INVESTIGATION OF FORMATION AND ANNEALING OF RADIATION DEFECTS IN III-V SEMICONDUCTORS UNDER ELECTRON IRRADIATION

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Effects of high-energy electron irradiation upon electrical and optical properties of InAs, InP, GaP crystals are discussed. Primary radiation defects in III-V semiconductors are shown to be mobile, in GaP being partly annealed even below room temperature. The role of dopants in the formation of complex radiation defects in III-V crystals is considered.

Introduction

III-V semiconductors, along with silicon and germanium, are the key materials for modern electronics, being the base for a variety of electronic devices. The improvement of their operating characteristics is closely related to the studies of various structural defects, essentially affecting the semiconductor properties. High-energy particle irradiation enabling wide controllable variation of concentration, type and spatial distribution of radiation defects (RDs) is one of the most convenient techniques for modelling physical processes in disordered systems.

Primary RDs in solids are known to be formed by crystal lattice atom displacements due to the energy being transferred to them from the bombarding particles [1]. The most probable mechanism of the energy transfer is elastic scattering. Under bombardment by low-energy particles (electrons, γ-quanta) mostly simple point defects are formed, while at irradiation with α-particles, protons, neutrons, high-energy electrons, displacement cascades can lead to more complex cluster-type defects. In this case the properties of semiconductors with point and cluster defects are essentially different [2]. From this point of view the use of M-30 microtron for formation of RDs in semiconductors seems attractive providing the opportunity to introduce both simple point defects under irradiation with 1–2-MeV electrons and clusters at irradiation with 15–30 MeV. Our first pilot irradiation sessions with the flux of 10^{12}–10^{13} electrons$\times$cm$^{-2}\times$s^{-1} have shown the samples to be heated to 200°C. In order to avoid this and to enable the low-temperature irradiation for studying the primary RDs evolution, a setup enabling the given sample temperature to be kept automatically within 78–400 K range, was elaborated. The sample temperature is provided by nitrogen vapour whose temperature being stabilized by a VRT-3 based system.

Irradiation effects on electrical properties

The changes in the physical properties of crystals irradiated at certain conditions, is closely related to the type of RDs being stable at these conditions. Primary RDs in III-V semiconductors are much more stable than those in silicon and germanium where they are mobile and are partly annealed already at liquid helium temperatures [3]. In InAs the primary RDs, introduced by low-temperature irradiation, start annealing above 200 K, and in GaAs and GaP – even above room temperature. The RD stability and electrical properties of *n*- and *p*-type InP crystals irradiated with 1–14-MeV electrons at 77 and 300 K and subsequent annealing are studied in [4]. Irradiation at 77 K was shown to result in the formation of RDs, about 90 % of which are annealed below room temperature, what essentially distinguishes InP from GaAs, where intrinsic RDs are stable at room temperature. Thus, the room-temperature irradiation-induced changes in InP properties are determined by more complex types of defects. The plots for charge-carrier concentration and mobility of *n*- and *p*-type InP on the fluence Φ of 14-MeV electrons are shown in Fig.1. In *n*-InP the concentration of electrons at first decreases, and at $\Phi > 10^{18}$ cm^{-2} reaches the limiting level of $n = (2.5 \div 4) \times 10^{12}$ cm^{-3}, corresponding to the limiting position of the Fermi level $E_F = E_i + 0.35$ eV, being onwards unchanged in the whole range of fluences under investigation. These limiting values have appeared to be independent either of the initial values of concentration of free electrons, or of the dopant type. In *p*-InP a *p*-*n*-conversion is observed with subsequent increase of *n* to the limiting value slightly below than that of *n*-InP. Such $n(\Phi)$ dependence is determined by irradiation-induced formation of two donor centres with energies $E_{d1} = E_c$ - 0.2 eV and $E_{d2} = E_c$ - 0.4 eV and compensating acceptor centres. Note that the E_{d1} centre recharging while being crossed with the Fermi level at its shift under irradiation the charge-carrier scattering mechanism is changed, resulting in the non-monotonous dependence of mobility on the irradiation dose (Fig. 1).

