

Surface band bending and surface conductivity of hydrogenated diamond

D. Takeuchi,* M. Riedel, J. Ristein, and L. Ley

Institut für Technische Physik II, Universität Erlangen-Nürnberg, Erwin-Rommel-Strasse 1, Erlangen, D91058 Germany

(Received 13 May 2003; published 11 July 2003)

We establish a strict correlation between the total photoelectron yield spectra and the surface conductivity of hydrogenated diamond. The decomposition of the yield spectra into electron and exciton derived contributions requires an upward surface band bending to accompany surface conductivity, while an essentially flat band or downward band bending is observed after removing the surface conductivity by annealing in vacuum. Between the two competing models proposed for surface conductivity with a sheet hole density of 10^{13} cm^{-2} , these results favor the surface transfer-doping model strongly over the subsurface acceptor model.

DOI: 10.1103/PhysRevB.68.041304

PACS number(s): 73.25.+i, 72.20.Jv, 79.60.-i, 81.05.Uw

Diamond with a band gap of 5.5 eV is a bona fide insulator in its undoped state and yet it exhibits a pronounced *p*-type surface conductivity (SC) provided the surface is terminated by hydrogen.^{1,2} The SC reaches values as high as $10^{-5} \text{ S } (\Omega^{-1})$ per square, independent of whether diamond is in the form of single crystals or polycrystalline films prepared by chemical vapor deposition. This SC is unique among all semiconductors and insulators and it has already been utilized for a variety of device applications such as Schottky diodes,³ field effect transistors,^{4,5} and pH sensors.⁶ The phenomenon is based on a surface-near hole layer with a concentration of the order of 10^{12} – 10^{13} cm^{-2} that shows little temperature dependence and thus requires acceptors that are very shallow above, or even degenerate with, the valence band.^{7,8}

Despite the exceptional nature of SC on diamond, there is no clear understanding of the nature of the doping mechanism that leads to the surface-near hole layer. Such an understanding is, however, highly desirable in order to be able to exploit fully the considerable potential of SC for applications.

There are currently two competing models which have been proposed. Based on the strong dependence of SC on ambient conditions, Maier *et al.* have elaborated former ideas of Ri *et al.*⁹ and suggested an electrochemical surface transfer-doping mechanism for which solvated ions on the surface play the role of effective acceptors.¹⁰ In this model electrons are transferred from diamond to a ubiquitous water layer where they neutralize hydronium ions. Overall charge neutrality is maintained by the negatively charged anions which remain in the water layer and are indicated as effective acceptors *A* in Fig. 1(a). In general, SC persists even in vacuum as long as the anions remain on the surface. Annealing in vacuum ($\geq 200^\circ \text{C}$) removes the anions and erases the SC. The complete process is reversible upon air exposure.

On the other hand, the junction properties of Schottky contacts and metal-semiconductor field effect transistors realized on diamond with SC have been explained in terms of a heavily *p*-doped surface layer. The layer requires conventional but as yet undefined very shallow acceptors with a density N_A between 10^{18} and 10^{19} cm^{-3} situated within a few nanometers below the surface.⁸ The influence of adsorbates on the SC can be reconciled with this model by assum-

ing permanent surface defects that lead, in the absence of adsorbates other than hydrogen, to a surface-near hole depletion layer [Fig. 1(b)].¹¹

Both models predict a substantially different surface band diagram, as shown in Fig. 1, that allows their distinction on the basis of the present results.^{9–12} In all the cases we are dealing with a fully hydrogenated diamond surface with negative electron affinity (NEA)^{13,14} and the only difference between the high conducting and low conducting state is the presence or absence of the surface acceptors labeled *A* in Fig. 1.^{9–11,15} The left-hand side of the band diagram refers, in each case, to the asymptotic situation inside the bulk of our specimens corresponding to a Fermi-level position E_F about 0.3 eV above the valence-band maximum E_V for the boron-doped type IIb crystal¹⁶ or deep in the gap for nominally undoped IIa crystals.

The surface transfer-doping model [Fig. 1(a)] is conceptually rather simple in terms of band bending. The negatively charged anions *A* balance the excess holes accumulated in the diamond. When they are removed by thermal annealing the hole accumulation disappears simultaneously, as required by overall charge neutrality, leading to flat band condition and low SC.

