

Heteroepitaxial growth of SiC films by carbonization of polyimide Langmuir-Blodgett films on Si

S.I. Goloudina^{1,*}, V.V. Luchinin¹, V.M. Pasyuta¹, M.F. Panov¹, A.N. Smirnov², D.A. Kirilenko², T.F. Semenova³, V.P. Sklizkova⁴, I.V. Gofman⁴, V.M. Svetlychnyi⁴ and V.V. Kudryavtsev⁴

¹ St. Petersburg State Electrotechnical University, 197376, 5 Prof. Popov st., St. Petersburg, Russia

² Ioffe Institute, RAS, 194021, 26 Politekhnicheskaya, St Petersburg, Russia

³ St. Petersburg State University, 199034, 7-9 Universitetskaya nab., St. Petersburg, Russia

⁴ Institute of Macromolecular Compounds, 199004, 31 RAS, Bol'shoy pr., St.Petersburg, Russia

Abstract. High quality single crystal SiC films were prepared by carbonization of polyimide Langmuir-Blodgett films on Si substrate. The films formed after annealing of the polyimide films at 1000°C, 1100°C, 1200°C were studied by Fourier transform-infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), transmission electron diffraction (TED), and scanning electron microscopy (SEM). XRD study and HRTEM cross-section revealed that the crystalline SiC film begins to grow on Si (111) substrate at 1000°C. According to the HRTEM cross-section image five planes in 3C-SiC (111) film are aligned with four Si(111) planes at the SiC/Si interface. It was shown the SiC films (35 nm) grown on Si(111) at 1200°C have mainly cubic 3C-SiC structure with a little presence of hexagonal polytypes. Only 3C-SiC films (30 nm) were formed on Si (100) substrate at the same temperature. It was shown the SiC films (30-35 nm) are able to cover the voids in Si substrate with size up to 10 µm.

Introduction

Among various semiconductor materials, silicon carbide (SiC) is an attractive material for high power, high frequency and high temperature microelectronics, owing in part to its wide band gap, high thermal conductivity, high break down field and high saturation velocity. Compared with Si or GaAs, it is chemically inert, extremely hard, radiation-resistant, and highly wear-resistant making it possible to fabricate microsensors and microactuators for harsh environments such as high temperature, aggressive media, and radiation-exposed environments. Additionally, SiC is inert to most chemicals at room temperature and has been found to be biocompatible with inert to bacterial growth, transparent to visible light, and show UV wavelength absorption. Furthermore, owing to its large ratio of Young's modulus to density, SiC has also attractive interest for use in ultra-high-frequency nanoelectromechanical system (NEMS) for wire-less signal-processing systems. However, this material has not been widely used because of the difficulties in growing high quality crystals and etching the material to form required pattern.

The motivation for the heteroepitaxial growth of SiC-on-Si has been to provide relatively inexpensive and large-area substrates of SiC for electronic devices and microelectromechanical system. Due to its large energy band and other promising semiconductor properties, 3C-SiC has potential for high performance as a wide band-gap emitter to the SiC/Si heterojunction bipolar transistor. Also SiC film on Si can be used as a buffer layer for the subsequent heteroepitaxial growth of gallium nitride and other group III-nitrides, which has application in blue and violet light-emitting diodes and lasers. However, the growth of SiC films on Si is one of the most difficult challenges of heteroepitaxy due to the large mismatches in lattice constant (20%) between SiC and Si, and the difference in the thermal expansion coefficient of SiC ($4.6 \times 10^{-6}/^{\circ}\text{C}$) and Si ($4.2 \times 10^{-6}/^{\circ}\text{C}$). The usual techniques to grow SiC-on-Si are chemical vapor deposition (CVD), laser sputtering, molecular beam epitaxy, and carbonization of a polyimide Langmuir-Blodgett (LB) film on silicon substrate. Currently, the high quality crystalline SiC films on Si can be fabricated by CVD method [1, 2], thickness of such films is often more than several microns. If the films thickness is less than one

* Corresponding author: goloudina@mail.ru

micron, it usually contains a large number of defects [3, 4].

