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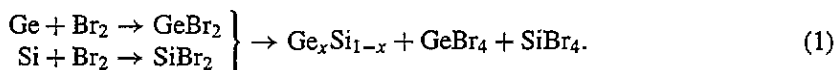‡ Polytechnic Institute, 290013, Lvov 13, Ukraine

Abstract. In this paper the results of an x-ray study of free-standing filament-like crystals of Ge_xSi_{1-x} solid solution are presented. The crystals were grown by a method of vapour transport reactions. The parameter x varied from 0.004 to 0.271. Independent measurements of both the lattice parameter and the composition have shown that the lattice parameter of filament crystals with diameters less than 1 μm is less than that of bulk crystals of the same composition. For example, in the crystals of 0.5 μm diameter with $x = 0.271$ the measured lattice parameter differed from its bulk value by 0.0047 Å. The effect is shown to be not connected with high concentrations of impurities of defects. It is explained by the disturbance of atomic bonds in the uppermost few layers of the crystal and accompanying reconstruction of these layers, which gives rise to a mechanical stress in the crystal bulk. From these data the strain decay length was calculated and was found to vary from 10 to 18 Å. The effect observed is unexpectedly large. We connect this value of the observed change with the cylindrical shape of the crystals. As we did not observe deviations from Vegard's law in the bulk crystals with diameters greater than 1 μm, we have discussed the possible origin of such deviations observed by other investigators.

1. Introduction

In recent years the investigation of growth mechanisms and properties of microcrystals is becoming of ever greater interest. Progress in this field opens the way to the creation of practically important objects such as artificial macromolecules. Widespread methods applied to obtain low-dimensional structures consist of preparation from bulk crystals using various kinds of etching. Such structures possess numerous surface defects and their properties are very unstable, strongly depending on the nature of the substrate and ambient. In connection with this, naturally grown free crystals raise considerable interest. They are characterized by high chemical stability and increased (compared with the bulk) crystal strength. Nevertheless, it might be expected that the properties of very small crystals would be defined by the atoms of the surface layer and should be quite different from those of the bulk. Recent x-ray investigations of submicron silicon whiskers [1] have confirmed that microcrystals having a filament diameter $d < 1$ μm form a lattice with the parameter smaller than that for bulk silicon. The results of the present work prove a certain universality of the facts mentioned. A similar effect has been found for filament crystals of Ge_xSi_{1-x} solid solutions. The origin of the given effect is connected with the increased role of the surface for the submicron crystal properties.

2. Experimental results

The filament crystals (whiskers) of Ge_xSi_{1-x} were grown using the technique of chemical transport reactions in a sealed tube containing bromine and the initial components (Si and Ge):

$$\left.\begin{array}{l} Ge + Br_2 \rightarrow GeBr_2 \\ Si + Br_2 \rightarrow SiBr_2 \end{array}\right\} \rightarrow Ge_xSi_{1-x} + GeBr_4 + SiBr_4. \tag{1}$$

The experiments were carried out using n- and p-type material. The types of conductivity of germanium and silicon were the same in each experiment. To provide this reaction, a temperature gradient was created in the reaction tube. The left-hand side of equation (1) describes the reactions occurring in the high-temperature part of the tube, while the right-hand side corresponds to its low-temperature part where the whiskers grow. The whiskers with diameters less than several microns grow in the {111} direction according to the vapour–liquid–crystal mechanism; on the other hand, whiskers of larger diameter grow according to both the vapour–liquid–crystal and the vapour–crystal mechanisms [2].

There are important peculiarities of the method used.

(1) Along the tube length, concentration gradients of the substances ($SiBr_2$ and $GeBr_2$) delivering the components for growing crystals exist.

(2) The temperature gradient created in the tube is small (about 35 and 90 K cm^{-1} for different initial compositions).

(3) The part of the tube in which submicron crystals grow is about 2 cm long.

(4) The smallest crystals grow in the cold part of the growth zone.

(5) The average temperature (T_{growth}) of the growth zone is about 1190 K.

