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Diamond / SiC heterojunctions

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***Abstract*—Diamond and SiC are wide bandgap (WBG) materials which can be used to fabricate high power devices with improved performance. The combination of these materials into one single device is expected to bring some benefits, like a better thermal management with a corresponding increase in the operating power. Diamond films deposited by Chemical Vapor Deposition (CVD) can be doped with boron, making them p-type semiconductors. Diamond films deposited on foreign substrates are intrinsically polycrystalline, so the quality of the interface, determined by deposition conditions and seeding method, plays a critical role in the heterojunction characteristics, impacting both reverse current and breakdown voltage. This work reports the fabrication and characterization of p-diamond / n-SiC hetero-junctions. P-type polycrystalline diamond (PCD) films were deposited directly on the surface on n-type SiC commercial wafers by Hot Filament CVD (HFCVD) using different seeding techniques. I-V characteristics of the obtained heterojunctions were measured at room temperature and the quality and morphology of the diamond films were assessed by scanning electronic microscopy (SEM) and Raman spectroscopy. The influence of the different seeding techniques on the I-V characteristics is discussed.**

***Keywords*—SiC, boron-doped diamond, p-n heterojunctions**

I. INTRODUCTION

High temperature (HT) electronics is a common denominator in many industries. For instance, petrochemical industry or geothermal power plants require sensors to monitor the environment around drilling equipment, where temperatures exceed 200°C. Distributed control systems in aerospace and automotive industries also pose additional requirements in terms of temperature (up to 200°C in avionics and 300°C in automotive applications) [1]. HT components will also impact renewable energy systems: in photovoltaic industry, they are expected to (i) increase inverters efficiency to values higher than 98% and (ii) reduce failure rate of passive components, footprint and installation costs [2]. Wind turbines can also benefit from HT electronics, by an improvement of 1% system efficiency that reflects in an operation cost benefit of $1.50 per hour per MW for electricity producers [3]. HT (> 300°C) devices also allow for a simplification of bulky cooling units, which are often implemented in common Si power converters.

SiC is considered a top material for these applications. It can overcome the ultimate performances reached by Si devices, in terms of power handling, maximum operating temperature and conversion efficiency in power module [4, 5]. The unique properties of the 4H-SiC poly-type include high critical electric field (3 MV/cm), large bandgap (3.2 eV), high saturation velocity (2×10^7 cm/s), high thermal conductivity (4.9 W/(cm K)) and good electron mobility (~1000 cm^2/Vs for //*c*-axis) [6]. SiC can operate efficiently in high-temperature environments [7] and at high switching frequencies [8]. In addition, as an indirect band gap material SiC is excellent for both unipolar and bipolar power device applications under high-temperature and high-power density conditions.

Diamond is a WBG material with properties such as high thermal conductivity (~20 W/cm/K), band-gap (~5.4 eV), critical field (~5.6 MV/cm) and chemical inertness [9]. It has a huge potential for high power / high temperature applications, whether as packaging or passivation material or as active semiconductor layer. Diamond can be deposited in the form of thin films by chemical vapor deposition (CVD) [9]; this process enables a precise and reproducible control of sp^2/sp^3 ratio and consequently specific material properties important for particular applications. Both p and n-type diamond films can be prepared by CVD, meaning that the desirable electronic properties exhibited by a few, very rare natural diamonds can now be achieved in an engineered diamond material [10-12]. The electrical properties of diamond and diamond-based devices have been widely published and different types of diamond devices have already been fabricated [13-20].

The combination of SiC and diamond is expected to lead to devices with improved thermal management and power capability. In 1993, optically transparent SiC contacts were deposited on natural semiconducting diamond [21]. More recently, both doped and un-doped nanocrystalline diamond (NCD) films were used as electrical contacts for both n- and p-type 4H-SiC, allowing for simultaneous measurement of both optical and electrical characteristics of the devices [22]. Highly-rectifying NCD / SiC hetero-junctions with high forward current densities and on / off current ratios have been demonstrated, with a curvature coefficient of 105 V^{-1}, amongst the highest known values for a diode [23]. Diamond can also be deposited directly on SiC devices to provide functionalities such as passivation or improved thermal management [24].

