The Structure and Properties of Nanocrystalline Ge

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Results of investigation of Ge films obtained by the method of thermal evaporation in vacuum at different substrate temperatures are presented. The structure and temperature dependence of the resistivity of obtained films are studied by different methods.

1. Introduction

The study of semiconductors is one of the principal trends in physics of condensed matter and very important in practice. In the last ten years interest in investigations of semiconductor objects has turned to nanostructural semiconductors or semiconductors with nano-sized inclusions. Compared to single crystals, qualitative, and often quantitative, changes of electrical and optical properties of nano-sized semiconductor materials offer possibilities in fundamental fields of investigation in physics of semiconductors and give hopes of creating practically new semiconductor devices. The central trend in study of nanocrystalline semiconductors is to develop methods of their synthesis providing good reproducibility of the properties of synthesized objects.

The results of Ge films investigation obtained by the method of thermal evaporation in vacuum at different substrate temperatures are reported in the present work. Techniques of obtaining nanocrystalline Ge films are found. The structure and temperature dependence of the resistivity of obtained samples are studied by different methods.

2. Preparation of samples.

Ge films were prepared in an ultra-high vacuum unit [1,2]. Evaporation was

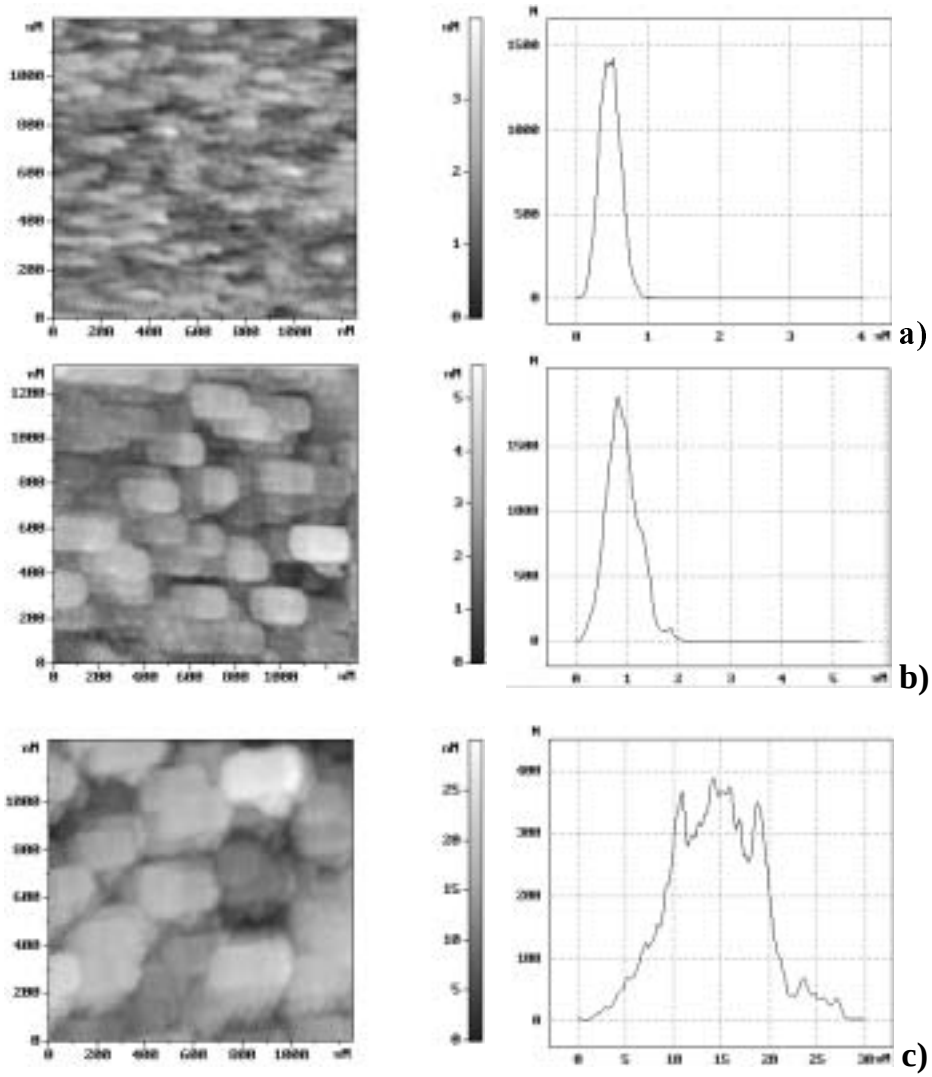

Figure 1. AFM images of surface and height distribution: a) 25°C, b) 150°C, c) 300°C.

produced on sitall substrates and polyimid films. The substrates surface was prepared by standard methods and by the procedure described in Ref. [3]. The substrate temperature during evaporation varied from 25 to 300°C. The film thickness was measured by microinterferometer.

