Semiconductor Physics, Quantum Electronics & Optoelectronics, 2015. V. 18, N 1. P. 53-56.
doi: 10.15407/ spqeo18.01.053

PACS 61.82.Fk

Changes in electrophysical properties of heavily doped *n*-Ge ⟨As⟩ single crystals under the influence of thermoannealings

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Abstract. Features of changes in the electrophysical parameters (concentrations of charge carriers n_e and their mobilities μ) in heavily doped *n*-Ge ⟨As⟩ single crystals, which occur as a result of the series of thermoannealings (each for 0.5 h) over a wide temperature range ($540 \le T \le 900$ °C), have been investigated and explained.

Keywords: germanium, thermoannealing, Hall effect, charge carrier concentration, charge carrier mobility.

Manuscript received 19.09.14; revised version received 25.12.14; accepted for publication 19.02.15; published online 26.02.15.

1. Introduction

Up to date and probably in the following decade, elementary semiconductors will remain a major material of the electronic engineering [1]. Thus, germanium is widely used in optical devices of infrared range. Very large scale integration circuits and very-high-speed integrated circuits, new elements of microelectronics, *etc.* are based on silicon [2]. In relation with the emergence of new technological materials and devices manufactured on the basis of germanium and silicon, the problem of controlling their physical properties after various treatments is especially urgent [3, 4].

The thermal treatment of the solid-state electronic devices based on the many-valley semiconductors under various conditions is a common feature of their production technique. Interaction of dopant with the lattice defects and residual impurities in the bulk of semiconductor crystals occur, in principle, at any nonzero temperature. However, at higher temperatures these processes run faster [5].

The doping of semiconductors with the necessary impurities to the desired concentration is one of the main technological methods when creating modern solid-state electronic devices, which allows directed changing the properties of materials. Impurity atoms introduced into semiconductor create local levels in the band gap, which act as suppliers of electrons to the conduction band (donors) or traps for them, providing the appearance of holes in the valence band (acceptors), or play the role of radiative or nonradiative recombination centers of non-equilibrium charge carriers. Impurity atoms are introduced into the bulk of ingots or layers at various stages of their growth, to purposefully alter their resistivity and to form the desired structures. The existence of inhomogeneities in the electrical, optical and other characteristics of real crystals is conditioned by the presence of the impurity atoms in the semiconductor bulk (which, in fact, are the defects in crystal) as well as by irregularity of their distribution [6].

2. Features of the heavily doped semiconductors

Intensive study of the heavily doped semiconductors and increased interest in them is mainly caused by two reasons. First, using heavily doped semiconductors

greatly expanded the capabilities of the semiconductor engineering and electronics, since they are the basis of such semiconductor devices as tunnel diodes, lasers, tensometers, Hall sensors. The second equally important reason is that in heavily doped semiconductors arises substantial in cognitive terms qualitatively new physical phenomena, compared with the studied crystals, which have normal level of the impurity content. These phenomena include manifestations of "individuality" of dopants in the kinetic effects, polytropy of the impurity, and appearance of "tails" inherent to the density of states in the band gap [7]. Moreover, the high content and associated non-uniform impurity distribution can lead to formation of defects in the crystal bulk that have a different physical nature.

First of all, we should define more specifically the notion of "weakly" and "heavily" doped semiconductor. Under weak doping, the impurity atoms that do not interact with each other form local energy levels in the band gap, and the charge carriers in this semiconductor obey the classical Boltzmann statistics.

By increasing the degree of doping, the wave functions of the neighboring impurity atoms begin to overlap, which leads to increased efficiency of interaction between the impurity atoms that removes the permutable degeneration and leads to the appearance of impurity bands on basis of the levels that were discrete at weakly interaction between impurity atoms. In [8], the doping level that leads to formation of an impurity band is conventionally called as the average.

Finally, at strong doping the impurity band merges with the conduction band (*n*-type semiconductor) or with the valence band (*p*-type semiconductor). The charge carriers, density of which is now very large, obey the quantum Fermi-Dirac statistics, and semiconductors with such a doping level are called as the heavily doped ones.

For example, the electrical conductivity of weakly doped *n*-Ge does not depend significantly on the type of the dopant of V group (As, P, Sb) in the temperature region where all donors are fully ionized. However, in the case of *n*-Ge heavily doped by these impurities this statement is not fair. Thus, in [9, 10] the concentration dependence of the resistivity is studied for *n*-Ge doped with As, P, Sb in a wide range of concentrations at the temperature of 300 K. It was found that starting from a certain concentration the resistivity depends on the type of dopant. The highest resistivity in the region of high concentrations was observed for Ge ⟨As⟩, and the least resistivity – for Ge ⟨Sb⟩. It should be also noted that the limiting values of concentrations, at which "individuality" of the impurities begins to manifest, differ for the germanium crystals doped with various impurities. Based on the study of the concentration dependence of resistivity and Hall effect, the conclusion was made concerning the effect that the electron mobility in Ge at the high level of doping with elements of V group depends on the type of dopant, beginning with a certain threshold concentration n_0.

