

Low resistance Cu_3Ge compounds formation by the low temperature treatment of Cu/Ge system in atomic hydrogen

A I Kazimirov¹, E V Erofeev¹, I V Fedin¹, V A Kagadei¹ and Y N Yurjev²

¹ Research Institute of Electrical Communication Systems of Tomsk State University of Control Systems and Radioelectronics, 47 Vershinina street, Tomsk, 634034 Russian Federation

² Institute of Physics and Technology, National Research Tomsk Polytechnic University, 30 Lenina av., Tomsk, 634050, Russian Federation

E-mail: erofeev@micran.ru

Abstract. The research deals with the regularities for Cu_3Ge compound formation under the low temperature treatment of a double-layer Cu/Ge system deposited on *i*-GaAs substrate in atomic hydrogen flow. The treatment of a Cu/Ge/*i*-GaAs system with layer thicknesses, respectively, of 122 and 78 nm, in atomic hydrogen with a flow rate of 10^{15} at·cm⁻²·s⁻¹ for a duration of 2.5–10 min at room temperature, leads to an interdiffusion of Cu and Ge and formation of a polycrystalline film containing stoichiometric phase Cu_3Ge . The film consists of vertically oriented grains of dimensions 100–150 nm and has a minimum specific resistance of 4.5 $\mu\Omega$ cm. Variation in the treatment duration of Cu/Ge/*i*-GaAs samples in atomic hydrogen affects Cu and Ge distribution profiles, the phase composition of films formed, and the specific resistance of the latter. As observed, Cu_3Ge compound synthesis at room temperature demonstrates the stimulative effects characteristic of atomic hydrogen treatment for both Cu and Ge diffusion and for the chemical reaction of Cu_3Ge compound generation. Activation of these processes can be conditioned by the energy released during recombination of hydrogen atoms adsorbed on the surface of a Cu/Ge/*i*-GaAs sample.

1. Introduction

The effects of treatment in hydrogen plasma or atomic hydrogen (hydrogenation) on the properties of near-surface layers of various semiconductor materials and solids have been intensively studied since the early 1990's. A number of effects have been discovered, including passivation of structural defects, deep and minor impurity centers, and also altering of electrophysical properties of materials [1–7]. The mechanisms of these effects are conditioned by atomic hydrogen penetration into the near-surface layers of semiconductor materials, followed by the formation of passive complexes with various types of crystal lattice defects.

In other studies, it is shown that the recombination of hydrogen atoms adsorbed on the surface of solids is accompanied by an energy release equaling $\cong 4.5$ eV per single recombination event. Under certain conditions, this energy can efficiently stimulate diffusion processes on the surface both in the surface and near-surface layers of semiconductor crystals and likewise, the desorption of residual impurities from the surfaces [8].

In paper [9], it is shown that under the action of atomic hydrogen generated in the gaseous discharge plasma, low temperature crystallization of thin polycrystalline Ni films occurs.



In paper [10], the research focused on low temperature diffusion of In into the near-surface layers of Ge stimulated by treatment of the samples in hydrogen plasma. The diffusion of In atoms from the thin film deposit on the surface of a Ge sample was observed in the so-called “active zone” (≈ 10 nm), where, according to the authors, the processes of defect formation take place and multiphonon dissipation mechanisms are brought into effect in the energy release, during recombination of hydrogen atoms. Localization of In atoms was observed both in the vacancies and in the interstitial sites of Ge crystal lattice. The factor of In diffusion into Ge, calculated for the hydrogen plasma treatment mode used in the study, amounted to $\sim 1.4 \cdot 10^{-19}$ m²/s, which corresponds to In thermal diffusion into Ge at $T = 610$ °C. The actual temperature of samples in these experiments did not exceed 30 °C.

The authors of paper [11] carried out research into low temperature diffusion of Au films into Ge substrate, stimulated by treatment in the hydrogen plasma of a gaseous discharge. It has been shown that treatment of this kind stimulates diffusion of Au atoms into Ge at temperatures close to room temperature. It has been shown that diffusion of Au within the crystal occurs by the interstitial mechanism, and a considerable part of Au atoms are localized on Ge lattice sites.

We have found earlier that treatment of semi-insulating GaAs samples, with thin Cu and Ge films deposited on their surface, in atomic hydrogen flow at room temperature, leads to interdiffusion of Cu and Ge and formation of polycrystalline film with vertically grains of dimension 100–150 nm [12].

