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Control of Parameters of III-V Compound Microcrystals and Epitaxial Layers by means of Complex Doping

Influence is studied of complex doping of InSb microcrystals and GaAs epitaxial layers with admixtures of Sn, Au, Al, Yb, Cr and Mn upon electrophysical parameters of the materials, their time stability and hardness to the fast neutron irradiation. It is found that for GaAs epitaxial layers considerable decrease in the free charge carrier concentration may be achieved by optimal quantitative combination of Al and Yb dopant during growth. For InSb microcrystals Sn admixture provides the desired range of free charge carrier concentrations from the intrinsic one up to 10^{19} cm^{-3} . Au admixture is a good catalyzer for whisker microcrystal growth and it facilitates InSb growth, while Cr admixture improves radiation resistance of the microcrystals. The possibility of application of the obtained materials for the development of Hall sensors operating efficiently under extreme external conditions, in particular under the conditions of high radiation loads, is verified.

Keywords: III-V semiconductor, crystal growth, complex doping, electrical properties

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Introduction

III-V semiconductors and structures based on them conventionally play one of the leading roles in scientific research and practical applications in various fields of electronics. At present investigations cover a wide-range spectrum of topics beginning from conventional techniques for the growth single crystals and epitaxial layers, and modification of their properties up to the development techniques for quantum-dimension structures like quantum wires, quantum dots, superlattices (GAO; HIDALGO; LUYKEN; LI). The present work continues our methodical studies of recent years concerning the possibility of obtaining III-V microcrystals and epitaxial layers with parameters, which could be applied for manufacturing of time-stable microsensors of physical quantities, intended for operation under extreme conditions, in particular under conditions of hard radiation exposure (BOLSHAKOVA; BOLSHAKOVA 2000). One of the basic technological methods widely used for solving such type of problems is complex doping of semiconductors. The main difficulty is to determine optimal qualitative and quantitative combination of impurities for doping certain materials. Below we present the results of experimental studies of the influence of various dopants on the electrophysical parameters of InSb microcrystals grown by chemical transport reactions (CTR) method and GaAs epitaxial layers grown by LPE method as well as on their time stability and hardness to fast neutron irradiation.

Growth of microcrystals and thin films

InSb whisker microcrystals were grown by the CTR method in a closed ampoule-like reactor (BOLSHAKOVA ET AL., 1998). Undoped polycrystalline indium antimony with charge carrier concentration of about $3 \cdot 10^{16} \text{ cm}^{-3}$ at the room temperature was used as the initial material. Halogenic compound J_2/Br_2 in 2:1 ratio was applied as transporting agent. Microcrystal growth was carried out at the temperature of crystallization zone of 450–460 °C. Duration of the growth process was 24 hours.

GaAs epitaxial layers were grown by the LPE method from gallium solution-melt with the use of piston graphite boxes in horizontal reactor. Semi-insulating GaAs oriented in (100) plane was used as the substrate. Growth temperature was equal to 620–560 °C, and the cooling rate was 1.5–2.0 K/min (KRUKOVSKII).

Modification of electrophysical parameters of microcrystals and thin films with the complex doping

