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# Influence of Growth Conditions on Morphology, Composition, and Electrical Properties of n-Si Wires

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A relationship between growth conditions of silicon wires and their morphology, composition, and electroconductivity is presented. In these crystals recently a lattice parameter change and a visible light emission have been found being almost the same as those observed in porous silicon. The crystals were grown by a method of gas-phase reaction in a sealed tube. Using electron microscopy, X-ray microprobe analysis, ion mass spectrometry, Auger electron spectrometry, and temperature dependencies of electroconductivity, it is shown that the crystals grown in different parts of the tube have various shapes, compositions, and electroconductivities. The study of the grown crystals allows to draw conclusions on the mechanisms of crystal growth and doping, and to find a method for controlling these processes. Varying the growth conditions, one is able to change (i) shape of crystals (cylindrical or prismatic), (ii) size of crystals in the ranges from 1  $\mu$ m to a few cm (axial) and from 0.1 to 100  $\mu$ m (transverse), (iii) specific electroconductivity from a few to 200  $\Omega^{-1}$  cm<sup>-1</sup> with various degrees of compensation.

## 1. Introduction

Practical needs in device miniaturization have initiated intensive search for new technologies. Nevertheless, up to now the basic methods of microstructure formation remain technologies of structure preparation from bulk materials using various etching processes. We believe that methods based on the ability of matter to self-organize are more preferable for this purpose. In the present paper we describe one of these methods and found relationships between growth conditions and morphology, composition, and electrical properties of crystals. A practical use of this method was already confirmed by our recent discovery of visible light photoluminescence [1] in filament-like silicon crystals. Taking into account the high chemical stability of the crystals we believe that they may become competitive with porous silicon.

#### 2. Experimental Results

The wires were grown by the method of the gas-phase reactions,

$$2\operatorname{Si} + 2\operatorname{Br}_2 = 2\operatorname{SiBr}_2 \underset{(\operatorname{Au})}{\rightleftharpoons} \operatorname{Si} + \operatorname{SiBr}_4, \qquad (1)$$

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in a sealed tube with a temperature gradient [2], where Au plays the role of a growth catalyst. The growth process based on this method is known [3] to consist of a few stages: 1. appearance of drops of the metal catalyst on the walls of the growth tube, 2. accumulation of silicon in these drops, and 3. growth of wires by the vapour-liquid-crystal (VLC) and vapour-crystal (VC) mechanisms.

In our case the initial n-silicon doped with antimony had a specific conductivity  $\sigma = 100 \ \Omega^{-1} \ \mathrm{cm}^{-1}$ . The bromine concentrations providing the proceeding of reaction (1) were 2.0 or 2.9 mg cm<sup>-3</sup>.

From the observation of the tube with an electron microscope after the growth process was finished, it was found that the crystals grow in a definite part of the tube, that position



Fig. 1. a) Schematic presentation of the tube, shaded regions are the zones of crystal growth and the distribution of the temperature (*T*) along the tube, b) the dependence of the diameter of the crystals on their growth position in the tube for two bromine concentrations:  $N_{\rm Br} = 2$  and  $\odot 2.9 \,\mathrm{mg}\,\mathrm{cm}^{-3}$ , c) gold and antimony concentrations vs. the position in the tube during crystal growth

depends on the bromine concentration and shifting towards the region of lower temperature with an increase of this concentration (Fig. 1). We have found also that the crystals were distributed in size along the growth zone. The corresponding dependencies of the diameter of wires on their position in the tube are presented in Fig. 1b for both bromine concentrations. As may be seen from Fig. 1a, b in the hotter part of the tube the wires of larger diameter grow, and crystals of different diameters grow at the same temperature, i.e. at the same position in the tube, if the bromine concentrations are different. Depending on temperature gradient, bromine concentration, and position in the tube, the wire diameters varied from 0.1 to  $100 \mu m$ .

The crystals were of regular hexagonal or rectangular prismatic, cylindrical, or weakly expressed conic shapes (Fig. 2). The crystals of submicron diameter had mainly cylindrical shape.

The lengths of the crystals range from a few  $\mu$ m to a few cm, sometimes they were longer than 5 cm. We have not found a marked correlation between length and diameter of the crystals. Both length and diameter depend strongly on the bromine and metal concentrations, and on the growth duration. Varying the growth conditions we are able to grow in a common tube either crystals of a large distribution of diameters or crystals having similar diameters.

