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Wire-like submicron crystal as a natural heterostructure

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Abstract

Silicon and silicon–germanium wire-like crystals grown by self-organizing processes have been studied by high-resolution transmission electron microscopy, scanning tunnelling microscopy, and ion and Auger spectroscopy. It is shown for the first time that such a crystal consists of a central part of bulk material and a nanoporous envelope and that these crystals represent the smallest Si-based heterostructures currently known. Possible reasons for such a structure developing for wire-like crystals are discussed, taking into account size effects in the growth process. The surprising thing is that they reveal Auger spectra particular to the atomically clean surfaces which do not vary upon storage in the atmosphere for a few years. It is also shown that the morphology and thickness of the envelope may be controlled by the growth conditions; therefore this technology may be applied in engineering new nanoelectronics materials.

1. Introduction

The self-organizing growth of various objects in the nanoworld is becoming of ever greater interest due to the promise for production of new-generation electronic materials. Nevertheless, there are many unsolved problems in nanophysics and nanotechnology. Metastability is a principal feature of nano-objects, which are usually obtained in out-of-equilibrium conditions [1]. Experiments with silicon and silicon–germanium wire-like crystals grown by self-organizing processes suggest that they may be useful for solving this problem.

It has been previously demonstrated [2–5] that these crystals not only have unique mechanical properties, but also reveal a change in the lattice parameter, optical properties, and state of the surface as their diameter decreases. Of prime importance is the high stability of their surfaces as compared with the stability of surfaces prepared artificially. The origin of these effects was presumed to be connected with the known [6] reconstruction of the uppermost layers of the crystal and the increased role of the surface as its diameter decreases. But such explanations could be open to question in view of the size effects operative even in crystals with diameters of about 1000 nm. According to the conventional viewpoint on surface reconstruction in a semi-infinite crystal approximation, the structural changes decay sharply with increasing distance from the surface and are already very small by the third or fourth

subsurface layer. On the other hand, in microcrystals of cylindrical shape, the role of the surface should be enhanced due to the greater ratio of the number of surface atoms to the number of atoms in the bulk part of the crystal. Moreover, in crystals with a curved surface, Laplace forces F_s act. Here

$$F_s = \sigma \sum_i 1/r_i$$

where σ is the surface tension and the r_i are the radii of curvature. All these factors should tend to increase the number of reconstructed atomic layers and their influence on the inner part of the microcrystal should be stronger than that in crystals with a plane surface.

The purpose of the present work is to elucidate how these crystals are constructed. Here we present the results of direct examination of the microstructure in the wire-like crystals using a high-resolution transmission electron microscope (HRTEM) and a scanning tunnelling microscope (STM). In order to characterize the composition of the crystals and their surfaces, we have used a secondary-ion mass spectroscope (SIMS) and an Auger electron spectroscope (AES). It is found for the first time that each crystal consists of a central part of bulk material and an envelope of different structure. The shape and thickness of the latter depend on the growth conditions and the diameter of the crystal; the envelope is present for all crystals.

2. Experiment

To grow the wire-like crystals, various technologies may be used [7]. Most of the crystals studied here were grown by the method of vapour-transport reaction in a closed tube containing the initial semiconductors, transporting gas (bromine or iodine), and metal catalysts, e.g. Au, Pt, Al, Ni, Cu [8]. The main reaction used in the process is $\text{Si} + \text{Br}_2 = \text{SiBr}_2 = \text{Si} + \text{SiBr}_4$.

In the case of the Si/Ge growth, there were similar reactions with Ge. The pure Si or Ge/Si that is rejected condenses on metal droplets created previously on a substrate. When the concentration of these atoms in the metal–semiconductor solution reaches a certain level, a filament-like crystal begins to grow.

In order to check the crystalline structure, double-crystal x-ray diffraction and electron microscopy were used. Individual microcrystals were characterized using a high-resolution transmission electron microscope.

All of the crystals grown may be divided into two groups. Figures 1 to 6 show micrographs of the cross-sections of two kinds of typical crystal. In each case, the plane of the micrographs is parallel to a long axis of the crystal and coincides with the $\langle 111 \rangle$ direction (indicated in the micrographs by arrows).

