ISSN 1027-4510, Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques, 2010, Vol. 4, No. 3, pp. 374–378. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © A.S. Gusev, S.M. Ryndya, N.I. Kargin, E.A. Bondarenko, 2010, published in Poverkhnost'. Rentgenovskie, Sinkhrotronnye i Neitronnye Issledovaniya, No. 5, pp. 18–22.

Low Temperature Synthesis of SiC Films by Vacuum Laser Ablation and Their Characterization

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Received August 10, 2009

Abstract—Thin films of silicon carbide were grown on Si(100) substrate by pulsed laser ablation of powder-pressed target. The influence of substrate temperature on both structure and surface morphology of SiC films was studied by scanning electron microscopy, X-ray diffraction, and IR spectroscopy.

DOI: 10.1134/S1027451010030031

INTRODUCTION

Thin silicon carbide films, due to their unique properties, have attracted considerable attention of researchers in the fields of semiconductor physics and technology of novel semiconductor devices for power, microwave, and optoelectronic applications. This is evidenced by a large number of studies on the growth of SiC based thin-film structures with a broad range of design solutions and technology parameters. Summarizing the literature data, we can conclude that, at present, one of the most common conventional methods to form thin silicon carbide films is the method of chemical vapor deposition (CVD) using mixtures of silane with hydrocarbons or various organosilicon compounds in the hydrogen flow. It allows forming good epitaxial silicon carbide layers, but the main drawback to the CVD method is a high process temperature above 1400°C [1, 2].

The increase in production of silicon carbide-based devices is stimulating a search for more economical and environmentally friendly technologies to form SiC layers. One of them could be the film growth by laser ablation in vacuum. This technology does not use chemically aggressive silicon-containing gases and allows forming thin continuous films several nanometers thick at relatively low substrate temperatures (there are indications that epitaxial growth of β-SiC was implemented at 900°C; α-SiC, at 1200°C [3, 4]). The ability to deposit all structure layers (including metalization) in a single technological vacuum cycle may be an advantage of the method. However, laser synthesis of silicon carbide structures has received little attention in our country, although the importance of such studies is determined by the prospects of developing fundamentally new devices for micro-, opto-, and nanoelectronics. It should be noted that amorphous silicon carbide films are also attractive for practical applications along with the epitaxial structures. The large energy bandgap, high thermal conductivity, high resistance to electric breakdown, and possibility of synthesis of large area layers at low temperature make amorphous nanocrystalline SiC a very promising material.

On this basis, the aim of this work was to study the physical and technology details of low-temperature synthesis of silicon carbide thin films by vacuum laser ablation and, in particular, to analyze the influence of substrate temperature on the structural properties and surface morphology of synthesized samples.

EXPERIMENTAL

Synthesis of thin film structures was carried out using an experimental processing system for pulsed laser sputtering based on a AYG:Nd^{3+} laser of LS-2138 type and a Varicoat 430 unit vacuum chamber [5]. Laser ablation was implemented using the powder target prepared by cold pressing of fine α-SiC powder in polymethylmethacrylate shell to form a tablet 40 mm in diameter followed by its annealing at 1000°C. Focused radiation of the Q-switched Nd:AYG laser ($\lambda = 532$ nm) was used for sputtering of the target material. The pump energy was 20 J; laser pulse duration, 15 ns; and repetition rate, 50 Hz. The target to substrate distance was 100 mm. The process was performed at substrate temperatures of 100–1000°C in high vacuum ($P \sim 10^{-4}$ Pa). Si(100) wafers cleaned in hydrofluoric acid solution and washed in distilled water were used as substrates.

Table 1 shows the film thickness estimated with an MII-4M microinterferometer. As follows from Table 1, in the course of the work two temperature series of samples with different synthesis time were prepared. The growth rate of films at a given temperature range hardly changed at all and was about 3.3 ± 0.1 nm/min.

