The structure, composition, and chemical state of the surface of wire-like silicon nanocrystal grown by self-organization technology

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Abstract

The surfaces of wire-like silicon crystals grown by self-organization processes are characterized using electron microscopy of high resolution, scanning tunnelling microscopy, x-ray microprobe analysis, secondary-ion mass spectroscopy, and Auger electron spectroscopy. The results obtained have shown that the upper layer of each microcrystal is a nanoporous envelope. The composition of the envelope is in general similar to the composition of the bulk part of the crystal but with some differences: the density of the matter—due to the porous nature of the envelope—is much smaller, and the density of metal impurities is slightly increased on the external surface. More striking was the fact that the external surface of the envelope is passive under exposure to oxygen. In Auger spectra of crystals stored in open air for several years, only the LVV and KLL peaks that are specific to the atomically clean silicon surface were observed.

1. Introduction

Technologies based on self-organization processes opened the way to engineering a wide range of nano-objects (nanocrystals or macromolecules). This has become a focus of a large amount of research, predominantly relating to carbon nano-objects [1]; but experiments with other materials, including the one most important for microelectronics, namely silicon, have also been carried out [2].

As the size of a microcrystal decreases, the role of its surface is enhanced. This is always the case, for any crystal prepared by any method, including the preparation of bulk material; but the effect is more pronounced for nanometre-sized and micrometre-sized crystals grown by self-organization technology, because the growth proceeds differently in crystals of

different sizes, and this leads to the formation of surface atomic layers of various structures and thicknesses.

Recent investigations of wire-like silicon crystals have shown that they have complex structure [3] and striking photoluminescence (PL) properties [4]. The crystals each consist of a central part composed of highly strained bulk silicon and a nanoporous envelope. The PL spectra of the crystals transform from the spectra of bulk silicon to completely new spectra with the decrease of the crystal diameter.

To elucidate what the surface of such as crystal consists of, we have characterized the state of the surface using high-resolution transmission electron microscopy (HRTEM), scanning tunnelling microscopy (STM), x-ray microprobe analysis (XMA), secondary-ion mass spectroscopy (SIMS), and Auger electron spectroscopy (AES). These investigations have shown that the surface has unique structure, a special composition, and high passivity under exposure to oxygen.

2. Experimental results

2.1. Technology of crystal growth

The crystals were grown by the method of vapour transport reactions in a closed tube containing bromine and the initial semiconductor:

$$2Si + 2Br_2 \Leftrightarrow 2SiBr_2 \Leftrightarrow Si + SiBr_4.$$

This reaction is reversible. In order to produce a reaction with rejection of pure silicon (the right-hand part of equation (1)), a temperature gradient was created in the tube. To control the deposition of the rejected atoms as well as further growth of microcrystals, various metals are used. To this end, droplets are formed on a silicon or dielectric substrate by different methods [5]. Due to the enormous difference between the sticking coefficients of metal and semiconductor (dielectric), the rejected silicon atoms are absorbed predominantly by the metal droplets. When the proportion of these atoms in the droplet reaches more than 70%, the growth of microcrystal begins. The first stage of the growth consists in capture of silicon atoms from a liquid metal–semiconductor droplet by the growing crystal. This is the so-called vapour–liquid–crystal (VLC) mechanism which leads to a fast elongation of the crystal, primarily along the $\langle 111 \rangle$ direction. The second stage is direct capture of the silicon atoms by the sides of the crystal, the so-called vapour–crystal (VC) mechanism. At this stage of growth, the crystal increases in thickness.

2.2. Structures of the upper layers of crystals

Using transmission electron microscopy of high resolution (a Philips CM 200 UT instrument), we have found that the microcrystals grown have a complex structure. They each consist of two distinguishable parts: the central part, of bulk silicon, and an extended envelope. The envelope has a nanoporous structure.

