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Structural and electrical transport studies of reduced in hydrogen surface of bismuth germanate glass

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Abstract

Bismuth nanoclusters embedded in germanate glass matrices and surface layer of bismuth grains have been obtained by thermal treatment in hydrogen atmosphere of $Bi_{0.33}Ge_{0.67}O_{1.83}$ glass. Confirmed by AFM and XRD measurements a simple model of two conducting layers is proposed. The influence of time and temperature of reduction on the properties of the reduced samples have been studied. A change in surface conductivity caused by melting of Bi granules has been observed in all studied samples. The possibility of existence of a superconducting state in reduced bismuth germanate glasses has been discussed.

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1. Introduction

Bismuth silicate glasses find a lot of industrial and special applications [1,2]. On the other hand, bismuth germanate glasses are less known and their applications are still rare. The interesting property of bismuth germanate glasses is that in the course of heat treatment in hydrogen atmosphere they change surface conductivity by several orders. Such a thermal procedure reduces Bi^{+3} ions into neutral atoms. Only a few works have been done on physical properties of non-reduced [3] and reduced [4,5] bismuth germanate glasses and there still remain many questions about conductivity and structures of these materials.

In this paper, we report the results of studies on bismuth germanate $Bi_{0.33}Ge_{0.67}O_{1.83}$ glass reduced under different conditions. The resulting glass–metal composite has been used for investigations of electrical properties of metallic bismuth in its nanocrystalline state. Possibility of existence of superconducting state in reduced bismuth germanate glasses have been discussed.

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2. Experiment

Bismuth germanate $Bi_{0.33}Ge_{0.67}O_{1.83}$ glass was synthesized as follows. Milled mixture of powdered GeO_2 and Bi nitrate, placed into a platinum crucible, was decomposed at 1000 K for 1 h. After the decomposition, the mixture was ground again and submitted to a gradual heating from room temperature to 1500 K. Melted glass was homogenized by mechanical stirring and than quenched by pouring onto a steel plate. Before further treatment the surface of samples was polished and cleaned carefully. The nominal oxygen content in the glass was calculated within the assumption that the original glass has a composition determined by the valency 3^+ of Bi and 4^+ of Ge.

Reduction process was carried out in the temperature range from 573 to 673 K in hydrogen atmosphere.

Surface morphology of non-reduced and reduced samples was tested by working in air AFM microscope. The glass and its reduced surface layer were examined by X-ray diffraction analysis with the use of Philips X'Pert diffractometer system.

Measurements of sample conductivity were made in the temperature range from 5.8 to 613 K in ambient atmosphere using two- or four-terminal methods. The

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surface conductivity of the samples has been calculated from equation: $\sigma_{\square} = R^{-1}d/l$, where R is the resistivity of sample, d the distance between the electrodes and l their length.

In this paper, we present results obtained for $Bi_{0.33}Ge_{0.67}O_{1.84}$ samples reduced at 613 K for 0.8 h (G1), 2 h (G2), 7 h (G3), 12 h (G4), 24 h (G5) and 44 h (G6). For comparison, samples reduced at 663 K for 0.12 h (H1), 0.22 h (H2), 1.4 h (H3), 24 h (H4) and 44 h (H5) also were studied.

3. Results

The plots of surface conductivity versus reduction time of $Bi_{0.33}Ge_{0.67}O_{1.83}$ sample reduced at five different temperatures (563, 588, 613, 643 and 663 K) are presented in Fig. 1. The behaviour seen in the figure is characteristic of bismuth germanate glasses subjected to the reduction process [5]. First, after some time a rapid of a few orders of magnitude increase in the surface conductivity of sample $Bi_{0.33}Ge_{0.67}O_{1.83}$ appears. Next, the surface conductivity of glasses attains a maximum (about $10^{-6}\ \Omega^{-1}$) and in a pronounced way decreases to a minimum. Further reduction causes increasing of conductivity of a few orders. The results confirmed that when reduction temperature increases the speed of changes of surface conductivity and the depth of the minimum increases too, but character of the dependence is still the same.

