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# Two-dimensional and zero-dimensional quantization of transfer-doped diamond studied by low-temperature scanning tunneling spectroscopy

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Hydrogen-terminated, humidity-exposed type-IIa diamond exhibits high-surface *p*-type conductivity explained by the electrochemical transfer-doping model. According to this model, electrons transfer from the diamond valence band into an adsorbed water layer on the surface, leaving behind a hole accumulation layer, thus forming a two-dimensional quantum well with discrete energy levels. In this paper, the existence of a surface upward band bending and the detailed structure of the discrete two-dimensional energy levels in the thus-formed quantum well are investigated. Ultrahigh vacuum scanning tunneling spectroscopy measurements at temperatures ranging from 30 to 750 K of hydrogen-terminated and humidity-exposed type-IIa diamond are used. The energy levels related to the transfer-doped surface conductive layer have been differentiated from those caused by the adsorbed water layer by measuring a hydrogen-terminated and atmosphere-exposed *p*-type B-doped diamond sample. These results corroborate the existence of an upward band bending and show the presence of localized zero-dimensional states and extended two-dimensional states in the local density of states, thus confirming the nonuniform nature of the quantum well on the surface. The energies of the quantized states in the transfer-doped two-dimensional well on the diamond surface, as extracted from the scanning tunneling spectroscopy measurements, agree well with theoretical predictions based on a self-consistent model.

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## I. INTRODUCTION

Hydrogen-terminated, humidity-exposed type-IIa diamond exhibits high *p*-type conductivity.[1] Although the model explaining this effect is still controversial, possible applications of the electronic properties of the high-surface *p*-type conductivity, including the fabrication of field effect transistors, biosensing devices, and various quantum devices, have been considered.[2,3] According to the accepted electrochemical transfer-doping model, the conductivity is due to the transfer of electrons from the diamond valence band into an adsorbed water layer on the surface, leaving behind a thin hole accumulation layer, which induces an upward band bending with two-dimensional (2D) properties near the surface.[4] The upward band bending is confirmed by Kelvin probe measurements, indicating that the Fermi level ($E_F$) resides roughly 0.7 eV *inside the valence band*.[5] The electrical properties of the so-formed *p*-type conductivity surface layer were found to be strongly dependent on surface properties. Surface sheet conductance of $10^{-4}$ to $10^{-5}$ $\Omega^{-1}$, carrier concentrations of $10^{12}$ to $5 \times 10^{13}$ holes/cm$^2$ , and a mobility of 30 to 70 cm$^2$V$^{-1}$s$^{-1}$ were deduced from room-temperature Hall effect and resistivity measurements.[1] The relatively low hole mobility was proposed to be related to the nonuniform quantum well caused by nonhomogeneous hydrogen termination and ionized adsorbate distribution.[6,7] Heating the sample to temperatures above 250 °C was shown to remove the surface conductivity, supporting the fact that the *p*-type conductivity is related to the presence of an adsorbed water layer on the diamond surface.[8]

A model based on the presence of shallow acceptors induced by the presence of hydrogen has recently been published suggesting a downward band bending near the diamond surface.[9] This model is strengthened by x-ray photoelectron spectroscopy (XPS) measurements showing that the Fermi level is as high as 0.52 eV *above the valence-band* maximum.[9]

Theoretical calculations based on the transfer-doping model show that, depending on the carrier concentration, the Fermi level may be as low as 1 eV below the valence-band maximum, forming a quantum well with discrete 2D states.[10–12] Most recently, a detailed study of these 2D states based on the self-consistent solution of the Poisson-Schrödinger equation for hydrogen-terminated diamond has been published.[12] It predicts that the quantized energy states are located only a few tens of meV around the Fermi level, and the position of the valence-band maximum is determined in this case by the lowest hole sub-band. For a hole sheet density above $9 \times 10^{12}$ cm$^{-2}$, the Fermi level is predicted to cross the lowest hole sub-band minimum supporting the existence of a 2D hole gas near the surface. Indeed, the presence of states in the 2D well has been confirmed by electron field emission experiments,[13,14] however, their exact energetic structure could not be inferred from these measurements.

An accurate and reliable spectroscopic study of the diamond surface is required to identify the exact structure of the quantized energy levels in the 2D quantum well. Scanning tunneling spectroscopy (STS), in particular when done at low temperature, is an ideal tool to determine the local density of states at the sample surface and to measure the energies of discrete energy levels.[15] For the specific case of transfer-doped diamond, STS measurements at different temperatures are complicated by the low conductivity of the diamond bulk and the presence of the adsorbed thin water layer on its surface. Previous scanning tunneling microscopy (STM) and STS measurements were performed on hydrogenated boron-doped diamond samples, however, with no water adsorbed on their surface.[16,17] Until now, no investigation of how the presence of an adsorbed water layer on hydrogenated type-IIa diamond affects the results of STM and STS was carried out, although it has been well documented that, in general, the existence of a thin, atmospherically adsorbed layer on sample surfaces can cause a dramatic decrease in the electronic tunneling barrier.[18–20] This water-related effect was shown to be caused by the existence of intermediate states in the tunneling gap due to the presence of adsorbed water molecule dipoles, violating the one-dimensional tunneling approximation. Recent STS measurements of an undoped hydrogenated diamond surface in electrolyte solution ($KNO_3$) at room temperature suggest that the Fermi level is located roughly 0.8 eV under the valence-band maximum and that 2D quantized hole states exist 0.3 eV above the Fermi level.[21]

