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Peculiarities of Si–Ge whisker growing by CTR method

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Growth peculiarities of doped $Si_{1-x}Ge_x$ (x = 0.01–0.05) solid solution whiskers of 1 to 100 μm in diameter in closed bromide system by chemical transport reactions method have been investigated. A dimensional dependence of specific resistance at 300 K has been revealed. The $Si_{1-x}Ge_x$ (x = 0.05) whiskers of 30 to 70 μm in diameter with dopant concentration in the vicinity of metal-insulator transition were obtained. Substantial changes of the specific resistance and gauge factor of the crystals depending on their diameters has been observed in temperature range 4.2–50 K.

Методом химических транспортных реакций в закрытой бромидной системе исследованы особенности выращивания легированных нитевидных кристаллов твердого раствора $Si_{1-x}Ge_x$ (x = 0,01–0,05) разного диаметра (0,1–100 мкм). Установлена размерная зависимость удельного сопротивления кристаллов при T = 300 К. Получены легированные образцы $Si_{1-x}Ge_x$ (x = 0,05) разного диаметра (30–70 мкм) с концентрацией легирующих примесей вблизи перехода металл-диэлектрик. Обнаружены существенные изменения их удельного сопротивления и коэффициента тензочувствительности в температурной области 4,2–50 К в зависимости от диаметра кристаллов.

Miniaturization of semiconductor devices makes a series of new demands to studies of physical properties of microcrystals at decreasing sizes thereof. In particular, it is necessary to take into account the recently revealed dimensional effects in Si and Si–Ge whiskers. Those include the change of submicron whisker lattice parameter [1], the shift of optical reflection edge, and the appearance of visible luminescence similar to that in porous silicon [2]. One of important tasks of Si–Ge whisker studies is to investigate the growth peculiarities thereof at various diameters and doping kinds. The aim of this work is to study peculiarities of $Si_{1-x}Ge_x$ (x = 0.01–0.05) solid solution whiskers growth in the closed bromide system by chemical transport reactions (CTR) method as well as the low temperature properties thereof. The whisker diameters range from 0.1 to 100 μm.

Si–Ge whiskers were grown by CTR method in closed bromide system [3, 4]. This technique makes it possible to dope the whisker immediately in the course of growth. The growth ampoule is loaded with silicon and germanium (growing materials), doping impurities, and bromine that is used as the transporting agent. The ampoule is evacuated down to a pressure of 10^{-5} Torr and placed into a temperature-gradient furnace. In the low-temperature part of furnace (so-called crystallization zone), the whisker growth takes place.

The main conditions of Si–Ge whisker growth are presented in Table. Gold and platinum are used as growth initiators according to vapor-liquid-crystal (VLC) mechanism, boron is used as doping impurity. The above-described method provides the growing of microcrystals both in the form of whiskers and needle-like crystals (with developed obliquity), as well as ribbons and isometric crystals. It is possible to manage morphology of microcrystals by selecting the crystallization temperature. In particular, it is shown that as the crystallization temperature increases, the microcrystal morphology changes from thin sub-

Table. Growth conditions of Si–Ge whiskers (T_e, temperature of evaporation zone; T_c, temperature of crystallization zone)

Compound	Impurity content, mg/cm^3	T_e, °C	T_c, °C	Transport agent, mg/cm^3	Whisker parameters ρ, Ω·cm
Si–Ge	Au $2\cdot10^{-3}$ Pt 7·10−3 B $8\cdot10^{-3}$	1150	800–950	$n_{\mathrm{Br}} = 2$	0.01–0.02

micron whiskers to ribbons, and further to the whiskers of large diameters ($d > 60$ μm) and isometric crystals (Fig. 1). The crystallization temperature influences also the whisker diameter: as the temperature rises from 800 to 950°C, the crystal diameter increases from 0.1 μm to 100 μm (the heat treatment duration 2 h).

