# Diamond-SiC heterojunctions – the influence of methane ratio on the electrical behavior of CVD diamond

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## Abstract

***Due to the properties of wide band gap materials, diamond / SiC heterojunctions are well-suited for high power / high temperature applications. Such devices can be fabricated by depositing p-type boron-doped diamond (BDD) films on n-type SiC substrates using hot filament chemical vapour deposition (HFCVD). The behaviour of the heterojunction depends on the properties of the diamond films and, as such, the fabrication of efficient devices requires previous knowledge of the impact the deposition conditions (such as gas concentration, substrate temperature and pressure). have on the morphology and electrical properties of the diamond film. Characteristics such as crystallite orientation and size, for instance, determine the concentration of boron doping which in turn affects the resistivity of the films (which lowers as the boron concentration increases). In order to calibrate the HFCVD system used in this work, diamond films were deposited using different experimental conditions; the films were characterised for morphological differences and differences in quality using SEM imaging and Raman spectroscopy. The effect of these parameters on the resistivity of the films was also studied.***

## Introduction

SiC is a material suitable for the development of optimal solutions for the high power requirements of modern electronics [1-4], providing highly efficient energy conversion at high powers, outside the current realm of technology. The extremely high thermal conductivity and breakdown field of diamond make it a good choice for applications where the thermal management is crucial for stable device operation.

Diamond films produced by CVD have been under investigation for high power and high temperature applications since 2004 [5]. The versatility of the CVD process allows for the fabrication of high quality diamond films (high $sp^3/sp^2$ ratio) on a wide variety of substrates [6]. The process usually involves the pre-treatment of the substrate in order to promote diamond nucleation; different methods, such as ultrasonic seeding or the novel nucleation procedure (NNP) [7], used in this work, can be used for this purpose. Using CVD, diamond films can also be doped with boron, for example, resulting in highly conducting films.

Semiconductor heterojunction interfaces, such as the one formed between doped diamond and SiC, exhibit useful electronic properties associated with the discontinuities in the local band structure at the interface. Some highly-rectifying NCD/SiC hetero-junctions have been demonstrated with high forward current densities and on/off current ratios. [8].

The properties of CVD diamond films have a direct impact in the electrical characteristics of the heterojunctions. It is known that growth parameters such as gas pressure, concentration of argon, $CH_4/H_2$ ratio and substrate temperature affect the diamond growth rate, as well as the quality and characteristics of the film itself [9-11]. High thermal energy during the growth process favours the growth of diamond grains [12]. The ratio of CH /$H_2$ is known to affect the crystallite size, determining whether a film is microcrystalline diamond (MCD) or nanocrystalline diamond (NCD) [13, 14]. Along with the crystal size, the orientation of the crystalline planes determines the efficiency of boron doping, and hence the electrical properties of the deposited film.

In the present work, BDD films were deposited on SiC substrates using HFCVD and differing experimental parameters. The characteristics evaluated using SEM, Raman spectroscopy and resistivity measurements.

## Experimental

For this study p-type BDD films were deposited on n-type 4H-SiC substrates using HFCVD. The SiC wafers underwent standard RCA cleaning (i.e., SC1-organic clean and SC2-ionic clean) prior to the CVD process. Post cleaning, the samples were introduced into the HFCVD chamber and underwent pre-treatment (PT) under diamond growth conditions. After PT, samples were "seeded" using an aqueous slurry of detonation diamond nanoparticles (DND) in ethanol, in an ultrasonic bath, for 60 minutes. These two steps constitute the aforementioned NNP. Finally the samples were introduced into the HFCVD chamber under doped diamond growth conditions. The filament temperature was kept in the interval 2100–2200°C for a total power of ~1000 W, a constant hydrogen flow of 128 sccm and different $CH_4$ flows. The doping source was a solution of boron oxide ($B_2O_3$), diluted in ethanol, with a B/C ratio of 10,000 ppm. The solution was placed inside a bubbler and dragged into the deposition chamber using a constant 6 sccm argon flow. The duration of the deposition was 3 hours. The deposition conditions are listed in Table 1.

| Film | $CH_4/H_2$ (%) | Pressure (kPa) | Ts (°C) |
|---|---|---|---|
| **MCD1** | 1.6 | 2.5 | 850 |
| **MCD2** | 1.6 | 15 | 850 |
| **NCD1** | 3.2 | 2.5 | 750 |
| **NCD2** | 4.8 | 2.5 | 750 |
| **NCD3** | 6.4 | 2.5 | 750 |

**Table 1.** Growth parameters of HFCVD deposition

Samples were then assessed under SEM (Hitachi SU70) and Raman spectroscopy (spectra were excited with an Ar+ laser, 514.5 nm).

