Recovery of surface conductivity of H-terminated diamond after thermal annealing in vacuum

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A unique feature of diamond among other semiconductors is the formation of a high conductive p-type layer which is usually obtained after hydrogen-termination of the surface. It is generally accepted that the appearance of surface conductivity (SC) requires the presence of atmospheric adsorbates. We present a combination of conductivity and spectroscopic measurements dealing with the loss and the formation of SC as a function of annealing in vacuum (temperatures 60–900 °C) and exposure to different atmospheres. For temperatures below 190 °C in vacuum the SC decreases by more than five orders of magnitude and comes back to its initial value when the sample is exposed to air. After annealing between 250 and 700 °C exposure to normal atmospheric conditions is no longer sufficient to recover SC, although the H termination is preserved. In this state the SC is fully restored upon air exposure after the surface has been exposed to ozone or oxygen radicals. We propose a model where oxygen-related sites are catalytically involved in the transfer-doping mechanism such that the rate of electron transfer from the diamond into solvated adsorbates is enhanced.

I. INTRODUCTION

Undoped diamond with a band gap of 5.5 eV is an excellent insulator with a high breakdown field of 10^7 V/cm. Thus, it is a remarkable phenomenon that an excessive surface conductivity (SC) of up to 10^{-4} S is observed in air, if the diamond surface is hydrogen terminated.[1,2] The SC has been identified as due to p-type carriers with a lateral concentration of up 10^{13} cm^{-2} and a mobility between 30 and 100 cm^2/Vs showing only weak temperature dependence in the range of 120–400 K.[3,4] The mobilities are not too different from those measured for B-doped diamond[5] and there is thus general agreement that the carriers are holes residing in an accumulation layer close to the surface. The microscopic mechanism which leads to the hole accumulation layer is still controversially discussed. In 1989 when Ravi and Landstrass first reported SC on single crystals and chemical vapor deposition (CVD) diamonds, the phenomenon was exclusively attributed to the presence of hydrogen.[1,2] However, in recent years the role of atmospheric species for the formation of the hole accumulation layer has become obvious. In several experiments it has been demonstrated that exposure to different gaseous species varies the SC by many orders of magnitude.[6,7] Maier *et al.*[8] have proposed an electrochemical model in which electrons are transferred from the diamond valence band to solvated H_3O^+ ions in a wetting layer that forms spontaneously in air. This model is supported in recent theoretical[9] and experimental studies.[10,11] Here we investigate the loss and recovery of SC upon annealing in vacuum and exposure to different kinds of atmospheres. The results imply that, in addition to hydrogen termination and air exposure, oxygen-related catalytic centers at the surface for the formation of the hole accumulation layer are required.

II. EXPERIMENT

In contrast to most other investigations we used for our experiments single-crystal diamond, namely, one undoped IIa single crystal and two undoped CVD diamond layers (150 and 300 nm) homoepitaxially grown on Ib substrates,

all of (100) orientation. This circumvents all ambiguities that might be connected with grain boundaries and crystallite edges. Prior to H-plasma preparation all samples were cleaned in concentrated (4:1 Vol. %) H_2SO_4: HNO_3 at 300 °C for 30 min in order to remove all nondiamond phases.[12] The surfaces were hydrogen terminated in a microwave assisted hydrogen plasma with the following parameters: 10 sccm H_2 flux at 50 mbar and a microwave power of 500 W. The samples were exposed to the plasma for 5 min at a temperature of 750 °C. Then the substrate temperature was reduced to 630 °C before the plasma was switched off and the sample was allowed to cool down to room temperature (RT) under H_2 flux. After plasma hydrogenation the samples were stored for 1 day under normal atmospheric conditions before commencement of the experiments. The surface conductivity was measured in a two-point configuration using gold coated, spring loaded tips. The conductance G was recorded by a computer controlled Keithley 617 electrometer using two operating modes.

(i) I-V measurements from -10 to $+10$ V were performed in order to confirm Ohmic characteristics. These measurements are indicated as discrete symbols in the figures.

(ii) The current was measured at a fixed bias of 1 V (or 10 V in the low-conductive state $G \leqslant 10^{-9}$ S) for recording conductance transients that are indicated by continuous lines in the figures.