In this paper, we present ultrahigh vacuum (UHV) scanning tunneling spectroscopy measurements at temperatures ranging from 30 to 750 K of hydrogen-terminated and humidity-exposed type-IIa diamond. The results of these measurements confirm the existence of an upward band bending yielding the detailed structure of the discrete 2D energy levels in the thus-formed quantum well. Furthermore, these results agree with the recently published self-consistent model in Ref. 12 Extra care has been taken to differentiate effects arising from the transfer-doped surface conductive layer from those caused by the adsorbed water layer. This was done by comparing spectroscopic results gathered from a hydrogenated highly boron-doped diamond ($N_A \approx 10^{19}$ cm$^{-3}$) in the presence of a surface adsorbed layer to those measured on the pure undoped transfer-doped diamond sample. The Fermi level in the highly boron-doped diamond is located close to the valence band, making the transfer-doping effect negligible compared to that of the pure IIa sample, thus allowing the energy levels related to the adsorbed layer on the diamond surface to be distinguished from those that are related to transfer doping.

## II. EXPERIMENT

A pure type-IIa single-crystal diamond ($3 \times 3 \times 0.25$ mm$^3$) and a type-Ib diamond homoepitaxially overgrown with a B-doped ($N_a = 2 \times 10^{19}$ cm$^{-3}$) layer were used in this work. Following cleaning from organic and nonorganic contaminants in a mixture of nitric, sulfuric, and perchloric acids, the samples were hydrogenated in a microwave hydrogen plasma for 30 minutes at a temperature of 640 °C and further exposed to the humid atmosphere allowing for the transfer doping to happen.

The STM and STS measurements were carried out in an Omicron ultrahigh vacuum variable temperature (UHV/VT) STM system in a vacuum of $4 \times 10^{-11}$ mbar. A tungsten tip conditioned by electron bombardment was used for the measurements. Two molybdenum plates pressed on the top edges of the diamond sample serve as top electronic contacts. The STM images were obtained with a bias voltage ($V_{\text{bias}}$) of 1.5 V and a set-point current of 500 pA, adjusting a feedback loop to keep a constant current. Sets of $I$-$V$ and $dI/dV$ curves were measured simultaneously, using a lock-in amplifier, in constant height mode at a bias voltage of - 1 V by interrupting the feedback loop. The reproducibility of the data was verified by recording $I$-$V$ and $dI/dV$ curves at the same point on the sample surface dozens of times. The presented data are an average over such measurements. For STM and STS measurements at low temperatures (30 and 110 K), the sample plate was cooled down through a copper braid connected to a liquid He reservoir. For STS and STM measurements with no water layer, the diamond was first indirectly heated *in situ* in an adjacent preparation chamber using a pyrolitic boron nitride heater allowing desorption of the moisture layer. The sample was then retransferred into the STM chamber, where it was cooled down to room temperature at which $I$-$V$ curves were measured. The same process was repeated for various temperatures until the sample surface conductivity was reduced to a point (550 °C) at which STM and STS measurements were no longer possible.

The resistivity, carrier concentration, and mobility of the samples were measured at room temperature by Hall effect in the Van der Pauw configuration using four silver paint contacts placed on the edges of the diamond surface. The type-IIa hydrogenated and air-exposed sample showed the expected $p$-type conductivity with a carrier concentration of $1.3 \times 10^{13}$ cm$^{-2}$, a mobility of 66 cm$^2$/V s, and a sheet resistance of $1.6 \times 10^4$ Ω /□.

## III. RESULTS AND DISCUSSION

Figure 1 shows a typical $I$-$V$ curve measured at room temperature (RT) on the type-IIa transfer-doped diamond. It should be noted that, unlike other STM experiments done in UHV, the water adsorbed layer that exists on the sample surface is not removed by heating, as its presence on the surface is essential for the existence of the surface conductivity and the 2D quantum well (QW) states measured here. The adsorbed water layer was shown in previous works[18–20] to lower the tunneling barrier height, reduce the dependence of the tunneling current on the tip-sample distance, and deteriorate the STM image resolution. Indeed, at this stage, a nonresolved image of the surface was noticed also in this work.