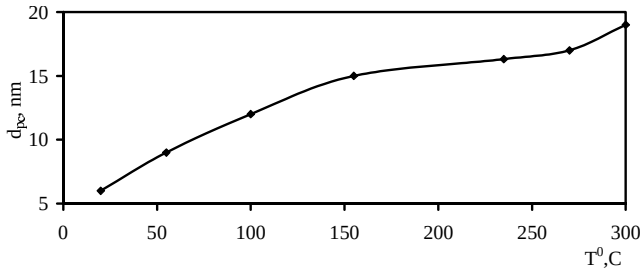

Figure 2. Temperature dependence of Ge-grain size.

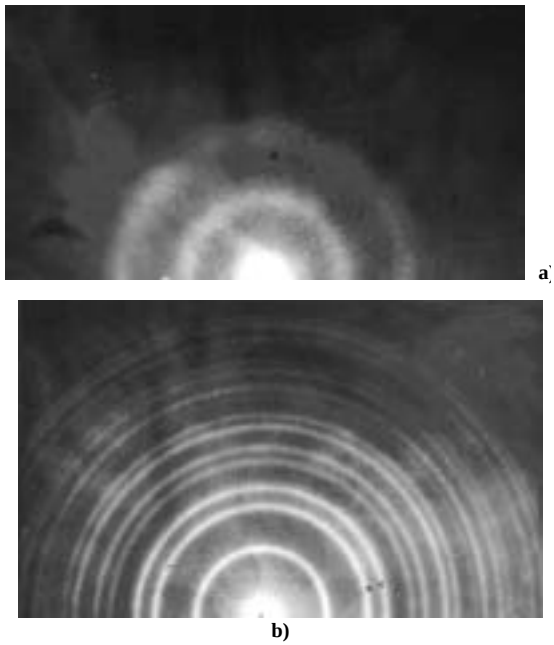

Figure 3. Electronograms of Ge samples obtained at 25°C (a) and 150°C (b).

3. Structure investigations.

The structure of obtained films was been certified by different methods: the atomic force microscopy (AFM), the X-ray diffraction, the transmission electron microscopy.

The atomic force microscope with the silicon cantilever made by NT-MDT [4], the X-ray diffractometer DRON-3, the transmission electron microscope UEMV-100K (the constant of the device is 3.4068 nm/min) were used. Ge films of 60–170 nm thickness evaporated on the polyimid film at substrate tem-

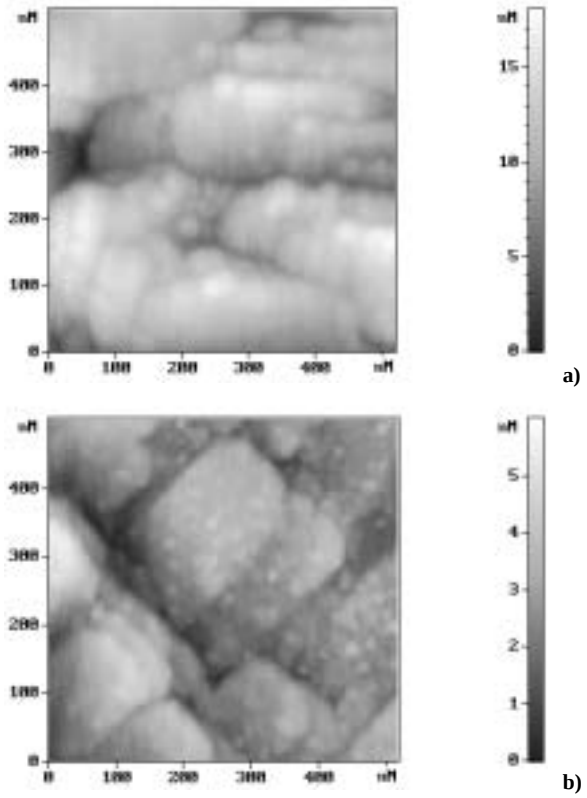

Figure 4. Magnified AFM-images of the surface of Ge-films obtained at temperature $T = 25°C$ (a) and 150°C (b).

peratures of 25, 150 and 300°C were presented for analysis. The substrate was first etched for studying by the transmission electron microscopy.

