Mechanical strain in the structure of array of silicon nanowires grown on a silicon substrate

A.I. Klimovskaya*, B.D. Shanina, A.S. Nikolenko, P.M. Lytvyn, Yu.Yu. Kalashnyk, V.V. Strelchuk

V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine
41, prospect Nauky, 03680 Kyiv, Ukraine
**E-mail: kaignn@gmail.com*

Abstract. We present experimental research on mechanical strains in the structure consisting of an array of silicon nanowires grown using the metal-enhanced CVD technique on boron-doped Si(111) and Si(100) substrates. Using the electron beam induced current on a cleaved substrate, electron spin resonance, and confocal micro-Raman spectroscopy, we found that growth of silicon nanowires on a native (silicon) substrate gives rise to a strain both of the substrate and grown nanowires, too. An occurrence of the strain in the substrate was revealed by an initiation of the electron spin resonance signal from boron atoms, which is not resolved usually in unstressed silicon due to a complex energy structure of a top of the valence band. Furthermore, the strain of the substrate was proved additionally by observation of spatial dependence of the current induced by electron beam on a cleaved substrate, and by the spectral shift of Raman peak related to 3C-Si near the interface "substrate – array of nanowires". Mechanical strain in the nanowires was more pronounced in the Raman spectra, which also revealed their complex crystal structure consisting of cubic and hexagonal phases of silicon. Model of the strain rise is discussed.

Keywords: array of silicon nanowires, mechanical strain, polymorphism of wires, CVD-technology, gold-enhanced growth.

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1. Introduction

In the recent years, great attention has been paid to the development of devices based on silicon nanowires due to a broad range of possible applications in nanoelectronics, optoelectronics and bio-nanoelectronics [1-3]. Special interest has been attracted to NEM devices that allow development of smart system for metrology, communication and information technologies [4, 5]. NEM system, especially like a compact array of NEM oscillators formed on a single crystal, proposed by Blick with coauthors [5], operates like "Carnot cycle" giving rise to solve partly a major problem of the current nanoelectronics, the so-called heat death. The central part of all NEM devices is nano- or micro-oscillators attached to a substrate. Stability, useful operation time and a mode of the device operation are evident to depend strongly on mechanical properties of the oscillating electrode and on a mechanical strength of its attachment. Therefore, a special attention has been paid to study mechanical properties of nanowires [6-9] and to different methods to strengthen the attachment of nanowires [10, 11].

Mechanical strains in a substrate covered by non-native films have been studied for a long time. Special interest to this problem arose with an increase of the packing density of multi-component IC's [12]. Effect of mechanical strain in these structures is known to originate from differences in translational symmetry and coefficients of thermal expansion of the substrate and the covering non-native films. One can expect a similar strain rise after growth of silicon nanowires on a non-native substrate. Application of a single wire (single NEM device) or an array of nanowires (array of NEM devices) grown on a native substrate as a comprehensive whole is expected to be more promising to improve a quality of NEM system.

In this paper, we present the results of experimental study of structures that consist of an array of silicon nanowires grown on silicon substrate and show that a strong mechanical strain may arise even in the structure of the array of nanowires grown on a native substrate. Complex geometry of the structure with nano-scale wires may initiate strong mechanical strains.

2. Experimental

Two sets of arrays of silicon nanowires were studied in the current work. Both sets were grown by similar technologies on boron-doped silicon substrates by using gold-catalyzed chemical vapor deposition in a flow of gas mixture (SiH_4+H_2+HCl) and which differs between each other by crystallographic orientation of the substrate. The first one was grown on Si (100) substrate in Hewlett-Packard Laboratories and kindly presented for this experiment by S. Sharma and T.I. Kamins [13]. The second set of the arrays were grown on Si (111) substrate in our laboratory in the framework of the STCU project #4080. In both cases, the substrates were doped by boron. The boron concentration was about 10^{15} cm^{-3}. Examples of the structures under investigation are shown in Fig. 1. The nanowires are known [14] to grow predominately along ⟨111⟩ direction independently of crystallographic orientation of the substrate. To study a mechanical strain of these structures, we used electron beam induced current (EBIC), electron spin resonance (ESR), and confocal micro-Raman spectroscopy (CMRS).

EBIC experiment was carried out using scanning electron microscopy. Energy of the electron beam was equal to 20 KeV, which does not produce structural damage [15] and induces phenomena analogues to those observed in a case of the light excitation. A SEM image of cleaved substrate with an array of nanowires and corresponding current induced by electron beam are shown in Fig. 2. At a large distance from the interface (more than 6 µm), it is seen a homogeneous distribution of the current that indicates no strain inside the substrate. A slow increase in the current in a region between 6 and 2 µm indicates increase in the strain and probably activation of interstitial formerly non-active boron atoms generating a p^+-p junction nearby the interface. Sharp increase of the induced current at a distance less than 2 µm from the interface and a strong oscillating behaviour of the current behind the interface are evidently caused by the growth of the nanowires on the substrate's surface.

