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SCIENCE DIRECT
Diamond & Related Materials 14 (2005) 137–143
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

# BEN-HFCVD diamond nucleation on Si(111) investigated by HRTEM and nanodiffraction

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Received 18 September 2003; received in revised form 14 September 2004; accepted 29 September 2004
Available online 5 November 2004

**Abstract**

The initial stages of diamond formation on firstly thinned Si(111) samples have been studied in a hot filament CVD (HFCVD) reactor by means of bright-field imaging and nanodiffraction experiments. Diamond crystals not resolved in high-resolution imaging are detectable using nanodiffraction. Nucleation mechanisms taking place during an HFCVD growth preceded or not by a bias treatment have been compared. The HRTEM observations strengthen previous reports concerning the smallest size of observable diamond islands. Finally, the bias effects on the surface morphology, on the nucleation density of diamond and on the orientation of diamond crystals versus the substrate are discussed. After bias, a matching between five {220} diamond and four {220} β-SiC planes in the [2–20] direction has been proposed. The former relationship is compared with previous studies of the diamond/β-SiC interface.


*Keywords:* Bias-enhanced nucleation; Diamond; Silicon; HRTEM; β-SiC

## 1. Introduction

The two main barriers to obtaining heteroepitaxial diamond films on Si substrates are the large lattice mismatch and the higher surface energy of diamond. Among the experimental attempts to overcome these obstacles, the bias-enhanced nucleation (BEN) pretreatment, first suggested by Yugo [1], remains the most powerful way to grow highly oriented diamond films on silicon [2]. Although better heteroepitaxial diamond films have been attained on β-SiC [3], on Ir [4] and on Pt substrates [5], silicon is the best candidate for electronic applications due to its wide use in microelectronics. The hot filament CVD (HFCVD) technique presents advantages like low cost and ease of scale-up. Nevertheless, only a few studies dealing with the bias treatment in HFCVD reactors are available [6–12]. Indeed, the presence of the filaments complicates the achievement of the biasing stage. Different systems have been suggested to enhance the uniformity and the stability of the plasma [13–15]. A recent work shows the possibility of growing a diamond film on a 4″ silicon wafer [11]. Unfortunately, the characterization of the film orientation has not been reported.

In a previous work, we showed the formation of β-SiC nanocrystals in the first stages of HFCVD synthesis on thinned Si(111) areas without any pretreatment, such as biasing or seeding [16]. The preferential structural relationship between β-SiC and silicon was β-SiC {220}//Si {220}. We also reported the existence of two pathways for nucleation under the same HFCVD conditions: The first involves a β-SiC interlayer, while the second arises directly

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doi:10.1016/j.diamond.2004.09.015

from the silicon substrate according to cross-section observations [17].

The present work reports nanodiffraction experiments performed on silicon carbide nanocrystals. The combination of nanodiffraction with high-resolution imaging is a powerful method to investigate the nucleation mechanisms. The early stages for HFCVD preceded or not by a BEN stage are compared. The size of the smallest observable diamond particle, as well as its stability, is also discussed. Finally, the BEN-HFCVD effects on the substrate surface and on diamond nucleation are compared with the literature.