This paper presents the results of further studies of phenomena occurring under the low temperature treatment in atomic hydrogen flow of a double-layer Cu/Ge system deposited on an *i*-GaAs substrate and, in particular, the regularities of Cu and Ge interdiffusion accompanied by formation of a polycrystalline film containing a considerable portion of the Cu₃Ge stoichiometric compound.

2. Experimental details

The semi-insulating *i*-GaAs (100) substrates were used in experiments. All substrates were cleaned from native oxides and contaminants in HCl:H₂O (1:10) solution, followed by rinsing in deionized water and drying in purified nitrogen flow.

The first series of experiments focused on a study of the regularities of profile changes in Cu and Ge distribution variant to the depth of samples, and of the changes of thin film phase composition variant to the duration of Cu/Ge/*i*-GaAs samples treatment in atomic hydrogen flow at room temperature. For that purpose, thin films of Ge and Cu, with thickness of 78 and 122 nm, respectively, were deposited on the surface of GaAs substrates by electron-beam evaporation in a vacuum, with residual pressure $p = 5 \cdot 10^{-7}$ mbar. The thickness of the films was chosen to complete mixing of the layers occurs, the Ge content in the mixture would amount to $N_{Ge} = 25$ at.%. This was supposed to ensure generation of the Cu₃Ge stoichiometric compound. On withdrawal of samples from the evaporator chamber, they were loaded into an experimental unit to treatment in atomic hydrogen flow with flow density $j = 10^{15}$ at.·cm⁻²·s⁻¹ for $t = 1, 2.5, 5,$ and 10 minutes at room temperature.

A reference sample of Cu/Ge/*i*-GaAs was subjected to heat treatment in a vacuum with residual pressure $p = 5 \cdot 10^{-6}$ mbar at temperature $T = 200$ °C for $t = 30$ min. According to the data [13], this mode of heat treatment leads to complete interdiffusion of Ge and Cu thin films and to generation of Cu₃Ge stoichiometric compound.

The second series of experiments dealt with a study of the dependence of the specific resistance of Cu/Ge thin film with a total thickness of 200 nm and with varying thicknesses of Ge film ($d = 65$ –102 nm) on the duration of Cu/Ge/*i*-GaAs samples treatment in atomic hydrogen flow at room temperature. After cleaning the surface of substrates from native oxides by electron-beam evaporation in a vacuum, deposition of Ge and Cu thin films would be performed, in which case Ge content amounted to $N_{Ge} = 20, 25, 30, 35$ at.%. Next, each sample would be divided into three parts. Each sample thus obtained would then be treated in atomic hydrogen flow with flow density $j = 10^{15}$ at.·cm⁻²·s⁻¹ at room temperature; $t = 5, 15,$ and 30 minutes, respectively.

The experiments were carried out using the atomic hydrogen source described in paper [14].

A cross section of the samples was examined using scanning electron microscopy (SEM), and the distribution of Cu and Ge elements by depth was examined using Auger electron spectroscopy (AES), with layer-by-layer etching. To determine the qualitative composition of phases of the obtained compounds, X-ray Diffraction (XRD) was applied. The specific resistance of Cu/Ge thin films was studied using a four-point probe method, with measurement error margin not exceeding 10 %.

3. Results and discussion

The profiles of Cu and Ge elements distribution by depth and phase composition of near-surface layers of the samples from the first series of experiments are presented in Figs. 1–5.

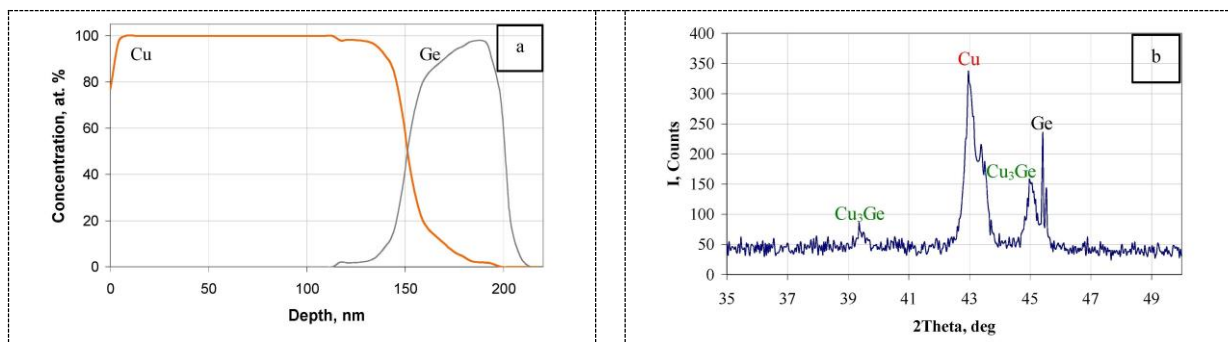


Figure 1. Profiles of Ge and Cu elements distribution by depth (a) and composition of XRD phases (b) of a Cu/Ge/i-GaAs sample treated in atomic hydrogen flow for $t = 1$ min.