The data of Fig. 1 show an abrupt increase of the tunneling current when the bias voltage is below –0.3 V or above 0.3 V, quickly reaching the amplifier saturation level of 3.3 nA at 1.5 V. Investigating the $I$-$V$ and $dI/dV$ (not shown) curves for $V <$ –0.3 eV and $V >$ 0.3 V reveals steplike features

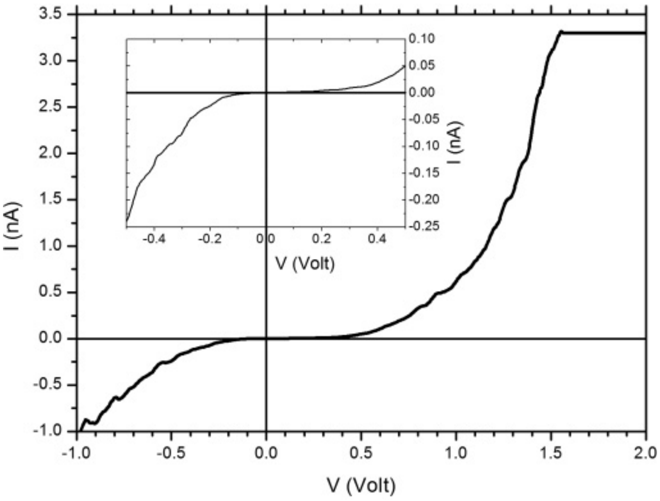

FIG. 1. Tunneling current vs sample bias voltage for a hydrogenated, atmospherically exposed IIa pure diamond at RT. The sample-tip approach parameters are $V_{\text{gap}} = -0.7$ V, $I_{\text{set point}} = 550$ pA. The STM amplifier saturates at 3.3 nA. The inset shows a zoom-in of the measured data around the Fermi level.