The local atomic structure was studied by the EXAFS spectroscopy method. Ge K-edge EXAFS spectra were obtained in "transmition" geometry on the laboratory spectrometer XAS-1. Bremsstrahlung of the X-ray tube BSV-27 with a Mo anticathode was used. Monochromatization was performed by the flexed SiO2 $(13\overline{4}0)$ (the interplanar distance $d = 1.18007$ Å at $T = 300$ K) crystal with focusing by Johann. Ge K-edge EXAFS spectra ($E_K = 11104$ eV) for Ge samples were obtained in the range between 10818 and 12114 eV, the signal to noise ratio being about 0.2%.

4. Study of the resistivity and activation energy.

In the study of the temperature dependence of the resistivity the temperature

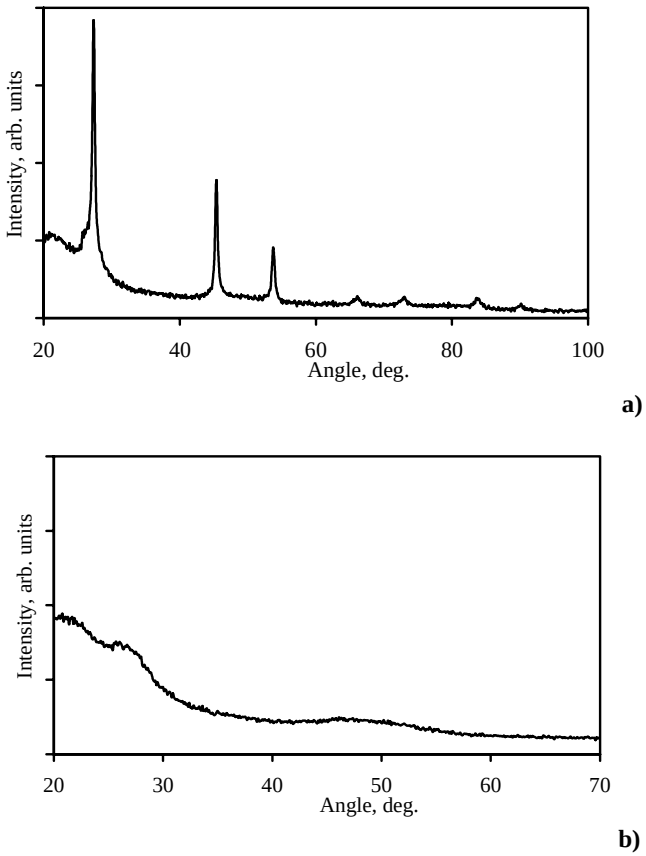

Figure 5. X-ray diffraction for Ge samples obtained at temperature $T = 300°$C (a) and 25°C (b).

was discretely changed with the step of 10∘C from the room one to 100°C. The activation energy was determined from the slope angle of the straight line for the dependence of conductivity on inverse temperature.

5. Results and discussion

In the experiment Ge films at the temperature of condensation from 25°C to 300°C were obtained. The obtained samples were studied by the AFM method (Fig. 1). It is clear that the surface relief changes at different temperatures. At room temperature the relief imperfections are about 0.5 nm. The size of crystallites and relief imperfections increase to 1.5 nm and more with the temperature rise to 150°C. At the temperature of 300°C imperfections reach 20 nm. It is known [5] that the films obtained by thermal sputtering at the different con-

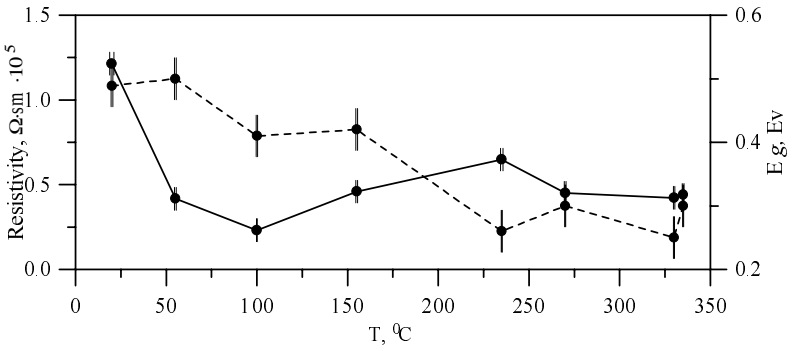

Figure 6. Activation energy E_g (dashed line) and resistivity (solid line) of the films versus condensation temperature.

