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**Overcoming the impact of post-annealing on uniformity of diamond (100) Schottky barrier diodes through corrosion-resistant nanocarbon ohmic contacts**

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**Abstract**

Diamond-based Schottky barrier diodes (SBDs) are involved in many technological applications. In a conventional SBD fabrication process that involves interface carbide forming ohmic contacts, a post-annealing step is necessary for ohmic contacts to achieve their operational efficiency. However, this step deteriorates the essential oxygen coverage at the diamond surface which in turn affects SBDs uniformity. So, an additional oxygen termination step is necessary prior to Schottky metal deposition. In this study, a non-conventional fabrication method is introduced using corrosion-resistant nanocarbon ohmic contacts fabricated by coaxial arc plasma deposition. As a result, The SBD parameters including ideality factors and barrier heights exhibited high uniformity with a very small standard deviation for the proposed fabrication process including a post-annealing step. Furthermore, the contact behavior of nanocarbon ohmic electrodes is investigated on a heavily boron-doped diamond film using circular transmission line model theory and a specific contact resistance of $\sim 10^{-3} \Omega \cdot cm^2$ is obtained, suggesting the practical application of nanocarbon ohmic contacts for diamond-based electronic devices.

**Introduction**

Semiconducting diamonds have been attracting much attention owing to their incomparable material properties and technological applications in several fields, including power electronics, quantum sensing, hard coating, electrochemistry, etc [1–4]. The high breakdown field of diamonds due to their stiff lattice has enabled them the candidacy in high voltage rectifying applications [5, 6]. The recent developments in diamond-based rectifiers such as Schottky barrier diodes (SBDs), field effect transistors, and bipolar junction diodes have successfully demonstrated the potential scope of diamonds in practical power electronics applications [7–9]. Recently, there have been focused studies on developing high-performance diamond-based SBDs to ensure foremost diode parameters like large breakdown voltage, high ON-state current, temperature stability, etc [10]. The performance of SBDs is highly dependent on the diamond/metal interface due to the Fermi level pinning induced by the surface termination [11]. Commonly, hydrogen and oxygen terminations (H- and O- terminations) are known to be the stable surface dangling bond terminations for diamonds and affect the properties of diamond-based electronic devices [12]. The H-terminated diamond surface usually exhibits a negative electron affinity (NEA) that tends to form low barrier height Schottky contacts with a metal interface [13]. This in turn decays the performance of diamond SBDs by allowing the carriers to cross the potential barrier at high reverse voltages. So that, the diamond SBD fabrication procedure usually includes an O-termination step before forming the Schottky metal contacts [14–16]. This achieves a large Fermi level pinning at the diamond / Schottky metal
interface due to the positive electron affinity of the O-terminated diamond surface leading to better Schottky junction properties than the H-terminated diamond/metal junction [17].

There has been intensive research on SBD properties with different surface termination of the diamond and, consequently, several O-termination methods have been proposed in recent years [11, 18, 19]. Among them, the UV/ozone and wet chemical O-termination methods are the most discussed O-termination methods included in diamond lateral SBD fabrication procedure. The UV/ozone O-termination is achieved through the diamond surface treatment in ozone plasma produced by ultraviolet irradiation of pure oxygen [20]. On the other hand, the wet chemical O-termination is achieved through immersing the diamond substrate in a boiling acid solution [18]. The diamond lateral SBD fabrication procedure usually includes the fabrication of ohmic contacts to a wet chemically O-terminated diamond film prior to Schottky metal deposition. Due to large fermi-level pinning for ohmic metal/diamond interface, interface carbide forming metals like Ti is experimentally employed as ohmic contacts to semiconducting diamonds [21]. These conventional ohmic contacts require a post-annealing at 450 °C–700 °C to form the interface carbide layer to achieve a good ohmic property. However, this post-annealing step causes the partial desorption of the oxygen atoms from the wet chemically O-terminated diamond surface which causes the non-uniformity of the SBD parameters [19, 22–24]. The wet chemical O-termination after the post-annealing step seriously affects the ohmic behavior and mechanical stability of Ti ohmic contacts due to their poor interfacial stability. So, an additional O-termination through UV/ozone is always employed to ensure the oxygen coverage at the diamond surface and thus the uniformity of the SBD parameters. The study by Navas et al compared the O-termination through UV/ozone and wet chemical methods, and the results confirmed the enhanced oxygen coverage on wet chemically oxidized diamond surfaces [25]. Despite that, the wet chemical O-termination is not widely employed for the diamond lateral SBD fabrication due to the reasons discussed above.

