Preparation of nanowires from silicon whiskers

A N Stepanova, V I Muratova, L N Obolenskaya, O M Zhigalina,
N A Kiselev, E I Givargizov
Institute of Crystallography RAS, Leninsky pr. 59, Moscow 119333, RF

E-mail: egivargiz@ns.crys.ras.ru

Abstract. Regularities of nanowire formation by thinning silicon whiskers at high-temperature oxidation in the range 900-1050°C were studied. The oxidation was performed in a flow of dry or wet oxygen. It is shown that a stopping of the oxidation process occurs at oxidation temperature below ~960°C. For example, at 930°C the oxidation process is stopped in 6 hours. It is shown that at temperature above 960°C such a stopping mechanism does not act and a through oxidation of the whisker is possible. In the wet oxygen, similar through oxidation takes place even at 930°C. On the other hand, during oxidation above 960°C it is possible to prepare nanowires with diameter lower than 5 nm in relatively thick whiskers; this is convenient for further manipulation with such objects. For example, during oxidation at 1000°C nanowires with diameter ≤ 5 nm in an oxide shell up to 200 nm were prepared. Also, it has been shown that gold as a separate phase segregates at the nanowire-SiO₂ interface provided that no special treatments were performed. This undesirable phenomenon was avoided by a special whisker treatment before oxidation.

1. Introduction
Silicon integrated microelectronics is a basis of the modern progress in science and technology. The principal trend in the Si microelectronics is a decreasing the electronic components sizes. Currently, the feature size is 0.1 – 0.3 µm, and the value continues to decrease. This results in significant enlargement of the packing density of the electronic components in integrated circuits. Accordingly, the length of interconnections is strongly increased resulting in strong decreasing the propagation velocity of the electric signals in the circuits and between circuits.

A possible decision of the problem consists in transferring from the electric signal to optical one, i.e. from the classic microelectronics to optoelectronics. In order to realize such an approach, Si light emitting diodes or injection lasers compatible with the silicon integrated microelectronics are necessary. Light emitting Si devices could open way to realization of Si optoelectronics.

However, the preparation of the light emitting Si devices represents a difficult problem. Because of the indirect energy gap, the bulk form of Si is not an effective light emitter. Therefore, during the last decade extensive studies of low-dimensional Si structures (porous Si, nanocrystals of Si in SiO₂ matrix, etc) have been undertaken. In the structures, effective photoluminescence (PL) and electroluminescence (EL) have been observed at the room temperature [1,2]. Observation of intensive PL and EL in low-dimensional Si structures makes it practicable to create effective Si light-emitting devices compatible with Si microelectronics. This could solve the problem of optical interconnections in integrated circuits and, in such a manner, develop Si integrated optoelectronics [3,4].

The greatest success in studies of PL and EL of low-dimensional structures has been achieved at investigation of light-emitting layers that contained Si nanostructures in isolated matrices [5-9].
However, last times one-dimensional structures, namely nanowires, are seemingly the most attractive ones. The techniques for preparation of semiconductor nanowires, including Si ones, are developed intensively.

The existing numerous techniques for preparation of nanowires can be divided for two principal groups:

1) preparation by etching, e.g., reactive ion etching with using electron lithography [10];

2) nanowire growing.

A detailed review of the techniques as applied to semiconductor nanowires has been recently published in [11].

A successful preparation of silicon nanowires by growing was seemingly described for the first time in 1998 [12]. Subsequently, the group from Harvard University has published a series of papers on improving their process for preparation of nanowires of Si and other semiconductors [13]. They published also their results on preparation of laboratory versions of devices from the nanowires, for example of a transistor based on Si nanowire [14].

Practically all the techniques for preparation of nanowires are based on the crystal growth mechanism according to the vapor-liquid-solid (VLS) process discovered in 1964 [4]. Later, the VLS process has been investigated in detail in papers [16,17] as applied to whiskers of silicon, as well as to whiskers of semiconductor compounds. In the work [17], a possibility for growing the array of regular whiskers, i.e., those having the same diameters and spaced at equal distances one of other, has been demonstrated for the first time.

