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# Synchrotron studies of top-down grown silicon nanowires

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ABSTRACT

Morphology of the top-down grown silicon nanowires obtained by metal-assisted wet-chemical approach on silicon substrates with different resistance were studied by scanning electron microscopy. Obtained arrays of compact grown Si nanowires were a subject for the high resolution electronic structures studies by X-ray absorption near edge structure technique performed with the usage of high intensity synchrotron radiation of the SRC storage ring of the University of Wisconsin-Madison. The different oxidation rates were found by investigation of silicon atoms local surrounding specificity of the highly developed surface and near surface layer that is not exceeded 70 nm. Flexibility of the wires arrays surface morphology and its composition is demonstrated allowing smoothly form necessary surface oxidation rate and using Si nanowires as a useful matrixes for a wide range of further functionalization.

Since many years silicon is the main material of micro- and nanoelectronics. The realization of the room temperature visible photoluminescence in porous silicon formed by the traditional electrochemical method [1] still causes active scientific interest. Nanostructured crystalline silicon nanowires (SiNWs) which are very popular nowadays have good perspectives of application in various fields, including optoelectronics, photonics and photovoltaics [2–6] all connected with the developed surface functionalization. Simple top-down technique such as metal-assisted wet chemical etching (MAWCE) which is involving only processes under the near ambient conditions and leading to a low-cost process can be applied for the formation of nanostructured silicon surfaces. The flexible engineering of electronic and optical properties in SiNWs can be effectively achievable by applying MAWCE approach. For that reason, a detailed study of local atomic and electronic structure features is strongly required, depending on the formation conditions specificity. Therefore, the usage of non-destructive methods of X-ray spectroscopy, which have a high sensitivity to the local surrounding of given sort of atoms is strongly demanded. The possibilities of X-ray Absorption Near Edge Structure (XANES) spectroscopy with the use of synchrotron radiation in the study of atomic and electronic structure were demonstrated earlier for different kind of nanomaterials [7–9] with different character of atomic ordering, composition and surface role [10–13].

SiNW arrays were fabricated by top-down wet-chemical method in details described previously [14]. Silver particles were deposited on the silicon surface and than immersed in a mixture of 5 M HF and $H_2O_2$ (volume ratio 10:1). During this step, the Ag particles sink into the substrate while forming silicon nanowires at the uncoated areas [14,15]. We produced the silicon nanowires on a highly and lowly boron doped substrate (doping concentration $10^{19}$ cm$^{-3}$ and $10^{16}$ cm$^{-3}$, resistivity $< 0.005\ \Omega$ cm and 1–5 $\Omega$ cm, respectively) so the final samples were named as HD-SiNW and LD-SiNW, respectively. The dopant in silicon is a potential defect and by all etching processes (wet or dry etching) the etching velocity is depending on the defect concentrations. It means that as higher is the dopant concentration as faster is etching of silicon and the porosity of SiNWs also increases [3,14]. LD-SiNWs array was formed in 20 min of etching time and HD-SiNWs array was formed for 60 min. The resulting silicon nanowires show a very high porosity as shown in Fig. 1. The morphology of the formed SiNWs array was studied using the dual beam FEI Helios Nanolab 600i scanning electron microscope (SEM). Synchrotron XANES spectra represent the distribution of the local partial density of electronic states in the conduction band [16] being really sensitive to the specificity of the local surrounding of given atoms [7–13]. XANES spectra relative to K core level of silicon were obtained with the DCM beamline of the SRC synchrotron (University of Wisconsin Madison, Stoughton, USA). Energy resolution was about 0.5 eV with beam energy in the ring of 800 MeV and current 160–250 mA. Probing depth was considered as 70 nm according to Ref. [10]. Vacuum in the analytical chamber was continuously kept at $10^{-7}$ Torr during spectra acquisition. Total

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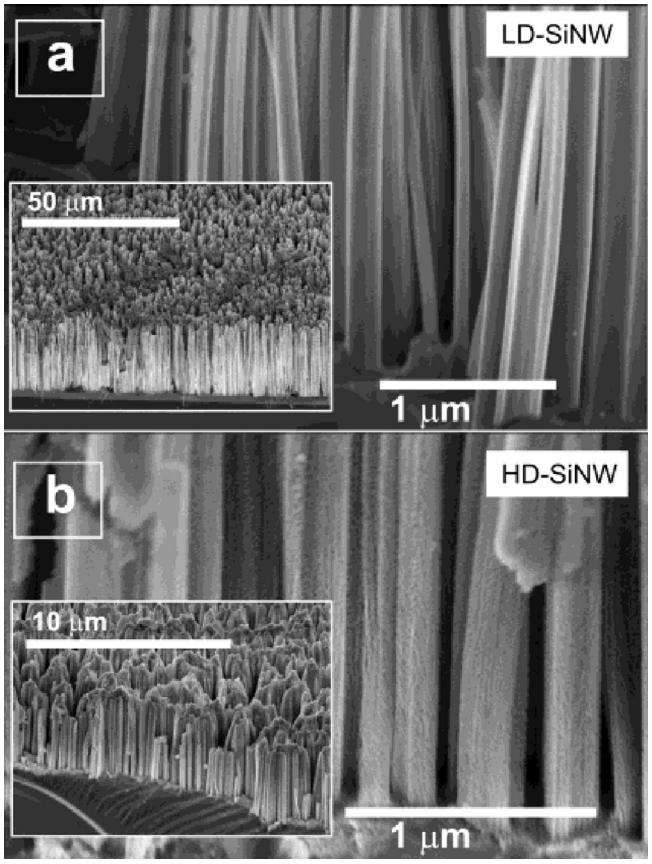


**Fig. 1.** Cross sectional and planar SEM views of the formed MAWCE SiNW arrays: (a) LD-SiNWs array; (b) HD-SiNWs array.