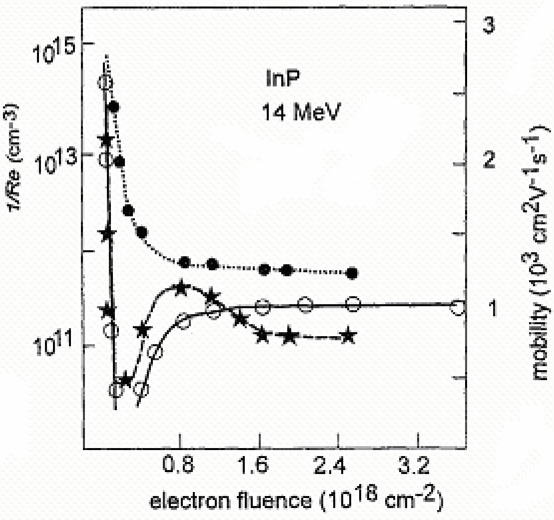

Fig.1. Concentration (circles) and mobility (stars) of charge-carriers in *n*- (dark symbols) and *p*-type (open symbols) InP crystals vs the fluence of 14-MeV electrons at 300K.

The initial carrier removal rate with Φ, being the measure of the defect formation rate, increases from 0.1 cm^{-1} at $E_e = 1$ MeV to 1.5 cm^{-1} at $E_e = 14$ MeV. Simultaneously, the calculation of the displaced atoms number has shown it to increase not more than twice. This discrepancy can be explained only by formation of thermally more stable defect complexes at higher electron energies. ESR and positron annihilation studies have shown that in irradiated InP crystals RD complexes, containing dopants, are formed [5, 6] .

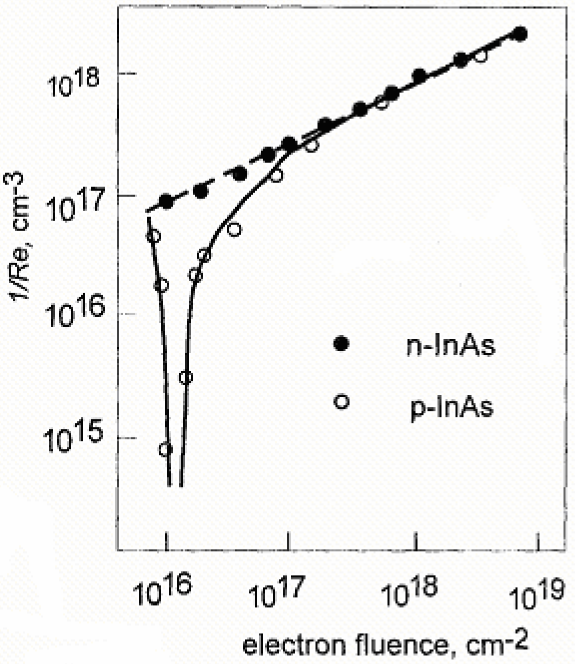

Fig. 2. Charge-carrier concentration in 10-MeV electron-irradiated at 300 K *n*- and *p*-InAs vs the electron fluence

