# OUT-OF-PHASE Bi NANOWIRES ON Si(001) SURFACE

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The structure of Bi nanowires on Si(001)2×1 surface was investigated by scanning tunneling microscopy (STM). In addition to in-phase nanowires, which are known from the literature, out-of-phase ones were revealed for the first time, and models of their structure have been proposed. It is shown that a relaxation of the stress originating from a difference in bond lengths between Si atoms in a substrate and Bi atoms in a nanowire gives rise to a rearrangement of defects into aggregations of the type of vacancy trenches arranged in parallel to the nanowire on the Si(001)2×1 substrate. At temperatures 20 — 40 °C higher than the nanowires formation temperature (520 °C), a degradation of nanowires begins due to the appearance of defects which are the substitutions of Si dimers for Bi atoms. The activation energy of the desorption of Bi from out-of-phase nanowires is 0.05 eV higher than that from in-phase nanowires, that is the evidence of higher stability of the out-of-phase Bi nanowires on the Si(001)2×1 surface.

## Introduction

In recent years, thin layers of Bi on Si(001) surface have intensively been studied in a number of laboratories throughout the world. They have attracted researchers' attention as surfactants, for instance, at epitaxial growth of germanium on Si(001), without Bi penetration into Ge layer [1]. In addition, under certain deposition conditions (at temperatures ∼500 °C), Bi forms almost defectless nanowires ∼ 1 nm wide and ∼ 200 nm long on the Si(001) surface [2—6]. Nanowires consist of the chains of Bi dimers arranged perpendicularly to the dimer rows of Si substrate [2—6]. They have proved to be less sensitive to the influence of hydrogen, oxygen, and ozone as compared with the sensitivity of silicon substrate atoms [6], which can be utilized in novel technologies of the metallization of nanoelectronic systems.

A few possible models of the nanowire structure have been suggested in the literature [2—6] and theoretically examined [7]. To make the ultimate choice of adequate model, further studies of Bi nanowires are required. In particular, a mechanism of defect formation has insufficiently been studied in both the nanowires and substrates of the Bi/Si(001) system. Such defects should appear in the system due to a difference in the dimer bond lengths of bismuth and silicon, which results in the stress in the surface layers of the system [8, 11]. Therefore, in this work with the usage of the STM technique, a further investigation of the structure of Bi nanowires has been undertaken with the aim to gain new information about their unusual features as well as about defects both in the nanowires and on the substrate surface near them.

## 1. Experiment

The experiments were performed in a high-vacuum chamber with a base pressure of $\sim 2 \times 10^{-10}$ Torr. The chamber was equipped with a scanning tunnel microscope, an Auger electron analyzer, a heater of both a tip and a specimen, as well as with a source of the thermal evaporation of Bi [9]. Si(001) specimens were cut from the $p$-type silicon (4.5 Ohm × cm). After chemical treatment, they were degassed in a vacuum $\sim(2\div5) \times 10^{-10}$ Torr at 700 °C for several hours, and, subsequently, by annealing cycles up to 1200 °C for 1 min. After the heat treatment, the specimens were cooled down with a rate of 100 °C/ min. The absence of impurities on the surface was verified by both the Auger electron spectra and STM images. After the treatment of silicon specimens, the STM images showed the well-ordered Si(001)-2×1 surface with sufficiently extended flat terraces between steps and negligible vacancy concentration. Bi was deposited from a heated tungsten crucible. Thickness of the Bi layers was monitored by a quartz resonator. Bi desorption from the Si(001) was carried out by heating the system up to ∼ 1200 °C for 1 min. This procedure allowed us to obtain the clean Si(001)-2×1 surface for carrying out further repeated investigations. STM images were taken with the use of a tungsten tip in the regime of a constant current.