For the contact geometry used here the conductances so obtained differ from the conductivities by a factor of the order of unity.[27] The conductivity measurements were performed in a vacuum chamber with a base pressure of 10^{-6} mbar. The latter will be referred to as high vacuum (HV) in the following and the corresponding conductances are plotted as open symbols in the figures. Filled symbols stand for conductances measured under controlled gas compositions. At selected preparation steps the sign of the electron affinity was inferred from the total photoelectron yield spectra (TPYS) measured in ultrahigh vacuum (UHV, $\leqslant 10^{-9}$ mbar). A negative electron affinity (NEA) is caused by heteropolar C-H bonds at the surface and can thus be taken as reliable evidence for a hydrogen terminated dia-
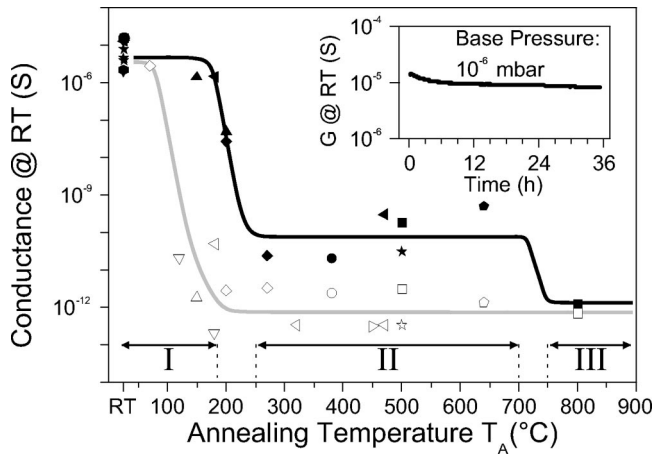
FIG. 1. Conductance of hydrogenated diamond (100) after annealing in vacuum. Open symbols and gray line: measured at room temperature in vacuum. Full symbols and black line: measured at room temperature after subsequent air exposure. The data points assigned to $T_A =$ RT represent the spread of conductances measured on the virgin samples in air. The inset shows the drop of conductance G measured after a virgin sample is placed into vacuum.

mond. In addition, the oxygen coverage of the surface was determined by x-ray photoelectron spectroscopy (XPS).

III. RESULTS

A. The three stability regimes of surface conductivity

As reported by Foord et al.[11] the initial formation of SC on freshly plasma hydrogenated polycrystalline CVD samples commences when the sample is exposed to ambient air and appears to saturate within hours. In our own experiments we confirm this observation. The samples to be discussed here were stored in air for 1 day after which the SC reached a stable plateau in the range of 10^{-6} to 10^{-5} S with local variations over the sample surface by less than a factor of 10. We denote these samples as virgin samples in the high-conductive state.

Figure 1 summarizes the results of annealing experiments on the conductivities of our samples. Each type of symbol represents a different series of measurements, always starting with a freshly hydrogenated virgin sample. Altogether more than ten such test series were performed. No characteristic differences, neither between the three samples nor depending on the initial hydrogenation process, were observed. The open symbols are conductances measured at RT in HV after the sample had been annealed for 10–30 min in vacuum at the temperatures indicated. The corresponding conductances after the samples have been subsequently exposed to air are plotted by solid symbols in Fig. 1.

In contrast to reports in the literature,[13] the SC of all our virgin samples were essentially stable at RT in vacuum (see inset of Fig. 1) with a drop of no more than a factor of 5 over a period of 36 h. The SC begins to decrease when the annealing temperature exceeds 60 °C and drops below 10^{-11} S for annealing temperatures higher than 150 °C. The general trend in the loss of SC as a function of annealing temperature is shown by the gray line in Fig. 1. With respect to the
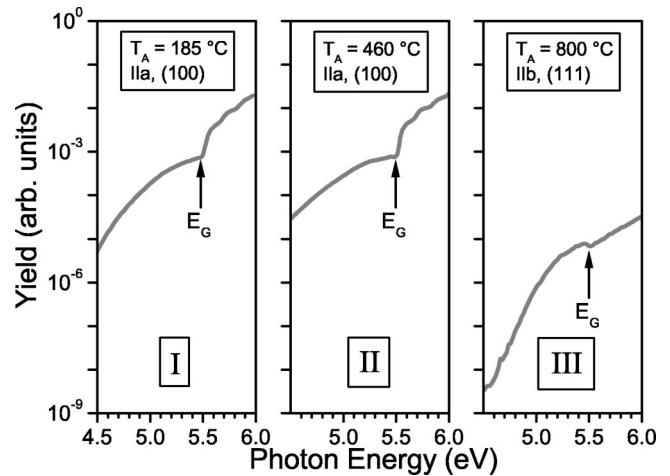

FIG. 2. Representative total photoelectron yield spectra (TPYS) of diamond after annealing in the temperature regimes I, II, and III, respectively. The increase in the yield at E_G in I and II is characteristic for intrinsic diamond with negative electron affinity (NEA) whereas the drop in III at E_G proves positive electron affinity (PEA).[14]

recovery of SC after exposure to air we distinguish three different regimes I, II, III (compare Fig. 1). For annealing temperatures below about 190 °C (regime I) the SC recovers fully to its initial value and can be repeatedly cycled between these extremes by annealing and air exposure. For annealing temperatures between 250 and 700 °C (regime II) the conductance increases only marginally upon air exposure to the nS range. Once the sample has been annealed above 750 °C (regime III) the SC is irretrievably lost. The transition between regime II and III is accompanied by the thermal desorption of hydrogen from the surface.[15] This fact is illustrated in Fig. 2 where for each of the three temperature regimes representative TPY spectra are shown for photon energies between 4.5 and 6.0 eV. The strong increase in the photoelectron yield at a photon energy corresponding to the band gap of 5.5 eV is a signature of negative electron affinity that requires a hydrogen termination of the surface.[16,17] The presence of this feature in regimes I and II and its absence in III attests to the loss of surface hydrogen for $T_A \geq 750$ °C as has been reported before.[14]

The recovery of SC upon air exposure after mild annealing in vacuum (regime I) and the complete loss of SC in regime III have been taken as supportive evidence for models of SC that depend on the transfer doping involving atmospheric species in conjunction with a sufficiently low electron affinity brought about by hydrogen termination.[18] In this context, the existence of regime II where despite an intact hydrogen termination (compare Fig. 2, I+II) air exposure alone does not reestablish the full SC (Fig. 1) requires a change in paradigm. We have therefore performed further experiments on the samples in regime II that we discuss in the following.

