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High forward current density of $10^3$ A/cm$^2$ (at 6 V) and a breakdown field larger than 7.7 MV/cm for diamond diodes with a pseudo-vertical architecture, are demonstrated. The power figure of merit is above 244 MW/cm$^2$ and the relative standard deviation of the reverse current density over 83 diodes is 10% with a mean value of $10^{-9}$ A/cm$^2$. These results are obtained with zirconium as Schottky contacts on the oxygenated (100) oriented surface of a stack comprising an optimized lightly boron doped diamond layer on a heavily boron doped one, epitaxially grown on a Ib substrate. The origin of such performances are discussed. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4864060]

Diamond high power devices are being intensively investigated according to the outstanding electrical and thermal properties of this wide band gap semiconductor such as its high breakdown field (higher than 10 MV/cm), high hole and electron mobility ($\mu_p = 2000\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$, $\mu_n = 1000\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$), and its high thermal conductivity ($22\,\mathrm{Wm^{-1}\,K^{-1}}$). Schottky diode, compared to other diamond power devices (Bipolar transistor,[1] junction field effect transistor,[2] Schottky-pn diode,[3] etc.), is the most promising because of the highest breakdown voltage reported (2.5 kV,[4] 6.7 kV,[5] 10 kV,[6] and 8–12 kV (Ref. 7)) and architectural progress to minimize its serial resistance. Indeed, the high serial resistance of the lightly doped Schottky active layer required to get high breakdown field, is one of the main limitations of such a device. The use of pseudo vertical (with a heavily boron doped buried layer) or vertical architectures (with a heavily boron doped substrate), allowed a significant reduction of the diamond diode serial resistance. The reported forward current for these diodes architectures are generally higher than 100 A/cm$^2$. A 1 Ω serial resistance[8] was recently demonstrated for a vertical diamond Schottky diode operating at 250 °C. However, the breakdown field reached in pseudo vertical and vertical Schottky diodes (2.1 MV/cm,[8] 2.7 MV/cm (Ref. 9)) even with a field plate structure used to avoid the edge field enhancement,[10] are much lower compared to those found for lateral diodes (7.7 MV/cm (Ref. 6)) and to the very first value reported for bulk diamond (higher than 10 MV/cm).[11] It is generally admitted that the main reason of such low breakdown field and high reverse currents of pseudo vertical and vertical diamond Schottky diodes lies in defects such as dislocations which propagate from heavily boron doped diamond substrate to the active layer.[12] On the other hand, diamond Schottky diode performance is closely linked to the thermal and chemical stability of the Schottky contact and to the interface states density. Schottky metal selection and surface pretreatment are crucial to get low enough barrier heights, low defect density at interface, and a thermally stable interface.

In this work, we demonstrate that a pseudo vertical architecture based on an oxygen-terminated diamond surface covered by an easily oxidizable metal like zirconium (Zr) combined with a heavily boron doped layer with optimal thickness fulfils these requirements. Diamond surface passivation with oxygen[13] is the first key point in our diode fabrication process, generally resulting in Schottky barrier heights larger than 2 eV. Moreover, according to the nature of the Schottky metal, barrier inhomogeneity may be observed due to partial oxygen desorption[13] when the metal does not react sufficiently with oxygen. On the contrary, we show here that a rather low barrier height (1 eV) can be obtained after annealing. These performances are presumably due to the formation of a very stable and uniform ultra-thin oxide film at the interface that acts as a chemical and electrical passivation layer, making the barrier height homogeneous and inhibiting interface defects responsible for the electrical leakage. A transparent conductive oxide (Indium Tin Oxide (ITO)) was also tested as a Schottky contact, resulting in a larger barrier height and a lower breakdown field.

