Influence of adsorbates on the surface conductivity of chemical vapor deposition diamond

M. Szameitat[a] and X. Jiang
Fraunhofer-Institut für Schicht- und Oberflächentechnik, Bienroder Weg 54e, 38108 Braunschweig, Germany

W. Beyer
Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich, 52425 Jülich, Germany

(Received 6 June 2000; accepted for publication 17 July 2000)

To investigate the mechanism of the diamond surface conductivity, temper experiments have been performed on chemical-vapor-deposited (CVD) diamond films under vacuum conditions. The surface conductivity of these films was measured as a function of temperature and in contact with different gas atmospheres. These results were compared with those obtained by gas evolution experiments performed on CVD diamond samples of the same kind, demonstrating the possible role of CO adsorption to the surface conductivity. © *2000 American Institute of Physics.* [S0003-6951(00)03436-7]

The surface conductivity of chemical-vapor-deposited (CVD) diamond is a well-known phenomena. It is of *p*-type character and appears only on hydrogen-saturated diamond surfaces. The increasing interest on the investigation of diamond surface conductivity is due to the fact that, in many electronic applications, it contributes to the bulk conductivity which influences the performance in most cases negatively. On the other hand, it was possible to use hydrogenated diamond surface to fabricate field-effect-transistor structures.[1] The mechanism of this kind of conductivity is still under controversial discussion. Experimentally it was found that, on diamond surfaces which were treated with an oxygen plasma, the surface conductivity vanishes. For this reason, it was proposed that hydrogen at the diamond surface promotes the formation of gap states which act as shallow acceptors leading to *p*-type diamond.[2,3]

In our laboratory, it has been observed that the surface conductivity of hydrogen-terminated diamond decreases slightly after the sample is put into vacuum. But much more dramatically dropped the conductivity after the sample had been annealed in vacuum to 572 K and then cooled down to 294 K. The resulted change in resistance was several orders of magnitude. After annealing in vacuum and bringing the sample in contact with atmospheric air the surface conductivity increased slowly to its former value. This finding provides us with strong evidence that the hydrogen termination with a desorption temperature over 1320 K[4] alone cannot result in such conductivity. Additional surface adsorption must be taken into account.

To study the influence of adsorbed gases on the surface conductivity of hydrogen-terminated diamond we performed annealing experiments in vacuum, brought the annealed diamond surface in contact with several gases, and performed gas evolution experiments. The dependence of the temperature on the desorption of adsorbates and on the surface conductivity of an untreated, hydrogen-terminated CVD diamond indicats that CO species adsorbed on hydrogen-terminated CVD diamond surfaces might be responsible to the surface conductivity.

Diamond films were grown by microwave plasma CVD on 2 in. *p*-type silicon wafers starting with a bias enhanced nucleation process. The as-grown diamond surface is hydrogen terminated. The diamond films are undoped and has a thickness of about 3 μm. They are of polycrystalline structure and some [001] textured character. The wafer was cut into four pieces for different experiments. For measuring the electrical conductivity two samples were contacted with carbon glue. The contacts on each sample are two parallel stripes. The ratio of stripe length to their distance is about 10. One contacted piece was mounted on a sample holder close to a Pt 100 thermoelement. The sample was heated up to 572 K under vacuum (<0.1 mbar, Baratron) at a heating rate of 10 K per minute and then cooled down to 294 K. In both heating and cooling periods the resistance of the sample was measured simultaneously. After cooling the sample different gases were introduced separately into the chamber and the resistance of the sample was measured as a function of time. These gases were hydrogen, nitrogen, methane, carbon dioxide, synthetic air (79% nitrogen, 21% oxygen), water vapor, mixtures of water vapor and carbon dioxide or synthetic air, and atmospheric air. After each of these adsorption experiments the sample was heated up to 572 K in vacuum again and cooled down to room temperature.

