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Superparamagnetism in $Si_{1-x}Ge_x$ <B, Hf> Whiskers

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The paper deals with studies of magnetization and magnetic susceptibility of $Si_{1-x}Ge_x$ <B, Hf> ($x = 0.05$) whiskers with a diameter of about 1 μm in the temperatures range 77-300 K and magnetic fields up to 4.28 kOe. The obtained results have showed that the whisker magnetic susceptibility differs substantially from the typical diamagnetic bulk material. The main difference is connected with the existence of paramagnetic centers localized in the nanoporous coating, the so-called core-shell structure, of $Si_{1-x}Ge_x$ whiskers. This leads to the emergence of magnetic ordering in them and appearance of a paramagnetic component in the magnetic susceptibility. An increase in the paramagnetic component was observed due to the introduction of Hf dopants as separate paramagnetic centers. The oxygen presence in the whisker core-shell structure was also found due to Auger spectroscopy associated with the VLS mechanism of the $Si_{1-x}Ge_x$ whisker growth. As a result, HfO_2 clusters are formed as a bulk material typical of diamagnets. The field behavior of the magnetic susceptibility component has a superparamagnetic character, which is characteristic of superparamagnetism saturation of magnetization and hysteresis absence in the temperature range 77-300 K. Therefore, the observed phenomena are explained by the existence of dangling bonds, as well as HfO_2 clusters, in the whisker nanoporous coating according to magnetic ordering and the superparamagnetism appearance in $Si_{1-x}Ge_x$ <B, Hf> whiskers.

Keywords: Whiskers, Silicon-germanium, Hafnium, Magnetic susceptibility, Superparamagnetism.

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1. INTRODUCTION

Boron-doped Si and Si-Ge whiskers with submicron size exhibit magnetic properties different from those of bulk silicon. In particular, they found at room temperature the paramagnetic component of the magnetic susceptibility and the nonlinear field dependence of the magnetization [1, 2]. It is worthy to note that bulk silicon or solid solution of silicon-germanium is a typical diamagnet [3]. The specific magnetic properties of Si-based whiskers are related to their core-shell structure [4], in particular, to the presence in the porous shell of Si nanowires of a high concentration of dangling bonds, which are known to be paramagnetic centers [5]. The interaction of paramagnetic centers in pores of small size can lead to low magnetization hysteresis in crystals at low temperatures [6].

Doping of crystals with rare earth elements such as Hf, Yb or Mn is known to change substantially their magnetic susceptibility [7]. For example, Mn_xGe_{1-x} nanostructures such as quantum dots have demonstrated field-controlled ferromagnetism up to 100 K [8]. From this point of view, it is interesting to investigate Si-Ge <B> whiskers with an admixture of hafnium to trace the potential change in magnetic characteristics. The obtained results can have not only theoretical significance for deepening the physics of processes in Si-Ge nanostructures, but also practical importance. The combination of good electronic properties of semiconductor Si-Ge whiskers with possible spintronic properties opens horizons for their wider practical application.

The aim of the present work is to study the magnetization and magnetic susceptibility of $Si_{1-x}Ge_x$ <B, Hf> ($x = 0.05$) whiskers in the temperature range 77-300 K and magnetic fields up to 4.28 kOe.

2. EXPERIMENTAL DETAILS

Samples ranging in size from micrometer fractions 0.1-1 μm to 100 μm were examined. We used the Faraday method for measuring the magnetic susceptibility of whiskers in a magnetic field within the intensity range of 0.3-4.0 kOe at temperatures of 4.2-300 K. Before the experiment, the whiskers were packed into cylindrical glass tubes 3 mm in diameter and fastened by wax. After that, the samples were pushed out off the glass tube. A sample without wax was also prepared to consider the wax magnetic properties. The experimental results show the magnetic susceptibility of wax, which is much less than the magnetic susceptibility of the whiskers. Nevertheless, due to the magnetic contribution of wax, the experimental data were corrected and taken into account in each measurement. It was found that the measurement error did not exceed 5 %.