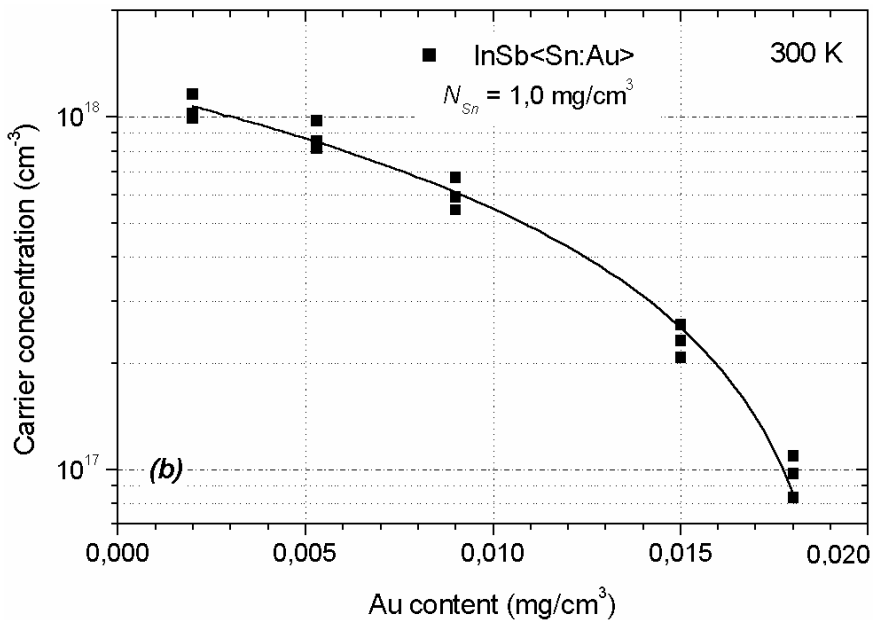
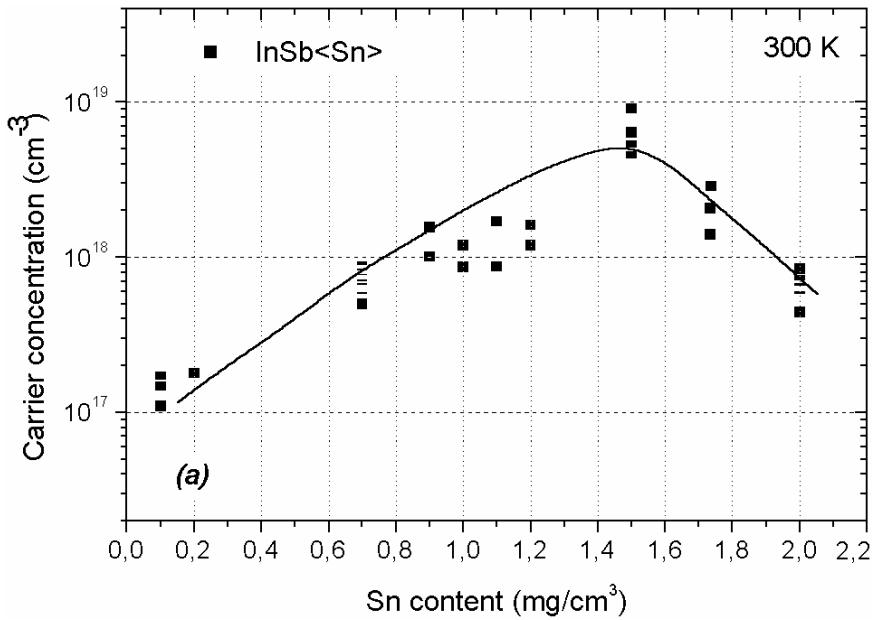
Complex doping of microcrystals and epitaxial layers was performed during their growth. For InSb microcrystals dopants were selected from the condition that they should not suppress (better – should promote) the growth of whisker crystals by the CTR process, should provide desired changes in their electrophysical parameters within a wide range while improving their time stability and hardness to high radiation loads. Main requirement to the admixtures applied for modification of electrophysical parameters of GaAs epitaxial layers is to provide considerable reduction in the concentration of free charge carriers and increase in their mobility, which is unreachable by means of conventional stock annealing at LPE conditions.

Donor tin impurity, traditional for III-V semiconductors, was used as the main dopant which should provide wide-range change of free charge carrier concentration for InSb microcrystals. It allowed to obtain microcrystals with free charge carriers concentration from $3 \cdot 10^{16} \text{ cm}^{-3}$ up to $1 \cdot 10^{19} \text{ cm}^{-3}$. Dependence of this concentration on Sn impurity in the microcrystal growth container is given in Fig. 1a. The figure shows that the maximum value of free charge carrier concentration about 10^{19} cm^{-3} is reached when the Sn content in the growth container is about 1.5 mg per 1 cm^3 of the reactor volume. An increase in the Sn content above this value leads to a decrease in the resulting free charge carrier concentration in the doped InSb microcrystals. It even suppresses the microcrystal growth, i.e. growth rate as well as the quantity and dimensions of growing microcrystals are decreased.

