Power Diode Structures Realized on (113) oriented Boron Doped Diamond

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Abstract

Molybdenum, ruthenium, and platinum contacts covered by the gold capping layer were used for preparation of pseudo-vertical Schottky barrier diodes on (113) oriented homoepitaxial boron-doped diamond. After metal deposition, diodes were stabilized by annealing for 20 minutes at 300 °C and their I-V characteristics were measured at temperatures from 30 to 180 °C. Results show that all three metals can be used to realize Schottky diodes with sufficient forward and blocking capability. Moreover, molybdenum and ruthenium can also be used to create a stable ohmic contact on heavily doped contact p\(^{''}\) layer. Molybdenum provides optimum properties: a sufficient Schottky barrier height providing low leakage at a level of 10\(^{-8}\) A/cm\(^2\) and an acceptable forward voltage drop of 3.80V@J\(_F\)=1kA/cm\(^2\) (measured at 150 °C), the rectifying ratio then reaches 10\(^{11}\) over the entire temperature range under study. Ruthenium contacts exhibit lower Schottky barrier, their forward voltage drop is thus lower (2.85V@J\(_F\)=1kA/cm\(^2\)@150 °C), but leakage increases rapidly with temperature. Platinum provides the highest Schottky barrier and guarantees the lowest level of the leakage (<10\(^{-8}\) A/cm\(^2\)). However, the diodes have poorer forward characteristics: their ideality factor and forward voltage is high (7.35V@J\(_F\)=1kA/cm\(^2\)@150 °C). Maximum realizable diode area and achievable breakdown field (0.8MV/cm) then depend on the number of crystal defects (namely threading dislocations) appearing in the diode low-doped drift region.

Keywords: diamond, Schottky diode, (113) orientation, molybdenum, platinum, ruthenium.

INTRODUCTION

Diamond has attracted considerable attention due to its unique material properties (large bandgap, high critical electric field, high thermal stability, high carrier mobility, and extremely high thermal conductivity), which makes it a candidate for future high-power devices capable of operating at extreme temperatures [1]. Due to its simplicity, the Schottky diode will likely be the first diamond commercial power component.

This device requires both the Schottky contact (with high blocking capability and low on-state resistance) and the highly conducting ohmic contact. In the case of the pseudo-vertical version of Schottky barrier diode (pVSBD) [1,2], which uses the more affordable insulating monocrystalline substrate coated by a heavily boron-doped p\(^{''}\) contact layer and then by a top low-doped p\(^{+}\) drift layer, both the ohmic and Schottky contacts are formed from above and, in principle, can be made by one metallic layer. This is because the top low-doped drift layer is removed at the point where ohmic contacts will be formed on the underlying p\(^{''}\) contact layer.

When designing a Schottky diode, it is necessary to optimize, in addition to the drift region, both contacts between the metal and the diamond. So far, (100) orientated diamond surface has been preferred [1-3] and several metals (aluminum [4], copper [5], gold [3], molybdenum [6], platinum [7], ruthenium [6], tungsten [3], and zirconium [8]) have been used to ensure sufficient and stable rectification characteristics.

In this contribution, we present the results of the development of pseudo-vertical Schottky barrier diodes realized on epitaxial boron-doped diamond layers with (113) orientation. This orientation offers an excellent trade-off between the surface morphology, epilayer roughness and electrical properties compared to (100) and (111) oriented boron doped diamond (BDD) layers [9]. pVSBD structures using different metals (molybdenum, ruthenium and platinum) to realize Schottky contacts were fabricated on an equivalent BDD bi-layer to eliminate the effect of the scatter in drift region parameters on diode characteristics. Diode forward and reverse characteristics were measured over a wide range of temperatures (30 to 180 °C), then differences in diode behavior are analyzed and discussed.
EXPERIMENTAL

A cross-sectional view of the fabricated pVSBD is shown in Fig. 1. The active part of the pVSBD consisted from the homoepitaxial boron-doped diamond p⁺/p bi-layer grown by a Microwave Plasma Enhanced Chemical Vapor Deposition (MWPECVD) system (AX5010 from Seki Diamond Systems) on (113) oriented insulating diamond substrate (see Fig.2). The substrate was produced from high-pressure high-temperature (HPHT) grown synthetic 0.5 carats Ib diamond crystal by polishing along the (113) crystalline plane using traditional scaife polishing techniques [9].

The first grown heavily boron-doped p⁺ contact layer (1.95 μm thick with boron concentration of 10²¹ cm⁻³) was overgrown by a lightly doped p⁻ drift region (thickness 1.35 μm and boron concentration of about 10¹⁷ cm⁻³).