The composition of crystals was examined by X-ray microprobe analysis (IC 845 Jeol), ion mass spectroscopy (IMS 4F CAMECA), and Auger electron spectrometry (AES Perkin Elmer). It is worth to note that the best equipment designed for such an investigation and used in our experiments does not allow to obtain quantitative data on the impurity distribution inside the wires, especially on submicron scale, due to the quasi-cylindrical shape of the crystals. Nevertheless, some conclusions on composition, integral concentration, and relative distribution of silicon and impurities in the crystals can be obtained from our study.

It was found that the total concentration of both gold and antimony in the crystals was



Fig. 2. Electron microscope images of wires with various shapes and sizes: a) two crystals of close (3  $\mu$ m) diameters but different shapes, b) a well faceted prismatic crystals of large ( $\approx$  50  $\mu$ m) diameter



Fig. 3. Dependence of specific conductivity ( $\sigma$ ) on diameter ( $d_i$ ) for crystals grown with different bromine concentrations:  $\bullet N_{Br} = 2$  and  $\circ 2.9 \text{ mg cm}^{-3}$ 

about or less than  $10^{18}$  cm<sup>-3</sup>. Additionally, a marked contamination by bromine was found. The bromine was located on the surface, and its surface concentration ( $\approx 10^{14}$  cm<sup>-2</sup>) did not depend on the crystal size.

Investigating simultaneously the profiles of silicon and impurities we can learn more about the degree of homogeneity of impurity distributions and on the relationship between their concentrations in wires of different diameters and in different parts of the crystals along their

large axis. It was found that the impurity concentration in the wires depends on the impurity concentration in the initial materials, the temperature gradient in the tube, and the transporting agent concentration, and the impurity concentration is approximately the same for crystals grown in a localized region (of several mm size at least) of the common tube.



For the study of electroconductivity wires of 0.5 to 60  $\mu$ m diameter grown in different parts of the tubes and with two bromine concentrations were used. The dependencies of specific conductivity on the diameter of crystals at room temperature are shown in Fig. 3. The conductivity values for crystals grown at low and high bromine concentrations amounted to  $\sigma_1 = 3$  to  $30 \ \Omega^{-1} \ cm^{-1}$  and  $\sigma_2 = 25$  to  $200 \ \Omega^{-1} \ cm^{-1}$ , respectively, i.e. they differ by about an order of magnitude. The increase in specific conductivity with the decrease of crystal diameter including those of submicron size was observed for the crystals grown at both bromine concentrations. Fig. 4 shows the depend-

Fig. 4. Temperature dependence of specific conductivity ( $\sigma$ ) for crystals of different diameters: (1)  $d_i = 43$ , (2) 27, (3) 10, (4) 54, (5) 26, (6) 6  $\mu$ m grown with different bromine concentrations: •  $N_{\rm Br} = 2$  and  $\circ 2.9$  mg cm<sup>-3</sup>

ence of specific conductivity  $\sigma(T)$  on temperature for crystals of different diameters and grown with different bromine concentrations. The measured dependence  $\sigma(T)$  for the crystals with specific conductivity 100  $\Omega^{-1}$  cm<sup>-1</sup> was found to coincide with that of the initial bulk silicon.

The main peculiarities in the behaviour of the observed electroconductivity are: (i) the conductivity increases with the decrease of wire diameter and with increase of bromine concentration, (ii) the position of the conductivity maximum versus temperature weakly depends on the parameters mentioned, (iii) the maximum value of conductivity strongly depends on these parameters.

#### 3. Discussion

The results obtained may be explained taking into account the VLC and VC mechanisms of crystal growth.

At the beginning of the growth process drops of the metal catalyst appear on the walls of the growth tube. The sizes of these drops depend on the gold concentration in the vapour. The silicon atoms arising according to reaction (1) are then captured by these drops as well as by the tube walls. Since the "sticking" coefficient to metal is known to be by several orders larger than that to a semiconductor or dielectric, the silicon atoms are absorbed generally by the metal, and the crystals start growing from the gold drops, which remain at the wire tops. This is the VLC mechanism, leading to the fast axial growth of wires. The transverse size of crystals depends on the initial size of the gold drops and should be varying for crystals growing in different parts of the tube, if the gold concentration in the vapour is varying along the tube. Furthermore, the greater the gold concentration in the vapour, the greater is the size of gold drops and, therefore, the diameter of the filament-like crystals. As an electron microscopic examination of the crystal diameter distribution along the tube showed that in the hotter part of the tube the crystals of larger diameter grow, we can suggest that the gold concentration increased towards the hotter part of the tube.