When diamond and SiC are brought into contact, a hetero-junction is obtained at the interface. In order to have a useful heterojunction, lattice constants of the two materials must be well matched, as in the case of 4H-SiC [25] and diamond [26],

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since lattice mismatch can introduce dislocations which result in interface states. In addition, challenges such as difficulty in relating the conduction mechanism to a pre-determined band structure or the causal variety of defect levels present in CVD diamond justify a fundamental study for characterizing the interface behavior and the parameters that affect it. Device performance itself depends on the quality of the diamond film and its surface termination, on the metal / diamond junction characteristics and on geometrical factors [27]. Even more critical than these parameters, however, is the diamond / SiC interface. Deposition of diamond films on foreign substrates requires a seeding procedure that enriches the substrate surface with diamond nanoparticles that grow and coalesce during the CVD cycle [9]. The density of these seeds, as well as the speed at which they grow and coalesce, are critical factors that determine the sp^2 / sp^3 ratio at the interface. This, in turn, deeply influences the rectifying ratio, as well as the leakage currents at the interface.

This paper reports the fabrication of p-diamond / n-SiC heterojunctions by HFCVD using different seeding procedures and gas phase compositions. I-V measurements reveal rectifying behavior as expected, however leakage currents are extremely high. The influence of seeding step on the I-V characteristics is discussed and a procedure to improve the quality of the interface is proposed.

II. DIAMOND-SIC HETEROJUNCTIONS

A. Fabrication

P-type boron-doped diamond (BDD) films were deposited on 25 mm^2 n-type 4H-SiC samples purchased from Cree Inc. using HFCVD. Carrier concentration on the top epitaxial layer was 1×10^{16} cm^{-3} and bulk resistivity was ≤ 0.025 $\Omega \cdot$cm. The samples were cleaned in acetone followed by ethanol in an ultrasonic bath (US) for 3 min each. Half of the samples were introduced into the HFCVD chamber and underwent pre-treatment (PT) under diamond growth conditions (Table 1). SiC samples (with and without PT) were then seeded with diamond particles. Two methods were used: US bath in aqueous nanodiamond (ND) slurry for 30 min and manual scratching method (by pressing the sample against a tissue with diamond particles). Seeded samples were introduced into the HFCVD chamber and boron-doped diamond was deposited for 4 hours, followed by a 1 hour-long cooling step. Boron doping source, boron oxide (B_2O_3) diluted in ethanol, was dragged by constant Ar flow at different CH_4/H_2 gas ratios and system pressures. Details can be found elsewhere [28]. Two samples (with and without PT) were simultaneously coated in each CVD run, to infer the effect of the PT on the characteristics of the heterojunction, if any.

Various deposition parameters were varied (pressure, composition of the plasma mixture and deposition time) (Table 1). These factors are known to affect features of the diamond film, such as crystalline size, and film roughness. For all runs (PT and), the SiC samples were placed in the sample holder and exposed during filament carburization.

TABLE I. SUMMARY OF EXPERIMENTAL CONDITIONS. SAMPLES NOT GIVEN PT ARE MARKED WITH '.

Sample	Seeding	Substrate temperature (°C)	$CH_4/Ar/H_2$ (sccm)	Pressure (mbar)
A1/A1'	ND	720	3/6/100	45
A2/A2'	ND	720	3/8/100	45
A3/A3'	ND	736	3/10/100	45
A4/A4'	scratch	720	3/8/100	45

The surface of the diamond-SiC heterojunctions was observed with a scanning electron microscope (SEM) Hitachi SU70 and diamond film quality was assessed using Raman spectroscopy. Spectra were excited with a 514.5 nm Ar+ laser focused to a 1 μm-diameter spot and with 5 mW incident beam power. Following the morphological characterization of the film, 10 μm-diameter copper wires were attached to the top surface of the diamond film and the back SiC side with silver conductive paint, which makes ohmic contacts. Estimated electrode area is $\approx 2.5\times10^{-3}$ cm^2. *I-V* characteristics of the vertical devices were measured at room temperature.