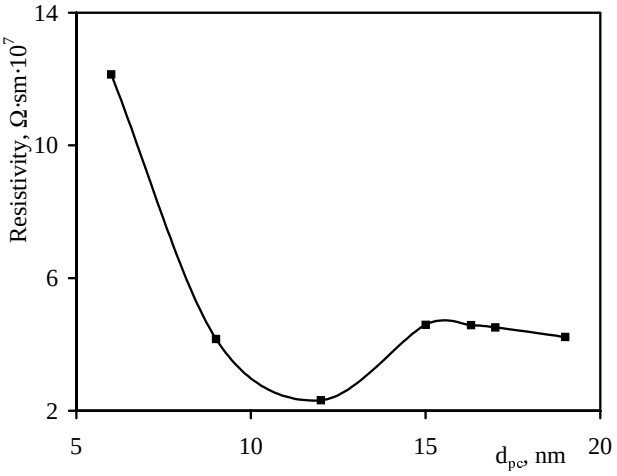

Figure 7. Resistivity of Ge-films versus grain size.

densation temperature have the columnar structure. On the other hand [6], the films obtained at lower temperatures are more porous and have lower density. It is also evident from the images obtained by AFM that as the condensation temperature increases, the number of pores decreases and grains grow in size.

According to the results of AFM studies the dependence of the mean grain diameter on the condensation temperature has been established (Fig. 2). At the temperature of about 150°C a change in the slope is observed that can be connected with the change of the structure. This is supported by transmission electron microscopy and X-ray diffraction methods.

Figure 3 (a, b) gives electronograms of the samples obtained at temperatures $T = 25$°C (a) and 150°C (b). It is clear that at room temperature an amorphous

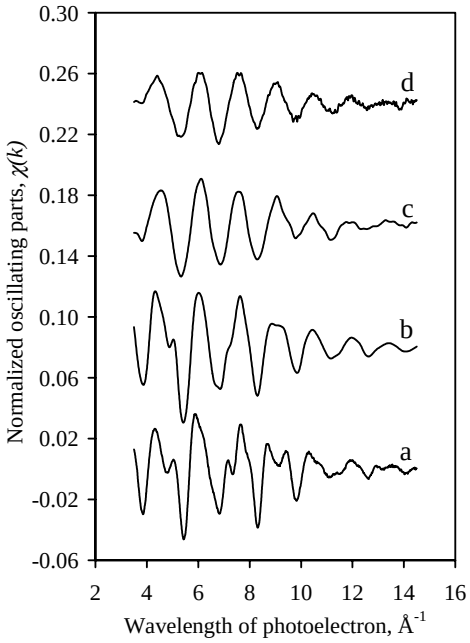

Figure 8. Normalized oscillating parts of EXAFS-spectra of Ge K-edge: a) calculated from crystallographic data with the experimental noise of 5%; b) experiment for the crystalline state; c) experiment for the nanocrystalline state; d) experiment for amorphous state. Curves *b*, *c* and *d* are shifted by 0.08, 0.16 and 0.24, respectively.

film is obtained and the film obtained at 150°C is polycrystalline. The characteristic size of grains in the AFM image (Fig. 1b) is about 120×200 nm. Point reflexes of crystallites of this size must be seen on the electronogram. In our case clearly defined rings are observed. Thus, these grains may consist of crystallites of smaller size (Fig. 4).

Investigations by the X-ray diffraction method (Fig. 5 a) have shown that Ge films obtained at 25°C are X-ray amorphous, and at 300°C (Fig. 5b) they have clearly defined peaks, suggesting that their structure is polycrystalline.

Fig. 6 presents the dependence of the resistivity on the grain size. It is seen that the curve has a maximum at $\sim$ 7 nm, then it decreases, and has a minimum at $\sim$ 12 nm (i.e. at nanocrystalline state). Next figure (Fig. 7) presents the dependence of the activation energy and the resistivity of the films on the condensation temperature. It is seen that the resistivity decreases in the range of condensation temperatures up to 100°C. This is connected with the growth of grain sizes and the decrease of intergranular boundaries which is favourable for better conductivity. The resistivity increases in the region from

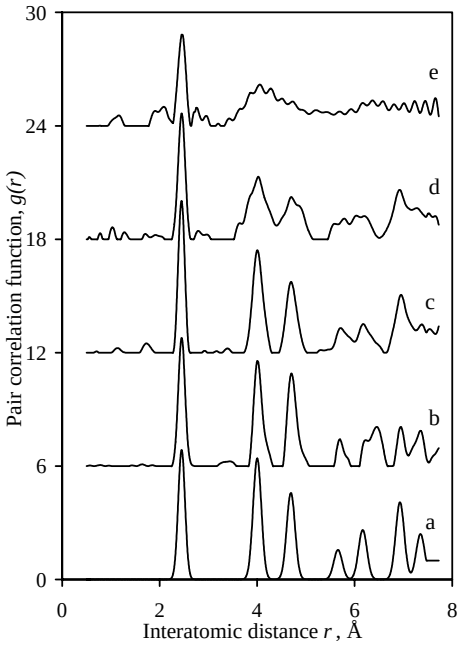

Figure 9. Pair correlation functions: a) calculated from the crystallographic data; b) restored from the calculated normalized oscillating part (Fig. 7a); c) restored from the experimental $\chi(k)$ for the crystalline state (Fig. 7b); d) restored from the experimental $\chi(k)$ for the nanocrystalline state (Fig. 7c); e) restored from the experimental $\chi(k)$ for amorphous state (Fig. 7d). Curves b, c, d and e are displaced to 6, 12, 18 and 24, respectively.