Another VC mechanism consists in the capture of silicon atoms from the vapour directly by the silicon surface of crystals. It becomes more important when the lateral surface of a wire becomes large and/or the gold drop disappears due to either solution of gold in the crystal bulk or for some other reason. In general, the growth mechanism is believed to be a combination of VLC and VC, but the contribution of each of them may be different for crystals of different diameter and grown in different parts of the tube.

It is obvious that the doping of crystals will be different for different growth mechanisms. The doping by the VLC mechanism is determined by the impurity concentration in the vapour, the sticking coefficient of this impurity to the gold drop, its solubility, and the diffusion coefficient inside the drop. The doping by the VC mechanism is also determined by the impurity concentration in the vapour and by the sticking coefficient to silicon.

Considering the impurity distribution in crystals it is necessary to take into account the diffusion processes as well. The impurities introduced into the wires during the growth may be redistributed due to diffusion. Since the diffusion coefficient of gold is by a few orders higher than that of antimony, it is more important to take account of a redistribution for gold.

From this consideration it might be suggested that wires of any diameter grown by the VLC mechanism have the same gold concentration because the main doping mechanism should be the doping from the gold drop. It is worth to note that since by the VLC mecha-

nism the growth rate of whiskers is very large (usually about 2 to 3  $\mu$ m/s or much more), the growth process is probably not occurring in a steady state, and crystals may capture gold from drops in concentrations exceeding the equilibrium solubility limit ( $N \approx 10^{16}$  cm<sup>-3</sup>). For the wires grown by the combined mechanism due to diffusion the gold concentration may be less and decrease in the direction from bulk to surface. Meanwhile, some quantity of gold might be captured in this case from the vapour as well. If the part of the crystal grown by the VC mechanism is large, the gold concentration in the crystal should be mainly defined by its concentration in the vapour.

The concentration of antimony should also be different for crystals grown by different mechanisms, but in contrast to gold it always depends on its concentration in the vapour. If the crystal grows by the VLC mechanism the antimony concentration will be constant over the crystal and depend on its concentration in the vapour, the sticking coefficient to gold, and its diffusion through the gold drop. For the VC mechanism this concentration is defined by the antimony concentration in the vapour also and by the sticking coefficient of antimony to a silicon surface. Since the diffusion coefficient for antimony is very small, its redistribution during the growth process may be ignored. Therefore, in crystals grown by a combined mechanism, the antimony distribution along the radius should be inhomogeneous.

We have really observed an inhomogeneity in brightness on a micrograph of the cross section of crystals grown by a combination of VLC and VC mechanisms. In Fig. 2a two crystals of about the same size but of different shape are shown. The cylindrical crystals are believed to be grown by the VLC mechanism, while the faceted ones by a combination of VLC and VC mechanisms. The cross section of the faceted crystal has a dark circle in its central part and bright edges. This may be assumed as the result of a potential relief. We believe that the central part of this crystal is cylindrical and grown by the VLC mechanism, while its faceted edge is grown by the VC mechanism. Since the diameter of a faceted crystal  $(d_i = 3 \,\mu\text{m})$  is about the diffusion length of gold but substantially larger than that for antimony, the contrast picture of this crystal is caused by different antimony concentrations, i.e. by different electroconductivities. From this observation one may additionally draw the conclusion that antimony is included into the crystal mainly by the VLC mechanism.