3. EXPERIMENTAL RESULTS

The study of $Si_{1-x}Ge_x$ <B, Hf> whiskers ($x = 0.05$) magnetization was performed using Kahn's weight by the Faraday method [9] in the temperature range 77-300 K. Fig. 1 and Fig. 2 show the temperature and field dependences of the magnetization and magnetic susceptibility of submicron $Si_{1-x}Ge_x$ <B, Hf> whiskers. The magnetic susceptibility of the whiskers (Fig. 1b) was calculated from the experimental dependence of the magnetization (Fig. 1a). Let us compare the data for the magnetization and the magnetic susceptibility of $Si_{1-x}Ge_x$ <B, Hf> and $Si_{1-x}Ge_x$ <B> whiskers [10] with the same diameter and boron concentration. It should be noted that the magnetization of whiskers doped with Hf is an order of magnitude greater than the magnetization of whiskers without Hf. It is worthy to underline one common peculiarity of the whiskers – the existence of a maximum magnetization at a certain magnetic field induction and a further slow decrease in magnetization with increasing magnetic field (see Fig. 1a). The maximum is well separated in $Si_{1-x}Ge_x$ <B> whiskers at about 1 kOe. The difference between doped with Hf and undoped whiskers consists in the shift of the maximum position to the region of higher magnetic field induction with increasing Hf admixture. The next difference is the change in the sign of the magnetic susceptibility of $Si_{1-x}Ge_x$ <B, Hf> whiskers [10]. As can be seen from Fig. 1b, the magnetic susceptibility of $Si_{1-x}Ge_x$ <B, Hf> whiskers is positive and shows a strong field dependence, but without changing the sign. Therefore, a paramagnetic component appears in submicron $Si_{1-x}Ge_x$ <B, Hf> whiskers, which is greater for Hf-doped whiskers.

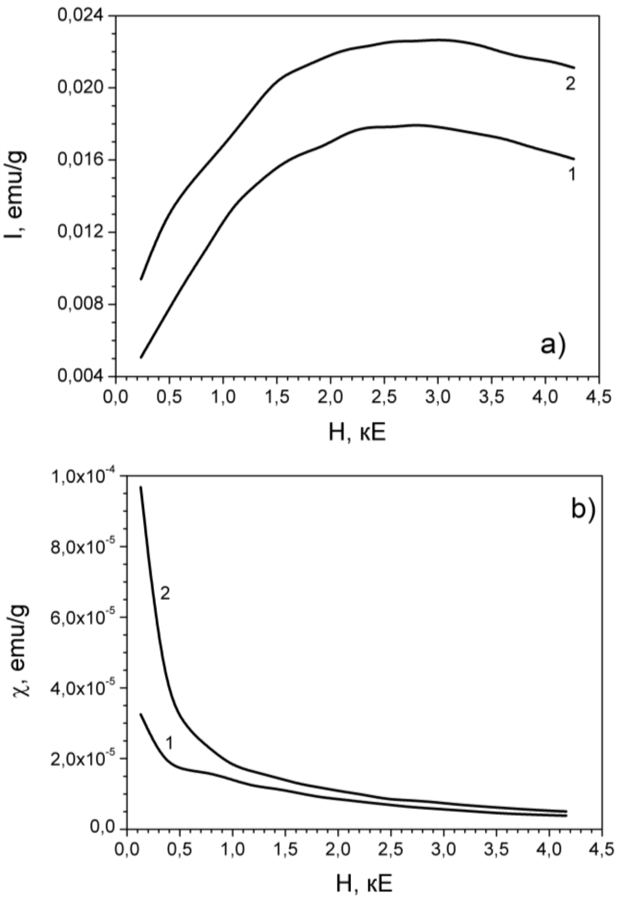

Fig. 1 – Magnetization (a) and magnetic susceptibility (b) of $Si_{1-x}Ge_x$ <B, Hf> whiskers with a diameter of $d \sim 1$ μm, $N_A = 5 \cdot 10^{18}$ cm^{-3}, at room temperature (1) and liquid nitrogen temperature (2)

It should be noted that the magnetic susceptibility of whiskers differs significantly from bulk $Si_{1-x}Ge_x$ (their magnetic susceptibility does not depend on the magnetic field and is equal to $-11.6 \cdot 10^{-6}$ emu/g at room temperature). The difference lies in two main points: 1) the value of the magnetic susceptibility of the whiskers does not change in fields above 4 kOe and is equal to $\chi = -0.5 \cdot 10^{-6}$ and $+1 \cdot 10^{-5}$ emu/g for $Si_{1-x}Ge_x$ <B> and $Si_{1-x}Ge_x$ <B, Hf> samples with $x = 0.05$ and $d = 1$ μm, respectively, which is less than for bulk $Si_{1-x}Ge_x$ crystals; 2) a strong field dependence of $\chi(H)$ is observed in the whiskers, which may indicate the presence of the magneto-dipole interaction between the centers. Another explanation for the detected effect may be the presence of superparamagnetism in the samples. That is, in the whiskers there is a certain magnetic interaction between the magnetic centers present in them.