The results of X-ray diffraction measurements of studied samples and rhombohedral bismuth are shown in Fig. 2. The spectra of as-quenched glass and reduced G1 and G2 samples show a halo pattern with no peaks (only G2 sample is shown in Fig. 2). Glasses annealed in hydrogen for 24 and 44 h (G5 and G6 samples) exhibit a series of peaks characteristic of rhombohedral crystalline Bi. They also show some peaks, which correspond to germanium.

AFM pictures of G1, G3 and G5 samples are presented in

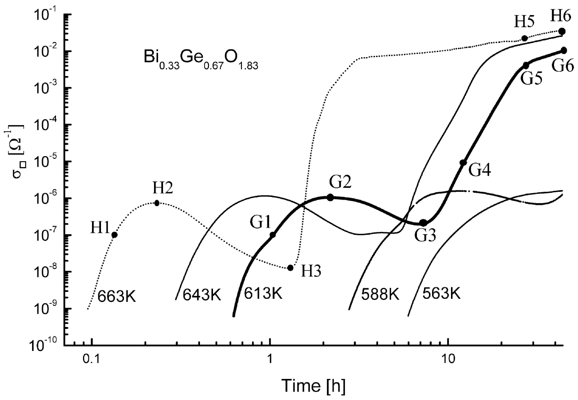

Fig. 1. The time dependence (log–log scale) of surface conductivity of $Bi_{0.33}Ge_{0.67}O_{1.83}$ glasses during heat treatment in five different temperatures (the letters G1…G6 and H1…H6 denote studied samples).

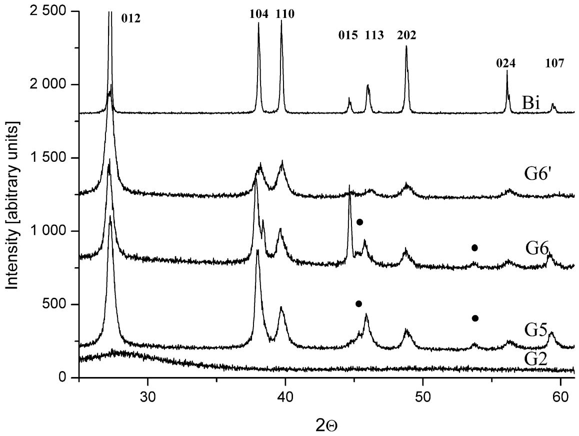

Fig. 2. X-ray diffraction spectra of rhombohedral bismuth, G2, G5, G6 and G6′ samples. The sample G6′ is G6 after removing outer Bi–Ge layer. (•) marks Ge peaks. The plots are shifted for better view.

Fig. 3. The flat surface of the glass (G1), a layer of connected or disconnected granules (G3) and multi-layer granular systems (G5) are visible in Fig. 3. We have obtained similar results for the samples reduced at 663 K.

The results of measurements of surface conductivity versus temperature in $Bi_{0.33}Ge_{0.67}O_{1.83}$ samples reduced for various times at 613 and 663 K are shown in Figs. 4–6.

4. Discussion

Properties of the bismuth germanate glasses reduced in

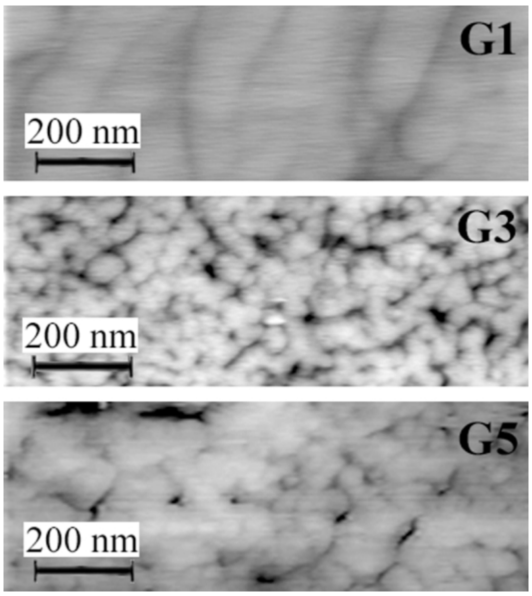

Fig. 3. Examples of AFM pictures of studied $Bi_{0.33}Ge_{0.67}O_{1.83}$ glass samples.

