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Silicon carbide nanowires: synthesis and cathodoluminescence

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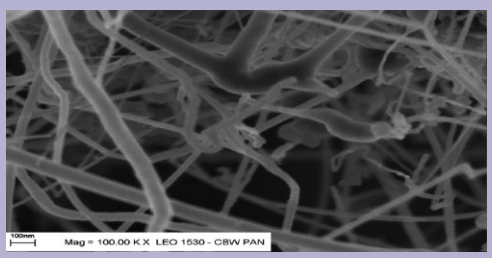
Silicon carbide nanowires have been synthesized via a combustion synthesis route. Structural studies showed that obtained SiC nanowires belong dominantly to 3C polytype with zinc-blend structure. Cathodoluminescence spectra from these nanostructures within the temperature range of 77...300 K, show obvious differences with respect to the bulk materials. The exciton band of the bulk 3C-SiC is significantly damped and the prevailing line is found to be at 1.99 eV (77 K), proving the key role of defect centers in optical properties of the investigated nanomaterial.



Purified SiC nanowires.

1 Introduction Silicon carbide (SiC) is a semi-conducting compound which exhibits unique thermal and mechanical properties, being highly resistive to radiation and is chemically inert and thus suitable for a wide range of technological applications [1–3]. For decades, SiC is in demand for microelectronics and widely used material in optoelectronics. The rapid progress of nanotechnology, stimulated the new wave of interest in the study of various SiC nanostructures such as nanowires, nanotubes, nanorods, etc [4]. These structures are promising from various viewpoints, and one of the foreseeable applications are LEDs with controlled wavelength of the emitted light. Therefore, many efforts are now being put in exploring the luminescent properties of the SiC nanostructures [5, 6].

The present report describes the chemical synthesis of silicon carbide nanowires and further structural and optical characterizations.

2 Experimental details

2.1 SiC nanowires synthesis Combustion synthesis in the Si/PTFE system yielded efficiently one-dimensional silicon carbide nanowires [7–9]. The final product was isolated and purified (up to 98 wt%), using wet-chemistry 3-stage protocol, see figure in the abstract.

2.2 Cathodoluminescence measurements The cathodoluminescence technique is based on the measurements of visible to UV emission from a material exposed to high-energy electron bombardment.

For the purpose of such measurements, we employed the set-up which includes the electron gun, MDR monochromator, N_2 liquid cryostat, photomultiplier-based detecting unit, and a PC-interfaced signal acquisition board. The electron gun was operating in a pulse regime, providing the beam energy up to 10 keV. Whereas, for this range of electron beam energies, the emission to be measured is excited from a several micron surface layer of SiC; for the purpose of measurement, the investigated powders were evenly deposited over the metallic substrate plate which, in turn, was placed into the cryostat. The emitted light was collected in the reflection geometry. This set-up was described in our previous works [10, 11].

The Gaussian deconvolution of the measured spectra was performed utilizing Focus optical functions creation software.

3 Results and discussion

3.1 XRD analysis Silicon carbide exists in different polytypes [12], therefore in order to determine the structure of produced SiC nanomaterial, the structural studies have been performed. XRD pattern of the purified nanowires obtained by combustion synthesis is shown in Fig. 1 for the 2Θ range from 15° to 70°.

Strong peaks at 35.68° and 60.11°, correspond to the 3C polytype of silicon carbide (zincblende unit cell, bandgap 2.39 eV [13]). Although the reaction product is composed mainly of the 3C polytype, there are also weaker signs of the 6H polytype (hexagonal unit cell, bandgap 2.86 eV [14]) at 38.25°, 41.44°, and 60.16°. Therefore, one may classify the obtained product as the 3C polytype with a small addition of the hexagonal phase.

3.2 Cathodoluminescence studies Cathodoluminescence from the SiC purified nanowires was analyzed with respect to the emission spectra of a standard commercial 3C-SiC micropowder. As illustrated in Fig. 2, the exciton band at 2.38 eV which is prevailing in the spectrum of the bulk material is essentially diminished in the spectrum of nanowires. On the other hand, dominating in the emission of SiC nanowires is the line at around 1.9 eV, which appears only as a weak shoulder in case of the commercial sample. One also has to notice that the spectrum of nanowires also exhibits two minor bands ranging within 1.9 and 2.8 eV.