## Results and discussion

Figure 1 shows the typical surface morphologies of the BDD films obtained in this work for the different deposition conditions given in Table 1. According to their observable microstructure, they can be organized in two distinct groups: one composed of samples MCD1 and MCD2 with surfaces showing well-faceted microcrystalline grains in the 0.1–1 μm range; and the second that comprises the other three samples (NCD1 to NCD3) with diamond grains in the nanometer size range (< 100 nm), and the typical 'cauliflower' morphology of nanocrystalline diamond. All the samples analyzed by Raman spectroscopy showed the characteristic diamond peak at 1332-1334 $cm^{-1}$ (results not shown). The D and G bands were observed around 1350 and 1550 $cm^{-1}$, respectively [15].

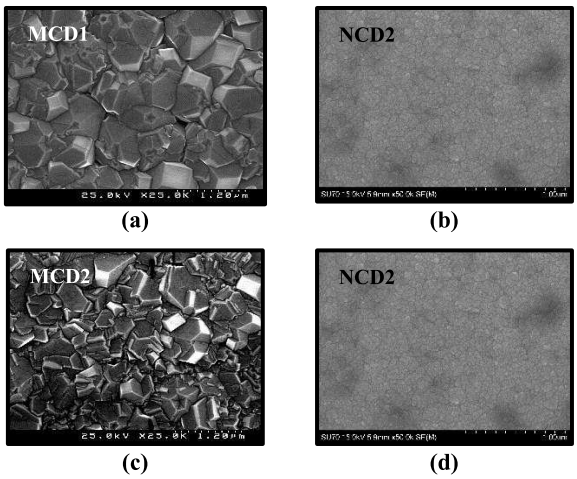


**Figure 1.** SEM of the surface of the diamond films obtained at various $CH_4/H_2$ ratios: (a) 1.6%, MCD1 and (b) MCD2; (c) 3.2%, NCD1 and (d)4.8%, NCD2

It is noted that with an increase in gas pressure from 2.5 kPa (MCD1) to 15 kPa (MCD2), there was a decrease in the grain size, which is an observation that contradicts most of the already published results for similar undoped and boron doped CVD films [16]. However, it must be noted that in these cases, Ar was not used as a B-carrier and hence did not affect the plasma composition during the deposition process.
The electrical resistivity (ρ) values are presented in Table 2.

| Film | Resistivity Ω.cm |
|---|---|
| **MCD1** | 0.8 |
| **MCD2** | 19.4 |
| **NCD1** | 1015 |
| **NCD2** | > 1M |
| **NCD3** | > 1M |

**Table 2.** Measured resistivity values of BDD films

MCD1, MCD2 and NCD1 coatings are semiconducting while the other NCD films are insulating. Nevertheless, comparing the resistivity value of NCD1 with MCD1 and MCD2, we can see that the boron doping efficiency drops considerably when the $CH_4/H_2$ ratio is increased from 0.016 to 0.032.
According to theoretical calculations, boron is preferably incorporated at the crystallites' surface and at the grain boundaries rather than in the bulk diamond electrically active sites [17]. This means that with decreasing grain size there is a tendency of decreasing boron doping efficiency. In our case, this behaviour can be observed in the heavily doped MCD1, MCD2 and NCD1 films, which presented with larger crystals when compared to the NCD2 and NCD3. In the last two films, the incorporation efficiency of boron in electrically active sites was much lower (since the resistivity was above the measurable limit value of the equipment used ($R > 1M\Omega$).
Since the amount of boron introduced into the chamber was the same for all depositions, the reported differences in resistivity are most likely related to variations of the chemical environment composition as a direct consequence of the increased $CH_4$ flow and the consequent lower relative hydrogen concentration.

## Conclusions

P-type BDD was deposited on n-type 4H-SiC substrates using HFCVD and the films' characteristics observed for differences with variation in experimental parameters of the HFCVD process. The characteristics of the film (such as crystallite size and density of grain boundaries) were seen to affect the boron doping efficiency during the CVD process and thus the values of electrical resistivity of the resulting films.

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