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ELECTRONIC PROPERTIES
OF SEMICONDUCTORS

On the Electronic Properties of GaSb Irradiated with Reactor Neutrons and its Charge Neutrality Level

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Abstract—The electronic properties and the limiting position of the Fermi level in *p*-GaSb crystals irradiated with full-spectrum reactor neutrons at up to a fluence of 8.6×10^{18} cm^{-2} are studied. It is shown that the irradiation of GaSb with reactor neutrons results in an increase in the concentration of free holes to $p_{\rm lim} = (5–6) \times 10^{18}$ cm^{-3} and in pinning of the Fermi level at the limiting position $F_{\rm lim}$ close to $E_V + 0.02$ eV at 300 K. The effect of the annealing of radiation defects in the temperature range 100–550°C is explored.

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1. INTRODUCTION

It is known that nominally undoped GaSb crystals, even when grown from melt enriched with Ga, are always of the *p*-type, with a hole concentration of $p \approx 5 \times 10^{15}–10^{17}$ cm^{-3}. Therefore, to produce GaSb material of the *n*-type, it is necessary to carry out overcompensation of the material with donor impurities during growth or to conduct the postgrowth diffusion of such impurities. Previously [1, 2], it was shown that irradiation with electrons or protons transformed *n*-GaSb into the *p*-type material and, in lightly doped *p*-GaSb, the concentration of free holes increased. Such features of GaSb are attributed to the predominant formation of acceptor-type defects, supposedly Ga vacancies ($V_{\rm Ga}$) and antisite defects typical of compositionally complex semiconductors, during growth of the material and upon exposure of the material to high-energy radiation.

The specifics of the electronic properties of as-grown and irradiated GaSb compared to other III–V semiconductor compounds is attributed to the low position of the charge neutrality level (CNL) in the band gap of this semiconductor. It should be noted that much attention is given to estimations of the CNL energy position in semiconductors, since this level not only defines the electronic properties of highly imperfect materials, but controls to a large extent the surface properties and the energy diagrams of interfaces in semiconductor materials as well. At the same time, experimentally, the CNL position can be most accurately determined by studying the electronic properties upon exposure of the semiconductor material to high-energy radiation. Under conditions of high-dose irradiation, the electronic properties of a semiconductor are controlled by radiation defects introduced upon irradiation, and the Fermi level of the crystal reaches the so-called limiting position ($F_{\rm lim}$) which is identified to the CNL of the semiconductor [3]. To date, the exact position of the CNL in GaSb has not been adequately studied.

2. EXPERIMENTAL

2.1. Irradiation

In this study, we explore the electronic properties of *p*-GaSb crystals ($p \approx (5–6) \times 10^{16}$ cm^{-3}) grown by the Czochralski method and irradiated with full-spectrum neutrons in the vertical channel of the VVR reactor (Karpov Institute of Physical Chemistry, Obninsk, Russia) at temperatures ≤70°C. The flux density of thermal neutrons (with an energy of $E < 0.1$ MeV) in the irradiation zone reached 5×10^{13} cm^{-2} s^{-1}, and the relation between the densities of fast ($E \geq 0.1$ MeV) and thermal neutrons in the flux was close to unity. In what follows, the neutron fluence is given in reference to the total integrated flux of reactor neutrons.

The changes induced in the electronic properties of the *p*-GaSb crystals by irradiation with full-spectrum reactor neutrons are illustrated in Fig. 1. Upon irradiation of the initial *p*-GaSb samples ($p = (5–6) \times 10^{16}$ cm^{-3}), we observe a slight change in the resistivity (ρ) and a decrease in the mobility of free holes (μ_h) to 10–15 cm^2 V^{-1} s^{-1} at 300 K, with an increase in the concentration of free holes to $(5–6) \times 10^{18}$ cm^{-3}, as the integrated neutron flux is increased to 8.6×10^{18} cm^{-2}. The experimental data shown in Fig. 1 are obtained by averaging the corresponding values of the electrical parameters for three samples.