The influence of deposition conditions on the dynamics of structural changes and the behavior of chemical bonds in thin films was studied by IR spec-

Table 1. Film thickness in relation to the temperature and deposition time

Temperature, °C / Time, min	100	300	500	700	850	1000
45 min	140 nm	160 nm	160 nm	140 nm	140 nm	140 nm
90 min	320 nm	300 nm	290 nm	380 nm	320 nm	300 nm

troscopy and X-ray diffraction. X-ray diffraction analysis of samples was carried out on a DRON-3M diffractometer using CuK_α radiation. The surface morphology of the experimental structures was examined by a Quanta 3D scanning electron microscope (SEM). IR spectra were recorded using an FSM-1201 infrared Fourier spectrometer. The measurements of transmission spectra were performed by means of the standard technique with a resolution of 2 cm^{-1}, an initial monocrystalline silicon wafer being used as a reference sample.

RESULTS AND DISCUSSION

Figures 1a, 1b, and 1c show typical surface images of the samples synthesized at substrate temperatures of 100, 700, and 1000°C. A characteristic feature of the surface morphology at the micro scale is the existence of quasi-spherical particles or microdroplets [6–8], the dimensions of which essentially range from 100 to 300 nm. Analysis of published data shows that the presence of such particles is typical for silicon carbide films formed by laser ablation in vacuum. The formation of microdroplets is considered likely to be due to splashes of molten layer on the target surface during its boiling and the spattering of liquid phase by pressure shock waves [8]. Whatever is the true reason for the formation of quasi-spherical particles, their content in the sample increases with increase in the substrate temperature, as is clearly illustrated in Fig. 1. In the temperature range studied, the surface concentration of particles increases from 4.5×10^6 cm^{-2} (t_{SUB} = 100°C) to 1.4×10^8 cm^{-2} (t_{SUB} = 1000°C). The values are in good agreement with the literature data. For example, the number of microdroplets per unit sample surface also increased with temperature and for a silicon carbide film synthesized at 500°C was about 10^7 cm^{-2} [8].

In contrast to low-temperature samples with nearly spherical microparticles, the particles on the surface of

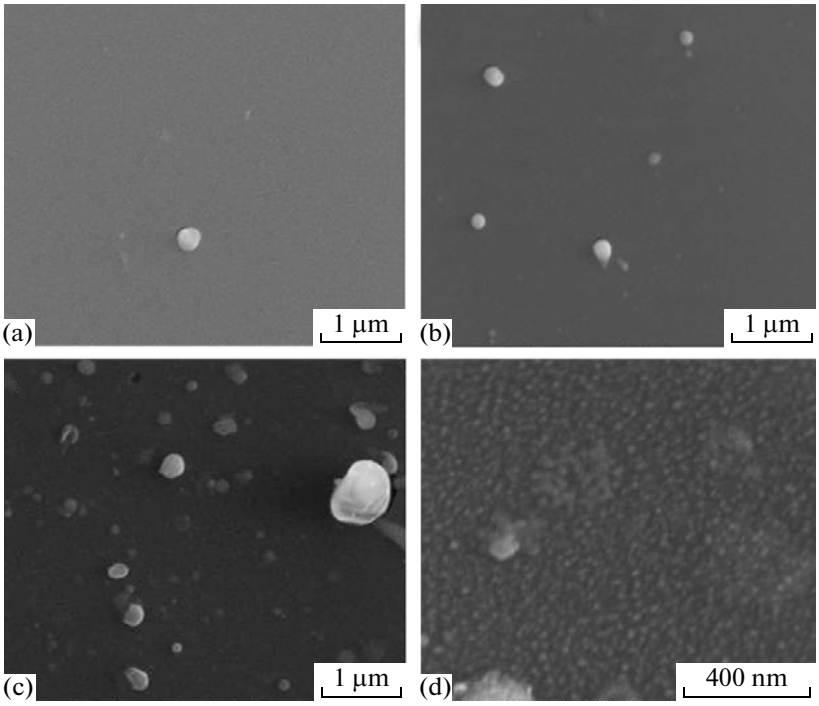

Fig. 1. SEM images of the surface of thin SiC films formed at the substrate temperature of (a) 100, (b) 700, and (c, d) 1000°C. Magnification for images (a), (b), and (c) is 50000; for image (d), 200000.

