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Si-Ge Whiskers for Thermoelectric Sensors Design

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The paper deals with studies of thermoelectric properties for $Si_{1-x}Ge_x$ (x = 0.01 - 0.05) whiskers doped with boron during their growth by CVD method. Temperature dependences of the resistance and the Seebeck coefficient for $Si_{1-x}Ge_x$ whiskers were measured in the temperature range 275 – 550 K. A method for determination of thermoelectric parameters of the whisker was proposed with use of the whisker joints, which allows us to define a ratio of Seebeck coefficient to thermal conductivity α/χ. Taking into account the obtained values of Seebeck coefficient, the whisker conductance and estimated values of thermal conductivity, parameter ZT was calculated for the whiskers and consists of 0.15 for at temperature about 500 K. The obtained value of ZT is in good coincidence with literature data for hot pressed Si-Ge nanocomposites. The humidity sensor was designed on the basis of Si-Ge whiskers.

Key words: Si-Ge, whiskers, Seebeck coefficient, thermal conductivity, figure of merit, sensor.

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Introduction

Si nanowires are widely used for sensor device application [1]. The main widespread their application is in biosensors [2-4]. Besides, nanowires are used for control of inertia environment [5], in particular for gas sensor design [6].

Si-Ge whiskers are prospective for sensor application. On their base sensors of mechanical (strain, pressure, liquid level) [7] and thermal (temperature, temperature difference) [8] values were elaborated. The studies of piezo-thermo-e.m.f. in heavily doped $Si_{1-x}Ge_x$ whiskers at low temperatures and strong magnetic fields open an outlook for sensor design [9]. The main problem here is obtaining of whiskers with predictable properties.

The paper deals with studies of Si-Ge whisker growth by chemical vapour deposition (CVD) method in closed bromide system with thermoelectric properties predicted beforehand for design of thermoelectric sensors.

I. Method of growth

We grow Si-Ge whiskers with Au as initiator of growth by vapour-liquid-solid (VLS) mechanism and with B, Zn as doping impurities. The purpose of growth is to obtain whiskers with impurity concentration in the vicinity to metal-insulator transition ($N_c \approx 5{\cdot}10^{18}$ cm^{-3}). Therefore, we should choose impurities which create shallow levels in Si-Ge band structure. Boron is shallow impurity as in Si and in Ge, while Zn creates deep level in Si and shallow level in Ge. So, we grow $Si_{1-x}Ge_x$ whiskers doped with B based on Si (x = 0.01 – 0.05) and the whiskers doped with Zn based on Ge (x = 0.95 - 0.99). As for intermediate compositions of solid solutions (x > 0.1 and x< 0.9), the whiskers have inhomogeneous distribution of Ge (or Si) which essentially influences on their low temperature parameters (such as hopping conductance, magnetoresistance, etc.) and the performances of sensors designed on their base.

The following temperature regimes were used: temperature of evaporation and crystallization zones were 1500 K (1150 K) and 1150 - 1220 K (850 - 920 K) respectively for $Si_{0.95}Ge_{0.05}$ ($Si_{0.05}Ge_{0.95}$) whisker growth. Bromine was loaded in a tube in amount of 0.1 - 0.2 mg/cm^3. A concentration of Au was of about 0.002 - 0.003 mg/cm^3.

As a result of processing during 2 hours the whiskers with diameters 0.1 - 50 μm are created in the tube. It should be noted that the whiskers of various diameters have different doping level, i.e., so called “geometric” effect of the whisker resistance exists: a resistance drops down when the whisker diameter decreases. Due to observed effect a whisker diameter can be regarded as critical for approach to (or removal from) metal-insulator transition (MIT). Then we can obtain the whiskers of 20 - 50 μm in diameter with impurity concentration as from metal and from insulator side of the MIT and study in detail the region of transition. The whiskers of such diameters are considered as bulk materials. The influence of surface on their properties is small and can be neglected. On the other hand, the whiskers of submicron diameters reveal specific effects: decrease of lattice parameter, special elecrophysical properties [10]. These effects are explained by influence of surface on physical properties of crystals with small diameters. So, submicron whiskers can be used for determination of surface contribution in hopping conductance at low temperatures. The above mentioned performances of Si-Ge whiskers grown can be used for application in sensors.

