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Three hydrogen-terminated diamonds with different surface roughness and morphologies have been investigated by conductivity and Hall experiments in the temperature regime 0.34–350 K. The sheet hole densities are weakly temperature dependent above a critical temperature T_c ($20\,\mathrm{K} \leqslant T_c \leqslant 70\,\mathrm{K}$), below T_c carriers freeze out. The mobilities of holes show a minimum at T_c increasing towards higher and even stronger towards lower temperatures significantly up to 400 cm^2/V s. A transport model is introduced where holes propagate in the valence band where a disorder-induced tail of localized states is present. © *2001 American Institute of Physics.*
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Diamond is a well known insulator with extremely high electrical resistivity. Surprisingly, Landstrass and Ravi reported in 1989 conductivities of the order $10^{-5} - 10^{-4}\,\Omega^{-1}$ on undoped as grown chemical vapor deposited (CVD) diamond.[1] Later, this observation was confirmed by several other groups revealing the *p*-type nature of the conductive surface layer,[2,3] typical sheet hole densities between 10^{12} and $10^{14}\,1/\mathrm{cm}^2$[3,4] and Hall mobilities between 3 and 70 cm^2/V s.[4,5] It is certain that the conductivity is related to hydrogen (for a review see Ref. 6), however, several controversial models have been proposed ranging from (i) surface band bending due to hydrogen surface termination where valence band electrons transfer into an adsorbate water layer ("transfer doping model"),[7–9] (ii) shallow hydrogen-induced acceptors,[2,10] and (iii) deep level passivation by hydrogen.[11]

In this letter we investigate transport properties of diamond surface conductive layers generated by hydrogen termination with Hall effect and conductivity experiments in the temperature range 0.34–350 K. We will show that the transfer doping model of Gi *et al.*[5] and later by Maier *et al.*[9] very well accounts for the detected properties. The transport characteristics are governed by a narrow hole accumulation layer at the valence band edge where disorder-induced localized states are also present. At low temperatures holes are trapped in these states. At these temperatures a small fraction of holes, however, propagates with mobilities up to 400 cm^2/V s which points towards transport in two-dimensional (2D) extended states.

To explore surface conductivity effects we characterized three undoped diamond samples with different surface properties: (I) An intrinsic polycrystalline CVD diamond with a thickness of 100 μm, an average grain size of 30 μm and an average roughness of 20–30 μm (named A). (II) An atomically flat homoepitaxially grown (100) monocrystalline CVD diamond (named B). The surface properties have been pub-

lished in Ref. 12. (III) A natural-type IIa (100) diamond with a surface roughness of about 15 nm (named C). Prior to hydrogen termination the diamonds have been cleaned in a solution of HNO_3/H_2SO_4 (1:3) at 350 °C for 30 min to remove graphitic carbon and to obtain oxygen termination. Then a hydrogen terminated in a microwave plasma at temperatures between 500 and 850 °C has been applied (for details see Ref. 6). Atomic force microscopy experiments performed on sample B (atomically flat) before and after hydrogenation show no etching damage of the surface. Standard photolithography processing was applied in combination with oxygen plasma etching to manufacture well defined hydrogen terminated squares of 2 mm×2 mm (Van der Pauw geometries) or Hall bars of 800 μm×5 μm size. Au layers 300 nm thick have been evaporated for ohmic contacts. The samples have been exposed to ambient atmosphere for at least 24 h prior to conductivity and Hall experiments to generate highly conductive surface layers on A of $6 \times 10^{-5}\,1/\Omega$, on B of $(1-5) \times 10^{-5}\,1/\Omega$, and on C of $10^{-3}\,1/\Omega$. The conductivity and Hall measurements were performed in vacuum of 10^{-7} mbar. Magnetic fields of 2 T for Hall measurements have been applied. As the thickness of the conductive layer is not known at present, the sheet conductivity σ_{Sh} and sheet hole density are calculated using standard equations.

