

Influence of Irradiation on the Electric Conductivity and Crystallization of Ge_{1-x}Si_x Films

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Abstract -In this work, the methodology of getting thin layers on the basis of Ge_{1-x}Si_x was used. The thin layers formation speed is 's' in 1 Å/s - 1000 Å/s. The ability of the quasi – amorphous condition of thin layers on the basis of Ge_{0.85}Si_{0.15} (h~100nm) to stay up to 530 K temperature was determined. It was shown experimentally that irradiation with electrons under an accelerating voltage enhances the crystallization in the films and lowers their electric conductivity.

[H. M. Mahdavi, R.S. Madatov, and U. F. Faradzov. **Influence of Irradiation on the Electric Conductivity and Crystallization of Ge_{1-x}Si_x Films.** *Researcher* 2014;6(1):77-82]. (ISSN: 1553-9865).
<http://www.sciencepub.net/researcher>. 14

Keywords: germanium–silicon alloy, epitaxial, film, electro physical property, hetero structure

1. Introduction

Ge and Si exhibit an unlimited mutual solubility both in the solid and the liquid state, and this agrees well with the nature of these elements. They possess analogous chemical properties and similar atomic radii and occupy adjacent places in the electrochemical series. Ge and Si possess a diamond-like crystal lattice. The ratio $a_{Ge}/a_{Si} = 1.042$; that is, the lattice parameters differ by less than 4.3% [1].

The authors of the phase diagram [2] noted that the alloy crystallization in the usual conditions is inhomogeneous. With a decrease in temperature, the solid phase that eliminates under cooling analysis.

The phase diagram was studied theoretically. It was found that, to provide the correlation between the theoretical and experimentally observed solidus and liquids curves, it is necessary to accept that the interaction between the like atoms Ge–Ge and Si–Si should be weaker than between the Ge–Si atoms; therefore, there is a tendency to ordering in the solid solution.

The results of work [3] have shown that the number of interstitial atoms in the Ge–Si solid solution is so small that it is beyond the sensitivity threshold of X-ray analysis.

According to the X-ray data, the lattice constant of Ge–Si alloys changes linearly with the change in the composition. The Si atoms deform the Ge lattice decreasing its parameter.

2. Material and Method

To perform the process of vacuum evaporation of the substance, an evaporation source is needed that can contain the evaporated substance and maintain its

temperature at a level high enough to provide the necessary vapor pressure. The deposition rate of the films can be varied from values of less than 1 Å/s to values exceeding 1000 Å/s. To approximately evaluate the operation temperature of the source, one should possess a steady vapor pressure of the evaporated material (germanium–silicon solid solution) on the order of 10–2 Torre to provide a rate of the film deposition on the order of 4.5–5 nm/s. Tungsten was used as the source material; the source temperature was maintained at a level of 2100 K. The source was made in the laboratory in the form of a boat 4 cm long and 1 cm wide. Tungsten is a brittle material, and this created the only problem that we experienced while making the source. The ends of the electric contacts were connected to the copper contact terminals.

The condensation of a molecular beam with some density (the number of atoms that reach the substrate in a unit of time) occurs only at a temperature that does not exceed some critical temperature T_{Cr} . The critical flux density is always present, and, at the specific temperature T_{Cr} , the condensation begins (on the given substrate) [8]. As is known, the migration of the adsorbed particles on the substrate surface exhibits isotropy. This idea is true for amorphous substrates, but it should be revised for the case when the condensation on a crystalline substrate is examined.

Nucleation of vacuum condensates on a neutral (in particular, amorphous) substrate can occur according to two main mechanisms: vapor–crystal [V→C]; that is, direct condensation from the vapor state into the crystal- line state occurs; and vapor– liquid [V→ (L→C)]; that is, the vapor transforms into the

liquid. Further, the liquid can remain in the overcooled amorphous state or crystallize [L→C].