The aim of this work was to prepare SiC films on Si by carbonization of rigid-rod polyimide (BPDA-oTD) LB films and studying their structure and morphology.

Materials and Methods

As polyimide prepolymer, we used polyamic acid alkylammonium salt (PAAS) synthesized on the basis of 3,3',4,4'-diphenyltetracarboxylic acid dianhydride and o-tolidine with tert-amine o,o',o''-trihexadecanoyltriethanolamine. The PAAS forms well-ordered and stable monolayers at the air-water interface. The PAAS monolayers were deposited on the silicon support at the surface pressure 30 mN/m. Y-type of deposition was observed. The transfer rate was 0.5 cm/min. [5].

PAAS LB films of 81, 121, 141 layers were deposited on Si(111) and Si(100) substrates. The polyimide (PI) films were then formed by thermal imidization of PAAS LB films (figure 1). The PI films had thickness of 47, 54 and 86 nm, respectively.

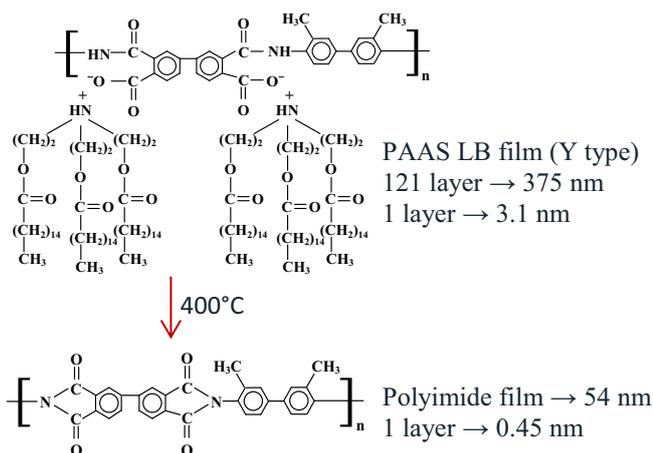


Fig. 1. The scheme of obtaining polyimide film.

For forming SiC the PI films on Si were annealed by two steps. Firstly the samples were heated to the temperature of 1000°C with the velocity of 10 degrees/min. and kept at this temperature during 1 h. After cooling down the samples were studied and then the films were heated again by the quick thermal heat annealing during 3 min. at the temperatures of 1100°C or 1200°C. The annealing was carried out in a vacuum (10^{-5} mm. of m.c.). The films formed after annealing were studied by Fourier transform-infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM), transmission electron diffraction (TED), and scanning electron microscopy (SEM).

The transmission spectrums of SiC films were obtained by using a Nicolet 6700 FT-IR Spectrometer. Raman spectra were acquired by using a Horiba Jobin Yvon T64000 micro-Raman system with a confocal microscope. The samples were excited by a continuous wave diode pumped Nd:YAG ($\lambda_{ex}=532$ nm) laser. Raman

spectra were measured at room temperature, with the spot size on the sample of about 1 μ m. The excitation power was limited to 1 mW to avoid sample heating. A standard Si(111) wafer was used for calibration of the micro-Raman system. X-ray investigations were carried out on a diffractometer with a Rigaku Ultima IV (CuK α radiation). TEM studies were performed by using a Jeol JEM-2100F transmission electron microscope (accelerating voltage 200 kV, point-to-point resolution 0.19 nm) equipped with an energy-dispersive X-ray spectrometer Oxford Instruments INCA. High resolution images were obtained in conventional bright-field mode using objective aperture of the optimal size. Specimens for TEM were prepared by mechanical polishing with subsequent ion milling using Ar⁺ at 4 kV. The surface morphology of SiC was examined by FEI Quanta Inspect SEM.

Results and Discussion

The infrared spectrum of the films after annealing at 1000°C is shown in figure 2. This spectrum was obtained at a "reflection" regime. Only one absorption peak is seen at 796 cm⁻¹, which indicate the TO phonon of the 3C-SiC phase.