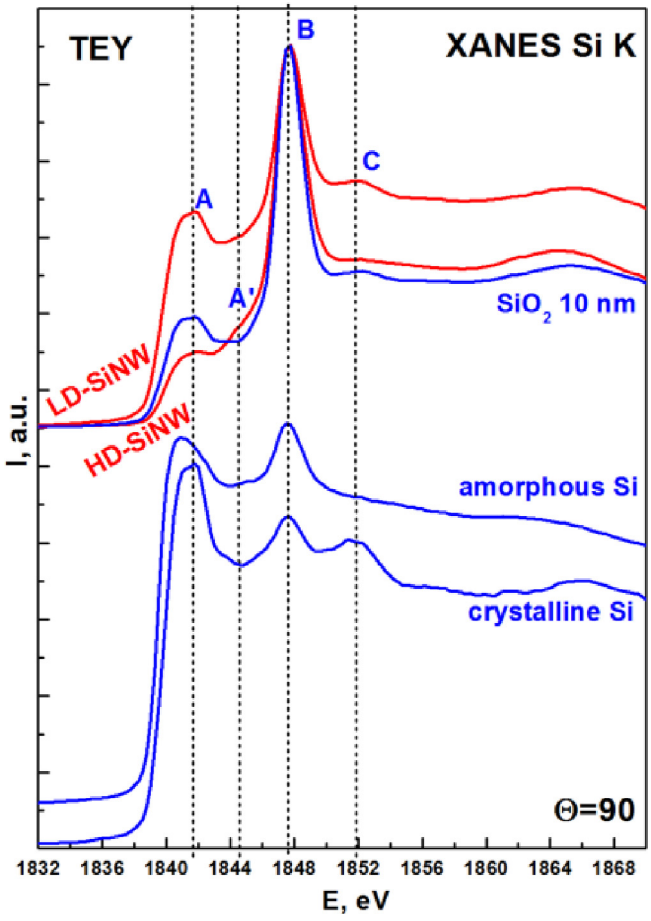


**Fig. 2.** Si K XANES for reference samples of c-Si, a-Si and $SiO_2$ (blue curves) together with SiNW arrays (red curves). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electron yield mode was used with the sample (drain) current detection technique. Synchrotron radiation grazing angle (Θ) was found 90° to the samples surface. Signal of pure Au mesh ($I_0$) was used for measured spectra normalization.

Morphology of the formed SiNWs is presented at the Fig. 1. Inserts in Fig. 1 show SEM planar views of the LD-SiNW and HD-SiNW arrays with morphological uniformity. One can see that for LD-SiNW the surface of the formed wires are smooth and similar to the bulk silicon. Length of the formed SiNWs is exceeding several micrometers with diameter of about tens of nanometers. From another side for the HD-SiNW considerably structured and highly porous surface morphology with relatively thicker wires have been observed. So by changing of the initial silicon substrate resistivity and certain formation parameters (e.g., etching time) we can effectively vary the morphology of the formed SiNWs array.

Fig. 2 presents XANES Si K edges (blue lines) observed for the crystalline silicon wafer (c-Si), amorphous (a-Si) silicon and 10 nm silicon dioxide ($SiO_2$) film on Si surface as references and their comparison with experimentally observed XANES Si K edges (red lines) for the lowly and heavily doped SiNW arrays. It is seen the presence of the fine structure distribution from XANES Si K spectra and presences of the Si atoms ordering in the analyzed surface layer. Peak A at ~1842 eV is generally attributed to Si atoms while by peak C presence at ~1852 eV we can specify the atomic ordering since this feature is peculiar only to c-Si [9,10]. Feature B is the evidence of the natural silicon oxide thin film at the c-Si and the a-Si reference samples and appearing dominant for the $SiO_2$ 10 nm reference film. Peak A' is related to silicon suboxide according to Refs. [11,17].

The relation between peaks A and B gives an information about the thickness of the silicon oxide layer formed over the probing surface depth [10]. Here we have to note that for SiNWs the estimation of the $SiO_2$ depth should be made carefully since falling X-rays of synchrotron radiation excites spectra not only the top parts of each wire but the wires side bevels.

Based on these results and relative intensities ratio between A and B peaks we can conclude that for nanowire arrays the thickness of the oxidized wire part for lowly doped substrate is at least two times lower in comparison to the highly doped SiNWs. For latter wires this may be caused by noticeably texturized surface of each wire side parts (see Fig. 1). Finally, this developed surface can be responsible for silicon suboxide traces found according to the peak A' observation (Fig. 2). Thus we can conclude that the flexibility of certain technology approaches opens up the possibility to controlled formation of the desired Si nanowires arrays aiming further wide range functionalization.

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