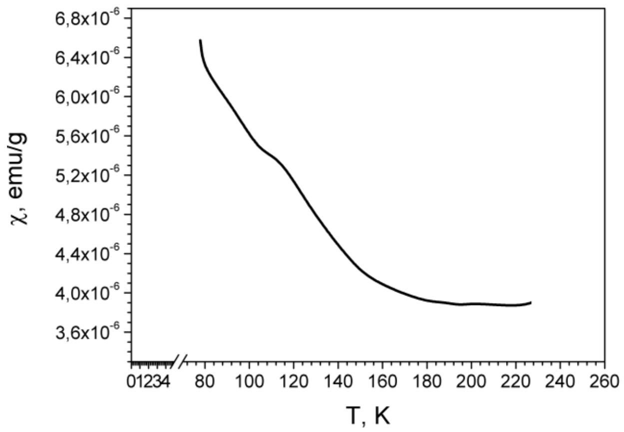

Fig. 2 – Temperature dependence of the magnetic susceptibility of $Si_{1-x}Ge_x$ <B, Hf> whiskers, with a diameter of $d \sim 1$ μm, $N_A = 5 \cdot 10^{18}$ cm^{-3}, and a magnetic field of 4.28 kOe

It should also be noted that all illustrated dependences exhibit a tendency to a decrease in the magnetic susceptibility with increasing transverse size of the whiskers (a decrease from $\sim 10^{-5}$ for submicron whiskers to $\sim -10^{-6}$ emu/g for crystals with sizes of 30-50 μm). This behavior of the magnetic susceptibility of the whiskers can be caused by the following factors: the degree of doping, the type of uncontrolled impurity, as well as the transverse dimensions of the solid solution whiskers.

4. DISCUSSION

Solid solutions of Si-Ge are a diamagnetic material with a constant negative value of the magnetic susceptibility at room temperature. The established features of the magnetic susceptibility in whiskers, in particular, the appearance of the paramagnetic component of the magnetic susceptibility, presuppose the presence of paramagnetic (or superparamagnetic) centers in the crystals. Therefore, the experimentally determined magnetic susceptibility can be considered as a superposition of two components:

$$\chi = \chi_d + \chi_p, \quad (1)$$

where χ_d and χ_p are the diamagnetic and paramagnetic components of the magnetic susceptibility, respectively. Similarly, we can talk about the corresponding contributions to the magnetization of crystals in a certain magnetic field:

$$I = I_d + I_p. \quad 2)$$

The analysis of the data in Fig. 1 allowed us to identify the corresponding components of the magnetization when a 4.2 kOe magnetic field is applied to the $Si_{1-x}Ge_x$ <B, Hf> whisker (see Fig. 3).

It is necessary to investigate the presence of impurities or defects in the crystals, which may cause the detected magnetic effects. We will analyze the influence of these factors below.

$Si_{1-x}Ge_x$ <B, Hf> whiskers were doped during growth with impurities of boron and gold. They are known to make a diamagnetic contribution to the magnetic susceptibility. The obtained value of $\chi = -0.5\cdot10^{-6}$ emu/g at high magnetic fields for $Si_{1-x}Ge_x$ <B> whiskers (Fig. 1b), including the contribution of the lattice and the impurity subsystem of the silicon-germanium crystal, is higher than that of bulk Si-Ge, which indicates an increase in the paramagnetic contribution to the magnetic susceptibility. For $Si_{1-x}Ge_x$ <B, Hf> whiskers, the paramagnetic contribution is greater. This fact indicates the presence of paramagnetic centers in crystals with concentrations exceeding the concentration of boron and gold. However, the results of microprobe analysis of the content of the whiskers (CAMEBAX) show that they contain only residual (for this analysis) boron concentrations $N_B \sim 5\cdot10^{18}$ cm^{-3}. No other impurities in the whiskers were detected by this method. However, the accuracy of microprobe analysis is too low for such studies. The results of studies of the whisker surface by Auger spectroscopy indicate the presence of a thin (several nm) layer of SiO_2, as well as C and N atoms. These materials are not magnetic impurities. Therefore, the detected behavior of the whisker magnetic susceptibility cannot be explained by the contribution of these impurities.

