

Investigation of SiC and C Nanostructures Obtained by MWCVD

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Article info

Received:

Received in revised form:

Accepted:

Keywords:

silicon carbide and carbon nanostructures, chemical deposition from the gas phase, microwave plasma, porous silicon, method of scanning electron microscopy, Raman scattering.

Abstract

The results of experiments on the synthesis of SiC and C nanostructures (NS) by chemical vapor deposition in microwave plasma are presented in this article. The single crystal silicon plates with orientations [100] and [111] which previously passed chemical purification were used as substrates. Also, the substrates of porous silicon (PS) were prepared in order to activate the surface during the synthesis. The synthesis temperature ranged from 700 to 900 °C in steps of 100 °C. The pressure in the chamber was changed depending on the power of the plasma. Studies by scanning electron microscopy showed that formed NS have a diameter of 200–350 nm and a rough surface. The formation of NS on the polished Si occurs on the SiC buffer layer. Analysis of SEM images of the samples shows that growth of NS on the surface of porous silicon is more widespread in contrast to the polished Si. The results of X-Ray spectral microanalysis showed that the carbon content in samples of nanostructures on polished Si varies from 10 to 20% and remains constant on porous silicon ~ 25%. The results of studies by Raman scattering (RS) confirmed that SiC film with structure of 3C-SiC is formed on the polished Si. Besides, the presence of main carbon peaks on both types of substrates in the range of 1338.2 and 1583 cm⁻¹ should be noted, which correspond to the carbon nanostructures.

1. Introduction

Nanostructures – silicon carbide nanotubes and nanofibers are promising targets for the creation of new materials. Nanostructures (NS) of silicon carbide possess a number of unique physico-mechanical and chemical properties: high mechanical strength and chemical stability, electrical conductivity that varies in wide intervals, depending on the structure of nanostructures, high emission characteristics.

Synthesis of SiC nanostructures is carried out in the presence of transition metal catalysts (Fe, Ni, Co) with additives of various promoters at a temperature in the range of 500–1500 °C [1].

One-dimensional (1D) semiconductor NS (fibers, tubes) have become the goal of intensive research, thanks to their unique applications in the production of electronic, optoelectronic and

sensor devices on a nanometer scale. Because of their potential use in nanodevices, 1D semiconductor nanomaterials were selected as one of the top 10 for technology in the Technical Review of the Massachusetts Institute of Technology in 2003 [2].

Filamentous silicon carbide crystals, as well as carbon nanotubes, have a high ratio of length to diameter (100–200 and more), the diameter of the SiC crystal can vary significantly, from 40 to 200–500 nm [3]. Filamentary form provides improved mechanical properties of whiskers [4]. In addition to the traditional use as components of ceramics and construction materials SiC whiskers are of interest for the development of new components of high-temperature electronic devices [1]. Advantages of using SiC in this area are associated with its high thermal and corrosion resistance, combined with the large value of the forbidden zone (2.4–3.3 eV, depending on the polytype of silicon carbide) [1].

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2. Experimental

2.1. Preparation of substrates

The single-crystal silicon plates of the brand KDB-20 (manufactured by Siegert Wafer GmbH, Germany) with sizes of 1×1 cm with [100] and [111] orientation were used as substrates.

The substrates of porous silicon (PS) were prepared in the Educational Laboratory of Semiconductor Instrumentation, Faculty of Physics and Technology, Kazakh National University in order to activate the surface during synthesis. Crystalline silicon was pretreated in acetone and placed in a solution of H₂SO₄:H₂O₂ for 5 min, followed by washing in deionized water. The plates were then immersed in the etch HF:H₂O for 1 min, after which they were thoroughly washed. The PS was formed by electrochemical anodizing in a modified solution with composition of HF (45%): ethoxyethanol: water in a ratio of 1:2:1. The current density and the anodization time were, respectively, 15 mA and 10 min. After etching, samples with porous silicon were thoroughly washed in deionized water and dried in air using lighting PS with a red lamp for 5 min.