In our recent report [26], we have proposed a low specific contact resistance and corrosion-resistant nanocarbon-based ohmic contact strategy for phosphorus-doped diamonds. The alternative nanocarbon ohmic contacts exhibited excellent contact behavior with low specific contact resistance than the conventional Ti-based ohmic contacts. In the current study, the nanocarbon ohmic contacts will be applied to boron-doped p-type diamonds with the aim of using their excellent corrosion resistance in boiling acid media to stabilize SBD parameters formed on wet chemically O-terminated p-type diamond surfaces.

**Experimental details**

For the characterization of nanocarbon ohmic contacts using the circular transmission line model (cTLM) theory, a homogeneous nanocarbon film was grown on a heavily boron-doped (~10^{20} cm^{-3}) diamond film using a coaxial arc plasma deposition (CAPD) system. The CAPD system employs the cathodic discharge of pure graphite targets to ejection the carbon species onto the substrate surface [27, 28]. The graphical representation of the CAPD apparatus is shown in figure 1. The detailed fabrication procedures can be found in our previous reports [26, 27]. Concentric nanocarbon electrodes with different inter-electrode spacings (d) ranging from 4 μm to 16 μm were formed using the standard photolithography lift-off technique and subsequent oxygen plasma reactive ion etching. The current-voltage (I–V) responses for different electrode spacings were recorded to accurately deduce the specific contact resistance using cTLM theory. In order to investigate the influence of a highly oxidizing acidic environment on nanocarbon ohmic electrodes, they were subjected to five consecutive acid treatment [H_{2}SO_{4} + HNO_{3} (3:1)] solution boiling at 250 °C] sessions of 50 min each, and the total resistance between concentric nanocarbon ohmic electrodes was recorded.

For the stabilization of SBD parameters on a wet chemically O-terminated p-type diamond surface, a stacked diamond film comprising a heavily boron doped (10^{20} cm^{-3}) contact layer and a lightly doped epilayer (~10^{16} cm^{-3}) was fabricated using hot filament chemical vapor deposition (HFCVD) and microwave plasma enhanced chemical vapor deposition (MPECVD), respectively on type-Ib (100) synthetic diamond substrate. The diamond film is cleaned in boiling acid solution [H_{2}SO_{4} + HNO_{3} (3:1) at 250 °C] to remove any surface contaminations. The nanocarbon ohmic contact was formed on the epilayer (~10^{16} cm^{-3}) through the CAPD method. After the formation of the nanocarbon contacts, the sample was re-immersed in the boiling solution for two sessions of 50 min each to ensure the wet chemical O-termination of the diamond epilayer surface. The subsequent deposition of Mo/Au stacking structure Schottky contacts with an interface area of 7.8 × 10^{-5} cm² was carried out in an electron beam evaporation chamber at a base pressure of 10^{-7} Pa. The I–V response of the Mo SBDs is then recorded with a micro-prober high resistance electrometer station (Keysight B2985A). For comparison, the same sample was subjected to 50 min of boiling acid treatment. Here, the Mo/Au contacts were peeled off due to their poor adhesion on the diamond surface. The diamond surface was then deliberately annealed at 450 °C using a rapid thermal annealing (RTA) system for 15 min and Mo/Au Schottky contacts were redeposited on the annealed diamond surface. The I-V response of the redeposited Mo/Au Schottky contacts
after post-annealing was compared with that of the same metal contacts fabricated on the wet chemically
O-terminated p-type diamond to analyze the uniformity of diode parameters.