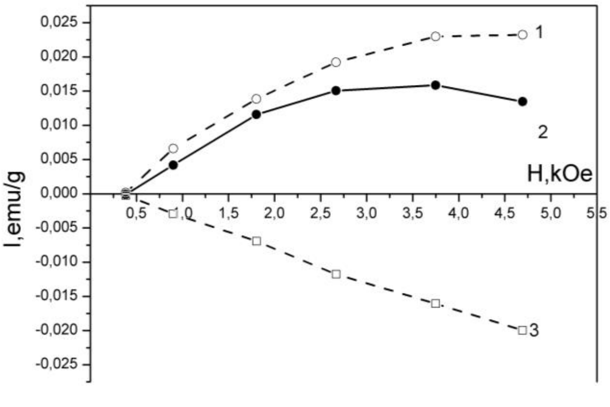

Fig. 3 – Decomposition of the experimental magnetization (curve 2) into two components: diamagnetic (curve 3) and superparamagnetic (curve 1)

As shown earlier, submicron $Si_{1-x}Ge_x$ <B> whiskers are known as heterostructures with a crystalline core and a nanoporous shell [10]. In addition, EPR data show that the porous shell contains a large number of dangling bonds [10]. The presence of the latter in the porous shell of Si-Ge whiskers is probably responsible for the difference between the whisker magnetic susceptibility and the magnetic susceptibility of bulk material. Dangling bonds are known to be paramagnetic centers. Therefore, their presence can explain the value of $\chi = -0.5\cdot10^{-6}$ emu/g for $Si_{1-x}Ge_x$ <B> whiskers at high magnetic fields in the saturation region (Fig. 1, $T = 296$ K). However, it is difficult to explain the positive value of the magnetic susceptibility of $Si_{1-x}Ge_x$ <B, Hf> whiskers and, moreover, the saturation of the paramagnetic component of the magnetic susceptibility (Fig. 3).

We tried to estimate the concentration of such paramagnetic centers in the whiskers. For this purpose, the temperature dependence of the susceptibility was constructed in coordinates $1/\chi$, T. As seen from Fig. 4, the dependence $1/\chi = f(T)$ is not a straight line, as it should be observed for a pure paramagnet or superparamagnet, where the Curie law is true. To determine the concentration of the centers, we approximated a certain section of the curve shown in Fig. 4 by a straight line, assuming that in this section the sample behaves like a typical paramagnet, for which the Curie law $\chi = C/(T - T_C)$ takes place. The angular slope of the obtained line determines the value of the Curie constant, which is equal to $C = 1.08\cdot10^{-4}$, and the parameter $T_C = -68$ K. A negative value of Tc indicates the presence of antiferromagnetic ordering in the crystal. At a magnetic field strength of 4 kOe, the relation $\mu B/kT \ll 1$ (where μ is the magnetic moment of the magnetic center, k is the Boltzmann constant) takes place, so the Curie constant can be described by the following equation:

$$C = \frac{N\mu^2}{3k}, \qquad (3)$$

where N is the concentration of magnetic centers. Assuming the magnetic moment of the centers to be equal to the Bohr magneton, we obtain the concentration of these centers equal to $N \approx 5.2\cdot10^{19}$ cm^{-3}.

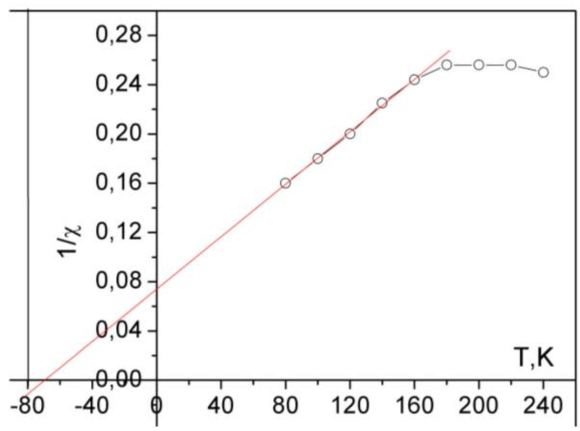

Fig. 4 – Checking the Curie law in $Si_{1-x}Ge_x$ <B, Hf> whiskers

The deviation of the dependence $1/\chi = f(T)$ from the straight line indicates the presence of a certain magnetic ordering in the whiskers at above room temperatures, which may be responsible for the exchange interactions between paramagnetic centers in the crystal. One can suppose that HfO_2 clusters localized in the region of the nanoporous shell of the whiskers could be the origin of the centers in $Si_{1-x}Ge_x$ <B, Hf> whiskers. It is known that neither Hf^{4+} nor O^{2-} are magnetic [11]. On the other hand, bulk HfO_2 is clearly diamagnetic. Magnetic ordering arises due to defect/oxygen vacancies at the interface of a thin HfO_2 film [12]. One can suppose that similar HfO_2 clusters were created in the nanoporous shell of the whiskers. The authors of [13] state that HfO_2 nanocrystals with a high defect concentration exhibit ferromagnetism and superparamagnetic behavior. Then, the magnetic interaction between paramagnetic centers located close to each other corresponds to magnetic ordering in the whiskers, leading to the superparamagnetic behavior of the whisker magnetic susceptibility (Fig. 3, curve 1) at the temperature of liquid nitrogen and room temperature.

