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Combustion Formation of Novel Nanomaterials: Synthesis and Cathodoluminescence of Silicon Carbide Nanowires

V. Savchyn[a], I. Karbovnyk[a], A.I. Popov[b,c] and A. Huczko[d,*]

[a]Department of Electronics, Ivan Franko National University of Lviv
107 Tarnavskogo, 79017 Lviv, Ukraine
[b]Institut Laue-Langevin, 6 rue Jules Horowitz, 38042 Grenoble, France
[c]Institute of Solid State Physics, University of Latvia, Kengaraga 8, LV-1063 Riga, Latvia
[d]Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

This paper presents the combustion synthesis and characterization of one-dimensional silicon carbide nanostructures (nanowires of 3C-SiC polytype with zincblend structure) by means of cathodoluminescence technique. Cathodoluminescence spectra of nano-SiC samples and, as a reference, of a commercially available SiC micropowder are compared. It is shown that the emission band at 1.97 eV which is slightly evidenced in the spectrum of the commercial SiC under 10 keV electron beam irradiation becomes the prevailing band in CL of the purified silicon carbide nanowires.

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1. Introduction

Because of its inherent properties silicon carbide (SiC) has several technological advantages over the other wide band gap semiconductors (high Debye temperature, large breakdown voltage, etc.) and has become an important industrial electronic material [1]. SiC exists in several different polytypes of which the 3C, 4H and 6H are the most common. The appropriate band gap values in eV are at 2.39, 3.20, 2.86, respectively [2].

One of the most interesting SiC features is a possibility to use it in light emitting devices for the entire visible range. Intensive research is now focused on that subject whereas novel SiC nanostructures allow us for obtaining of enhanced and tunable emission by varying the size of nanoparticles or the length/diameter of nanowires as well [3, 4]. The present study deals with the fabrication of stable 1D silicon carbide nanostructures by means of combustion synthesis and its further optical characterization that originates from the deep defect levels in the band gap. Comparative cathodoluminescence (CL) measurements allow us for understanding the factors influencing the change of the luminescence yield and the emission lines shifts when one moves from bulk material to confined structures.

2. Experimental

We have investigated a sample of SiC nanowires obtained by combustion synthesis route from Si/Teflon® composition according to the procedure outlined in detail elsewhere [5, 6]. Three different powder samples of nano-SiC were prepared, hereafter denoted as A, B and C. Sample A was an unpurified as-obtained combustion product, containing, as contaminations, soot, un-reacted Si and SiO_2, while samples B and C were chemically purified in one and two stages, respectively. We also investigated commercially available 3C-SiC micropowder (BDH Chemicals Ltd.) in order to obtain the reference spectrum. Figure 1 shows typical scanning electron images of as-obtained and purified silicon carbide nanostructures. One has to notice that the raw product contains not only SiC nanowires (diameter between ≈ 10 nm and ≈ 100 nm, and typically a few micrometers long) but also certain amounts of 3D nanostructures, i.e. carbon nanocrystallites and un-reacted silicon. The elaborated protocol of chemical purification allowed us for the preparation of SiC nanowires in the purified samples at the level of 98 wt.% [5]. The material balance of the process, made on the basis of the mass and chemical composition of solid and gaseous products, indicated that the almost 50% of starting silicon was converted to SiC. Surprisingly, the highest conversion was obtained for the runs carried out in air atmosphere. This finding shows that (i) the process is far from thermodynamic equilibrium (otherwise silicon should be mostly oxidized to silica) and (ii) probably gaseous SiO is an intermediate reactant participating in transport and diffusion of reacting silicon.

The optical characterization of the samples listed above was performed employing the cathodoluminescence experimental setup, used earlier to study the emis-

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[*] corresponding author; e-mail: `ahuczko@chem.uw.edu.pl`

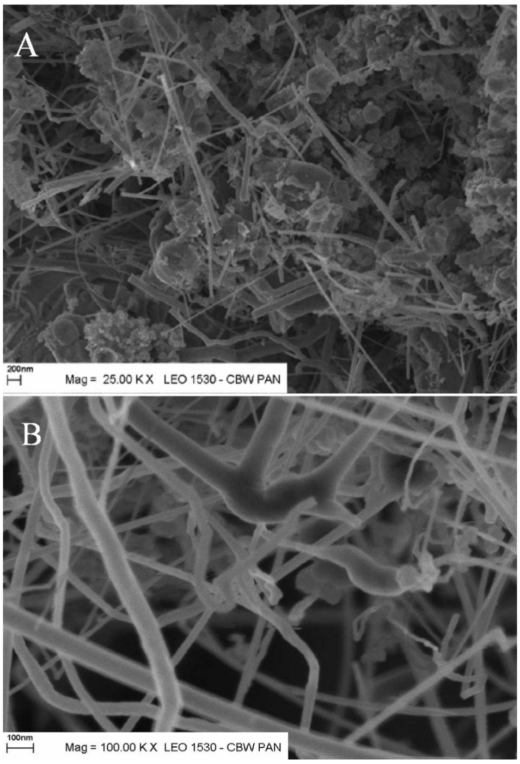

Fig. 1. Typical SEM images of the fabricated SiC nanostructures: (A) raw combustion product, (B) purified nanowires.