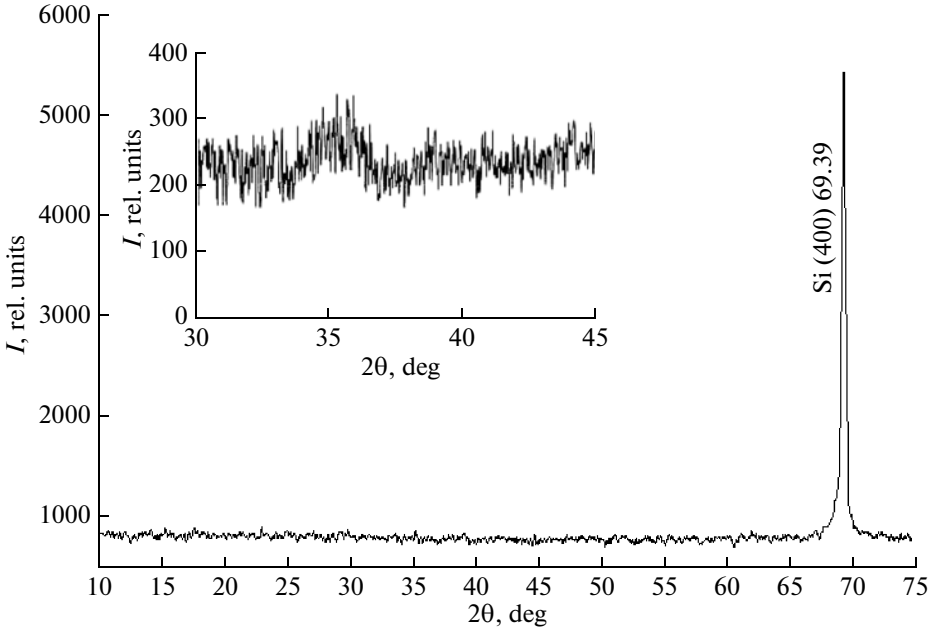

Fig. 2. Typical X-ray diffraction spectrum for samples formed at substrate temperatures of 100–850°C (diffraction peak $2\theta \approx 69°$ corresponds to the (400) reflex from the silicon substrate). Inset shows the section of the spectrum ($2\theta = 30–45°$) for the sample formed at 1000°C.

films deposited at 1000°C (Fig. 1c) have an irregular shape. Some changes in the surface morphology are also observed at the nanoscale for thin films synthesized at higher temperatures. The surface of the samples formed at temperatures of 100–850°C is smooth in microdroplet-free areas, which indicates the amorphous structure of the film. This assumption was confirmed by X-ray diffraction analysis. Reflections corresponding to silicon carbide are entirely absent in the X-ray diffraction patterns of these samples (Fig. 2). The situation changes somewhat with the increase in substrate temperature to 1000°C. Figure 1d is an SEM image of this film surface at magnification of 200000. Here there are nanoparticles like formations with sizes not exceeding 20–30 nm. It should be noted that the traces of nanocrystalline silicon carbide phase in this sample were also revealed by X-ray diffraction analysis (see the inset to Fig. 2). Here in a typical for silicon carbide range of angles $2\theta = 33–37°$ [9, 10], a weak broad band is observed, which indicates the formation of nanocrystalline SiC. The formation of SiC nanoclusters embedded in an amorphous matrix is also possible.