Results and discussion

The nanocarbon ohmic contacts were characterized in terms of specific contact resistance on a heavily boron-
doped diamond film (∼10^{20} \text{ cm}^{-3}) using cTLM theory. According to cTLM theory, the total resistance $R_T$ between the concentric circular electrodes can be related to the inter-electrode spacing ($d$) through the following expression when $r_1 + r_2$ is a constant [29]

$$R_T = \frac{R_s}{2\pi} \left[ L_T \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \ln \left( \frac{r_2}{r_1} \right) \right] \approx \frac{(2L_T + d)}{2\pi r_0} R_s. \quad (1)$$

Where $r_1$ and $r_2$ are the radii of the inner and outer circular electrodes with $r_0 = r_1 + d/2 = r_2 - d/2$. The parameters $R_s$ (sheet resistance of diamond film) and $L_T$ (transfer length of the nanocarbon ohmic electrode) can be deduced by fitting $R_T$ versus $d$ points to expression 1. Thus the specific contact resistance ($\rho_c$) can be obtained as,

$$\rho_c = R_s \times L_T. \quad (2)$$

The sheet resistance $R_s$ and transfer length $L_T$ were deduced to be 3 kΩ and 0.55 μm, respectively from the slope and x-intercept of the $R_T$ versus $d$ plot shown in figure 2. The specific contact resistance is calculated as $9.1 \times 10^{-6} \text{ Ωcm}^2$.

In parallel, to explore the influence of acid treatments sessions on the electrical durability of nanocarbon
ohmic contacts, the total resistance between concentric electrodes with an inter-electrode spacing of 8 μm is
recorded with respect to the number of acid treatment sessions as shown in figure 3.
The inter-electrode resistance followed a near linear increasing behavior from the first acid treatment to the fifth acid treatment session. This can be ascribed to the deterioration of the sp² carbon phase that existed in the nanocarbon film and at the diamond/nanocarbon interface which acts as electrically active states in the ohmic electrode. The sudden hike in the resistance from pristine to the first acid-treated nanocarbon ohmic contacts can be attributed to the Au metal employed as the photolithography lift-off mask getting dissolved in the first acid treatment session which in turn increases the contact resistance between the electrometer probes and the nanocarbon electrodes. The I-V curve preserved the linear nature during acid treatment sessions without inducing any potential barrier which shows high interfacial stability. This interfacial stability and mechanical adhesion in a highly corrosive medium are due to the partial sp³ bonds at the diamond/nanocarbon interface which then becomes less susceptible to degradation. The complete removal of the nanocarbon ohmic contacts from the diamond surface has been observed after twelve acid treatment sessions similar to those observed for nanocarbon ohmic contacts for phosphorus-doped diamonds [26].

This anti-corrosive efficiency of nanocarbon ohmic contacts in acid media is utilized for wet chemical O-termination of the diamond surface after fabricating the nanocarbon ohmic contacts. This strategy cannot be afforded by the conventional interface carbide forming Ti ohmic contacts due to their poor interfacial stability in

Figure 2. Dependence of inter-electrode resistance on inter-electrode spacing.

Figure 3. Dependence of inter-electrode resistance on the number of acid treatment sessions for nanocarbon ohmic contact (d = 8 μm).
a highly corrosive boiling acid medium. As discussed in the experimental session, the I-V response of the Mo/Au Schottky contacts after post-annealing was compared with that of the same metal contacts fabricated on the wet chemically O-terminated p-type diamond to analyze the uniformity of diode parameters as shown in figure 4. Hereinafter, we shall refer to the wet chemically O-terminated process involved with post-annealing as (PWC-O) and the other wet chemically O-terminated to (WC-O).

Regarding the Schottky diodes fabricated by WC-O process, the I-V responses of 42 diodes were measured and they have shown good uniformity in their forward bias region. A rectification ratio of almost 8 orders has been achieved for all the SBDs at a voltage region of $-11$ to $11$ V. The 20 SBDs fabricated through the PWC-O process have shown a degraded uniformity in their I-V responses at the forward bias region. The forward current at $+11$ V has slightly decreased from the previous experiment. This might be due to the interface degradation of the nanocarbon ohmic contact after the acid treatment session before the post-annealing step.