Figure 1 shows micrographs of fragments of the envelopes of different nanocrystals grown under different conditions. A common property of the envelopes is some ordering of the pores. The smallest diameter of the pores reaches a few diameters of silicon atoms (figure 1(a)); however, it can be much greater and may be equal to a few nanometres (figures 1(b) and (c)) depending on the conditions of the crystal growth. There are conditions under which the pores create concentric cylinder-like surfaces, giving rise to strong periodicity around the central part of the crystal. A fragment of such an envelope is shown in figure 1(c). The difference
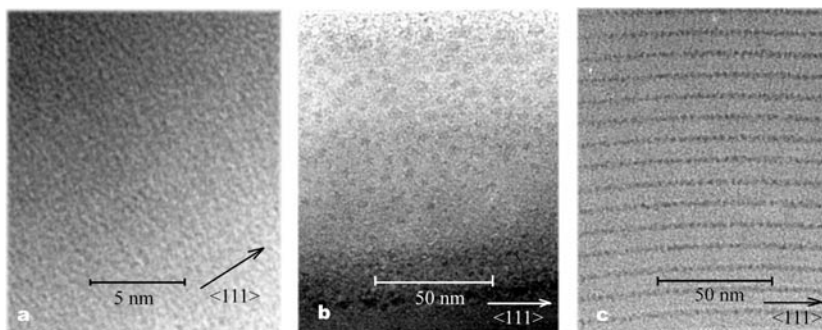
Figure 1. HRTEM (Philips CM 200 UT instrument) images of various envelope structures of different microcrystals grown under different conditions: (a)—homogeneous; (b), (c)—complex. The long axes of all of the wire-like crystals coincide with the ⟨111⟩ direction indicated by arrows. The direction from the core of the crystals to the external surface is always normal to the ⟨111⟩ direction and oriented: (a) from the upper left corner; (b) from the top; and (c) from the bottom of the figures.
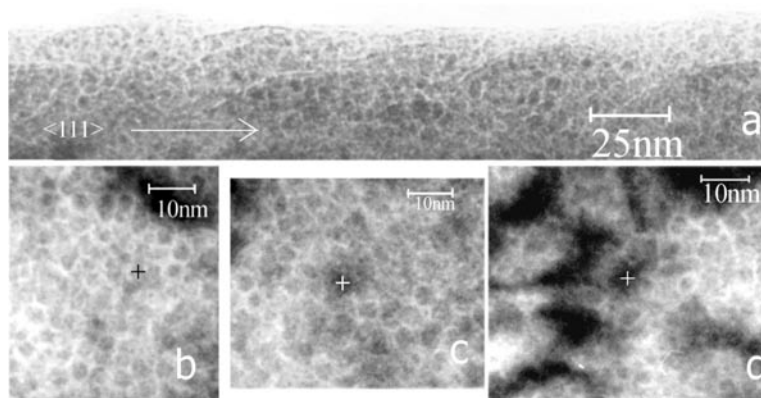

Figure 2. Views of a crystal from different angles: from the side (a) and from the top (b)–(d). Crosses indicate the centres of the valleys and ridges on the surface. The micrographs are produced using HRTEM (Philips CM 200 UT) with an unfocused electron beam.

between the envelope structures for different crystals was found to be produced by a difference in crystal growth temperature regime and in concentration of Si atoms in the vapour.

Figure 2 presents views of the external surface from different directions: from the side (figure 2(a)) and from the top (figures 2(b)–(d)). The direction of the long axes of the crystals always coincide with the ⟨111⟩ direction indicated by arrows in the micrographs. The surface consists of 'ridges' and 'valleys' that create some periodic substructure on the surface. This may be seen from figure 2(a). Figure 3 (obtained with a scanning electron microscope, Hitachi SEM S806) shows this more clearly. The valleys and ridges are formed by the nanopores symmetrically ordered around the axis normal to the surface. This is seen in figures 2(b)–(d). Here the centres of the valleys and ridges are indicated by crosses.