The critical temperature was found experimentally to be $T_{cr1} \approx 2/3T_m$. Below this temperature, the mechanism V→C takes place, and, over this temperature, the mechanism V→L occurs (T_m is the melting temperature of the condensed material in its bulk form). The T_{cr1} values can vary in definite limits in dependence on the properties of the condensate and the substrate material, the binding energy between them, the condensation rate, and other conditions of the condensation process. Some authors [9] suggested that a second critical temperature exists: $T_m = T_{cr2} \approx 1/3T_m$. Over this temperature, the V→C mechanism takes place, and, temperature, the V→C mechanism takes place, and, temperature, the V→C mechanism takes place, and, this assumption is based on various experimental data related to research on the condensation of a large number of metals as well as some alloys. The data of microscopic and X-ray methods and micro hardness measurements give evidence that an interval ΔT_{cr} exists, where heterogeneous condensation according to both mechanisms occurs (V→C and V→L). The T_{cr} and ΔT_{cr} values can vary in some limits dependent on the condensation conditions. In the low temperature range of condensation ($T_m < T_{cr}$), the condensation according to the V→L mechanism sometimes leads to the formation of meta- stable crystalline and amorphous (vitreous) phases (V→L→C or V→L→A, where A is an amorphous phase) that completely or partly transform into more stable phases at long storage or heating [10].

In the case, when an “active” (single-crystalline) substrate is used and the epitaxial or au to epitaxial growth of single-crystalline layers takes place characterized by strong bonds with the substrate, the condensation mechanism V→L is suppressed and the temperature range ($T_{cr1} - T_{cr2}$) widens where the mechanism V→C occurs.

→ The examined condensation mechanisms refer to the initial stage only. At the following stages, the nuclei of the liquid phase are not stable, and the transition into the crystalline phase (L→C) occurs. However, the preceding mechanism VL leaves its imprint in the form of defects of the crystalline structure in the condensate, which in turn influences the structure-sensitive properties. This was used for the indirect detection of the V→L mechanism at $T_m < T_{cr2} \sim 1/3T_m$ in bulk condensates.

However, each field of technical application of semi- conductors advances its specific demands concerning their principal characteristics. At the

present time, the influence of the temperature on the electro physical properties of germanium and silicon has been studied rather well, and it was established that these two elements, while containing oxygen, exhibit thermal instability. The point is that oxygen reveals both the neutral and the electrically active character in germanium and silicon and substantially changes their electro physical properties with the temperature changing [11]. Film condensates of germanium–silicon solid alloys are especially sensitive to oxidation both during the evaporation and during the quenching processes.

3. Result and Discussion

In $Ge_{1-x}Si_x$ alloy ($x = 0-0.15$), the atoms of silicon and germanium are randomly located in the sites of the diamond-like lattice. Since the alloy is not an ideal crystal, but a crystal with imperfections in the periodicity of the lattice structure, it does not possess an energy band structure in the strict sense of this term. However, it is possible to examine some features of the energy band structure of the alloy.

The electron energy spectrum consists of a large number of energy intervals with a high density of destroyed states in them. The energy spectrum of the alloy also consists of a large number of intervals where a low density of destroyed states is present; those are mainly forbidden gaps. The electron energy spectrum of the alloy can be represented as consisting of a large number of destroyed bands with a high density of states possessing small “tails” (regions with a low density of states), which penetrate the forbidden bands (regions with a negligibly low density of states). Since the lattice constants for ideal crystals of silicon and germanium only differ by several percent and germanium and silicon atoms possess the same valence, it is probable that the “tails” in the energy spectrum of the germanium– silicon alloy are rather of secondary (not of primary) importance in the energy spectrum. Much attention is paid to the study of the electric properties of strongly doped and compensated solid solutions [4].