Figure 1 shows the SEM image of PS.

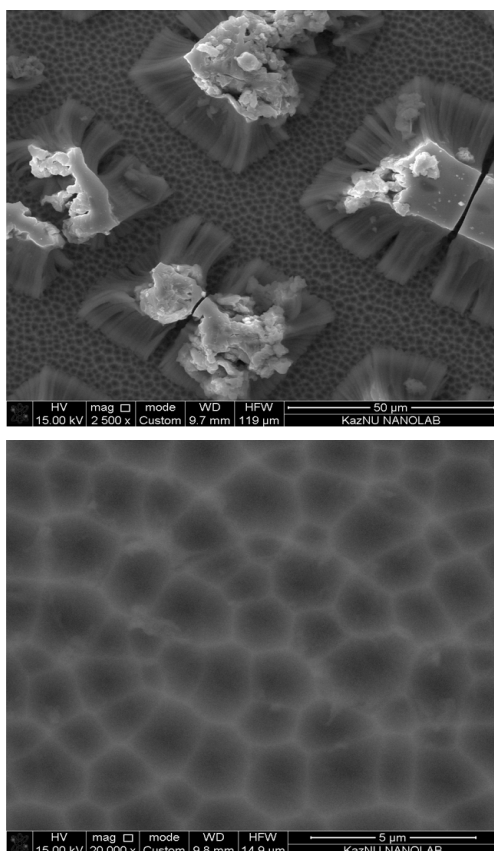


Fig. 1. SEM images of PS surface.

2.2. Synthesis of nanostructures

Synthesis of nanostructures was carried out in the Department of Surface and Technology of New Materials at the Institute of Materials Science, University of Siegen, Germany, on equipment of microwave plasma assisted chemical vapor deposition (MWCVD) of the ASTEX system (frequency 2.45 GHz).

Prior to the experiments, the substrates were purified with ethanol and then washed with distilled water, drying was carried out at room temperature. The synthesis temperature ranged from 700 to 900 °C in steps of 100 °C. The temperature was measured using an infrared pyrometer of model Chino IR-AP M0011 (Japan). The experiments were carried out at three plasma power levels of 1800, 2000 and 2200 W. The pressure in the chamber was changed depending on the power of the plasma. Table 1 shows the parameters of the experiments.

The mixture of trimethylsilane ((CH₃)₄Si) and hydrogen was used as working gas, the flow rates of which were 10 and 400 cm³/min, respectively. The duration of the experiments was 120 min.

3. Results and discussion

3.1. Method of scanning electron microscopy

The obtained samples were studied by the method of scanning electron microscopy (SEM), which was also carried out at the Institute of Materials Science of the University of Siegen. The field emission scanning electron microscope with ultra-high resolution of model Gemini Ultra 55 of the company Zeiss, with a device for X-ray microanalysis of the company «Thermo Scientific» was used to study the morphology and thickness of the samples.

Figure 2 shows the results of studies of samples synthesized at a substrate temperature of 700 °C by SEM. Figure 2a shows that the formation of NS on polished Si occurs on a buffer layer of SiC with height of 235 nm. Figure 2b and c show SEM images of the formed NS, which have diameter of 200–250 nm and a rough surface. Figure 2d represents a fairly extensive (~ 40–50 µm) NS. Energy dispersive X-ray spectra indicate that the carbon content in NS is up to 25%. Experiments have shown that the growth of NS is not of a mass character over the entire surface of the substrate.

