Demonstration of Diamond-Based Schottky p-i-n Diode With Blocking Voltage > 500 V

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***Abstract*— Diamond is considered to be the ultimate semiconductor for power devices due to its high breakdown electric field, high carrier mobility, and superior thermal properties. The success of diamond-based electronic devices has been difficult due to critical challenges involved with poor doping efficiency and achievement of ohmic contacts. Achieving n-type diamond has proved to be more difficult over p-type so far. In this letter, we report the achievement of n-type doping in diamond, verified using Hall measurements, which was then used to fabricate Schottky p-i-n diodes measuring a forward current density greater than 300 A/cm^2 at 4 V and breakdown voltage of over 500 V with a 3.5-μm-thick drift layer. A Silvaco simulation was performed which agreed well with the experimental data showing turn-ON voltage of 1 V and an ideality factor of 1.04, consistent with the model of a p-i-n diode with a fully depleted n-type contact.**

***Index Terms*— Diamond, P-I-N diodes, power semiconductor devices.**

I. Introduction

WITH a bandgap of 5.47 eV diamond offers a large critical electric field, enabling a roadmap for high voltage power switches beyond GaN and SiC. The predicted bulk mobility (1800 cm^2/Vs for holes and 2100 cm^2/Vs for electrons), although remains untapped [1], [2], is ideal for achieving high output current. Its high thermal conductivity along with a low coefficient of thermal expansion would allow device operation at elevated temperatures. The development of electronic devices using diamond has been impeded mainly due to difficulties involved in growing homoepitaxial n-type diamond and unavailability of single crystalline diamond substrates. The lack of a suitable metal with work function lower than n-type diamond (0.9 eV) [3] is yet another issue that makes the formation of ohmic contacts very challenging. Phosphorus (P) is the only relatively shallow n-type dopant to diamond ($\sim$ 0.5-0.6 eV). Even though multiple approaches have been employed in growing homoepitaxial n-type diamond, only few have been successful [4]–[7].

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TABLE I

Growth Parameters for Type IIa Substrate P-Doped and I-Layer

	n-layer	i-layer
Source Gases	H_2, CH_4,$P(CH_3)_3$	H_2, CH_4
Temperature	1100 ºC	900 ºC
CH_4/H_2	2 sccm / 388 sccm	2 sccm / 398 sccm
$P(CH_3)_3/H_2$	10 sccm	0
Pressure	80 Torr	80 Torr
Microwave Power	2500 W	1700 W

In this letter we report the development of PIN diodes using (100) orientation of the crystal grown homoepitaxially on single crystal bulk diamond substrates. The reverse blocking voltage realized in these devices exceeds 500 V over a 3.5 μm i-layer at a current level of 10^{-2} A/cm^2. We also report our P-doping study that was done to achieve the n-type layer. Although the standalone n-type diamond films exhibit good conductivity, the fabricated devices behaved like Schottky PIN diodes (SPINDs) with high forward current, demonstrating an on:off ratio $>10^7$ at $+/-$ 4 V. A Silvaco ATLAS two-dimensional drift diffusion simulation was also performed and compared to experimental data to validate the theory of operation in these devices.

II. Homoepitaxial Diamond Growth

All the semiconducting layers for the diode were grown using Plasma Enhanced Chemical Vapor Deposition (PECVD) technique on 3 mm $\times$ 3 mm type IIa insulating and type IIb Boron (B)-doped single crystal diamond (100) substrates.

For the type IIa substrates, at first a 5 μm-thick p-type diamond with a B-concentration $\sim 10^{20}$/cm^3 was grown at Fraunhofer USA Center for Coatings and Diamond Technologies. The intrinsic and n-type (P-doped) layers were subsequently grown in our lab using the growth conditions summarized in Table I. A wet chemical etch was performed to remove organic or metallic contaminants, followed by a H-plasma treatment to remove graphitic impurities. The i-layer was grown using 2 sccm methane (CH_4) as the carbon source and 398 sccm of hydrogen (H_2) as carrier gas. A 50-70 nm n-type layer was grown on the i-layer to complete the p-i-n structure. A mixture of H_2 and Trimethylphosphine (TMP) $P(CH_3)_3$ (200 ppm/10 sccm) as the P-source for the n-type doping. CH_4 (2 sccm) acts as the additional carbon source with H_2 (388 scm) as the carrier gas.