The mentioned features of the electrical properties of heavily doped Ge crystals become apprehensible to a certain extent, if we assume that the charge carrier concentration obtained from the Hall measurements is less than the true concentration of impurity in the bulk of the investigated crystal. Taking into account the fact that the dopant atoms are completely ionized, and the Hall factor in heavily doped Ge is not very different from unity (though it is not exactly equal to unity up to the highest concentration of the dopant), this discrepancy can be explained by the fact that a part of the dopant atoms is not included in the Ge lattice and is located in its bulk in an inactive state. In [11], for germanium the theoretical calculations were adduced, which show that when the number of impurity atoms is changed from 10^{18} up to 10^{22} cm^{-3}, i.e., by 4 orders, the number of charge carriers is changed only by 2 orders. Therefore, it is conceivable that with a high level of doping, the dopant is located in a germanium crystal in several forms simultaneously. This property of the impurity in the heavily doped Ge is called as polytropy.

There are many causes of generation of impurity polytropy in germanium. The main among them are as follows: formation of different types of structural complexes, the dopant deposition on the various structural defects (for example, formation of "impurity atmospheres" on dislocations), the inclusions of second phase, and the presence of the impurity atoms in the interstitials. All these causes lead to the fact that the part of impurities is not included into the substitutional solid solution. Such system is not stable from the thermodynamic point of view, because polytropy appears at the impurity concentrations when the solid solution is still far from saturation. Therefore, it is natural to assume that over time there will be a gradual recovery of the solid solution, i.e., the charge carrier concentration will increase due to the additional transition of the part of dopant into the solid solution.

Study of decomposition of the solid solution of germanium and its influence on the kinetic effects is of great scientific and practical interest. It should be noted that the crystal lattice of the basic substance is significantly deformed at the decomposition of the solid solution of impurity. The impurity that is not included in the substitutional solid solution and forms (as noted above) the various kinds of defects creates local disturbances in the crystal. These disturbances can be investigated using the structural methods based on X-ray diffraction (for example, the Lang method or the method of anomalous transmission of X-rays) [12].

In recent years, germanium doped with arsenic attracts greater interest. This interest is due to the fact that in heavily doped *n*-Ge ⟨As⟩ crystals the phenomena of decomposition of solid solution occur relatively easily. The arsenic atoms have significant diffusion mobility in the germanium lattice, which allows observing the decomposition of impurity solid solution in a wide temperature range.

The thermoannealing of semiconductor crystals is studied in [6, 13]. The authors compared the data obtained, which were the result of the annealings carried out at different temperatures (T_{ann}) and various durations (t), when the initial crystals were characterized by the usual level of the impurity content.

The aim of this study was to carry out a series of sequential thermoannealings of equal duration in a wide temperature range of heavily doped *n*-Ge ⟨As⟩ single crystals and to investigate changes in their electro-physical parameters that arise under the influence of these thermoannealings.

3. Results and discussion

In this paper, the research of changes in the concentration of charge carriers n_e and their mobility μ as a result of thermoannealings of the heavily doped *n*-Ge ⟨As⟩ single crystals at different temperatures within the range from 540 to 900 °C was performed. The concentration of the arsenic dopant for all the germanium samples was approximately equal to $3.9 \cdot 10^{19} \text{cm}^{-3}$. The samples were studied in the initial state (the concentration and mobility of charge carriers in their bulk were calculated), and then were subjected to the thermal treatment in a vacuum furnace at temperatures of 540, 600, 640, 725, 800, 830 and 900 °C. The annealing time of crystals at each temperature was 0.5 h. After the thermal treatment, the study of the same parameters as in the initial state, using standard methods of measuring the Hall effect and conductivity, was carried out.

The results of these experiments are presented in Figs 1 and 2. The reasons of changes that occur in the dependences of n_e and μ on the annealing temperatures, probably, boil down to the manifestation of the factors described below, which inevitably accompany these annealings.

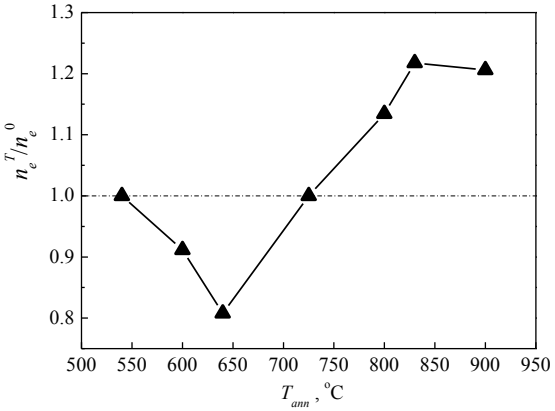

Fig. 1. Dependences of the charge carrier concentration after annealing n_e^T normalized by the corresponding values in the initial state n_e^0 on the annealing temperatures T_{ann} = 540, 600, 640, 725, 800, 830, 900 °C in the heavily doped *n*-Ge ⟨As⟩ samples.