The composition of $Si_{1-x}Ge_x$ solid solution whiskers was investigated by micro-probe analysis and corresponded to $x = 0.01–0.05$. It was much more difficult to determine the admixture content in the crystals. As the crystals of different diameters grow under different technological conditions, their doping will differ also. In addition, the elemental composition must vary somewhat along the crystal radius, taking into account two stages of its creation. At the first stage, the thin crystal grows in length, the so-called leader being formed according to the VLC mechanism [5]. At the second stage, the leader thickness increases due to deposition from vapor according to the vapor-crystal (VC) mechanism. The presence of two growth mechanisms causes a different doping of central and peripheral part of the crystal. Of course, the resulting distribution of impurities in a crystal is defined by the diffusion coefficients of impurities at the growth temperature, by the crystal transversal dimensions and the heat treatment duration.

Elemental composition of impurities in Si–Ge crystals was examined by micro-probe analysis, Auger spectroscopy, and mass-spectral analysis. The micro-probe analysis has revealed trace Pt concentrations in all the samples, the method sensitivity being about 10^{18} cm^{-3}. Thus, Pt concentration in the whiskers did not exceed that limit. Using the Auger spectroscopy with gradual anode etching of surface, Br was found only at the whisker surface at the surface concentration about 10^{14} cm^{-2}. The results of mass-spectral analysis differ substantially for the crystals of submicrometer and submillimeter diameters. The whiskers of the latter group are homogeneous as for structure and element composition. In submicrometer whiskers, two structural regions are clearly distinguishable, the crystalline core and porous shell. These structure distinctions are confirmed by the results of TEM and ASM [6]. As mass-spectral investigations have shown, impurities in each of the structural regions in the whisker are distributed homogeneously [7].

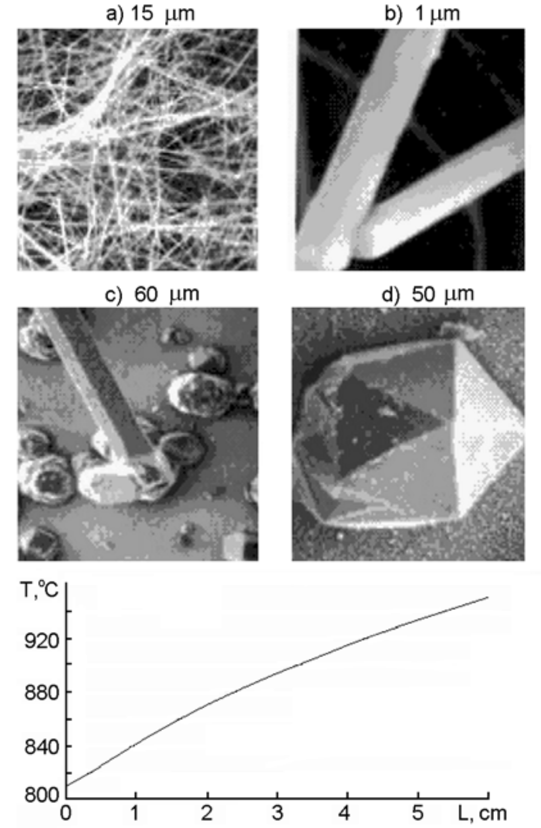

Fig. 1. Formation of Si–Ge whiskers with various morphology in the crystallization zone: (a) submicrometer whiskers; (b) ribbons of 1 μm in diameter; (c) whiskers of 2–60 μm in diameter; (d) isometric crystals.

An interesting peculiarity of Si–Ge whiskers is the existence of so called "geometrical effect" therein related with differ-

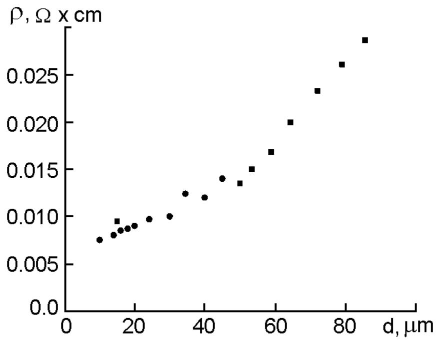

Fig. 2. Dependence of specific resistance on Si–Ge whisker diameter (T = 300 K).