The conductivities of the three layers at room temperature are in the range $10^{-5} - 10^{-3}\,1/\Omega$ which is typical for hydrogen terminated diamond.[3–5] No correlation between surface roughness and conductivity or structural (polycrystalline/monocrystalline) properties and conductivity can be deduced from this data. The conductivities are weakly temperature dependent showing activation energies between 3 and 20 meV (see Ref. 13). In all cases a positive Hall coefficient is detected indicating that holes dominate transport properties. Figure 1 summarizes sheet hole densities
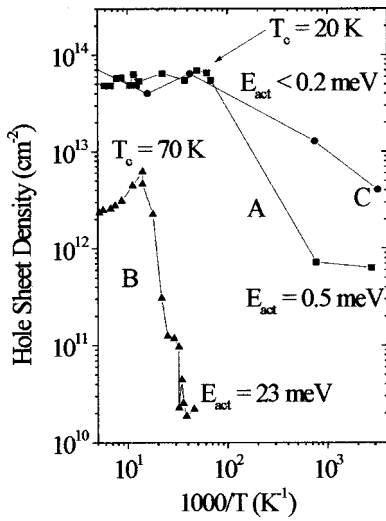
FIG. 1. Hole sheet densities measured from 0.34 to 200 K. Below a critical temperature T_c the carrier density is activated with energies $\cong 23$ meV (B) and $\cong (0.2–0.5)$ meV (A, C).

measured between 0.34 and 200 K. Below a critical temperature T_c [$\cong 70$ K (B), $\cong 20$ K (A, C)] the densities decrease with activation energies ranging from 23 meV (B), to $\cong (0.5–0.2)$ meV (A, C). Above T_c the density is about constant (A, C) or slightly decreasing (B). The freeze-out temperature T_c is dependent on the hole density shifting from about 70 K for 6×10^{12} cm^{-2} to about 20 K for 6×10^{13} cm^{-2}.

Hall mobility (μ_h) of holes, shown in Fig. 2, is decreasing towards lower temperatures showing a minimum at T_c. In B μ_h follows a $T^{1.5}$ law which indicates scattering at ionized impurities.[14] In A and C the decrease is weaker. Below T_c a strong rise in mobility in all three samples is detected. Obviously, a small fraction of holes (1%–10%) propagates with increasing mobilities. The highest detected mobilities are 14 (B), 70 (A) and 400 cm^2/V s (C).

The deduced results indicate no correlation between surface quality and electronic properties. We assume that the
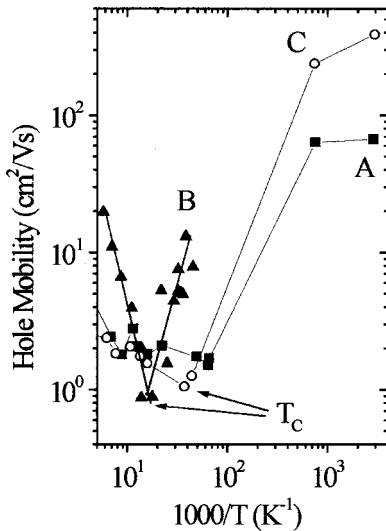

FIG. 2. Hole mobilities measured in the temperature regime 0.34–200 K. Below T_c mobilities are increasing several orders of magnitude. Above T_c the $T^{1.5}$-temperature dependence on sample B indicates scattering at ionized impurities.
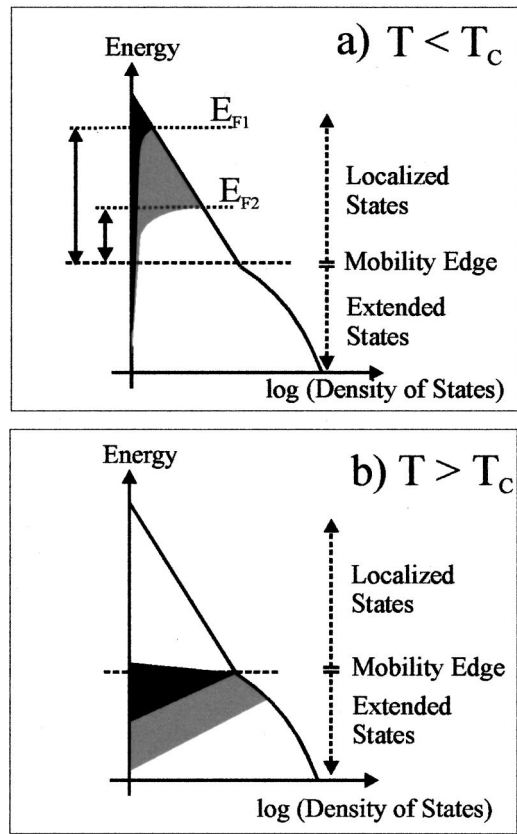