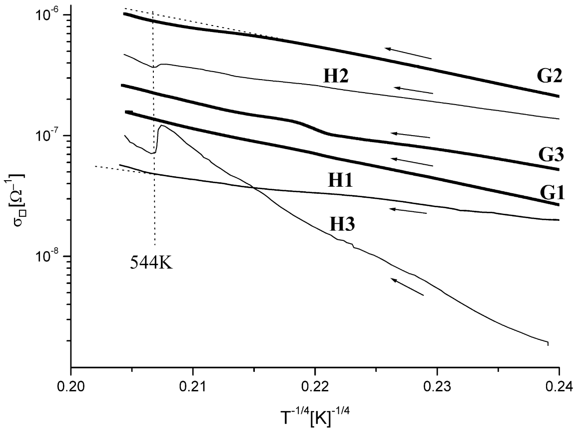

Fig. 4. The plots of surface conductivity versus $T^{-1/4}$ in $Bi_{0.33}Ge_{0.67}O_y$ samples reduced for 0.8 h (G1), 2 h (G2), 7 h (G3) at the temperature 613 K and 0.12 h (H1), 0.22 h (H2), 1.4 h (H3) at the temperature 663 K. Measurements range is from 300 to 573 K.

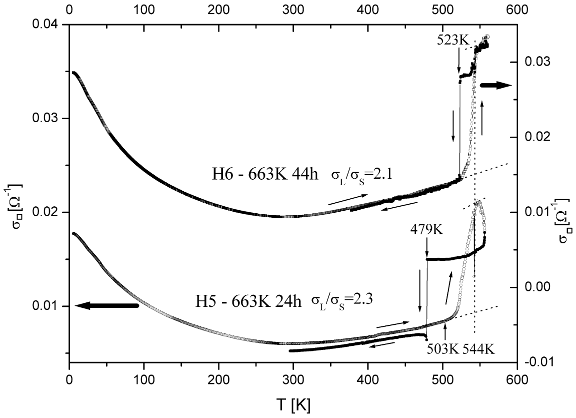

Fig. 6. The plots of surface conductivity versus temperature in $Bi_{0.33}Ge_{0.67}O_{1.83}$ samples reduced for 24 h (H5) and 44 h (H6) at the temperature 613 K. Measurements range is from 5.8 to 560 K.

hydrogen atmosphere depend both on time and temperature of reduction. We propose a simple model of the glass subjected to the reduction process, which is illustrated in Fig. 7. Forming of two conductive layers can be distinguished. One is the layer, which contains Bi particles embedded in a GeO_2 glass matrix, and the latter is the very top layer containing either connected or not grains of Bi and a small amount of Ge. The both layers are created simultaneously during annealing of the samples in hydrogen in appropriately high temperatures. First, on account of reduction, neutral bismuth atoms occur and next they agglomerate into clusters. As long as the distance between Bi nanostructures is too large for an electron tunnelling to take place, the conductivity is determined by ionic mobility and does not change with reduction time. While the reduction is carried on, the concentration and dimension of Bi clusters grow. When the Bi concentration on a surface layer of glasses is sufficient, an electrons tunnelling trough the potential barrier between metallic granules appears and the conductivity rapidly increases (Fig. 1). It means that the 2D layer of Bi granules embedded in GeO_2 matrices is created. Further reduction causes rising of layer thickness. In reduced bismuth germanate glasses, apart from the processes described above, both the migration of bismuth atoms to the surface of samples and reduction of GeO_2 is observed. This phenomenon is a reason of changing surface morphology and decreasing to minimum of surface conductivity of studied glasses. Up to this point (sample G3) the conductivity by electron tunneling dominates in reduced bismuth germanate samples. The electrical transport by tunneling of electrons in granular systems has been a subject of intensive experimental and theoretical studies for more than tree decades [7–10]. It well known that the $n = 1/2$ index in $\ln[\sigma(T)] \sim -T^{-n}$ function is characteristic in disordered granular systems in the case of Coulomb interaction (e.g. in cermets [7]). It is known also that some materials (diamond-like carbon films containing tungsten [15], disordered semiconductors [16]) exhibit a dependence $\ln[\sigma(T)] \sim -T^{-1/2}$ at low temperatures with the cross-over to $T^{-1/4}$ at high temperatures. Sandoe et al. [17] found $n = 1/3$ in reduced lead–silicate glasses (where a layer of lead embedded in SiO_2 matrices is created) which he