Local strain at the interface of the structures was additionally found by occurrence of an electron spin resonance (ESR) signal of boron atoms that dope the substrate. It should be pointed that in stress-free silicon, ESR from acceptors is not observed due to degeneracy of the valence bands of light and heavy holes. Paramagnetic absorption by acceptors in silicon is observed usually under an external mechanical strain σ giving rise to a splitting of the valence bands, which has to be much greater than the Zeeman energy. The first experimental research of ESR from boron in silicon was performed by Feher *et al.* [16]. That experiment was carried in a wide range of external stress up to 900 GPa. The concentration of boron atoms in that experiment varied between $5\cdot10^{15}$ and $2\cdot10^{17}$ cm^{-3}, and the *g*-factor values in this range of concentrations were found to be concentration independent. According to this research, stress dependence of the

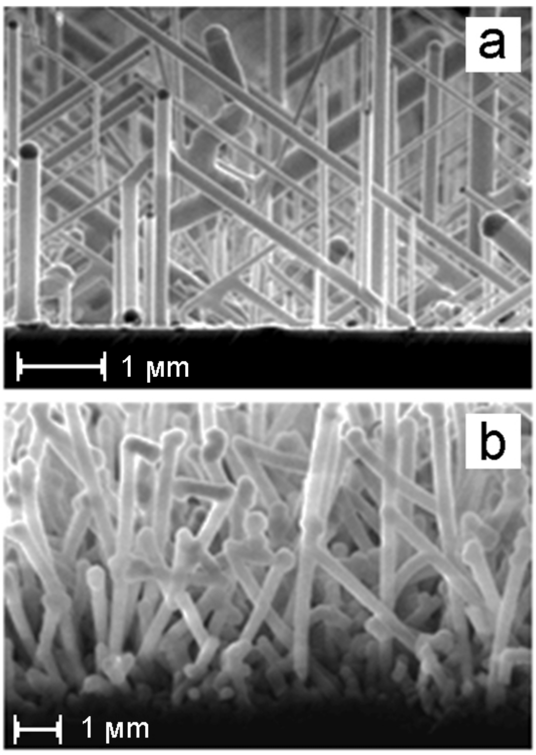

Fig. 1. SEM images of cross-sections for cleaved substrates with different densities of nanowires grown on: (a) Si (100) and (b) Si (111); tilt angles of the view relative to a plane of the figure are ~ 70° and 90°, correspondingly.

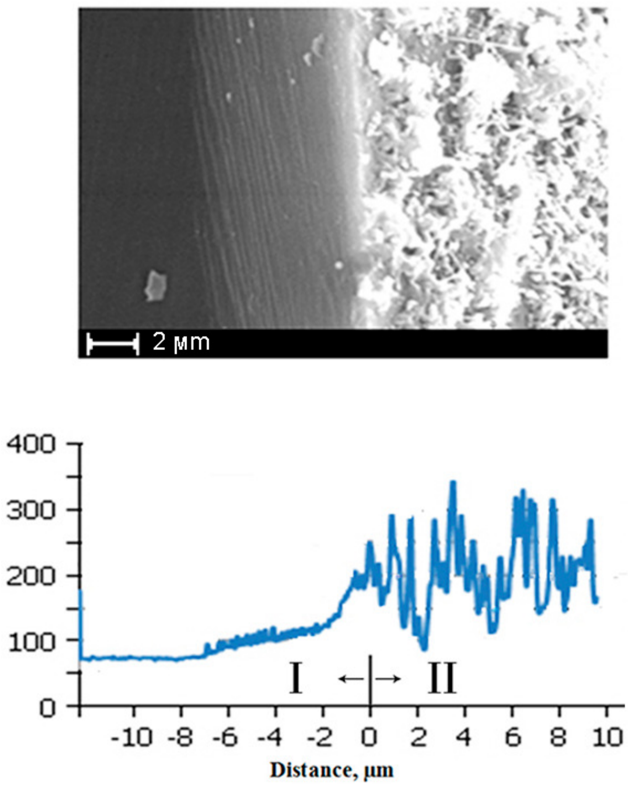

Fig. 2. SEM image and EBIC signal of the cross-section of a cleaved substrate with an array of nanowires.