This is why during the growth process a flow of growth species exists provided by two diffusion fields originating from the temperature and concentration gradients, and in the cold part of the tube there is a smaller concentration of growth species. Since the difference between the thermal energies kT (where k is the Boltzmann coefficient and T is temperature) of the crystals growing in various parts of the tube is much smaller than the energy of the crystal chemical bonds, the flows from the surface of crystals of different sizes (which grow in different parts of the tube, i.e. at different temperatures) should be much the same. Therefore, the supersaturation (determined by the difference between the flows of growth species on the surface and from the surface) should be smaller in the colder part of the growth zone. This means that the growth conditions for the thinnest crystals are close to equilibrium and, hence, more perfect structures form. These conclusions are proved by the experimental observation of increases in the crystal strength and chemical stability as the crystal size decreases.

The crystal strength was studied by stressing a set of whiskers and subsequent examination of bent crystals by electron microscopy. In figure 1(a) an electron micrograph of a bent crystal is presented. By using the measured values of curvature radius and bent crystal thickness, we can calculate the relative compression and extension in the inner and external surfaces of the crystal. On the other hand, by examining the crystal surface in the vicinity of the bend, we can detect plastic deformation of the crystal (see figure 1(b)) and from this assess the crystal strength. The results obtained in these experiments have shown that the crystal strength in submicron crystals is close to the theoretical limit.

The crystal strength of thin crystals is known to depend strongly on the surface defect concentration. In addition, the rate of chemical dissolution also strongly depends on this
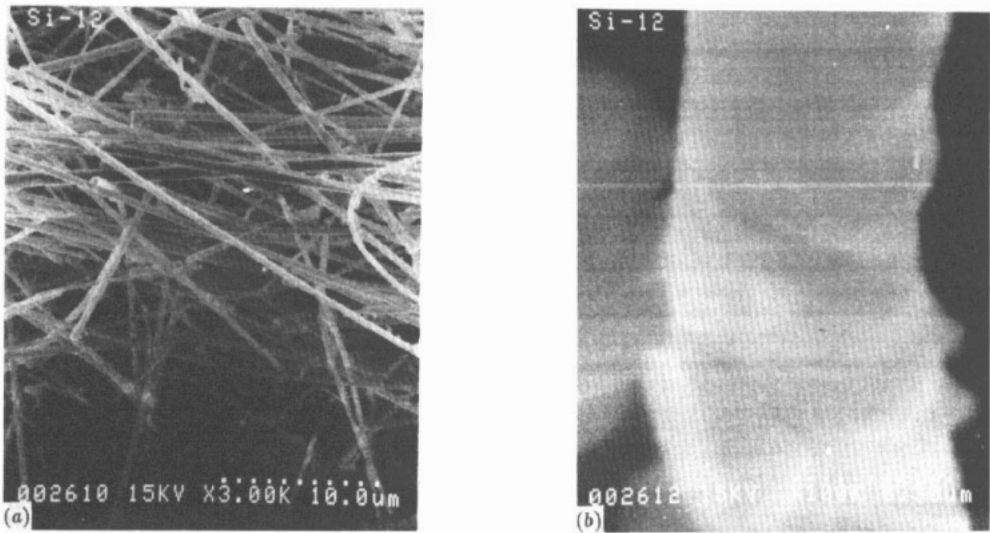
Figure 1. (*a*) Bent crystal in a set of crystals; (*b*) a plastic deformed crystal.

concentration. By studying the rate of chemical dissolution of submicron crystals, we have established that it is one to two orders of magnitude less than that in the crystals with an artificially prepared surface. Furthermore, with the help of Auger spectroscopy we have found that the thickness of the dioxide grown on the surface does not exceed 10–15 Å if the crystals had been stored in the atmosphere for 3 years. The high perfection of the dioxide was confirmed by the Auger spectra. Additionally, it was found that the dioxide thickness is less in crystals of smaller diameter. All these experiments substantiate our conclusion that the submicron crystals have both a perfect bulk and a perfect surface.

These results are in agreement with the results of computer simulation of the growth process by the Monte Carlo method [3], where the decrease in supersaturation was shown to lead to an improvement in the quality of the crystalline structure.