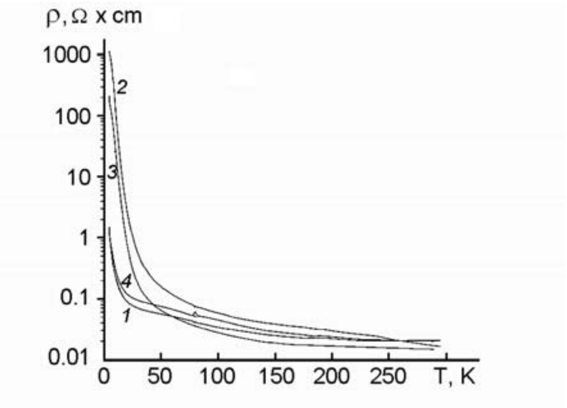

Fig. 3. Temperature dependences of specific resistance for the $Si_{1-x}Ge_x$ (x = 0.05) whiskers: free (*1*) and strained by various substrates: copper (*2*), aluminum (*3*), quartz (*4*) d = 40 μm ($\rho_{300\ K}$ = 0.012 Ω·cm). The dependences for d = 50 and 60 nm are quite similar.

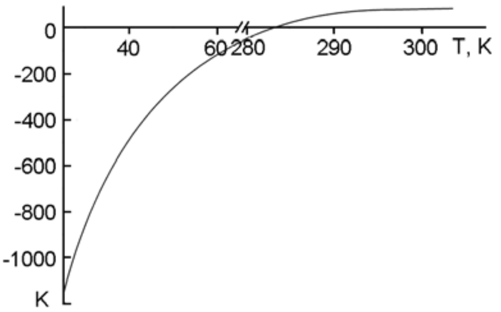

Fig. 4. Temperature dependences of gauge factor for $Si_{1-x}Ge_x$ (x = 0.05) whiskers: d = 40 μm, $\rho_{300\ K}$ = 0.012 Ω·cm (copper substrate). The dependences for d = 50 and 60 nm are quite similar.

ent doping of the whiskers of various diameters. This effect becomes apparent as a dependence of the whisker specific resistance on its diameter (Fig. 2). Such geometrical dependence of resistance indicates that the crystals of smaller diameter are doped stronger (that is, contain a higher concentration of boron) as compared with those of large diameters. Using the appropriate amount of the dopant, the whiskers can be obtained with impurity concentrations in the vicinity of critical concentration for metal-insulator transition (MIT) ($N_c = 7 \cdot 10^{18}$ cm^{-3} that corresponds to specific resistance of uncompensated samples ρ = 0.009 Ω·cm). Then, as the specific resistance (or concentration of doping impurity) depends on the diameter (Fig. 2), the whisker size becomes critical with respect to approaching (or moving off) MIT. That is, we can obtain the whiskers of 20–70 μm in diameter with dopant concentrations approaching MIT both from metallic and from dielectric side and study in detail the change of properties in the transition region. It should be noted that the whiskers of such diameters can be regarded as bulk material, i.e. an influence of surface on their properties can be neglected. We have studied the peculiarities of low-temperature resistance of $Si_{1-x}Ge_x$ (x = 0.05) whiskers of various diameters (40–60 μm) and impurity concentrations at the dielectric side of MIT obtained from one growth charge. In particular, we have measured temperature dependence of resistance for free and strained whiskers in the temperature range 4.2–300 K using the procedure described in detail in [8] (Fig. 3). The whisker straining was provided by fixation on a substrate and cooling to the liquid helium temperature due to the difference of thermal expansion coefficients of the whisker and substrate. Basing on the investigations, the whisker gauge factor can be estimated, which characterizes the piezoresistive effect level in the whisker:

