Phys. Status Solidi A **207**, No. 9, 2088–2092 (2010) / **DOI** 10.1002/pssa.201000055

physica status solidi a
www.pss-a.com
applications and materials science

High breakdown voltage Schottky diodes synthesized on p-type CVD diamond layer

Pierre-Nicolas Volpe[*,1,6], Pierre Muret[1], Julien Pernot[1], Franck Omnès[1], Tokuyuki Teraji[2], François Jomard[3], D. Planson[4], Pierre Brosselard[4], Nicolas Dheilly[4], Bertrand Vergne[5], and Sigo Scharnholtz[5]

[1] Néel Institute—CNRS, 25 Avenue des Martyrs 38000 Grenoble, France & Université Joseph Fourier, BP53, 38041 Grenoble, France
[2] National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[3] GeMaC—Campus CNRS de Meudon, 1 place Aristide Briand, 92195 Meudon, France
[4] AMPERE—UCBL—INSA, 20 Avenue Albert Einstein, 69621 Villeurbanne Cedex, France
[5] ISL, French–German Research Institute of Saint Louis, 5 rue Général Cassagnou, 68301 Saint Louis, France
[6] Present address: CEA, LIST, Diamond Sensors Laboratory, Gif-sur-Yvette 91191, France

Received 26 March 2010, revised 9 June 2010, accepted 16 June 2010
Published online 10 August 2010

Keywords breakdown, diamond, Schottky diode

* Corresponding author: e-mail Pierre-nicolas.volpe@cea.fr, Phone: +33 1 69 08 21 69, Fax: +33 1 69 08 78 19

Diamond is a very promising material for power electronics and electrical energy management devices. Several architectures have been implemented in the past for the fabrication of Schottky diodes on boron doped microwave plasma enhanced chemical vapour deposition (MPCVD) layers and on lowly and highly boron doped stacked structures. Meanwhile, the performances often suffered several limitations, mainly due to insufficient crystalline quality of the layers or a non-optimized diamond/metal interface. In this study, we will especially show that the achievement of diamond Schottky diode with high breakdown reverse voltage and high breakdown field goes through the optimization of several factors: a net acceptor concentration below $10^{16}\,cm^{-3}$, the epilayer growth conditions, the implementation of efficient surface passivation techniques and the integrity of the metal/diamond interface. Optimizing the previous conditions enabled us to fabricate a lateral gold Schottky diodes withdrawing reverse voltages up to 7.5 kV before avalanche breakdown induced by an electric field in the range 7–9.5 MV/cm. These findings open the route for unipolar diamond devices operating in high power electronics without the use of guard rings or edge terminations contrary to other wide band gap semiconductors.

1 Introduction Low boron doped diamond is a very promising material for high power and high frequency application due its intrinsic properties like a wide band gap (5.45 eV), high breakdown field (10–20 MV cm^{-1}), a high hole saturation velocity (2.2×10^7 cm s^{-1} [1]) and an important thermal conductivity ($22\,W \cdot cm^{-1}\,K^{-1}$). These properties are far higher than those known from other semiconductors like silicon or SiC especially in the field of power applications, which make diamond an interesting material for the fabrication of high breakdown voltage devices. In this study, we synthesized several Schottky diodes on a thick low boron doped diamond layer grown by microwave plasma enhanced chemical vapour deposition (MPCVD), exhibiting a breakdown voltage higher than 7.5 kV and, for such a reverse voltage, an electrical field in the range 7–9.5 MV/cm at the centre of the Schottky contact. These values are higher than the actual state of art for Schottky diode breakdown voltage [2, 3] and avalanche electric field [4]. It will be especially stressed that these record values have been obtained thanks to an optimization of the layer growth conditions, metal/diamond interface and efficient surface oxidizing treatment. It will be also shown that the latter treatment permits both a stable electrical passivation of the surface as well as a chemical passivation of the metal/diamond interface, thus revealing the true dielectric strength of diamond.