In general, the crystals have complex structures and consist of two distinguishable parts: a central part and an external envelope. This is clearly seen from figure 1. The central part, for both types of crystal, is diamond-like silicon (silicon/germanium) and has homogeneous structure. But the crystals differ from each other in the structure of their envelopes. By varying the growth conditions (temperature gradient in the reaction tube, temperature of crystal growth, transporting gas concentration, and type of metal catalyst) we may grow crystals with homogeneous or structurally complex envelopes. The crystal shown in figure 1 and on an enlarged scale in figure 2 represents the first type of crystal. It is evident from the micrographs that the transition layer between the two parts of the crystal is very small and its thickness is just a few nanometres. Moreover, the envelope has a nanoporous structure. The size of individual pores and the thickness of the separating walls are equal to 0.4 nm. These sizes increase moderately with distance from the crystal centre.

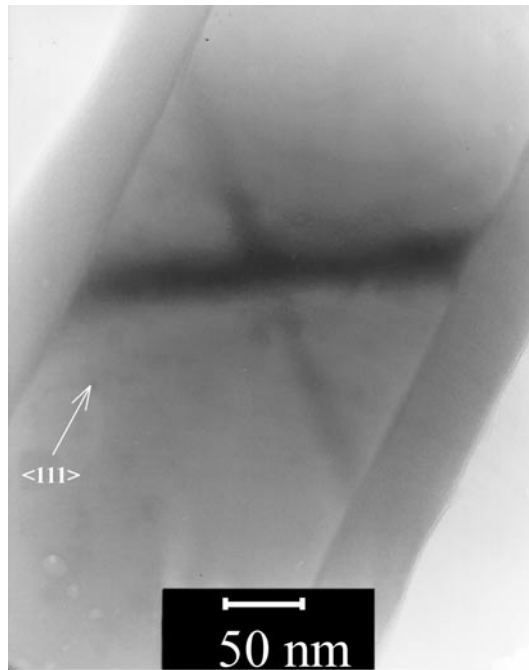


Figure 1. A micrograph of a cross-section of a crystal. The plane of the figure is parallel to the long axis of the crystal coinciding with the $\langle 111 \rangle$ crystallographic direction (indicated in the figure by an arrow). The dark line in the central part suggests that this is a twin crystal.

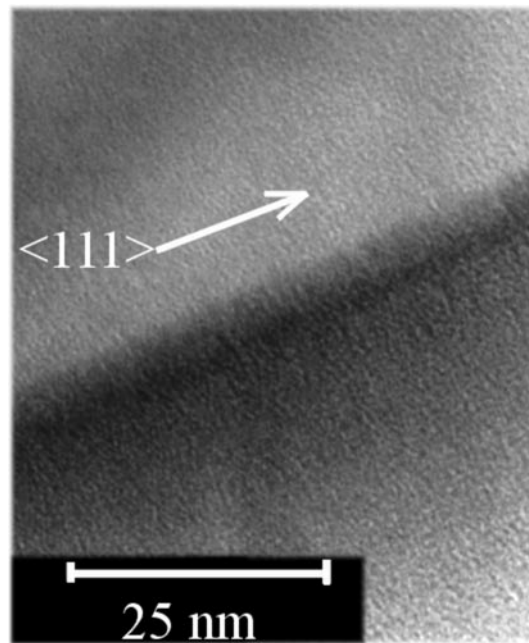


Figure 2. A fragment of a crystal. The upper left and lower right parts of the figure represent the central part and the envelope of the crystal, respectively. The dark band (along the $\langle 111 \rangle$ direction) is an interfacial layer separating these parts.

A micrograph of a fragment of another type of crystal grown under different conditions is presented in figure 3. The bulk part of the crystal is seen in the upper right corner of the figure (light region). It is homogeneous, without any substructure. But the envelope incorporates several layers separated by sharp interfaces parallel to the long axis of the crystal ($\langle 111 \rangle$). The outside of the envelope consists of semi-spherical nuclei and reveals nanoporosity. The linear size of the nucleus is 150 nm, and the pore size and wall thickness are greater than in the crystals of the first type and equal to 3 and 1.5 nm, respectively. Other parts of the envelope are more homogeneous; nevertheless, nanostructure may be seen here too. It should be emphasized that the innermost layer of the envelope (immediately adjacent to the bulk part of the crystal) has pores of larger sizes and densities than those observed at its interface with the nuclei. This may be seen from figure 4 where the direction from the top of the figure to the bottom corresponds to the direction from the central part of the crystal to its outer surface.



Figure 3. A fragment of a crystal. The central part of the crystal is seen in the upper right corner of the figure. Layers immediately adjacent to this part represent the complex envelope.

Closer examination of the envelopes of the two types of crystal (presented in figures 5 and 6) reveals some *ordering* of the pores. In view of the fact that the size of the smallest pores and the thicknesses of the walls separating the pores are comparable with the sizes of the atoms (Si, Ge) and that the pores are ordered, the envelope may be considered as a new type of structure.