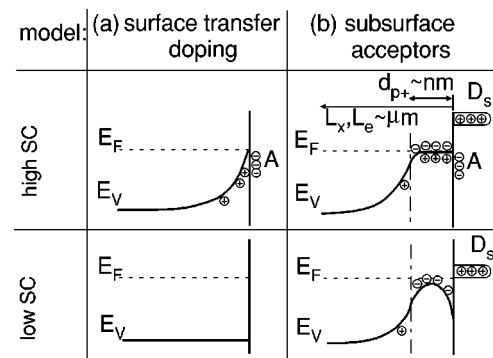


FIG. 1. Schematic band diagrams (valence band only) for the two alternative models of SC on diamond. E_F is the Fermi level, E_V the valence-band maximum, and d_{p+} the extension of the subsurface acceptor layer. D_s denotes donor type surface defects and *A* denotes negatively charged ionic adsorbates. The diffusion lengths of electrons (L_e) and excitons (L_x), which define the probe depth of total photoelectron yield spectroscopy (TPYS), are orders of magnitude larger than d_{p+} .

In the subsurface acceptor model [Fig. 1(b)], donorlike surface defects D_s with a density that exceeds the hole sheet concentration have to be assumed in order to account for the fact that a hydrogenated surface that has not been exposed to atmosphere does not exhibit SC. In the absence of any surface adsorbates they lead to a depletion of the holes, leaving behind the negatively charged subsurface acceptors in the doped layer and a tail of free holes spreading towards the bulk. This results in the band profile shown in the lower panel of Fig. 1(b). In the high SC state atmospheric surface acceptors balance the defects and re-establish the holes in the p^+ layer, as shown in the upper panel of Fig. 1(b). The extension d_{p^+} of the p^+ layer in the subsurface acceptor model has been estimated to lie between a few and 20 nanometers,^{5,7,8} which is also the range of the hole accumulation profile in the surface transfer doping model.²³

It is evident from the band diagrams of Fig. 1 that conventional methods to determine the surface potential, such as photoelectron spectroscopy (PES) and the measurement of contact potentials by the Kelvin method, are unable to distinguish between the two models. Both determine the difference in energy between E_F and E_V . The Kelvin method does so right at the surface and PES averages this difference over the elastic mean free path of hot electrons, which amounts, at most, to a few nm. On these scales there is essentially no difference between the two models.

The difference between the two models is evident in the band profile **below** the hole layer. Here, the transfer-doping model switches between upward band bending for high SC and no band bending for low SC whereas in the subsurface acceptor model an upward band bending is always present.¹⁷ This is, however, exactly the region that can be probed by total photoelectron yield spectroscopy (TPYS) of surfaces with NEA.

In TPYS the quantum efficiency of photoelectron emission is measured as a function of photon energy. In the absence of any barrier between the conduction-band minimum (CBM) and the vacuum level, i.e., for NEA surfaces, *thermalized* electrons and excitons dominate the yield and the effective sampling depth is determined by diffusion lengths L_e of electrons and L_x of excitons.^{14,16,18,19} Different values for L_e and L_x have been published but all exceed a few μm ^{18,19} and the electron contributions to the yield spectrum should thus depend on the band bending in the region where the two models differ.

For the measurements we used a synthetic type IIa (001) and a natural type IIb (001) single-crystal diamond. The samples were boiled in a mixture of H_2SO_4 and HNO_3 at 200 °C to remove contaminants and nondiamond carbon. Both were hydrogenated in a microwave hydrogen plasma at 750 °C. In order to guarantee identical treatment during the following experiments, both crystals were mounted on the same Ta sample holder and introduced into a UHV system with a base pressure of 10^{-10} mbar for TPYS [at room temperature (RT)] and annealing.²⁰ Each annealing step lasted 10 minutes. Conductance measurements with two Au tips as contacts were performed at RT either under high vacuum conditions of 10^{-7} mbar [high voltage (HV)] in a load lock attached directly to the UHV chamber or in air.^{10,21}