The type IIb substrates with a B-concentration $\sim 5 \times 10^{19}$/cm^3 were obtained from the Technological

TABLE II
GROWTH PARAMETERS FOR TYPE IIb SUBSTRATE P-DOPED AND I-LAYER

	n-layer	i-layer
Source Gases	H_2, CH_4,$P(CH_3)_3$	H_2, CH_4
Temperature	980 ºC	900 ºC
CH_4/H_2	3 sccm / 367 sccm	2.25 sccm / 398 sccm
$P(CH_3)_3/H_2$	30 sccm	0
Pressure	80 Torr	60 Torr
Microwave Power	2500 W	1200 W

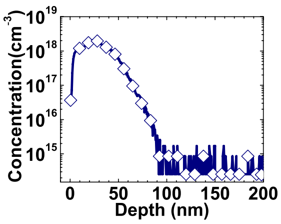


Fig. 1. Representative SIMS plot showing P-incorporation in the n-layer [8].

Institute for Super-hard and Novel Carbon Materials. The growth conditions for P-doped and i-layer were slightly different due to the difference in plasma focusing as summarized in Table II.

A. P-Doped Diamond Growth Optimization

A preliminary set of growth experiments was performed on type IIa non-conducting substrates to obtain parameters enabling high P-incorporation while maintaining homoepitaxial growth. The growth was performed with microwave power set at ∼ 2500 W and a temperature of 1100 °C which showed promising reduction in defect density. The higher pressure helped achieve a more confined plasma discharge enabling P-incorporation through growth rates greater than the surface segregation velocity of P-atoms. A P-doping of $2 \times 10^{18}/cm^3$ was achieved and verified using Secondary ion mass spectroscopy (SIMS) as shown in Fig. 1 [8].

P-doping of diamond is most commonly achieved by a phosphine/hydrogen gas mixture. Here TMP, a liquid, dissolved in H_2 is used - as it presents a less toxic doping source. P-doping of (100) oriented diamond is still a challenge that is addressed by preparation of miscut or off-axis substrates with a miscut angle several degrees toward the (110) direction. A temperature controlled sample holder that utilizes plasma focusing at a protruding geometry is used to establish a high density plasma discharge adjacent to the substrate. With a pulsed deposition technique phosphorus was incorporated along the (100) surface. The process of using short, incremental, doping cycles presents a novel approach for growing electronic grade n-type diamond.

B. Hall Measurements on P-Doped Diamond

Hall measurements were performed on P-doped films grown on undoped type IIa substrates to verify their n-type nature. A comprehensive study of free electron mobility versus carrier concentration was performed at room temperature as shown in Fig. 2 [8]. The mobility decreases with the increase in doping concentration due to the increase in impurity scattering [5].

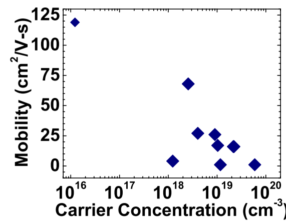


Fig. 2. Variation of free electron mobility with carrier concentration [8].

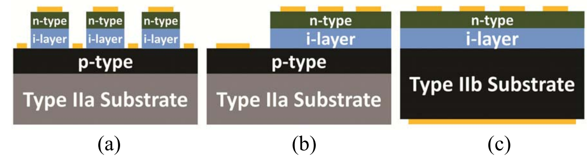


Fig. 3. Schematic representation of (a) conventional mesa etch (b) edge contact (c) back contact diode structures.