To achieve a better understanding of the reasons for such morphology of the crystals developing, we have used additional methods of characterization: SIMS, STM, and AES. The results of these studies will be published in detail elsewhere [9], although we present some of them (to elucidate, for the first time, the complex structure and composition of the crystals) here.

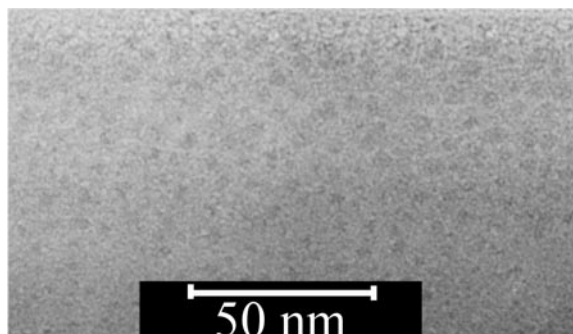


Figure 4. A HRTEM micrograph of the innermost layer of the envelope immediately adjacent to the bulk part of the crystal in a crystal of the second type. The direction from the top of the figure to the bottom corresponds to the direction from the central part of the crystal to its outer surface. Dark spots correspond to the pores.

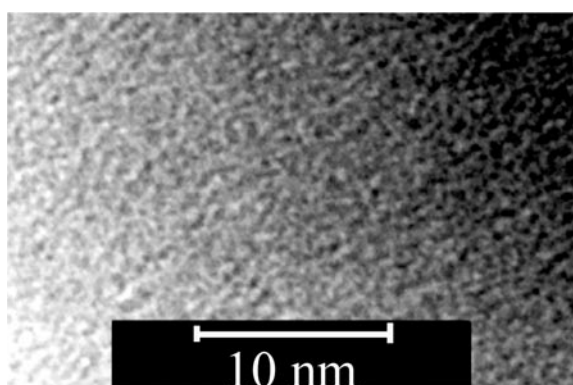


Figure 5. A HRTEM image of a cross-section of the different inner parts of the homogeneous envelope in a crystal of the first type. The pore size and wall thickness are about 0.4 nm.

The porous nature of the envelope was proved by SIMS investigations of the depth profile of the crystals. The measured profiles showed clearly a step-like distribution of the main as well as the background atoms and proved the existence of the complex structure of the crystals. Furthermore, the step-like transition from the envelope to the bulk of the crystal is not accompanied by a marked change in the relationship between the densities of different atoms. The density of the envelope was found to be much smaller (by one or two orders of magnitude) than that of the central part of the crystal. Similar profiles were observed for all of the crystals, while the envelopes of the crystals differ in density and/or thickness. The estimated values of the thickness match well with the ones obtained from the direct HRTEM examination. The main results of this study are the following:

- (i) both the envelopes and the bulk parts of the crystals consist of the main material (Si or GeSi), and there are background impurities;
- (ii) the density of the envelope is one or two orders of magnitude smaller than that in the bulk part; and
- (iii) the relationship between the concentrations of the main and background atoms does not markedly differ between the two parts of the crystal.

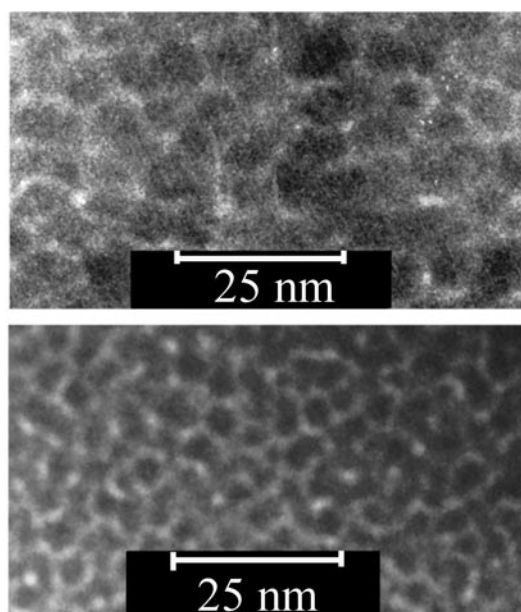


Figure 6. HRTEM images of a cross-section of the different inner parts of the complex envelope in a crystal of the second type.

STM study has shown that the curved cylinder-like surface of the crystal is formed by a series of nanoscale steps. It is striking that the STM experimental study may be carried out in the ambient atmosphere.