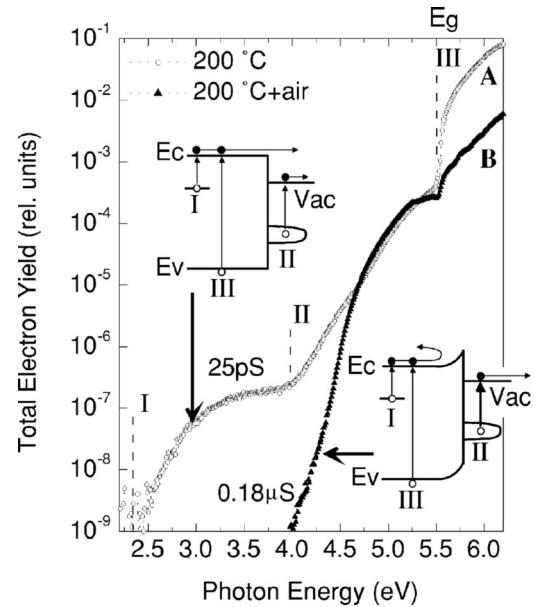


FIG. 2. TPY spectra of plasma hydrogenated type IIa (001) diamond. The first spectrum marked A (open circles) was taken after the sample was annealed at 200 °C in UHV and showed a low sheet conductance of $\sigma = 25$ pS. The spectrum marked B (filled triangles) was taken after subsequent air exposure ($\sigma = 0.18$ μS).

Figure 2 shows TPY spectra of the IIa (001) diamond. The first spectrum was taken after the freshly hydrogenated sample was annealed at 200 °C (open circles). After that the sheet conductance, measured in HV, was 25 pS, i.e., the sample was in the low SC state. The sheet conductance increased to 0.18 μS by exposing the sample to air, confirming the formation of the hole layer. In this state the sample was reintroduced into UHV and characterized again by TPYS (filled triangles). Because TPYS is an integrating spectroscopy (no energy discrimination of the electrons) and photoelectrons are excited into a continuum of states, different excitation processes show up as characteristic thresholds followed by a power-law increase in the TPY spectra. With this in mind, three distinct excitation channels can be identified in Fig. 2. Channel I with a threshold of about 2.4 eV corresponds to photoelectrons excited from bulk defects situated 2.4 eV below CBM into the conduction band. Channel II, starting at a threshold energy of about 4.0 eV, is due to the direct excitation of electrons out of surface defects or graphitic patches at the surface, i.e., without any transport step inside the diamond.¹⁸ Channel III, finally, corresponds to the excitation of electrons from the valence band. The fact that the threshold energy of 5.5 eV coincides with the band gap of diamond proves the NEA of the hydrogenated surface.^{13,14,16,18,19} The different excitation mechanisms are schematically indicated in the upper left insert of Fig. 2, and they obviously all contribute to the yield spectrum of the annealed sample with low SC. We shall term samples showing this spectral signature as in state A. After re-establishing SC by air exposure contributions that require electron transport to the surface after excitation, are suppressed by more than one order of magnitude (state B). This holds for the bulk defect contribution of channel I and the band-to-band

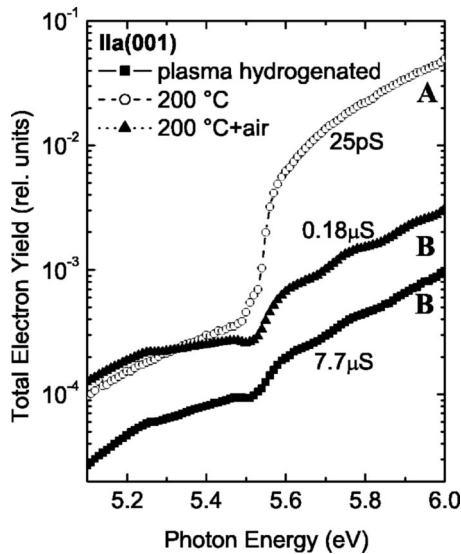


FIG. 3. TPY spectra of type IIa diamond in the band-gap region. The sample is right after plasma hydrogenation (full squares), after annealing at 200 °C in UHV (open circles), and after subsequent exposure to air (full triangles).

excitation of channel III. It obviously does not apply to channel II to which only electrons originating directly from the surface contribute. We interpret this observation as due to a transition in the surface band diagram from flat band to upward band bending because—as explained before—electrons photoexcited well below the surface are susceptible to diffusion barriers, as schematically indicated in the lower right insert of Fig. 2. Obviously, the change in band bending is correlated with that of SC.

