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Heteroepitaxial diamond growth on 4H-SiC using microwave plasma chemical vapor deposition

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Abstract

Deposition of heteroepitaxial diamond via microwave chemical vapor deposition has been performed on a 4H-SiC substrate using bias enhanced nucleation followed by a growth step. In future work, the diamond film will serve as a protective layer for an alpha particle sensor designed to function in an electrorefiner during pyroprocessing of spent fuel. The diamond deposition on the 4H-SiC substrate was carried out using a methane-hydrogen gas mixture with varying gas flow rates. The nucleation step was conducted for 30 minutes and provided sufficient nucleation sites to grow a diamond film on various locations on the substrate. The resulting diamond film was characterized using Raman spectroscopy exhibiting the strong Raman peak at 1332 cm^{-1} . Scanning electron microscopy was used to observe the surface morphology and the average grain size of the diamond film was observed to be on the order of $\sim 2\text{--}3\text{ }\mu\text{m}$.

Keywords: Condensed matter physics, Nuclear engineering, Nanotechnology, Materials science

1. Introduction

The deposition of heteroepitaxial diamond has shown to be useful in the context of semiconductor electronics. A method of depositing diamond on non-diamond

substrates is via chemical vapor deposition (CVD). Microwave plasma-assisted CVD has proven to be a reliable method of heteroepitaxial diamond growth on semiconductors such as silicon. Change et al. has reported successful diamond growth on 6H-SiC [1] as well as Yaita et al. reported diamond growth on 3C-SiC [2]. These polytypes vary in the order of the stacking of Si-C layers. This paper will report diamond growth on the polytype 4H-SiC which has a stacking sequence of ABCB. The lattice mismatch between 6H-SiC and diamond is slightly below 16% while the lattice mismatch between 4H-SiC and diamond is slightly above 16%. While 4H-SiC is not superior for diamond growth in terms of lattice compatibility, it does however have a wider band gap than other SiC polytypes at 3.2 eV [3]. The wider band gap is one main reason 4H-SiC was used for this study since it is relevant for the device's future intended use as an alpha particle sensor.

In future work, the diamond film in this paper is to serve as a protective layer for a semiconductor based charged-particles detector that must function in a high temperature, high corrosive, and high radiation environment. During reprocessing of spent nuclear fuel, it is important to protect against misuse of nuclear material. A method of doing so is by the monitoring of actinide concentrations present during pyroprocessing, one of a closed fuel cycle technologies, via alpha spectroscopy. It is then necessary to fabricate an alpha particle detector that can operate effectively in the high temperature and highly corrosive pyroprocessing environment. An electrorefiner at Idaho National Laboratory operates at a molten salt melting temperature of approximately 500 °C [4]. The alpha detector would need to function effectively under this temperature range and a protective diamond film is a proposed solution.

This molten salt temperature is much too high for a common silicon radiation detector to function effectively without performance degradation, mainly from an increase in thermal noise and unacceptable leakage current [5]. A wide band-gap semiconductor would not have as much leakage current as silicon and would be a more desirable material to base an alpha particle detector on in a pyroprocessing environment. Fabrication has started on an alpha particle detector using 4H-SiC due to its wide band-gap of 3.2 eV. In addition to high temperature, the molten salt environment is also highly corrosive. This brings motivation to creating a protective layer around the 4H-SiC detector that can withstand the high temperature and corrosive molten salt environment but is still conductive. A similar detector was fabricated and tested by Tran et al. using a silicon PIN diode with a boron doped CVD diamond film layer [6]. Boron doped diamond has been reported to be a viable conductive electrode capable of withstanding electrochemical environments and should serve well for the intended application of the alpha detector proposed [7]. Kado et al. has previously shown that a diamond film of around 2–3 μm in thickness exposed to a molten salt environment up to around 800 °C remains electrochemical stable and the diamond crystalline structure remains intact [8],

thus lending validity to the use of a diamond film as a durable electrode in molten salt. The diamond film may be doped with a high boron concentration, forming p-type conductive diamond, via ion beam implantation or by introducing trimethylboron into the hydrogen gas used in the diamond growth process which creates the ability to dope the diamond during growth [9]. Diamond grown using microwave plasma chemical vapor deposition (MPCVD) on 4H-SiC has been performed in this work and will serve as a protective film. The details of the diamond growth is the focus of this paper. The deposition conditions along with scanning electron microscope (SEM) images and Raman spectra confirming the growth of diamond on 4H-SiC are reported.