To study the surface adsorption and the desorption phenomena in dependence of the temperature gas evolution experiments were performed on not contacted samples. For a comparison to the hydrogen-terminated samples some samples were treated in an oxygen electron cyclotron resonance plasma for 2 min time. To control the influence of the backside of the samples (silicon) a bare silicon piece of similar size was also examined. For the gas evolution experiments the samples were inserted into a quartz tube evacuated by turbomolecular pump. The samples were heated to 672 K at a heating rate of 20 K/min. The partial pressure of several masses was monitored by a quadrupole mass analyzer. For

[a]Electronic mail: szameitat@ist.fhg.de

TABLE I. List of the analyzed masses in the gas evolution experiments and the corresponding species.

Mass	Specie	Mass	Specie	Mass	Specie
2	H_2	16	O, CH_4	32	O_2
4	He	17	OH, NH_3	41	
12	C	18	H_2O	44	N_2O, CO_2
14	N, CH_2	28	N_2, CO	48	O_3
15	CH_3	30	NO		

fixed pumping speed of the turbomulecular pump the partial pressure is a measure of the evulotion rate dN/dt. In a first run all masses up to 50 u were detected and then those selected which showed a signal. Table I shows a list of the analyzed masses and the corresponding species.

The contacts of the untreated sample show ohmic character as the current–voltage characteristic is a straight line. The resistance between the contacts is about 300 kΩ. The sample which was treated in an oxygen plasma has a resistance higher than 2000 MΩ.

The temperature dependence of the conductivity for the untreated sample under vacuum is shown in Fig. 1(a). During pumping down to the ultimate pressure (<0.1 mbar) of the chamber the resistance increased to around 500 kΩ. Heating the sample from room temperature to 377 K the resistance slightly falls reaching a local minimum of 446 kΩ. Continuing heating up the sample the resistance reaches a local maximum of 1523 kΩ at 475 K. Increasing the temperature the resistance of the sample decreases continuously. At the maximum temperature of 563 K it is 113 kΩ. Cooling down the sample the resistance increases continuously. At temperature of 390 K, the resistance is 1054 MΩ. Keeping this sample at room temperature under vacuum the resistance remained higher than 2000 MΩ.

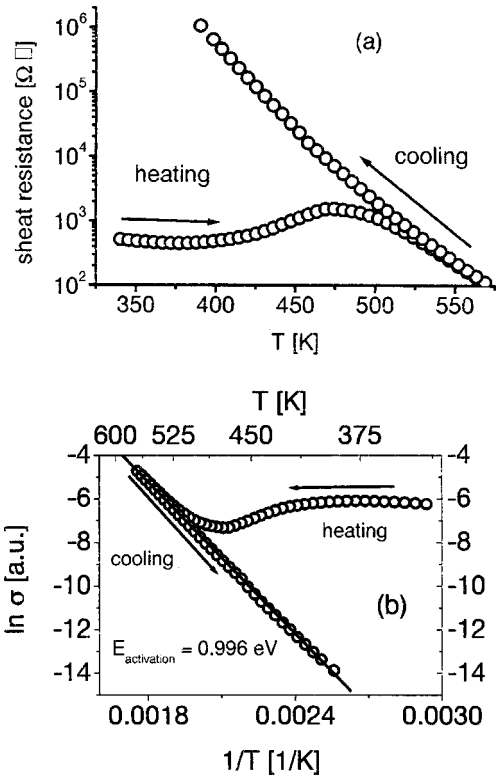

FIG. 1. (a) Sheat resistance vs temperature of a hydrogen-terminated CVD diamond film heated up and cooled down under vacuum. (b) Arrehnius plot of the same data.

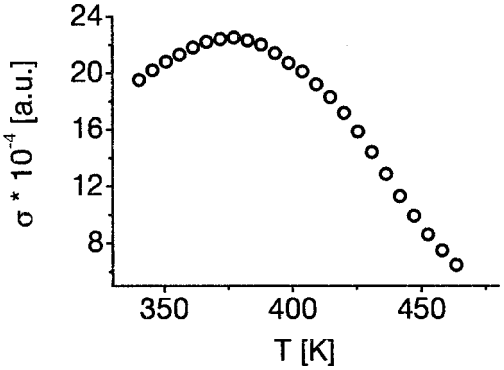

FIG. 2. Surface conductivity vs temperature of a hydrogen terminated CVD diamond film heated up under vacuum.