B. Influence of different atmospheric gas compositions on the surface conductivity

The experiment shown in Fig. 3 was carried out with a homoepitaxial CVD-diamond sample that was annealed at
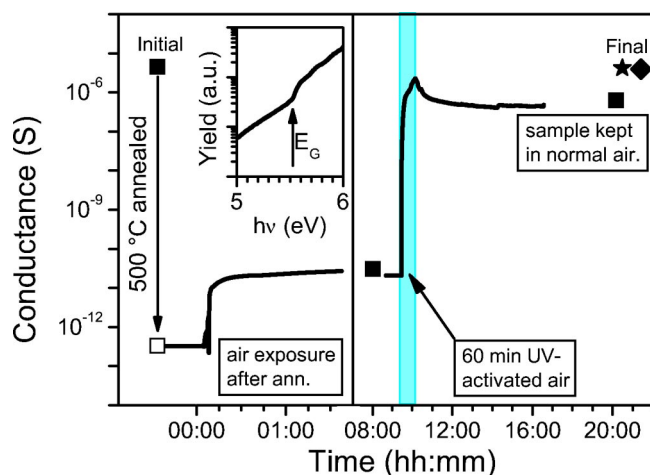
FIG. 3. Conductivity transients after annealing a homoepitaxial CVD layer on Ib diamond to 500 °C and exposure to air. After 9 h, UV-activated air was for 1 h (shaded area) admixed to the atmosphere to which the sample was exposed in complete darkness. After the UV-activated air flow was terminated the sample was kept in normal air again. The inset shows the TPY spectrum with typical NEA feature at the band gap.
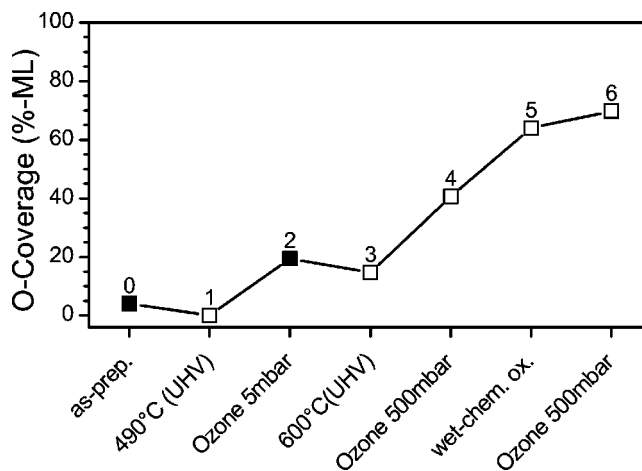

FIG. 4. Oxygen coverage of an initially H-terminated (100) surface after successive annealing in UHV and exposure to ozone-oxygen mixtures. The data were obtained from peak-area-ratios of the O1s to C1s signal measured by XPS. Samples in stages 5 and 6 are shown as reference for the oxidized surfaces. Solid symbols represent samples in the state of high SC and open symbols indicate the absence of SC in air.

500 °C for 10 min in UHV. The hydrogen termination after annealing was confirmed by the TPY spectra as shown in the inset. At the start of the experiment ($t=0$) the sample devoid of any SC was exposed to air while kept in complete darkness. In the first 15 min the conductance increases by two orders of magnitude and saturates after 8 h in air and in the dark at 2×10^{-11} S. This is the level of conductance typically obtained for the samples in regime II after air exposure.

At $t=9$:15 h the sample was exposed to a continuous air stream that was UV activated by passing it over a 1000 W Xe-arc lamp in such a way that no light was shed onto the sample. After 1 h the air was changed back to normal conditions. During UV-activated air exposure (shaded region in Fig. 3) the conductance rises steeply to about 10^{-6} S and essentially remains on this level in normal air. The slight decrease of the conductance after switching off the Xe-arc lamp is due to a concomitant drop in air temperature by about 15 °C. After 20 h the final SC was measured at different positions on the sample as indicated by the solid symbols in Fig. 3.

UV light induces various photochemical reactions in air. The previous experiment strongly suggests that one of the resulting species is responsible for the final full recovery of SC in air. One of the more abundant species is ozone. Hence, a complementary experiment was performed to test ozone explicitly as a candidate using an ozone generator fuelled with pure oxygen that uses an electrical discharge for ozone production. The output of the generator was an O_3: O_2 mixture with a ratio of about 1. Due to the high concentration of ozone used in these experiments the degree of oxidation[19] of the sample was monitored by XPS in addition to the conductance measurements.