Experimental In this study, we used a Ib (100) made by high pressure and high temperature technique (HPHT) ($3 \times 3 \times 0.5\,mm^3$) diamond substrate on which we grew an intrinsic epilayer in a NIRIM type MPCVD reactor composed of a 2.45 GHz microwave generator and vertical silica chamber, using only methane and hydrogen with a ratio of $[CH_4]/[H_2] = 4\%$, at a temperature of 830 °C and a pressure of

30 Torr. The layer thickness has been evaluated at 13.5 μ thick; thanks to secondary ion mass spectroscopy (SIMS) measurements. The cathodoluminescence (CL) analysis has been performed at 5 K in a QUANTA 200 SEM microscope coupled with a collecting mirror and charge coupled device (CCD) array through an HR 460 JOBIN YVON spectrometer. CL spectra have been recorded for different primary electron energies ranging from 5 up to 30 kV, and CL images has been recorded at 5 kV for the following photons energies: 5.26 eV (Fe^{TO}), 3 eV (A band) and 2.47 eV (H3). Planar Schottky diodes have been processed. They consist of 400 nm thick titanium–gold ohmic contacts annealed under vacuum at 450 °C, and 49 circular gold Schottky contacts, with a diameter of 150 μm, after a surface treatment by vacuum ultra-violet (VUV) [5] with the help a deep ultraviolet xenon lamp (wavelength of 172 nm). The metal deposition has been made through holes in a metallic mask, without any lithography step. Capacitance–voltage measurements have been performed with an Agilent E4980A bridge at a frequency of 1.2 kHz and a temperature of 400 K. Such conditions were checked as adequate to determine the depletion zone thickness and net ionized acceptor charge because of the insensitivity of the capacitance to frequency variations within the range 120 Hz–3 kHz. Current–voltage $I(V)$ analysis has been performed under a vacuum of 10^{-6} mbar with a power supply delivering voltages up to 20 kV and current-density *versus* voltage. $J(V)$ values have been deduced thanks to the knowledge of the diodes area. Numerical simulations were done with the two dimensional software Sentaurus technology computer aided design (TCD), using a finite element method with mesh size in the range 10–100 nm,and the parameters deduced from the diode geometry and doping profile.

3 Measurements and simulated results

CL spectra performed on the sample are presented in Fig. 1(a) and (b). The latter shows that the free excitonic peak has a small full width half maximum (FWHM) of 8.1 meV and low defects band intensities at 3 and 3.7 eV. These findings indicate that the CVD layer has low concentrations of point-like and extended defects and by the way confirm its good crystalline quality. As can be seen in Table 1, the ratio of the H3 peak intensity over the Fe^{TO} peak intensity increases from 50 up to 91 for an acceleration voltage ranging from 5 to 30 kV, which induced the excitons generation in a pear-shaped volume whose depth goes, respectively, from 0.3 to 5 μm.

As the H3 peak indicates the presence of nitrogen inside the substrate, one can conclude that, even for the lowest accelerating voltage, excitons do reach the substrate interface, implying that the excitonic diffusion length value λ is of same magnitude as the layer thickness of 13.5 μm (see Fig. 3(b)). Such a value is indicative of a high crystalline quality of the epilayer, consistent with the λ value of 11 μm derived in Ref. [6].

Figure 2 shows SEM and CL images of the CVD epilayer, taken, respectively, at the Fe^{TO}, A band and H3 energies. Correlation between Fig. 2(a) and (b) indicates that