II. Results and discussion

Temperature dependences of the resistance and the Seebeck coefficient for solid solution $Si_{1-x}Ge_x$ whiskers were measured in the temperature range 275 - 550 K. The whiskers of two boron concentrations with specific resistance $\rho = 0.004$ Ohm·cm and $\rho = 0.005$ Ohm·cm were under a consideration. The temperature dependences of the whiskers resistance is presented in Fig. 1. As we can see in Fig. 1, the samples have metallic conductivity, their resistance raises with temperature growth. The temperature dependence of Seebeck coefficient for $Si_{1-x}Ge_x$ whiskers with specific resistance $\rho = 0.004$ Ohm·cm is presented in Fig. 2. As obvious from Fig. 2, the Si-Ge whiskers have rather large values of Seebeck coefficient up to 1 mV/K.

To adequately assess thermoelectric parameters of $Si_{1-x}Ge_x$ whiskers in certain temperature range it is important to know the real value of the coefficient of thermal conductivity (χ). As is known, that parameter χ is highly dependent on the composition, degree of solid solution perfection.

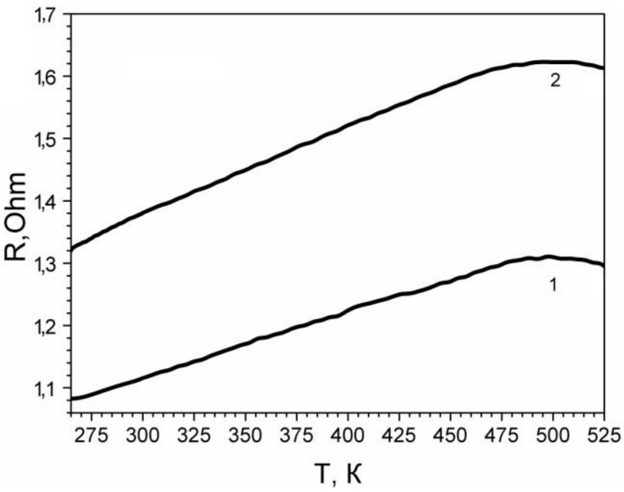

Fig. 1. The resistance for $Si_{0.95}Ge_{0.05}$ whiskers versus temperature for specimens with specific resistivity: 1 – $\rho = 0.004$ Ohm·cm; 2 – $\rho = 0.005$ Ohm·cm.

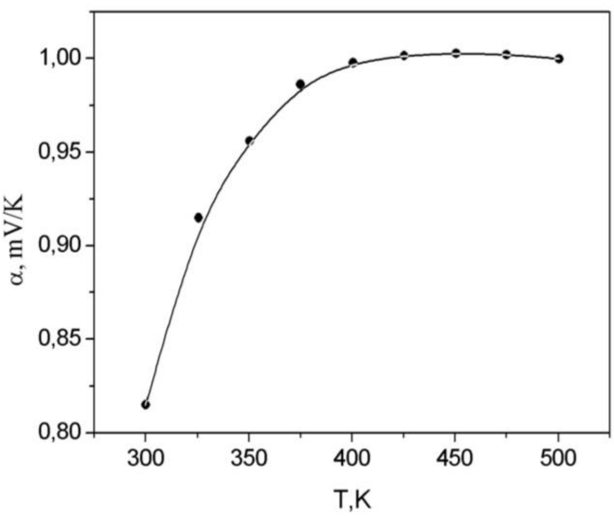

Fig. 2. The Seebeck coefficient for $Si_{0.95}Ge_{0.05}$ whiskers versus temperature for specimens with $\rho = 0.004$ Ohm·cm.