Table 1
Parameters of the experiments

Substrate		Si orientation	Power of plasma, W	Temperature of substrate, °C	Pressure, Torr
Si	Polished	[100]	1800	700	47
			2000	800	50
			2200	900	57
	Porous	[111]	1800	700	47
			2000	800	50
			2200	900	57

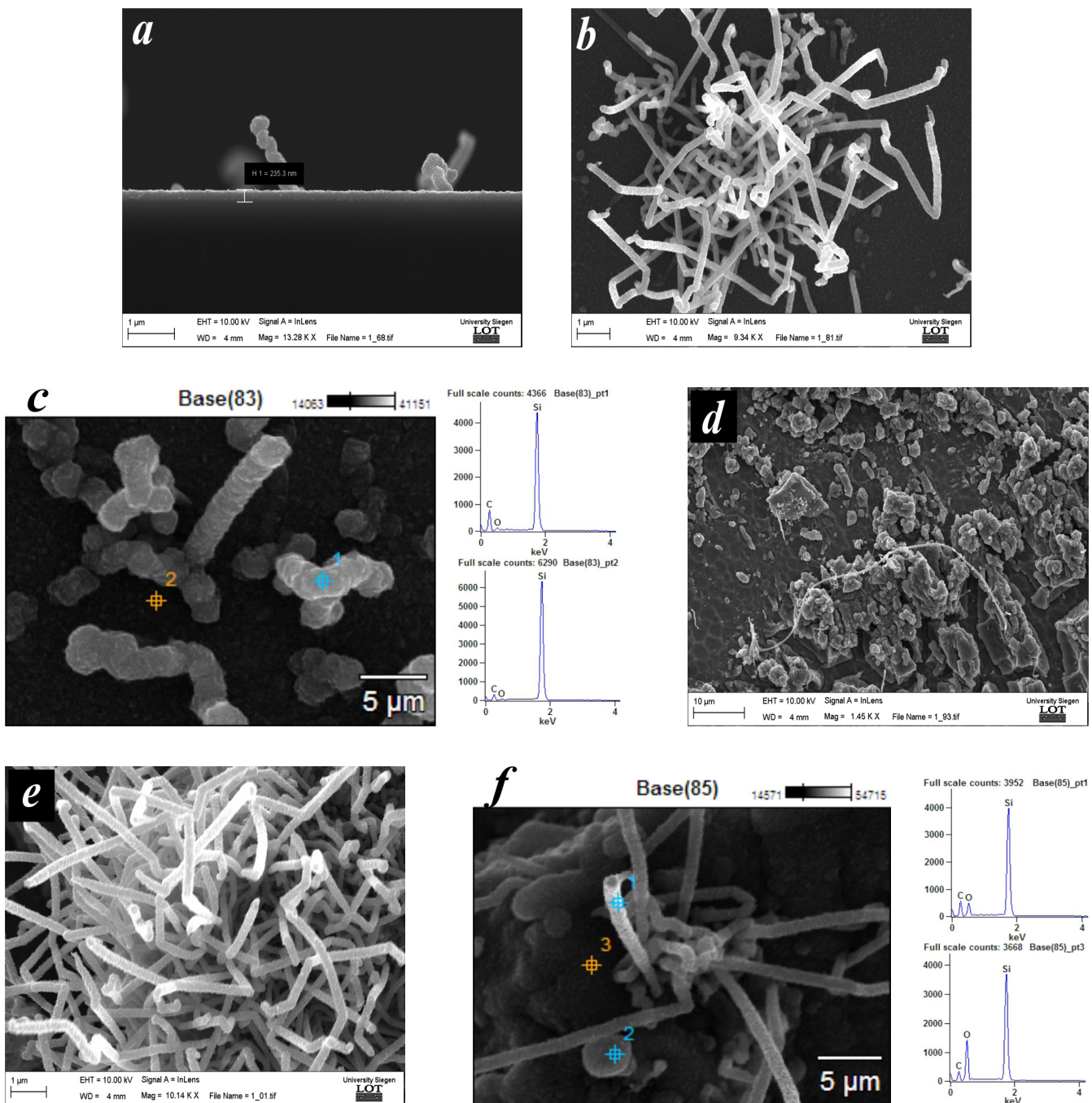


Fig. 2. SEM images and energy dispersive X-ray spectra of samples synthesized at substrate temperature of 700 °C: a, b, c – on polished Si (111); d, e, f – on PS (111).

