Silicon carbide nanowires: chemical characterization and morphology investigations

A. Busiakiewicz 1, A. Huczko 2, H. Lange 3, P. J. Kowalczyk 1, M. Rogala 1, W. Kozłowski 1, Z. Klusek 1, W. Olejniczak 1, K. Polan 1, and S. Cudziło 3

1 Department of Solid State Physics, University of Łódź, 149/153 Pomorskastr., 90-236 Łódź, Poland
2 Department of Chemistry, Warsaw University, 1 Pasteurstr., 02-093 Warszawa, Poland
3 Department of Chemistry, Military University of Technology, 2 Kaliskistr., 00-908 Warszawa, Poland

Received 28 April 2008, revised 17 June 2008, accepted 18 June 2008
Published online 26 August 2008

PACS 68.37.Hk, 68.37.Ps, 68.65.La, 78.67.Li, 79.60.Jv, 81.07.V

** Corresponding authors: e-mail adambus@std2.phys.uni.lodz.pl, Phone: +48 42 6355694, Fax: +48 42 6354325
** e-mail ahuczko@chem.uw.edu.pl, Phone: +48 22 8222375, Fax: +48 22 8225996

Silicon carbide nanowires (SiCNWs) were efficiently obtained via self-combustion high-temperature synthesis (SHS) route from silicon-bearing/poly(tetrafluoroethylene) (PTFE) mixtures. The SEM and AFM studies were carried out to find out the lengths and diameters of the nanowires (20-100 nm dia. and several microns in length). XPS was used to investigate the chemical composition of the nanowires. These studies showed that the SiCNWs are N-doped. The ARXPS results revealed that outer regions of the nanowires are C-rich. These results along with a low resistance of the nanowires suggest that nitrogen dopant and the carbon rich surface are responsible for good conducting properties of SiCNWs.

1 Introduction Silicon carbide (SiC) has been widely studied for tribological and structural applications, and has also promising applications in high temperature technology, because of its high Young’s modulus and hardness, excellent oxidation and corrosion durability, high strength at elevated temperatures, and good thermal shock resistance [1]. If fabricated in the form of 1-D nanostructures, SiC would have, obviously, new properties resulting from both its marked shape-specific and quantum-confinement effects. However, the existing methods of preparing 1-D SiC nanostructures [2, 3] are quite involved, require high temperature and long processing times. We found earlier [4, 5] that a complex set of parallel gas phase reactions with participating silicone-fluorine radicals yielded solid SiC nanowires as the main reaction product during the combustion (SHS) of silicon-bearing/PTFE mixtures. In fact, SHS technique [6], which makes use of the heat generated by exothermic reactions, can be applied to synthesize different unusual nanomaterials [7]. We report here on the chemical and structural characterization of the produced SiCNWs.

2 Experimental SiC nanowires were obtained using the procedure outlined elsewhere [4, 5]. The initial reactant composition comprised of polytetrafluoroethylene (PTFE, 57.8 wt%) and calcium disilicide (CaSi₂, 42.2 wt%). Samples in two forms were investigated: pristine sponge-like material and nanowires deposited on Au (111). In the case of the first sample a small clod of pristine material was glued to the holder. The solution used in preparation of the second sample was prepared by sonication (30 min.) of a few µg’s of the SiCNWs in 2 cm³ of dichloroethane. Then, a droplet of that solution was deposited on commercially available 300 nm gold film evaporated on mica (Georg Albert PVD-Beschichtungen) cleaned by repeated cycles of Ar⁺ sputtering and annealing. After the treatment the sample was dried in the air for 1h. AFM and XPS was carried out in the Omicron UHV system working at the base pressure lower than 5×10⁻⁸ Pa equipped with the EA 125 HR hemispherical analyzer with the resolution better than 0.8 eV. Mg Kα1,2 source was used with power set to 75 W in all experiments. The three-point correction of the energy scale based on Au 4f7/2 (83.95 eV), Ag 3d5/2 (368.22 eV) and Cu 2p3/2 (932.62 eV) lines was applied to all spectra [8]. This technique is reliable for pristine material due to its good conducting properties (charging effects could be excluded). It is also reliable for SiCNWs deposited on Au (111) which was confirmed by the proper position of all gold peaks. The WSPECTRA and XPSPEAK
packages were used to perform analysis of the collected data. ARXPS data were recorded by tilting the sample to 60° from analyzer axis. Obtained results have not been corrected to eliminate influence of the sample tilt. SEM used in this experiment was Tescan Vega 5135 MM (BSE detector, HV: 30 kV) working at the base pressure lower than 5×10⁻³ Pa.

3 Results and discussion

3.1 SiC characterization

Long nanowires, typically a few micrometers long, can be clearly seen in SEM image (Fig. 1).

The diameters were in the range from a few up to tens of nanometers. To check the homogeneity of the sample (pristine material) we performed the XPS scan across the sample using the Mg Kα1,2 line. It has to be pointed out here that using XPS we were able to investigate only a relatively thin fragment of the sample surface. Taking into account that typical diameters of SiCNWs were larger than 10 nm (which is attenuation depth) we can claim that the measurements were performed only on the surface of nanowires. What is more, we believe that in our sample there are no identical nanowires. Thus, all XPS measurements shown below should be treated as a sum over many similar SiCNWs. The results in the form of Energy, Distance, Intensity (EDI) maps are presented in Fig. 2.

The intensity in the EDI map is presented using gray scale colors. Each map was normalized individually so minimal intensity corresponds to black color and maximum intensity to white color. The measurements were collected on the length of 10 mm while the sample was slightly smaller which is clearly seen on the EDI maps. For the distance ca. 8–10 mm, the influence of the sample holder can be seen evidently. It is also clearly seen that the region of the other edge of the sample at distances ca. 0–2 mm is not only SiC but also with low intensity of silicon and nitrogen peaks and double carbon and oxygen peaks. The central region of the sample at distances ca. 3–7 mm is free from peak distortions which proves the homogeneity of the sample.