Increase in the growth of microcrystals may be reached by means of using additional doping impurities. An increase in the quantity of crystallizing nucleus and crystals was observed during Au doping when its concentration in the growth container did not exceed 0.02 mg/cm^3 . In this case increase in Au in the growth chamber at a constant concentration of the main donor dopant Sn decreases the charge carrier concentration in microcrystals (Fig. 1b). This confirms the acceptor behaviour of Au impurity during the doping of InSb. A similar effect is also observed in the case of Mn dopant but the concentration of Mn required to have the effect is 7–8 times higher than that for the Au impurity (Fig. 1c). However, with the main Sn dopant Cr dopant results in a small increase in the free charge carrier concentration in InSb microcrystals (Fig. 1d) as well as reduces spread in electrophysical parameters of microcrystals and improves their time stability.

For GaAs epitaxial layers their primary purification from the background impurities was provided by means of annealing of Ga/GaAs solutions/melts at optimally selected hydrogen streams. This allowed to reach the threshold concentration of free charge carriers at the level

of $(1-2) \cdot 10^{16} \text{ cm}^{-3}$, typical for this technology. Complex doping with rare-earth (Yb) and isovalent (Al) impurities was used for deeper purification and complementary decrease in the free charge carrier concentration. Dependence of free charge carrier concentration on the contents of mentioned impurities is presented in Fig. 2a. As seen from the figure, the free charge carrier concentration for complex doped epitaxial layers of GaAs is decreased by over 2 orders in comparison with the undoped samples.



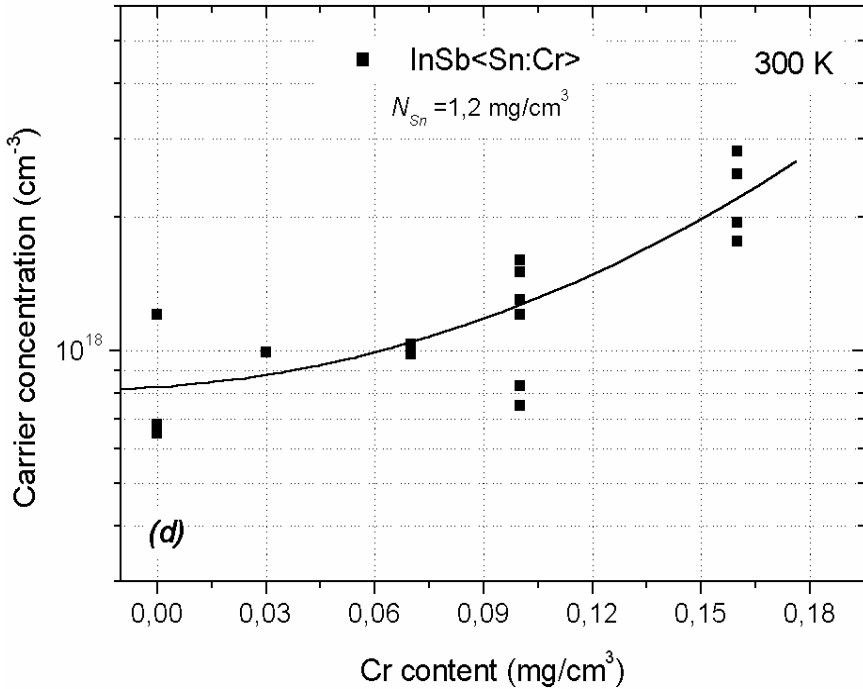
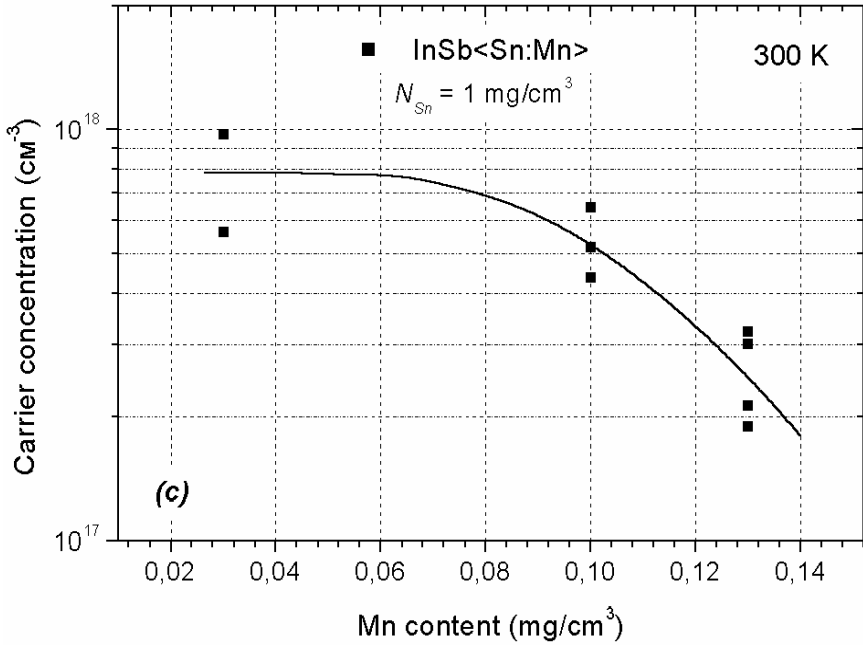


