Supplementary Informations for : "Local Detection of Nitrogen-Vacancy Centers in a Nanodiamond Monolayer"

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Materials and Methods

Nanodiamonds synthesis. The nanodiamond particles of this study were synthesized by detonation of an explosive composed of 70 wt% of trinitrotoluene (TNT) and 30 wt% of hexogen (RDX) and purified by an acidic treatment followed by oxidation under air at 670 K.^{1,2} Ultracentrifugation was then applied to the nanodiamond suspensions in order to select individual particles and electrophoretic deposition (EPD) was performed with the resulting suspensions onto highly oriented pyrolitic graphite (HOPG) (see Fig. S1).³ Thereafter, the HOPG sample was clamped on a Mo sample holder by metallic contact at its surface and introduced in ultra high vacuum (UHV) (2×10^{-10} mbars). In this way, we ensure a good contact required for accurate bias-dependent spectroscopic measurements. The sample was then heated up to 850 K for several hours to remove all contaminants of the surface.

Scanning tunneling microscopy experiments. The STM experiments were realized at 5K in ultra-high vacuum (UHV) with a low-temperature STM/AFM microscope (Omicron Nanotechnology GmbH) based on a tuning fork sensor in the qPlus configuration (stiffness of k = 1800 N/m, resonance frequency f_0 = 26 kHz, Q factor = 35000). All STM images were recorded in the constant current mode with the voltage applied to the tip. Prior to measurements, gentle tip indenting into a clean Cu(111) surface were systematically conducted to ensure the tip quality and material.

Spectroscopic measurements under illumination. The spectroscopic experiments under illumination were conducted with a multi-wavelengths LED system from Mitech (P = $10 \text{ mW}/\text{ cm}^2$, wavelengths available : 400 nm, 470 nm, 530 nm and 590 nm) continuously shining through a glass window of the microscope. A relative increase of the microscope temperature ($\approx 4.8 \text{ to } 5 \text{ K}$) was usually observed just after illumination. The piezo-drift was compensated by thermalizing the microscope for $\approx 30 \text{ min}$. Meanwhile, the

thermal displacement was corrected by dynamically tracking the nanodiamond position.⁴ The tip height was set with respect to a reference height given by the STM set point above nanodiamonds at I = 10 pA and V = -3.1 V, parameters taken in accordance to the conductance measurements shown in Figure 2b. They ensure that no relevant variations of the conductivity occur due to illumination which could modify the relative tip-sample distance. Scanning tunneling spectroscopy (STS) was performed with the lock-in technique (f = 600 Hz, $V_{AC} = 5-10$ mV) and bias dependent-frequency shift spectroscopy, $\Delta f(V)$, with typical oscillation amplitudes of A = 150 pm. Spectroscopic measurements were always acquired above the same nanodiamond without any tip changes.

Supplementary Discussion

STS under illumination on wide band-gap semi-conductors and impurities: The interaction of light with semiconductors is a fascinating subject that has occupied scientists for several decades. With the advent of STM, the study of surface photo-voltage effect (SPV) has become of interest and numerous publications have reported light-assisted STM/STS data on various semi-conducting surfaces 5-9. Experimentally, it is known that the SPV created at the sample by irradiation alters the tunneling junction during STM/STS experiments inducing a lateral shift of the I/V characteristics. The interpretation of these STS shifts are however difficult since the local band structure beneath the STM probe can be affected by the strong electric field and high current density required for the STM observation (tip-induced band bending). Nevertheless, the differentiation of p- and ndoped hydrogenated silicon surface or the carrier dynamics in an operating p-n junction have been successfully demonstrated by light-assisted STS measurements.^{8,9} The study of sub-surface impurities has also been conducted by STM.^{10,11} Koenradd et al. showed the possibility to modify the charge states of such defects depending on the voltage applied to the STM tip.^{12,13} Furthermore, the pioneer work of Bonnell *et al.*¹⁴ has also reported the charge transfer transitions from sub-surface defect states (Co²⁺ and Mn²⁻ doped ZnO) to

the conduction band of ZnO Under illumination.