Another character of charge-carrier concentration with irradiation is observed in InAs crystals (Fig. 2). In InAs *n* increases proportionally to $\Phi^{0.7}$ in the whole fluence range under investigation. The temperature behaviour of the irradiated InAs has shown the increase of *n* with irradiation is caused by the formation of shallow donor levels which at $\Phi > 10^{17}$ cm^{-2} form an impurity band overlapping with the conduction band bottom, resulting in metallic conductivity type (*n* being independent of Φ). Shallow donor level formation is also observed in *n*-InAs heavily doped with Sn, Te, as well as in *p*-InAs, leading to *p*-*n* conversion with subsequent *n* variation with dose like in *n*-type material. The obtained result is in qualitative agreement with those of [7, 8] where 2-MeV electron irradiation effect upon InAs crystals is studied. Taking into account that primary RDs in InAs are stable up to 165 K [9], $n(\Phi)$ dependence was studied with electron energy variation for lower temperatures. The corresponding results are shown in Fig. 3 where in the inset the experimental and calculated (normalized per the experimental value at the energy of 1 MeV) carrier introduction rates are shown. Nonlinear $n(\Phi)$ dependence as well as the discrepancy between the experimental and calculated carrier introduction rates give the evidence of primary RDs being mobile in InAs at 77 K, the change of its electrophysical properties being determined by defect complexes. This is also confirmed by the studies of low-temperature irradiation and annealing of heavily doped *n*-InAs:Sn [10].

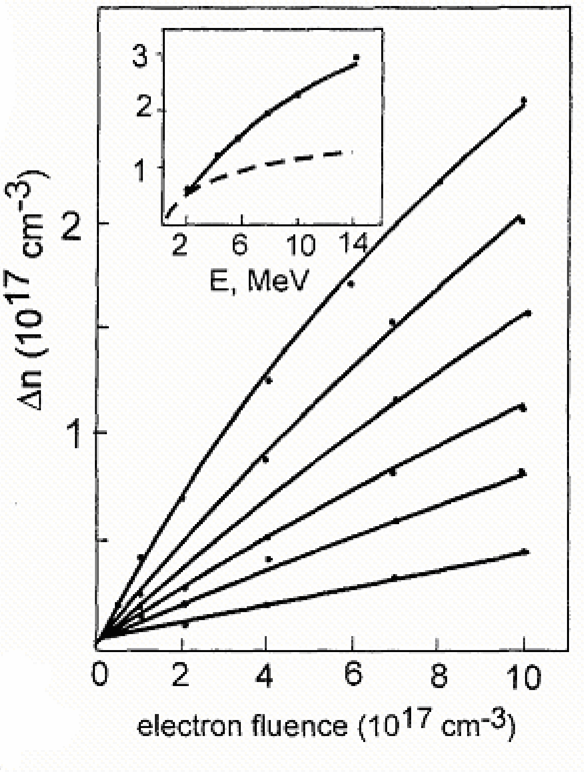

Fig. 3. Charge-carrier concentration vs irradiating electron fluence for undoped InAs irradiated at 77 K with electron energies 2.0 (1), 4.5 (2), 6.0 (3), 7.8 (4), 10.0 (5), 14.5 (6) MeV. The inset shows the calculated and experimental dependences of charge-carrier introduction rate on the electron energy.

Effect of irradiation upon optical properties

Irradiation of semiconductors, as a rule, results in a considerable decrease of charge-carrier mobility caused by additional scattering by the RDs, its mechanism determination encountering certain difficulties. Additional information can be taken from light absorption by free charge-carriers in the infrared spectral range, characterized by a monotonous featurell spectrum of $\alpha \sim \nu^{-r}$ form where the power index depends on the scattering mechanism. The free charge-carrier absorption spectra at room temperature of 10-MeV electron-irradiated undoped and Sn-doped InAs crystals are shown in Fig. 4. Simultaneously for these samples charge carrier concentration was measured and light absorption cross-section $\sigma = \alpha/n$ was determined. The analysis of the presented data shows the power index r to decrease and the absorption cross-section to increase with irradiation, this enabling a conclusion to be made on a mechanism of "inelastic" scattering on the whole defect system appearing in irradiated InAs [11].

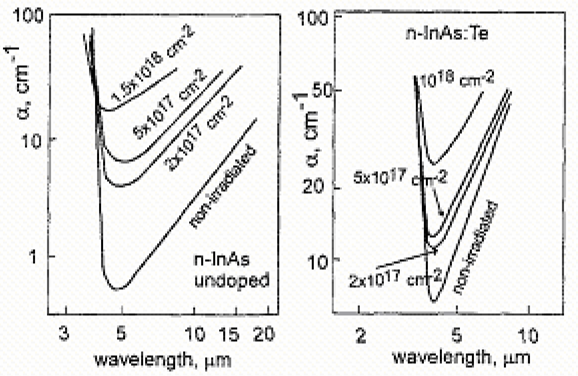

Fig. 4. Free-carrier optical absorption spectra of 10-MeV electron-irradiated InAs crystals.

