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Selective growth of p-doped SiC on diamond substrate by vapor–liquid–solid mechanism from Al–Si liquid phase☆

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ABSTRACT

This works deals with the localized growth of SiC on monocrystalline (100) diamond surface. It describes an attempt of selective epitaxy using vapor–liquid–solid (VLS) transport. Patterns of Al–Si stacking were melted and fed by propane. Morphology, structure and doping type of the SiC deposit were evaluated. The deposit was found to be successfully selective but polycrystalline, with the 3C-SiC polytype. Study of the initial step of growth showed that SiC nucleation occurs without any propane addition but just through the interaction of liquid Al–Si and diamond via a dissolution/precipitation process. The VLS transport mainly assists the growth of these nuclei by providing a secondary carbon source. This explains the random nucleation and the polycrystalline growth. Despite this, the deposit was dense enough to perform some preliminary electrical measurements which show encouraging results.

1. Introduction

The market of power electronic devices continues to expand and there is a great interest for the study of wide bandgap semiconductor heterojunctions. Diamond can be seen as the ultimate semiconductor when considering its outstanding properties but its development is hindered by many technological issues. Among them, fabricating good electrical contacts to diamond, with low resistance, good adherence and high reliability, is very difficult. Metallic contacts are usually studied but the best solution is still to be found. Varied types of electric contacts were studied: Al/Si [1,2], Au/Ta [3] or Mo [4]. In some studies the resistance of the ohmic contacts did not reach low values because of oxidation of the metals. In this work, we propose to use for this contact a highly doped semiconductor instead, namely SiC. The experience accumulated by the authors on the Al-doped 4H-SiC homoepitaxial growth by vapor–liquid–solid (VLS) transport could be transposed to diamond substrate, and more especially VLS induced selective deposition (VLS-SD) which is more suited for contact formation [5,6]. Direct SiC epitaxial growth on diamond was hardly studied probably due to the difficulties related to this heterosystem. Usually, the reverse is performed, i.e. diamond growth on 3C-SiC because this material was used as seed, either as a thick (few micrometers [7]) or thin (few nanometers [8]) interlayer with the Si substrate. The closest work to the present study was performed by Unifantowicz et al. who investigated the reaction between diamond crystals (150 μm average diameter) and silicon powder under microwave heating up to 1700 °C [9]. The formation of micrometric silicon carbide crystals was observed, with a growth mode depending on the crystalline orientation of the diamond facets. However, if one wants to study the SiC/diamond heterojunction, another approach should be used. Furthermore, for ohmic contact to diamond, high p-type doped SiC such as the one obtained by VLS transport is a promising solution.

2. Material and methods

In the present study, VLS-SD of SiC was carried out on monocrystalline CVD diamond (100) substrates (3×3 mm^2) from the Element Six Company. No specific surface treatment was done on the diamond seeds except cleaning (H_2O_2–H_2SO_4, BOE, acetone, ethanol). After that, Si (1.1 μm) and Al (1.5 μm) layers deposition was made using sputtering and these layers were patterned using photolithographic process in order to form different kinds of shape and size of patterns: micrometric squares and circles from few tens to several hundreds of micrometers. The samples were then introduced inside the RF heated vertical cold wall reactor working at atmospheric pressure for VLS growth. After reactor evacuation, samples are heated under H_2 (10 slm) and propane flows up to the temperature plateau of 1100 °C for the growth. The

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Table 1
Summary of the growth conditions studied in this work.

Sample	Propane flow (sccm)	Temperature (°C)	Plateau duration (min)	Average deposit thickness (μm)
1	1	1100	10	2
2	0.5	1100	10	2
3	1	1100	0	1.1[a]
4	0	1100	0	1.1[a]
5	0	1100	5	1.3
6	1	1100	5	1.7

[a] Deposit constituted of single grains.

standard procedure involves propane introduction during the heating ramp since it was found beneficial for avoiding liquid dewetting [6]. The sample growth conditions studied in this work are summarized in Table 1. Some experiments carried out at higher temperature (1200 °C and 1300 °C) showed that evaporation of the alloy was significant and led to unwanted deposit outside the initial patterns. We thus limited the working temperature to 1100 °C. To study the influence of the propane flow during the plateau duration, two samples (1 and 2) have been performed at the C_3H_8 flows of 1 and 0.5 sccm. To investigate the first steps of the growth and to isolate what is happening during the heating ramp alone, samples 3 and 4 were done without plateau duration, with (1 sccm) or without C_3H_8 addition. At last, a reduction of the plateau duration from 10 to 5 min was done for samples 5 and 6 without and with C_3H_8 introduction to characterize the evolution of the growth during the plateau. After the growth, the unreacted alloy, which remains on top of the grown material, was wet etched using HF-HNO_3-HCl followed by hot NaOH.

The samples were then characterized by X-ray diffraction and Raman spectroscopy for phase and doping identification. Elemental information was obtained from energy-dispersive X-ray (EDX) spectroscopy performed in an FEI Quanta 250 FEG microscope. Deposit thickness was measured using a mechanical profiler. The morphology of the deposit obtained here being rough, the values noted in Table 1 correspond to average thickness, although grown features may locally be significantly thicker. This average thickness is mainly used to compare samples grown in different conditions, because it does not give an accurate value of the amount of grown material due to the morphology of the deposit.