III. DEVICE FABRICATION

The as-grown samples which could be either H- or OH- terminated, were treated in an acid mixture (HNO_3: H_2SO_4 = 1:3) to ensure that the surface is O-terminated. It has been reported earlier in literature that a two-dimensional hole gas forms a surface conductive layer when the surface is H-terminated [5], [9]. Metal contacts to the n-layer using Ti/Pt/Au/Ni:50 nm/50 nm/150 nm/50 nm were deposited by e-beam evaporation using standard bi-layer photolithography.

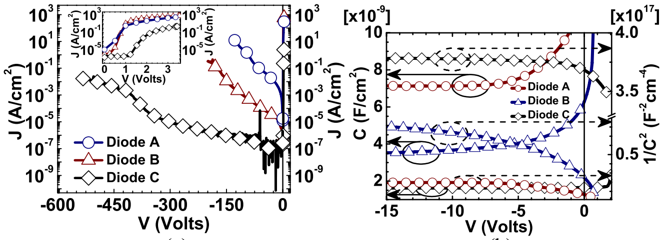
Mesa isolation was achieved using a SiO_2 hard mask process. SiO_2 was deposited on the sample using PECVD, patterned and then etched using RIE at 200 W and 30 mTorr, using CHF_3 and Ar (25 sccm each). The diamond was then etched using the patterned hard mask in an Oxygen(O)-plasma at 300 W RIE power and 7 mTorr process pressure. SF_6 was added to increase anisotropy of the etch.

The hard mask was etched away using RIE before the p-layer contacts (Ti/Pt/Au:50 nm/50 nm/150 nm) were deposited. Square diodes with side 50 μm to 300 μm in length and circular diodes with diameters 50 μm to 300 μm were fabricated as shown in Fig. 3 (a). The diodes showed a high forward current density but suffered from high reverse leakage possibly due to conduction along the side walls. Attempts at passivation using SiN_x, Al_2O_3 and O-plasma failed to show reduction in reverse leakage characteristics.

In the absence of suitable passivation, the mesa-etch was replaced with a single p-layer contact placed at the edge of the sample as depicted in Fig. 3(b). Two approaches were explored for growing the i-layer. The first approach involved growing the i-layer in a chamber used for growing Nitrogen (N)-doped diamond (Diode A). The second approach involved growing in the same chamber used for growing the n^+ layer (Diode B). The type IIb substrates were used to fabricate vertical diode structures (Diode C) as shown in Fig. 3(c).

IV. RESULTS

Current density-voltage (J-V) and capacitive-voltage (C-V) measurements were performed to investigate the electrical properties of the diodes. Figure 4(a) shows a representative set of J-V characteristics from diodes showing the lowest leakage current. Diode A (area=333×10^{-6} cm^2),



(a) (b)

Fig. 4. (a) J-V characteristics of diodes (Inset shows the forward characteristics) (b) C-V and 1/C^2 vs V characteristics of diodes at 1 MHz.

B (area=169 $\times$ 10^{-6} cm^2) and C (area=415 $\times$ 10^{-6} cm^2) were chosen for the plot based on their lowest measured current density. Not shown in the plot, Diode B with a comparable area of 315 $\times$ 10^{-6} cm^2 offered a slightly higher current density (3 $\times$ 10^{-2} A/cm^2 at 150V). The fabricated diodes showed clear rectification behavior with an on:off ratio $> 10^7$ at +/− 4 V. The forward current density for Diode A and Diode B was >300 A/cm^2 at 4 V and 7.5 A/cm^2 in the case of Diode C. In reverse bias, Diode A broke down catastrophically beyond 120 V. Diode B and C had a blocking voltage > 100 V and 400 V respectively at a current level of 10^{-3} A/cm^2 and >150 V and 500 V at a current level of 10^{-2} A/cm^2.