Essential irradiation-induced changes are observed in the edge and near-edge range of optical absorption spectra. As a rule, irradiation results in strong additional absorption in the near-edge range due to the formation of density-of-states tails, described by Urbach rule. Radiation-induced density-of states tails can be formed by both RD levels and fluctuation levels due to local band deformations by large-scale Coulomb potentials of charged RD clusters or at high compensation of conductivity by charged donors and acceptors.

The effect of room-temperature electron irradiation upon the near-edge absorption of undoped [12] and Te-doped [13] GaP, in both cases similar behaviour of the spectra being observed (See Fig. 5).

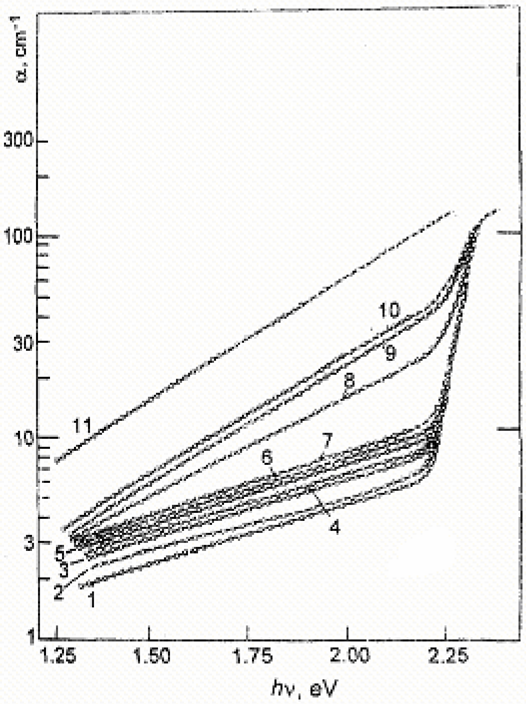

Fig. 5. Optical absorption spectra of non-irradiated (1) and irradiated with 4.5-MeV electrons GaP:Te crystals. $\Phi = 5\times10^{15}$ (2), 10^{16} (3), 2×10^{16} (4), 3×10^{16} (5), 5×10^{16} (6), 10^{17} (7), 3×10^{17} (8), 5×10^{17} (9), 7×10^{17} (10), 10^{18} (11) cm^{-2}.

In the non-irradiated samples the absorption edge is seen to be formed by two parts, the first of them, related to indirect optical transitions, being described by

$$\alpha h\nu = B(\alpha h\nu - E_o)^2 \quad , \qquad (1)$$

E_0 being the energy gap, B – a constant, and the second one – by

$$\alpha = \alpha_o(h\nu - E_o)/E_e \quad , \qquad (2)$$

E_e being the characteristic energy.

With Φ increase E_e and B decrease nonlinearly, therefore at $\Phi > 10^{17}$ cm^{-2} the edge part, corresponding to ihe indirect transitions, is not observed, and considerable additional absorption in the whole near-edge range is described by Eq. (2). The absorption spectra recover at annealing to 500°C.

Doping with Zn or S results in new absorption bands in the range 1.75–2.3 eV, increasing with Φ, and evidently related to the processes of photoionization of RD complexes with dopants [14]. The studies of irradiation effect upon GaP:Fe also indicate involving of Fe atoms into RD formation process [15].

Near-edge absorption behaviour at low-temperature (77 K) irradiation with 4.5- and 14.5-MeV electrons of undoped and Te-, S- and Zn-doped GaP crystals was studied in [16, 17]. Isochronal annealing of optical absorption in GaP:Te irradiated at 77 K revealed three stages below 300 K where the sample transmittance practically recovers. The obtained results prove the mobility of RDs introduced into GaP by low-temperature irradiation.