In order to check the chemical state of the surface, we have used AES. In the Auger spectra, we have observed the LVV and KLL peaks of pure silicon. Furthermore, these peaks have been observed both for the as-grown crystals and for crystals stored in air for a few years. Such spectra have *never been observed* for real silicon surfaces. The peaks of pure silicon appear only in the spectra of atomically clean surfaces in ultrahigh vacuum or in spectra of surfaces covered by ultrathin (<1 nm) film, transparent to secondary Auger electrons. Such a film might be created by the transporting gas (bromine or iodine) that plays a role in the growth process. Notwithstanding the fact that the depth profile shows the incorporation of some amount of this gas into both the envelope and the bulk part of crystal, we have not observed Auger spectra particular to these gases. Therefore, from the results obtained we cannot reach a conclusion as regards the nature of the film, if it does indeed exist. It is more likely that the surfaces of wire-like crystals grown by self-organized processes have saturated atomic bonds. But this is still an assumption that needs further investigation.

So, AES experiment suggests different properties of the crystal surfaces as compared with the properties of artificially prepared ones—e.g. by etching of bulk material.

3. Discussion

To discuss the appearance of the envelope that causes the special properties of the wire-like crystals, we focus attention on the mechanisms of crystal growth. The process of growing the crystals using the method involves a few basic steps: the creation of crystal-growth seeds and growing crystals by the vapour–liquid–crystal (VLC) and vapour–crystal (VC) mechanisms.

The VLC growth includes the capture of atoms from vapour by liquid-metal droplets (growth seeds), diffusion of the captured atoms towards the interface between the droplet and growing crystal, and their incorporation into the crystal. The VLC mechanism provides fast elongation of microcrystals.

The VC growth includes the direct capture of atoms by the side surface and leads to an increase in thickness. In this case, the character of the incorporation of the atoms into the crystal should depend strongly on the relationship between the atomic flux J_d due to the surface diffusion and the flux J_c of atoms captured by the surface from the vapour. Regardless of the curvature of the surface, the main characteristics of the process should be similar to those found previously [10, 11] for growth of films on plane surfaces. Therefore, one may expect, under the condition $J_d > J_c$, the atoms captured by the surface to be homogeneously redistributed over the surface creating a film (in our case, a curved film) that is uniform in thickness. This condition corresponds to the condition for growth of the first type of crystal (figures 1, 2, and 5), while crystals of the second type (figures 3, 4, and 6) were grown when the opposite condition $J_d < J_c$ was obeyed, and 3D nuclei (figure 3) were created during the growth process.

The curvature of the surface should affect both the fluxes: J_d via the micromechanism of diffusion over the curved surface and J_c due to the Gibbs–Thomson relation. The Gibbs–Thomson effect leads to the dependence of the growth rate on the crystal diameter and, as a consequence, it changes the diameter distribution. But the difference of the surface diffusion over the curved surface from the diffusion over a plane surface may be more important in shaping a filament-like crystal and in the creation of a sharp boundary between the central part of the crystal and the envelope.

We assume that during the fast growth of a crystal by the VLC mechanism, the central part of the crystal with the diamond-like structure (the so-called leader) is formed, and its outer surface, in order to minimize the surface energy, is reconstructed. By this means, atoms adsorbed from vapour (in the next stage of the growth by the VC mechanism) cannot create the regular strong bonds required for diamond-like crystals. The new atomic layers formed by the VC mechanism can grow similarly to a film on a mismatched substrate [12], the only difference being that the growth involves monotonic change in the surface curvature, i.e. the substrate (leader) is subjected to differing stress due to Laplace forces. A sharp interface between the central part of the crystal (figures 1 to 3) and its envelope as well as monotonic decay of the size and density of the pores (dark spots in the micrograph of figure 4) with distance away from the crystal centre support this viewpoint. But the concrete reason for the growth of the envelopes with special structure calls for further investigation.

4. Conclusions

The crystals grown by self-organizing processes are shown to be wire-like heterostructures each composed of a central part of bulk material and a nanoporous envelope. They are the smallest Si-based heterostructures known of currently. The total linear size of the heterostructure can be a few tens of nanometres, and the characteristic size of its substructure (the envelope) is of nanometre scale. By varying the growth conditions one may grow crystals of different shapes and structures. Furthermore, these heterostructures, being natural objects, are highly stable, in contrast to those prepared by bulk material etching. More striking was the feature that they reveal Auger spectra particular to the atomically clean surfaces which do not vary upon storage in the atmosphere for a few years. Taking into account additionally that these crystals emit visible light [3], one may consider growing wire-like crystals by using self-organizing processes as a promising technology for the engineering of new materials.

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