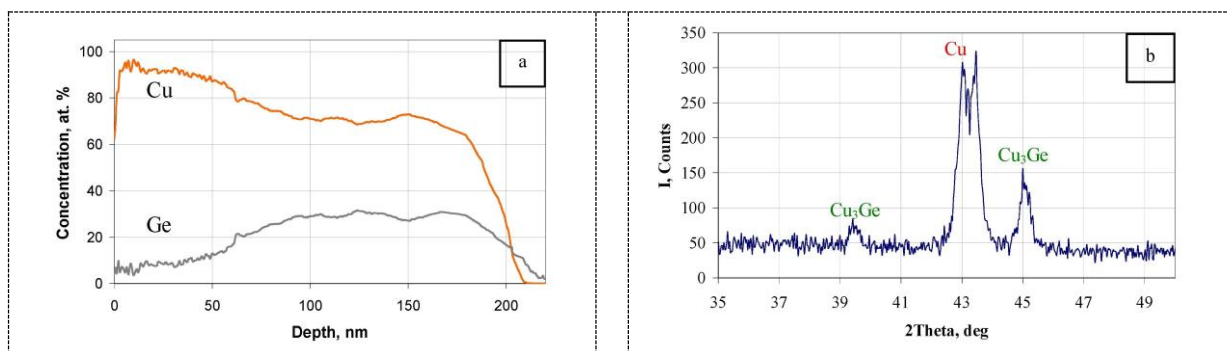


Figure 2. Profiles of Ge and Cu elements distribution by depth (a) and composition of XRD phases (b) of a Cu/Ge/i-GaAs sample treated in atomic hydrogen flow for $t = 2.5$ min.

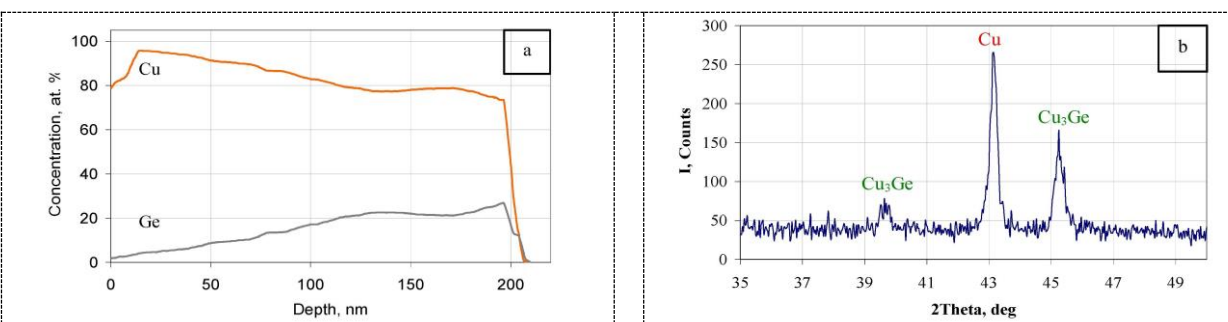


Figure 3. Profiles of Ge and Cu elements distribution by depth (a) and composition of XRD phases (b) of a Cu/Ge/i-GaAs sample treated in atomic hydrogen flow for $t = 5$ min.