After the deposition of Bi with a coverage level $\theta_{\rm Bi} > 0.5$ monolayer and the subsequent annealing at ∼ 420 °C, Bi/Si(001)-2×$n$ structure was obtained, as was observed by other authors [2, 10]. The following annealing at ∼ 520 °C for several hours has lead to

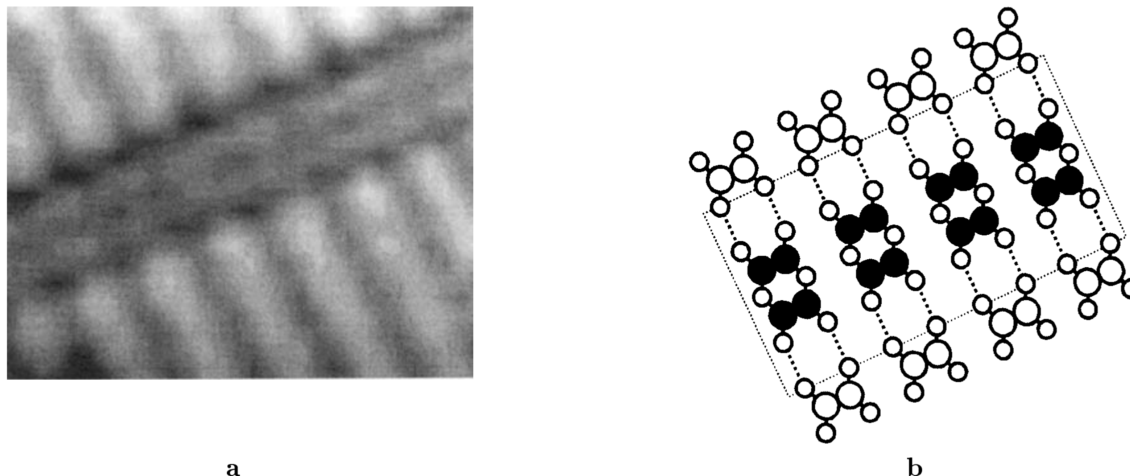

Fig. 1. STM image (∼4.5×4 $nm^2$, –2.0 V, 46 pA) (*a*) and structure model (*b*) of a in-phase Bi nanowire on the Si(001)-2×1 surface. Greater and smaller white circles correspond to Si atoms of the first and second layers, respectively; black circles — to Bi atoms

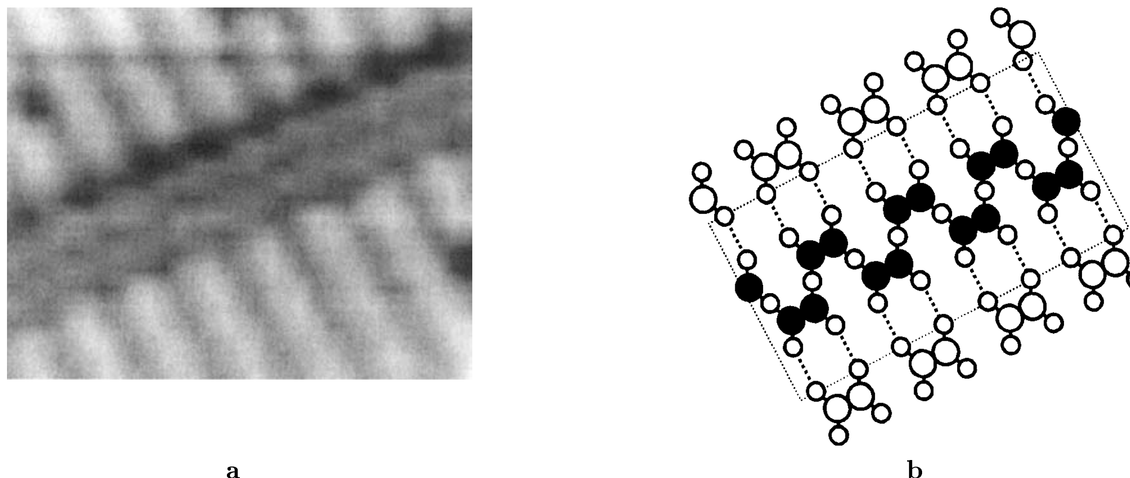

Fig. 2. The same as in Fig. 1, for the out-of-phase nanowire

the formation of Bi nanowires similar to those obtained by the authors of [2—6]. A typical nanowire image is shown in Fig. 1,*a*. It has a width about 1.5 nm, i.e. it replaces 4 dimer rows on the substrate, and extends over ∼ 200 nm in the direction perpendicular to the dimer rows of the Si substrate. A model of the structure of such a Bi nanowire is presented in Fig. 1,*b*. The STM image of nanowires and their model agree with the recent data reported in the literature [5, 6]. Taken as a whole, this gives a firm foundation to claim that our method of fabrication and investigation of Bi nanowires enables one to obtain reliable experimental data on their structure.