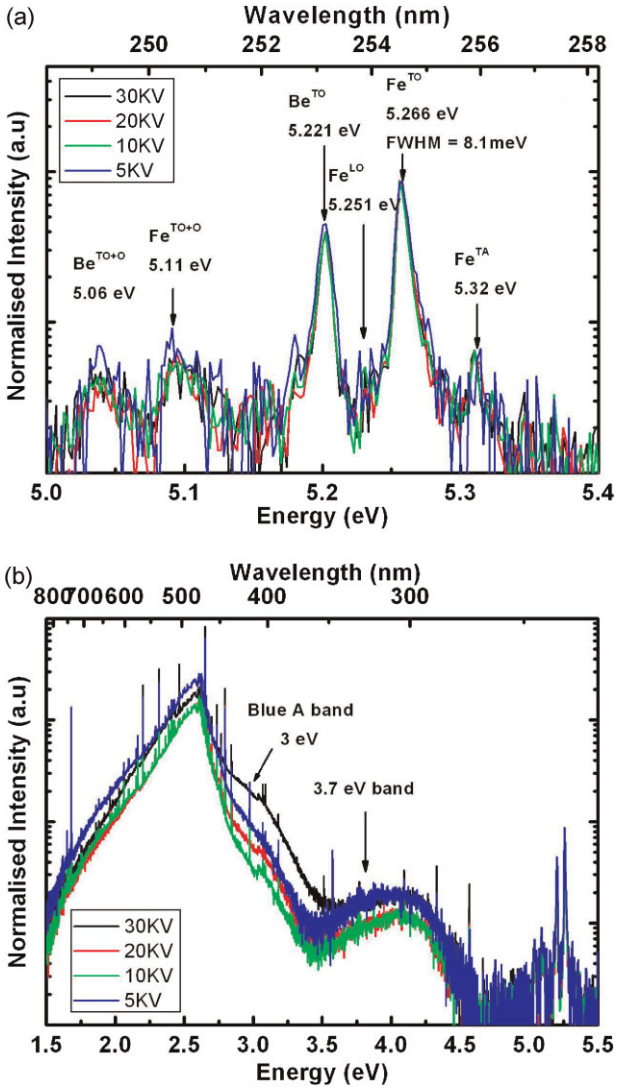

Figure 1 (online colour at: www.pss-a.com) Cathodoluminescence analysis performed at different primary electron energies for a spot size 8 and a temperature of 5 K, (a) on the exciton peaks energy range, (b) on the whole energy range.

the exciton signal is weakened in unepitaxial crystallites and hence, the signal of the A band and H3 in Fig. 2(c) and (d) are also attenuated because less excitons diffuse and reach the substrate. The evaluation of boron doping by use of CL spectra gives the following result for accelerating energies ranging from 5 to 30 kV: $[B]_{CL} = (2.1 \pm 0.7) \times 10^{16}\,cm^{-3}$.

Table 1 Evolution of the ratio of the H3 peak intensity over the Fe^{TO} peak intensity *versus* the accelerating voltage.

energy (kV)	I_{H3}/I_{FETO}
5	50
10	55
20	60
30	91

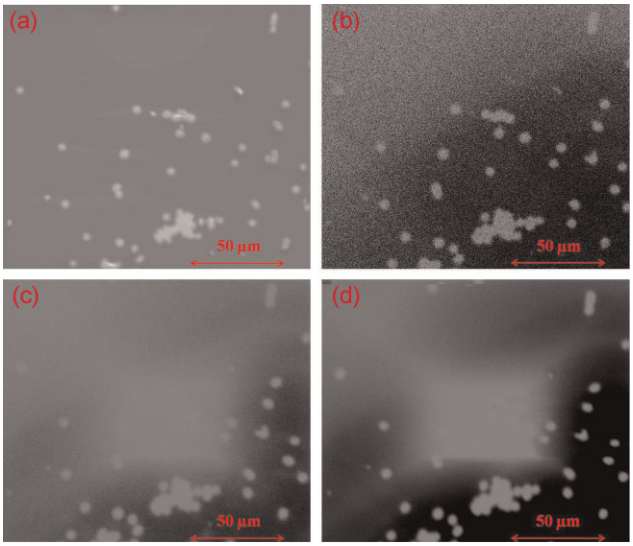

Figure 2 (online colour at: www.pss-a.com) SEM (a) and CL images taken for an accelerating voltage of 5 keV and a spot size 8 at a temperature of 5 K, for an energy of (b) 5.26 eV (Fe^{TO}), (c) 3 eV (A band) and (d) 2.47 eV (H3).