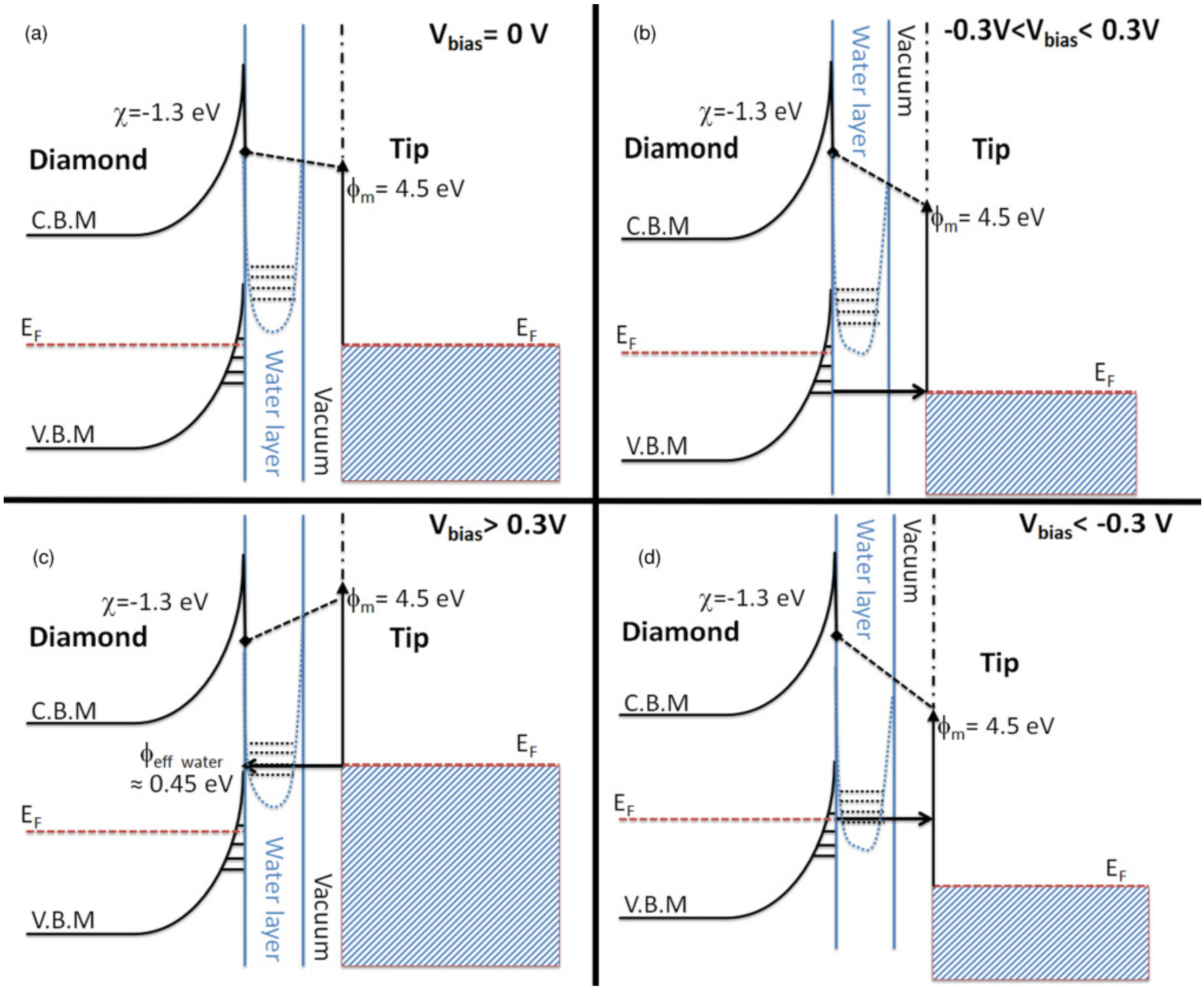

FIG. 2. (Color online) Schematic energy band diagram of the tunneling junction between the hydrogenated transfer-doped diamond surface, the adsorbed water layer (out of scale), and the STM tip. The upward band bending is 0.55 eV ($E_V$-$E_F$ at the surface) (Ref. 12). $\chi = -1.3$ eV and $\phi_{\text{tip}} = 4.5$ eV. (a) Shows the junction with no bias voltage applied. (b) Shows the tunneling junction under a negative sample bias voltage greater than –0.3 V. The arrow indicates electron tunneling from filled states of the QW into the tip. (c) Shows the tunneling junction under a positive sample bias voltage greater than 0.3 V. $\phi_{\text{eff}} = 0.45$ eV indicates the reduced tunneling barrier due to intermediate states in the water adsorbed layer. The arrow indicates electron tunneling from the tip into empty intermediate states in the adsorbed water layer. (d) Shows the tunneling junction under negative bias voltage lower than –0.3V. The arrow indicates tunneling from full states in the sample into intermediate states in the adsorbed water layer.

indicating the existence of filled states below –0.3 eV and empty states above 0.3 eV. The inset in Fig. 1 shows the same data on an extended scale in the region around the Fermi level (–0.5 V to +0.5 V). The slope of the curve gradually increases for negative bias voltages; however, it remains constant for positive bias voltages below 0.3 V, thus suggesting that filled valence-band states are located close to the Fermi level.

The abrupt increase in current accompanied by the appearance of steps observed at positive sample bias above 0.3 V (Fig. 1) may, in principle, be interpreted as (i) direct tunneling from the tip to empty states in the quantized 2D well related to transfer doping and/or (ii) tunneling from the tip through empty surface states and/or (iii) tunneling from the tip through the intermediate states in the thin adsorbed water layer on the diamond surface. The features observed at negative voltage below –0.3 eV may be interpreted as direct tunneling from filled states in the quantized 2D well to the tip (i) or tunneling from filled states near the sample $E_F$ through the energy levels in the thin adsorbed water layer to the tip (iii).

The likelihood of the above options is discussed below: A schematic energy band diagram of the tunneling junction based on the transfer-doping model, and taking into account the tunneling barrier resulting from the thin water layer adsorbed on the diamond surface and the vacuum between them, is displayed in Fig. 2 for different bias voltages. Figure 2(a) shows the tunneling junction under equilibrium conditions with no bias voltage applied. The Fermi levels of the metallic tip and transfer-doped diamond are aligned. The values used for the construction of this figure are as follows: The hydrogen-terminated diamond surface exhibits a negative electron affinity of $\chi = -1.3$ eV.[4] The work function of the tungsten tip is $\phi_m = 4.5$ eV. The transfer-doping process induces an upward band bending. The Fermi level is located close or below the valence-band maximum, depending on the hole sheet conductivity. For the present case, with a measured carrier density of $10^{13}$ cm$^{-2}$, $E_F$ is located 0.55 eV below the VBM according to the latest published calculation.[12] If the energy levels related to the water are ignored, the tunneling barrier between the tip and sample would have been 4.625 eV (the average between the work functions of the tip and the diamond surface). However, it is clear that, in the present case, the effect of the water layer on the STM measurements must be taken into account. Various mechanisms, including the existence of intermediate states due to dipole arrangement of water molecules in the adsorbed layer on diamond, have been suggested as a cause for lowering the tunneling barrier.[19,20] As discussed by others,[19,20] the density of states in a water layer is unknown. The exact location of these states in Fig. 2 is, thus, schematic only. The thin water layer adsorbed on the diamond surface was found to exhibit a barrier height of $\phi_{\text{eff}} = 0.45$ eV, as determined from the maximum of the $dI/dV$ curve at sample bias exceeding 0.3 V.[18–20] We also assume that there exists a vacuum gap between the water-covered sample and the tip under the UHV conditions of this experiment. Figures 2(b)–2(d) described the sample-tip junction under bias. The applied voltage causes the energy levels of the tip and of the adsorbed water layer to shift energetically upward or downward compared to the sample depending on the bias polarity. Figure 2(b) shows the tunneling junction for –0.3 V $\ll V \ll$ 0.3 V. In this case, the system is in the direct tunneling regime for which tunneling is through a square potential well, described by the standard WKB model. The surface local density of states is detected by the injection of electrons from the tip to empty states above the Fermi level for positive sample bias voltages. For negative voltage values, electrons tunnel from filled states below the Fermi level to the tip. For the case in which the positive voltage approaches the intrinsic tunneling barrier of the water layer $V = 0.45$ V [Fig. 2(c)], electrons tunnel from the tip through intermediate states within the thin adsorbed water layer, giving rise to an exponential increase in the measured current for positive sample bias voltages above 0.3 V and to steps in the *I-V* curve (see Fig. 1). For bias voltage smaller than –0.3 V [see Fig. 2(d)], and assuming the voltage drops entirely on the sample-tip junction, the water-related intermediate empty states will align with occupied levels in the sample 2D quantum well, causing an increase in tunneling current. This effect is noticeable in Fig. 1 for bias voltages lower than –0.3 V in the form of additional features unrelated to the energy levels of the 2D quantum well. Therefore, information regarding the LDOS of the 2D QW formed in the transfer-doped pure IIa diamond may be extracted *only from data taken at voltages lower than 0.3 V and higher than -0.3 V*. It turns out from the analysis of Fig. 1 and the above discussion that the strong increase in tunneling current that occurs above $V_{\text{bias}} = 0.3$ V and below –0.3V should be related to hypothesis (iii), i.e., tunneling from the filled states of the tip to empty states in the thin adsorbed water layer (see further experimental proof for this below) or from the filled states around the sample Fermi level through the energy levels in the thin adsorbed water layer to the tip. The first hypothesis (i) assumes that direct tunneling from the tip to empty states in the quantized 2D well related to transfer doping or direct tunneling from filled states in the quantized 2D well to the tip is not compatible with the theoretically predicted and experimentally measured[5,10,12] position of the Fermi level, being 0.4 to 0.7 eV below the valence-band maximum at the surface. The energies of the quantum states for this high Fermi level are predicted by Ley *et al.*[12] to be only a few tens of meV around the Fermi level, in contrast to the high currents and steps measured here for fairly high voltages (above 0.3 V). Had there been empty states at energies above 0.3 eV on the diamond surface, this would require a much higher quantum well for holes, which is not the case for carrier concentration around $1.3 \times 10^{13}$ cm$^{-2}$.[10,12] The tunneling to empty surface states related to carbon dangling bonds [hypothesis (ii)] can also be ruled out since it can occur only if the hydrogen is desorbed from the surface, which is known to happen only at $T > 680$ °C.[16]