We start with the evolution of the oxygen coverage of the IIa (100) single-crystal diamond in the course of the experiment as summarized in Fig. 4. The different stages of the

sample are numbered consecutively for easy reference. The as-prepared virgin sample (stage 0) shows a total amount 0.04 monolayers (ML) of oxygen. This amount consists of physisorbed oxygen in the form of hydrocarbons or water because no O1s signal is detected after annealing at 490 °C in UHV (stage 1). The subsequent exposure to ozone [$p(O_3)=5$ mbar, $t=5$ min] results in a 0.19 ML coverage of oxygen (stage 2). Part of this coverage, namely, the equivalent of 0.04 ML is due to physisorbed oxygen because it disappears after annealing at 600 °C in UHV (stage 3). The remaining 0.15 ML are apparently due to a surface oxidation. In step $3 \rightarrow 4$ the sample was exposed again at RT to a higher concentration of ozone [$p(O_3)=500$ mbar, $t=13$ h]. This results in a further increase of the O1s signal to 0.41 ML and a loss of NEA. Wet chemical oxidation (stage 5) and further exposure to an ozone-oxygen atmosphere [$p(O_3)=500$ mbar, $t=28$ min, stage 6] results in 0.64 ML and 0.70 ML of oxygen coverage, respectively.

We now turn to the corresponding conductance measurements as summarized in Fig. 5. Starting point in Fig. 5 is the sample in stage 1 after exposure to air and brought back to HV (stage 1$'$). After 5 min of ozone exposure (stage 2) the SC is fully established and NEA is preserved. After the second annealing step at 600 °C in UHV (stage 3) the SC is lost as expected for annealing in regime II. The subsequent exposure to a higher concentration of ozone [$p(O_3)=500$ mbar, $t=13$ h, stage 3] results again in an initial rise in SC by more than seven orders of magnitude that lasts for about 4 h. Thereafter the SC gradually decreases to about 10^{-10} S under ozone. As soon as the ambient is changed to normal air the SC drops rapidly to less than 10^{-14} S. The loss of SC in air is accompanied by the loss of NEA. This points towards a loss of hydrogen termination as a consequence of partial oxidation in accordance with Fig. 4 (stage 4). The rightmost panel of Fig. 5 shows the conductance of the wet chemically
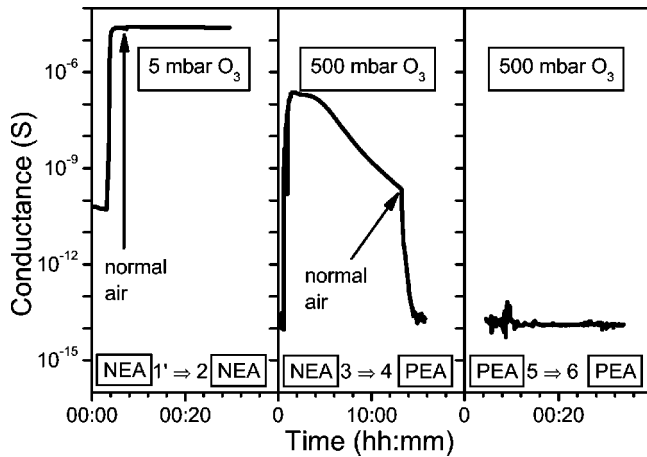
FIG. 5. Influence of ozone exposure on the conductance of the sample of Fig. 4. The numbers in the figure correspond to the stages of Fig. 4. (Left) Within 5 min exposure to ozone, the SC recovers while NEA is preserved. (Middle) At high partial pressure and 13 h of ozone the sample progressively oxidizes and NEA and SC are lost. (Right) For samples showing PEA the ozone has no effect on SC.

oxidized sample (stage 5) as measured during ozone exposure [$p(O_3) = 500$ mbar]. The negative result excludes the possibility that ozone induces SC on an oxidized surface.

C. Influence of UV illumination on the surface conductivity

For these experiments a low-pressure mercury discharge lamp ($\lambda = 254$ nm, $h\nu = 4.9$ eV) was used to illuminate the sample in vacuum through a quartz window. After annealing the sample in UHV at $450\,°C$, a temperature at which the hydrogen termination is preserved, it is exposed to UV light for 40 min and was transferred *in situ* within a minute into HV where the conductance is measured. A value in the pS range is obtained. While venting the chamber with normal air, the transient behavior is recorded over 18 h as shown in Fig. 6. The conductance increases by three orders of magnitude in air. In a second step, the sample is illuminated for 15 min under atmospheric conditions (shaded area in Fig. 6).
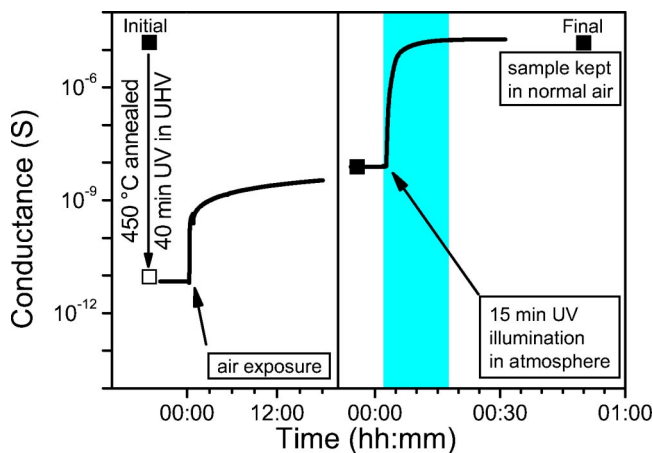