To realize the ohmic contact on the p⁺⁺ contact layer, its outer part was etched away using a chromium hard mask covering the central part of the sample. Etching to a total depth of 1.5 μm was carried out by inductively coupled plasma using O₂ reactant gas (Oxford Instruments PlasmalabSystem 100). After etching, the sample was cleaned in hot KNO₃ + H₂SO₄ acid, placed in a hydrogen plasma at high temperature for 10 min to remove any remaining contamination, and, finally, the diamond surface was ozone treated to obtain a clean oxygen terminated surface. A 10 nm thick layer of Mo, Ru or Pt covered by a 100 nm thick Au capping layer was evaporated by an e-beam evaporation system (Leybold-Heraeus) to realize the Schottky contact of the diode. In the case of Mo and Ru, the same metallic bi-layer (single metallization) was used as the ohmic contact, while Ti/Au ohmic contact was used for Pt pVSBDs. After the deposition, circular (100 or 60 μm in diameter) Schottky contacts on the mesa and the ohmic contact ring on the p⁺⁺ layer were defined using a laser lithography system (Microwriter ML) and wet chemical etch [10].

RESULTS AND DISCUSSION

First, the quality of ohmic contacts on the contact p⁺⁺ layer was investigated. Fig. 4 compares the measured values of the specific contact resistance $R_{Csp}$ as a function of annealing temperature for all metallic systems used (Mo/Au, Ru/Au, and Ti/Au). The contacts were deposited on an ozone treated (113) homoepitaxial BDD layer with boron concentration of 8×10²⁰ cm⁻³. As mentioned in the experimental section, for Ru and Mo pVSBDs, the same metallization was used for the ohmic as for the Schottky contact. For Pt diodes, due to the higher work function (barrier) of the Pt contact, Ti/Au was used for an ohmic contact. As one can see, at very high boron concentrations, very low values of $R_{Csp}$ (~10⁶ Ω·cm²) can be achieved for all types of contacts.
The as-deposited contacts show a very low specific contact resistance due to the tunneling of holes through the Schottky barrier from highly doped \( p^{++} \) contact layer. Increasing the annealing temperature gradually improves \( R_{\text{Csp}} \) and all contacts keep excellent quality up to 850 °C, at which we observed a significant degradation of the Au capping layer [11]. Fig. 4 also shows that after annealing at 300 °C, which was used to stabilize the characteristics of the realized diodes, the specific contact resistance of all types of ohmic contacts should be more or less identical (~10^{-3} \, \Omega \cdot \text{cm}^2).

The quality of ohmic contacts on the contact \( p^{++} \) layer of the realized pVSBDs was compared after their stabilization by 20 minutes of annealing at 300 °C. Measurements made on c-TLM structures placed on the outer contact ring (see Fig. 3) showed the following values of the specific contact resistance: Mo/Au (\( R_{\text{Csp}} = 0.95 \, \mu \Omega \cdot \text{cm}^2 \)), Ru/Au (\( R_{\text{Csp}} = 6.2 \, \mu \Omega \cdot \text{cm}^2 \)), and Ti/Au (\( R_{\text{Csp}} = 17.8 \, \mu \Omega \cdot \text{cm}^2 \)). This confirms that Mo and Ru can also be used to create a stable ohmic contact on heavily doped contact \( p^{++} \) layer.

Figs. 5-7 compare room temperature \( I-V \) characteristics of typical Mo, Ru, and Pt pVSBDs fabricated on equivalent BDD bi-layers recorded after 20 minutes annealing at 300 °C. The insets then show forward characteristics which were measured subsequently at temperatures ranging from 30 to 180 °C. Results show that all three metals can be used to realize Schottky diodes with sufficient forward and blocking capability. The characteristics of Mo and Ru pVSBDs are very similar. Both diodes were fabricated on equivalent BDD bi-layers and the maximal forward current densities thus achieve almost identical values. Due to the lower Schottky barrier of Ru, the built-in voltage of Ru diodes is lower \( V_B = 1.40 \text{V} \) compared to Mo pVSBDs \( V_B = 1.65 \text{V} \). On the other hand, the forward \( I-V \) characteristics of Pt pVSBDs are significantly worse: the built-in voltage is high (~ 5.5 V) and the ideality factor \( n \) is far from one. This may be due to the high barrier of the Pt Schottky contact and its inhomogeneity.
At room temperature, the reverse current of all measured diodes is close or below the resolution limit of our measuring station \((10^{-15} \text{ A})\). This results in an excellent rectification ratio \(I_{\text{OFF}}/I_{\text{ON}}\) defined as the ratio of the diode current at \(V_T = 3 \text{ V}\) (Mo and Ru diodes) or \(V_T = 8 \text{ V}\) (Pt diodes) to that at \(V_T = 10 \text{ V}\). The room temperature \(I_{\text{OFF}}/I_{\text{ON}}\) value is of the order of \(10^{10}\), which is fully comparable to the values reported for the best Schottky diodes prepared on diamond with (100) orientation [6,8]. The reverse current of Mo and Pt pVSBDs increases only slightly with temperature and at 150 °C the reverse current density \(J_R@V_T = 10 \text{ V}\) is still of the order of \(10^{-7} \text{ A/cm}^2\). As a result, the \(I_{\text{ON}}/I_{\text{OFF}}\) ratio of Mo and Pt pVSBDs increases with temperature. On the other hand, the leakage of Ru pVSBD increases rapidly with temperature due to the lower barrier of the Ru/Au Schottky junction.