To experimentally verify that the steep increase of the tunneling current for $V > 0.3$ V is indeed related to the adsorbed water layer on the type-IIa diamond [hypothesis (iii)], or to degenerated valence-band empty states [hypothesis (i)], temperature-dependent STS measurements were performed on a transfer-doped highly boron-doped ($N_a = 10^{19}$ cm$^{-3}$) diamond layer. This sample was hydrogenated and exposed to air under the same conditions as the IIa diamond. The high hole concentration and the low Fermi level in the boron-doped sample nullify the effect of the transfer doping. The high conductivity of the native sample (not related to transfer doping) enabled STM and STS measurements at temperatures where the water layer has been desorbed, allowing the investigation of the effect that the adsorbed water layer has on the boron-doped diamond *I-V* and $dI/dV$ curves.

Figure 3 shows the resulting *I-V* curves measured for the hydrogenated air-exposed B-doped sample at RT, 250 °C,

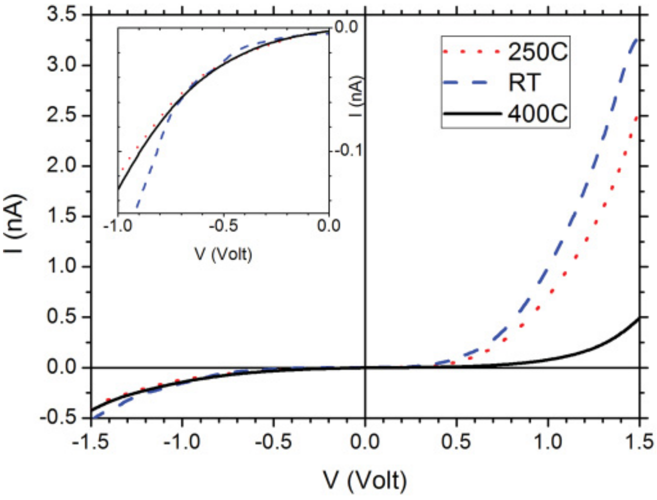

FIG. 3. Tunneling current vs sample bias voltage for a hydrogenated, atmospherically exposed, boron-doped diamond layer at RT (blue dashed line), 250 °C (red dotted line), and 400 °C (solid black line). The tip sample approach parameters are $V_{\text{gap}} = -1$ V, $I_{\text{setpoint}} =$ 150 pA. The inset shows a zoom-in of the measured data for negative bias voltages.