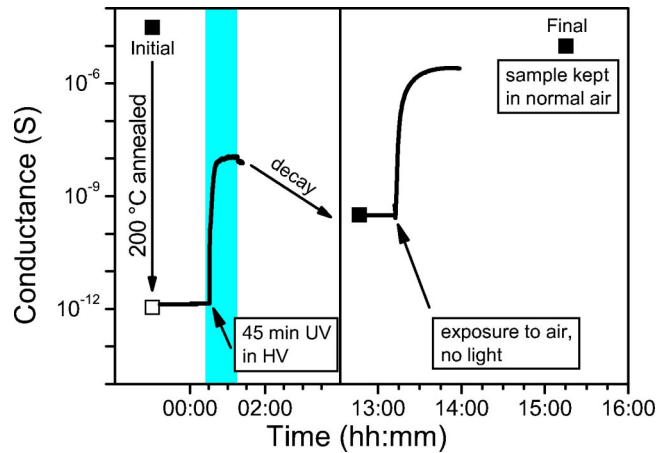FIG. 6. Effect of UV illumination on the SC of a sample annealed at $450\,°C$.

FIG. 7. Effect of UV illumination at $p = 10^{-5}$ mbar on a sample annealed at $200\,°C$.

The high conductive state is restored within 5 min and after the illumination is switched off it stabilizes at 10^{-5} S, identical to the initial level. The final value was stable over weeks in air.

The first part of this experiment proves that after annealing in regime II UV illumination as specified above under UHV conditions is not able to restore the diamond surface to a state where air exposure reinstates SC. Therefore, we studied the effect of UV-light exposure on the sample's conductance when residual gas ($p = 10^{-5}$ mbar) was present during the illumination process. Figure 7 refers to a sample after annealing at $200\,°C$ in the nonconducting state that is UV-illuminated for 45 min at RT in a vacuum of $p = 10^{-5}$ mbar. During the illumination process an increase in conductance is observed with a long decay time after the end of the illumination. After 13 h in darkness the conductance has decayed to the nS range. At this stage simple air exposure to ambient air restores the SC fully.

We repeated this experiment on the same sample with different annealing temperatures ($380\,°C$ and $550\,°C$) and a prolonged exposure time (2 h) to UV light in an similar vacuum (Fig. 8). In these experiments we kept the sample in darkness until the conductance dropped to the pS range. Then the sample was exposed to ambient air and the recovery of SC recorded over a period of 15 h. Finally, this same sample was annealed at $150\,°C$ upon which the conductance dropped to 10^{-12} S. In air the SC was recovered without any UV illumination and thus it behaved like that of a virgin sample in regime I.

IV. SUMMARY OF EXPERIMENTAL RESULTS

The SC of diamond disappears ($G \leq 10^{-12}$ S) upon annealing in vacuum. For annealing temperatures not exceeding $190\,°C$ it recovers to its initial value (μS range) upon exposure to air. We call this the fully reversible state I of the diamond surface. For annealing temperatures between $250–700\,°C$ the conductance increases only marginally upon exposure to air and remains below 10^{-9} S. We refer to these samples as in the intermediate state II. However, by appropriate surface preparation such samples can be conditioned
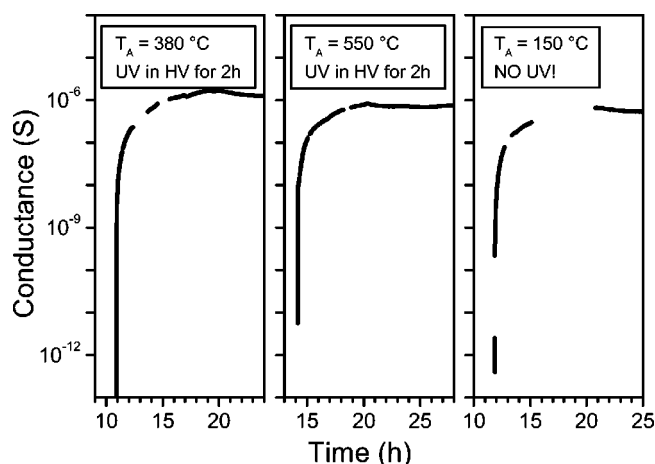
FIG. 8. Chronology of the recovery of SC upon air exposure after different annealing temperatures. The transients in the first two frames were recorded after UV illumination while for $T_A = 150\,°C$ (right panel) no UV illumination was employed.

such that SC upon air exposure is again fully recovered. We shall call this kind of treatment "surface reactivation" in the following. For annealing temperatures above $750\,°C$ the SC is irretrievably lost together with the hydrogen termination of the surface (irreversible state III).

The experiments performed in order to identify the surface reactivation of samples brought into state II can be summarized as follows.

(1) After UV illumination under UHV conditions the conductance remains in the 10^{-11} S range and does not recover to its initial value upon air exposure. (Fig. 6, left-hand side). This excludes that the surface reactivation is solely due to an electronic effect of UV illumination of the diamond as concluded in Ref. 10.

