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Quantization of 2D Hole Gas in Conductive Hydrogenated Diamond Surfaces Observed by Electron Field Emission

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Discrete jumps are observed in the emitted current density (J) versus extraction electric field (E) curves in electron field emission measurements from a conductive, hydrogen-terminated air-exposed diamond surface. These jumps are well reproduced by computations based on the assumption that a 2D nanoscale quantum system with discrete energy levels exists in the diamond near-surface layer. The present results confirm the formation of well-defined quantum states of holes in the 2D surface layer present on hydrogenated air-exposed diamond surfaces.

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Diamond is a wide band-gap semiconductor with excellent electronic properties [1,2] making it a promising candidate, when successfully doped, for the realization of various electronic devices [3,4]. The discovery that undoped diamond, when hydrogenated, has a negative electron affinity and, when further exposed to air, exhibits high (p-type) surface conductivity [5–7] enables the fabrication of nanometer sized diamond based devices such as field effect transistors [7] and pH sensors [8]. The mechanism responsible for the appearance of the near-surface hole conduction was recently attributed to the formation of a 2D-hole gas due to a hole accumulation layer in the very near-surface region of diamond [6,9] resulting in an upwards band bending in the near-surface region. The existence of this band bending was confirmed by photo-emission yield spectroscopy measurements [10]. Kelvin force experiments have shown that the Fermi level at the surface is located below the valence band [11]. However, up until now, it was not experimentally proven that discrete energy levels do exist in the so-formed quantum well (QW).

In the present work, we investigate, by electron field emission measurements, the properties of surfaces of intrinsic diamond which have been rendered conductive by hydrogenation and exposure to air. Peculiar steps observed in the J-E curves provide experimental proof for the existence of discrete energy levels in the surface potential well due to the formation of a 2D hole-gas on the diamond surface.

The field emission from two $\langle 100 \rangle$ and from one $\langle 111 \rangle$ oriented natural type IIa diamonds was measured. The samples were well polished (rms = 1 nm as measured by AFM on both $\langle 100 \rangle$ and $\langle 111 \rangle$ diamonds) and surface hydrogenated by exposure to a hydrogen microwave plasma at 700 °C for 1 h followed by exposure to ambient conditions, hence inducing surface conductivity [5,6]. The surface resistivities and hole mobilities were measured by Hall-effect as a function of temperature prior to and following hydrogenation. Silver paint dots, deposited at the 4

corners on the sample surface, were used as contacts. I-V measurements (from $+80$ to -80 V) have shown the contacts to be Ohmic, thus indicating that the measured J-E curves are only related to field emission (FE) and are not due to the contacts. Whereas the nonhydrogenated samples have had resistances greater than $10^{12}\ \Omega/\square$ and no measurable Hall-effect at RT, resistances of the order of $10^4\ \Omega/\square$ with sheet hole concentrations of about $5 \times 10^{12}\ cm^{-2}$ and RT hole mobilities of $\sim 60\ cm^2\ V^{-1}\ s^{-1}$ were measured for the hydrogenated samples. Almost no temperature dependence of the conductivity was observable following hydrogenation and air exposure, in accord with the reported conductivities of air-exposed hydrogenated diamonds [6]. For the FE measurements the samples were mounted in a high vacuum chamber (10^{-9} torr) with a spherical ''extraction'' electrode (2 mm diameter) placed on a computer controlled piezo-driven stage, set at distances of 10–40 μm from the surface. Variable negative voltages (0–5 kV) were applied to the surface relative to the extraction electrode. The measurements comprised of gradually ramping up the voltage between the sample and the extraction electrode (set at fixed distances from the surface), while measuring the emission current (J) as function of voltage, i.e., as function of electric field (E). Several up/down cycles were performed at the same spot as well as at different spots on each sample with the extraction electrode set at different distances from the sample. The entire experiment was done automatically under computer control. In the present FE measurements, in contrast to the commonly used configuration in which a back contact is used as a cathode, topside contacts to the hydrogenated conductive surface were employed, thus allowing the carriers to flow through the conducting surface to the emission sites and be emitted to the extraction electrode. Similar results were consistently obtained for the different measurement modes on the different samples (when converted to current density versus electric field curves).