Figure 1 shows the temperature dependence of the mobility of holes in crystals Ge_xSi_{1-x} ($x = 0 \div 15$). As can be seen from Fig. 1 in crystals of solid solutions Ge-Si with silicon content up to 15% of the mobility of holes in the scattering by lattice vibrations in the 100-280 K varies as $\mu_r \sim T^{-2.33}$ in pure germanium [7]. It was found that $T > 100$ K all the crystals Ge_xSi_{1-x} ($x = 0 \div 15$) is practically negligible scattering by ionized holes and neutral /, as well as dislocations [5]. It was stated that the mobility decreased in the temperature range of $T = 300-700$ K as $T^{-1.1}$ and $T^{-0.9}$ in uncompensated and compensated samples, respectively [4]. Using these data, the ionic

component of the mobility was determined (Fig. 1) [5]. In this calculation, the dependence $\mu \sim T^{-0.8}$ was taken for the dispersion on in homogeneities of the solid solution and $\mu_t \sim T^{-3.5}$ for the dispersion on lattice vibrations, and in the range of 50–100 K $\mu_t \sim T^2$.

It is assumed that, in the case of flash evaporation, a pure V→C condensation mechanism takes place (without the film sub melting). In practice, a satisfactory film structure can be obtained only after additional recrystallization of the deposited film.

A number of peculiarities associated with the character of the conductivity were found during the thermal treatment of the deposited $\text{Ge}_{0.85}\text{Si}_{0.15}$ films. The films of $\text{Ge}_{0.85}\text{Si}_{0.15}$ solid solutions are rather resistant to thermal treatment. The condensates prepared at $T_s = 490$ K (Fig. 2) were of a quasi-amorphous type. Fig. 2 shows that with increasing annealing temperature electrical conductivity of the film decreases, due to the partial crystallization of the amorphous film. In the temperature range of 300–600 K, they exhibit a semiconductor behavior of conductivity with thermal activation energy of 0.052 eV.

This value was determined from the slope of the plot $\lg \sigma = f(1/T)$ drawn according to the experimental values (Fig. 3). In the temperature ranges of 450–500 K and 500–680 K, the semiconductor type of conductivity is retained and the activation energy somewhat increases and amounts to 0.096 eV. In these temperature ranges, the three intervals (350–420, 510–540, and 590–620 K) are observed with more sharp changes in the electric conductivity; they can be associated with crystallization processes in the condensates (Fig. 4), and corresponds to the values of the activation energy of 0.054 and 0.022 eV.

The kinetics of the crystallization and the thermal stability were studied via heating the amorphous film directly in the column of a UEMV-100K electron microscope using a PRON-2 attachment (Fig.5). The thermal stability of the amorphous state was determined via the appearance of the most intensive diffraction reflections of the crystalline phase against the background of the diffuse maxima of the amorphous phase. The thermal stability of the amorphous state was studied in the films deposited on the substrates at room temperature and at 490 K. Figure 5 shows the successive stages of the structure transformations in the amorphous films. The amorphous $\text{Ge}_{0.85}\text{Si}_{0.15}$ films in their initial state are not in a state of thermal equilibrium but relax to a metastable state. With the temperature increase, the quenching of defects and changes in the free volume and topological short range ordering occur. The composition order does not change in this process. The

amorphous films possess some quantity of stored heat, which liberates during the crystallization of the amorphous phase; in this process, the properties of the film change irreversibly. It is important to know the crystallization mechanism on the microscopic level for the practical application of $\text{Ge}_{1-x}\text{Si}_x$ ($x = 0.15$) amorphous films. These studies would allow one to draw conclusions concerning the possible widening of the temperature range where the amorphous films can be effectively used. The controlled crystallization can be used for making super dispersed structures.

The amorphous $\text{Ge}_{0.85}\text{Si}_{0.15}$ films crystallize at a temperature of 530 K. The rate of the continuous heating directly in the column of the electron microscope amounts to 10 K/min. The initiation of the crystallization process is registered by the appearance of the most intensive diffraction lines [(111), (220), and (311)] of the crystalline phase of the solid solution in the electron-diffraction patterns against the background of the diffuse haloes.

The growth of the crystalline phase occurs in a dendrite fashion with formation of multiple bifurcations in the amorphous phase. When the temperature increases by 15–20 K, the crystallizations terminate with the formation of a continuous polycrystalline film of the solid solution.