Heavily boron doped ($p^+$) and non-intentionally doped ($p^-$) homoepitaxial diamond layers were grown by Microwave Plasma enhanced Chemical Vapor Deposition (MPCVD) on $3 \times 3$ mm$^2$ Ib(100) high pressure high temperature (HPHT) diamond substrates (sample #1 and #2). A 200 nm thick $p^+$ layer was first grown with a gas mixture of diborane ([B]/[C] = 1200 ppm), methane ($[CH_4]/[H_2] = 4\%$) and hydrogen using a pressure of 33 Torr and a temperature of 830 °C to get a doping level higher than $10^{20}\,\mathrm{cm^{-3}}$ and a highly conducting behavior.[15] The $p^+$ epilayer was used as a substrate for the 1.3 $\mu$m thick $p^-$ layer growth with 0.75% of $CH_4$ and 0.25% of $O_2$ in hydrogen gas, using a 50 Torr pressure and a temperature of 910 °C. An average doping level close to $N_a = 1.5 \times 10^{15}\,\mathrm{cm^{-3}}$ evaluated by 5 K cathodoluminescence[16] for both samples #1 and #2, was attributed to the residual boron in the growth reactor. An Inductively and Capacitively coupled Plasma (ICP) etching step was performed to reduce the $p^-$ layer to a $2 \times 2$ mm$^2$ square centered at the middle of the $p^+$ layer, thus delineating a pseudo vertical Schottky diode structure.[17] The ohmic contact was then

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made on the $p^+$ layer by Ti, Pt, and Au layers deposition, followed by 30 min annealing at 750 °C under ultra high vacuum. In this way, the $p^+$ layer will act as a contact layer and the $p^-$ layer as the drift layer.[17] An ozone treatment produced by deep UV light[13] was performed to passivate the drift layer surface before Schottky contacts deposition.

Zirconium and Tin doped ITO were deposited on sample #1 to fabricate Schottky contacts with a diameter of 100 $\mu$m corresponding to an area $S = 7.85 \times 10^{-5}\,cm^{-2}$. ITO contacts were deposited by sputtering and annealed at 200 °C during 30 min allowing crystallization.[18] An electron beam evaporator was used to deposit Zr contacts and the first metallic material was subsequently covered with different cap layers to obtain three distinct metallic stacks on the same sample, defined as follows: Zr(20 nm)/Au(20 nm), ITO(20 nm)/Au(20 nm), Zr(30 nm)/Pt(20 nm)/Au(10 nm).

Zr (20 nm) Schottky contacts with a metallic stack Pt(30 nm)/Au(20 nm) were fabricated on sample #2.

A constant capacitance of 3.65 fF (sample #1) versus reverse bias voltage, indicating a full depletion of the drift layer, agrees well with $C = \varepsilon S/d = 3.04$fF, $\varepsilon$ being the diamond absolute permittivity and $d$ the thickness of the $p^-$ layer. An effective doping level $N_a - N_d$ of $8.5 \times 10^{14}\,cm^{-3}$ has been calculated from capacitance measurements under forward bias because the active layer is fully depleted at zero and reverse biases. This doping level is in good agreement with the cathodoluminescence results.

The current-voltage (I–V) characteristics at room temperature (RT) of diamond Schottky diodes based on zirconium and ITO are shown on Figure 1. Zirconium Schottky contacts exhibited an extremely good rectification behavior characterized by a high current density $10^3$ A/cm$^2$ (at 6 V), a reverse current density less than $1 \times 10^{-8}$ A/cm$^2$ up to the maximum voltage ($|V_{max}| = 1000$ V) available with our measurement set up, and an ideality factor near 1.3. The breakdown ($V_{br}$) of ITO/p-diamond diodes occurred at −200 V and a forward current density of 640 A/cm$^2$ (at 6 V) was obtained. According to the drift layer thickness of 1.3 $\mu$m, a reverse field ($F = |V_{max}|/d$) of 7.7 MV/cm has been reached for Zr/p-diamond diodes without any change on the reverse current level. It must be noticed that the equation used for the electrical field evaluation gives a lower boundary (assumption of an insulative diamond between Zr and $p^+$ layer). A Baliga's Power Figure Of Merit[19] $BFOM = (V_{max})^2/(R_{on}S)$, where ($R_{on}$) is the specific on-resistance, of 244 MW/cm$^2$ at RT was calculated for Zr/p-diamond. This value above the Si limit (10 MW/cm$^2$),[20] is today the largest value reported for diamond Schottky diodes. This experimental BFOM is not far from the theoretical one[20] (1000 MW/cm$^2$) for the same breakdown voltage and temperature, and would reach it if the effective breakdown voltage was doubled. The BFOM in the case of ITO/p-diamond diode is much lower, about 8 MW/cm$^2$, mainly due to the lower breakdown field (1.5 MV/cm). Figures 2(a) and 2(b) show the reproducibility of Zr/p-diamond diodes I–V characteristics for samples #1 and #2. The good reproducibility of I–V characteristics observed for both ITO and zirconium Schottky contacts indicates a uniform interface and barrier height for the diodes fabricated with each metallic contact. The detrimental influence of crystalline defects mentioned by Ohmagari and co-workers[12] is inhibited to a large extent. To illustrate these properties, a cumulative frequency plot of the average current densities found for a reverse bias range of [0,−10 V] in 83 diodes (Fig. 2(c)), demonstrated that 85% of diodes have a reverse current below the threshold of $1.3 \times 10^{-9}$ A/cm$^2$.