Figure 1(a) shows typical FE results obtained from $\langle 100 \rangle$ and $\langle 111 \rangle$ intrinsic diamond samples [lines (a) and (b)]
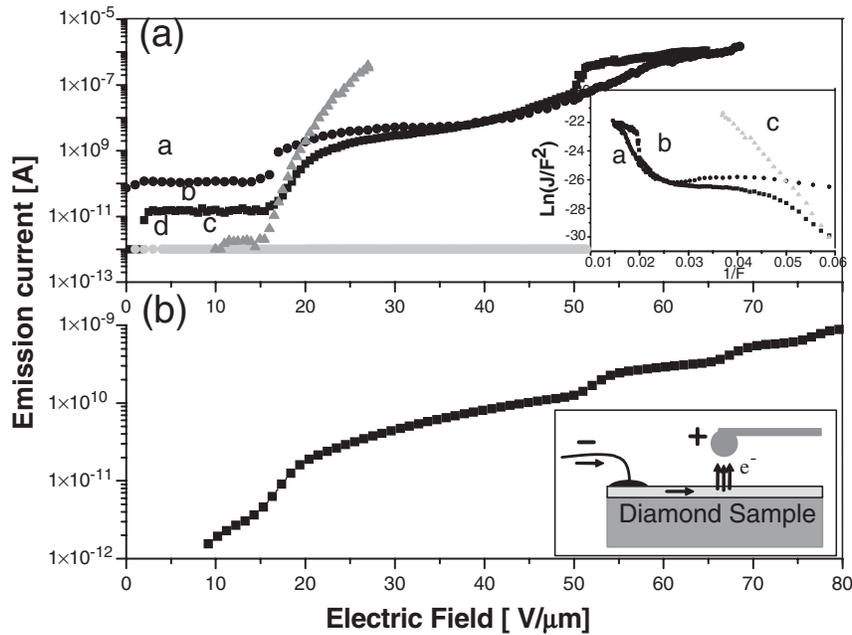
FIG. 1.   (a) Results of FE measurements from different samples: (a) hydrogen-terminated, air-exposed, top contacted $\langle 100 \rangle$ type IIa natural diamond (sample #1). (b) Same for a different $\langle 111 \rangle$ type IIa diamond (sample #2). (c) Hydrogen-terminated polycrystalline B-doped CVD diamond on Si, contacted on the front corner side. (d) Sample #1 after, *in situ*, heating to 250 °C (H_2O removed), prior to breakdown. The insets show the same data when plotted in the Fowler Nordheim presentation. (b) Results of calculations of the expected emission current from a triangular surface potential well of width $w = 49$ Å and depth $d = 115$ meV. The inset shows the experimental arrangement.

with a top contacted hydrogen-terminated conductive surface and from the same $\langle 100 \rangle$ sample, with the same top contacts, following electrical conduction removal by *in situ* thermal treatment above 250 °C [line (d)]. Line (c) shows, for comparison, the results of field emission for a bulk conductive boron doped chemical vapor deposition (CVD) grown polycrystalline diamond. Identical data were repeatedly obtained for the other, similarly treated, samples at different anode distances and on different spots on the same sample. The marked difference between the *J-E* curves of the differently treated samples should be noted: For the intrinsic hydrogen-terminated diamonds [lines (a) and (b)], steps in the emission current densities with increasing field are noticed at well-defined values of the field (at about 17 V/μm, 52 V/μm, and perhaps at 67 V/μm). Never before were such jumps observed in field emission measurements. In contrast, the emission current for a bulk conductive boron doped CVD grown polycrystalline diamond [line (c)] exhibits the well-documented FE behavior; i.e., it increases abruptly at a defined value of the electrical field (turn-on field) and then smoothly and continuously rises as a function of the electric field, in accord with the Fowler Nordheim (FN) FE theory, thus giving confidence in the staircase-shape results measured for the surface conductive samples [lines (a) and (b)]. For a nonconductive sample obtained by surface conduction removal [line (d)], no emission current can be detected. The small currents measured for the top contacted samples [lines (a) and (b)] at very low electrical fields (less than 10 V/μm) are due to

charging and current leakage effects. The inset in Fig. 1(a) shows the FN presentations of the above FE results. As can be seen the FE, behavior of the B-doped CVD diamond is in accord with FN FE behavior (straight line) while FE from hydrogen-terminated IIa diamond cannot be explained by the FN theory.