Since bromine forms different chemical bonds with Ge and Si as well as with impurities doping these semiconductors, the chemical reactions (1) for these materials occur at different temperatures, i.e. in different parts of the tube. By direct investigation of the chemical composition and by studying the temperature dependence of the electroconductivity [4] in the crystals grown in different parts of the tube, it was found that, as the melting temperature of a material decreases, then the maximum concentration shifts towards the colder part of the tube. Therefore, the crystals grown in different parts of the growth zone differ not only in size but also in the concentrations of germanium, silicon, and doping donors or acceptors. So, in the colder part of the growth zone, smaller crystals with higher contents of germanium and doping impurities form. The composition of the grown crystals was measured with x-ray microprobe spectroscopy, and for some crystals ion mass spectroscopy was also used. The lattice parameters of the crystals was determined using x-ray diffractometry. In all, several tens of crystals were studied. Typical results are shown in table 1.

For the same crystal compositions, table 1 presents both the experimentally measured lattice parameters (a_w) of the whiskers and the lattice parameters (a_b) of the bulk crystals calculated by Vegards's law [5].

The error in measuring a_w was ±0.0005 Å. The inaccuracy in the measurement of x by

Table 1. The lattice parameter values a_w (measured in the whiskers) and a_b (calculated according to Vegard's law for the bulk) versus the Ge_xSi_{1-x} crystal diameter d_i and Ge concentration x' and x, which characterize (in weight fraction) the compositions of the initial materials and grown whiskers, respectively.

x' initial	T_{growth} (K)	d_i (μm)	x	a_w (Å)	a_b (Å)
0.15	1300	20–30	0.0180	5.4338	5.4342
	1180	1.0	0.1495	5.4634	5.4631
	1110	0.5	0.271	5.4854	5.4901
0.01	1315	20–30	0.0004	5.4306	5.4305
	1200	1.0	0.0100	5.4327	5.4328
	1020	0.5	0.015	5.4321	5.4339

x-ray microprobe analysis is equal to about 0.0001 weight fraction (i.e. about 10^{18} cm^{-3}). That is why the errors in evaluating a_b (from the inaccuracy in x measurement) were ±0.0002 Å and ±0.0001 Å for crystal diameters less than 1 μm and greater than 1 μm, respectively.
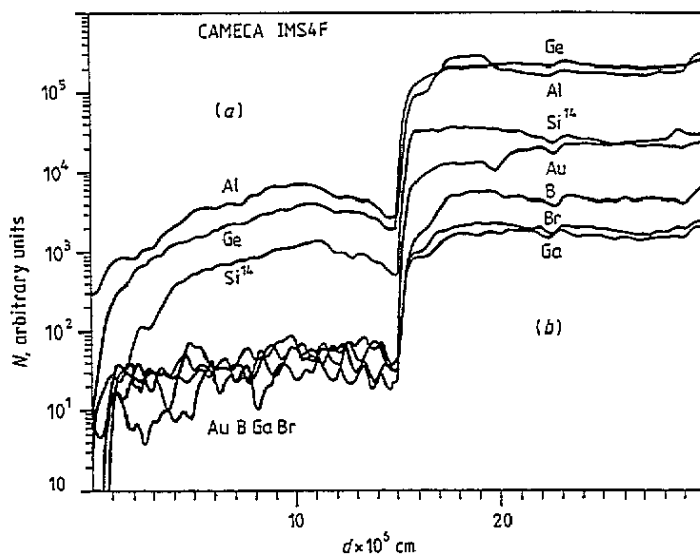
Figure 2. Depth profiles of Si, Ge, Al, Ga, B, Br and Au in two crystals of different diameters; (a) $d = 0.15$ μm; (b) $d = 1$ μm.

Using a mass spectroscopy method we have found that bulk distribution of germanium (as well as of other impurities) in our crystals is homogeneous with a spatial resolution of almost 50 Å for crystals of any diameter. In figure 2, profiles of some components are presented for two crystals of 0.15 and 1 μm diameter. Taking into account that the analysed area was changing during the analysis time owing to the cylindrical shape of crystals, we can only draw conclusions regarding a spatial distribution of the ratio of the silicon to germanium concentrations. From the profiles presented it is seen that in the bulk of the crystals the former is approximately constant.