## 2. Results of Studies

Apart from the ordinary, well described in the literature [2—6] and shown in Fig. 1 Bi nanowires, which we called the *in-phase* nanowires, we have revealed their new species, namely the *out-of-phase* ones. Typical image of an out-of-phase Bi nanowire is depicted in Fig. 2. Out-of-phase Bi nanowires differ from the in-phase ones in the directions of silicon dimer rows on the Si(001)-2×1 surface: in the latter, the directions are invariable on the both sides of a nanowire, whereas in the former, they are shifted by a half-period of Si(001)-2×1 domain structure,

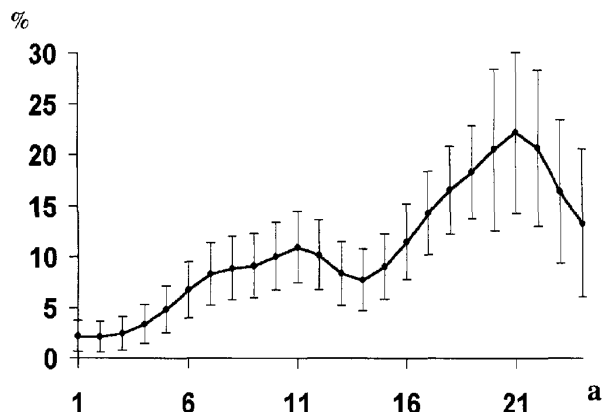


Fig. 3. Defect concentration on the Si(001)-2×1 surface as a function of the distance to a Bi nanowire ($a$ = 3.86 Å is a distance between the neighboring Si dimers)

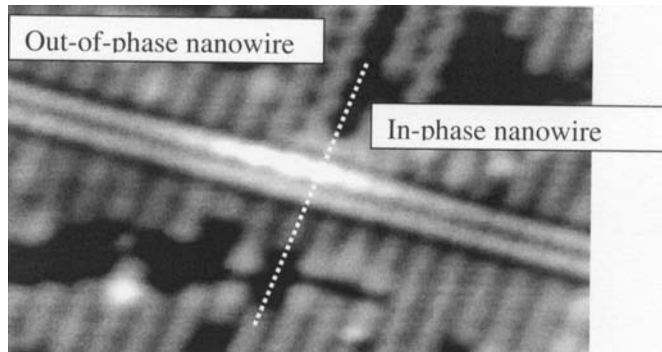


Fig. 4. STM image (~12.5×8 nm$^2$, –1.0 V, 25 pA) of the complex Bi nanowire, which is formed at the intergrowth of in-phase and out-of-phase Bi nanowires on the Si(001)-2×1 surface. Dashed line is the boundary of the intergrowth of the nanowires of both types

i.e. by one dimer row of the silicon substrate. We have proposed a model of the structure of such a out-of-phase Bi nanowire, which is schematically shown in Fig. 2,*b*. It implies that one chain of Bi dimers, which is the part of the out-of-phase nanowire, is shifted by a half-period relatively to the other one.

As a result of both the difference in bond lengths of Bi and Si dimers and interaction between the chains of Bi dimers in the Bi/Si(001)-2×$n$ system, the additional stress arises in the Si substrate. Its relaxation may give rise to the appearance of defect aggregations in the form of vacancy trenches. Earlier publications also indicate the presence of such aggregations [1, 4]. We have calculated the number of the defects, which are mainly the dimer vacancies (rows of missed silicon dimers) on the silicon surface in the vicinity of a nanowire, and built the dependence of their average quantity on a distance to the nanowire. This dependence is shown in Fig. 3. It is seen that the number of the defects is almost by an order smaller in the vicinity of the nanowire than on the Si(001)-2×1 terraces which do not contain adsorbed Bi, and that the relaxation of the stress caused by Bi addimers occurs, as was also observed in [4], by the formation of the vacancy defect aggregations located on the silicon substrate at the distances $(6\div7)a$ and $22a$, where $a$ is a distance between neighboring silicon dimers and equals 3.86 Å. This relaxation is likely to be an additional factor that ensures the stability of Bi nanowires.