Figure 3 shows SEM images of samples synthesized at a substrate temperature of 800 °C.

As can be seen in Fig. 3a, the thickness of SiC buffer layer on polished Si decreased to 163 nm. Figure 3b and c show SEM images of the formed NS, which have an average diameter of 250 nm and, as in the previous experiments, have a rough surface. Figure 3d shows that the growth of NS on the PS surface is more massive in contrast to polished Si. Energy dispersive X-ray spectra in Fig. 3c and f indicate that the carbon content in NS on polished Si is up to ~ 10% and on PS ~ 25%.

Figure 4 shows SEM images of samples obtained at a substrate temperature of 900 °C.

As can be seen in Fig. 4a, the thickness of SiC buffer layer on polished Si decreased to 115.5 nm. Figure 4b and c show SEM images of the formed NS, which have an average diameter of 350–400 nm. Figure 4d confirms that the growth of NS on the PC surface is more massive than on polished Si.

The energy-dispersive X-ray spectrum in Fig. 4c shows that the carbon content in NS on polished Si is from ~ 10% to ~ 20%, in contrast to NS at PS ~ 25% (Fig. 4f). All samples of NS, as in previous experiments, have a rough surface.

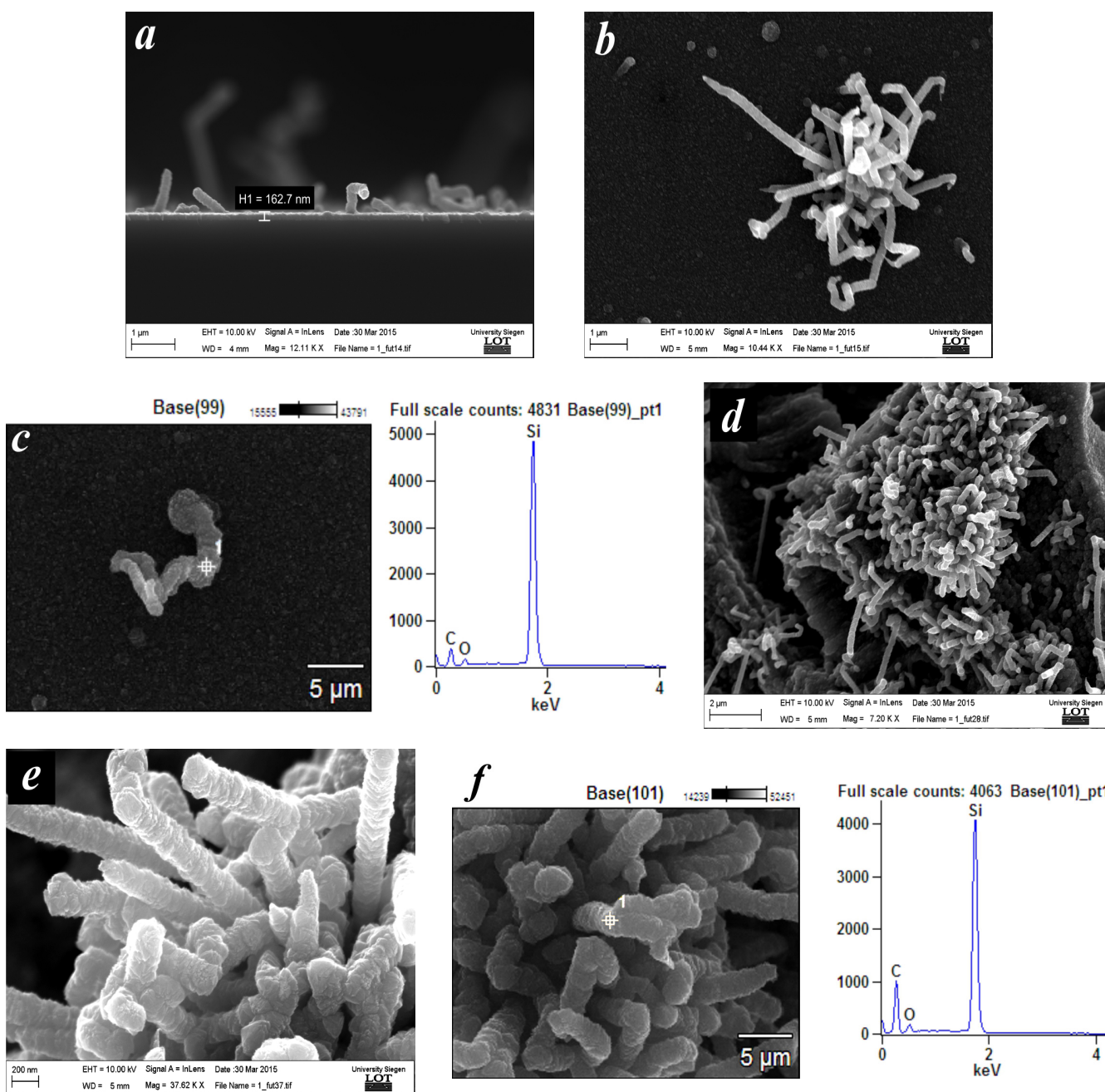


Fig. 3. SEM images and energy dispersive X-ray spectra of samples synthesized at a substrate temperature of 800 °C: a, b, c – on polished Si (111); d, e, f – on PS (111).