In this work, the process for preparation of Si nanowires from Si whiskers by high-temperature oxidation is studied. Earlier, the oxidation technique was used for the preparation of Si nanowires from Si columns obtained by reactive ion etching [10].

The first communication on preparation of Si nanowires by the high-temperature oxidation of Si whiskers was published in 1994 [18]. Here, the process has been studied on arrays of non-regular Si whiskers having small diameters. (The non-regular whisker array means that the whiskers have various diameters, and distances between them are different, too). Our aim is to investigate optimal oxidation conditions for whiskers having different diameters so that, then, the results obtained could be used for preparation of regular oriented arrays of nanowires.

2. Experimental techniques

2.1. Whisker growing

Silicon whiskers were grown on (111)-oriented Si substrates according to the VLS process with gold as liquid-forming agent [16,17]. Special Si substrates were used for studies of the nanowire formation at the high-temperature oxidation. A scheme of such substrates is shown in Fig. 1. The whiskers were grown on the narrow top butt-end that had the crystallographic orientation (111). Using the substrates that had the indicated sizes and orientation allowed to study the nanowires formed inside the oxidized whiskers by high-resolution transmission electron microscope (HRTEM) without any additional treatments of the samples studied. The sample was installed in the microscope so that the electron beam fell on the face (110) of the sample. This allowed, in principle, to observe the nanowires with the atomic resolution.

Growth conditions and the thickness of the Au layer were chosen so that whisker diameters were in the range 100-150 nm. It is to note that, in order to prepare nanowires from them, the whiskers must be of cylindrical shape. Meantime, due to some parameters of the whisker growing processes whiskers with slightly-conical shape were often formed. Height (length) of the whiskers must be ≤10 μm, otherwise the whiskers could bend.
The whiskers have different diameters. This is convenient for given investigations because it allows to measure on the same sample (by photos taken in the HRTEM) the dependences of the nanowire diameters or the oxide thicknesses on the whisker diameters. It is to note that we measured diameters of the whiskers that have been already oxidized, because in dense arrays of thin oxidized whiskers practically impossible to identify any concrete whisker before and after the oxidation.

2.2. Whisker oxidation
Oxidation of whiskers directed to their thinning was performed in tube furnace. A flow of dry or wet oxygen was passed through the furnace. The furnace was heated up to temperatures 900-1050°C, duration of the oxidation was up to 9 hours. Before the oxidation whiskers were studied in scanning electron microscope JSM-840 (JEOL). The oxidized whiskers were studied in HRTEM BS-230 (Philips).

3. Results and discussions
It was shown in the paper [10] that, at the oxidation of Si columns with diameters ≤40 nm Si nanowires (SiNW) with the diameters ≤5 nm inside the oxide envelope (shell) can be prepared. It was shown in the same paper that during the oxidation in dry oxygen at temperatures <950°C the oxidation process stops when the nanowire diameter reaches down to a certain value. Thus, the temperature 950°C is, in some sense, a critical value, T_c. That case, the nanowire diameter formed depends on the diameter of the initial whisker. The self-limiting mechanism considered in [10] (the stopping the oxidation) the authors relate to the strains that are developed at the Si-SiO_2 boundary. Existence of the stopping mechanism is very convenient from the technological point of view: that case, a danger of through oxidation is here absent.

On the other hand, it is desirable to have such thin SiNW’s in relatively thick whiskers (e.g., ≥100 nm). This could facilitate further manipulations with such a system. It is this task that we try to solve.

It is to note that our whiskers differ from the columns used in [10], e.g., on their impurity content and, hence, on their properties. Therefore, taking into account the results [10], we have studied the formation of the SiNW’s at both the lower T<T_c (950°C) and the higher temperatures.