(2) The same experiment performed under poor vacuum conditions (10^{-5} mbar) restores upon air exposure the SC to its initial value (Fig. 7, right-hand side). In combination with (1) this proves that the surface reactivation is due to a UV-mediated reaction between a residual gas species and the diamond surface.
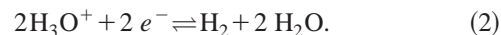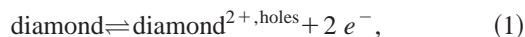
(3) Reactivation is also achieved when the diamond is kept in the dark while exposed to a UV-illuminated atmosphere (Fig. 3). This experiment proves that the optical excitation of the diamond surface is not necessary. Instead, a species created by UV illumination of air must be responsible for the reactivation of the surface.

(4) Among the possible candidates of UV-generated species, ozone as the most abundant was tested explicitly (Fig. 5). The positive outcome of this experiment strongly suggests that it is the reaction of ozone with the diamond surface which reactivates the surface and restores the diamond to state I, where the SC can be repeatedly cycled between pS and μS by annealing in vacuum below $190\,°C$ and reexposure to air. However, ozone exposure above a critical limit leading to oxidation of more than 20% of the surface destroys the SC irretrievably (Figs. 4 and 5).

V. DISCUSSION

The strong influence of atmospheric adsorbates on the p-type surface conductivity of hydrogenated diamond led

Maier *et al.* to suggest a surface-near doping of the diamond by an electron transfer from the valence band to solvated hydronium ions in an aqueous layer on the surface.[8] This electron transfer results in the formation of hydrogen and water, and thus the electron is effectively transferred to the H_3O^+/H_2 redox couple. Within this concept the doping mechanism is the result of the following redox reaction that is driven towards an equilibrium between two electronic reservoirs: the diamond (valence band) on the one side and the H_3O^+/H_2 redox couple on the other:

$$\text{diamond} \rightleftharpoons \text{diamond}^{2+,\text{holes}} + 2\,e^-, \tag{1}$$

$$2\,H_3O^+ + 2\,e^- \rightleftharpoons H_2 + 2\,H_2O. \tag{2}$$

The role of the hydrogen termination of the surface is only indirect, albeit essential, by lowering the ionization energy of the diamond sufficiently and thus lifting its chemical potential (Fermi level) above that of the electrons of the H_3O^+/H_2 redox couple. On the basis of this electrochemical surface transfer-doping process, holes are formed in a surface-near layer and are responsible for the observed p-type conductivity. Their charge is exactly balanced by the anions originally accompanying the hydronium ions and residing on the surface. In the model of Maier *et al.* they were identified with HCO_3^- of the slightly acidic aqueous layer that is formed by the dissolution of atmospheric CO_2. The decrease of SC in vacuum in the fully reversible temperature regime I can in fact easily be understood within the surface transfer-doping model as the desorption of the anions from the surface. For charge neutrality reasons the holes must either recombine with the anions prior to their desorption or be swept out into contacts on the diamond surface. Air exposure leads again to surface transfer doping as described above and thus also restores the SC. The fully reversible temperature range reported by us here and also by others[13,20] finds a natural explanation in the present model.

The experiments described in detail in this paper, however, focus on the intermediate state II of hydrogenated diamond where the surface conductivity cannot be induced by exposure of the sample to normal air although the hydrogenation of the samples is still intact. The mere existence of this state implies that, in addition to the presence of atmospheric adsorbates and a sufficiently low ionization energy of the diamond surface, a further condition is necessary for the creation of holes in diamond. This condition is lost during thermal annealing above a critical temperature threshold ($\approx 250\,°C$), but it can be reestablished by the different techniques discussed above. We have called this process which transforms samples from state II back to state I surface reactivation.

Our experiments show that one possibility for the reactivation of the hydrogenated diamond surface is an exposure to ozone. This leaves both a reaction of O_3 and of oxygen radicals with the diamond surface as possible mechanisms for the reactivation. However, the reactivation achieved by UV illumination under HV conditions (10^{-5} mbar) favors oxygen radicals as the responsible species. Considering the low O_2 partial pressure in HV it is very unlikely that the
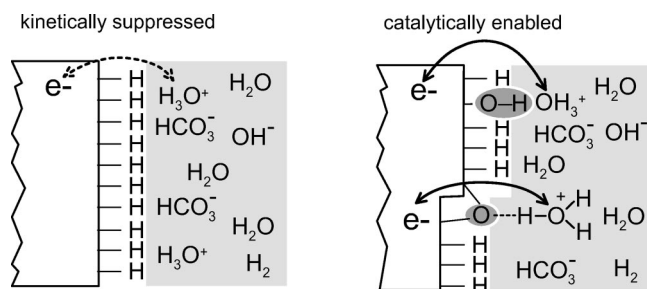
FIG. 9. Schematic model for the inactive, perfectly hydrogen terminated diamond surface (left-hand side) and the reactivated diamond surface with oxygen-related catalytic defect sites that allow an electron transfer from the diamond to H_3O^+ ions acting as surface acceptors (right-hand side).