Kelvin Probe Force Spectroscopy : The basic of Kelvin probe force microscopy (KPFM) experiments is to dynamically compensate the electric field arising from the difference of work functions between an AFM tip electrically contacted to the sample.¹⁵ By varying the tip-sample voltage V, the minimum value of this local field, so-called local contact potential difference (LCPD), is determined by measuring the voltage-dependency of the frequency shift Δf of the oscillating sensor. The typical parabolic behaviour of the Δf vs. applied voltage V is shown in (Figure 2d). The maxima of the $\Delta f(V)$ parabola corresponds to the LCPD value, V_{lcpd} , at a certain height and position of the sample. The absolute contact potential difference (CPD) is defined as CPD = $(\phi_{sample} - \phi_{tip})/e$. Knowing that the work function of C(111) is $\phi_C \approx 4.7$ eV (sample)¹⁶ and the Cu-terminated tip ϕ_{Cu} pprox 4.95 eV 17 (the tip was always gently indented in Cu(111) before measurements), the expected CPD during our measurements is expected to be -250 meV. We remark that, at large tip-sample distances (z = 2 in Figure 2e), a value of \approx -300 meV is experimentally found in the so-called long-range electrostatic force regime. Approaching the tip towards the sample allows to probe the short-range regime (SRE) of the electrostatic forces.^{18,19} In this case, the LCPD measurement becomes sensitive to local variation of work function at the surface such as induced by trapped charges at defects. Experimental works have indeed reported the identification of charges localized at the step edges of bulk insulators,²⁰ the differentiation of charge states of adatoms on NaCl/Cu(111),²¹ point defects in oxyde surfaces²² or within single molecules.²³ All these results were essentially obtained at low temperature by means of KPFM spectroscopy. At low temperature and by means of a tuning-fork sensor, the acquisition of spatially resolved LCPD maps (KPFM image) is rather challenging since it requires the built-up at constant height of the LCPD(x,y) map containing several $\Delta f(V)$ curves. This approach has been successfully demonstrated by resolving the charge distribution within a single naphthalocyanin.²⁴ However, the major

drawback of such measurement is the impact of the sample corrugation. In our case, nanodiamonds are highly corrugated (3D-object with few nm height) and the NV centers are distributed in the three spatial dimensions of the nanodiamond core. Such LCPD map is thus strongly affected by the tip-sample distance variations.

To determine the LCPD variation *vs*. the tip-sample distance *z* as shown in Figure 2f, we followed the same procedure than L. Gross *et al.*²¹ Several $\Delta f(V)$ curves were acquired above a single nanodiamond at different tip-sample separations. For each curve, we determined by fitting the parabola the minimum of the sample voltage value (LCPD) V_{CPD} and plotted them *vs*. the tip-sample distance (Figure 2f).

References

- Pichot, V.; Comet, M.; Fousson, E.; Baras, C.; Senger, A.; Le Normand, F.; Spitzer, D. Diamond Rel. Mat., 2008, 17, 13-22.
- (2) Pichot, V.; Stephan, O.; Comet, O.; Fousson, E.; Mory, J.; March, K.; Spitzer, D. J. Phys. Chem. C, 2010, 114, 10082-10087.
- (3) Schmidlin, L.; Pichot, V.; Josset, S.; Pawlak, R.; Glatzel, T.; Kawai, S.; Meyer, E.; Spitzer, D. *Appl. Phys. Lett.*, **2012**, *101*, 253111–253115.
- (4) Kawai, S.; Glatzel, T.; Koch, S.; Baratoff, A.; Meyer, E. Phys. Rev. B, 2011, 83, 035421-1/7.
- (5) Hamers, R. J.; Marker, K. J. Vac. Sci. Technol. A, 1009, 8, 3524–3530.
- (6) Kuk, Y.; Becker, R. S.; Silverman, P. J.; Kochanski, G. P. J. Vac. Sci. Techno. B, 1991, 9, 545–550.
- (7) Takeuchi, O.; Yoshida, S.; Shigekawa, H. Appl. Phys. Lett., 2004, 84, 3645–3646.
- (8) Arima, K.; Shigetoshi, T.; Kakiuchi, H.; Morita, M. Physica B, 2006, 376, 893–896.
- (9) Yoshida, S.; Kanitani, Y.; Oshima, R.; Okada, Y.; Takeuchi, O.; Shigekawa, H. *Phys. Rev. Lett.*, 2007, 98, 026802–1/4.
- (10) Rose, M. K.; Borg, A.; Mitsui, T.; Ogletree, D.F.; Salmeron, M. J. Phys Chem., 2001, 115, 10927–10934.
- (11) Koenraad, P. M.; Flatte M. E. Nat. Mater., 2011, 10, 91–100.
- (12) Teichmann, K. M.; Wenderoth, S.; Loth, R. G.; Ulbrich, J. K.; Garleff, A. P.; Wijnheijmer, P. M.; Koenraad P. M. *Phys. Rev. Lett.*, **2008**, *101*, 076103.
- (13) Garleff, J. K.; Wijnheijmer, A. P.; vand der Enden, C. N.; Koenraad, P. M. *Phys Rev. B*, 2011, 84, 075459.