3. Discussion

As evident from table 1 the measured lattice parameters of the whiskers and those calculated by Vegard's law using the x measurement coincide within the experimental accuracy for all whiskers with $d > 1$ μm. On the other hand, the lattice parameters measured in the crystals with $d < 1$ μm are smaller than those calculated for both small and large values of x.

Before discussing this discrepancy between the behaviours of submicron crystals and those with diameters larger than 1 μm, we must emphasize that, contrary to the results obtained in [6–9], we did not obtain a deviation from Vegard's law in the crystals of large diameters (larger than 1 μm, i.e. for the bulk material). It should also be noted that the results obtained by various workers were markedly different from each other, and the methods of crystal preparation used in [6–9] and in the present work were different. We believe that one of the most probable reasons for deviations from Vegard's law observed in [6–9] is inhomogeneity in solute distribution appearing during the growth process. As the crystals are being grown, some of the solute atoms aggregate into clusters of various sizes. Then, the higher the concentration of solute atoms, the greater is the number of clusters of larger sizes that form. As a result, some of the total solute material (which is determined, for example, from chemical, spectral, or other integral analyses) does not change the lattice parameter and should not be accounted for in evaluating its magnitude. Only in [9] was the homogeneity of component distribution in the mixed crystals studied. However, as a spatial resolution of the method was not indicated in [9], it is impossible to account for cluster creation in the lattice parameter calculation.

By studying the Ge and Si distributions in our crystals (see figure 2) we found both components to be distributed uniformly in the bulk. The spatial resolution in our experiment was about 50 Å. If clusters form, then the number of atoms in a cluster did not exceed ten. Thus, the lattice parameter in our mixed crystals was determined by the overall amount of the solute introduced into the crystals.

As the theoretical calculations which have been reviewed in [10] are employed, it turns out that for the same Ge–Si system some calculations give positive deviations from Vegard's law, while others give negative deviations. Therefore, these calculations did not confirm the experimental results in [6–9].

Taking into account the above consideration, we have concluded that in submicron crystals grown by the vapour transport reactions method used in our work the deviations from Vegard's law have nothing in common with those observed in [6–9].

The effect observed could also not be accounted for by a high doping concentration [11] as the total impurity concentration measured in the crystal was too small to change the lattice parameter (about 10^{18} cm^{-3}). These changes also cannot be explained by an increase in the defect density as the filament diameter decreases. The density of defects should be low. This follows from the microcrystal growth peculiarities described above as well as from the experimentally observed increase in crystal strength and chemical stabiilty as the diameter decreases.

The changes in lattice parameter observed in submicron crystals of Ge_xSi_{1-x} solid solution coincide in sign and are comparable in value with those found for submicron silicon crystals [1]. We think that similarly to the case of silicon whiskers the most probable mechanism of the changes observed is the influence of a surface reconstruction on the bulk layers of the whiskers. According to a conventional viewpoint on surface reconstruction in a semi-infinite crystal approximation the structure changes decay sharply with increasing distance from the surface and are very small already by the third to fourth subsurface layer [12]. On the other hand, we observed lattice parameter changes in the crystals containing as

many as 1000 atomic layers. We believe that such great changes result from the cylindrical shape of the crystals, since in this case the inner atoms are affected by the uppermost reconstructed layers of a crystal more strongly than in the case of a crystal with a plane surface because of the greater ratio of the number of surface atoms to the number of atoms in the bulk.

According to the model proposed, each submicron crystal may be regarded as a crystal with the 'lattice parameter' depending on the distance from its surface. This must give rise to inhomogeneous broadening of Bragg reflections and to a shift in its maximum, which was observed in our experiment. The lattice parameter corresponding to the Bragg reflection maximum may be regarded as some 'average' lattice parameter and may be presented in the form [1]

$$a(d_i) = a_0 \left(1 - \gamma \frac{\tanh(d_i/L_a)}{d_i/L_a} \right) \tag{2}$$

where L_a is the strain decay length and γ is a phenomenological parameter. From the theoretical crystal strength, $\gamma = \frac{1}{4}$. Then, using equation (2) and the experimental results for various compositions we have obtained values of L_a ranging from 10 to 18 Å.

Acknowledgments

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