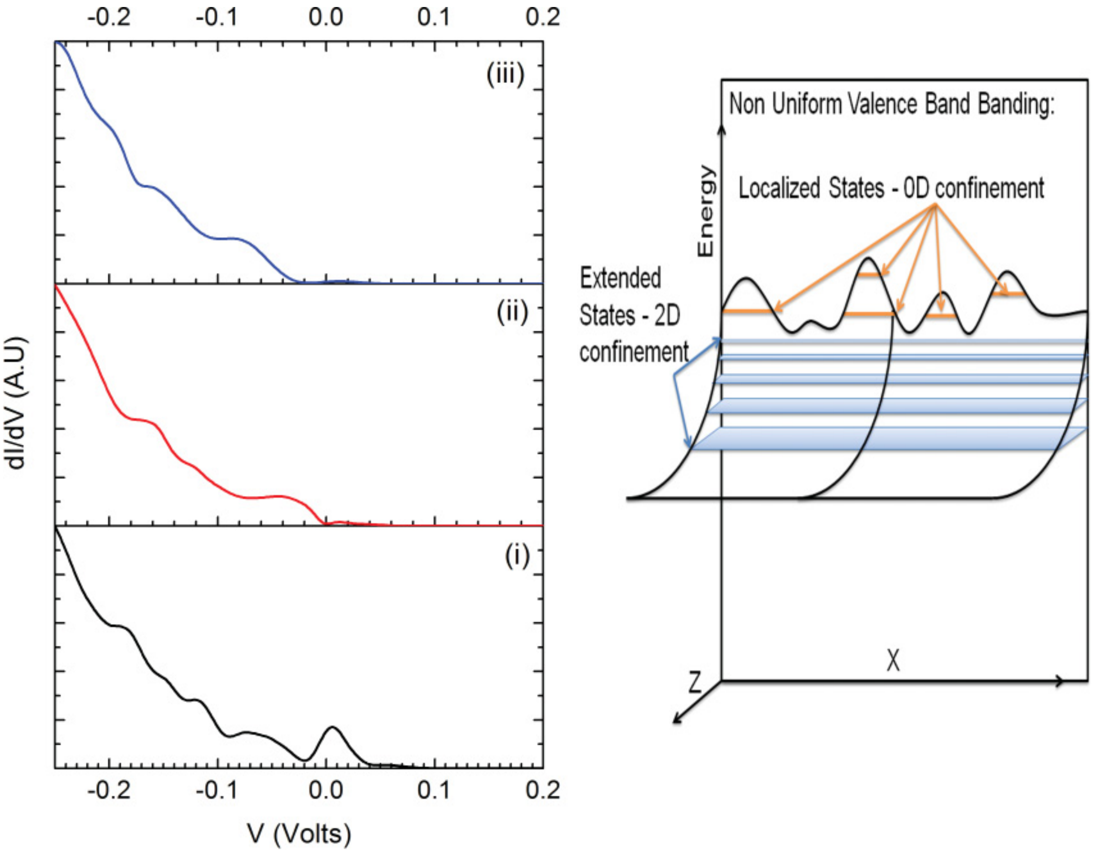

FIG. 4. (Color online) (a) Shows $dI/dV$ (normalized) vs sample bias voltage for a hydrogenated transfer-doped pure IIa diamond measured at 30 K at different points (i), (ii), and (iii) on the sample surface. The tip approach parameters are $V_{\text{gap}} = –0.5$ V, $I_{\text{set point}} = 450$ pA. (b) Shows a schematic description of the nonuniform QW and the resulting localized states created due to the nonhomogeneous hydrogen termination and adsorbate coverage of the diamond surface (Ref. 6).

and 400 °C. The *I*-*V* curves measured at all temperatures are almost similar at negative bias voltages and show that the Fermi level is close to the valence-band maximum, as expected for the highly boron-doped sample ($E_A \sim 0.2$ eV). At room temperature, for positive sample bias values above 0.3 V, the same abrupt increase in tunneling current that was measured on the hydrogenated IIa diamond sample is observed. This increase in tunneling current vanishes progressively as the sample is heated to temperatures at which the adsorbed layer is removed, until it is barely visible at 400 °C.

The results presented in Fig. 3 prove that there is a direct connection between the existence of an adsorbed water layer and the increasing tunneling current at positive sample bias voltages greater than 0.3 V, regardless of sample doping. This clearly proves that the high tunneling current measured above 0.3 V is unrelated to the transfer-doping effect. The results of Fig. 3 obtained for a B-doped sample also exclude the contribution of hydrogen-plasma-induced surface states to the tunneling current. Had this been the case, then the tunneling currents should remain high as long as the temperature range is below the hydrogen desorption temperature (~700 °C). The increase in tunneling current at high positive voltages must therefore be attributed to the decrease in the effective tunneling barrier at the STM junction caused by intermediate states in the adsorbed water layer covering the diamond surface. In fact, the jumps observed in the tunneling current at high positive voltages are most probably related to resonant tunneling through these intermediate states in the water layer. In addition, the *I*-*V* curve measured at RT exhibits clear features for bias voltages lower than –0.3 V (as shown in Fig. 3 inset). These features are not present in the *I*-*V* curves measured at higher temperatures, suggesting that they are related to electron tunneling out of the diamond through empty levels related to the adsorbate water layer.