Figure 3 shows the results of the XPS investigations carried out in the central region of the sample. The presence of silicon, carbon, oxygen, fluorine and nitrogen was identified using XPS. It is worth mentioning that nitrogen which is donor dopant of SiC [9] was found in the spectrum. It suggests that the analyzed SiCNWs were N-doped. In addition to the lines attributed to Si, C, O, F and N, some other additional lines are clearly seen in the spectrum. Each of these lines is associated with Si, C and O lines. These lines result probably from the collective oscillations of the electron gas – plasmons. The inset shows carbon and associated plasmon peak located at 283.35 eV and 305.87 eV respectively. Previously, it was shown that for the bulk SiC the plasmon oscillation is shifted 22.5 eV from the carbon peak [10]. It is in perfect agreement with our results which clearly show that we dealt with the sample rich in crystalline SiC. Our results show that atomic concentrations of carbon, silicon, oxygen, nitrogen and fluorine were equal 45.4%, 33.4%, 16.2%, 3.6%, and 1.4% respectively. Thus, the C:Si ratio is equal 1.34.
Figure 4 presents the XPS results for silicon and carbon peaks. Each of the peaks was split into several Gaussian-Lorentzian peaks. Two peaks located at 100.94 eV and 101.34 eV were obtained after applying a fitting procedure to the silicon peak. We think that one of them is related to Si-C (which should be located ~101.0 eV [11-13]) while the other one is related to Si-N located at ~101.34 eV [14, 15]. The presence of SiN could be easily explained due to the presence of nitrogen in the sample. Our measurements showed that nitrogen is located at 398.1 eV which corresponds quite well with the location of N in Si$_3$N$_4$ located at ~398.4 [16, 17]. Carbon C 1s peak shown in Fig. 4 has four components located at 283.2 eV, 284.1 eV, 284.2 eV and 286.4 eV. These binding energies are representatives of SiC (283.2 eV), carbon in sp$^2$ configuration (284.1 eV, 284.2 eV) and C-O-H (286.4 eV) compounds respectively [12, 13, 18-20]. In our opinion the presence of hydrocarbons in the sample is related to atmospheric contaminations. A strong sp$^2$ peak suggests the existence of graphite in the sample. However, conducting properties could also result from the presence of nitrogen which donor electronic states located close to the Fermi level.

3.2 SiCNWs deposited on Au (111) A typical AFM image recorded on SiCNWs deposited on Au (111) is shown in Fig. 5. Typically SiCNWs were a few micrometers long and their diameters were in the range 10–100 nm which is in perfect agreement with SEM measurements. What is more, our AFM investigations revealed that the surface of SiCNWs is not flat. A large number of defects can be found on the surface. The defects (bamboo-like structures) are clearly seen in Fig. 5 – especially in the inset which depicts magnification of the central part of the wire. This kind of defects are very often observed in case of (111) 3C-SiC wires. Its origin is related with local change in the atomic arrangement of 3C-SiC layers. Such rearrangement is responsible for local change of the 3C polytype into hexagonal one (2H, 4H, 6H) [21].

XPS measurements recorded on SiCNWs deposited on Au (111) are shown in Fig. 6. The comparison between sponge-like SiCNW material and deposited nanowires (Fig. 6(a)) shows a significant shift towards higher energy of C1s peak for SiCNWs + Au system. The shift was estimated to 0.83 eV. We think it is the result of the Schottky contact potential between SiC (semiconductor) and gold (metal). A similar shift was also observed for silicon peaks. What is more, a shift of C 1s peak at the level of 0.78 eV was reported [22] upon deposition of Au on the crystalline SiC. The reported value is in good agreement with our measurements. This additionally proves that we dealt with contact potential. By the increase of the analysis’ angle the information about the chemical composition of the surface could be collected. In our opinion angle measurements on randomly oriented nanowires are possible as long as we measure large diameter SiCNWs (up to 100 nm in our case). In such situation the amount of photoelectrons emitt-
ed with proper angles starts to dominate over photoelectrons emitted eg perpendicularly to nanowires’ walls. Our results (Fig. 6(b)) showed increase of carbon peak intensity with increasing analysis’ angle. The intensity of silicon peak remains unchanged. It suggests an increase of carbon concentration in the outer region of SiCNWs. It is additionally confirmed by the ARXPS results which clearly show lowering of the SiC component and increasing of the graphite component (Fig. 6(c)). These observations lead us to a conclusion that the outer region of the SiCNWs is carbon rich. What is more, carbon is rather in $sp^2$ configuration which suggests graphitization of the surface. These findings are additionally confirmed by our previous STM investigations [23].

4 Conclusions

The characterization of the SiCNWs prepared by the SHS route was carried out using different techniques. SEM and AFM was used to analyze nanowires’ lengths (within tens of micrometers) and diameters (from single nanometers up to hundreds of nanometers). The XPS analysis of silicon and nitrogen peaks shows the existence of Si-N bonds in the SiCNWs which suggests the existence of donor levels in the electronic structure of the SiCNWs. The Schottky barrier potential was observed at SiC–gold interface. The barrier height was estimated and is equal 0.83 eV. The ARXPS results showed increase of carbon concentration in $sp^2$ configuration in outer regions of the nanowire. It suggests graphitization of SiCNWs surface.

Acknowledgements

This work was supported by the Ministry of Education and Science through the Department of Chemistry, Warsaw University, under Grant No. 3 T08D 012 28.

References