FIG. 3. Exponential tail of localized states at the valence band edge. At temperature below T_c holes are localized in the tail. Only a small fraction can propagate in extended states (a). Above T_c most of the holes are thermally excited into extended states of the valence band (b). The black and gray regions represent two hole densities. E_{F1} and E_{F2} are the activation energies of trapped holes.

detailed properties of the hole accumulation layer are governed by the hydrogen plasma process which is up to now not well characterized. Due to the metallic properties of holes down to lowest temperatures (see Fig. 1) we adopt the transfer doping model as published in Refs. 7 and 9. Here, a hole accumulation layer is generated in the valence band by transfer of valence band electrons into the surface adsorbate layer which acts as an electron sink. As the Fermi level is in the valence band and the sheet hole density is ($10^{13}–10^{14}$) 1/cm^2 the surface band bending extends only about 1–5 nm into the diamond[15] giving rise to quantum size effects. For a perfect hydrogen terminated and smooth surface a two-dimensional electronic system is therefore expected. However, our real surface is most likely dominated by hydrogen which may not be arranged in a perfect periodic way. Adsorbates which are negatively ionized may generate Coulombic disorder and the surface roughness may cause additional carrier scattering. The resulting disorder will modulate the up bending of the valence band, destroy the long range order and generate electronic traps. These traps are distributed in energy. As first order approximation we assume an exponential distribution which is schematically shown in Fig. 3, given by

$$g(E) = g_0 \exp\left[-\frac{E - E_{mob}}{E_0} \right], \tag{1}$$

where E_{mob} is the mobility edge and E_0 is the characteristic

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energy of the tail. In the following we discuss this model based on data shown in Fig. 1. In sample B, the hole density below 70 K is activated with 23 meV indicating that the center of charge is about 23 meV above the mobility edge ($=E_{\mathrm{F1}}$ in Fig. 3). At temperatures above 70 K all holes ($p_{\mathrm{SH}} \approx 3 \times 10^{12}\,\mathrm{cm}^{-2}$) are in extended states as the density of holes is approximately constant. We estimate E_0 to be about 6 meV ($=k_B \times 70\,\mathrm{K}$, where k_B is the Boltzmann constant), for details see Ref. 16. As below 70 K basically all holes are trapped, the density of states at the mobility edge, g_0, can be calculated by

$$g_0 \approx \frac{p_{\mathrm{Sh}}(T > 70\,\mathrm{K})}{E_0} \exp\left[\frac{23\,\mathrm{meV}}{6\,\mathrm{meV}}\right]$$

$$\approx (1-5) \times 10^{16} [\mathrm{cm}^2\,\mathrm{eV}]^{-1}. \qquad (2)$$

The total density of localized electronic states at the surface is therefore about $(1-5) \times 10^{14}\,\mathrm{cm}^{-2}$ which is 10% of the diamond surface density of atoms.[17] The hole density in samples A and C is about $6 \times 10^{13}\,\mathrm{cm}^{-2}$. Assuming the same tail-state distribution as in B, the tails are nearly filled and the activation energy E_{F2} therefore approaches zero. This is in good agreement with the detected activation energies for A and C of $E_{\mathrm{act}} < 0.5\,\mathrm{meV}$.

At temperatures below T_c hole mobilities are rising. Obviously, a small fraction propagates in states which are less distorted. These states form extended 2D electronic levels. These results and recently published data by Tachiki *et al.*[18] indicate that the narrow width of the accumulation layer at the surface gives rise to 2D properties, however further experiments are required to confirm these results.

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