The experimental results presented here clearly prove that an electron diffusion barrier towards the surface exists in the surface conductive state, which vanishes along with the hole layer. This correlation is naturally explained in the surface transfer-doping model where both holes and surface acceptors disappear simultaneously upon annealing. In the subsurface acceptor model, the acceptors, being situated inside the diamond lattice, are inherently of permanent nature. The disappearance of the holes can thus only be explained by their complete capture within the surface defects illustrated in Fig. 1(b). In order to be compatible with the reversible cycling of the surface conductivity by annealing and air exposure, a quite restrictive requirement for the subsurface acceptor model is a sufficiently high concentration of surface defects, of the order of 10^{13} cm^{-2} . On an average, one out of twelve surface atoms in a row would have to carry a defect such as a dangling bond in that scenario. This seems to be hardly compatible with the high quality of the surfaces used in this study and frequently adopted for experiments on surface conductivity as well. We have calculated the tolerable extension of the subsurface acceptors such that the remaining diffusion barrier is only kT over a typical diffusion length of electrons in diamond.¹⁷ The result is a maximum critical product of acceptor sheet density and layer width such that for 10^{13} cm^{-2} , a confinement of surface acceptors within 6 nm is necessary. For this estimate a rectangular acceptor profile has been assumed, but it is straightforward along the

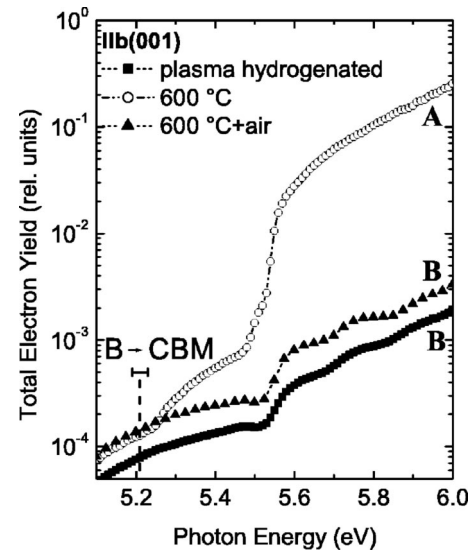


FIG. 4. TPY spectra of type IIb (001) diamond, treated analogously to Fig. 3. Note the additional yield contribution with a threshold energy of 5.21 eV. That we assign to the excitation of electrons from boron acceptor states into the conduction band.

lines of reference¹⁷ to extend the analysis also to nonconstant acceptor densities decaying into the diamond bulk. For example, using a linearly or exponentially graded acceptor profile with the same total amount of acceptors as for the rectangular case yields 4.5 and 2.1 nm, respectively, for the maximum allowed full width at half maximum of these two profiles.

Nevertheless, one could argue that the changes in TPY are only accidentally linked to the change in SC and rather a direct consequence of the annealing process. In addition, the reduction in yield of channel III is less (about 1.5 orders of magnitude) than that of channel I (more than 2 orders of magnitude) and a distinct contribution remains even in the conducting state.

In order to dispel this notion we show in Figure 3 the previous spectra on an expanded scale, focused on the band-gap region. In addition, a spectrum of the same sample in its initial state right after plasma hydrogenation and with high sheet conductance around $7.7 \mu\text{S}$ is also shown. It is evident that the spectral signature is that of a sample in state *B* just as one of the samples that exhibit high SC after annealing in UHV and subsequent exposure to air. The direct correlation between spectral shape *B* and high SC is thus established, also for the sample in its initial state prior to any annealing.

We now turn to the remaining emission above 5.5 eV in state *B*. The well defined step in the TPY spectra, at about 5.5 eV, is a clear indication that an emission channel with a threshold close to the band-gap energy remains superimposed on the surface defect emission (channel II). This contribution is obviously not suppressed by the diffusion barrier connected with the upward band bending in samples with high SC. As has been first pointed out by Bandis and coworkers,^{14,19} excitons as well as free electrons contribute to the TPY of diamond, starting with slightly different thresholds around the band-gap energy of 5.5 eV. An oscillatory yield spectrum is characteristic for the exciton contri-

bution. It is a result of the thermalization process after photoexcitation via multiple emissions of optical phonons. Depending on the photon energy, the thermalization process leaves the exciton with a final kinetic energy between zero and the optical phonon energy (160 meV) that determines the breakup probability of the exciton.^{14,22} Therefore, the spectral oscillations in Fig. 3, in state *B* (and also Fig. 4), identify the above-band-gap contribution as exciton mediated. Clearly, excitons as neutral entities are not affected by band bending. In this sense their contribution to the yield of the samples with high SC and upward band bending strengthens rather than refutes our interpretation of the changes in TPY with SC. For samples with low SC (state *A*) the oscillatory exciton contribution is masked by the much more intense contribution of free electrons.