B. Results and Discussions

Fig. 1 shows SEM images of deposited films. Images revealed that after 4 hour deposition, samples seeded with ND suspension (a,c) were covered with closed and highly adherent polycrystalline diamond films, with an average crystal size of 600 nm. On the contrary, films deposited on samples seeded with scratch method showed areas where the film was not fully closed yet (b,d). The same tendency was observed with other samples. These results are not surprising since it is known that the exposure of the substrates to diamond growth conditions before the seeding step increases nucleation density and decreases coalescence time [29].

Raman spectra (Fig. 2) showed the characteristic diamond sp^3 peak at 1332 cm^{-1}. The G band of graphite is clearly seen in all spectra around 1550 cm^{-1}. The smaller band around 1150 cm^{-1} has been associated to NCD [30], however, A.C. Ferrari and J. Robertson [31] showed that this band is a signature of trans-polyacetylene and is connected to the presence of hydrogen in the films.

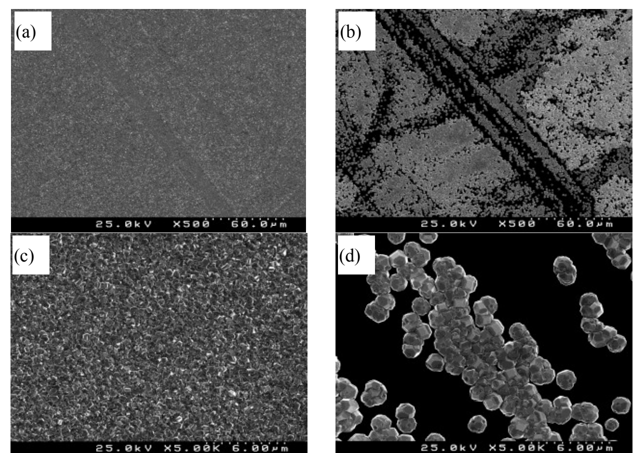

Fig. 1. SEM images of (a,c) ND seeded sample A2 and (b,d) scratch seeded sample A4.

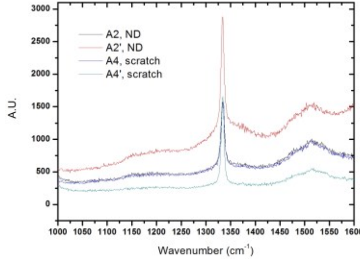

Fig. 2. Raman spectra of samples of series A.

The heterojunctions exhibit poor rectifying behavior (Fig 3a) with correspondingly low rectifying indexes (Table 2). The predicted energy band diagram is shown in Fig 3b [32]. Electrons that flow from the SiC towards the diamond face a high barrier and the current in reverse mode is expected to be negligible [22]. The high leakage currents observed in our case suggest a high density of defects at the interface.

To get further insight on the conduction mechanisms across the heterojunctions, the *I-V* characteristics were plotted on a log-log scale, as shown in Fig 4a. The function $\alpha = \frac{\partial \log I}{\partial \log V}$ gives information on the conduction mechanisms: when the number of thermally generated free carriers is larger than the number of injected carriers, the current follows Ohm's law ($\alpha = 1$), otherwise it switches to space charge limited current (SCLC). In this regime, the current (in the absence of traps) is described by the Mott-Gurney law [33]:

$$I_{SCLC} = q \cdot p_0 \cdot \mu \cdot \frac{V}{d} + \frac{9}{8} \cdot \varepsilon \cdot \mu \cdot \frac{V^2}{d^3} \quad (1)$$

where ε is the dielectric constant of the material, μ is the mobility and L is the electrodes distance. In the presence of shallow traps, the current shows the same behavior but is decreased by a factor θ, which is the ratio between free charge density and total charge present inside the film. In both cases, $\alpha = 2$. In the presence of deep traps or distribution of exponential traps, $\alpha > 2$ [34]. In our case (Fig 4a), α increases to a value larger than 2 in all samples, suggesting the presence of deep traps or an exponential distribution of traps.