The crystallization temperature of $\text{Ge}_{1-x}\text{Si}_x$ amorphous films is only 15 K greater than that of the films of amorphous germanium. This fact gives evidence that the same non diffusion crystallization mechanism occurs in both cases. That is, the silicon addition to germanium does not lead to a substantial increase in the thermal stability of the amorphous state. It is known that the thermal stability of the amorphous state can be considerably increased by doping with an impurity that does not form solid solutions with the host material or possesses significantly different atomic dimensions. Taking this into account, one should expect increasing of the thermal stability of the amorphous films in the system $\text{Ge}_{0.85}\text{Si}_{0.15}$ in such an interval of compositions where the destruction of the solid solution occurs. In this case, the mechanism of the diffuse stratification of the amorphous material with the temperature increasing will be the defining crystallization process; this will substantially retard the crystallization processes and lead to the increasing of the thermal stability of the amorphous state.

An additional crystallization at continuous heating at the rate of 25 K/min was performed to clarify the crystallization mechanism. The temperature of the initiation of the crystallization process is virtually the same in the case of the continuous heating with rates of 10 and 25 K/min; this proves the nondiffusional character of the interatomic

reconstructions in $\text{Ge}_{0.85}\text{Si}_{0.15}$ amorphous films, as well as gives evidence of the highly homogeneous interatomic distribution in the amorphous films.

The irradiation of the samples by an electron beam can be performed using a defocused or focused spot (projective or objective mode of operation) at an accelerating voltage of 35 kV. The attachment allows using replaceable cutting diaphragms to vary the dimensions of the irradiated area, to measure the resistivity of the samples in the process of irradiation, and to control the temperature of the samples.

The $\text{Ge}_{1-x}\text{Si}_x$ ($x = 0 \div 15$) samples were irradiated by an electron beam with a surface area of 5×2 mm for 1.5 hours. The temperature dependence of the electric conductivity of the Ge–Si samples show that the electric conductivity decreases and the slope of the line $R = f(T)$ increases as a result of the irradiation (Fig. 6); this suggests that the thermal activation energy increases. This phenomenon is most pronounced in the high temperature range. This behavior of the electric conductivity of the $\text{Ge}_{1-x}\text{Si}_x$ ($x = 0.15$) amorphous films gives evidence that the conductivity gap broadens. Evidently, the action of the electron flux accelerates the partial crystallization and leads to the capture of oxygen atoms.

Figure 6 shows the temperature dependence of the electrical conductivity of the film $\text{Ge}_{1-x}\text{Si}_x$ ($x = 0.15$) before and after irradiation. As seen from Fig. 6, when irradiated with a dose of 10^{15} sm^{-2} samples annealed at temperatures of 490 and 530 K, the conductivity decreases. It was established that, when the silicon content in the *n*-type $\text{Ge}_{1-x}\text{Si}_x$ thin films increases, the rate of formation of radiation defects also increases (Fig. 7), and the dose necessary to produce the *n* to *p* conversion decreases. The higher the silicon content in the $\text{Ge}_{1-x}\text{Si}_x$ samples irradiated with the same relative doses of electrons, the higher the concentration of holes after the conversion of the conductivity type. It was found that when the content of silicon in the *p*-type $\text{Ge}_{1-x}\text{Si}_x$ thin films increases, the rate of radioactive defects are also reduced (Fig. 7).

The data collected during the experiments concerning the action of fluxes of accelerated electrons on the mechanical properties of the crystals on the basis of $\text{Ge}_{1-x}\text{Si}_x$ can be explained if we suppose that the simplest defects in the crystal structure induced by the irradiation are vacancy-type lattice defects [12].

4. CONCLUSION

One can suppose that empty sites (vacancies) and displaced atoms introduce a set of energy levels into the forbidden gap. Complexes are formed in the presence of uncontrolled impurities in the crystal.

Unlike the pure components, the Ge–Si solid solution is an inhomogeneous material, and it can be represented as a two-phase system. The interface between the phases is a source of strong elastic strains and is characterized by the maximal density of dislocations.