$$K = \frac{\Delta\rho}{\rho_0 \cdot \varepsilon}, \qquad (1)$$

where Δρ is the specific resistance change due to straining; ρ_0, the specific resistance of unstained whisker; ε, relative strain. Taking into account that the whisker relative strain remains practically unchanged in the temperature range 4.2–50 K (in accordance with our computations [8]), we have constructed the temperature dependences of gauge factor (Fig. 4) basing on the data of Fig. 3. As is seen from Fig. 4, the gauge factor of a whisker of 40–60 μm in diameter attains $3 \cdot 10^4$ at T = 4.2 K. Such great values of the whisker gauge factor at low temperatures are explained by strain-induced change of conductance mechanism, which is well described within the framework of Habbard model in heavily doped semiconductor crystals [9].

To conclude, the following features of the Si–Ge whisker growth in the closed bromide system using CTR method have been established. At growing in a temperature gradient, the whisker diameters are determined by the growth temperature. The whiskers of different diameters (formed at different temperatures) differ in the dopant content, the boron concentration being increasing at reduction of the whisker diameter from 100 μm to 20 μm. In heavily doped whiskers, their size becomes critical with respect to approaching (or moving off) MIT. The whiskers with impurity concentrations at the dielectric side of MIT have been obtained and the change of their low-temperature characterstics (specific resistance, gauge factor) in the vicinity of transition have been revealed. Thus, we have shown a possibility to manage the low-temperature parameters of $Si_{1-x}Ge_x$($x = 0.01-0.05$) whiskers by varying their diameters in the course of growing.

References

1. A.I.Klimovskaya, I.P.Ostrovskii, R.I.Baitsar et al., *J.Phys.:Condens.Matter.*, **7**, 1229 (1995).
2. E.G.Gule, G.Yu.Rudko, A.I.Klimovskaya et al., *Phys.Stat.Solid.*, **B 161**, 565 (1997).
3. V.A.Voronin, I.I.Maryamova, A.S.Ostrovskaya, *Cryst.Prop.and Prepar.*, **36–38**, 340 (1991).
4. A.A.Druzhinin, I.P.Ostrovskii, *Phys.Stat. Solid.C*, **181**, 333 (2004).
5. E.I.Givargizov, Growth of Needle-like and Plate Crystals from Vapor, Nauka, Moscow (1977) [in Russian].
6. A.I.Klimovskaya, I.V.Prokopenko, I.P.Ostrovskii, *J.Phys.: Condens.Matter.*, **13**, 5923 (2001).
7. A.I.Klimovskaya, I.P.Ostrovskii, A.S.Ostrovskaya, *Phys.Stat.Sol.A.*, **153**, 465 (1996).
8. A.Druzhinin, E.Lavitska, I.Maryamova et al., *Cryst.Res.Technol.*, **37**, 243 (2002).
9. J.A.Chroboczek, F.H.Pollak, H.F.Staunton, *Phil.Mag.*, **50**, 113 (1987).

Особливості вирощування ниткоподібних кристалів Si–Ge методом ХТР

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Методом хімічних транспортних реакцій у закритій бромідній системі досліджено особливості вирощування легованих ниткоподібних кристалів твердого розчину $Si_{1-x}Ge_x$ ($x = 0{,}01-0{,}05$) різного діаметра (0,1–100 мкм). Встановлено розмірну залежність питомого опору кристалів при $T = 300$ К. Одержано леговані зразки $Si_{1-x}Ge_x$ ($x = 0{,}05$) різного діаметра (30–70 мкм) з концентрацією легуючих домішок поблизу переходу метал-діелектрик. Виявлено істотну зміну їх питомого опору та коефіцієнта тензочутливості у температурній області 4,2–50 К в залежності від діаметра кристалів.