The steps measured in the *J-E* curves from the conductive hydrogenated air-exposed layer on the diamond surface can be understood as follows: a 2D potential well is formed on the surface. Changing the external electrical field modifies the dimensions of the well and consequently changes the number of discrete energy levels in it. The observed steps with increasing field are due to the appearance of new energy levels in the well.

To reproduce the data, we rely on the electrochemical transfer-doping model for surface conductivity in hydrogen-terminated and air-exposed diamond. This model predicts the formation of a hole accumulation layer on the sample surface, resulting in an upwards band bending at the diamond-vacuum interface [10,12] [see Fig. 2(a)]. Once the carrier concentration on the surface reaches a certain value the bending of the valence band maximum (VBM) can be so large as to give rise to the formation of a QW containing a 2D hole gas with discrete energy levels [13]. In order to obtain FE of electrons from these hole levels, they must be populated by thermally exited electrons that must overcome the surface barrier. Application of an external electric field has two effects on the band diagram of the near-surface region of the dia-
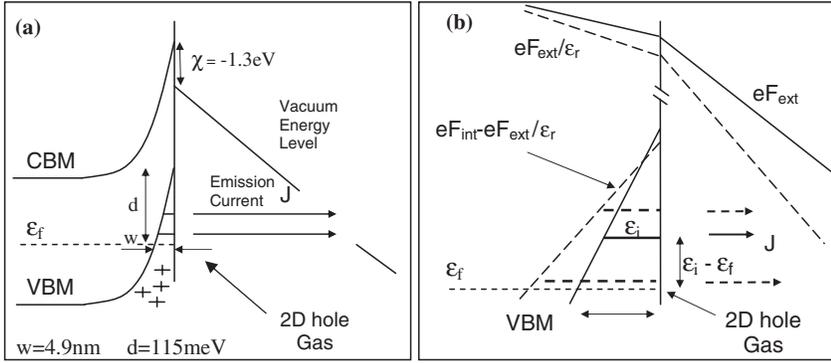
FIG. 2. (a) Schematic energy band diagram of the interface between hydrogen-terminated, air-exposed, diamond, and vacuum in the presence of an external electrical field according to the "charge transfer-doping" model [6]. (b) Schematic drawing of the effect of different external electric fields on the band diagram of the near-surface region of H terminated diamond (low field: solid line, higher field: dashed line).

mond, both affecting the FE probability [see Fig. 2(b)]. (i) With increasing field its profile on the vacuum side steepens, hence the tunneling barrier for electrons to the vacuum is reduced and their escape probability is enhanced. (ii) Once an external field is applied to the sample, the dimensions of the well are modified and they can be approximated by the sum of the internal potential energy and the potential energy induced by the external electrical field. This results in the widening of the QW, leading to an increase of the number of levels that it can accommodate. At certain values of the electric field the QW will be wide enough to accommodate new energy levels. The additional energy states will contribute to the emitted current. Hence jumps in the J-E curve, as reflected in the appearance of steps in the measured FE curve, are to be expected. It should be mentioned that in FE, the tunneling probability of electrons out of the surface depends only on the energy corresponding to their momentum component perpendicular to the surface, which, in our case, is quantized. Therefore, the appearance of jumps in the FE emission (J-E) data is directly associated with the presence of quantum states in the surface potential well.

The experimentally observed jumps in the field emission from a hydrogenated diamond surface at well-defined values of the extracting electric field are theoretically reproduced by us as described below. We perform numerical calculations which, when using physically reasonable parameters, reproduce very well the experimentally measured J-E curves.

In general, the current density (J) of electrons emitted from a surface is given by:

$$J = \Sigma_i N(\varepsilon_i) f(\varepsilon_i) D(\varepsilon_i), \qquad (1)$$

where ε_i is the energy of the ith discrete energy level, $N(\varepsilon_i)$ is the density of occupied states in this level, $f(\varepsilon_i)$ is the "attempt frequency" for escape of the electrons from the QW, and $D(\varepsilon_i)$ is the tunneling probability of an electron from the ith energy level through the barrier into the vacuum.