5. CONCLUSIONS

It was shown that the magnetic susceptibility of $Si_{1-x}Ge_x$ <B> ($x = 0.01$-0.05) differs from the magnetic susceptibility of bulk silicon-germanium solid solutions, which are typical diamagnets. The main difference is the presence of a rather high concentration of dangling bonds localized in the nanoporous shell in the core-shell structure of whiskers. The small distance between the dangling bonds, which are paramagnetic centers, leads to the emergence of some magnetic ordering in them and the appearance of a paramagnetic component of the magnetic susceptibility. The aim of this work was to observe the change in the magnetic susceptibility upon the introduction of Hf impurities into whiskers. Hf as a single atom is known to be a paramagnetic center. Thus, an increase in the paramagnetic component should be observed with its introduction into crystals.

Investigation of the magnetization and magnetic susceptibility of $Si_{1-x}Ge_x$ <B, Hf> ($x = 0.05$) whiskers in the temperature range 77-300 K and magnetic fields up to 4.28 kOe was conducted. Indeed, the experiments fulfilled showed the substantial (in order of magnitude) enlargement of the paramagnetic component of the whisker magnetic susceptibility. Nevertheless, it was not only the paramagnetic contribution. The field behavior of the magnetic susceptibility component in a magnetic field has a superparamagnetic character, since saturation of magnetization typical of superparamagnetism and the absence of any hysteresis were observed in the temperature range 77-300 K. Therefore, we suppose the presence of superparamagnetic clusters in the whiskers. The main probable place of their localization is the whisker nanoporous shell. The results of Auger spectroscopy showed the presence of oxygen in the shell. Hafnium and other impurities (B, Au) have the highest concentration on the whisker surface that is resulted from the whisker growth according to the VLS mechanism. Then, the formation of HfO_2 in the whisker nanoporous structure is very probable. Despite the fact that HfO_2 as a bulk material is typical diamagnet, numerous literature sources indicate its paramagnetic nature in nanostructures. Therefore, the presence of clusters in the whisker nanoporous shell and their interaction due to the very small distance between them leads to the appearance of magnetic ordering, which manifests itself in the superparamagnetic phase on the $Si_{1-x}Ge_x$ <B, Hf> surface. It should be noted that subsequent comprehensive investigations of the surface structure of whiskers and their elemental content should be conducted to explain the observed phenomena in more detail.

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Суперпарамагнетизм в ниткоподібних кристалах $Si_{1-x}Ge_x$ <B, Hf>

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Стаття присвячена дослідженню намагніченості та магнітної сприйнятливості ниткоподібних кристалів $Si_{1-x}Ge_x$ <B, Hf> ($x = 0,05$) діаметром близько 1 мкм в діапазоні температур 77-300 К та магнітних полях до 4,28 кЕ. Отримані результати показали, що магнітна сприйнятливість ниткоподібних кристалів суттєво відрізняється від типового діамагнітного об'ємного матеріалу. Основна відмінність пов'язана з існуванням парамагнітних центрів, локалізованих в нанопористому покритті, так званій структурі ядро-оболонка, ниткоподібних кристалів $Si_{1-x}Ge_x$. Це призводить до виникнення їх магнітного впорядкування та появи парамагнітної складової в магнітній сприйнятливості. Збільшення парамагнітної складової спостерігалося завдяки введенню домішок Hf як окремих парамагнітних центрів. Було також виявлено наявність кисню в структурі «ядро-оболонка» відповідно до результатів Оже-спектроскопії, що пов'язано з ПРК-механізмом росту ниткоподібних кристалів $Si_{1-x}Ge_x$. В результаті відбувається утворення HfO_2-кластерів як об'ємного матеріалу, що характерно для діамагнетиків.

Поведінка польової залежності магнітної сприйнятливості має суперпарамагнітний характер, що є типовим для насичення намагніченості суперпарамагнетизму та відсутності гістерезису в інтервалі температур 77-300 К. Отже, виявлені явища пояснюються наявністю обірваних зав'язків, а також кластерів HfO_2 в нанопористій оболонці ниткоподібних кристалів, що приводить до магнітного впорядкування та появи суперпарамагнетизму в зразках $Si_{1-x}Ge_x$ <B, Hf>.

Ключові слова: Ниткоподібні кристали, Кремній-германій, Гафній, Магнітна сприйнятливість, Суперпарамагнетизм.