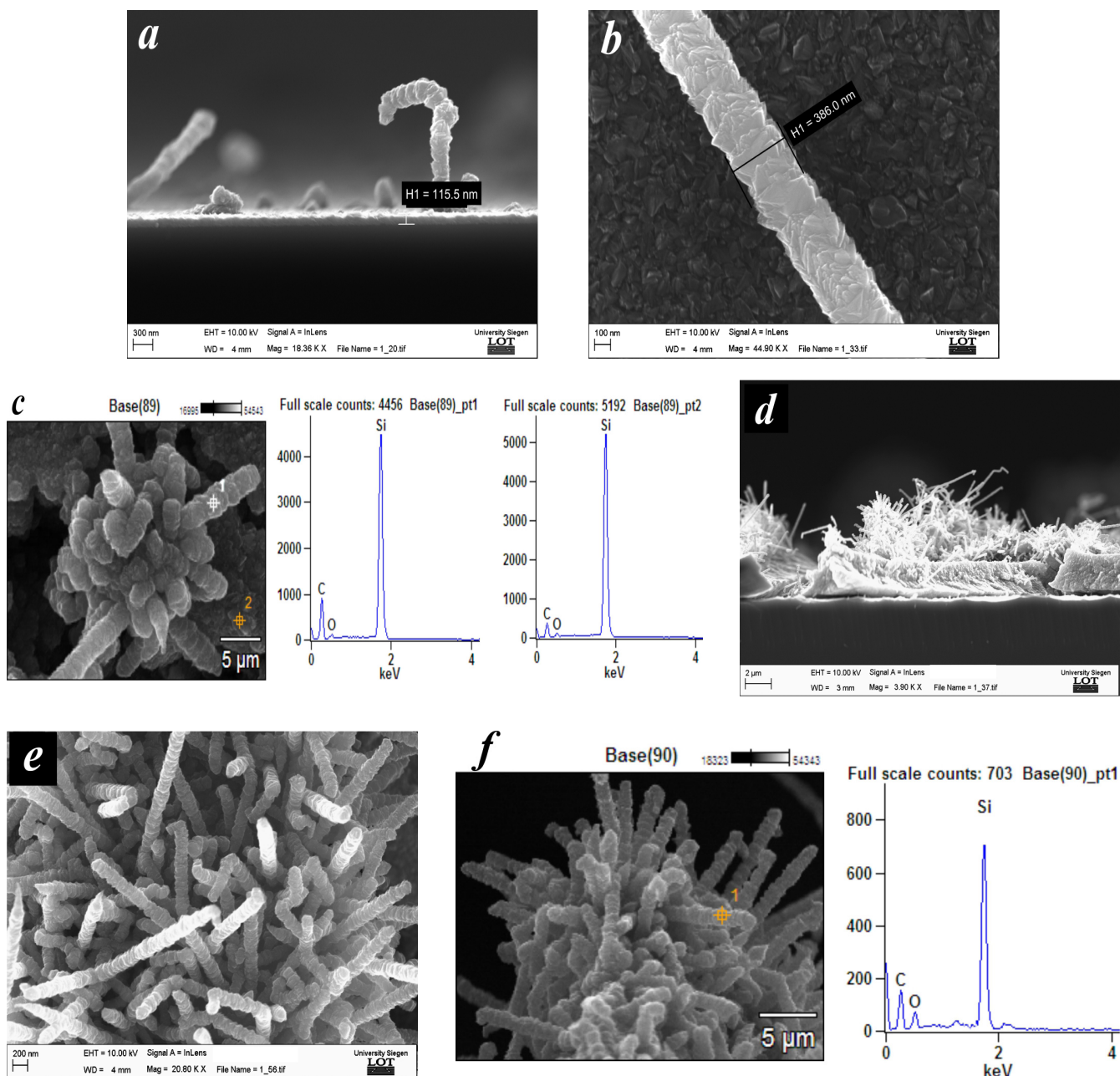


Fig. 4. SEM images and energy dispersive X-ray spectra of samples synthesized at a substrate temperature of 800 °C: a, b, c – on polished Si (111); d, e, f – on PS (111).

3.2. Method of Raman scattering

The obtained samples were investigated by Raman spectroscopy using spectrometer NT-MDT NTegra Spectra (laser wavelength $\lambda = 473$ nm) at The National Nanotechnology Laboratory of open type (Almaty, Kazakhstan). Figures 5 and 6 show the Raman spectra of some samples.

The Raman spectrum of Sample 5a is rather complicated. There are intense peaks of silicon carbide in the region of 795.1 and 972.7 cm^{-1} , which can indicate the formation of silicon carbide film with a 3C-SiC structure [5]. Peaks in the region of 614.4

and 663.4 cm^{-1} correspond to silicon oxide [6]. One can note a peak within 1432.4 cm^{-1} , which belongs to CH_3 groups [7]. The peak at 1703.2 cm^{-1} corresponds to the stretching mode $\text{C}=\text{O}$ [8]. The groups in the region of 2616.3–3278.9 cm^{-1} correspond to the C-H stretching [9]. The spectrum of Sample 5b also contains peaks of silicon oxide SiO_2 and silicon carbide 3C-SiC. In addition, one can see the main carbon peaks in the range of 1338.2 and 1583 cm^{-1} , which correspond to carbon nanostructures. Moreover, peaks of the second order are observed in the region of 2678.9 and 2902.7 cm^{-1} , which correspond to 2D and D + G groups [10, 11].