The following discussion now concentrates on the data obtained for voltages lower than 0.3 V and higher than –0.3 V, yielding results related to the transfer-doped diamond. Figure 4 shows typical $dI/dV$ curves measured at 30 K at different points on the sample surface. Each curve represents the average of up to 30 measurements taken at the same point on the sample surface. The majority of the points measured on the diamond surface show $dI/dV$ curves with the energetic structure similar to that of curve (i). The spectral resolution of the $dI/dV$ measurements is a convolution between the derivative of the Fermi-Dirac function of the tip and the LDOS of the sample. The resulting temperature broadening is expected to be of the order of $3.2 \times k_B T$.[22] The improvement of the spectral resolution from 100 meV at room temperature to 10 meV at 30 K allows the clear observation of discrete energy levels. The Fermi level position in the QW is temperature dependent. However, the shift in $E_F$ is predicted to be only of the order of

10 meV; thus, the results of the set experiments are insensitive to it due to the low (0.1 eV) experimental resolution at RT.

All the measured spectra indicate that the Fermi level resides several meV away from the first quantized energy level and that the energetic structure of the $dI/dV$ curves measured at various points is different. In particular, the $dI/dV$ curve (i) displays both the distinctive steplike features of 2D confined DOS and peaks that suggest zero-dimensional confinement. These can be understood by considering the transport model introduced in Ref. 6 to explain the strong dependence of the $p$-type conductivity on surface properties, most likely adsorbates, and the hole mobility increase detected at low temperature ($T < 25$ K) by Hall effect measurements. This model is based on the fact that the transfer-doping process is affected by the hydrogenation of surface dangling bonds and adsorbed water coverage, which are not uniform throughout the sample surface. The resulting upward band bending and, therefore, quantum well will not be uniform throughout the sample surface, as schematically shown in Fig 4(b).[6] In Ref. 6, this disorder is shown to cause a tail of localized zero-dimensional states that trap holes at low temperatures ($T < 25$ K), thereby decreasing the measured hole concentration. The remaining holes are delocalized and can propagate along the 2D extended states at the surface, hence, increasing their mobility.[6,7] In our work, the quantum-well disorder results in $dI/dV$ curves displaying different energetic structures at different measured points on the sample surface and in the appearance of zero-dimensional states in the $dI/dV$ curves measured on spots with higher upward band bending. Indeed, the first energy level measured on point (i) is located above $E_F$, while it is located below $E_F$ for points (ii) and (iii), thus proving that the local hole concentration of point (i) is higher than that of the two other points. The $dI/dV$ for point (i) exhibits the first three quantized energy levels located at $E_0 = +6$ meV, $E_1 = -77$ meV, and $E_2 = -120$ meV from the Fermi level with additional levels at 150 and 185 meV. The first feature, at 6 meV, is a relatively sharp peak, typical for a localized zero-dimensional state in the quantum well, as expected for higher upward band bending [see Fig. 4(b)]. The other features of the same $dI/dV$ curve are steplike, as expected for energy levels in a 2D well. The difference between the first $E_0$ and second $E_1$ quantized levels in these spectra is of the order of a few meV, being of the same order of magnitude of the energies deduced from the hole-transport activation energies obtained from Hall effect experiments at low temperatures (23 meV).[6] The spacing between the higher levels (at –150 and –185 meV) is smaller, as expected, for levels in a triangular quantum well. In contrast, the LDOS curves measured at the two other locations on the sample surface [Fig. 4(a), (ii) and (iii)] have their first state at –15 and –55 meV below the Fermi level. Their measured LDOS show only steplike features typical for 2D confinement. Therefore, these points correspond to lower local hole densities. The differences in the measured LDOS curves clearly indicate a nonuniform quantum-well structure on the nanoscale, with different local hole concentrations, as schematically shown in Fig. 4(b).

The difference between the second quantized energy level and the Fermi level is larger than $k_BT$ in all the $dI/dV$ measurements performed at 30 K. Thus, indicating that the hole occupation of $E_0$ (the first quantized state) is significantly larger than that of $E_1$ (the second quantized state), confirming that the positively charged holes in $E_0$ can be treated as a two-dimensional hole gas according to Ref. 12.

Figure 5 shows a comparison between the computed energies of the three first levels around $E_F$ as calculated in Ref. 12 and those experimentally deduced from the present STS measurements. These first levels are of particular interest as they determine the electrical transport properties of the transfer-doped diamond surface. The hole concentration measured by Hall effect ($1.3 \times 10^{13}$ cm$^{-2}$) yields the theoretically predicted energies of the three first levels around the Fermi level.[12] These levels were found to fit those measured in