In order to assess the barrier height and to investigate the thermal stability of these diodes, current-voltage measurements over a wide temperature range (300 K to 723 K) have been performed on sample #1. ITO/p-diamond diodes preserved their rectification behavior up to 723 K (Fig. 3(a)) and were not affected by high temperature measurement since a quasi-identical room temperature I-V curves were obtained after the thermal cycling study. The main change observed so far was a forward current decrease linked to an increase of the series resistance. The resistivity of the homoepitaxial drift layer cannot be affected by the dissociation of boron-hydrogen pairs which already took place after the 30 min annealing at 750 °C performed to achieve the ohmic contact.[21] So, the resistivity increase must be ascribed to the ITO film. As shown by Joshi *et al.*[18] the resistivity of ITO

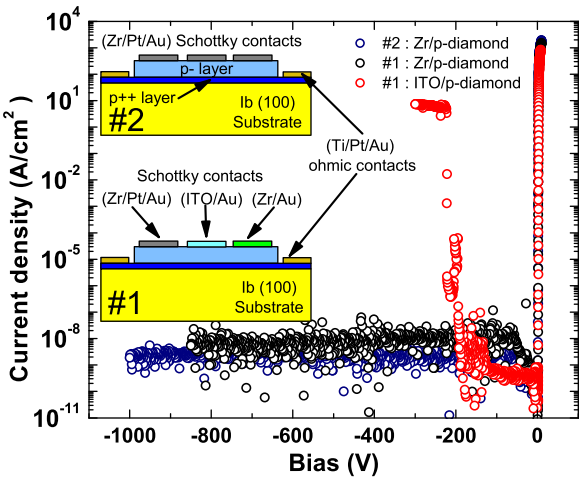


FIG. 1. Current-voltage characteristics of Zr/p-diamond (samples #1 and #2) and ITO/p-diamond (samples #1) Schottky diodes at 300 K.

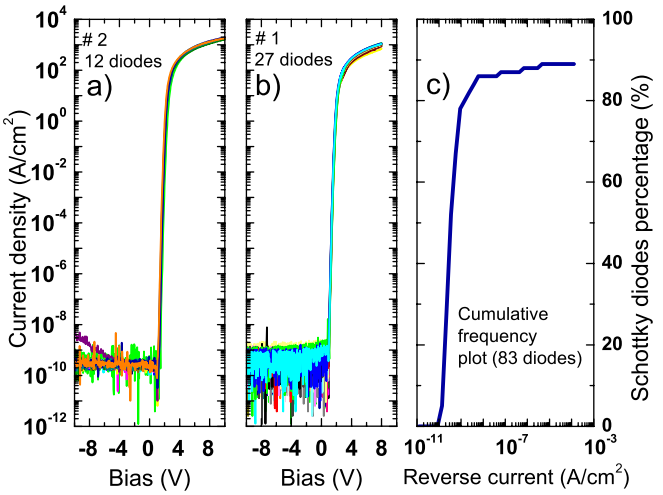


FIG. 2. (a) and (b) Reproducibility of Zr/p-diamond diodes characteristics (at 300 K) for samples #1 and #2, (c) Cumulative frequency plot of reverse current density for 83 Zr/p-diamond diodes showing that 85% of diodes have a reverse current below $10^{-9}$ A/cm$^2$.