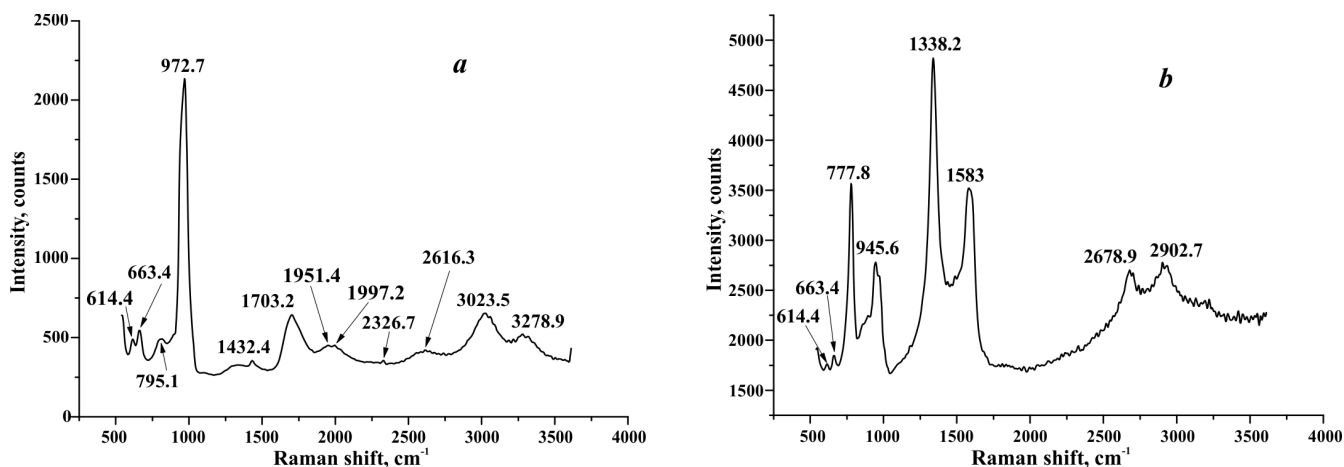


Fig. 5. Raman spectra of nanostructures obtained on polished silicon substrates with orientation [100]: a – 800 °C and b – 900 °C.