Taking into account these considerations, we proposed a model to explain the radiation effects in $\text{Ge}_{1-x}\text{Si}_x$ involving the concept of the structural inhomogeneity of the solid solutions, which consist of the regions enriched with silicon or with germanium.

The interface between these regions acts as an effective drain for interstitial atoms formed owing to the radiation. The intensive adsorption and accumulation of free vacancies in the bulk of the material define the peculiarities of the radiation processes in $\text{Ge}_{1-x}\text{Si}_x$ solid solutions and devices on their basis.

According to the proposed model, the point defects formed in $\text{Ge}_{1-x}\text{Si}_x$ interact with structural defects and form complexes that act as recombination centers and decrease the concentration of charge carriers. This results in changes in the mechanical and electrical characteristics of the irradiated samples.

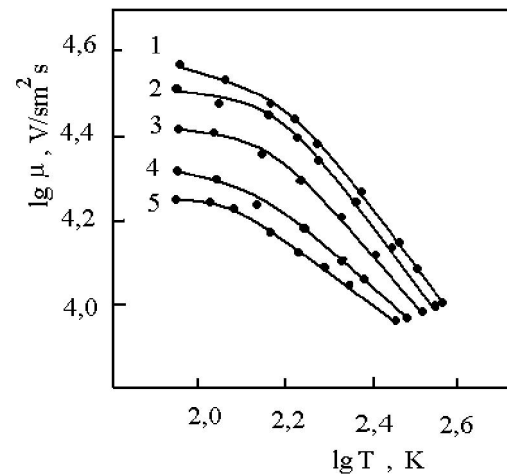


Fig.1. The temperature dependence of the mobility of holes in crystals $\text{Ge}_x\text{Si}_{1-x}$ ($x = 0 \div 15$): 1-0 at.%, 2-5 at.%, 3-10 at.%, 4-10 at.%, 5-15%.

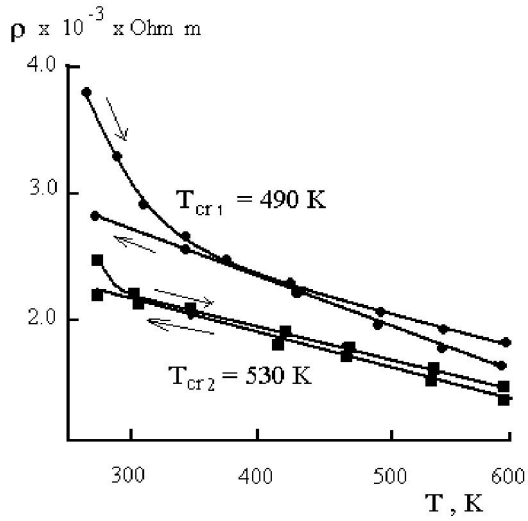


Fig. 2. Temperature dependence of the resistance of $Ge_{1-x}Si_x$ ($x = 0.15$) films; $n = 100$ nm.

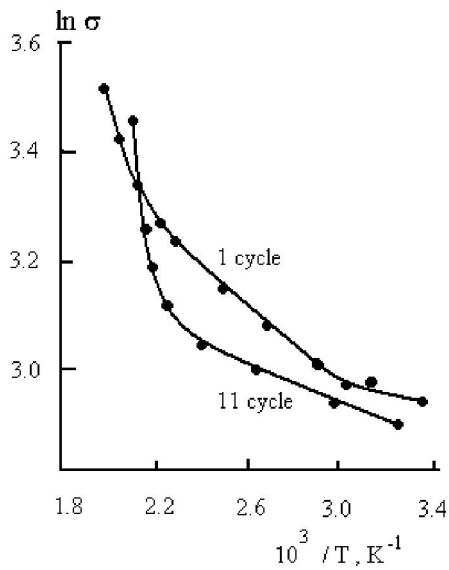


Fig. 3. Dependence of the conductance versus the temperature of $Ge_{1-x}Si_x$ ($x=0.15$) films at thermocycling.