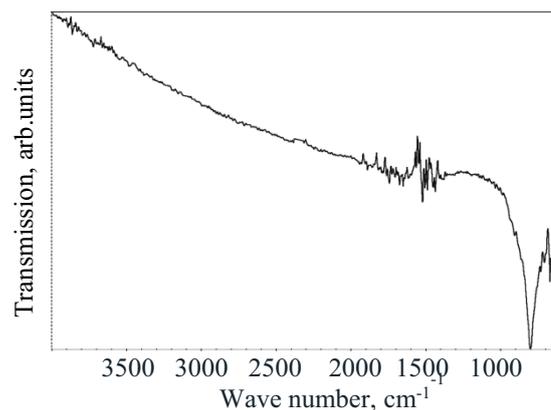


Fig. 2. FTIR spectrum of SiC films

The interesting details of SiC formation on Si were found by Raman spectroscopy. The results show that after heat treatment at 1000°C the films on Si consist mainly of amorphous carbon (figure 3 a). After annealing at 1100°C the films contain both the carbon and SiC phases (figure 3b). Mainly the SiC phase was formed at 1200°C (figure 3 c, d).

At the same time, the cross section TEM image of the film formed at 1000°C shows the presence of SiC nanocrystals on the Si surface (figure 4). Furthermore, it is clearly seen that five planes in 3C-SiC(111) structure are aligned with four Si (111) planes at the SiC/Si interface.

Formation of high quality SiC crystalline phase at 1000°C was confirmed by X-ray diffraction (figure 5). The peak 1 on the XRD spectrum corresponds to 3C-SiC(111) structure or H-SiC (table 1). The FWHM of this peak is 0.060° which indicates the single crystal SiC phase formation on Si [1].

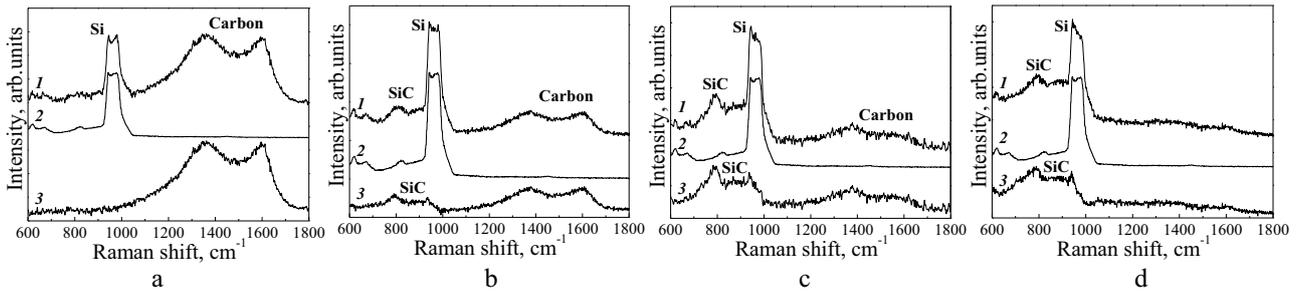


Fig. 3. Raman spectra of films formed on Si substrate at various temperature: Si(111) - 1000°C (a), 1100°C (b), 1200°C (c); Si(100) - 1200°C (d): 1 – SiC/Si, 2 – Si, 3 – difference spectrum (the spectrum 1 – the spectrum 2).

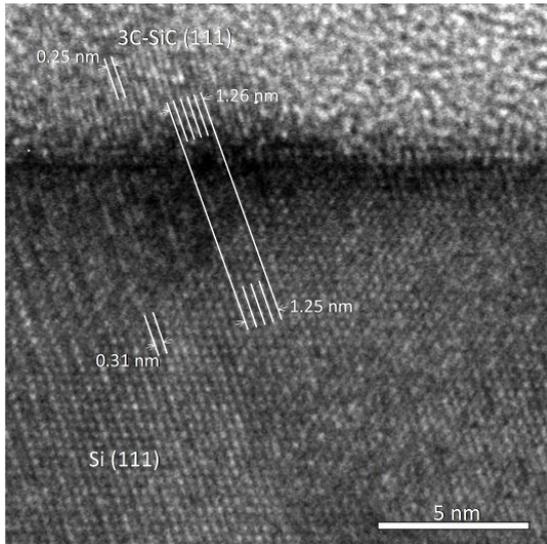


Fig. 4. Cross section TEM image of a SiC nuclei on a Si surface.