In order to calculate the J-E curve we first calculate the energy levels ε_i of carriers confined in the QW following the procedure described in Ref. [14]. We approximate the near-surface potential experienced by holes by a triangular

potential well [15] of depth d and width w, extending from the surface into the diamond. This well will accommodate energy levels $\varepsilon_i(F)$, the positions of which depend on the dimensions of the well, hence on the value of the external field as given by Eq. (2).

$$\varepsilon_i(F) = \left(\frac{\hbar^2}{2m_z^*}\right)^{1/3}\left[\frac{3}{2}\pi e(F_{\text{int}} - F/\varepsilon_r)\left(i - \frac{3}{4}\right)\right]^{2/3}. \quad (2)$$

Here i is the energy level number, m_z^* is the effective mass of a hole perpendicular to the surface (taken as $0.75m_e$) [16], F_{int} is the internal electrical field calculated from the dimensions of the potential well, F is the applied electrical field, and ε_r the material dielectric constant. These energy levels, calculated as a function of the external field (using realistic values for the potential well, $w = 4.9$ nm and $d = 115$ meV) according to Eq. (2), are shown in Fig. 3. As can be seen in Fig. 3 (solid line), for very low values of the applied electric field the well already contains one energy level. However, with increasing electric field more levels enter so that at values of the field of about 17 V/μm, 52 V/μm, and 67 V/μm the well contains 2, 3, and 4
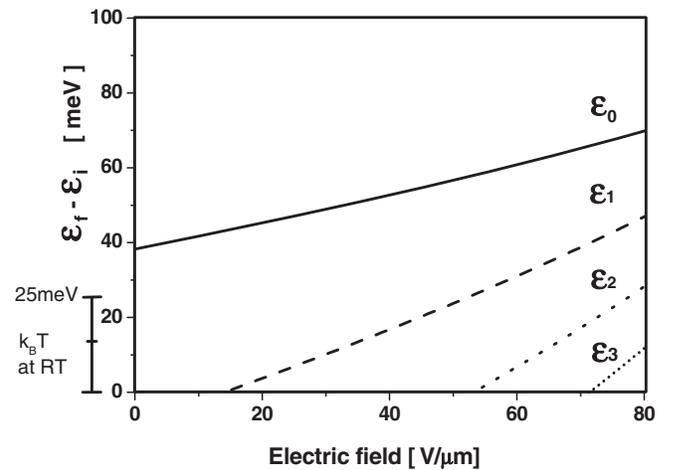

FIG. 3. Calculated energy levels in a triangular QW of width $w = 4.9$ nm and height $d = 115$ meV as a function of the applied external field [values used for the FE simulation shown in Fig. 1(b)]. Note that without any external field the QW can accommodate one energy level (ε_0) only, hence electron emission is already measured at very low fields.

levels, respectively. Once the energies of the levels are known their electron occupation $N(\varepsilon_i)$ at any given temperature can be calculated using the Fermi distribution.

$$N(\varepsilon_i) = n\left(\frac{m_z^*}{\pi\hbar^2}\right)kT\ln\left[1 + \exp\left(\frac{E_{QW} - \varepsilon_i - E_f}{kT}\right)\right], \quad (3)$$

where E_f is the Fermi energy level, E_{QW} is the depth of the potential QW, n is the degree of hole degeneracy, and $m_z^* = (m_x^* m_y^*)^{1/2}$ is the state density mass. The total sheet carrier concentration N_s is the sum over all electrons at the different energy states:

$$N_s = \sum_i N(\varepsilon_i). \quad (4)$$

The attempt frequencies for escape from the different levels in the well $f(\varepsilon_i, F)$ can be calculated from fundamental quantum mechanics [14].

$$f(\varepsilon_i, F) = \frac{e(F_{int} - F/\varepsilon_r)}{2(2m_z^*\varepsilon_i)^{1/2}}. \quad (5)$$

The escape probability $D(\varepsilon_i)$ of an electron from an energy level ε_i, through the triangular barrier at a given value of the applied field F, is given by [17]:

$$D(\varepsilon_i, F) = \exp\left(-\frac{4\sqrt{2m_z^*}}{3e\hbar F}[\chi + E_g - (E_{QW} - \varepsilon_i)]\right), \quad (6)$$

where χ is the electron affinity of the semiconductor, being negative in the case of hydrogenated diamond ($\chi = -1.3$ eV) [18].