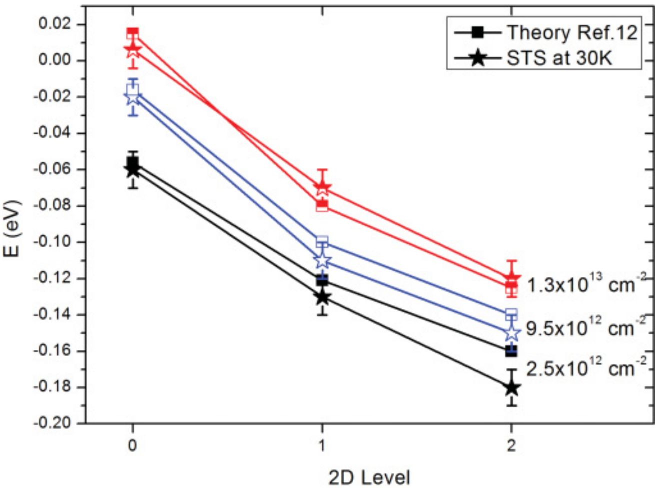

FIG. 5. (Color online) Comparison between the 2D energy levels measured on different points of a transfer-doped pure IIa diamond surface at 30 K (stars) and the corresponding single-band 2D levels calculated in Ref. 12 for a hole sheet density of $1.3 \times 10^{13}$ cm$^{-2}$ (half-full red squares, $9.5 \times 10^{12}$ cm$^{-2}$ (empty blue squares), and $2.5 \times 10^{12}$ cm$^{-2}$ (full black squares). Error bars are 10 meV, with the optimal spectral resolution at 30 K.

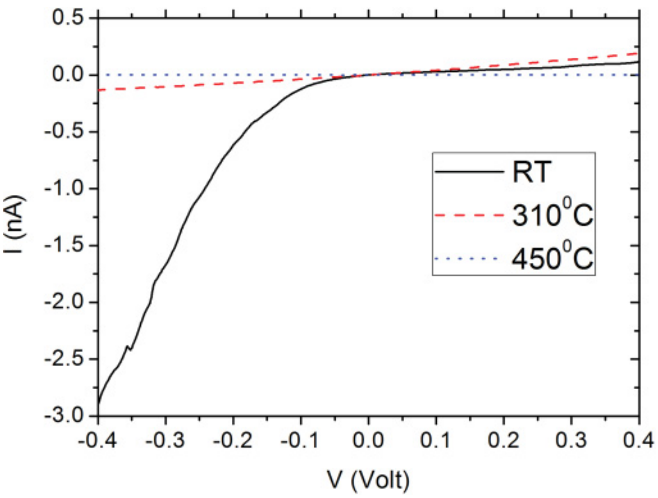

FIG. 6. (Color online) Tunneling current vs sample bias voltage for a hydrogenated, transfer-doped pure IIa diamond at RT (solid black line), 310 °C (red dashed line), and 450 °C (blue dotted line.

curve (i) of Fig. 4(a). For the other points [(ii) and (iii)], the local hole concentration was extracted by comparing the energy levels obtained by the experimental STS measurements with those calculated in Ref. 12 As seen in the figure, most of the experimental results agree with the theoretical predictions within the error due to temperature spectral resolution.

To verify that the measured quantized energy levels are indeed related to band bending generated by the transfer-doping effect, the overall electrical conductivity was measured at temperatures ranging from 300 to 750 K. The results of these measurements are displayed in Fig. 6, showing the current voltage dependences for $-0.4$ V $< V < +0.4$ V. At 300 K, the $I$-$V$ shows a Fermi level that is located near the valence-band maximum, and the tunneling current is of the order of a few nanoamperes for negative sample bias voltages and it is extremely small for positive voltages. When the sample was measured after it was heated (*in situ*) to 310 °C, the tunneling current decreased by an order of magnitude and the valence-band maximum was no longer located near the Fermi level. Following further heating on this sample to 450 °C, extremely small currents in the picoampere range are measured. Hence, the decrease in the tunneling current is clearly related to the gradual loss of the thin water layer setting in at about 250 °C, as previously reported in Refs. 4 and 8, eliminating the hole accumulation layer produced by the transfer-doping process.

## IV. CONCLUSIONS

The presence of the discrete quantized levels in the 2D quantum well formed as a result of hydrogenation and exposure to atmospheric humidity ($H_2O$ adsorbates) of a type-IIa diamond was proven by variable temperature STS measurements. The effect that the adsorbed water layer has on the measured tunneling current was separated from that due to tunneling from states in the QW on the type-IIa diamond surface by comparing the STM obtained for the undoped diamond to those obtained for a similarly treated heavily B-doped sample (assumed to be covered with a similar $H_2O$ surface layer). The presence of a moisture layer on the surface was shown to reduce the tunneling barrier, resulting in high tunneling current as observed in $I(V)$ curves above $+0.3$ eV and below $-0.3$ V. These are unrelated to the quantized energy levels of the QW of the transfer-doped diamond.

The existence of an upward band bending and the presence of 2D states very close to the Fermi level on the treated type-IIa diamond surface are confirmed by the stepwise gradual increase in $dI/dV$ curves, which sets in already at very small voltages. Local nonuniformities on the nanometer scale on the single-crystal diamond surface, possibly caused by nonuniform H and $H_2O$ uptake similar to those inferred from conductivity measurements, are noticed by the appearance of quantum states at some spots on the sample, which resemble those expected for the zero-dimensional confinement.

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