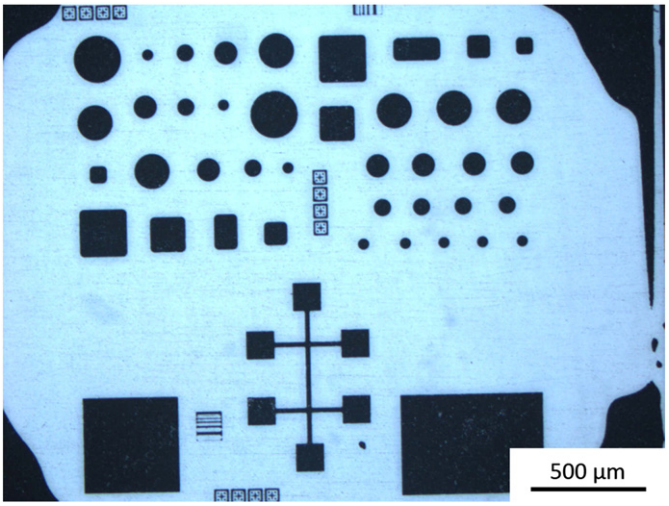

Fig. 1. Optical microscopy picture after VLS-SD growth on diamond (sample 6); the deposit on the edges of the sample is due to undesired Si/Al stackings remaining after the photolithographic process which was not well adapted for such small samples.

3. Results and discussion

Fig. 1 shows optical microscopy picture of a typical sample grown by VLS-SD at 1100 °C. First of all, it is obvious that some deposit was formed which is selectively grown in the areas delimited by the Al–Si patterns. Second, it shows that the shape of the patterns did not change after VLS growth. There is no liquid movement. When zooming inside one of these patterns (Fig. 2), one can see the presence of facetted grains agglomerates with typical size of ~2–3 μm. This morphology was found to be identical for all the samples of this study. One can also see from Fig. 2a that the limit of the deposited areas is sharp which means that the deposition is highly selective.

Using X-ray diffraction, the deposit is identified as 3C-SiC, polytype which was expected according to the cubic symmetry of diamond. However, no particular crystalline relationship with the (100) orientation of the substrate was detected (Fig. 3). Using Raman spectroscopy, the deposit could be also indentified as SiC, with the Fano interference located on each side of the TO mode at 796 cm^{-1} (Fig. 4). Although Raman

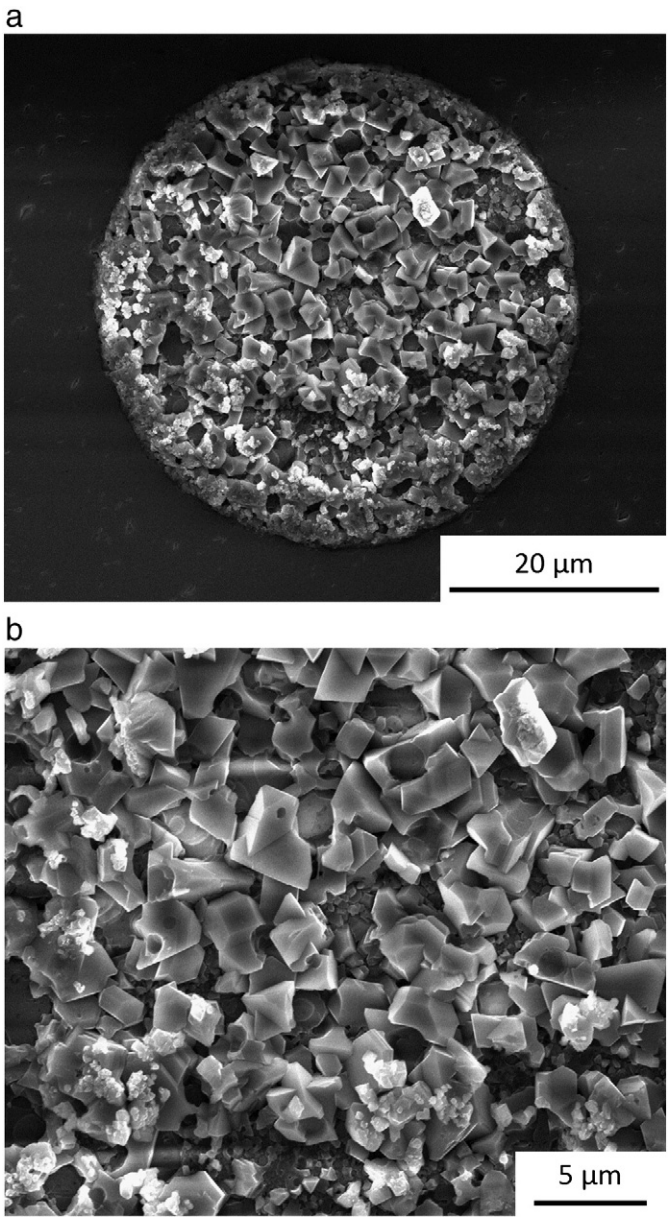

Fig. 2. SEM pictures of the sample 6 showing (a) a general view of a circular pattern and (b) a close up at the center of this pattern for illustration of the deposit microstructure.