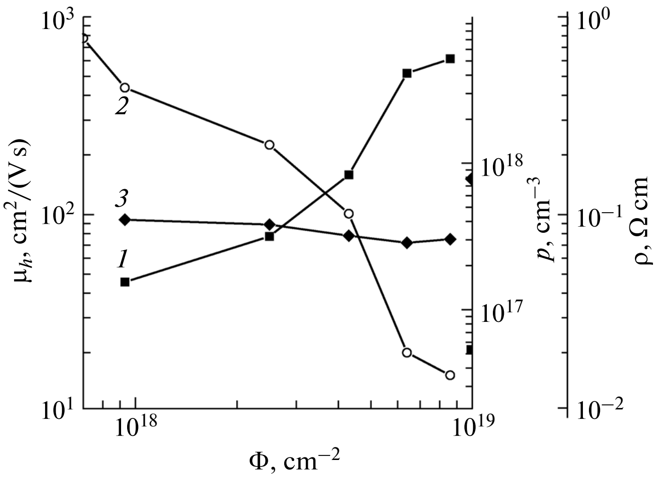

Fig. 1. Dependences of (*1*) the concentration p, (*2*) the mobility of free holes μ_h, and (*3*) the resistivity ρ of the p-GaSb crystals (with the initial concentration $p = (5–6) \times 10^{16}$ cm^{-3}) on the fluence of reactor neutrons Φ. The measurement temperature is $T = 300$ K.

From the data presented above, it follows that the limiting position of the Fermi level F_{lim} in p-GaSb can be estimated as being on the level of $E_V + 0.01$ eV at 300 K, where the energy E_V corresponds to the top of the valence band. To date, the parameter F_{lim} has been experimentally studied also for n- and p-GaSb crystals irradiated with protons (with an energy of $E = 5$ MeV and fluence of $\Phi = 1.7 \times 10^{16}$ cm^{-2}) [1] and electrons ($E = 2$ MeV and $\Phi = 1 \times 10^{19}$ cm^{-2}) [2]; the experimentally determined values of F_{lim} are listed in the table. With consideration for the data obtained in this study, we can estimate the average value of F_{lim} in the GaSb compound irradiated with electrons, protons, and neutrons at a level of $E_V + (0.02 \pm 0.01)$ eV at 300 K.

The CNL plays an important role in determining not only the electronic properties of a semiconductor, both as-grown and irradiated with high-energy particles, but also the energy diagrams of the interphase boundaries in semiconductors. For this reason, the CNL position is sometimes estimated from the studies of interfaces. The corresponding results for the CNL position estimated from the offsets of the energy bands of semiconductor heteropairs [4] and from the heights of Schottky barriers [5, 6] involving GaSb are given in the table. As can be seen from the table, the CNL positions estimated from the studies of interfaces are considerably spread in energy and substantially differ from the experimental data on F_{lim} for the irradiated GaSb samples. This is a consequence of the complexity and, hence, the inaccuracy of estimations of the CNL energy position from studies of GaSb-involving interphase boundaries, as compared to estimations for the bulk material irradiated with high-energy particles.

The results of theoretical calculations [7–10] of the CNL position in GaSb in different studies performed to date within the context of different analytical models are also given in the table. The estimates show that, in the GaSb compound, the CNL is in the lower part of the band gap, near the level Γ_{8V}, and the averaged CNL position calculated from the data of the table is estimated at $E_V + (0.01 \pm 0.05)$ eV. Thus, the calculated CNL positions and the experimentally determined quantities F_{lim} are rather close, suggesting that the CNL is close to the top of the valence band of the GaSb compound.

2.2. Annealing

The curves of isochronous annealing for the concentration and Hall mobility of free holes in the p-GaSb samples irradiated with reactor neutrons are plotted in Figs. 2 and 3, respectively. In the dependences of the concentration on annealing temperature, $p(T_{\text{ann}})$, for the samples moderately irradiated with reactor neutrons, we distinguish the stage of the gradual annealing of acceptor defects in the temperature range 100–350°C and the stage of "reverse" annealing in the temperature range 350–400°C, with the further annealing of acceptor defects at temperatures above 400°C (Fig. 2). The stage of "reverse" annealing of the free-hole concentration can be associated with the disappearance of donor defects, whose energy levels are above the Fermi level. In samples highly irradiated with neutrons, the stage of "reverse" annealing is unobservable in the curves $p(T_{\text{ann}})$, and the concentration of holes decreases upon annealing in a wide temperature range from 100 to 500°C.

The recovery of the Hall mobility of free holes in the p-GaSb samples irradiated with different integrated fluxes of reactor neutrons also occurs in a wide range of annealing temperatures from 100 to 400°C. The main stage of recovery of μ_h corresponds to the temperature range 250–400°C (Fig. 3), which is coincident with the range of the main stage of the annealing of acceptor and donor defects (Fig. 2).