The SBD parameters were calculated using the thermionic emission (TE) model. The TE model Schottky junction carrier transport at forward biasing voltages can be evaluated by the following expression [30],

$$I = A A^p T^2 \exp \left( - \frac{q \phi_b}{kT} \right) \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right]$$

(3)
The ideality factor ($n$) and barrier height ($\phi_b$) were obtained by fitting the linear region in the semilogarithmic I-V curve of SBDs with equation (2). The constants involved TE model were ascribed to Richardson’s constant ($A^*$), Schottky junction area ($A$), temperature ($T$), charge constant ($q$), and Boltzmann constant ($k$).

The SBD parameters $n$ and $\phi_b$ has exhibited an enhanced uniformity for the WC-O process when compared with PWC-O process. The $n$ values for PWC-O process showed a large distribution in their values as shown in figure 4 with a standard deviation of 0.35, while the distribution was limited for WC-O process with a small standard deviation of 0.04. This shows a near-ideal diode behavior uniformity for SBDs fabricated without post-annealing. A similar trend has been observed for $\phi_b$. The standard deviation of the $\phi_b$ data points have been found to decrease from 0.13 to 0.03 for WC-O process as shown in figure 5. This uniformity of the Schottky barrier height may have arisen from the uniform O-termination at the diamond/Mo interface. The post-annealing step can induce pinning-free surface states due to the partial desorption of oxygen atoms at the interface which can adversely affect the uniformity of the diode parameters.

Most of the SBDs after the PWC-O process exhibited relatively high ideality factors which are near to 2. This might be due to the inhomogeneous Schottky barrier formed at the metal/diamond interface due to partial oxygen desorption from the diamond surface. The formation of additional non-passivated surface states can influence the interface current transport and can change to TFE (Thermionic field emission) model with

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**Figure 5.** Distribution of ideality factors of the Schottky barrier diodes fabricated through (a) WC-O process (b) PWC-O process.
substantial tunneling across the Schottky barrier, in turn suggesting a deteriorating Schottky interface. Even though some PWC-O SBDs ([15%] 3 SBDs out of 20) show barrier heights ($\phi_b$) greater than 1.5 eV as shown in figure 6, the mean $\phi_b$ for PWC-O process was found to be decreased to 1.37 from 1.45 (WC-O process). This decrease in Schottky barrier height can be considered as an indication of tunneling-assisted carrier transport at the diamond/metal interface due to non-oxygen passivated dangling bonds. A similar effect of increased Schottky barrier height values due to interfacial oxygen dipoles has been already reported for electrochemically deposited Au contacts on candidate semiconducting material n-GaAs [31].

In conclusion, we have simplified the lateral diamond Schottky fabrication process by avoiding the post-annealing step which is generally employed in fabrication procedures involving conventional interface carbide forming ohmic contacts. The $O^{-\theta} - C^{+\theta}$ interfacial dipoles ($\theta$ is the averaged elementary charge per atom) at the diamond/metal interface are essential for the supreme performance of the Schottky barrier junction owing to their large potential barrier which in turn reduces the leakage current when compared with the $H^{+\theta} - C^{-\theta}$. The post-annealing step for a wet chemically O-terminated diamond substrate at high temperatures (>450 °C) employed in conventional fabrication procedure often causes the cancellation of partial O^{-\theta} - C^{+\theta} electric dipoles and in turn produces non-passivated dangling bonds at the surface, which deteriorates the uniformity of the SBDs [17]. By skipping the post-annealing step, the uniformity of SBD parameters fabricated on wet chemically O-terminated diamond surfaces has been obviously improved with a very small standard deviation. The potential of nanocarbon ohmic electrodes over conventional Ti ohmic contacts has been proposed for both phosphorus-doped [26] and boron-doped diamonds. The proposed nanocarbon ohmic electrodes for

\[\text{Figure 6. Distribution of barrier heights of the Schottky barrier diodes fabricated through (a) WC-O process (b) PWC-O process.}\]
semiconducting diamond-based electronic applications could enhance the degree of freedom of diamond lateral Schottky device fabrication.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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