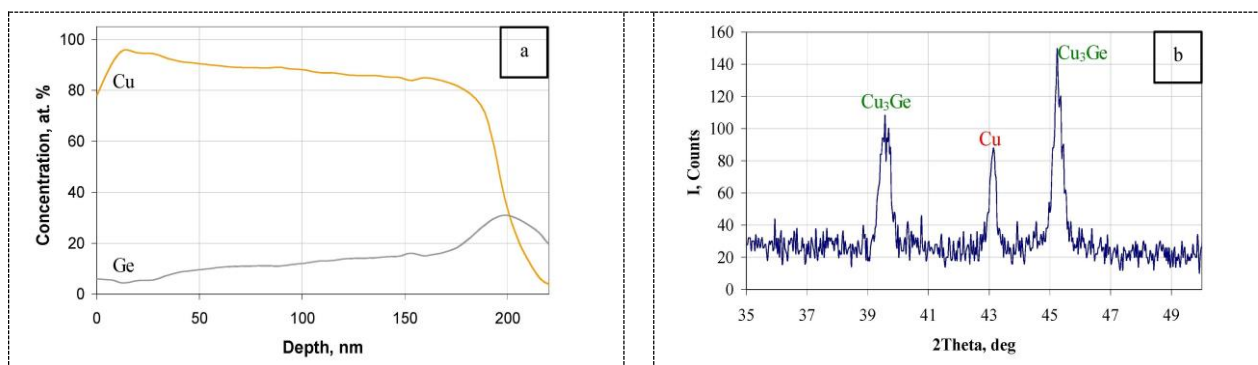


Figure 4. Profiles of Ge and Cu elements distribution by depth (*a*) and composition of XRD phases (*b*) of a Cu/Ge/*i*-GaAs sample treated in atomic hydrogen flow for $t = 10$ min.

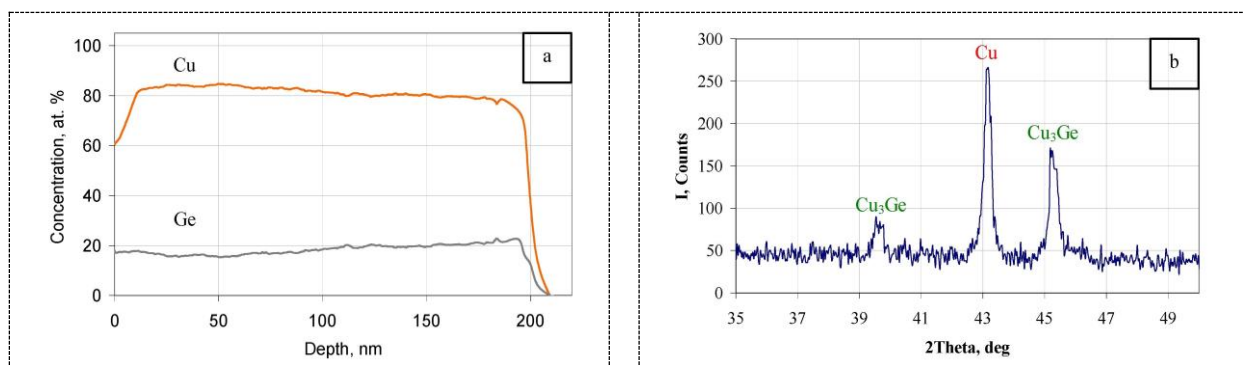


Figure 5. Profiles of Ge and Cu elements distribution by depth (*a*) and composition of XRD phases (*b*) of Cu/Ge/*i*-GaAs samples after high-temperature vacuum annealing at temperature $T = 200$ °C for $t = 30$ min.

The data in Fig. 1, *a* demonstrates the fact that treatment of a two-component Cu/Ge/*i*-GaAs system in atomic hydrogen flow at room temperature for $t = 1$ min does not result in any noticeable diffusion of Cu and Ge by sample depth. The profiles of elements distribution are similar to the profiles characteristic of the sample before its treatment in atomic hydrogen flow (not shown in the figure).

With the time of sample treatment in atomic hydrogen flow being $t = 2.5$ min (Fig. 2, *a*), the profiles change considerably, forming a pattern typical of a complete mixing of Ge and Cu films. With the treatment time increased to $t = 5$ and 10 min (Figs. 3 and 4, *a*), no further considerable change in the distribution profiles pattern occurs. The concentration of Ge in the near-surface layers remains at the level of 4–8 at.%, gradually increasing to 25–30 at.% at a depth of 200 nm.

A reference sample obtained through vacuum annealing at temperature $T = 200$ °C for $t = 30$ minutes (Fig. 5, *a*) also demonstrates complete mixing of Ge and Cu films, but with more uniform elements distribution by depth. The concentration of Ge is at a level of 20 at.% through the entire thickness of the film examined.

The X-ray pattern of a sample treated in atomic hydrogen flow for $t = 1$ min (Fig. 1, *b*) demonstrates that with treatment durations being small, considerable amounts of Cu and Ge are in a chemically free state, which correlates with data obtained using the AES method. However, even in the absence of any substantial Cu and Ge interdiffusion, the X-ray pattern features a peak corresponding to Cu₃Ge phase.