In addition to the in-phase and out-of-phase Bi nanowires, the ones with more complex structure appear in the Bi/Si(001)-2×$n$ system. An STM image of such a nanowire is shown in Fig. 4 as an example. As can be seen, its right part is the in-phase nanowire, whereas the left one is the out-of-phase nanowire. Out-of-phase Bi nanowires are formed near the lacking dimer rows of the silicon substrate (dashed line in Fig. 4), where there is a boundary between the out-of-phase silicon domains on the substrate. This boundary serves as a nucleus for an out-of-phase nanowire, which proceeds to grow even when it crosses a phase boundary of silicon domains and turns into the in-phase nanowire. The in-phase and out-of-phase nanowires are converted into one another on the boundary of a vacancy row. In the STM image, the area of the matching of nanowires looks brighter and slightly wider than other nanowire areas. Its extension reaches ~10 rows of the Si dimers that is a typical distance of the relaxation of the stresses originating from a missed dimer row in the silicon substrate.

As a rule, the nanowires itself are almost ideal and contain a little number of defects even after the interaction with hydrogen, oxygen, and ozone [6]. However, at temperatures by 20—40 °C higher than a nanowires formation temperature (i.e. at 540—560 °C), when a partial Bi desorption and degradation of in-phase and out-of-phase nanowires may occur, the defects arise on them and their number grows with temperature and the annealing time. Typical STM image and possible structural models of substitution defects on the in-phase and out-of-phase nanowires are presented in Fig. 5. The defects look like spots, which are slightly elongated along the nanowires, and their brightness and location are similar to the silicon dimers of the substrate. This allows us to identify these defects as the silicon dimers which substitute for bismuth desorbed from nanowires.

A comparative analysis of the amount of substitution defects on the nanowires of both types after the