Figure 1(b) is an Arrehnius plot of the data in Fig. 1(a). Form this plot an activation energy of $E_{\text{activation}}=0.996$ eV can be derived. This value corresponds very well to activation energies of 0.9, 0.93, and 0.85 eV reported in Refs. 5–7, respectively, for oxygenated undoped CVD diamond. Keeping the sample under vacuum and heating it up again the only charge carrier, which contributes to the conductivity, had an activation energy of 0.996 eV.

Subtracting the conductivity arising from this activation from the total conductivity one obtains the surface conductivity as a function of temperature shown in Fig. 2. From this diagram it can be seen that the surface conductivity increases in the beginning of the heating period, reaches its maximum at 377 K and then falls continuously. Converting these diagram in an Arrhenius plot an activation energy of the surface conductance of 0.055 eV can be evaluated.

After the sample was cooled down different gases were introduced separately into the chamber at a pressure of 100 mbar. In the case of hydrogen, nitrogen, methane, carbon dioxide, synthetic air (79% nitrogen, 21% oxygen), water vapor (21 mbar), and mixtures of water vapor and carbon dioxide or synthetic air the resistance of the surface remained after 100 min over 2000 MΩ. Then each experiment was aborted and the sample heated up to 572 K in vacuum again. Exposing the sample at room temperature to atmospheric air at a pressure of 100 mbar, the resistance decreased significantly after 5 min. This experiment lasted 976 min thereafter the resistance dropped down to 3.86 MΩ as Fig. 3 shows.

For almost all species the gas evolution spectra of the

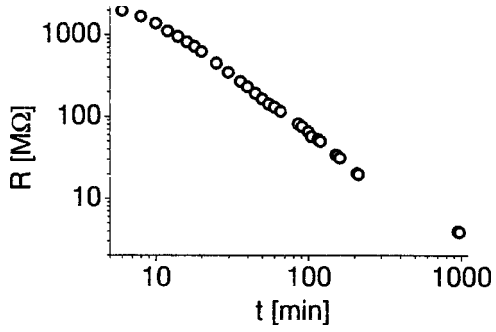

FIG. 3. Resistance of a hydrogen-terminated CVD diamond film vs exposition time to atmospheric air at 100 mbar. Before the exposition to air the sample was heated up to 572 K and cooled down to 292 K under vacuum.

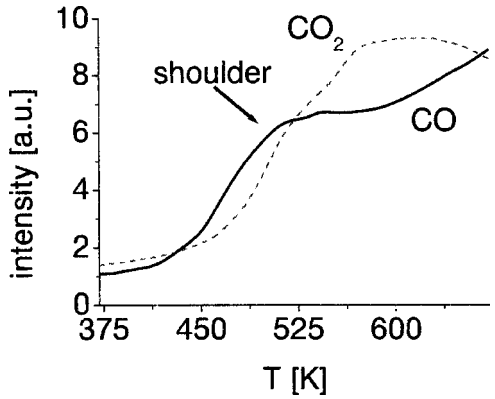

FIG. 4. Gas evolution spectra of a hydrogen-terminated CVD diamond sample.

hydrogenterminated diamond surface showed no specific features in the region from 373 to 672 K, except for CO (mass 28 u) and CO_2 (mass 44 u), which are shown in Fig. 4. Between 430 and 600 K the CO spectrum shows a shoulder, which indicates a higher effusion rate. A similar behavior shows the CO_2 spectra, which shoulder starts at a temperature of about 470 K and seems to end over 670 K. In this temperature range the spectra of both masses are in the same order of magnitude. The gas evolution spectra of the oxygen-terminated diamond surface showed almost the same behavior.