An increase in the duration of Cu/Ge/*i*-GaAs samples treatment in atomic hydrogen flow ($t = 2.5$ –10 min, Fig. 2–4, *b*) results in a decrease of the intensity of the peaks which correspond to elementary Ge and Cu and in an increase of the intensity of peaks of the Cu₃Ge stoichiometric compound phase. It goes to show that even though a more uniform distribution of Ge and Cu elements by film thickness is

not achieved with treatment time $t = 5$ and 10 min, chemical reaction of compound formation proceeds successfully, leading to an increase of Cu_3Ge phase content in the samples.

A reference sample obtained through vacuum annealing (Fig. 5, *b*) has an X-ray pattern similar to the one which is typical for a sample obtained by treatment in atomic hydrogen flow for $t = 5$ min (Fig. 3, *b*). This demonstrates the fact that, although film elements in the reference sample have a more uniform distribution, the maximum content of the Cu_3Ge phase is not achieved in the film, whereas the content is observable in a sample treated in atomic hydrogen flow for $t = 10$ min.

It should be noted that changes in the sequence of Ge and Cu films deposition on *i*-GaAs substrates during treatment of samples in atomic hydrogen flow has never resulted in any considerable changes in the behavior regularities of the processes of formation of a continuous polycrystalline film containing the Cu_3Ge phase.

To further elaborate the pattern of Cu and Ge films interaction, microscopic examination was carried out for the cross section of the initial Cu/Ge/*i*-GaAs samples, as it was for samples having undergone a control vacuum annealing and for those treated in atomic hydrogen for $t = 5$ min (Fig. 6).

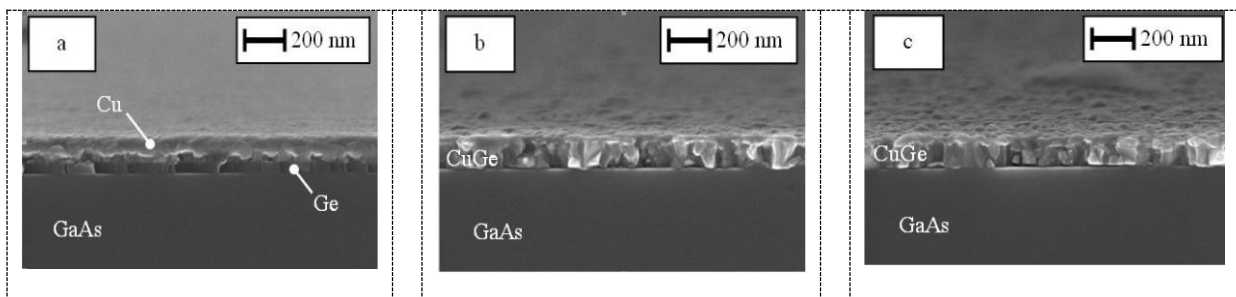


Figure 6. Cross section of Cu/Ge/*i*-GaAs samples before treatment (*a*), after treatment in atomic hydrogen flow for $t = 5$ min (*b*), and after heat treatment in a vacuum at temperature $T = 200$ °C for $t = 30$ min (*c*).

For the initial Cu/Ge/*i*-GaAs sample (Fig. 6, *a*), the boundary between the two films of Cu and Ge is clearly visible. After heat treatment in a vacuum ($T = 200$ °C, $t = 30$ min), interdiffusion of films occurs, leading to formation of a polycrystalline film with vertically oriented grains (Fig. 6, *b*), similar to those obtained in study [15]. Treatment of a Cu/Ge/*i*-GaAs sample in atomic hydrogen at room temperature for $t = 5$ min leads to a result similar to that obtained in a reference sample with vacuum annealing. Formation of a polycrystalline film with vertically oriented grains of 100–150 nm average size (Fig. 6, *c*) is observed.

The results shown in Figs. 1–6 correlate well with each other and testify to the fact that during treatment of Cu/Ge/*i*-GaAs samples in atomic hydrogen flow at room temperatures, interdiffusion of Cu and Ge occurs, accompanied by generation of a Cu_3Ge compound having polycrystalline structure.

Fig. 7 shows the dependencies of specific resistance, ρ of Cu/Ge thin film on the duration of the treatment of Cu/Ge/*i*-GaAs samples from the second series of experiments in atomic hydrogen flow at room temperature. The content of Ge, N_{Ge} in the samples varied within a range of 20 to 35 at.%.