To assess the composition and structural features of the samples under study, their IR transmission spectra were recorded in a range close to the Si–C vibration modes (Fig. 3). IR spectra of synthesized films have an absorption region in the range 500–1200 cm^{-1} with complex structure, which is a superposition of two bands. According to the literature (Table 2), the long-wavelength absorption band with a peak at 780 cm^{-1} is due to Si–C vibrations. It is indicative of the formation of silicon carbide films. The short-wavelength band with a peak at 1000 cm^{-1} is apparently due to carbon-hydrogen bending/swing vibration modes in CH_n groups chemically bound to silicon atoms ($Si–C–H_n$) [11] and/or swing motion of CH_n groups in $Si–CH_n$ [12]. At low temperatures of the substrate this band dominates the transmission spectra for the samples synthesized for 45 min (Fig. 3a) and is comparable in intensity with the band at 780 cm^{-1} for the samples deposited for 90 min (Fig. 3b). This points to the rela-

Table 2. The main absorption bands of SiC thin films in the spectral range studied

No.	IR bands with peaks	Group	References
1	670–800 cm^{-1}	Si–C (stretching vibrations)	[11, 12, 13, 14]
2	950–1000 cm^{-1}	Bending and rocking vibrations of C–H bonds in $Si–C–H_n$ Rocking vibrations of CH_n group in $Si–CH_n$	[11] [12]
3	2080–2100 cm^{-1}	$Si–H_n$ (stretching vibrations)	[11, 13, 14]
4	2800–3100 cm^{-1}	$C–H_n$ (stretching vibrations)	[12, 13, 14]

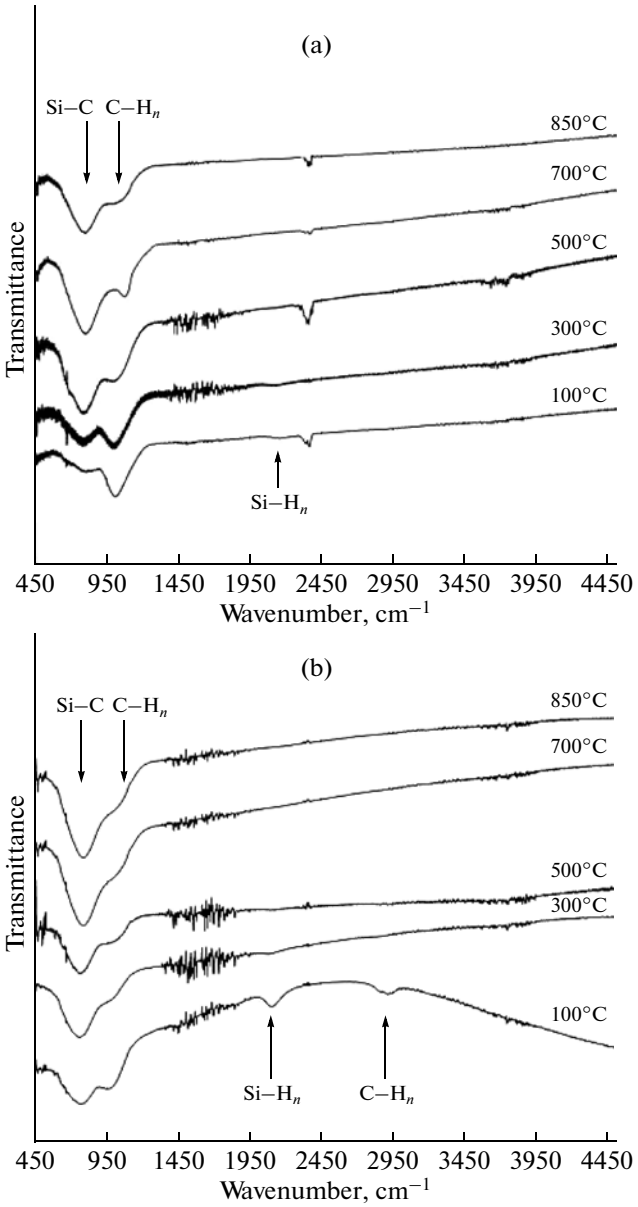

Fig. 3. IR transmission spectra for the samples deposited for (a) 45 and (b) 90 min.

tively high concentration of hydrogen bonds in the film material. In addition, the existence of hydrogen in the samples is also evidenced by the bands at 2100 and 2800 cm^{-1} caused by stretching vibrations of Si–H bonds [11, 13, 14] inC–Si–H$_n$ chains and vibrations in C–H$_n$ groups [12, 13, 14], respectively. These bands are most pronounced in the transmission spectra for thicker samples (Fig. 3b) formed at substrate temperatures below 500°C.