UV-created oxygen radicals O_1 undergo a further gas phase reaction before hitting the diamond surface. Therefore, it is the reaction of O_1 with the diamond surface that changes the surface in such a way that the transfer-doping process becomes possible again after it had been quenched by annealing above 250 °C in vacuum. On account of the high reactivity of O_1 it is plausible that the surface changes involve specific bonding configuration of C, O, and possibly H which we shall refer to as oxygen-related centers. The concentration of these centers is below 0.01 ML which is the O1s XPS the detection limit. The centers act catalytically on the SC in the sense that O_1 exposure alone does not lead to the high SC state unless the sample is subsequently exposed to air. Reactivation by oxygen radicals or ozone and doping are independent processes as proven in experiments documented in Figs. 7 and 8 where in all cases surface reactivation takes place prior to and independent of doping by air exposure.

The catalytic action of the oxygen-related centers could, in principle, be brought about by a change in the kinetics or a change in the energetics of the transfer-doping process. We exclude the last possibility for the following reasons. A crucial aspect of the charge transfer from the diamond to the H_3O^+/H_2 redox couple is the lowering of the ionization energy of diamond by the $C^{\delta-}\text{-}H^{\delta+}$ dipole layer of the hydrogenated surface.[8] Replacing C-H dipoles by C-O or C-O-H dipoles increases the ionization energy on account of the opposite sign of the C-O, C-O-H dipoles compared to C-H (O is more electronegative than C). The introduction of oxygen-related defects would therefore lead to an energetically less favorable situation for charge exchange and their thermal removal to a more favorable one—the former leading to an enhanced SC and the latter to a reduced SC in contrast to what has been observed. We therefore favor an interpretation whereby the oxygen-related defects enhance the kinetics of the charge-transfer process. In their absence the electron transfer to a redox couple acting as surface acceptor is kinetically suppressed although it is energetically allowed with respect to the electrons' chemical potential. As examples for such a defect we have sketched in Fig. 9 an isolated O-H group on a hydrogen terminated terrace and an O atom bridging two dangling bonds at a surface step. Such oxygen-related defects may in fact lead to a strong localized dipole moment superimposed on the homogeneous dipole

layer of opposite sign connected with an otherwise perfect hydrogen termination of the surface bonds. As a consequence, a stronger interaction between potential acceptors and the diamond surface may result, enhancing electronic tunneling between both. In case of hydronium ions as surface acceptors and a bridging oxygen atom this kind of interaction is in fact somewhat similar to the formation of a pseudo-hydrogen-bond between the H_3O^+ and the oxygen chemically bonded to the carbon surface atoms. Electron transfer along such hydrogen bonds is in fact a well-known phenomenon and the key factor in the diffusion of hydronium ions in water.[21] One can thus imagine that oxygen groups on the diamond surface can accelerate an electron transfer that is kinetically suppressed on the perfect hydrogenated surface. This appears to contradict the considerations given above where we argued that electron exchange is energetically less favorable at the site of a C-O or a C-O-H defect on account of the dipole orientation. This is clearly a question that ultimately has to be solved by quantum mechanical calculations of the charge exchange process. Recent results in this direction provide the following picture.[22] The lowest molecular orbital (LUMO) of a solvated hydronium consisting of 1 H_3O^+ and 3 H_2O molecules extends over an area of about 9–12 carbon atoms on a hydrogen terminated surface. Electron transfer from diamond to the LUMO takes place even if one C-O-C bridge replaces two C-H surface bonds. This implies, that one "wrong" C-O dipole among the otherwise undisturbed hydrogen terminated C atoms is not sufficient to suppress the charge transfer on energetic grounds. Obviously, the change in potential due to the C-O dipole averaged over the lateral extension of the solvated hydronium does not raise the LUMO relative to the valence-band maximum of the diamond enough to prevent the electron transfer doping. Acting catalytically, each center may be involved in many charge-exchange processes and thus their lateral density can be far less than that of the holes.

Aside from the surface reactivation a progressive oxidation of the surface by ozone has an obvious but maleficent effect on the surface conductivity as well. Increasing oxygen coverage eventually raises the electron affinity from -1.3 eV for the fully hydrogenated to $+1.7$ eV for the fully oxidized surface.[23] This is directly proven by the conversion from NEA to PEA ($3\rightarrow4$ in Figs. 4 and 5). At the same time, the chemical potential of the diamond with respect to potential surface acceptors is reduced and the formation of the hole accumulation layer suppressed.

The conductance transient measured during the second reactivation of the diamond sample by ozone exposure (middle panel of Fig. 5) reflects an interesting intermediate oxidation stage. In the beginning of the transient the ozone exposure successfully reactivates the surface and *simultaneously* leads to surface conductivity. After passing through a maximum at about 2 h the conductance decays and rapidly vanishes completely when the ambient is changed from ozone to normal air after 13 h. This transient can be understood if we realistically assume that traces of water vapor are also present in the ozone/oxygen atmosphere used for reactivation. Then we have to consider the O_3/O_2 redox couple

as an alternative surface acceptor instead of the H_3O^+/H_2 couple discussed so far. The electron transfer doping will proceed via

