawn in Fig. 3 in the form of Arrhenius plots. Actually, straight line with the slope corresponding to the activation energy of the conductivity is to be expected herein; however, as seen in Fig. 3 each curve is of rather complicated shape. In general, at least two



Fig. 3. The surface resistance against temperature characteristics of the same untreated CVD diamond sample (measured in vacuum of 10^{-3} Torr) at different stages of its spontaneous oxidizing under normal condition for, respectively: 3, 33, and 57 months. Room-temperature surface resistance substantially increases with elapsed time. Apart from that, two distinct resistance peaks are observed, first of which disappears, whereas the second one sharpens in the course of spontaneous oxidizing.

distinct surface resistance peaks are evident at approximately 310 and 435 K, that is at thermal excitation energies of about, respectively, 27 and 38 meV. As in Fig. 2, the room-temperature surface resistance of CVD diamond markedly increases under spontaneous oxidizing, and furthermore the peak centered at 310 K gradually vanishes, whereas that at 435 K becomes in contrast much more distinct.

To explain such an evolution, low-rate exchange of adsorbed gaseous species in the same vicinity of the crystal must be taken into consideration that involves activated desorption of hydrogen in the presence of oxygen atoms followed by chemical adsorption of oxygen. Thus, the sp³-hybridization of surface carbon atoms is no longer sustained by hydrogen atoms solely, but also by oxygen ones. Apart from relatively low temperature of about 300 K of the spontaneous oxidizing, the rate of this process is considerably limited by the valency of adsorbed species. In fact, hydrogen atoms form single bonds once chemisorbed onto diamond, while to entirely adsorb those of oxygen, two neighboring carbon atoms with dangling bonds are required. In such a case, however, re-hybridization of surface carbon atoms would be possible resulting in higher contribution of non-diamond impurities that would inevitably cause the surface resistance falling down unlike it is seen in Figs. 2 and 3. Therefore, no neighboring carbon atoms with dangling bonds are allowed at the same time. Hence, oxygen adsorption presumably proceeds as a two-step process, in which the appropriate bonds are formed independently. To corroborate such a reaction path, however, additional measurements must be carried out (e.g. ESR).

Peaks in surface resistance shown in Fig. 3 can be explained making use of the dipole model, in which the two contrary processes are considered, namely intense desorption of gaseous species accompanied by thermal generation of charge carriers. This concerns, however, physisorbed species solely, taking account into relatively low energies of the thermal excitations. The coverage made of adsorbed gases resembles to a certain extent a two-dimensional system, where phase transformations take place similar to those of ordinary three-dimensional systems. Along with increasing temperature, the coverage gets progressively disordered and even damaged once still gas molecules become free to move along the surface and then they start to desorb. This results in variations of the given accumulation layer geometry that has a detrimental influence on the current flow and hence gives rise to observed surface resistance increase. Fig. 3 shows, however, that this depends on the coverage thickness since disorder within layer closer to the crystal surface is found to induce the higher peak.

In summary, there are experiments on spontaneous oxidizing of hydrogenated diamond surfaces described in this Letter. Obtained results are explained in terms of the dipole model, according to which chemisorption of hydrogen atoms with electronegativity lower than that of carbon pre-induces accumulation of holes in the subsurface region of diamond. Similarly, accumulation of electrons should be possible due to chemisorption of oxygen that subsequently would give rise to n-type conductivity in diamond. Unfortunately, such an assumption is no longer valid since the surface resistance is found to monotonically increase under oxidizing. Hence, this reflects depletion of holes on account of low concentration of free electrons in wide-bandgap semiconductors. Moreover, asymmetry in charge carrier injection from contacts might be relevant to that effect as

well because injection of holes proceeds actually as withdrawal of electrons. Regardless, problems concerned with generation of n-type conductivity in diamond remain open. As to potential diamond applications in microelectronics, spontaneous oxidizing along with the HSEC degradation is found undesirable since it makes active devices defective. Another limiting factor is that the HSEC in diamond rapidly vanishes at elevated temperatures even if kept in vacuum. In spite of that electrical measurements described in this Letter make a great opportunity to give insight into subtle surface processes unavailable for other methods (e.g. Raman spectroscopy).

Acknowledgements

Authors acknowledge Mr. Zbigniew Polakowski for his valuable technical support.

References

- K. Hayashi, H. Watanabe, S. Yamanaka, T. Sekiguchi, H. Okushi, K. Kojimura, Diamond Relat. Mater. 6 (1997) 303.
- [2] H.J. Looi, L.Y.S. Pang, A.B. Molloy, F. Jones, J.S. Foord, R.B. Jackman, Diamond Relat. Mater. 7 (1998) 550.
- [3] F. Maier, M. Riedel, B. Mantel, J. Ristein, L. Ley, Phys. Rev. Lett. 85 (2000) 3472.
- [4] S. Kulesza, F. Rozploch, Diamond Relat. Mater. (in press).
- [5] M.I. Landstrass, K.V. Ravi, Appl. Phys. Lett. 55 (1989) 1391.
- [6] K. Hayashi, S. Yamanaka, H. Okushi, K. Kojimura, Appl. Phys. Lett. 68 (1996) 376.
- [7] Y. Mori, Y. Show, M. Deguchi, H. Yagi, H. Yagyu, N. Eimori, T. Okada, A. Hatta, K. Nishimura, M. Kitabatake, T. Ito, T. Hirao, T. Izumi, T. Sasaki, A. Hiraki, Jpn. J. Appl. Phys. 32 (1993) L987.
- [8] A. Denisenko, A. Aleksov, A. Pribil, P. Gluche, W. Ebert, E. Kohn, Diamond Relat. Mater. 9 (2000) 1138.
- [9] F. Rozpłoch, S. Kulesza, J. Patyk, W. Bala, P. Borowski, Polish J. Appl. Chem. 2–3 (2000) 81.
- [10] Y. Saito, M. Aomori, H. Kuwano, J. Appl. Phys. 81 (1997) 754.
- [11] M.A. Lampert, Rep. Prog. Phys. 27 (1964) 329.