Due to the large value of λ, CL will give an average value of the whole layer boron doping, while the evaluation of a precise depth profile of the net acceptor concentration can be obtained by capacitance–voltage. Figure 3 shows the net acceptor concentration deduced from $C(V)$ measurements and the SIMS analysis of boron and nitrogen, the latter being useful only to detect the interface with the substrate and hence the epilayer thickness. $C(V)$ is performed up to a reverse voltage of 800 V, corresponding to a probed depth of 7 µm, which is around 50% of the whole CVD layer thickness. From this latter measurement, one can see that the sample does not display a uniform doping profile. The net acceptor concentration is fluctuating from 2×10^{14} up to $3 \times 10^{16}\,cm^{-3}$. Such a situation results most probably of the passivation of boron by hydrogen (presence of B–H pairs) which is not necessarily homogeneous as testified by a non-monotonic deep trap profiles in similar epilayers [7], eventually due to boron–hydrogen complexes. It has been recently shown [8] that feeding simultaneously small amounts of B_2H_6 and O_2 during the growth permits to decrease and control the doping level as well as obtaining transport properties close to state of art for (100) low boron doped diamond layers. Conversely, the growth has been achieved here by using only H_2 and CH_4, which confirms the beneficial role of O_2 in the development of high purity diamond layer. Moreover, we must also mention that for layers with a boron level close to the SIMS detection limit of $10^{16}\,at \cdot cm^{-3}$, SIMS measurements are not an appropriate method to evaluate small doping fluctuations, both because of a too small sensitivity and because SIMS probes all the boron atoms, not only the active acceptor sites as detected by $C(V)$. One can also see on the depth profile of Fig. 3 that, after the first 7 µm, the doping level reaches $3 \times 10^{16}\,at \cdot cm^{-3}$ which gives a value compatible with the previous one found by CL if the average doping concentration is taken into account over the whole thickness, and if it is assumed that this concentration remains constant down to the layer/substrate interface located at 13.5 µm from the surface. This hypothesis will be kept in the following.

The evaluation of the Schottky junction properties from the $J(V)$ curves presented in Fig. 4 is summarized in Table 2. One can see that ideality factors (n) and Schottky barrier heights (SBH) are far away from the values expected in the case of optimal gold Schottky junctions made by ozone treatment [9]. In the latter case, Teraji et al. [9] showed that, for an extrapolated ideality factor equal to unity, the SBH is around 2.6 eV. In our case, the extrapolated SBH value at

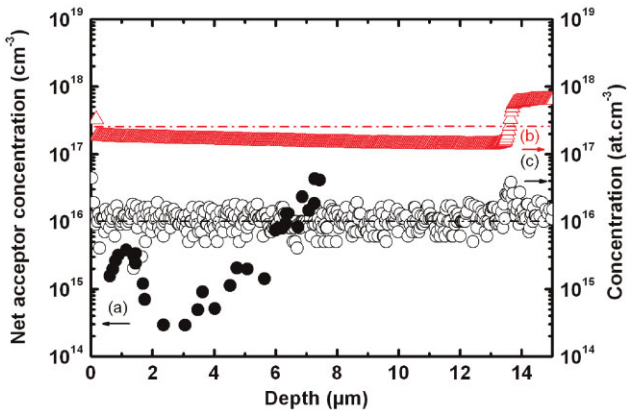

Figure 3 (online colour at: www.pss-a.com) (a) (black filled circles) Net acceptor concentration deduced from capacitance–voltage performed at 1.2 kHz and 400 K, up to a reverse voltage of 800 V, (b) (red empty triangles) nitrogen and (c) (black empty circles) boron content in the layer evaluated by SIMS. SIMS detection limits are symbolized by broken lines.