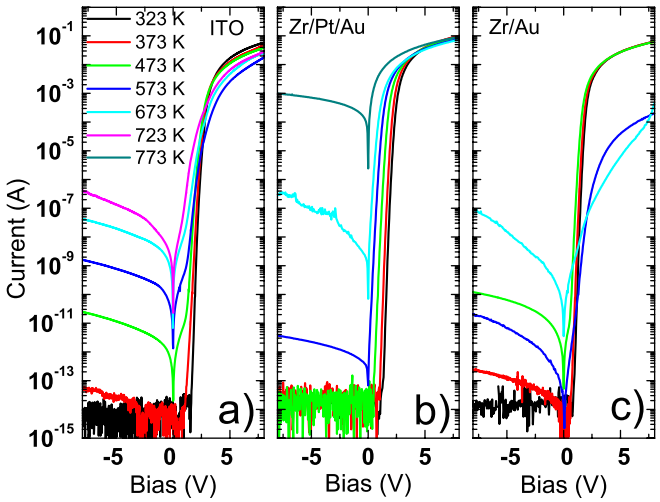


FIG. 3. Temperature dependence of I-V characteristics: (a) ITO/p-diamond, (b) (Zr/Pt/Au)/p-diamond, and (c) (Zr/Au)/p-diamond.

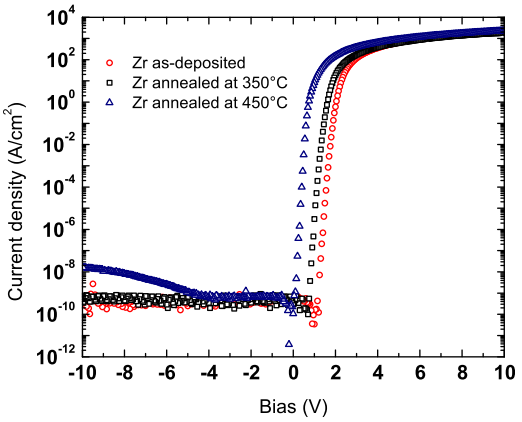


FIG. 4. Current-voltage characteristics for as-deposited and annealed (Zr/Pt/Au) Schottky contacts.

film deposited by sputtering increases after annealing (temperature range 50 to 450 °C) in air. The same phenomenon is expected to occur here for the ITO electrodes.

Conversely, zirconium contacts covered directly with a gold layer lost their rectification behavior at 523 K (Fig. 3(c)) while (Zr/Pt/Au) Schottky contacts was stable up to 773 K (Fig. 3(b)). This degradation points out the role of the platinum layer used as diffusion barrier avoiding oxygen migration through the Au layer, leading to Zr oxidation, and/or metals intermixing.

Anyway, the current in ohmic regime (bias >3 V) of Au/Pt/Zr/p-diamond diodes, was almost temperature independent (Fig. 3(b)) in disagreement with a conduction increase related to boron ionization versus temperature. This is due to a self-heating effect even with sample holder temperature below RT, leading to both the full ionization of dopants and temperature variations during measurements. Thus, the serial resistance exhibited an increase because the conductivity of the active layer was controlled by the carrier mobility which decreases versus temperature due to optical phonon scattering.[22] The self-heating still occurred even in pulse mode measurement with a pulse width of 100 $\mu$s (the exchange between diamond and outside was not optimized).

Moreover, the thermal cycling measurements showed the possibility of lowering the forward losses of Au/Pt/Zr/p-diamond Schottky diodes by annealing. To illustrate this effect, the as-deposited and Zr/Pt/Au Schottky contacts on sample #2 were successively annealed at 350 °C and 450 °C. The forward characteristics of both as-deposited and annealed Zr/Pt/Au Schottky contacts (350 °C and 450 °C) were compared on Figure 4. To assess the corresponding barrier height $\Phi_{Bp}$ for each case, a Richardson plot was performed, assuming that the forward current relies on the equation $I = SA^*T^2 \exp(-q\Phi_{Bp}/k_BT)\exp[q(V-RI)/nk_BT]$, $q$ being the elementary charge, $A^*$ the Richardson constant, $R$ the serial resistance, $k_B$ the Boltzmann constant, $T$ the absolute temperature, and $n$ the ideality factor. The obtained barrier heights for as-deposited diodes and diodes annealed at 350 °C are, respectively, 1.88 eV and 1.49 eV. However, several uncertainties affect the results because barrier inhomogeneities have been neglected, temperature might have changed due to self-heating and finally the series resistance $R$ is not constant both because of eventual self-heating and saturation velocity in the drift layer.[17] So, barrier heights are also calculated at RT using the theoretical Richardson's constant[23] of 90 A cm$^{-2}$ K$^{-2}$ and summarized in Table I. But it must be stressed that the diodes (Zr/Pt/Au)/p-diamond annealed at 450 °C display a barrier height of 1 eV and remain stable up to 500 °C.