CNL energy position estimated for GaSb from measurements of F_{lim} [1, 2], studies of interfaces [4–6], and calculations [7–10]. (The CNL position (eV) is reckoned from the top of the valence band)

Reference (year)	[1] (1988)	[2] (1991)	[4] (1997)	[5] (1996)	[6] (2006)	[7] (1986)	[8] (1995)	[9] (1998)	[10] (1998)
CNL	0.02	0.03	–0.28	0.16	0.14	0.07	0.00	–0.07	0.05

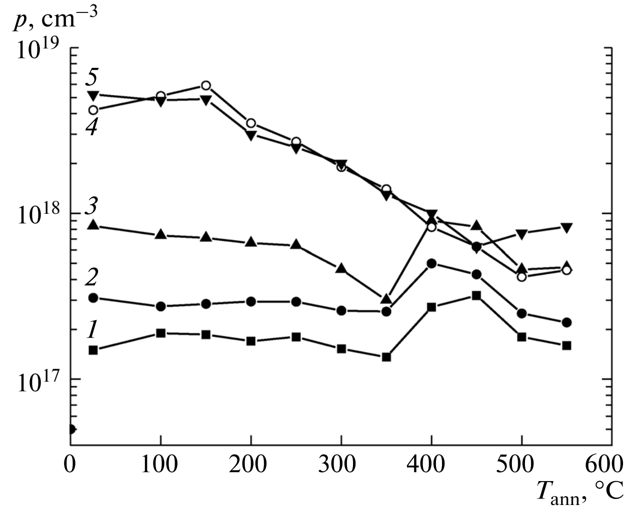

Fig. 2. Dependences of the concentration of free holes p on the temperature of isochronous annealing T_{ann} (the annealing time $\Delta t = 20$ min) for the p-GaSb crystals (with the initial concentration $p = (5–6) \times 10^{16}$ cm^{-3}) irradiated with different fluences of reactor neutrons Φ. Φ = (*1*) 9.3×10^{17}, (*2*) 2.15×10^{18}, (*3*) 4.3×10^{18}, (*4*) 6.4×10^{18}, and (*5*) 8.6×10^{18} cm^{-2}.

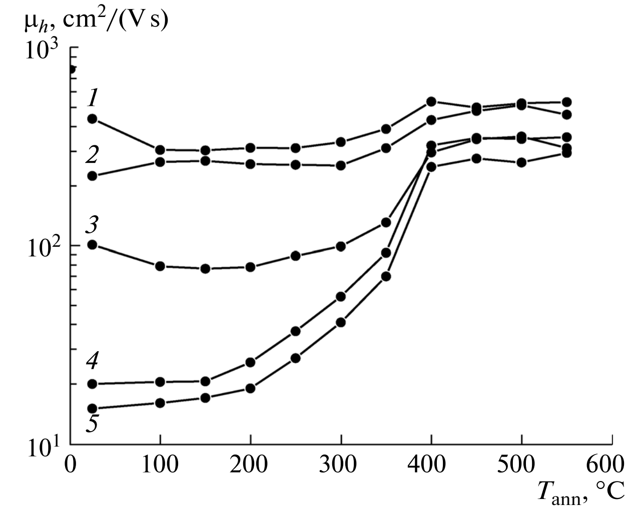

Fig. 3. Dependences of the mobility of free holes μ_h on the temperature of isochronous annealing T_{ann} (the annealing time $\Delta t = 20$ min) for the p-GaSb crystals (with the initial concentration $p = (5–6) \times 10^{16}$ cm^{-3}) irradiated with different fluences of reactor neutrons Φ. Φ = (*1*) 9.3×10^{17}, (*2*) 2.15×10^{18}, (*3*) 4.3×10^{18}, (*4*) 6.4×10^{18}, and (*5*) 8.6×10^{18} cm^{-2}.

The residual values of parameters p and μ_h of the material annealed at 550°C are several times larger than the corresponding initial values determined before irradiation and are larger at higher irradiation doses. This suggests that, after annealing at temperatures up to 550°C, the fraction of residual radiation defects is still rather high. In addition, studying the annealing of radiation defects in GaSb crystals at high temperatures of heating is complicated by the effect of thermally stimulated transmutation doping of the material and by the partial activation of Se and Te donor impurities formed in GaSb during nuclear reactions with the participation of thermal neutrons [11, 12].