Fig. 1: Dependence of free charge carrier concentration for InSb microcrystals on the content of main dopant Sn (a); the content of main dopant Sn together with additional dopant Au (b), Mn (c), and Cr (d)

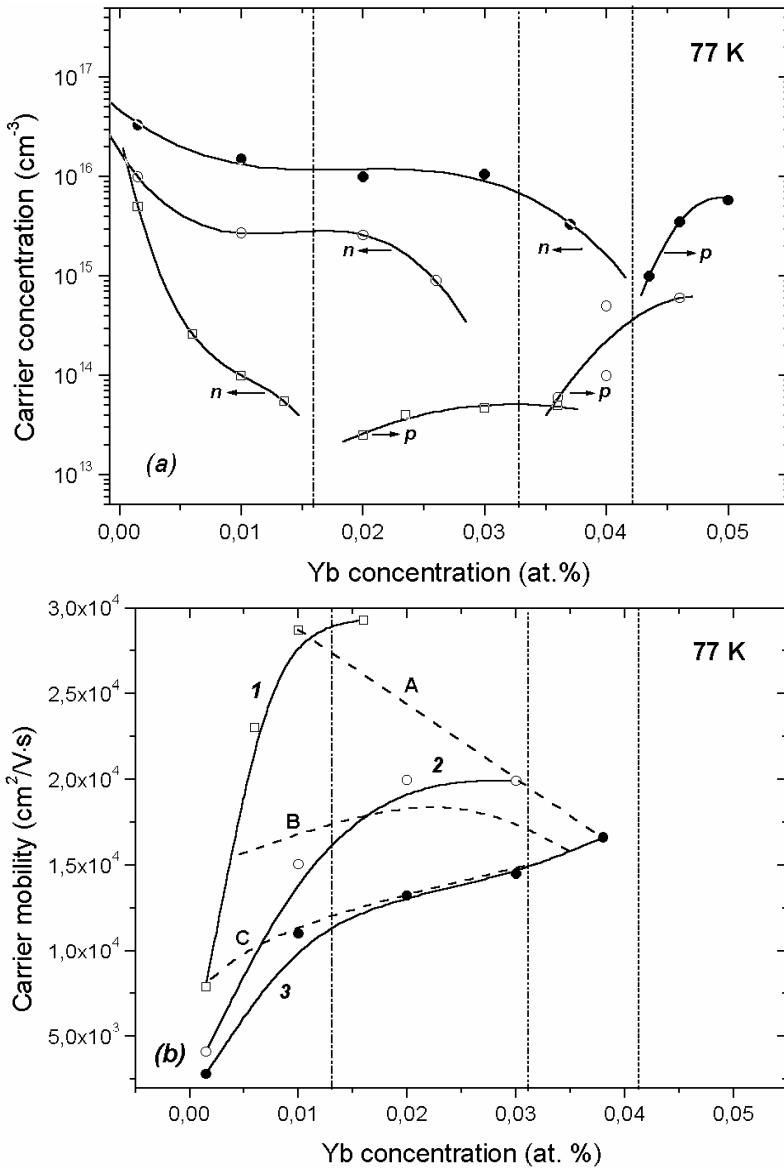


Fig. 2: Dependence of free charge carrier concentration (a) and mobility (b) for GaAs epitaxial layers on Yb impurity concentration in gallium solution-melt for different contents of additional Al impurity: (1) no impurity, (2) 10⁻⁴ at.%, and (3) 5·10⁻⁴ at.%. Dashed curves in (b) correspond to isoconcentration lines of mobility for free charge carrier concentration (A) 10¹⁴ cm⁻³, (B) 10¹⁵ cm⁻³, and (C) 2·10¹⁵ cm⁻³.

Discussion

The results presented above show that successful control of free charge carrier concentration in epitaxial layers as well as in microcrystals of the studied semiconductors and obtaining of materials with predefined parameters are possible by means of optimum combinations of

specially selected impurities. The contents of a doping combination depend on the problem at hand. For example, if GaAs epitaxial layers with free charge carrier concentration $1 \cdot 10^{15} \text{ cm}^{-3}$ and maximum mobility are required, then it is rational to use combination of Yb and Al dopants with the contents of $2.3 \cdot 10^{-2}$ and $1 \cdot 10^{-4}$ at.