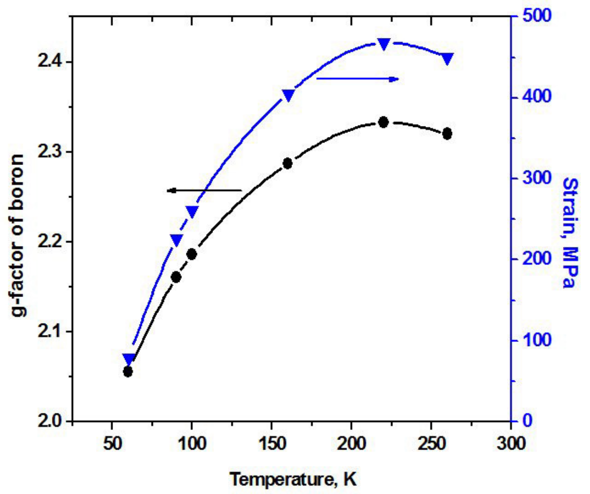

Fig. 3. Temperature dependence of the g-factor of boron atoms and strain of the interface layer of the substrate.

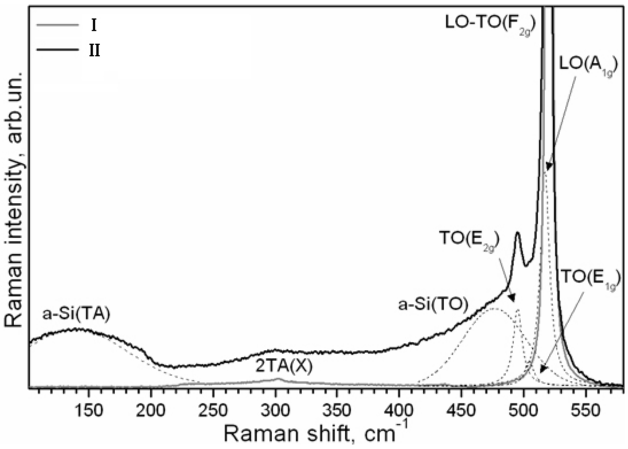

Fig. 4. Raman spectra measured on the cleaved edge of the investigated structure: (i) in the region from 6 down to 2 µm in the substrate and (ii) directly in the vicinity of interface. Spectra are normalized on the intensity of LO-TO(F_{2g}) mode of 3C-Si.

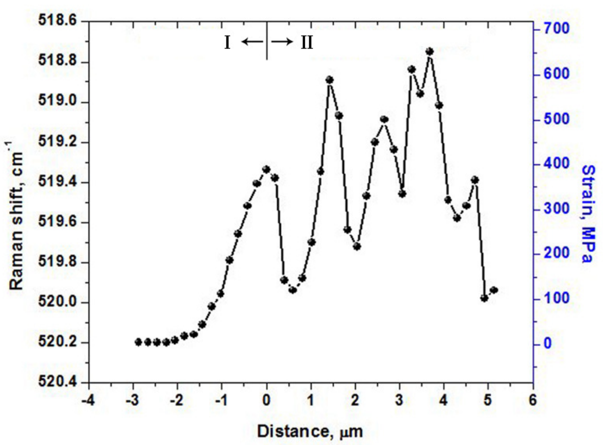

Fig. 5. Distribution of Raman shift of LO-TO (Si) phonon mode and strains in the lateral scan measured on the cleaved edge of the investigated structure from Si substrate to nanowire top.

g-factor for a stress σ along [100] direction and for the magnetic field orthogonal to this direction, which corresponds to conditions of our experiment, was found to be:

$$\frac{dg_{\perp}}{d\sigma} = 7.0 \cdot 10^{-10} \text{ Pa}^{-1}. \quad (1)$$

In spite of the fact that our experiment was performed without external stress, appearance of the paramagnetic signal from boron atoms proves a spontaneous occurrence of a strain in the substrate. We found that the magnitude of strain strongly depends on temperature. So, the strain dependence of the *g*-factor we may present as follows:

$$\frac{dg_{\perp}}{d\sigma} = \frac{dg}{dT} \cdot \frac{dT}{d\sigma}. \quad (2)$$

So far as the concentration of boron atoms in the substrate used in the current experiment is close to the concentration in the experiments performed in [16], we can recalculate our experimental data on temperature evolution of *g*-factor, presented in Fig. 3, using the magnitude of $\frac{dg_{\perp}}{d\sigma}$ found in Ref. [16], into a temperature dependence of the strain σ(*T*). According to this assessment, we found that the strain in the investigated substrate changes from 50 up to 450 MPa within the temperature range 60 to 260 K.