Figure 6 shows cross section images and TED of SiC films formed on Si at 1200°C. For preparing these films, PI films containing 121 layers were used. As can be seen in figure 6, the thickness of the SiC film is 35 nm on Si(111), and 30 nm on Si(100).

The SiC film grown on Si(111) has a 3C-SiC structure with a small presence of a hexagonal phase. Only 3C-SiC films were formed on Si(100) substrate. It was shown that the SiC film on Si(100) consist of two layers. The

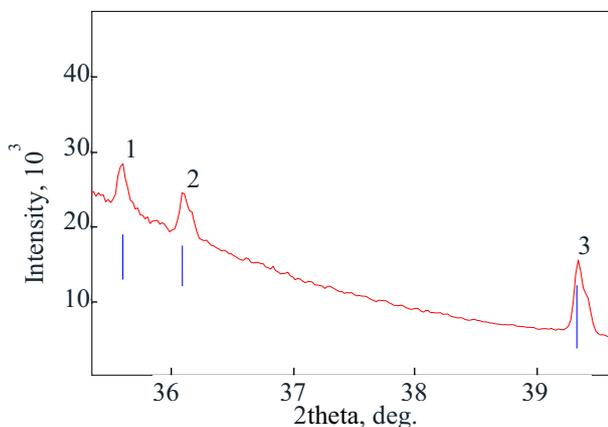


Fig. 5. XRD spectrum of the films after annealing at 1000°C.

Table 1. The characteristics of XRD spectrum.

N	2theta (deg.)	d (ang.)	FWHM (deg.)	Phase name
1	35.619	2.518	0.060	3C-SiC or H-SiC
2	36.100	2.486	0.080	8H-SiC
3	39.308	2.290	0.080	unknown

lower layer (10 nm) has crystalline structure and the upper layer (20 nm) is polycrystalline.

The surface morphology of SiC films was examined by SEM. Figure 7 (a, b) shows the presence of faced voids at the SiC/Si interface. Most of the voids are closed by SiC film. It was observed that the shape of voids depends on the symmetry of the substrate surface. The facets of voids are parallel to the lowest surface energy faces, i.e. {111} planes (figure 8). Thus, it is approximately square in shape on Si (100) and triangular on Si (111) substrates. The formation of the voids at the SiC/Si interface is caused by the diffusion of the Si atoms from the Si substrate.

Conclusion

In the present work we demonstrate an easy strategy to produce high quality single crystal SiC films on Si through carbonization of polyimide Langmuir-Blodgett films. To the best of our knowledge, this is the first report of the growth of single crystal SiC hetero-epitaxial film on Si with thickness of about 30 nm. The SiC {111} lattice planes are well aligned with those of the Si substrate. Moreover, every fourth Si plane is aligned with every fifth plane in 3C-SiC(111) structure at the SiC/Si interface. It was shown that the SiC films (30-35 nm), obtained at 1100°C and 1200°C, are able to close the voids in Si substrate. The size of these voids can reach 10 μm.