2. Materials and methods

Diamond deposition was performed on 4H-SiC wafers grown by Cree Labs. On the substrates, there existed a bulk layer of thickness 300 μm and an epitaxial layer grown on top with a thickness of 21 μm . The doping concentration of the epitaxial layer was 5.0×10^{14} atoms/cm³ of nitrogen. The diamond deposition was performed on the epitaxial layer of the 4H-SiC wafer and the surface was silicon terminated, as opposed to carbon terminated.

The diamond deposition was performed in an ASTEX AX5200 M 1.5 kW CVD reactor. The sample was placed in the middle of a molybdenum sample holder in the CVD chamber. The sample was cleaned by H₂ plasma for 15 minutes prior to the nucleation step. The bias enhanced nucleation step consisted of applying a bias on the sample holder at -400 V for 30 minutes. The microwave power used was 700 W. The substrate temperature was 840 °C. The H₂ and CH₄ flow rates were 300 sccm and 15 sccm, respectively. The pressure was held at 20 Torr. After the bias enhanced nucleation step, a growth step was performed on the sample for a duration of 5 hours. The growth step consisted of a microwave power of 1300 W, a substrate temperature of 705 °C, a pressure of 50 Torr, and the H₂ and CH₄ flow rates were 300 sccm and 3 sccm, respectively.

Studies have been done previously on the effects of temperature, pressure and CH₄/H concentration on growth rate. Li et al. reported a growth rate of around 0.5 $\mu\text{m}/\text{hour}$ with a 300 sccm hydrogen flow rate at 50 Torr [10]. This growth rate was reflected in the diamond film grown in this paper, which will be discussed in more detail in the next section. It should be noted that since the 4H-SiC substrate used in this paper had a silicon terminated surface, it was believed that using a growth condition valid for Si may also be valid for silicon terminated 4H-SiC. Changa et al. reported successful diamond growth on 6H-SiC using a 1% methane concentration and temperature above 700 °C [1]. Growth conditions similar to these were factored into the recipe used in this paper.

After seizing all plasma, gas, and heating to the sample, the temperature was then decreased to room temperature and the pressure decreased to atmospheric pressure using argon gas. The sample was then characterized using electron microscopy and Raman spectroscopy, which will be discussed in the next section.

3. Results

Raman spectroscopy is a common method of analyzing diamond films due to its ability to easily identify the constituents of a material and diamond specifically having a strong wavelength shift at 1332 cm^{-1} [11, 12], making it stand out from amorphous carbon and other non-diamond materials. In addition to Raman spectroscopy serving as an accurate method of diamond identification, there is no special sample pretreatment which makes the method not only accurate but convenient.

Fig. 1 shows the Raman spectrum of the sample after the diamond deposition and exhibits the characteristic diamond peak at 1332 cm^{-1} confirming successful deposition of diamond on the 4H-SiC substrate. The Raman measurements were performed using at 514 nm excitation wavelength.

As a reference spectrum, Fig. 2 shows a Raman spectrum of the bare 4H-SiC substrate prior to diamond deposition to show the spectrum features of the substrate with no diamond present. The absence of any peaks near 1332 cm^{-1} is very apparent, removing any possibility of a wavelength shift from a constituent in 4H-SiC substrate causing a false positive peak that could be mistaken for diamond. In addition, if there is any graphite or amorphous carbon present in the diamond film, they are overshadowed by the strong diamond peak. This claim is from the

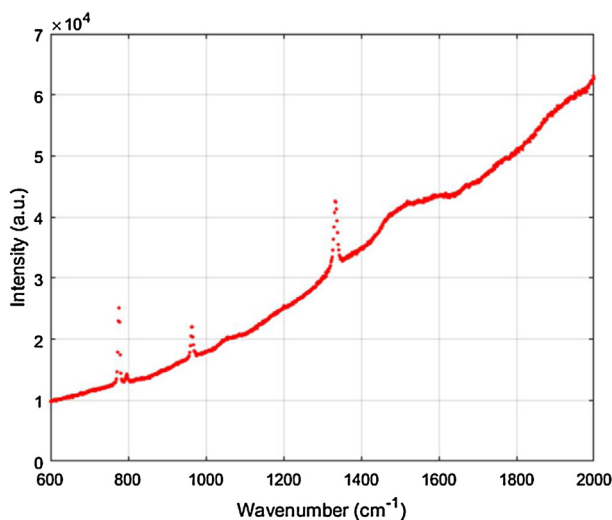


Fig. 1. Raman spectrum measured of diamond film on 4H-SiC sample after deposition.