The minimum value of Cu/Ge film specific resistance was $\rho \approx 4.5$ $\mu\Omega\cdot\text{cm}$, this being observed for samples with $N_{\text{Ge}} = 20$ –25 at.% and $t = 5$ min. Increase of samples treatment time from $t = 5$ to 30 min results in a gradual increase of thin film specific resistance value, irrespective of N_{Ge} value. At the same time, for all treatment durations, the minimum value of ρ is observed for samples with Ge content at the level of 20–25 at.%, which is close to a stoichiometric composition characteristic in a Cu_3Ge compound.

The value of film specific resistance of a sample having a similar N_{Ge} magnitude but formed through vacuum annealing at temperature $T = 200$ °C for $t = 30$ min amounted to $\rho = 7.0$ $\mu\Omega\cdot\text{cm}$. The obtained data concurs with the results of study [13], in which the value of specific electrical resistance of the

film of Cu₃Ge compound, with Ge content in the system amounting to about 27–30 at.%, after heat treatment in a vacuum at $T = 400$ °C for $t = 30$ min resulted in $\rho \approx 5\text{--}6$ $\mu\Omega\cdot\text{cm}$.

Thus, proceeding from the results obtained from the experiments a conclusion can be drawn concerning the simulative character of the effect of treatment in atomic hydrogen flow on both the interdiffusion of Cu and Ge and the chemical reaction of Cu₃Ge compound generation in Cu/Ge/*i*-GaAs samples. Activation of these processes, according to the data of studies [8–11], can be conditioned by the energy released during recombination of hydrogen atoms on the surface of Cu/Ge/*i*-GaAs samples.

4. Conclusion

It has been shown that treatment of Cu/Ge/*i*-GaAs samples in atomic hydrogen flow with density $j = 10^{15}$ at. $\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ for $t \geq 2.5$ min at room temperature leads to interdiffusion of Cu and Ge atoms and formation of a polycrystalline film with a Cu₃Ge compound stoichiometric phase. The film consists of vertically oriented grains of 100–150 nm average size. The minimum value of polycrystalline film specific resistance, with Ge content at the level of 20–25 at.%, is $\rho \approx 4.5$ $\mu\Omega\cdot\text{cm}$. Activation of diffusion processes, as well as the process of Cu₃Ge chemical compound generation, can be conditioned by the energy released during recombination of hydrogen atoms on the surface of Cu/Ge/*i*-GaAs samples.

Acknowledgments

The authors of this study express their appreciation to the staff of the “Nanotechnology” Education & Research Center, Tomsk State University of Control Systems and Radioelectronics, and of the “Microelectronics” Research & Production Department, “Micran” Research & Production Company, for their involvement and assistance in the work, and also to Ivan A. Shulepov and Artyom A. Kachayev, staff members of the National Research Tomsk Polytechnic University, for carrying out measurements using the AES and XRD methods.

This work was supported by the Ministry of Education and Science of the Russian Federation under the Contract № 14.577.21.0204 from 27.10.15.

References

- [1] Tyurin Y I 2000 *The storage properties of hydrogen in solids* (Moscow: Energoatomizdat)
- [2] Alefeld E 1978 *Hydrogen in metals. Basic Properties* (New York: Springer-Verlag)
- [3] Golban A N 1976 *The interaction of atomic particles with solids* (Kharkov)
- [4] Pearton S J 2010 *Chem. Vap. Deposition* **16** 266
- [5] Seager C H, Myers S M, Wright A F 2002 *J. Appl. Phys.* **92** 7246
- [6] Seager C H, Mayers S M, Wright A F 2000 *J. Appl. Phys.* **88** 4676
- [7] Polyakov A Y, Smirnov N B, Govorkov A V 2003 *J. Appl. Phys.* **94** 3960
- [8] Lavrenko V A 1973 *Hydrogen atoms recombination on solid surfaces* (Kiev: Naychnaya misl)
- [9] Zhavzharov E L, Byalik G A, Matyushin V M 2007 *Technical Physics Letters* 33 571
- [10] Matyushin V M 2001 *Semiconductors* **35** 287
- [12] Matyushin V M 1999 *Zh. Tekh. Fiz.* **69** 73
- [13] Kazimirov A I, Erofeev E V, Kagadei V A 2013 *Proc. of SPIE* **8700** 870005
- [14] Kagadei V A, Proskurovsky D I 2004 US Patent 6765216 B2
- [15] Aboelfotoh M O, Oktyabrsky S, Narayan J 1997 *J. Mater. Res.* **12** 2325