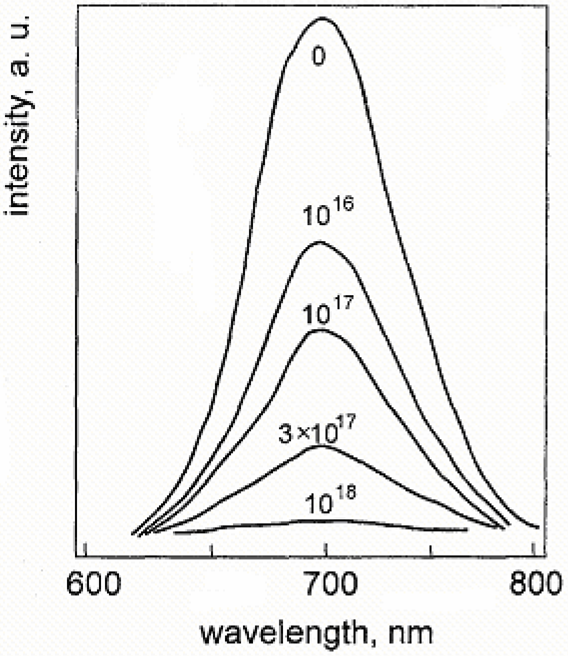

Fig. 6. "Red" photoluminescence of GaP:S quenching under irradiation of 10-MeV electrons, the fluence values in cm^{-2} being indicated near the corresponding curves.

In Raman spectra of GaP crystals, irradiated with 7-MeV electrons, at $\Phi > 10^{18}$ cm^{-2}, besides the known LO and TO phonon bands, we observed much weaker broad bands centered at 100 and 220 cm^{-1}, coinciding with the phonon density-of-states maxima and corresponding to the disorder-activated first-order Raman scattering by acoustic phonons due to the selection rules breakdown [18].

Photoluminescence (PL) studies of S- and Te-doped GaP crystals have revealed 10-MeV electron irradiation to result in much faster quenching of the "red" PL band (700 nm) due to donor-acceptor pairs with Φ than that of the "green" one (570 nm) due to bound excitons recombination (Fig. 6). Comparison of these results with those of other authors [19, 20] and the analysis of the discrepancies enabled us to assume the luminescence quenching under 10-MeV electron irradiation is related rather to complex RD formation involving S or Te donors than to radiation-induced centres of non-radiative recombination. This conclusion is confirmed by low-temperature annealing studies of optical absorption in electron-irradiated GaP where the RD mobility below room temperature is shown [16, 17].

Conclusions

Summarizing the performed results, the foolowing features of RDs behaviour in III-V semiconductors can be pointed out:

- primary RDs in III-V crystals are much more mobile than it had been considered earlier [2], in GaP they are partly annealed even below room temperature;
- radiation-induced changes in electrical and optical properties of III-V crystals are determined mostly by RD complexes being formed at low energies (1–3 MeV) due to the primary RD mobility, and at higher energies – also by secondary displacement cascades;
- dopants usually are involved into the RD complexes.

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ДОСЛІДЖЕННЯ УТВОРЕННЯ Й ВІДПАЛУ РАДІАЦІЙНИХ ДЕФЕКТІВ У НАПІВПРОВІДНИКАХ A^3B^5 ПРИ ОПРОМІНЕННІ ЕЛЕКТРОНАМИ

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Обговорюється вплив опромінення високоенергетичними електронами на електричні й оптичні властивості кристалів InAs, InP, GaP. Показано, що первинні радіаційні дефекти в напрівпровідниках групи A^3B^5 рухливі, а в GaP частково відпалюються навіть при температурах, нижчих за кімнатну. Розглядається роль домішок в утворенні складних радіаційних дефектів у кристалах групи A^3B^5.