The standard model for thermionic emission [1] of the current conduction including the influence of the diode specific on-resistance \(R_{\text{on,sp}}\) was used to extract values of the zero-bias Schottky barrier height \(\Phi_{\text{BO}}\) and the ideality factor \(n\), and to characterize the temperature behavior of fabricated pVSBDs:

\[
I = I_S \left( \frac{q(V - R_{\text{on,sp}})}{n k_B T} \right)^n - 1
\]

where \(n\) is the ideality factor, \(k_B\) is the Boltzmann constant and \(T\) is the temperature. The saturation current density \(I_S\) is given as

\[
I_S = A' T^2 e^{-\frac{q \Phi_{\text{BO}}}{n k_B T}}
\]

where \(A'\) is the Richardson’s constant. Using the theoretical value of \(A'\) for holes in diamond \((A' = 90 \text{ A}\cdot\text{cm}^{-2}\cdot\text{K}^{-2})\), \(J_s\), \(n\), and \(R_{\text{on,sp}}\) values at different temperatures were determined by fitting of forward I-V characteristics. The values of \(J_s\), \(n\), and \(\Phi_{\text{BO}}\) obtained are presented in Table I where we also included the values of the rectification ratio \(I_{\text{OFF}}/I_{\text{ON}}\) subtracted from the I-V characteristics. We can see that the ideality factor \(n\)

| TABLE I | PARAMETERS OF PSEUDO-VERTICAL SCHOTTKY BARRIER DIODES WITH Mo, Ru, AND Pt CONTACTS ON (113) ORIENTED BORON DOPED DIAMOND |
|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Contact    | \(J_s\)       | \(n\)    | \(\Phi_{\text{BO}}\) | \(I_{\text{OFF}}/I_{\text{ON}}\) | |
| Mo          | 1.1×10^{-2}  | 1.35       | 1.68        | 3×10^{10}  | |
| Mo          | 4.8×10^{-2}  | 1.24       | 1.70        | 1×10^{10}  | |
| Ru          | 1.6×10^{-3}  | 1.41       | 1.31        | 8×10^{7}   | |
| Ru          | 2.9×10^{-3}  | 1.28       | 1.33        | 7×10^{7}   | |
| Pt          | 8.0×10^{-3}  | 3.25       | 1.32        | 3×10^{4}   | |
| Pt          | 2.8×10^{-3}  | 2.60       | 1.66        | 2×10^{3}   | |

in the diode drift region was fitted by the functional dependence, which assumes that the drift region is a non-degenerate p-type semiconductor containing an acceptor concentration \(N_A\) and compensating, fully ionized donors with a concentration \(N_D\). The hole concentration \(p\) at temperature \(T\) was calculated using the relation [15]:

\[
p(p + N_D) = \frac{2}{\beta} \left( \frac{2\pi m^* k_B T}{\hbar^2} \right)^{3/2} e^{-\frac{E_A}{k_B T}}
\]

where \(\beta\) is the spin degeneracy of acceptors, \(m^*\) is the effective density of state hole mass and \(E_A\) is the acceptor ionization energy. The best fit of the measured data provided \(E_A = 0.37 \text{ eV}\), which agrees well with the boron activation energy in diamond [1], the acceptor concentration \(N_A = 1.3 \times 10^{17} \text{ cm}^{-3}\), and the concentration of deep donors \(N_D = 3 \times 10^{16} \text{ cm}^{-3}\). The donor compensation, which is due to residual contamination of the MWPECVD reactor, should be eliminated because it causes considerable uncertainty in setting the hole concentration in the drift region, which is critical for the proper operation of the diode.