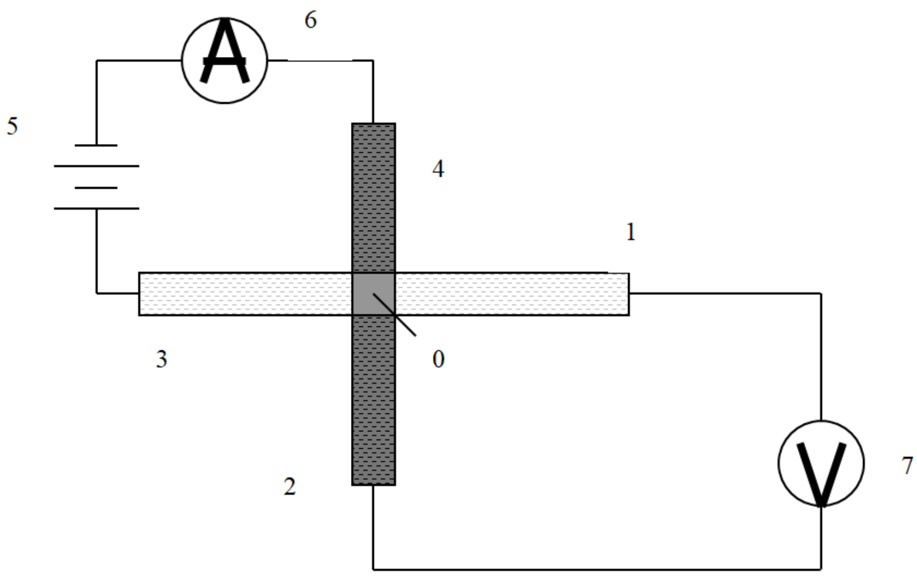

Fig. 3. A way to measure the thermoelectric parameters of Si-Ge whiskers.

Table 1

Thermoelectric parameters of cross-like Si-Ge whisker joints

№	U_1, mV voltage diference 0-1	U_2, mV voltage diference 0-2	R_3, Ohm resistance of measuring branch	I_3, μA heating current	χ /α, A/cm	α/χ, cm/A
1	49.0	33.8	224	9.6	4.2	0.24
2	73.5	57.5	242	11.6	4.05	0.26

One can propose a method for determination of thermoelectric parameters. For this purpose, the whiskers of certain geometry and morphology were obtained. In particular, various aggregates with cross-like and X-like shape were obtained. Such whisker structures were used for estimation of their thermoelectric parameters. We have proposed a method, which allows us to define a ratio of Seebeck coefficient to thermal conductivity α/χ. According to the method, current is passed through a heating branch, namely two adjacent cross-shaped contacts of joint 3 and 4; two others contacts 1 and 2 serve as a measuring branch (Fig. 3).

The main measurable parameters were: 1) the potential difference U_1 and U_2 between the ends of measuring branch and the node of joint, 2) the impedance of measuring branch R_3 and 3) the current through heating branch I_3. Therefore, warming up the node of joint by current I_3 creates two heat flows from the growth middle to points 1 and 2 of the measuring branches that could be recorded as $W_1 = \frac{\chi S}{l_1}\Delta T_1$ and $W_2 = \frac{\chi S}{l_2}\Delta T_2$ (S – sectional area of the growth, l_1 and l_2 are the length of measuring branch, respectively). Taking into account that temperature gradients ΔT_1 and ΔT_2 can be expressed due to value of thermopower $U_1 = \alpha\Delta T_1$ and $U_2 = \alpha\Delta T_2$, and the difference in heat flow creates between points 1 and 2 an electrical power, we get the equation

$$I_3^{\,2} R_3 = \frac{\chi S}{\alpha l_1}(nU_2 - U_1)\,, \qquad (1)$$

where $n = l_1/l_2$.