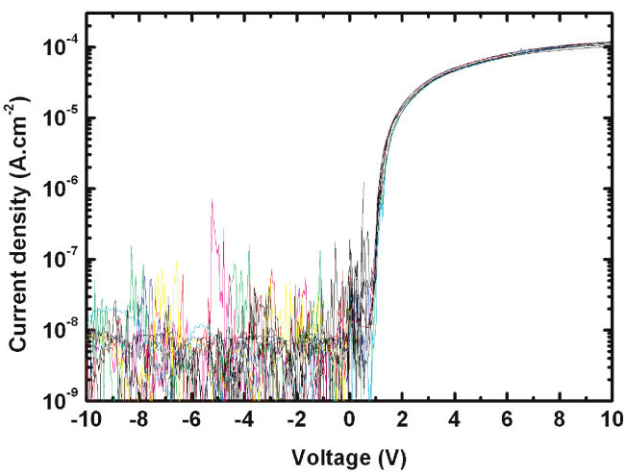

Figure 4 (online colour at: www.pss-a.com) Current density–voltage $J(V)$ tests performed on 20 diodes, at room temperature between +10 and −10 V.

Table 2 Schottky junction properties extracted by the Richardson model from the $J(V)$ analysis.

ideality factor (n)	SBH (eV)	rectifying ratio
2.3–4.06	1.08–1.31	10^4

$n = 1$ gives an SBH equal to 1.46 eV which is quite lower. Mönch [10] has shown that the presence of oriented B–H pairs located below the metal/diamond interface could create electrical dipoles and induce a Schottky barrier lowering of approximately 1 eV. These findings are consistent with data summarized in Table 2 and the $C(V)$ profile of Fig. 3(a), confirming the residual passivation of the layer by subsurface hydrogen. Ideality factors larger than two cannot be justified by the standard recombination currents in junctions made with small bandgap semiconductors, but they are very common in inhomogeneous barriers [11], which are here very likely if one relies on the CL images shown in Fig. 2.

The current density–voltage $J(V)$ characteristics of the diodes have been investigated with the help of experimental setups providing increasing maximum voltages up to 1, 12 and 20 kV, respectively. The first reverse $J(V)$ measurements performed up to 1 kV gave similar $J(V)$ curves as previously published by Teraji et al. [9], with very low dispersion even 9 months after the last VUV ozone treatment and metallization. $J(V)$ tests at higher reverse voltages have been performed, by covering the sample with an insulating gel (fluorinert) to avoid a surface breakdown [5] or by putting the sample into a vacuum chamber at a pressure of 10^{-6} Mb. The two latter $J(V)$ measurements are shown in Fig. 5.

The breakdown observed on the latter at 5.6 kV resulted from air ionization between the parts of the metallic tips connecting the contacts and emerging from the fluorinert. Conversely, the $J(V)$ performed with the sample under vacuum does not show any indication of avalanche breakdown and was stopped at 7.5 kV due to limitations of the measurement set-up.

Relying on the net acceptor profile previously determined by $C(V)$, a simple integration of the Poisson equation gave an electric field of 9.5 MV/cm for the reverse voltage of 7.5 kV, while two-dimensional numerical simulations led to a central field of 7 MV/cm with the help of the software Sentaurus TCD. Figure 6 shows the calculated potential and electric field mapping for a reverse voltage of 7.5 kV, deduced from the same parameters and diode geometry. One can see that the electric field is constant beneath the whole Schottky contact, but undergoes an enhancement at its edge, as expected. Estimates based on several distances and mesh sizes all give values of more than 20 MV/cm. However, the true electric field at the edge depends on the details of the metal geometry, dielectric characteristics of the coating and precise doping profile very close to the diamond surface, all being not accurately known. Therefore, the electric field enhancement at the edge can only be qualitatively assessed, without certainty about the real value.