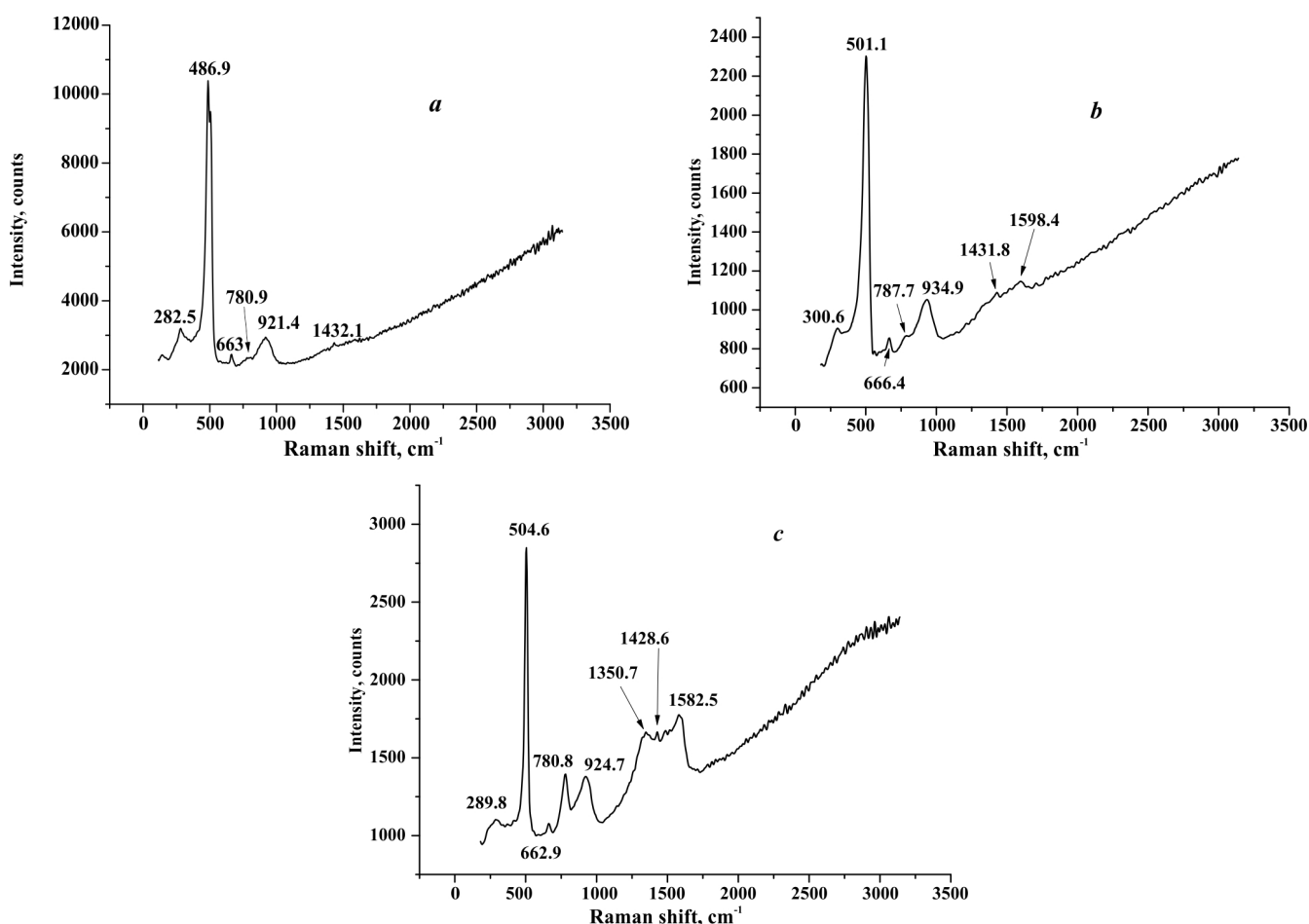


Fig. 6. Raman spectra of nanostructures obtained on porous silicon substrates with orientation [111]: a – 700 °C, b – 800 °C and c – 900 °C.

The second-order silicon peak is observed in the region of 486.9, 501.1, and 504.6 cm^{-1} in all three spectra. Groups within 282.5–300.6 cm^{-1} and 662.9–666.4 cm^{-1} correspond to silicon oxide [6]. In addition, shift of silicon carbide peaks in the region of 780.8–787.7 cm^{-1} are observed, which correspond to the transverse mode, while the longitudinal mode is observed in the range of 921.4–934.9

cm^{-1} . Displacement can occur due to the presence of a different crystal structure, i.e. silicon carbide nanofibers [12]. There is a peak corresponding to CH_3 groups in all spectra. G peak with low intensity in the region of 1598.4 cm^{-1} is observed in Sample 6b. In Sample 6c, peaks D and G are present in the region of 1350.7 and 1582.5 cm^{-1} . It can be assumed that these peaks belong to amorphous carbon.

It is difficult to estimate the quality and purity of the obtained carbon formations in relation to the I_D/I_G intensities, since nanostructures are present in some samples, whereas on others, amorphous carbon films.

4. Conclusions

In the course of the research, experiments on the synthesis of SiC and C nanostructures by the method of microwave plasma assisted chemical vapor deposition were carried out.