Such surface structure was observed by STM also. In this experiment a current contact was formed on the crystal. An STM view of the free-of-contact surface is shown in figure 4. It is clearly seen that the ridges are shaped as concentric discs, whose diameters increase with distance from the surface. The surprising thing is that the STM experiment was carried out
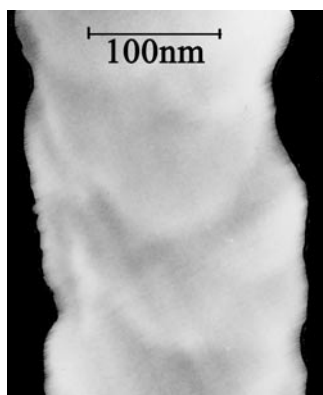
Figure 3. A micrograph (Hitachi SEM S806) of a microcrystal with some periodic substructure on its external surface.

x=24.0nm, y=24.0nm, z=49.3nm
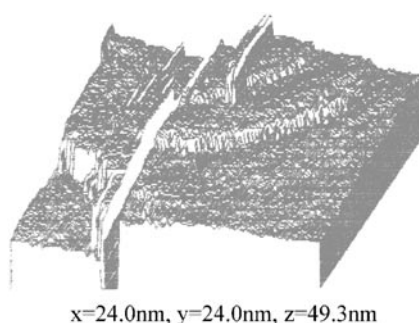
Figure 4. An STM view of ridges on the surface. The light band in the left-hand part of the figure probably indicates the presence of an oxide cluster.

in the atmosphere. In places, the tunnel current disappears sharply, possibly indicating the existence of oxide clusters on the surface; a destruction of the regular structure is observed as a rule in such places.

### 2.3. Composition of the crystals

To check the composition of the crystals, we have used a high-performance x-ray microanalysis and imaging system (AN 10000) and a fibre ion mass spectroscope (CAMECA IMS 4F).

Figure 5 presents an energy-dispersive x-ray spectrum (AN 10000) of a wire-like crystal. It is seen that the main component of the crystal is silicon, even if a metal catalyst is present also. The concentrations of all other contaminants were below the sensitivity of the method ($<10^{18}$ cm^{-3}).

Typical depth profiles (SIMS) of two crystals grown under different conditions are shown in figure 6, where the distributions of the main components taking part in the growth process are presented. In order to compare the profiles of the main substance (Si) and background (Al, Au, Ga, Ge, B, Br) atoms, for silicon Si^{2+} ions were used because their concentration (N) is much smaller than that of Si$^+$ ions ($N_{Si^{2+}}/N_{Si^+} \approx 10^{-3}$) and comparable with the concentrations of all other impurities. The latter allows one to avoid noise induced by automatically switching the amplifier and to enhance the sensitivity of the method. On the other hand, in the magnetron of the ion mass spectrometer, Si^{2+} ions act as atoms with 'mass 14' and cannot be distinguished
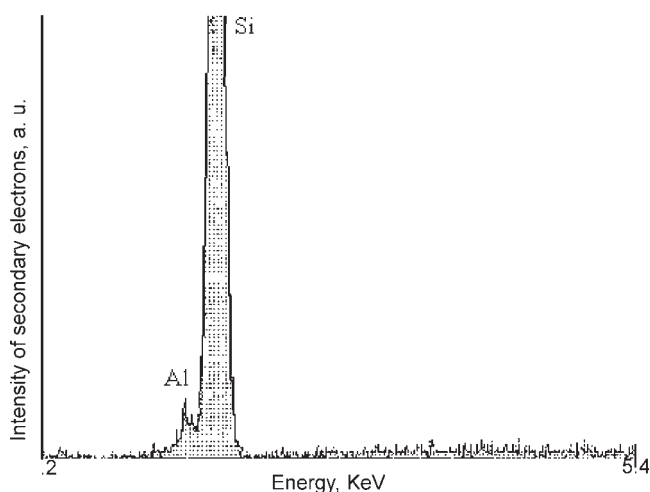
Figure 5. An energy-dispersive x-ray spectrum (AN 10000) of a wire-like crystal. The main component of the crystal is seen to be silicon, while it is also apparent that a metal catalyst is present in the crystal.
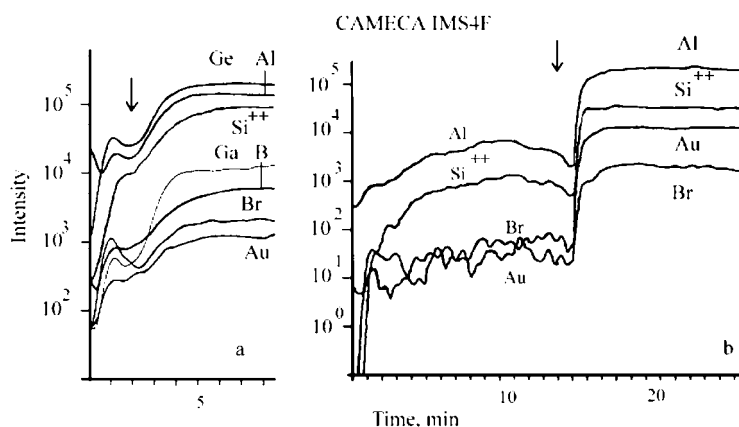
Figure 6. Depth profiles (CAMECA IMS 4F) of two crystals grown under different conditions. SIMS measurements were performed using a CAMECA IMS 4F. The intensities of the main substance (Si^{2+}) and background (Al, Au, Ga, Ge, B, Br) atoms are given versus the time of etching. The rate of the crystal core etching is (a) 20 and (b) 10 nm min^{-1}. The rate of envelope etching differs from that of the core and cannot be exactly estimated due to the porous nature of the envelope. Arrows in the figures indicate the transition layers between the envelopes and the centrals part of the crystals.