In the case of IIB (001) hydrogenated diamond, the TPY spectra (Fig. 4) are in perfect agreement with the results of the IIa specimen despite the fact that the SC could not be directly measured on account of the high bulk conductivity of the boron-doped sample. When the sample is freshly hydrogenated, the spectral signature is that of state *B*, i.e., of a

sample with high SC. When annealed, the SC is presumably lost and the spectral shape is that of state *A*, as expected. Again, state *B* related to high SC can be restored by exposure to atmosphere.²⁴ A special feature in the yield spectrum of the annealed IIB sample to which we fit an excitation threshold of 5.21 ± 0.02 eV, is assigned to the excitation of an electron from the boron acceptor state into the conduction band. Details will be discussed elsewhere.

In summary, total photoelectron yield spectroscopy and conductance measurements show a strict correlation between the suppression of electron emission from the conduction band and the occurrence of surface conductivity. This is direct evidence for an upward surface band bending connected with SC and flat bands without SC. These results are consistent with the surface transfer doping mechanism as developed by Maier *et al.* They contradict subsurface acceptor models as they have been published so far with a sheet carrier density of 10^{13} cm⁻².

The authors would like to thank H. Okushi for fruitful discussions.

*Corresponding author. Electronic address: d.takeuchi@aist.go.jp; permanent address: Diamond Research Center, National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, 305-8568 Japan; CREST, Japan Science and Technology Corporation (JST).

¹M.I. Landstrass *et al.*, Appl. Phys. Lett. **55**, 1391 (1989).

²T. Maki *et al.*, Jpn. J. Appl. Phys., Part 1 **31**, L1446 (1992).

³D. Takeuchi *et al.*, Appl. Surf. Sci. **159-160**, 572 (2000).

⁴A. Hokazono *et al.*, Jpn. J. Appl. Phys., Part 1 **36**, 7133 (1997).

⁵E. Kohn *et al.*, J. Phys. D **34**, R77 (2001).

⁶R. Müller *et al.*, Diamond Relat. Mater. **11**, 651 (2002).

⁷K. Hayashi *et al.*, Appl. Phys. Lett. **68**, 376 (1996).

⁸S. Yamanaka *et al.*, Mater. Res. Soc. Symp. Proc. **423**, 353 (1996).

⁹R.S. Gi *et al.*, Jpn. J. Appl. Phys., Part 1 **34**, 5550 (1995).

¹⁰F. Maier *et al.*, Phys. Rev. Lett. **85**, 3472 (2000).

¹¹D. Takeuchi *et al.*, Diamond Relat. Mater. **11**, 355 (2002).

¹²J. Shirafuji *et al.*, Diamond Relat. Mater. **5**, 706 (1996).

¹³F.J. Himpsel *et al.*, Phys. Rev. B **20**, 624 (1979).

¹⁴C. Bandis *et al.*, Phys. Rev. B **52**, 12 056 (1995).

¹⁵M. Szameitat *et al.*, Appl. Phys. Lett. **77**, 1554 (2000).

¹⁶J. Ristein, Diamond Relat. Mater. **9**, 1129 (2000).

¹⁷J. Ristein *et al.*, (unpublished).

¹⁸J.B. Cui *et al.*, Phys. Rev. B **60**, 16 135 (1999).

¹⁹J. Ristein *et al.*, Phys. Rev. Lett. **78**, 1803 (1997).

²⁰J. Schäfer *et al.*, Rev. Sci. Instrum. **64**, 653 (1993).

²¹J. Ristein *et al.*, Diamond Relat. Mater. **10**, 416 (2001).

²²C.D. Clark *et al.*, Proc. R. Soc. London, Ser. A **277**, 312 (1964).

²³Solving Poisson's equation for surface hole accumulation of 10^{13} cm⁻² on intrinsic diamond yields 90% of the holes concentrated within the first 2 nm and 99% within the first 20 nm, at RT.

²⁴In this case, due to the considerably higher annealing temperature (600 °C) of the IIB sample as compared to the IIa diamond (200 °C), simple air exposure turned out to be not sufficient to recover state *A* unless the atmosphere (not the sample!) was activated by UV light. The same procedure restores the SC of intrinsic IIa diamond annealed in vacuum between 250 and 650 °C and is currently under investigation.