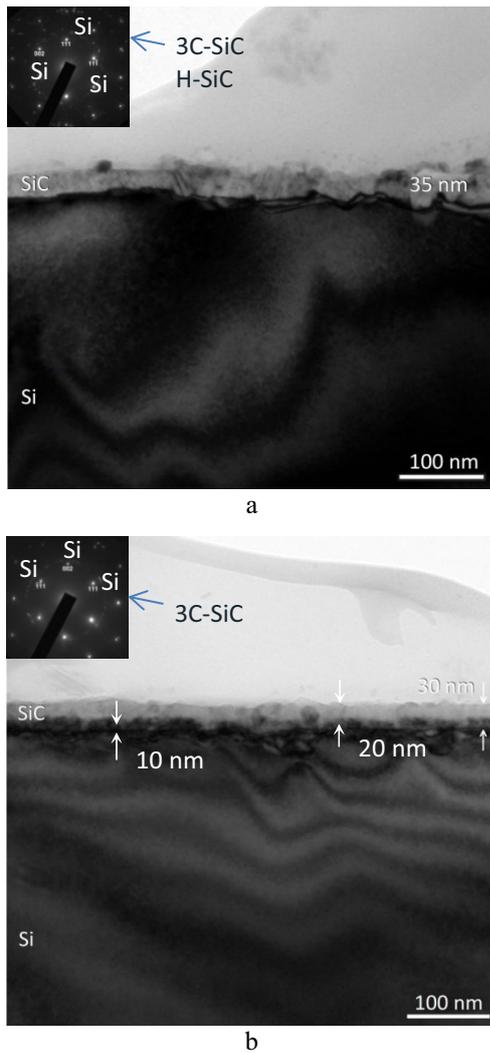


Fig. 6. Cross section images and TED of SiC films formed on Si at 1200°C: a) The SiC film (35 nm) on Si (111) substrate has a 3C-SiC structure with a small presence of a hexagonal phase; b) The SiC film on Si(100) substrate consist of two layers, the lower layer (10 nm) has 3C-SiC structure, and the upper layer (20 nm) is polycrystalline.

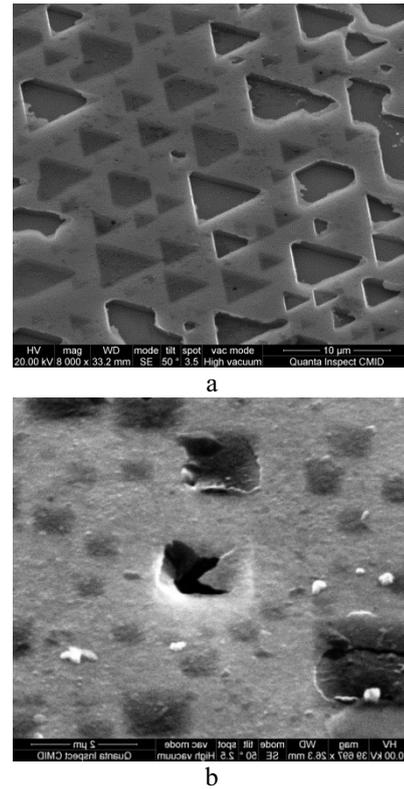


Fig. 7. SEM images of the SiC films covering the voids in Si (111) (a) and Si(100) substrates (b). The SiC films on the surface of Si substrate and the SiC films covering the voids have the different contrast. The broken SiC films are also observed.

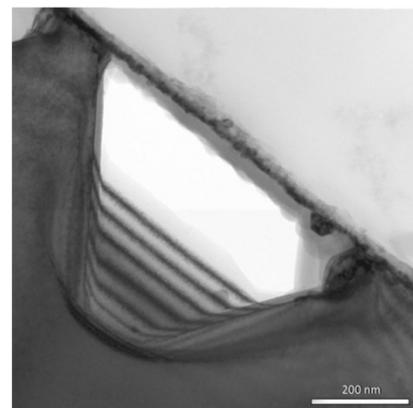


Fig. 8. Cross section TEM of SiC film with thickness 30nm, covering a pyramidal void in Si(100) substrate.

References

1. S. Madapura, A. J. Steckl, M. Loboda. Journal of Electrochemical Society. P.1197-1202. **146**(3) (1999)
2. C. Locke, R. Anzalone, A. Severino, C. Bongiorno, G. Litrico, F. La Via, S.E. Sadow. *Materials Science Forum*. P.145-148. **615-617** (2009)
3. G.-S. Chung, K.-S. Kim. Bull. Korean.Chem.Soc. P.533-537. **28**(4) (2007)
4. A. Severino, R.Anzalone, M.Camarda, N. Piluso, F. La Via. *Materials Science Forum*. V.**711**, P.27-30 (2012)
5. S. I. Goloudina, V. V. Luchinin, V. M. Pasyuta, V.V Klechkovskaya, Yu. G. Baklagina, V.V. Rozanov, M.F. Panov, V.P. Sklizkova, V.V. Kudryavtsev. *Crystallography Reports*. P 468-476. **54**(3) (2009)