In principle, Mo and Ru Schottky contacts can be operated up to 400 °C without substantial breaking of the oxygen termination of the diamond surface [6]. At
this temperature, it can be expected that the hole concentration in the drift region of our diodes will increase to $2.6 \times 10^{16}$ cm$^{-3}$. At the same time, the mobility of holes drops to 115 cm$^2$V$^{-1}$s$^{-1}$ as determined by the Hall measurement on an equivalent p' epilayer. Thus, at 400 °C, the $R_{on,sp}$ of the drift region can be expected to fall below 100 µΩ.cm$^2$, which is lower than the $R_{on,sp}$ value of the pVSBD contact layer. Various improvements in the layout of the diode that decrease the distance between anode and cathode contacts can then be used to further reduce the ON-state resistance of the diode.

Room temperature reverse I-V characteristics of different Mo pVSBDs measured up to the point of diode destruction (breakdown) are shown in Fig.9 (bottom). As can be seen, the breakdown field of the diodes vary and its maximum 0.8MV/cm (diode G21) is far below the value expected for the diamond device. The breakdown (destruction of the diode) does not occur at the edge of the contact, where the highest electric field strength can be expected, but at various locations inside the contact. Evidence is provided by optical images of the anode contact taken before and after destruction (see the top of Fig. 9).

![Fig.9 Room temperature reverse I-V characteristics of Mo pVSBDs measured up to the destruction/breakdown (bottom) and the optical image of the anode contact recorded prior to and after the destruction (top).](image1)

In general, the breakdown field of diamond Schottky diodes is degraded by number of defects (namely threading dislocations [16]) appearing in the MWPECVD grown low-doped p' drift region. These defects cause a local increase in the reverse current, which can lead to charge carrier multiplication when the electric field increases with reverse bias. This is shown in the reverse I-V characteristics of diodes F51, F81, and G21 in Fig.9. Their characteristics have a regular shape at first, but after exceeding the reverse voltage of approx. 20 V a gradual uncontrolled increase of the leakage occurs, which is followed by a breakdown. High number of defects in the drift region leads to loss of blocking capability of the diode (G21). Fig.10 shows a detail SEM image of the mesa structure (taken before the metal deposition) of the diode chip with (the presented Ru pVSBDs) and without (not presented) blocking capability. On the right, one can register etch pits appearing in the p' contact layer after the removal of the p' epilayer by oxygen plasma. The etch pits are connected with different types of crystal defects (threading and edge dislocations, stacking faults). In the bottom image, the etch pit density reaches a value of $10^8$ cm$^{-2}$ and none of the diodes realized on this chip showed blocking properties. The etch pit density corresponding to the top image was two orders of magnitude lower, but still did not guarantee the regular blocking characteristics of 100 µm diameter diodes. In summary, the reduction of crystal defects is necessary to achieve the expected breakdown voltages for larger devices.

![Fig.10 Detail SEM image of the mesa structure (taken before the metal deposition) of the diode chip with (top) and without (bottom) blocking capability. The top p' layer is on the left, the edge of the mesa is in the middle, and the surface of the p'+ layer exposed by oxygen plasma etching is on the right.](image2)

### CONCLUSIONS

Mo, Ru, and Pt contacts covered by the gold capping layer were used for preparation of pseudo-vertical Schottky barrier diodes on (113) oriented homoepitaxial boron-doped diamond. Results show that all three metals can be used to realize Schottky diodes with sufficient forward and blocking capability. Moreover, molybdenum and ruthenium can also be used to
simultaneously create a stable ohmic contact on heavily doped contact p⁺ layer. Molybdenum provides optimum properties: a sufficient Schottky barrier height providing low leakage (< 10⁻⁸ A/cm²) and an acceptable forward voltage drop of 3.80V@J₁=1kA/cm² at operation temperature of 150 °C. The rectifying ratio of Mo pVSBDs stays at 10¹¹ over the entire temperature range from 30 to 180 °C. pVSBDs with ruthenium contacts exhibit lower Schottky barrier, their forward voltage drop is thus lower (2.85V@J₁=1kA/cm²@150 °C), but their leakage increases rapidly with temperature and rectification ratio drops to 7×10⁵ at 150 °C. Platinum provides the highest Schottky barrier and guarantees the lowest level of the leakage (<10⁻⁸ A/cm²). However, the diodes have poorer forward characteristics: their ideality factor and forward voltage is high (7.35V@J₁=1kA/cm² at 150 °C). The maximum achievable breakdown field (0.8MV/cm) of realized pVBDs is then given by the number of crystal defects (namely threading dislocations) in the low-doped drift region.

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REFERENCES


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