100 to 230°C where the activation energy changes abruptly. An increase in the resistivity and the abrupt change of activation energy result from the structural changes in the film. The film becomes nanocrystalline (Fig. 2b) and textured (Fig. 1b).

Probably, changes of the resistivity and the activation energy are connected with changes in local atomic structure of the films obtained at different condensation temperatures. The local atomic structure was studied by the EXAFS spectroscopy method. EXAFS spectra normalized oscillating parts for crystalline, nanocrystalline and amorphous samples were extracted from EXAFS experimental data. These parts are presented in Fig. 8 in comparison with the spectra calculated by the FEFF program [7] for single crystal Ge. Pair correlation functions (PCF) are calculated from these normalized oscillating parts by the solution of inverse problems with iterations and a trial function. The crystallographic PCF is taken as a trial function [8]. These functions together with

the function reconstructed from "noisy" model data (the noise level was 0.5% of the maximum of the envelope) are given in Fig. 9. Obtained parameters of the local atomic structure are presented in Table 1.

Parameters of the first sphere are well restored from both the model and experimental data in the case of the crystalline state. The radius of the first coordination sphere in the nanocrystalline state has changed little or not at all within the error as compared to the crystalline state, and in the amorphous state it is 0.01 Å greater, the peak is and has the asymmetrical form (see Fig. 9 and Table 1) that, within the error, is in agreement with the data of other authors [9–12]. Parameters of the second and the third coordination spheres for crystalline and nanocrystalline states are determined with no confidence (except interatomic distances) that is probably connected with neglect of the contribution of multiple scattering (it is especially great for the crystalline state and substantially less for the amorphous one). But it is seen that in the nanocrystalline state the second and the third peaks are wider which may be connected with the topological disorder. It is also seen that the changes of the resistivity and the activation energy may be connected with the changes of local atomic environment. For example, dependence of resistivity on condensation temperature has a minimum when coordination number is smaller, i.e. at nanocrystalline state. The behaviour of activation energy is similar.

	R_1, Å	N_1	σ_1, Å	β_1	R_2, Å	N_2	R_3, Å	N_3
Crystallografic model	2,450	4	0,070	1	4,001	12	4,692	12
Restored from model $\chi(k)$	2,452 (0,005)	3,92 (0,20)	0,071 (0,010)	0,97 (0,04)	4,008 (0,008)	10,2 (1,0)	4,704 (0,010)	13,5 (1,5)
Crystalline state	2,447 (0,005)	4,18 (0,20)	0,072 (0,010)	0,97 (0,04)	4,005 (0,008)	8,0 (1,0)	4,695 (0,010)	7,2 (1,5)
Nnocrystalline state	2,452 (0,005)	3,76 (0,20)	0,87 (0,010)	1,04 (0,04)	4,022 (0,008)	-	4,698 (0,010)	-
Amorphous state	2,460 (0,005)	3,89 (0,20)	0,110 (0,010)	1,26 (0,04)	—	—	—	—

Table 1. Parameters of the coordination spheres extracted from the PCFs. Here R_i are the coordination sphere radii, N_i are the coordination numbers, σ_1 is the mean square displacement of the interatomic distance, β_1 is the asymmetry coefficient.

6. Conclusions

Ge samples have been obtained in the range of temperatures from 25 to 300°C by the method of thermal evaporation on the polyimid and sitall substrate at different slope angles of the substrate with respect to the molecular beam. The structural investigations by various methods have shown that at the condensation temperature of 25°C amorphous films are formed, at 150°C nanocrystalline films are formed, and at temperatures higher than 230°C crystal films are produced. Morphology and the local atomic structure of the samples obtained at the slope angle of 0∘ have been investigated by different methods such as AFM, X-ray diffraction, and EXAFS spectroscopy. The EXAFS investigations have made it possible to determine more accurately the structure state of the samples.

In the temperature range from 100 to 230°C the activation energy jump and a rise in resistivity are observed that can be a consequence of structural transformations in films.

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