The equation (1) allows us to determine the ratio of χ/α. The calculation were firstly successfully checked at Si whiskers. The results are presented in the Table 1.

The data of Table 1 shows that obtained value of χ/α consist of 4.1. The value was compared with data of [9] for bulk silicon at room temperature, which was equal to 4.6. Therefore, the results evidence that good agreement of our estimations with literature data was obtained.

The above results allow us to estimate a ratio of χ/α in $Si_{1-x}Ge_x$ (x = 0.05) whiskers in the temperature range 300 - 500 K. Firstly we have measured the temperature dependence of the whisker Seebeck coefficient (see Fig. 2). Then taking into account the measured parameters of the whiskers joint and obtained ratio χ/α we have obtained the following temperature dependences of coefficient of thermal conductivity (see Fig. 4).

The obtained data of the whisker thermal conductivity are in 30 times lesser than the correspondent parameters for bulk silicon. It is unexpectedly large change due to rather small composition of solid solution (x = 0.05). So, the obtained data should be checked by other direct measurement, in particular by 3ω method.

The obtained data allow us to estimate a figure of merit for the investigated whiskers according the following equation:

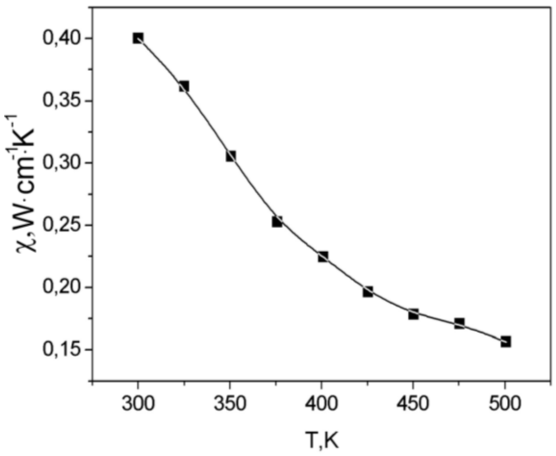

Fig. 4. The thermal conductivity χ of $Si_{0.95}Ge_{0.05}$ whiskers versus temperature for specimens with specific resistivity: $\rho = 0.004$ Ohm·cm.

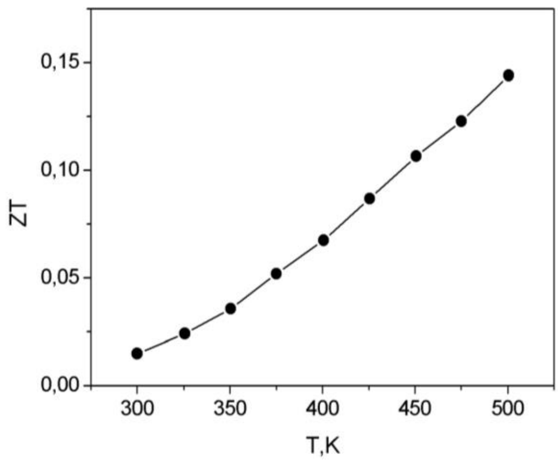

Fig. 5. Figure of merit (parameter ZT) for $Si_{0.95}Ge_{0.05}$ whiskers versus temperature.

$$ZT = \frac{\alpha^2 \sigma}{\chi} T , \qquad (2)$$

where σ is conductivity of Si-Ge whiskers.

The obtained ZT parameter versus temperature for Si-Ge whiskers is presented in Fig. 5. A comparison of ZT parameter for Si-Ge whiskers and nanocomposite hot pressed Si-Ge samples [12] have shown a good coincidence. As follows from Fig. 5, value of ZT parameter for Si-Ge whiskers at temperature 500 K consists of 0.15 that is a little less than for nanocomposite hot pressed Si-Ge samples [12].