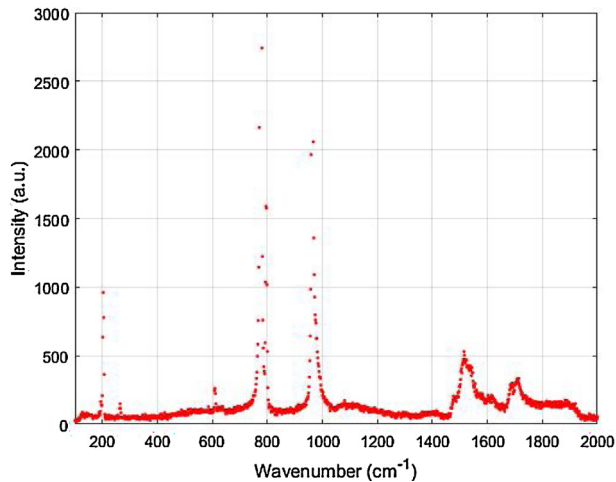


Fig. 2. The Raman spectrum of the bare 4H-SiC substrate.

absence of a G-band or D-band appearing in the spectrum near the narrow diamond peak.

SEM images can give helpful insight into the average grain size of the diamond film as well as analyzing the uniformity of the diamond film on the sub-micron scale. Fig. 3 shows an image of the diamond film on 4H-SiC taken via scanning electron microscopy.

As can be seen in Fig. 3, the average grain size of the diamond film was on the order of $\sim 2\text{--}3\ \mu\text{m}$, which indicates growth rate of around $0.5\ \mu\text{m}/\text{hour}$. The SEM image taken in Fig. 3 was from a location on the substrate where the diamond

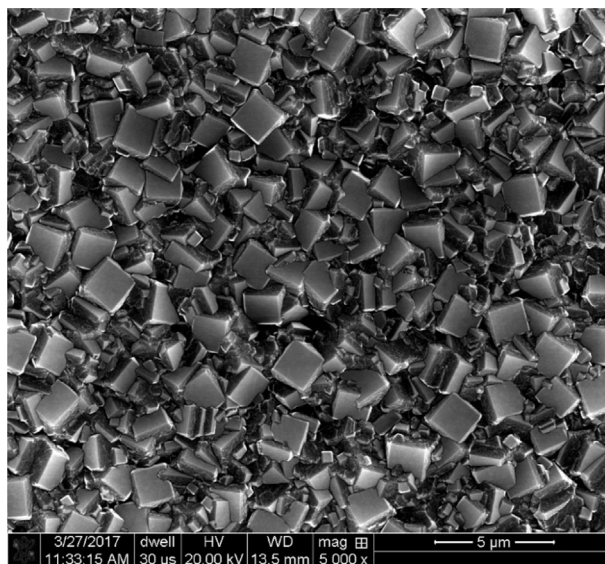


Fig. 3. SEM image showing surface morphology of the diamond film on 4H-SiC.

film had grown to confluence with no substrate left exposed. The diamond film did not grow this uniformly across the entire substrate however. Fig. 4 shows an SEM image of a location on the substrate where diamond did not grow to confluence.

The diamond had a tendency to grow near the outer perimeter of the substrate surface having the highest grain density around this perimeter and then decreasing in grain density towards the center of the substrate and out to the very edge of the surface. SEM images of this growth tendency can be seen in Fig. 5 and Fig. 6.

The shape of this growth formation may be impacted by the location of the sample in the CVD chamber. This sample location may be a changed variable in future work to attempt to achieve more uniform nucleation sites resulting in a more uniform diamond film across the substrate surface.

The SEM images of the diamond film are helpful with determining the average grain size and the confluence of the film but important characterization of the diamond film yet to be performed is of the cross section. An analysis of this would give important insight into the adhesion of the diamond film to the 4H-SiC substrate which may play an important role in its purpose as a conductive layer for the proposed alpha particle detector. Since poor adhesion may produce undesirable and non-negligible effects towards this purpose, a cross section analysis will be performed in future work to determine the quality of the film adhesion.

The resistivity of the diamond film was measured using a Keithley 2410 SourceMeter. Electrical contacts were placed 1 cm apart in contact with the diamond film on the surface of the substrate and the resistivity measured to obtain

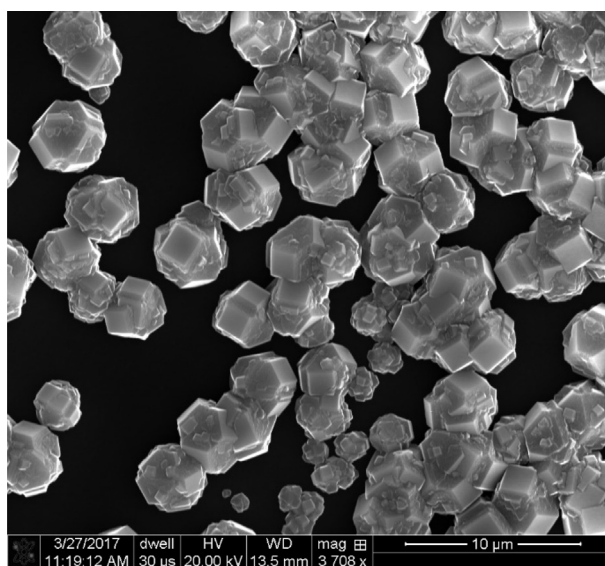


Fig. 4. SEM image of nonuniform diamond film location on 4H-SiC.