- (14) Bonnell, D. A.; Rohrer, G. S.; French R. H. J. Vac. Sci. Techno. B, 1991, 9, 551.
- (15) Sadewasser, S.; Glatzel, T. Kelvin Probe Force Microscopy: Measuring and Compensating Electrostatic Forces. Springer Berlin, (2012).
- (16) Diederich, L.; Küttel, O. M.; Aebi, P.; Schlapbach, L. Surface Science, 1998, 418, 219–230.
- (17) Takeuchi, K.; Suda, A.; Ushioda, S. Surface Science, 2001, 489, 100–106.
- (18) Nony, L.; Bocquet, F.; Loppacher, C. Phys. Rev. B, 2011, 83, 035411–13.
- (19) Sadeghi, A. *et al.* Multiscale approach for simulations of Kelvin probe force microscopy with atomic resolution. *Phys. Rev. B* **86**, 075407 (2012).
- (20) Barth, C.; Henry, C.R. Phys. Rev. Lett., 2007, 98, 136804.
- (21) Gross, L.; Mohn, F.; Liljeroth, P.; Repp, J.; Giessibl, F.J.; Meyer, G. Science, 2009, 324, 1428–1431.
- (22) Köning, T.; Simon, G. H.; Rust, H.-P.; Pacchioni, G.; Heyde, M.; Freund, H.-J. J. Am. Chem. Soc., 2009, 131, 17544–17545..
- (23) Leoni, T. et al. Phys. Rev. Lett., **2011**, 106, 216103–1/4.
- (24) Mohn, F.; Gross, L.; Moll, N.; Meyer G. Nature Nanotechnol., 2012, 7, 227–231.
- (25) Burke, S. A.; Ledue, J. M.; Topple, J. M.; Fostner S.; Grütter, P.Adv. Materials, 2009, 21, 1–5.
- (26) Eren B. et al. Beil. Journ. Nanotechnol., 2013, 3, 852–859.
- (27) Pohl D. W.; Möller, R. Rev. Sci. Intrum., 1998, 59, 840-843.



Figure 1: Topographic images of the nanodiamond layer. (a) and (b) constant-current STM images of Figure 1a and b respectively.



Figure 2: Collection of I/V curves recorded at different tip-separations z under illumination. (a)-(e) I(V) spectra where all tip-sample variation are superimposed obtained in dark condition, $\lambda = 530$ nm, $\lambda = 400$ nm, $\lambda = 470$ nm, $\lambda = 590$ nm respectively. Both measurements are performed at the same relative height according to the conductance measurements (Figure. 2) by interrupting the STM feedback at I_t = 10 pA, V_t = -3.1 V. All irradiation conditions lead to the appearance of the HOMO-LUMO states of the NV⁻¹ with a gap of ≈ 1.8 eV. The step height are varying depending on the used wavelength. The maximum is observed for $\lambda = 530$ nm corresponding to the zero-phonon line of the NV⁻¹ centers.