%, respectively. If charge carrier concentration is to be equal to $1 \cdot 10^{14} \text{ cm}^{-3}$ at the maximum mobility condition, then the contents of these impurities should be $1.1 \cdot 10^{-2}$ at.% Yb and $5 \cdot 10^{-4}$ at.% Al. This is confirmed by the isoconcentration curves (Fig. 2b) of electron mobility in GaAs epitaxial layers obtained by complex doping with Yb and Al impurities.

The use of aluminum in technological growth processes of the studied materials allows to increase charge carrier mobility not only as the additional dopant for the growth of GaAs epitaxial layers, but also for InSb microcrystals. This is shown in Fig. 3, which presents the concentration dependence of electron mobility in InSb microcrystals obtained at various combinations of doping impurities. Despite a considerable spread in the experimental data, it is clear that introduction of aluminum impurity to the vapor phase of InSb microcrystals for the growth increases their electron mobility, especially in the range of charge carrier concentrations below 10^{18} cm^{-3} . The simplest description for this conclusion might be additional purification of InSb microcrystals from uncontrolled background impurities during growth by means of aluminum.

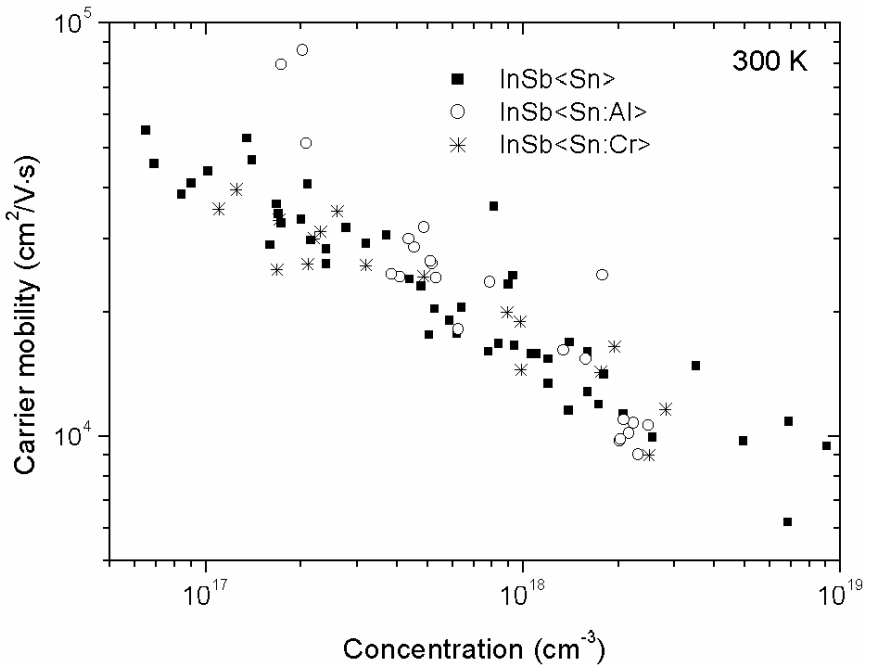


Fig. 3: Concentration dependence of free electron mobility for InSb microcrystals for different doping combinations