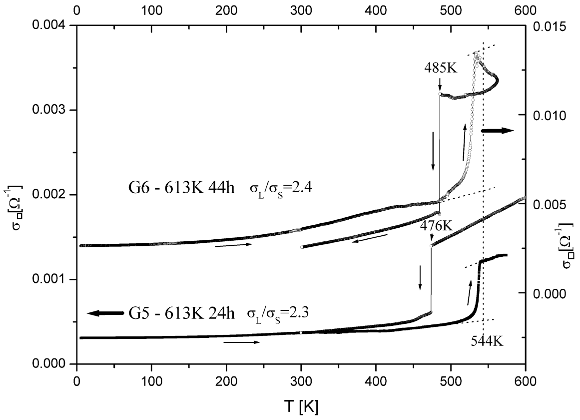

Fig. 5. The plots of surface conductivity versus temperature in $Bi_{0.33}Ge_{0.67}O_{1.83}$ samples reduced for 24 h (G5) and 44 h (G6) at the temperature 613 K. Measurements range is from 5.8 to 560 K.

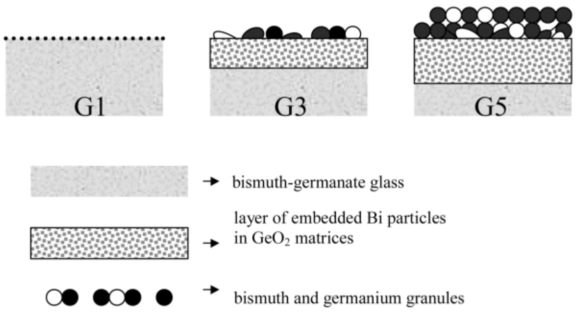

Fig. 7. Model of two-layered structure of reduced in hydrogen bismuth–germanate glasses.

interpreted as VRH in 2D system. Our results suggest that G1 and G2 samples are 3D systems with $n = 1/4$ in high temperature regime but because of too narrow measurement temperature range (300–520 K) $n = 1/2$ cannot be excluded. The measurements down to cryogenic temperatures are needed to resolve the problem. Detailed analysis of surface conductivity in a layer of Bi clusters embedded in GeO_2 matrices will be a subject of the next paper.

The migration of bismuth atoms to the surface of samples cause that the very top layer containing either connected or not connected grains of Bi is created. When the concentration of Bi nanoclusters attains a percolation threshold (near point G3 in Fig. 1) the increase in conductivity is observed. The continuous layer of Bi granules is created and its electrical properties determine surface conductivity of the reduced samples. Further reduction causes increase of thickness of this layer.

The model agrees very well with results of XRD analysis, which can observe both the layers. The creation of the very surface layer of Bi and Ge granules in G5 and G6 samples is detected (Fig. 2). The inner layer containing bismuth nanoparticles embedded in GeO_2 matrixes was studied after removing the outer one (Fig. 2 sample G6′). The analysis of broadening of XRD peaks shows that diameter of embedded Bi nanoparticles in reduced sample G6′ is less than 10 nm. The thickness of the inner layer of G5 sample is 1.6 μm, whereas that of G6 sample is 4.2 μm. In the case of samples reduced at 663 K the thickness of inner layer of H5 i H6 samples are 3.4 and 5.2 μm, respectively.

Further support for the above model comes from AFM results (Fig. 3) where the outer layer of Bi granules is visible. The diameter and height of granules on the surface of G3 sample are about 30 and 10 nm, respectively. The granules in the layer of G5 sample have diameter about 30–50 nm. The AFM pictures of cross-section of G5 and G6 samples show that thickness of granular layer is about 50 and 170 nm, respectively.