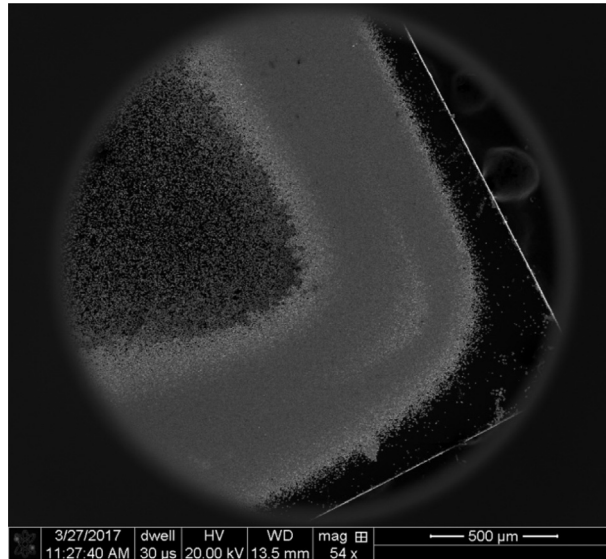


Fig. 5. SEM image showing the tendency for the diamond to grow near the perimeter of the substrate.

an average value. The average resistivity was $\sim 10^6 \Omega \text{ cm}$ which is consistent with resistivity measurements of other diamond films grown from chemical vapor deposition, such as Landstrass et al. [13]. It is also proposed in [13] that the low resistivity may be attributed to hydrogen passivation in defect sites in the diamond film from the hydrogen gas present during the diamond deposition process.

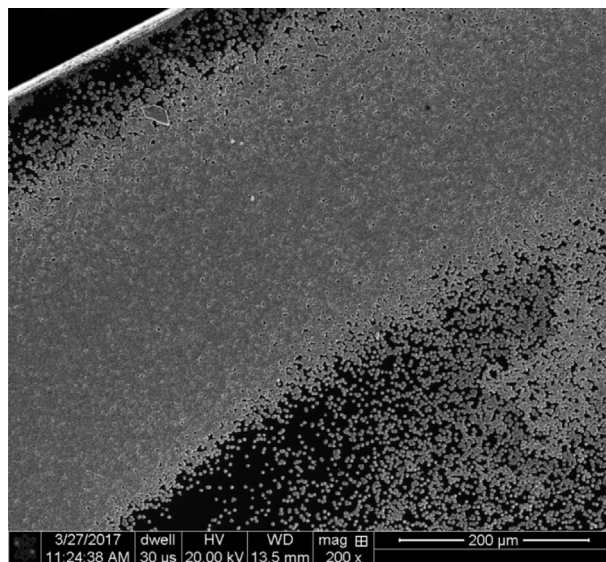


Fig. 6. A zoomed-in SEM image of the diamond growth near the edge of the substrate.

4. Conclusions

Deposition of heteroepitaxial diamond was successfully performed on a 4H-SiC substrate using MPCVD. Once uniformity of the film is achieved in future work, it will serve as a protective conductive layer for an alpha particle sensor in a molten salt environment. The resulting thickness of the diamond film in this paper (2–3 μm) was consistent with the work of Kado et al., [8] where a diamond electrode was shown to successfully function and remain intact in a molten salt environment. The deposition process consisted of a nucleation step of applying a negative bias with respect to the substrate was used to create nucleation sites for the resulting diamond film. The deposition of the final diamond film was performed for 5 hours with no bias applied. The existence of diamond was confirmed via Raman spectroscopy where the characteristic diamond peak at 1332 cm^{-1} was easily observed. There were no observable G-band or D-band peaks present in the Raman spectrum lending to higher purity of the diamond film. The resistivity of the diamond film was measured to be $\sim 10^6\ \Omega\text{ cm}$, which could be made highly conductive upon ion beam implantation of boron and is the current intended path forward in future work. The quality and morphology of the diamond film was observed using SEM images at various locations on the surface of film.

Declarations

Author contribution statement

Eric Moore: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Joshua Jarrell: Contributed reagents, materials, analysis tools or data.

Lei Cao: Conceived and designed the experiments; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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