from nitrogen. We have not used nitrogen in this experiment; therefore we did not expect it to appear. But to avoid any possible mistake, we have carried out an additional experiment to elucidate the relationship between Si^{2+} and other isotopes (Si_{29}, Si_{30}). We have found that the Si^{2+} profile corresponds to the profile of the silicon material.

The depth profiles are presented with respect to time. Notwithstanding the fact that the etching rates of the central part of crystal and the envelope differ due to the porous nature of the envelope, these results reflect the main character of the crystal profile. First and foremost, the step-like distributions of all the components draw one's attention. The profiles of the doping
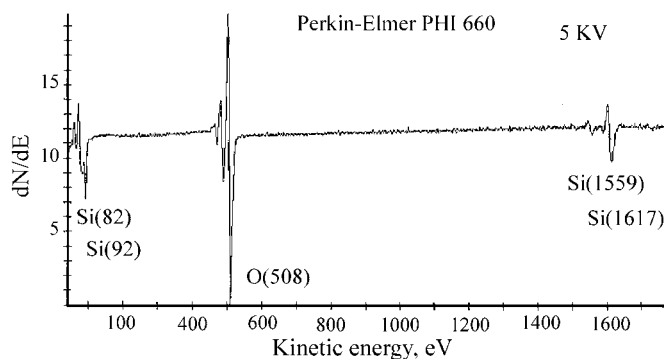
Figure 7. Auger spectra of a crystal (Perkin-Elmer PHI 660). The LVV peaks consist of the known peak of pure silicon at the energy of 92 eV and an additional peak at 82 eV, while the KLL peaks are very close to those for pure silicon and correspond to 1559 and 1617 eV.

impurities repeat in general the step-like profile of silicon, although in a few upper monolayers the concentrations of all of the metals (and only the metals) are somewhat greater than inside the envelope. It should be pointed out that the densities of all the components at the interface between the envelope and central part of the crystal (indicated in the figure by arrows) are somewhat smaller not only than the densities in the central part of the crystal but also than those in the envelope.