sion from aluminum nitride nanostructures and described elsewhere [7]. Here, we would only like to note that electron beam energy was 10 keV and according to the estimation, reported recently in [8], in this case electron excitation of SiC can extend beyond a μm.

3. Results and discussion

The CL spectrum of the commercial SiC sample obtained at 77 K is shown in Fig. 2. It resembles well the shape of photoluminescence (PL) emission spectrum for 3C-SiC polytype (reported earlier [9]) and exhibits main peak at 2.38 eV, which is in a good agreement with zinc-blende 3C-SiC band gap 2.39 eV at 2 K [2, 4]. A shoulder at the low-energy side of the main peak is also noticeable. Gaussian decomposition of the spectrum suggests that this shoulder originates from the additional band at nearly 1.97 eV.

Low-intensity maximum at nearly 3.0 eV can be resolved as well. Luminescence peak at ≈ 3.0 eV was already observed earlier for thin films and some of 3C-SiC (or beta-SiC) nanomaterials. In particular, in [10] a strong PL band at 400 nm (3.1 eV) is reported for β-SiC nanowires and in [11] hexagonal-shaped nanowires of the same material (with a small content of α-SiC) were shown to emit light at 391 nm (3.17 eV). Stable emission in the range of 360 to 400 nm was also observed from SiC/SiO nanocables [12]. Although this emission from nano-SiC is often thought to originate from nanotube core defects, here it is not obvious because we observed this for both SiC bulk and nanostructures (see below). Hence, we suggest that 3.0 eV peak is rather a manifestation of OH and other environment-related groups adsorbed on some defects and/or may be assigned to the structural defects, which exist on the SiC surface [3, 8]. However, even in bulk SiC the true origin of this band is uncertain, especially in view of experimental fact that the small peak at about 3.1 eV was observed in 20 keV CL spectra from 4H-SiC epitaxial layers [13]. This luminescence is also attributed by some authors to inclusions of 15R-SiC polytype [14].

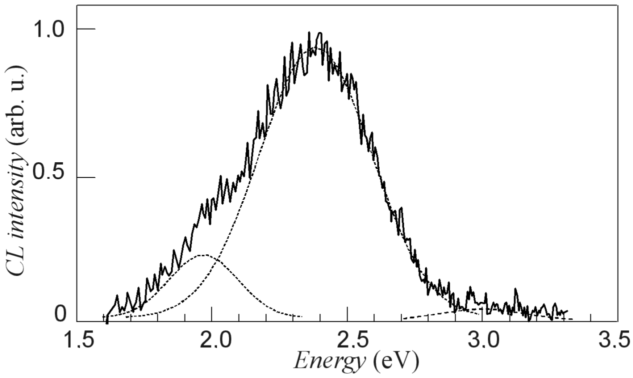

Fig. 2. Normalized cathodoluminescence spectra of commercial 3C-SiC powder at 77 K. Dotted lines are Gaussian contributions.

Taking into consideration comprehensive previous PL [15] and CL [16] studies of 3C-SiC material exposed to electron beam irradiation one can ascribe 1.97 eV peak to radiative transitions between the defect level (silicon vacancy) and the conduction band.

Figure 3 shows CL spectra of the synthesized SiC nanowires samples obtained at 77 K, denoted as A (a), B (b) and C (c), respectively. The intensity in Fig. 3 is normalized with respect to the spectrum in Fig. 2. In the spectrum of raw SiC product it is possible to resolve only weak signatures of emission bands at ≈ 2 eV, ≈ 2.5 eV and 3.0 eV, being, most likely, of the same origin as in the spectrum of the commercial SiC sample. Obviously, the as-obtained product contains not only nanowires but also a fraction of carbon nanoparticles and un-reacted silicon (see Fig. 1). Referring to the absorbance spectra of colloidal 3C-SiC nanoparticles [17], one can notice that due to the size distribution, a significant absorption is observed within 2.4–3.2 eV. Thus, ≈ 2.5 eV and 3.0 eV emissions might be strongly damped in the samples under consideration.