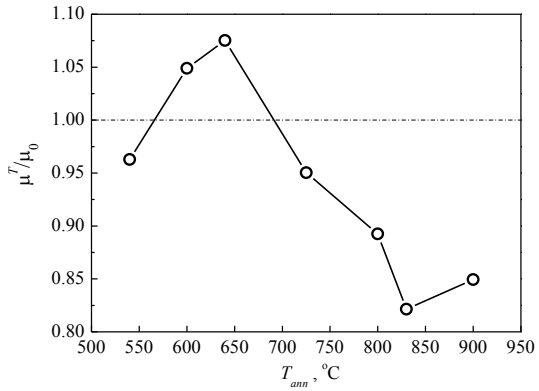

Fig. 2. Dependences of the charge carrier mobility after annealing μ^T normalized by the corresponding values in the initial state μ_0 on the annealing temperatures T_{ann} = 540, 600, 640, 725, 800, 830, 900 °C in the heavily doped *n*-Ge ⟨As⟩ samples.

At the annealing temperature 540 °C, the charge carrier concentration n_e is not changed as compared with its value in the initial state (Fig. 1).

Within the range from 600 to 725 °C, the performed electrical measurements showed that intensive decomposition of arsenic solution in germanium occurs. As shown in Fig. 1, decomposition of supersaturated solid solution of arsenic in germanium is accompanied by a decrease in the charge carrier concentration, because part of impurities under decomposition becomes electrically inactive. The carrier mobility at the same time, respectively, increases, because the number of the effective electrically-active scatterers decreases.

It should be noted that the measurement of the electrical parameters was carried out at the temperature of liquid nitrogen. At this temperature, taking into account the very high charge carrier concentration, the system approaches to the degeneracy and the Hall factor approaches to the unity. Consequently, the obtained values of the carrier concentration will be more accurate than those measured at room temperature.

Investigation of the samples after the thermal treatment at the annealing temperatures $T_{ann} > 725$ °C showed that the carrier concentration n_e is not reduced but increased relative to the values in the initial state (Fig. 1), although probably the phenomenon of decomposition of solid solution at these temperatures to a certain extent takes place. This discrepancy is likely related to the fact that at these annealing temperatures, taking into account the high concentration of impurities, the electrically-active complexes (up to the annealing temperature of $T_{ann} \approx 830$ °C) are formed. This process causes an increase in the carrier concentration.

The annealing even at higher temperature ($T_{ann} > 830$ °C) causes the electrically-active complexes to be decomposed, therefore, the carrier concentration is decreased, while the mobility is increased. At these

annealing temperatures, perhaps, another process may take place: the impurities precipitated earlier will be returned to the crystal lattice, which can be accompanied by the recovery of its structural perfection. As a result of this process, the charge carrier concentration will increase and their mobility will decrease.

As can be seen from comparison of Figs 2 and 1, the change in the charge carrier mobility is correlated in the opposite phase with changes in the concentration of the electrically-active complexes (scattering centers) both in the area of n_e growth (and, therefore, of the concentration of scattering centers), and in the initial area of their thermal dissociation.

It was also experimentally found that the changes in the concentrations and mobilities of charge carriers that occur at each annealing, after cooling the samples to the room temperature, are very stable and can remain unchanged for six months, i.e. the diffusion processes in the annealed crystals at the high temperatures ($T_{ann} >$ 500…600 °C) do not subjected to the appreciable influence of the room temperatures for a long time. It opens practical possibilities to change the physical parameters of germanium (such as n_e and μ) in the desired direction (within the changes provided by the thermoannealings at the elevated temperatures) and to use the achieved changes at lower temperatures (for example, at room temperatures). At the same time, surely, you must take into account the changes (in the values of the charge carrier mobility, lifetime of the minority carrier and other parameters), which inevitably accompany annealings of the crystals at various temperatures. After all, these changes can be not only useful but also quite undesirable. For example, if you want to increase the carrier concentration in the crystal due to annealings, then in *n*-Ge⟨As⟩ the charge carrier mobility will only decrease within the region of the annealing temperatures 500…850 °C (which is urgent for practice).

4. Conclusions

Features of changing in the electrophysical parameters (concentrations of charge carriers n_e and their mobilities μ) in heavily doped *n*-Ge⟨As⟩ single crystals, grown using the Czochralski method, that occurred as a result of the series of thermoannealings (each for 0.5 h) over a wide temperature range, were investigated and explained. It has been ascertained that a change in the basic parameters of the samples under conditions of using the thermoannealing regimes that are commonly used in manufacturing the semiconductor devices occur non-monotonic. As a result of the analysis of carried out thermal treatments of samples, it has been found that the dependences of concentrations and mobilities of charge carriers (normalized by the corresponding values in the initial state) on the values of the annealing temperatures possess two extrema corresponding to the values approximately 640 and 830 °C. Information allows understanding the physical meaning of the above changes has been adduced.

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