The step-like profile is not surprising, because the envelopes of the crystals have nanoporous structure, as found in HRTEM studies. An increased concentration of metals in the uppermost monolayers of the envelope suggests selective gettering at the surface.

So, this experiment shows that the central part of the crystal and the envelope consist of silicon and background impurities nearly homogeneously distributed inside both parts of the crystals: the envelopes and the central parts.

2.4. Chemical state of the surface

In order to characterize the chemical state of the surface, we have used the Auger electron spectrometer Perkin-Elmer PHI 660. The residual gas pressure in the vacuum chamber was 10^{-9} Pa. The primary exciting electron current and energy were 100 nA and 5 keV, respectively. The energy resolution was better than 2 eV.

In the spectra of the crystals, we have observed LVV and KLL peaks of pure silicon. Figure 7 shows a typical spectrum. The positions of the KLL peaks are very close to those for pure silicon and correspond to 1559 and 1617 eV. But the LVV peaks consist of the known peak of pure silicon at 92 eV and an additional peak at the energy of 82 eV. Scanning an electron beam over the surface did not reveal serious modification of the LVV peaks as regards position and shape, but the peak-to-peak height ratio was slightly changed. The intensity of the additional peak was comparable to the intensity of the peak of pure silicon, but sometimes, depending on the position of the test electron beam on the surface, it was larger or smaller.

Similar LVV spectra were observed in [6]. The authors attributed this peak as proof of the presence of a SiN_x layer on the surface, because a more pronounced nitrogen peak at 379 eV [7] was also observed. But we cannot ascribe the additional LVV peak (82 eV) to a contamination of the surface by nitrogen, because we have not detected in our spectra any other peaks related to nitrogen.

In addition to the silicon peaks, the oxygen peak at 508 eV was detected. Therefore, the appearance of peaks specific to silicon dioxide (the LVV peak at 76 eV and KLL peaks at 1547

and 1606 eV) might be expected. However, we have not found any indication of these peaks in the crystals studied.

More striking in this experiment was the fact that the spectra of the wire-like crystals did not markedly change after storage for a long time (a few years) in the atmosphere. This suggests a high passivity of these crystal surfaces, in contrast to surfaces prepared artificially by etching bulk material. Such passivity may be ascribed to saturation of the surface with bromine, which occurs during growth. But we have not seen any indication of peaks appertaining to bromine, although SIMS shows that the crystals do contain bromine. This suggests that its concentration on the surface is too small to explain the passivity of the surface.

3. Discussion

Special properties of the surface of wire-like crystals may be caused by special structure of the envelope as well as its external surface. In order to understand the reasons for the occurrence of such structure, we should focus our attention on the mechanisms of crystal growth. It involves a few basic steps: growth of the crystal by the VLC mechanism (leading to fast elongation of the crystal—so-called growth of the leader) and by the VC mechanism (leading to thickness increase, when the crystal becomes large enough).

Since the rates of these two growth mechanisms differ each from other by a few orders of magnitude [8], it is very possible that during the growth of the leader its side surface (in order to minimize the surface energy) becomes reconstructed [9, 10] in such a manner that the atoms absorbed from the vapour (during the next step of the growth by the VC mechanism) cannot create strong bonds on this surface, as for bulk diamond-like crystals.

A factor contributing to this may be size effects, e.g. those caused by Laplace forces. The latter leads to the appearance of components of the surface tension directed normally to the curved surface of the crystal. The components of the Laplace forces $F_s = 2\sigma/d$ (where σ is the surface tension, d is the diameter of the crystal) give rise to a strain in the crystal, and this may influence the crystal growth. The components of the Laplace forces estimated for the crystals studied are large: they may reach magnitudes up to 100 MPa.

Also, from the depth profiles one may conclude that chemical bonds inside the envelope as well in the bulk part of the crystal (leader) are stronger than those in the interface between these two parts of the crystal. The evidence for this can be derived from the fact that the density on the boundary between the envelope and leader (indicated by arrows in figure 6) is smaller than the density inside the envelope as well in the leader. This means that the envelope grows as a tube bound slightly to the leader, and, therefore, it has its own structure.