TABLE II. RECTIFICATION INDEXES.

A2'	A2	A4'	A4
1.2	2.4	8	76

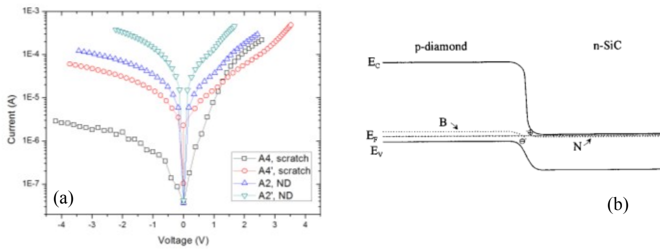

Fig. 3. (a) I-V characteristics of the heterojunctions. (b) Qualitative energy band diagram of a p-type diamond / n-type SiC heterojunction [32].

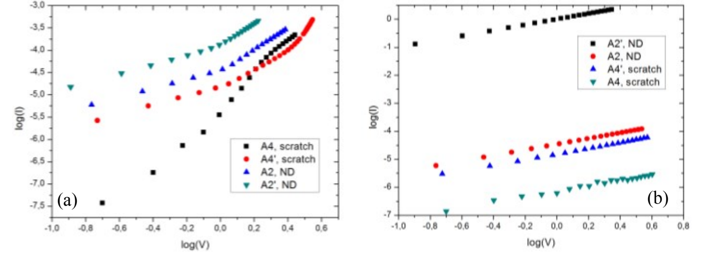

Fig. 4. Log(I) *vs.* log(V) under (a) forward and (b) reverse bias.

Current under reverse bias (Fig 4b) does not follow common Fowler-Nordheim or Poole-Frenkel mechanisms. Instead, log(I)-log(V) can be fitted by a straight line, which suggests Poole conduction. This type of transport occurs when the density of states is so high that the Coulomb potential of neighbor states overlap and trapped carriers escape from one of the centers through a lower barrier according to Poole Law [35]. Again this is evidence of a high density of interface states that influence the *I-V* behavior of the devices.

The presence of interface states that compromise the behavior of diamond-based devices has already been reported [34, 36, 37]. In addition, polycrystalline diamond films may be regarded as a network of grains (sp^3 carbon) and grain boundaries (non-sp^3 carbon) [38]; the latter act as conductive paths and, if their density is high enough, the current that flows through them dominates the conduction under reverse bias. For each seeding procedure used (ND *vs.* scratch), the PT has a positive influence, since it increases the rectification index. In fact, the PT is known to lead to higher diamond nucleation densities and improved interface uniformity [29], with the decrease of grain boundaries density at the diamond/SiC interface – and corresponding decrease of interface states.

Regardless of this, and even taking into consideration the intrinsic polycrystalline nature of the diamond film, reverse currents are still abnormally high. The origin of this effect may be related with the fact that, due to limitations of the HFCVD system, the SiC sample was exposed to the plasma during the filament carburation; during this step, non-sp^3 carbon species were deposited on the SiC surface, creating an abnormally high density of defects at the interface. This layer may have been partially removed by the manual scratch given to samples A4 and A4', hence the higher rectification indexes.

III. FUTURE WORK AND CONCLUSIONS

P-diamond / n-SiC heterojunctions were fabricated by HFCVD using different seeding methods. Even though rectifying behavior was observed, reverse currents are extremely high. Analysis of *I-V* curves (both in forward and reverse bias) show evidence of the presence of a high density of interface states that compromise the devices' performance. These states may have been created by the exposure of the SiC surface during filament carburation. In order to improve the performance of the devices, the SiC substrates should be protected during this step.

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