The existence of chemically bound hydrogen in synthesized films can be explained by the presence of water adsorbed by porous target. It is known that a small amount of hydrogen always exists in residual gases in the vacuum chamber.

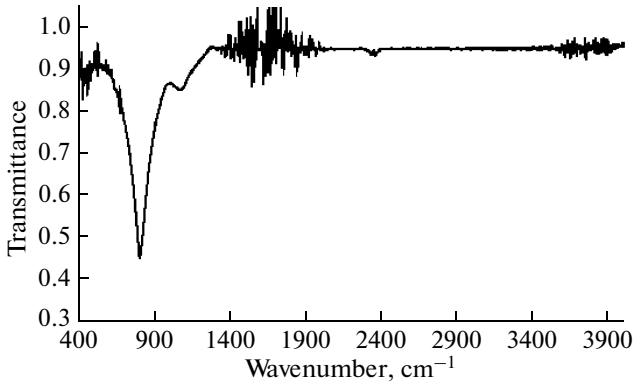

Fig. 4. A typical IR transmission spectrum for samples formed at substrate temperature of 1000°C.

With an increase in substrate temperature, the IR spectra of studied structures are significantly modified. The relative intensity of the band with a maximum around 1000 cm^{-1} decreases. In the transmission spectra of films formed at 500°C and higher, the Si–C absorption band dominates in both cases (Fig. 3a, b). Peaks in the spectral regions of 2100 and 2800 cm^{-1} are almost absent. Thus, we can suggest that with the increase in synthesis temperature there are structural changes in samples being accompanied by breaking Si–H and C–H bonds and the formation of Si–C bonds. For example, films of amorphous hydrogenated silicon carbide formed by reactive magnetron sputtering behave similarly during their vacuum annealing [11].

It should be noted that, at substrate temperatures of 850°C or lower, no decrease in the half-width of the band at 780 cm^{-1} was observed. Therefore, in this temperature range, there is no significant ordering of angles and lengths of Si–C bonds. The films are amorphous. However, the spectrum shape changes significantly even at 1000°C (Fig. 4). The half-width of the Si–C vibrations band decreases. The line has become Lorentz lineshape indicating, together with the X-ray diffraction data, the appearance of a silicon carbide crystalline phase.

CONCLUSIONS

Submicron SiC thin films were deposited on silicon wafers by vacuum laser ablation of powder target. The effect of synthesis temperature on the structural properties and surface morphology of the samples was studied. It was shown that the formation of crystalline SiC phase in the form of silicon carbide nanoclusters begins at substrate temperature of 1000°C. The first piece of evidence of this is the presence of 20- to 30-nm particles revealed by scanning electron microscopy on the sample surfaces; the second, the appearance of a weak broad band in typical silicon carbide range of angles $2\theta = 33°–37°$ in X-ray diffraction

spectra; and the third, the IR spectroscopy data. At substrate temperatures of 850°C or lower, the films are amorphous. Reflections corresponding to silicon carbide are entirely absent in the X-ray diffraction patterns of these structures.

The existence of chemically bound hydrogen in SiH- and CH-groups was identified in the samples by IR spectroscopy. The temperature dependence of transmission spectra indicates that, with an increase in synthesis temperature, there are structural changes in samples being accompanied by breaking Si–H and C–H bonds and forming Si–C bonds.

ACKNOWLEDGMENTS

This work is part of research conducted under the project "Multifunctional Homo- and Heterostructures Based on $A^{IV}B^{IV}$ and $A^{III}B^{V}$ Compounds to Develop a New Generation of Devices for Power and Microwave Electronics" on the assignment of Russian Federal Agency on Science and Innovation, state contract no. 02.513.12.3019.

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