To elucidate reasons of the strain rise in the substrate and its temperature dependence, we performed confocal micro-Raman mapping in the vicinity of the interface. Micro-Raman spectra were measured at room temperature using triple Raman spectrometer T-64000 Horiba Jobin-Yvon equipped with electrically cooled CCD detector. Experiment was performed in backscattering geometry. The line 488 nm of Ar-Kr ion laser was used for excitation. Exciting radiation with power less than 1 mW was focused on the sample surface with the 100×/0.9 Olympus objective. Experiment was performed in backscattering geometry.

Fig. 4 shows typical micro-Raman spectra measured: (i) in a substrate at a distance more than 2 µm from the interface (in the homogeneous region of the substrate) and (ii) directly at the interface where nanowires start to grow. The Raman spectrum of the homogeneous region of the Si substrate consists of two peaks associated with the triply degenerated long-wavelength optical phonons LO-TO(T_{2g}) and the second-order Raman scattering assigned by 2TA(X) phonons. These Raman spectra are typical for the unstrained silicon with the cubic (Si I) structure. Quite different Raman spectra are observed at the interface region. Along with LO-TO peak of Si cubic phase (3C-Si), additional Raman peaks appear, which are related to the TO(E_{1g}) and TO(E_{2g}) phonons proper to the hexagonal phase of silicon [17] and quite wide bands at about 150 and 480 cm^{-1} associated with TO and TA vibration modes of the amorphous silicon (a-Si), respectively. Intensities of Raman bands of a-Si increase with moving to the interface and are sensitive to the nanowire growth conditions. It is worth to note that contribution of the cubic phase to Raman spectra remains prevalent for all the regions of the structure, however, the frequency position and width of TO and TA bands in the amorphous silicon depends on the distance from the interface.

A spatial distribution of the band related to the cubic phase of silicon along the cleaved surface is shown in Fig. 5 (the left hand *y*-coordinate). The Raman peak related to 3C-Si band in all regions of the structure was found to shift towards smaller energies and indicate a crystalline lattice expansion. In order to assess a magnitude of the strain from Raman spectra, we recalculated the shifts of Raman peak into the strain according to [12]. Results of the assessment are presented in Fig. 5 (the right hand *y*-coordinate). According to this experiment, the strain in the interfacial region of the substrate at 300 K reaches the value 400 MPa. Its magnitude is in a good agreement with the results of the ESR study. Therefore, strong oscillating behaviour of the strain behind the interface, found in the CMRS experiments, may be related to inhomogeneous distribution of the nanowires over the substrate. A magnitude of the strain in this region is much larger, then in the interface, and ranges from 100 up to 600 MPa.

3. Discussion

Let us consider what reasons initiated this quite high strain in the complex structure under investigation. Summarizing the experimental results, we found that the structure consists of bonded together several layers with essentially different thicknesses, namely:

(i) thick substrate of the unstrained silicon with the cubic (Si I) structure (~ 500 µm);

(ii) strained interface region of the substrate with the cubic (Si I) structure (~ 2 µm);

(iii) array of nanowires (~ 10 µm) surrounded by the thin epitaxial layer of hexagonal and amorphous phase that grows simultaneously with the nanowires;

(iv) slight amount of a thin oxide layer over all surface of the structure.

Taking into account the strong temperature dependence of the strain found using ESR, we may assume that the substrate and layers covering the substrate have different thermal expansion. Technology for the structure formation consists of two major stages: patterning of the substrate with growth-seeds and growing the array of nanowires [18]. Both of these stages take place at the temperatures from 500 to 700 °C, and then the structures are cooled down to the room temperature.

The interface layer may generate a strain, but it is doubtful that this difference may cause a significant tension, because the inclusions of hexagonal and amorphous silicon in the interface layer are small, and the thermal coefficient of amorphous silicon weakly vary from that of cubic silicon [19]. A simple assessment of contribution from the residual catalyst may result in an appreciable strain, only if a fraction of surface area occupied by the catalyst is sufficiently large. For instance, the gold coverage of ~ 0.3 gives rise to the strain about 50 MPa. This value is by order of magnitude smaller than that observed in our experiments. Thus, neither difference in thermal coefficients of the interfacial layer, nor residual catalyst may result in the strain close to 600 MPa or higher at room temperature.