By inserting Eqs. (2)–(6) into Eq. (1) we can generate J-E curves of the emission current versus applied electric field for different values of the dimensions of the QW. The computed curve that best fits the data is obtained by using a width of 4.9 nm and a depth of 115 meV, as shown in Fig. 1(b). The similarity between the computed J-E curve obtained by using these parameters [Fig. 1(b)] and the experimental data [Fig. 1(a) lines (a) and (b)] is remarkable.

The dimensions of the potential at the hydrogen-terminated diamond surface found here to best reproduce the positions and heights of the steps in the J-E experimental curve can be compared to those estimated by others. Takeuchi et al. [10] have deduced, using Nernst's equation, the height of the QW to be around 100 meV above the VBM. Nebel and co-workers [13] have calculated for a surface carrier concentration of 5×10^{12} cm^{-1}, a potential well of height 237 meV, and width of 2.7 nm. These values are in agreement with the dimensions of the QW obtained by us, taking into account the carrier concentrations and vacuum conditions of the different experiments.

In conclusion, we have experimentally shown, by FE measurements, the formation of well-defined quantum states of holes in the 2D surface layer present on hydrogenated air-exposed diamond surface. This quantization is evident from the appearance of discrete jumps in the electron emission current, at well-defined values of the extracting electric field. The fact that quantum effects are found, at RT, in the FE from a front contacted surface-conducting diamond and that they can be theoretically reproduced, supports the hypothesis that it is the surface "transfer-doping model" [6] that gives rise to surface conduction in hydrogen-terminated air-exposed diamond. In contrast to most quantum effects, observable in nanostructures only at very low temperatures, our finding shows that quantum effects of carriers confined in two-dimensional nanostructures may be observed at high temperatures. These are expected to be enhanced when the temperature is increased, thus increasing the carrier concentrations at the various energy levels. The fact that in surface-conducting diamond, plateaus in the J-E curves exist in which the electron emission is nearly independent on the extracting field (in sharp contrast to the regular exponential FN dependence), may find application in diamond based FE devices.

[1] J. E. Field, *The Properties of Natural and Synthetic Diamond* (Academic, New York, 1992).
[2] J. Isberg et al., Science **297**, 1670 (2002).
[3] C. E. Nebel and J. Ristein, *Thin-Film Diamond II*, Semiconductors & Semimetals Vol. 77 (Elsevier, New York, 2004).
[4] S. Koizumi et al., Science **292**, 1899 (2001).
[5] M. I. Landstrass and K. V. Ravi, Appl. Phys. Lett. **55**, 975 (1989).
[6] F. Maier, M. Riedel, B. Mantel, J. Ristein, and L. Ley, Phys. Rev. Lett. **85**, 3472 (2000).
[7] H. Kawarada, Surf. Sci. Rep. **26**, 205 (1996).
[8] D. Takeuchi et al., Appl. Surf. Sci. **159–160**, 572 (2000).
[9] P. Strobel, M. Riedel, J. Ristein, and L. Ley, Nature (London) **430**, 439 (2004).
[10] D. Takeuchi, M. Riedel, J. Ristein, and L. Ley, Phys. Rev. B **68**, 041304(R) (2003).
[11] B. Rezek et al., Appl. Phys. Lett. **82**, 2266 (2003).
[12] J. Ristein, L. Ley, and M. Riedel, J. Electrochem. Soc. **151**, E315 (2004).
[13] C. E. Nebel, B. Rezek, and A. Zrenner, Diam. Relat. Mater. **13**, 2031 (2004).
[14] V. G. Litovchenko and Yu. V. Kryuchenko, J. Vac. Sci. Technol. B **11**, 362 (1993).
[15] T. Ando, A. B. Fowler, and F. Stern, Rev. Mod. Phys. **54**, 437 (1982).
[16] A. T. Collins, in *Properties and Growth of Diamond*, edited by G. Davis (INSPEC, London, 1994), p. 275.
[17] A. Modinos, Solid-State Electron. **45**, 809 (2001).
[18] F. Maier, J. Ristein, and L. Ley, Phys. Rev. B **64**, 165411 (2001).