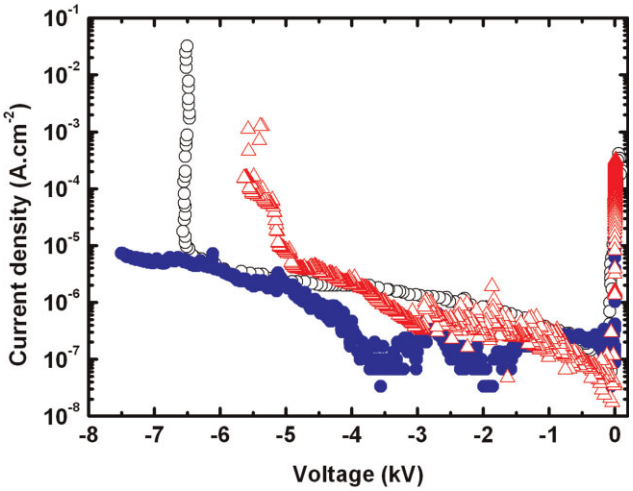

Figure 5 (online colour at: www.pss-a.com) High voltage $J(V)$ measurements from Butler et al. [1] (black empty circles) and those performed in our gold Schottky diode under fluorinert (red empty triangle) and under vacuum (blue filled circles).

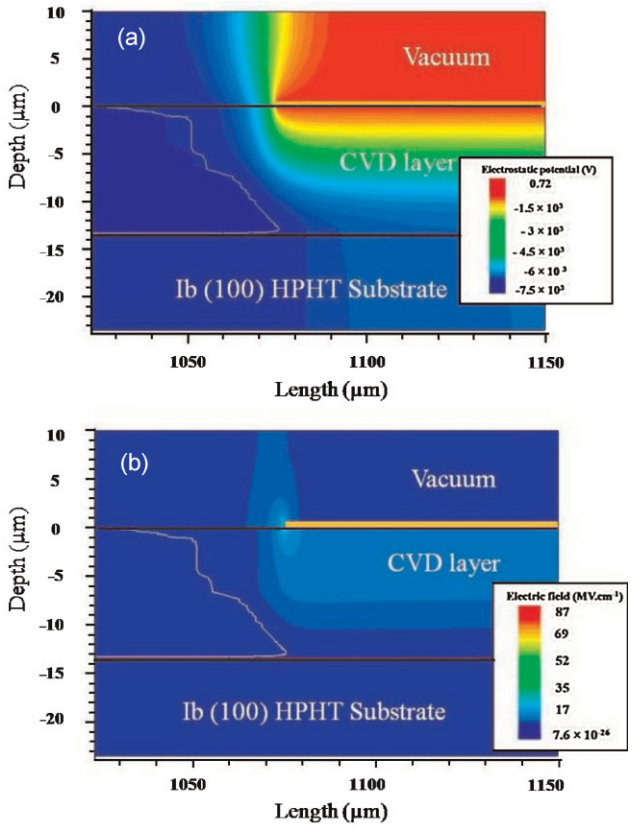

Figure 6 (online colour at: www.pss-a.com) (a) Potential mapping and (b) electrical field cartography around the Schottky contact for a reverse voltage of 7.5 kV. The white broken line represents the space charge zone extension limit. These simulations were made by using the doping profile determined by $C(V)$.

Meanwhile, these values of the reverse voltage and electric field higher than those previously published for Schottky diodes became possible only because the VUV ozone treatment of the diamond surface has created a passivation coating which reduces very efficiently the surface conductivity and hence leakage currents. This is a consequence of the very low density of states within the bandgap on the oxygenated surface of diamond which has been recognized previously [12]. Consequently, the first mechanism able to increase significantly the reverse current in our diodes consists in the avalanche multiplication of carriers, which takes place at the location where the field is maximum: near the Schottky contact periphery, in the space charge zone sketched in Fig. 6 by a white line extending several tens of μm outside the metallic edge, inside the diamond layer but close to its surface. This is the reason why avalanche breakdown inside the diamond layer can be well identified in these diodes.