Summarizing the results of this consideration we can state that if most of the crystal grows by the VLC or VC mechanism, the impurity distribution inside the crystal may be treated approximately as homogeneous. Taking into account that the crystals of small diameter  $(\leq 1 \ \mu\text{m})$  have a cylindrical shape, these crystals are believed to grow by the VLC mechanism mainly, whereas crystals of large diameter  $(\geq 10 \ \mu\text{m})$ , being well faceted, grow by the VC mechanism generally. Therefore, for all these crystals the impurity distribution may be treated as homogeneous. Following these considerations a corresponding calculation of the theoretical dependencies  $\sigma(T)$  for these crystals was carried out within the temperature range 77 to 300 K. The electron scattering on ions was considered by the Conwell-Weisskopf formula and phonon scattering of electrons was accounted for by the relaxation rate estimated from the empirical dependence for pure Si,  $\mu \approx \mu(T_0) (T/T_0)^{-2.5}$ , where  $\mu(T_0) = 1250 \ cm^2 \ V^{-1} \ s^{-1}$ ,  $T_0 = 300 \ K$ . Gold and antimony concentrations in the wires were evaluated from a comparison of the theoretical and experimental dependencies  $\sigma(T)$  and for some crystals are presented in Table 1. Since the electron–electron interaction was ignored in this treatment, the given impurity concentrations correspond to a material more compensated than it is in reality.

From these calculations it may be seen that crystals of different diameters have different concentrations of gold and antimony manifesting some monotonic dependence on the crystal diameter for both bromine concentrations used.

Table 1 Wire parameters				
$\overline{N_{\mathrm{Br}}}$ (mg cm <sup>-3</sup> )	$\sigma$ ( $\Omega^{-1}$ cm <sup>-1</sup> )	$\frac{N_{\rm Sb}^{\rm w}}{(10^{17} {\rm ~cm^{-3}})}$	$N_{\rm Au}^{\rm w}$ (10 <sup>17</sup> cm <sup>-3</sup> )	d <sub>i</sub> (µm)
2.9	100	40	_	6
	40	3	0.2	26
	25	3	0.7	54
2.0	22	3	0.7	10
	10	2	1	27
	3	2	1.7	43

Since the doping by antimony depends on the antimony concentration in the vapour (independent of the growth mechanism of the crystal) we can conclude that the calculated dependence of antimony content on the diameter reflects the real distribution of antimony in the vapour along the growth zone.

The observed dependence of the gold concentration in the wires on the diameter shows that the main mechanism of growth for wires of large diameter (>5  $\mu$ m) is the VC mechanism. It means that the gold concentration in wires with various diameters, i.e. grown in different parts of the tube, reflects the distribution of gold in the vapour along the tube similarly to the case of antimony.

Therefore, accounting for the distribution of crystals of different diameters versus their growth position in the tube (Fig. 1b) we can calculate the real distribution of the impurity (antimony and gold) concentrations in the vapour during the crystal growth. These are shown in Fig. 1c. As may be seen from this figure, the maximum gold and antimony concentrations are in the hot and cold parts of the tube, respectively. We did not find a marked change in impurity distribution for different bromine concentrations.

To understand the influence of the bromine concentration on the wire conductivity it is necessary to pay attention to the fact that wires of the same diameter grown at low and high bromine concentrations are localized in different parts of tube (Fig. 1b). Taking into account the impurity distribution along the tube we can see that an increase in the bromine concentration leads to an increase in the doping of wires of the same diameter by antimony, to the simultaneous decrease of the doping by gold, and, as a result, to the increase in wire conductivity. The total impurity concentration in all crystals investigated (excluding those grown in the coldest part of the tube) was about the same (3 to 3.7)  $\times 10^{17}$  cm<sup>-3</sup>, which is in good agreement with a direct study of the composition by methods of composition analysis.

### 4. Conclusion

The dependencies of morphology, composition, and electroconductivity on diameter and transport agent concentration were studied for wires of 0.1 to 100  $\mu$ m diameter grown in a sealed bromine-containing system. Both the decrease in wire diameter and increase in bromine concentration lead to the same result: the wire electroconductivity grows. This is explained by two growth mechanisms (VLC and VC), as well as by peculiarities of antimony and gold distributions along the tube.

The crystalline silicon wires studied here are known to be highly efficient microcathodes and sensitive microelements used to measure various physical quantities [4 to 6]. Recently found visible light emission from these crystals [1] enhances the importance of the material for micro- and optoelectronics. In contrast to the microdevices prepared from bulk materials (using the methods of integral technology) the devices based on crystalline wires have stable properties. They are formed during the growth process, may be different from that of bulk material [7], and cannot be charged by further treatment. The data presented give the opportunity to exert control over the properties of wires and to provide the production of devices with required performances.

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