To have a deeper insight, we measured the temperature dependence of the cathodoluminescence from SiC nanowires. The results are depicted in Fig. 3.

By performing the Gaussian deconvolution, three bands can be resolved at the highest measured temperature: the band A (1.98 eV at 290 K)the most intense emission, the band B (2.30 eV at 290 K) and the band C (2.77 eV at 290 K). Parameters describing each of the three observed bands in the temperature range of 77. . .290 K, were obtained by the non-linear least squares fitting procedure. Peak positions of the bands B and C exhibit negligible temperature shift and were determined to be 2.35 and 2.74 eV, respectively, for the range of temperatures denoted above. The band marked as A

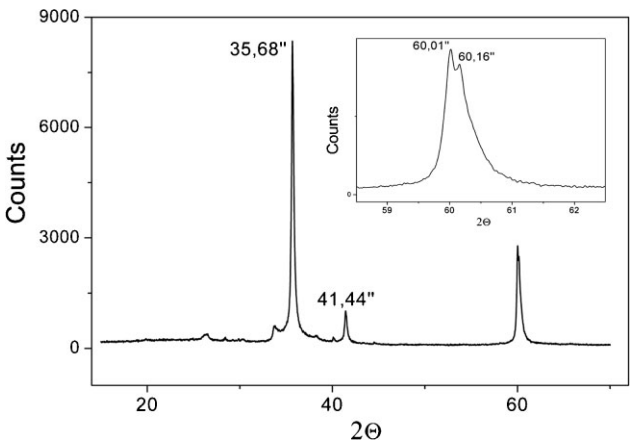


Figure 1 XRD pattern of as-obtained SiC nanowires.

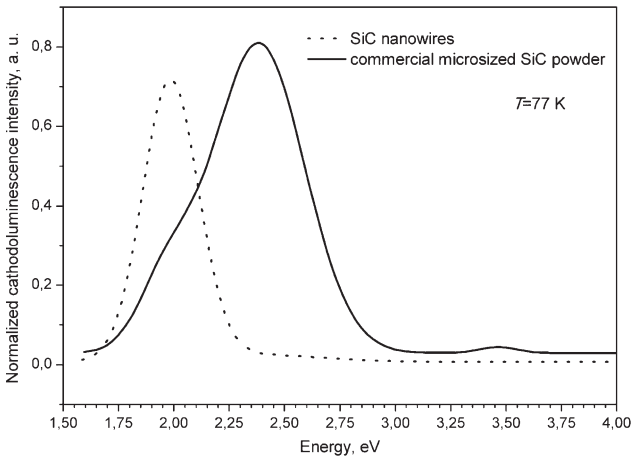


Figure 2 The difference in the catholuminescence from the bulk 3C-SiC and obtained silicon carbide nanowires. Intensities are normalized for the purpose of comparison.

shows a different trendpeaked at 1.938 eV (290 K), it is blue-shifted to 1.993 eV at 77 K (see Fig. 4), the respective estimated activation energy value is nearly 20 meV.

Full width at half maximum values at 77 K are 0.30, 0.18, and 0.32 eV for A, B, and C bands respectively. All revealed bands show typical temperature broadening.