Such barrier height variations already observed were interpreted as a consequence of the interface modification because of oxygen desorption used to passivate diamond surface as in the case of Au/p-diamond.[14] But in our case, oxygen desorption is supposed not to occur for (Zr/Pt/Au)/p-diamond diodes since an ultrathin zirconia film is expected to form between zirconium and oxygen terminated p-diamond after annealing because of the migration of dissolved oxygen atoms toward the interface under the effect of a chemical gradient due to oxygen consumption at interface. Such an ultrathin zirconia film can be extremely stable as demonstrated by Jeon *et al.*[24] for silicon substrates where this kind of film was stable up to 800 °C. The origin of the barrier height decrease shown in this study is presumed to be either the disappearance of the oxygen-carbon dipole layer initially present at the oxygen terminated diamond surface or the onset of other dipoles. Indeed, as demonstrated in Ref. 25 and 26, a dipole layer was induced by the adsorbed atoms on diamond surface. This layer can affect diamond electron affinity (EA) as illustrated for hydrogen and oxygen terminated diamond where negative and positive EA were, respectively, observed.[25,26] This interfacial dipole induced a barrier height lowering (below 1 eV) of metal/hydrogen-terminated diamond diodes[27,28] whereas, for metal/oxygen-terminated diamond, the reported barrier heights were generally close to

TABLE I. Schottky barrier heights $\Phi_{Bp}$ calculated using the theoretical Richardson constant $A^* = 90$ A cm$^{-2}$ K$^{-2}$

| Schottky contact | Annealing | $\Phi_{Bp}$ (eV) |
|---|---|---|
| Zr/p-diamond | no | 1.97 |
| Zr/p-diamond | 350 °C, 30 min | 1.4 |
| Zr/p-diamond | 450 °C, 30 min | 1 |
| ITO/p-diamond | 200 °C, 30 min | 2.45 |

2 eV. So, inhibiting the interfacial dipole can minimize the positive EA of oxygen-terminated contribution to this high barrier height and lead to a lower value. Several mechanisms linked to the presence of an interfacial oxide layer as supposed for Zr/oxygen-terminated diamond diodes, can produce this effect: (i) the effective disappearance of the oxygen-carbon dipole layer due to a new bonding arrangement at the diamond interface after annealing; (ii) the compensation of the initial dipole layer by positive charges in the oxide, as usually due to extrinsic deep levels, often related to oxygen vacancies; (iii) intrinsic gap states within the oxide layer resulting in a new dipole induced by the alignment of the charge neutrality levels in the oxide and diamond; (iv) a combination of these mechanisms or a change in the oxide properties which eventually have promoted one of them after annealing. Concurrently, lateral oxidation of zirconium layer at its periphery probably occurred because the cap layers do not cover the lateral face of Zr. This effect can explain the different breakdown fields observed for ITO and Zr/p-diamond diodes, since this natural oxide around Zr contacts plays a role similar to that of the field plate used to reduce electric field enhancement at diode corners.[10] The performances reported here for Zr/p-diamond Schottky diodes (high breakdown combined to high current density), confirm the interest of diamond properties for high power electronics applications.

In conclusion, diamond Schottky diodes based on zirconium and ITO contacts have been developed. Zirconium Schottky contacts with platinum/gold capping layers exhibited high current density near $10^3$ A cm$^{-2}$ (at 6 V) and very low leakage currents (under 1 pA) at RT up to at least 1000 V. The corresponding bulk electric field across the active layer which is only 1.3 $\mu$m thick, exceeded 7.7 MV/cm. Contrary to what is generally found in intimate metal-diamond Schottky contacts, the dispersion of the I–V characteristics is extremely weak for 85% of the whole diode population, opening the route for industrial upscaling. An unprecedented BFOM larger than 244 MW/cm$^2$ at room temperature was obtained. A 450 °C annealing of zirconium Schottky contacts was able to decrease the barrier height to about 1 eV, thus reducing the forward power losses to fairly acceptable values. These diodes remain stable up to 500 °C.

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