More strong and complex three-dimensional strains can be set up with a coating layer having non-planar geometry. In contrast to multilayered planar two-dimensional structures, the highly developed nano-relief of the base of the growing nanowires may more strongly affect the strain. Let us consider forces that act in this structure. An initial stage of the nanowire growth leads, as a rule, to shaping a nanowire base with a negative curvature of the surface [20]. The curvature sign of a surface is known to specify the direction of the force $\mathbf{F}_{st}^{i}$ related to a surface tension [21]. The negative curvature of the surface corresponds to the force that is orientated outside of the nanowire base with the components parallel f_l^i and orthogonal f_n^i to the plane of the substrate, which is shown in Fig. 6. Summarizing action of both components of the force $\mathbf{F}_{st}^{i}$ related to a surface tension and taking into account a high density of nanowires on the substrate (~10^8 cm^{-2}), we may conclude that the interfacial layer of the substrate undergoes tensile strain.

Furthermore, force $\mathbf{F}_{st}^{i}$ related to a surface tension gives rise also to strong stress of whole nanowires that sometimes lead to appearance of polymorph phases of silicon [22].

It should be additionally noted that growth of nanowires is accompanied by significant (by several orders of magnitude) increase of surface area that means increase in relation the surface atoms to the bulk ones. Inasmuch as a cohesive energy of the surficial atoms has to be smaller than that of bulk atoms, thermoelastic properties of nanoobject has to depend on the object size. There are a number of theoretical and experimental researches on this topic. Using reasonable assumption that cohesive energy of the surficial atoms is about twice smaller than that of bulk atoms, the thermal expansion coefficient of nanocrystalline materials was calculated in Ref. [23]. According to this calculation, the thermal coefficient of the layer with nanowires has to be larger than that of the substrate, and therefore, may explain the temperature dependence of the strain observed in the ESR measurements.

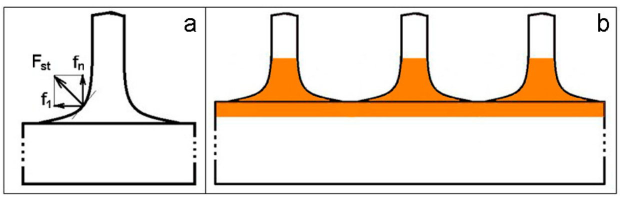

Fig. 6. Sketch of a nanowire base (a); and an array of nanowires, colored part of the structure correspond to a region subjected to tensile strain (b).

4. Conclusion

Summarizing, we may conclude that a complex structure like an array of nanowires grown even on a native substrate is strongly strained due to highly developed nano-relief of the base that arise during nanowire growth. The strain of the interface and the grown nanowires imply as well on fundamental properties on both the substrate and nanowires that should be taken into account in development of nanoelectronic devices based on these complex structures.

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Authors and CV

A.I. Klimovskaya, Doctor of Sciences in Physics and Mathematics, Leading Researcher at the Department of Ion Beam Engineering, V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. The area of scientific interests includes surface science, hot electrons and intervalley electron redistribution at silicon surface; magnetic properties of surface layers at quantum limit; current and/or voltage instability in MOS-structures; femtosecond optical pulse generation; intelligent microsensors of temperature, humidity, light intensity, micro moving and DC-AC micro converters; magnetic sensors for high power cryogenic turbo generators operating at extreme temperatures, vibration and rotation loads; magnetic sensors of short magnetic pulses and for diagnostic space distribution of very small magnetic fields; growth silicon and silicon/germanium wires and their application for regeneration of nervous tissue.

B.D. Shanina, Doctor of Sciences in Physics and Mathematics, Professor, Leading Researcher at the Department of Optics and Spectroscopy, V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. The area of her scientific interests includes the theory of semiconductor electron structure and magnetic resonance in semiconductor materials.

A.S. Nikolenko, Ph.D., Senior Researcher at the Optical Submicron Spectroscopy Laboratory, V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. Field of research: semiconductor physics, semiconductor nanostructures and heterostructures, Raman, photoluminescence and FTIR spectroscopy. He is the author of more than 60 science papers and technical patents.

P.M. Lytvyn, PhD in Physics and Mathematics, Senior Researcher of the Laboratory of Electron probe methods of structural and elemental analysis of semiconductor materials and systems, V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. The area of scientific interests includes the AFM and X-ray investigation of semiconductor materials and systems.

Yu.Yu. Kalashnyk, PhD student, Researcher at the Department of Ion Beam Engineering, V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. The area of scientific interests includes the nanowires growth, silicon nanowires, study of the properties of low-dimensional structures.

V.V. Strelchuk, Professor, Doctor of Sciences in Physics and Mathematics, Head of Optical Submicron Spectroscopy Laboratory at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. Field of research: physics of semiconductors, Raman and photoluminescence spectroscopy of semiconductors, nanostructures and nanoscale materials. He is the author of more than 100 scientifical publications and technical patents.