3. DISCUSSION

As in other semiconductors, in p-GaSb when irradiated with reactor neutrons, radiation defects of the donor or acceptor types are introduced. As a result, the Fermi level is shifted from its initial position, defined by the level of doping with chemical impurities, towards the valence band of the compound and subsequently stabilized near the level Γ_{8V}. The average energy position of the level F_{lim} estimated from experimental data on the electronic properties of GaSb crystals irradiated with protons ($E = 5$ MeV, $\Phi = 1.7 \times 10^{16}$ cm^{-2}) [1], electrons ($E = 2$ MeV, $\Phi = 1 \times 10^{19}$ cm^{-2}) [2], and reactor neutrons ($\Phi = 8.6 \times 10^{18}$ cm^{-2}) corresponds to $E_V + (0.02 \pm 0.01)$ eV, which is rather close to the averaged result of theoretical estimations of this parameter, $E_V + (0.01 \pm 0.05)$ eV (see table).

Thus, according to experimental studies of the electronic properties of irradiated GaSb crystals and to the results of calculations, the CNL ($\equiv F_{lim}$) is actually located near the top of the valence band of GaSb. This feature makes GaSb substantially different from other III–V semiconductors (arsenides, phosphides, nitrides): as follows from the experimental data and the results of calculations, the CNL in these semiconductors is located in the band gap (GaAs, AlAs, GaP, GaN, etc.) or in the region of allowed energies of the conduction band (InAs, InN) [8, 10, 13].

It should be noted that location of the CNL in the lower part of the band gap is a characteristic feature of semiconductor compounds based on “heavy” antimony (AlSb, GaSb, and InSb) and is defined by considerable spin–orbit splitting Δ_{SO} of the valence bands of these compounds (0.67 eV for AlSb, 0.67 eV for GaSb, and 0.85 eV for InSb). This feature of the energy spectra of III–Sb semiconductor compounds is responsible for “narrowing” of their minimum band gap by ~ $\Delta_{SO}/3$ because of the shift of the Γ_{8V} level towards the bottom of the conduction band and, as a result, for the highly asymmetric position of the CNL with respect to the edges of the minimum band gap of these semiconductors.

4. CONCLUSIONS

The CNL position near the top of the valence band defines the shift of the Fermi level towards the level Γ_{8V} upon the accumulation of intrinsic lattice defects during the growth of GaSb and upon high-energy irradiation of the initial material. This feature is responsible for *p*-type conductivity in both as-grown GaSb and GaSb irradiated with high-energy electrons, protons, and neutrons. In addition, it is worth noting that the "low" CNL position in the energy spectrum of this compound controls the electronic properties of its surface and the small height of the energy barrier for holes in metal/GaSb structures.

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REFERENCES

1. V. N. Brudnyi and I. V. Kamenskaya, Phys. Status Solidi A **105**, K141 (1988).
2. I. V. Kamenskaya, Extended Abstract of Cand. Sci. Dissertation (Tomsk. State Univ., Tomsk, 2007).
3. V. N. Brudnyi, Extended Abstract of Doctoral Dissertation (Tomsk. State Univ., Tomsk, 1993).
4. C. G. van de Walle, and J. Neugebauer, Appl. Phys. Lett. **70**, 2577 (1997).
5. W. Monch, J. Appl. Phys. **80**, 5076 (1996).
6. J. Robertson and B. Falabretti, J. Appl. Phys. **100**, 014111 (2006).
7. J. Tersoff, J. Vac. Sci. Technol. B **4**, 1066 (1986).
8. V. N. Brudnyi, S. N. Grinyaev, and V. E. Stepanov, Phys. B **212**, 429 (1995).
9. S. H. Wei and A. Zunger, Appl, Phys. Lett. **72**, 2011 (1998).
10. V. N. Brudnyi and S. N. Grinyaev, Semiconductors **32**, 315 (1998).
11. N. G. Kolin, D. I. Mercurisov, and S. P. Solov'ev, Phys. B **307**, 258 (2001).
12. N. G. Kolin, Russ. Phys. J. **46**, 543 (2003).
13. W. Walukiewicz, Phys. B **302–303**, 123 (2001).

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