## 2. Experimental

Samples were cut from P-doped Si(111) wafers with a resistivity of 1–3 Ω cm. The plan-view geometry allows the determination of the azimuthal misorientation between diamond crystals and silicon carbide. Si discs with a diameter of 3 mm were polished, ground and milled to perforation [18,19]. The ion milling was performed at liquid nitrogen temperature to limit the sample amorphization. After rinsing in acetone and ethanol, the samples were introduced into the UHV chamber. A cleaning procedure combining heating at 1123 K and flashes up to 1573 K [18] led to Si(111) monocrystalline areas close to the middle hole [12]. Samples were further transferred in an HFCVD reactor connected to the UHV chamber, where a $CH_4/H_2$ mixture is activated by tungsten hot filaments. This setup is equipped with a double biasing system, which enhances the plasma stability [15]. A more detailed description of this equipment is given in Ref. [12]. A negative bias voltage $V_P$ is applied between an anode grid located above the upper filaments and a cathode grid placed between the two pairs of filaments. Positive ions are then accelerated by an extraction voltage $V_e$ produced between the cathode and the sample. The sample current $I_S$ was measured through the thermocouple contact. An insulating MACOR substrate holder is used to concentrate the electrical field lines above the sample to provide a homogeneous deposition. A first set of samples underwent HFCVD syntheses, including a prior UHV cleaning procedure and a CVD growth. Successive syntheses were carried out on the monocrystalline thinned areas corresponding to cumulative deposition times of 7 and 15 min. The HFCVD parameters are listed in the Table 1. The second set of samples was prepared following three processing steps: a cleaning under pure hydrogen, a BEN step and a CVD growth (Table 1). HRTEM studies have been carried out using a TOPCON 002B microscope operating at 200 keV with a point-to-point resolution of 0.18 nm.

Table 1
CVD experimental conditions for syntheses preceded or not by a BEN step

| CVD parameters | First set | Second set | | |
|---|---|---|---|---|
| | Growth | Etching | BEN | Growth |
| $CH_4$ in $H_2$ (%) | 0.5 | – | 4 | 1 |
| Total pressure (mbar) | 30 | 15 | 15 | 30 |
| Filament activation power (W) | 185 | 155 | 155 | 185 |
| Substrate temperature (°K) | 1073 | 973 | 973 | 1123 |
| Bias voltage $V_P$ (V) | – | 120 | 170 | – |
| Extraction voltage $V_e$ (V) | – | 20 | 15 | – |
| Sample current $I_S$ (mA) | – | 0.08 | 0.2 | – |
| Time (min) | 7+8 | 2 | 15 | 5 or 15 |

Table 2
Standard $d$-spacing values for silicon, β-SiC and diamond planes

| Si | | β-SiC | | Diamond | |
|---|---|---|---|---|---|
| $d_{hkl}$ (nm) | {hkl} | $d_{hkl}$ (nm) | {hkl} | $d_{hkl}$ (nm) | {hkl} |
| 0.385 | {100} | 0.252 | {111} | 0.206 | {111} |
| 0.313 | {111} | 0.154 | {220} | 0.126 | {220} |
| 0.192 | {220} | 0.131 | {311} | | |
| 0.110 | {422} | | | | |

Complementary results obtained from the nanodiffraction pattern and the high-resolution image enabled the structural characterization of diamond nanocrystals. For nanodiffraction, a diaphragm with a 14-nm diameter was used. In the plan-view configuration, this led to multiple contributions in the diffraction pattern coming from several crystalline stacked lattices. To clarify the analysis of the diffraction pattern, the standard $d$-spacing values for silicon, β-SiC and diamond planes are listed in Table 2. Since beam alignment is critical during nanodiffraction, slight misorientations with respect to the zone axis are sometimes underlined on the patterns. High-resolution imaging is obviously extremely sensitive to the sample thickness, which must be lower than 100 nm. In the plan-view geometry, Moiré patterns are observed in the bright-field images.

## 3. Results

### 3.1. HFCVD deposition without BEN

Among 30 particles analysed in nanodiffraction, diamond reflections were observed for one half. The case we will discuss is singular for its orientation relationship with the carbide. At least, three different orientations have been determined for the other diamond particles [19]. This evidences the multiple orientation of diamond crystals without BEN.

Prior to CVD, the SAD pattern shows the expected sixfold symmetry of the (111) silicon plane [12]. After 7 min of HFCVD synthesis, the formation of silicon carbide crystals with a preferential structural relationship β-SiC {220}//Si {220} was reported [12,16]. After a second HFCVD deposit of 8 min, corresponding to a total deposition time of 15 min, no significant change could be distinguished on the SAD pattern. Nanodiffraction experiments have been performed on several locations to investigate the crystallographic relationship between the nanoparticles and the substrate. Fig. 1a displays the bright-