$$O_3 + H_2O + 2\,e^- \rightleftharpoons O_2 + 2OH^-, \qquad (3)$$
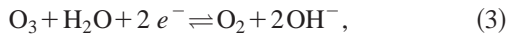
which replaces Eq. (2) in the redox reaction and leads to holes in the diamond and OH^- ions as counter charge on the surface. Assuming realistic conditions for our experiment (pH$=7$ and an ozone/oxygen ratio of 1:1) yields a chemical potential 5.7 eV below the vacuum level for the electrons of the redox couple [Eq. (3)], i.e., about 1.5 eV lower than for the H_3O^+/H_2 couple.[8] In the presence of ozone (and traces of water) the creation of holes should therefore be possible even for a surface that is partially oxidized and does for energetic reasons no longer allow electron transfer to the H_3O^+/H_2 couple in normal air. At the end of the ozone exposure documented in the middle panel of Fig. 5 (state 4 of the sample) the surface is covered by 0.40 ML of oxygen (Fig. 4). This corresponds to a positive electron affinity[23] where indeed the electron transfer to the H_3O^+/H_2 redox couple is no longer possible. After the next (wet chemical) oxidation leading to 0.64 ML of oxygen coverage (Fig. 4) the electron affinity of the surface has increased further so that even the O_3/O_2 redox couple is no longer able to induce any conductance during ozone exposure.

When the surface reactivation is performed by softer methods such as UV illumination in air or in HV, the oxygen-related catalytic defect centers can also be generated in sufficient concentration without a significant overall oxidation of the surface such that the electron affinity necessary for surface transfer doping in air is maintained.

Finally, we address the thermal transition from the fully reversible to the intermediate state of the diamond surfaces. We interpret this as a thermal transformation of the catalytic defect centers into an inactive state, probably by the desorption of oxygen and the formation of dangling bonds or distorted π bonds. The transition temperature for this transformation of around 250 °C is rather low when compared with the desorption temperature of oxygen from fully oxidized surfaces and the transformation to the clean reconstructed surface.[24–26] One has to keep in mind, however, that the oxygen-related catalytic defect centers probably involve specific bonding configurations at steps or edges that may show a considerably lower stability than the regular oxygen termination of extended diamond terraces. The surface reactivation obtained in our experiments, either by UV activation of atmospheric or residual vacuum species in HV or by direct exposure to ozone, is interpreted as a reformation of the catalytic defect centers by oxygen radicals. In view of their small concentration their identification by spectroscopic techniques remains a challenging task for the future.

The results presented here raise the question whether the same active centers are present right after plasma hydrogenation because samples that are reactivated from state II to state I behave in all aspects like virgin samples, i.e., they develop SC right upon exposure to air. This question cannot be answered unambiguously at present. However, our own experience shows that storing samples in state II in air under fluorescent lights reactivates them over a period of hours. The weak UV-component of the light is apparently sufficient to create the necessary oxygen radicals needed for the active centers. In view of this experience, experiments which show development of SC by *in situ* air exposure right after plasma hydrogenation without intentional UV illumination might not be conclusive examples for SC without the presence of active centers as postulated here. That the more so, since plasma hydrogenation is often performed in transparent quartz tubes which allow UV excitation even after plasma switch off and cool down of the sample.

VI. CONCLUSION

There is mounting evidence that the transfer-doping model as first insinuated by Ri *et al.* and later fully developed by Maier *et al.* is able to account for virtually all observations that deal with effects of environmental conditions on the SC of diamond. The model is also able to account for the reversible loss and recovery of SC for annealing in vacuum below temperatures of about 190 °C as reported by us and others. It finally explains the irretrievable loss of SC after oxidation and for annealing temperatures above about 750 °C by the increase in ionization energy of diamond brought about by oxidation or the loss of terminating hydrogen at the surface.

However, the transfer doping in its original form appears to be unable to account for the loss of SC after annealing in an intermediate temperature range ($250\,°C \leqslant T_A \leqslant 700\,°C$) and its recovery after UV illumination despite the fact that the H termination remains intact. The detailed studies presented here yield strong evidence that in samples in this intermediate state (state II in our nomenclature) the reestablishment of SC upon air exposure is energetically possible but kinetically hindered. The hindrance is removed if the sample is exposed to ozone or oxygen radicals and UV illumination is neither necessary nor sufficient. Consequently, we postulate oxygen-related catalytic centers in addition to H-termination and exposure to air as a third necessary ingredient in order to establish SC on diamond in a matter of minutes to hours. The detailed bonding configuration and concentration of these catalytic centers can only be speculated about at present. Nevertheless, we present arguments why these centers could be inadvertently present on virgin samples, i.e., samples that exhibit SC right after plasma hydrogenation when exposed to air without being intentionally exposed to ozone or oxygen radicals.

As a serendipitous finding we could also establish that for surfaces with somewhat raised ionization potential (compared to the fully hydrogenated case) the O_3/O_2 redox couple in aqueous atmosphere can still induce SC where the H_3O^+/H_2 couple fails to do so. This is in keeping with the low electrochemical potential of the former (-5.7 eV with respect to the vacuum level) compared to the latter (-4.2 eV).

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[27] For two circular tips of diameter δ and a center distance D it is straight forward to show that the conductance G is related to the two-dimensional surface conductivity $\sigma_\square$ by $\sigma_\square = G \cdot \pi/\ln(2D/\delta-1)$ in which the geometry factor $\pi/\ln(2D/\delta-1)$ for common tip geometries ($D/\delta \approx 5, \ldots, 10$) is always of the order of one.