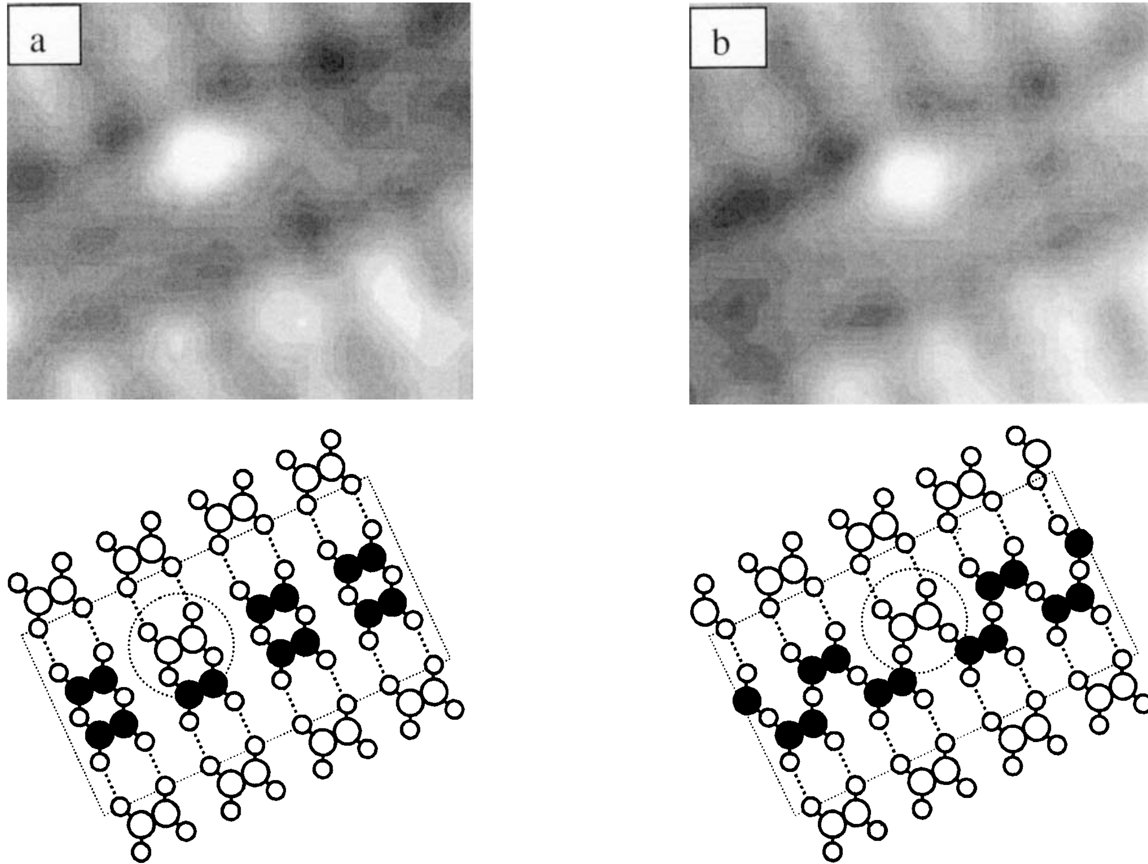


Fig. 5. STM image ($\sim 3.1\times 2.9$ nm$^2$, –2.0 V, 25 pA) and models of the defect structure of in-phase (*a*) and out-of-phase (*b*) Bi nanowires on the Si(001)-2×1 surface. Greater and smaller white circles correspond to Si atoms of the first and second layers, respectively; black circles — to Bi atoms

beginning of the desorption of Bi from them shows that their number in the in-phase nanowires is twice as that in the out-of-phase ones. Assuming that the processes of both the Bi desorption and creation of the substitution defects are thermodynamically equilibrium ones, it is possible, with the help of the Arrhenius relation, to estimate a difference in the energy of Bi desorption from the in-phase and out-of-phase nanowires ($\Delta E = E_{\text{out}} - E_{\text{in}}$ )

$$\Delta E = k_{\text{B}} T \ln 2.$$

When $T = 560$ °C, $\Delta E = 0.05$ eV. This means that, under equal conditions, the out-of-phase nanowires are more stable than the in-phase ones, and, under certain conditions, the number of the former may be greater than that of the latter. A search for these conditions is the subject of our further investigations.

## Conclusions

Thus, it has been shown for the first time that, after the annealing of the Bi/Si(001)-2×1 system up to $\sim$520 °C, the new species of almost defectless out-of-phase nanowires is formed, aside from the in-phase ones known from the literature [2—7]. They extend in the direction perpendicular to the dimer rows of the silicon substrate. Their size coincides with that of the in-phase Bi nanowires. The structure model of out-of-phase Bi nanowires has been proposed. It has been shown that an out-of-phase nanowire may cross the domain phase boundaries on the surface of silicon, turning in such a way into an in-phase one, and vice versa.

It has been shown that the relaxation of the stress arising due to the difference in the Si and Bi dimer bond lengths, gives rise to the appearance of defect aggregations in the form of vacancy trenches on the Si(001)-2×1 substrate.

The defects have been studied in the nanowires, which arise at the Bi desorption. The structure models have been proposed for the defects in both the in-phase and out-of-phase nanowires. It has been revealed that the activation energy of the defect formation is ~0.05 eV higher in the latter comparing to the former. Further theoretical and experimental investigations are necessary to do the ultimate conclusion about the areas of intergrowth of nanowires and areas, in which the stress relaxation occurs.

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АНТИФАЗНІ НАНОНИТКИ Bi НА ПОВЕРХНІ Si(001)

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Р е з ю м е

Методом скануючої тунельної мікроскопії (СТМ) досліджено структуру нанониток Bi на поверхні Si(001)2×1. Крім відомих з літератури синфазних нанониток, вперше виявлено антифазні нанонитки Bi та запропоновано їх структурні моделі. Показано, що релаксація напружень, що виникають через різницю довжин зв'язків між атомами Si в підкладці і атомами Bi в нанонитці, приводить до перерозподілу дефектів у скупчення типу вакансійних траншей, паралельних нанонитці на підкладці Si(001)2×1. При температурах на 20—40 °C вищих, ніж температура формування нанониток (520 °C), останні починають руйнуватись через появу дефектів, які являють собою заміщення атомів Bi на димери Si. Енергія активації десорбції Bi з антифазної нанонитки на 0,05 еВ вища, ніж із синфазної, що свідчить про більшу стабільність антифазних нанониток Bi на поверхні Si(001) 2×1.