Contrary to the sample A, isolated and purified SiC nanowires (sample B) exhibit much stronger CL peak at 1.97 eV. It follows from Fig. 2 that the intensity of this peak is more than three times larger than that of band gap luminescence at 2.38 eV. Further purification leads to continuing increase of the 1.97 eV band intensity

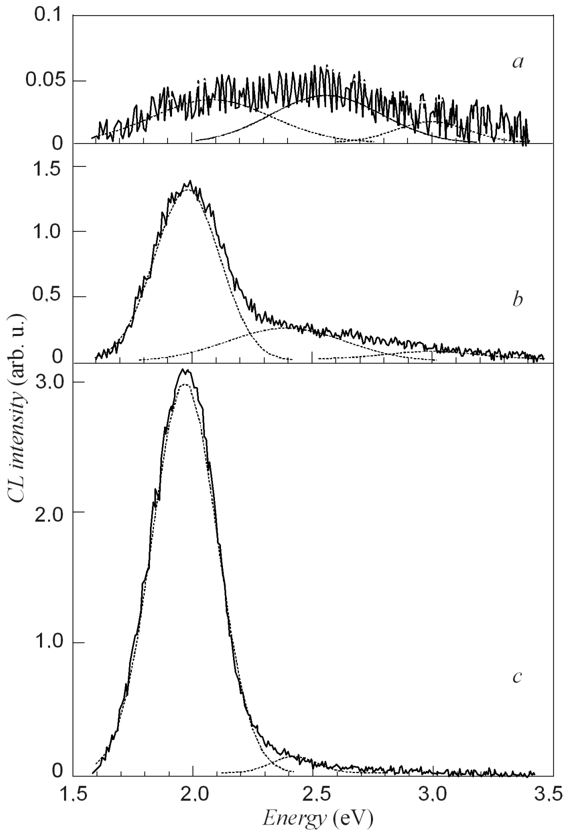

Fig. 3. Cathodoluminescence from 3C-SiC nanomaterials: (a) unpurified combustion product, (b) isolated nanowires after purification; (c) pure nanowires, after the second stage of purification.

(Fig. 3c), which becomes completely dominating. The peak position is in excellent agreement with the CL line marked as A_0 [16] and well-known D_1 center [3, 9, 15, 16]. This line is present in bulk SiC due to simple defects which can be introduced by electron beam irradiation. However, electron beam energy in our experiment is relatively low, therefore the 1.97 eV peak is manifested only as a weak shoulder on the background of the band-to-band emission at 2.38 eV. The situation with purified nanowires is quite different and this allows us to make a conclusion that produced nanowires of 3C silicon carbide are defects enriched, providing a larger number of D_1 irradiative centers [18]. Relatively broad measured CL band with respect to reported sharp photoluminescence lines [9] can be explained assuming that emission peak might shift slightly depending on the size of 1D nanostructures while the collected CL spectrum represents an integral contribution.

4. Conclusions

The results of cathodoluminescence studies on silicon carbide 1D nanostructures are compared with the CL data collected for the commercial SiC micropowder, in which the band at 2.38 eV and a less intensive one at 1.97 eV are prevailing. 2.38 eV line corresponding to band-to-band transition in 3C-SiC was found to be much less intensive in nanopowders than in commercial sample. Further experiments indicated that isolated and purified 3C-SiC nanowires exhibit stronger emission line at 1.97 eV. The intensity of this line depends on the purification degree. Luminescence yield at 1.97 eV is enhanced significantly when one compares a bulk SiC to double-purified silicon carbide SiC nanowires. The origin of this band can be ascribed to D_1 irradiative centers. The obtained experimental results lead to the conclusion that deep vacancy states density (that determines the 1.97 eV line intensity) is higher in nano-SiC than compared to the bulk material. Another additional reason of the enhancement of 1.97 eV luminescence in double-purified SiC nanowires is that the energy transfer from band-to-band electronic states (2.38 eV) to D_1 irradiative center is more efficient. In this case the purification process leads to the strong decrease of the concentration of the imperfection/defect states responsible for non-radiative relaxation of electronic excitations. As a result, luminescence yield at 1.97 eV is significantly higher that that observed from the commercial bulk SiC or less purified nanowires. Summarizing, a morphological characterization of the fabricated 3C-SiC 1D nanostructures has been performed by combining electron microscopy with cathodoluminescence measurements. Using those techniques as complementary tools can be helpful in the analysis of various nanomaterials having pronounced defect structure.

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