Figure 4(b) shows the C-V characteristics of the diodes measured at 1 MHz. The doping concentration of the fully depleted "i-layer" was obtained using[10]

$$\frac{1}{C^2} = \frac{2}{q\varepsilon_s N_I}\left(V_{bi} - V - \frac{2kT}{q}\right) \tag{1}$$

$$\frac{d\left(\frac{1}{C^2}\right)}{dV} = -\frac{2}{q\varepsilon_s N_I} \tag{2}$$

From the slope of 1/C^2 vs V characteristics, the doping concentration of the fully-depleted "i-layer" was found to be $\sim 1.24 \times 10^{16}$/cm^3, 4×10^{15}/cm^3 and 2.57×10^{16}/cm^3 for diode A, B and C respectively. The thickness of i-layer was calculated to be 0.68 μm (Diode A), 1.12 μm (Diode B) and 3.5 μm (Diode C) from the capacitance under full depletion. The ideality factors for diode A, B and C was calculated to be ∼1.5,1.04 and 3.12 respectively.

V. Discussion

Diamond has a bandgap of 5.47 eV and therefore the expected turn-on voltage for diamond PIN junction is ∼ 4-5 V. In our present non-isolated devices, the measured turn-on voltage varied between 0.2-1 V. TLM measured after the full diode fabrication indicates depletion of the top n$^+$ layer. The possible cause of such a change in the surface barrier height is currently being investigated under a separate study.

To verify the theory of operation, a Silvaco ATLAS simulation was performed on a p$^+$-i-n diamond diode. The material parameters, such as mobility of electrons and holes in diamond, were calibrated by fitting to experimental resistivity versus temperature data [11] for different n-type and p-type doping concentrations (discussed in [12]). The simulated structure was a p$^+$-i-n diode with a 50 nm n-layer, 1 μm i-layer and a 0.8 μm p$^+$ layer. The doping concentration of the n and p-type layers was assumed to be 10^{17}/cm^{3}and

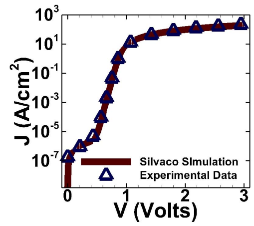
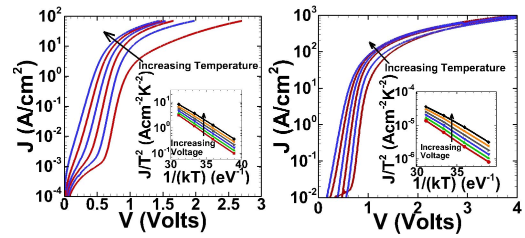


Fig. 5. Comparison plot between a Silvaco ATLAS simulation of a PIN diode with fully depleted n-layer and the corresponding experimental data.



(a) (b)

Fig. 6. Forward Diode Characteristics as a function of temperature (25°C to 275°C in steps of 50°C) for (a) Diode A (b) Diode B. Inset shows Richardson Plot used to extract barrier height (V=700 mV to 750 mV in steps of 10mV).

10^{20} /cm^3 respectively. The doping concentration was appropriately chosen to account for a fully depleted n-layer.

A good fit between simulated and experimental data at room temperature was obtained as shown in Fig. 5 by assuming a Schottky contact to the n-layer. From the simulation, the band diagram shows a barrier value of ∼1.0 eV to holes and ∼4.45 eV to electrons. The constant slope of the Richardson plot as shown in the inset of Fig. 6 demonstrates the current is limited by thermionic emission. The value of the Richardson constant was found to be 2.52 A/cm^2/K^2 and 1.02 A/cm^2/K^2 for Diode A and B respectively. The higher barrier to the electrons at the n-layer depletes the layer of electrons and lower barrier to holes implies that once the device turns on, the majority current is due to holes being injected over the barrier and collected at the n-layer contact. The lower turn-on voltage is in agreement with the Schottky behavior of the n-type layer. An ideality factor of 1.04 was obtained, which matches very well with the experimental value as depicted in Fig. 5. Makino et al. [7] observed similar results in diamond pn diodes with a fully depleted n-layer.

VI. Conclusion

Diamond diodes reported in this letter measured a forward current density >300 A/cm^2 at a forward bias of 4 V and a blocking voltage >500 V. The low turn on voltage, good forward current density, ideality factor close to 1 and scaling of the blocking voltage with i-layer thickness, as reported in this letter, make these devices very promising for high power switching applications.

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