Since the estimated peak position of the band marked as B is very close to the main emission maximum in the spectrum of the bulk 3C-SiC, the band B most likely to represent the band gap luminescence in the nano-SiC under study. Considering that the band gap of 6H-SiC is 2.86 eV [14] and taking into account the XRD data presented in the Section 3.1, one may ascribe the band C to the characteristic emission of the 6H polytype of silicon carbide. The deviation which is within 0.1 eV, can be explained by very low CL yield and consequently, the error in the exact peak position determination. Due to the same reason, the correct analysis

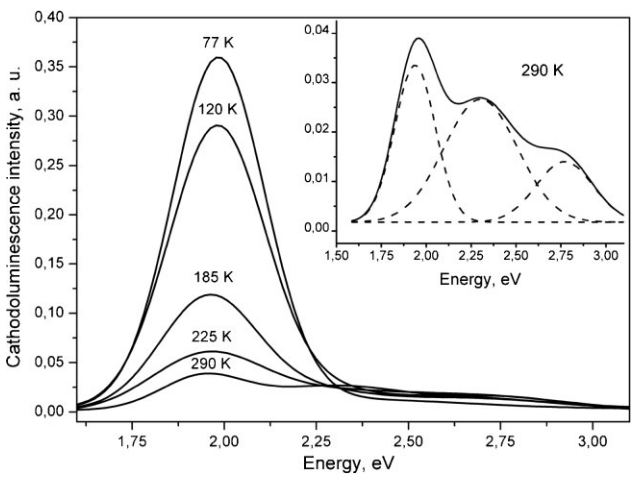


Figure 3 CL from obtained SiC nanowires at elevating temperatures. The inset illustrates the spectrum at 290 K in which three Gaussian components are shown as dashed lines.

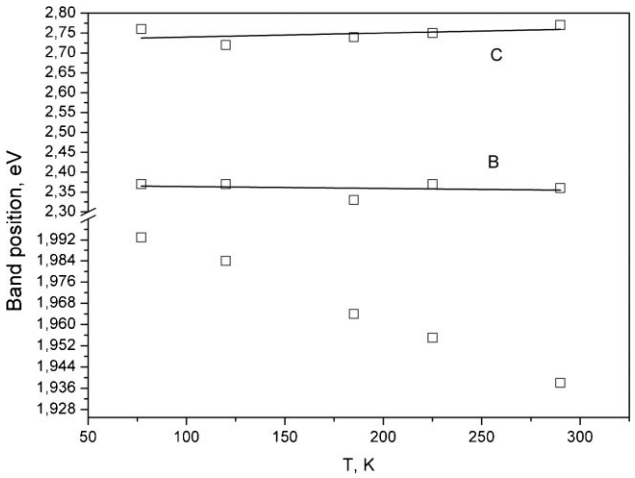


Figure 4 Peak positions of luminescence bands versus temperature (SiC nanowires). Solid lines represent linear fit for bands B and C.

of the temperature behavior of the 6H-SiC related band is not possible here.

The prevailing characteristic luminescence of the investigated nanowires (A) at 1.938 eV (290 K) is fairly close to the known CL band reportedly being ascribed to the D_1 center. Similar band appears also in the bulk SiC, due to the defects, introduced by the high energy electron irradiation [15, 16].

Since the electron beam energy in the present experiment is rather low for the efficient formation of radiative centers, the most probable origin of the observed 1.938 eV peak can be the transition between the Si vacancy level within the bandgap and the bottom of the conduction band. Considering that the band gap of 3C-SiC is 2.39 eV, the vacancy level is suggested to be located at 0.5 eV above the top of the valence band, so the respective radiative transition produces the emission around 1.9 eV [17].

Although there still is a certain probability that such vacancies could be created by irradiation, it is also very likely that the density of the vacancy states is significantly higher in nano-SiC, having pronounced defect structure, as compared to the bulk material. Another way of increasing the yield at $\sim$1.9 eV in case of the nanowires, is more effective energy transfer from the bandgap electronic states, since the chemical purification of the nanomaterial lowers the probability of non-radiative relaxations on defect states.

4 Conclusion Novel silicon carbide one-dimensional nanostructures have been synthesized. Structural studies identified that obtained SiC nanowires belong dominantly to 3C polytype with zincblend structure. Cathodoluminscence spectra from these nanowires within the temperature range of 77. . .300 K, show obvious differences with respect to the bulk materials. The exciton band of the bulk 3C-SiC is significantly damped and dominated line is found to be at 1.99 eV (77K), proving the key role of defect centers in the optical properties of investigated nanomaterial.

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