Investigation of Auger spectra leads to a similar suggestion that Si–Si bonds in the envelope differ from those in bulk silicon. A real surface of single-crystalline silicon is always oxidized. The thickness of the oxide layer depends on the previous treatment and the time of storage in the atmosphere. An atomically clean surface emerges on removing the oxide layer but is preserved only under high-vacuum conditions. The so-prepared atomically clean surface oxidizes in the atmosphere in a few seconds. Therefore, the Auger peaks of pure silicon have never been observed for a real silicon surface stored in the atmosphere for a long time. These peaks appear only in the spectra of atomically clean surfaces in ultrahigh vacuum, although they may be observed if the surface is covered with a very thin oxide layer (<1 nm), which is transparent to Auger electrons [11]. On real surfaces a single LVV peak (76 eV) and the KLL peaks (1547 and 1606 eV) of silicon dioxide are usually observed [7]. We have not observed these peaks for the crystals studied, even when the crystals were stored for a few years in the atmosphere. So, the spectra observed for wire-like crystals differ from the spectra specific to atomically clean surfaces and from

those specific to the surface covered by silicon dioxide. The difference is observed not only in the energy position but also in the ratio of the intensities of the LVV and KLL transitions.

We cannot yet explain this surprising result properly—in particular, because the envelope is porous and the surface area is enlarged. But we note two peculiarities characterizing the crystals studied:

 (i) The surface under consideration is formed on a wire of small radius; therefore it is strained.
(ii) The porous surfaces of the crystals are formed during the growth process—in contrast to common porous silicon, which is prepared by etching. The etched surface of silicon is well known to oxidize very quickly.

The influence of strain on silicon oxidation as well as on the kinetics of the latter [12] has been considered by many researchers. But the results obtained are not comparable with the results of the current work because of different methods of surface preparation of wafers and the crystals studied here—which were grown in vacuum and subjected to strain during growth but not after growth—and the chemical–mechanical treatments applied in the earlier work. The strain usually induces many defects in the wafers, and, therefore, increases the speed of oxidation. Wire-like crystals have a strength approaching the theoretical limit [13]. This suggests low concentrations of defects in the bulk and on the surface, and this makes oxidation difficult.

A recent PL study [4] of these crystals has indicated also special atomic bonds in the envelope. It was shown there that, besides visible PL, a new infrared PL band was observed. Its energy (1.139 eV) was close to the energy of the bond excitons in bulk silicon (1.149 eV). The intensity of the new band increases, while the intensity of the band of bulk excitons decreases and eventually disappears completely as the diameter of the crystal decreases. This suggests that the new PL band may be ascribed to the special structure of the envelope, because the role of the surface increases with decrease of the crystal diameter.

Elucidation of concrete reasons for the complex structure of wire-like crystals grown by self-organized processes, as well as the striking properties of the surface, would require further theoretical calculations taking into account both of the mechanisms of crystal growth, the conditions of growth, and size effects (e.g., Laplace forces).

4. Conclusions

The upper layers of wire-like crystals grown by self-organization processes have nanoporous structure. The morphology of these layers depends strongly on the growth conditions, but their common property is that some pores are ordered and have quasi-spherical shape.

XMA, SIMS, STM and AES characterization of the crystals indicated that

  (i) the upper layers of the crystals as well as the bulk part consist of silicon, even if there is contamination;
 (ii) the Auger spectra differ from the spectra of real silicon surfaces and those of atomically clean ones, although they are closer to the latter;
(iii) the external surfaces of the crystals are highly stable and chemically inert in the atmosphere;
(iv) the unique properties of the surfaces of wire-like crystals may be attributed to size effects that influence the crystal growth and to the variety of their manifestations under different conditions of crystal growth (temperature, supersaturation, etc), although elucidating concrete reasons for the striking properties of the surfaces would require further investigation.

Acknowledgments

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