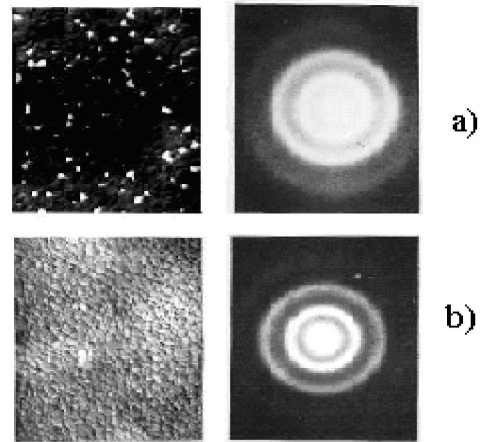


Fig. 4. Micrographs and electron-diffraction patterns of $Ge_{1-x}Si_x$ ($x = 0.15$) films: $n = 100$ nm, $\times 3500$. T_s , K: (a) 490, (b) 530.

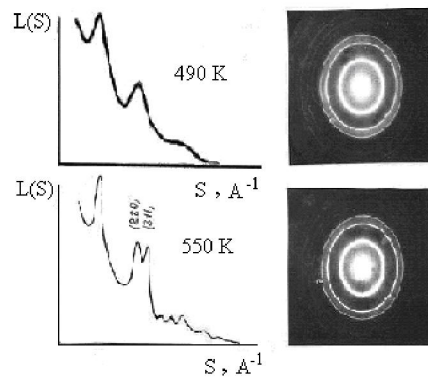


Fig. 5. Crystallization kinetics of $Ge_{1-x}Si_x$ ($x = 0.15$) solid solution.

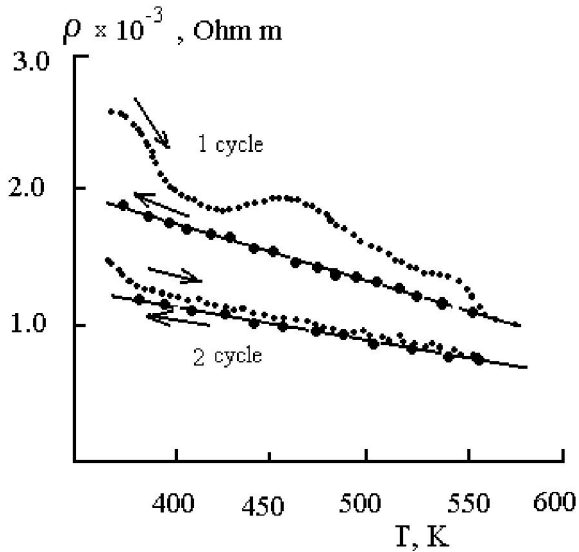


Fig. 6. Dependence of the resistivity of $Ge_{1-x}Si_x$ ($x = 0.15$) solid solution versus the temperature: (1) before irradiation, (2) after irradiation.

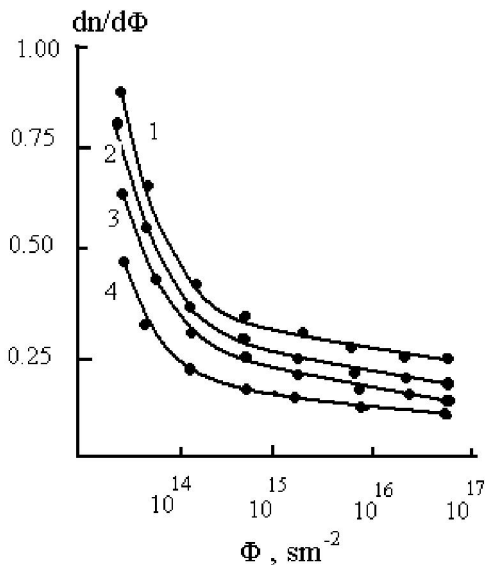


Fig. 7. Dependence of the rate of generation of defects versus the irradiation dose for various Si contents in $n-Ge_{1-x}Si_x$ solid solution: (1) $x = 0$, (2) $x = 0.05$, (3) $x = 0.10$, (4) $x = 0.15$.

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12/22/2013