III. Design of the thermoelectric humidity sensor

Thermoelectric humidity sensor of psychrometric type is designed on the base of Si-Ge whisker. Two electrical contacts to Si-Ge p-type whisker ($\rho = 0.004$ Ohm·cm) serving as dry and wet thermometers (the second contacts is situated in sensitive to humidity polymer) are connected with the measurement device, in which voltage difference is calibrated in humidity reading. Calibration curve of the sensor is shown in Fig. 6.

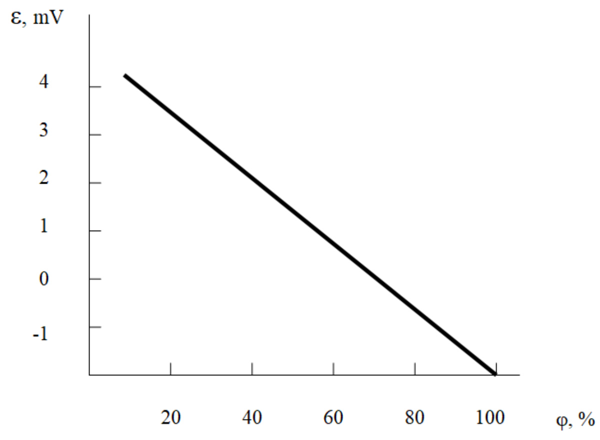

Fig. 6. Thermo-emf ε versus humidity φ dependence for the thermoelectric sensor of humidity.

A linear dependence of thermo-emf ε on humidity φ was observed. However, due to the low values of thermo-emf (ε is about a few mV) an accuracy of humidity measurement should by low. Nevertheless, the sensors are simple in design, cheap, and can be used for approximate detection of humidity in the wide humidity range $\varphi = 10 - 100$ %.

Conclusions

Temperature dependences of the resistance and the Seebeck coefficient for $Si_{1-x}Ge_x$ (x = 0.05) whiskers were investigated in the temperature range 275 – 550 K. Investigation of thermoelectric parameters of the whisker joints shows a possibility their using for estimation of a ratio of Seebeck coefficient to thermal conductivity α/χ. Estimation of the thermoelectric quality of the whiskers was done. In particular, the parameter ZT was calculated based on measured values of Seebeck coefficient and the whisker conductance as well as estimated values of the whisker thermal conductivity. ZT parameter was equal to 0.15 at temperature 500 K, while its temperature dependence showed linear growth in the temperature range 350 – 500 K that promises rather high values at temperature 1200 K. The results obtained are in good agreement with literature data for hot pressed Si-Ge nanocomposites. Thermoelectric sensor of humidity of psychrometric type is designed on the base of Si-Ge whisker. The sensor can be used for approximate measurement of humidity in the wide humidity range $\varphi = 10 - 100$ %.

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Ниткоподібні кристали Si-Ge для створення термоелектричних сенсорів

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У статті розглянуто термоелектричні властивості ниткоподібних кристалів $Si_{1-x}Ge_x$ (x = 0,01 - 0,05), легованих бором під час їх росту методом хімічних газотранспортних реакцій. Температурні залежності опору та коефіцієнт Зеєбека ниткоподібних кристалів вимірювали в діапазоні температур 275 - 550 К. Запропоновано метод визначення термоелектричних параметрів ниткоподібних кристалів із застосуванням зростків кристалів, що дозволяють визначити відношення коефіцієнта Зеєбека до теплопровідності α/χ. Враховуючи отримані значення коефіцієнта Зеєбека, електропровідності ниткоподібних кристалів та розрахункові значення параметра теплопровідності, проведені оцінки параметра ZT, який становить 0,15 для температури порядка 500 К. Отримане значення ZT співпадає з літературними даними для сучасних нанокомпозитів Si-Ge, отриманих методом гарячого пресування. На основі ниткоподібних кристалів Si-Ge був розроблений прецизійний сенсор вологості повітря.

Ключові слова: Si-Ge, ниткоподібні кристали, коефіцієнт Зеєбека, теплопровідність, термоелектрична добротність, сенсор.