VUV ozone oxidation, which is a rather strong process because both excited radicals and photochemical reactions at the diamond surface act simultaneously, generated a carpet of oxygenated groups on the diamond surface with an electrical passivation efficiency and probably an homogeneity never reached before. Different oxidation techniques have been already developed, like chemical oxidation, oxygen plasma treatment and ozone treatment [12–14]. The ozone treatment seems more favourable to synthesized optimal Schottky diodes with a minimal leakage current [9]. Work is in progress to better know such a coating layer. This layer is also believed to be useful for preventing carbide formation, which would otherwise generate or enhance detrimental defects at the Schottky metal/diamond interface.

4 Conclusion In this study, we demonstrated that diamond displays huge potentialities for high voltage applications. According to all the results previously presented, one can conclude that the route for high voltage devices fabrication is open only if a special attention is paid to the growth conditions in order to optimize the layer crystalline quality even when Ib (100) HPHT diamond substrates are used, to decrease the net acceptor concentration below some $10^{16}\,cm^{-3}$ and to remove all possible passivation or compensation of the boron acceptors. We also showed that a second key parameter for high voltage devices development is the oxidizing surface pre-treatment. This step is necessary to remove all possible surface conduction by the creation of a passivation coating able to reveal the true dielectric strength of diamond, and optimizing the Schottky metal/diamond interface. We finally demonstrated, by optimizing all the conditions mentioned above, that Schottky diamond diodes can withdraw breakdown voltages higher than 7.5 kV and avalanche electric field in excess of 7–9.5 MV/cm at the diode centre and at least twice at the diode edge. Therefore, the route for implementing unipolar electronic devices on diamond without the need for guard rings or other special edge terminations, contrary to other wide gap semiconductors, is open.

Acknowledgements The authors wish to thank NIMS, the Rhône Alpes Regional Council (France) and the 'Agence Nationale pour la Recherche' (France) through the contract 'DIAMOOND' 06-2-134411 for their financial supports, and F. Donatini (Néel Institut, CNRS, Grenoble, France) for his assistance in CL measurements.

References

[1] P. Muret, P.-N. Volpe, T.-N. Tran-Thi, J. Pernot, C. Hoarau, F. Omnès, and T. Teraji, submitted to Diam. Relat. Mater.
[2] J. E. Butler, M. W. Weis, K. E. Kohn, J. Lawless, D. Denault, T. M. Lyszczarz, D. Flechtner, and R. Wright, Semicond. Sci. Technol. **18**, S67–S71 (2003).
[3] R. Kumaresan, H. Umezawa, N. Tatsumi, K. Ikeda, and S. Shikata, Diam. Relat. Mater. **18**, 299 (2009).
[4] D. J. Twitchen, A. J. Whitehead, S. E. Coe, J. Isberg, J. Hammersberg, T. Wikström, and E. Johansson, IEEE Trans. Electron Devices **51**, 826 (2004).
[5] T. Teraji, S. Koïzumi, and Y. Koide, Appl. Surf. Sci. **254**, 6273 (2008).
[6] P.-N. Volpe, P. Muret, F. Omnès, J. Achard, F. Silva, O. Brinza, and A. Gicquel, Diam. Relat. Mater. **18**, 1205 (2009).
[7] P. Muret, J. Pernot, T. Teraji, and T. Ito, Appl. Phys. Express **1**, 035003 (2008).
[8] P.-N. Volpe, J. Pernot, P. Muret, and F. Omnès, Appl. Phys. Lett. **94**, 092102 (2009).
[9] T. Teraji, Y. Garino, Y. Koide, and T. Ito, J. Appl. Phys. **105**, 126109 (2009).
[10] W. Mönch, Europhys. Lett. **27**, 479 (1994).
[11] J. H. Werner and H. H. Güttler, J. Appl. Phys. **69**, 1522 (1991).
[12] P. Muret and C. Saby, Semicond. Sci. Technol. **19**, 1 (2004).
[13] H. A. Girard, N. Simon, D. Ballutaud, and A. Etcheberry, Chimie. **11**, 1010 (2008).
[14] H. Notsu, I. Yagi, T. Tatsuma, D. A. Tryk, and A. Fujishima, Electrochem. Solid-State Lett. **2**, 522 (1999).