3.1. Oxidation at T<T_c
Principal studies were performed at 930°C, duration of the oxidation varied in the range 1 to 9 hours. Fig. 3 shows a group of whiskers that were oxidized at this temperature in dry oxygen during 6 hours. The diameter of the SiNW’s in the shell is ~10 nm (in the middle part of the photo). The upper parts of
the whiskers shown in Fig. 2 have slightly conic shape seemingly due to partial evaporation of gold during whisker growing.

**Figure 2.** A group of the oxidized Si whiskers with SiNW inside in SiO₂ shell. Oxidation temperature 930°C, oxidation duration – 3 hours, medium – dry oxygen.

Fig. 3 shows dependence of the diameter of the SiNW on the oxidation duration at 930°C in dry oxygen. As it is seen, the stopping mechanism at the oxidation in dry oxygen is acting. It is seen that the stopping mechanism is acted at the oxidation in dry oxygen at 930°C, the minimal reached diameter of the nanowire being ~13 nm when the whisker diameter after the oxidation was 80 nm.

**Figure 3.** The dependence of the diameters of nanowires on oxidation duration at 930°C, medium – dry oxygen.

At the oxidation at 930°C in wet oxygen the stopping mechanism does not act, and the whiskers are oxidized through. HRTEM studies of such oxidized whiskers do not discover any crystalline phase inside the whiskers.

### 3.2. Oxidation at T>Tₘ (950°C)

The preparation of SiNW with diameters <5 nm in relatively thick whiskers at the oxidation at 930°C was unsuccessful, therefore we have studied the temperature dependence of the nanowire diameters. Such a dependence for the oxidized whiskers having diameters 85 nm is given in Fig. 4. The
The temperature range of the oxidation was 900-1050°C, process duration is 3 hours for all the temperatures, the oxidation was performed in dry oxygen.

**Figure 4.** Temperature dependence of Si nanowire diameters for whiskers that had (after oxidation) diameter 85 nm. The oxidation was performed in dry oxygen.

It is seen in Fig. 4 that the oxidation at 930 and 960°C gives practically the same result. At higher temperatures, the nanowire diameters decreased drastically down to complete through oxidation at 1050°C.

In Fig. 5 the dependences of the nanowire diameters of the oxidized whiskers for three oxidation temperatures 930, 1000 and 1050°C are given.

**Figure 5.** Dependence of nanowire diameters on diameters of Si whiskers at various oxidation temperatures.

The dependences for 930 and 1000°C are approximated by straight lines. However, at the temperature 930°C the linear dependence is not correct for thinner whiskers due to a retardation and, then, a complete stopping the oxidation. Also, it is seen in Fig. 5 that at 1050°C the oxidation occurs very fast, and all the whiskers with diameters up to 120 nm were oxidized through. Such a fast process is technologically inconvenient.

At 1000°C it was possible to prepare thin nanowires with diameter ≤ 5 nm. In Fig. 6, a nanowire with diameter 2.5-5 nm inside the oxidized whisker with diameter 200 nm is shown. A conic shape of the nanowire is, most probably, due to a conic shape of the initial whisker that is difficult to recognize due to its large diameter.
3.3. Influence of gold on internal structure of SiNW

Au that was used for the growing the Si whiskers can negatively influence to properties and structure of SiNW. Firstly, Au is captured by the whiskers during their growth according to the distribution coefficient of the impurity and even in larger concentrations if their growth process is significantly non-equilibrium one. Secondly, a Si-Au globule remains on the whisker top after completion the growth process. The gold can diffuse into whisker during the oxidation. In addition, the gold can segregate at the Si-SiO₂ interface as a separate phase. The precipitates were observed not on all the whiskers, namely they were absent on the whiskers that had a slightly-conical shape (such as shown in Fig. 2). This means that gold evaporated during the growth process, and globules were absent on the whisker top after the cease of the growth. It is concluded from the observations that the gold precipitation at the Si-SiO₂ interfaces is caused by the presence of the Si-Au globule on whisker tops during the oxidation.

During the whisker oxidation at 1000°C a new phenomenon was observed: a part of SiNW formed has been dissolved resulting in rupture of the SiNW. Such a phenomenon is demonstrated in Fig. 7.