Our experiments show that the surface conductivity of hydrogen-terminated CVD diamond is induced by adsorbates. The adsorbates lead to the formation of states, which are ionized by a very little activation energy less than 0.1 eV. Once a diamond sample is put into vacuum they start to desorb. Hence, less states are induced at the diamond surface and the conductivity of the surfaces decreases. Heating up the sample this process is accelerated. At low temperatures this process is encountered by the ionization of more charge carriers within the diamond surface being induced by the adsorbates. For this reason the conductivity increases slightly with raising temperature at low temperature range reaching in this experiment its maximum at 377 K. At higher temperatures the loss of charge carriers becomes the dominant process as more and more adsorbates desorb and less states are induced at the diamond surface. Hence, the conductivity is decreasing. Continuing heating up the sample carriers of the diamond bulk are ionized with an activation energy of about 1 eV. They become the major charge carrier and the conductivity of the sample is increasing again. Cooling down the sample they are frozen in and the conductivity decreases. As there are no adsorbates on the samples surface (they are all desorbed) the freezing in of bulk charge carriers is the only process which influences the conductivity of the sample. For this reason the cooling data in Fig. 1(b) are a straight line and show the typical behavior of charge carriers of a not degenerated semiconductor.

Once the adsorbates are removed the hydrogen-terminated diamond conductivity versus temperature characteristic behaves as it is reported of an oxidized diamond surface and shows no surface conductivity at room temperature. Exposing the sample to atmospheric air the surface conductivity recovers very slowly indicating that the species, that causes the surface conductivity on hydrogen-terminated diamond, must be very rare in air. Therefore, it is not surprising that the diamond surface conductivity is not sensitive to nitrogen (78% in atmospheric air), synthetic air (79% nitrogen, 21% oxygen, oxygen content in air 21), carbon dioxide (0.034% in atmospheric air).

Gas evolution spectra in the temperature range between 372 and 672 K show that both diamond surfaces (the hydrogen terminated and the oxygen terminated) effuse in the same manner. The shoulders in the CO spectra is due to a desorption peak between 430 and 600 K indicating a higher desorbtion rate.

As the contribution of CO_2 to the conductivity can be rolled out from our study these spectra indicate that carbon monoxide might be involved to the surface conductivity of hydrogen-terminated diamond is induced by. Although the gas evolution spectrum shows a shoulder for CO starting at 430 K while the drop in conductivity occurs in our experiments at a temperature of 380 K, this miss fit was, however, originated in the different heating rates. The heating rate of the gas evolution spectra were twice of the annealing experiment, in which the samples conductivity versus temperature was obtained. Therefore the gas evolution spectra show a delay in temperature.

The oxygen-terminated diamond surface is not conducting, although the same species are adsorbed on it as the gas evolution spectra show. The mechanism, which leads to the formation of charge carriers in a hydrogen-saturated diamond surface but not in an oxygen-saturated diamond surface, is still unclear. It might be a result adsorbates on an oxygen-terminated surface induces other surface states, which are not ionized at low temperatures.

In conclusion, for a better understanding of the mechanism of diamond surface conductivity temper experiments have been performed on CVD diamond films under vacuum conditions and in contact with different gas atmospheres. These results show that the surface conductivity of hydrogen-terminated diamond surfaces is induced by adsorbates. Gas evolution experiments demonstrating the possible role of CO adsorption to the surface conductivity.

[1] A. Hokazono, T. Ishikura, K. Nakamura, S. Yamashita, and H. Kawarada, Diamond Relat. Mater. **6**, 339 (1997).
[2] H. J. Looi, L. Y. S. Pang, A. B. Molloy, J. S. Foord, and R. B. Jackmann, Diamond Relat. Mater. **7**, 550 (1998).
[3] K. Hayashi, H. Watanabe, S. Yamanaka, T. Sekiguchi, H. Okushi, and K. Kajimura, Diamond Relat. Mater. **6**, 303 (1997).
[4] I. I. Arkhipov, B. V. Spitsyn, A. E. Gorodetsky, A. P. Zakharov, G. Popvici, T. Sung, M. A. Prelas, and S. Khasawinah, Diamond Relat. Mater. **5**, 121 (1996).
[5] J. Shirafuji and T. Sugino, Diamond Relat. Mater. **5**, 706 (1996).
[6] Y. Muto, T. Sugino, J. Shirafuji, and K. Kubashi, Appl. Phys. Lett. **59**, 843 (1991).
[7] P. Gonon, A. Deneuville, E. Gheeraert, and F. Fontaine, Diamond Relat. Mater. **3**, 654 (1994).