As shown in Fig. 3, unlike aluminum chromium impurity does not lead to an increase in the electron mobility by the doping of InSb microcrystals. However, sensitive elements of Hall sensors of magnetic field, produced from InSb microcrystals grown under the complex influence of Sn and Cr dopants, are featured with the highest radiation hardness under the fast neutron irradiation among all tested sensors. Experiments performed for such Hall

elements with charge carrier concentration within the range of $(1-3) \cdot 10^{18} \text{ cm}^{-3}$ showed that concentration changes under fast neutron irradiation with doses up to 10^{15} n/cm^2 do not exceed 0.04% of the initial value.

The technology for obtaining microcrystals and thin films of the studied materials with required parameters, described here, also provides high long-term stability of these parameters. This was confirmed by experimental measurements carried out within 6 months for the samples obtained with different combinations of doping impurities. Time stability of carrier concentration for several samples with different doping combinations is presented in Fig. 4. As may be seen from the figure, within the limits of the 0.1% experimental errors, no changes are observed in the free charge carrier concentration in the studied samples.

These results presented here lead to the general conclusion that the developed technology for the growth of III-V microcrystals and epitaxial layers under the influence of different doping combinations allows to obtain high-stable materials for sensitive elements of magnetic field sensors to be operated under hard radiation exposure with fast neutrons.

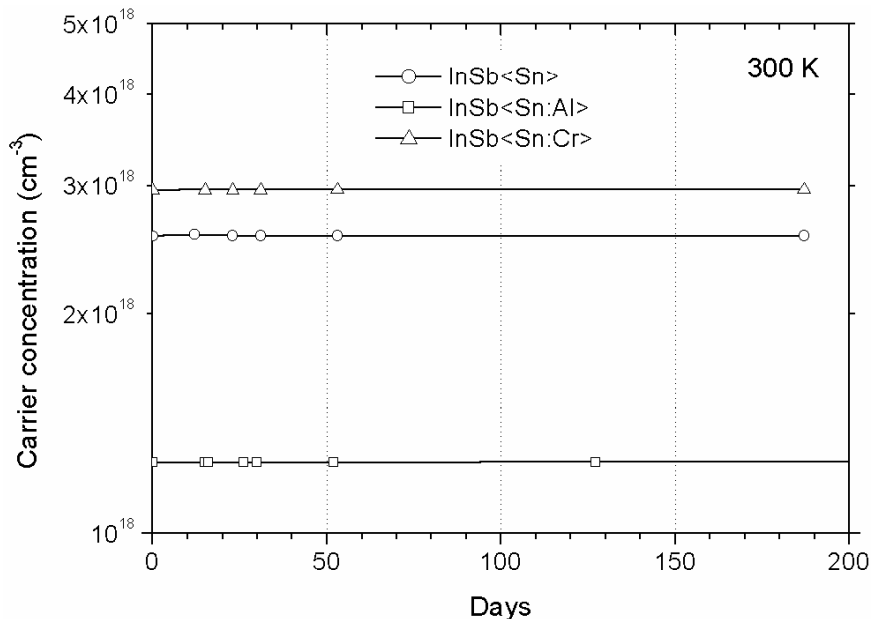


Fig. 4. Time dependence of free charge carrier concentration of complex-doped InSb microcrystals after irradiation with fast neutron dose of $10^{15} \text{ n}\cdot\text{cm}^{-2}$ with average energy of 1.35 MeV. Zero of abscissa axis corresponds to 10-th day after irradiation (after the induced radioactivity is lost).

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