Studies by the method of scanning electron microscopy have shown that the formed NS have a diameter of 200–350 nm and a rough surface. The formation of NS on polished Si occurs on the SiC buffer layer. The height of the SiC film decreases with increasing substrate temperature. Analysis of SEM images of the samples shows that the growth of NS on the PS surface is more massive than on polished Si. According to the results of X-ray spectral analysis, the carbon content in samples of NS on polished Si varies from 10 to 20% and remains constant at PS ~ 25%.

The results of studies by Raman scattering confirmed that SiC film with structure of 3C-SiC is formed on the polished Si. Besides, the presence of main carbon peaks on both types of substrates in the range of 1338.2 and 1583 cm^{-1} should be noted, which correspond to the carbon nanostructures.

It is necessary to conduct additional studies using transmission electron microscopy and diffraction of electrons, as well as X-ray diffraction analysis for a more detailed analysis of the structure of the produced NS.

Acknowledgements

The authors thank candidate of physics and mathematics Dikhanbaev K.K for assistance in the preparation of porous silicon samples, Professor Xin Jang – Director of the Institute of Materials Science, University of Siegen (Germany) for the opportunity to use the equipment.

The work was carried out with partial financial support of the grants of the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan No. 3823/ГФ4, and No. 3816/ГФ4.

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