As it was mentioned above, the gold precipitation is caused by the presence of the Si-Au globule on whisker tops during the oxidation. Accordingly, were taken care to avoid the precipitation of gold at the Si-SiO₂ interface: the Si-Au globule has been removed before whisker oxidation. The process of
globule removing has been developed on regular array of relatively thick whiskers that had diameters of several µm. Such procedures are inapplicable for thin, dense irregular whisker arrays that we used in this investigation because the whiskers bent and stuck together. In future, we hope to use the regular arrays of relatively thin whiskers (with diameters ≤ 200 nm) for preparation of SiNW regular arrays. In this case we will use this method for removing Si-Au globules before oxidation of whiskers.

3.4. Conclusion
Preparation of Si nanowires (SiNW) from Si whiskers has been described. The preparation procedures consist in high-temperature oxidation Si whiskers. At oxidation of Si in flow of dry oxygen at relatively low temperatures (930°C) self-limiting oxidation (“stopping”) has been observed when the diameter of Si decreased down to a certain value. The minimum diameter depends on initial whisker diameter. The minimum SiNW diameter reached at 930°C is ~10 nm for the whisker diameter after oxidation ~60 nm. At the oxidation in wet oxygen the stopping was not observed so that the whiskers could be oxidized through. SiNW’s with diameters ≤5 nm were prepared by oxidation at 1000°C in whiskers that had (after the oxidation) diameters up to 200 nm. At the oxidation temperatures the stopping was not observed.

It was observed the influence of Au on the structure of SiNW’s. The metal can segregates at the SiNW-SiO₂ interface as a separate phase and even dissolve partly the SiNW resulting in its rupture. This phenomenon is explained by the presence of the Si-Au globule on the whisker top during the oxidation. A procedure for removing the globule from the whisker top before its oxidation has been developed.

This work has been made with the support from International Science and Technology Center, Grant 2559.

References
[1] Canham L T 1990 Appl. Phys. Lett. 57 1046
[2] Cullis A G, Canham L T and Calcott P D J 1997 J. Appl. Phys. 82 909
[3] Hirschman K D, Tsybeskov L, Duttapauta S D and Fauchet P M 1996 Nature, 384, 338
[4] Silicon based optoelectronics 1998 Mater. Res. Bull. 23(4)
[5] Zhang Qi, Bayliss S C and Hutt D A 1995 Appl. Phys. Lett., 66, 1977
[6] Baru V G, Bradley I V, Stepanov G V et al. 1996 Appl. Phys. Lett. 69 4148
[7] Baru V G, Duyuzikov I N, Pokalyakin V A, Shevchenko O F, Skryleva E A and Zhigalina O M Cond. Mat. (2004) 0511602
[8] Pavesi L, Van Negro L, Mazzoleni C, Franco G, and Priolo F 2000 Nature 408 440
[9] Valenta J, Juhasz R and Linnros J, 2002 Appl. Phys. Lett. 80 1070
[10] Liu H I, Biegeisen D K, Ponce F A, Johnson N M and Pease R F W 1994 Appl. Phys. Lett 64 1383
[11] Fan H J, Werner P and Zacharias M 2006 Small 2 700-717
[12] Morales A M and Lieber C M 1998 Science 279 208
[13] Cui Y, Lauhon L J, Gudiksen M S, Wang J and Lieber C M 2001 Appl. Phys. Lett. 78 2214
[14] Cui Y, Zhong Z, Wang D, Wang W U and Lieber C M 2003 Nano Lett. 3 149
[15] Wagner R S and Ellis W C 1964 Appl. Phys. Lett. 4 89
[16] Givargizov E I J. Cryst. Growth 1975 31 20-30
[17] Givargizov E I 1978 Current Topics in Mater. Sci. 1 ed E. Kaldis (North-Holland) 80-145
[18] Plekhanov P S, Zhirnov V V, Givargizov E I and Kiselev A N 1994 Abstracts Int. Symp. on Nanostructures:Physics and Technology (St. Petersburg, Russia) 160