In the temperature dependence of conductivity of the layer of bismuth granules embedded in glass matrices (sample G2, H1, H2 and H3) interesting phenomena can be observed. The characteristic changes in the slope of $\sigma_\Box(T)$ plots around melting point of Bi (544 K) are seen (Fig. 4). The surface conductivity decreases and changes the slope during the heating at melting temperature. We think that phenomenon is caused by decreasing volume of Bi nanoparticles during melting which leads to growing of s/d ratio where s is a distances between granules and d their diameter. So that the probability of activated tunnelling between grains decreases which is seen as a decrease of conductivity. More pronounced changes of $\sigma_\Box(T)$ in the samples reduced at 663 K (H1, H2 and H3) are connected with larger dimensions of bismuth granules in the glass reduced at higher temperature.

In contrary to G2, H2 and H3 sample the increase of conductivity in the case of G5, H5, G6 and H6 samples near the melting point is observed. Conductivity of bulk bismuth changes 2.3 times [6] during the phase transition. The jumps ($\sigma_{liquid}/\sigma_{solid}$) in reduced samples are practically the same or a little smaller than 2.3 (see H6 in Fig. 6). We think that a process of partial damage of the Ag electrodes by the melting of bismuth layer is responsible for the smaller value of the jump. An abrupt conductivity decrease (about 2.3 times) on cooling as a result of solidification of overcooled bismuth is also visible in Figs. 5 and 6 (e.g. at 479 K in H5 sample). The phenomena of changing of conductivity at Bi phase transition support the thesis that outer layer contain metallic granules of bismuth. Our investigations by differential scanning calorimetry (DSC) confirmed that large changes in surface conductivity of reduced glasses are induced by melting and solidification of bismuth nanocrystals [18].

Another thing characteristic of the temperature dependence of conductivity of G5 and G6 samples is its activated character (Fig. 5), whereas in the bulk bismuth a metallic dependence would be expected. As our results show the top conductive layer contains weakly connected Bi granules, which, we believe, determines the character of $\sigma_\Box(T)$ function in reduced bismuth germanate glasses. We think that a difference in thermal expansion coefficients of surface of reduced glass and that of a layer of granular bismuth is responsible for activated character of conductivity. Probably the dimensions of Bi granules decrease quicker than dimensions of glass matrices with decreasing temperature. This may disconnect some paths of conducting granules and cause a decrease in conductivity during cooling (and inverse process during heating). When reduction temperature increases the thickness of outer layer increases and Bi granules conglomerate into bigger system. The $\sigma_\Box(T)$ function changes into typical metallic character (Fig. 6 in temperature range from 5 to 290 K).

Rhombohedral bulk bismuth is a semimetal, which do not display superconductivity under ordinary circumstances. However, under pressure (over 25 kbars) bulk Bi shows superconductivity with a T_c ranging from 3.9 to 8.6 K [11]. Bi in amorphous state also shows superconductivity with a $T_c = 6.2$ K [12]. The superconductivity with a T_c up to ~ 5.8 K in granular Bi films prepared from Bi clusters with well-defined size was confirmed by some authors [13,14]. Heat treatment in hydrogen of bismuth germanate glasses creates Bi granular layer. When these granules are relatively big they have non-superconducting rhombohedrical form. The dimensions of granules depend on Bi contents in glass, on temperature and time of annealing in hydrogen. We think that smaller reduction temperature, shorter time and changes of Bi content in $Bi_xGe_{1-x}O_{2-0.5x}$ glasses could lead to creating smaller bismuth granules. In such a 2D monolayer of distorted rhombohedrical granules existence of superconductivity is possible [14]. The measurements at lower temperature are necessary to confirm this hypothesis.

5. Conclusion

The interesting property of bismuth germanate glasses is that in the course of reduction in hydrogen atmosphere they develop two conducting layers at their surface. One of them is a layer of Bi nanoclusters embedded in germanate glass matrix. The second is a mixture of Bi and Ge granules on the surface.

A gradual change of the slope or a jump of conductivity observed during heating or cooling in all studied samples near the temperature of 544 K is caused by a phase transition of the Bi granules.

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