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Transport and generation–recombination mechanisms of nonequilibrium charge carriers in ZnO/In_2O_3/InSe:Cd heterojunctions

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ABSTRACT

Current–voltage characteristics, spectral characteristics of short-circuit photocurrent and charge generation–recombination kinetics in InSe layer from the contact region of ZnO:Al/In_2O_3/InSe:Cd heterojunctions are investigated. The structures show photosensitivity in the photon energy range 0.96–3.30 eV. The photosensitivity in the low energy range is determined by absorption threshold of InSe:Cd, while in higher energy range, the optical transparency region of ZnO film prevails. For doping levels of 0.5–1.0 at.%, the ratio of the ambipolar diffusion coefficient and the recombination rate at the InSe surface is decreasing from 1.8 to 0.9 μm.

1. Introduction

In recent years, III–VI layered semiconductors, a typical representative of which is InSe, have attracted considerable attention, due to their specific features: enhanced anisotropy of mechanical, electric and optical properties, strong excitonic emission, and large optical nonlinearity [1]. Because of weak bonding (of Van der Waals type) between stratified packages, facile crystal cleavage in plan-parallel plates, atomically smooth and optically homogeneous is enabled.

With a band gap of 1.3 eV, InSe is a promising candidate for solar cell technology [2–4]. This applicative direction is also stimulated by the fact that, by thermal treatment in normal open-air atmosphere, a native oxide (In_2O_3) film, with high electric conductivity and optical transparency, in the range of 300 to ~1300 nm, is formed on the surface of InSe lamellas [5]. As-obtained In_2O_3 film can serve as the window layer in InSe-based photovoltaic cells [6–8].

Stoichiometric indium selenide crystals are *n*-type semiconductors, however, by doping with Sb, As, Zn and Cd, in concentrations of 0.05–0.50 at.%, their electric conductivity may be changed to *p*-type [9–12].

Weak bonding between stratified Se–In–In–Se packages, as well as the presence of practically compensated chalcogen valence bonds at the packages surface, enables low surface-state density, which determines the efficiency of minority charge carrier transport through junctions. Recent studies have demonstrated that during the In_2O_3 formation at the surface of *p*- or *n*-InSe, in the contact region of *p*-InSe/*n*-InSe heterojunctions, high surface-state densities occur. This results in a marked photocurrent diminution for the photon energy range 2.0–2.2 eV [6,8,13], which decreases quantum efficiency of *n*-In_2O_3/*p*-InSe based photovoltaic cells.

To diminish the influence of technological factors on InSe surface-state density, a thin ZnO:Al film may be placed in the contact region with In_2O_3 ($d<500$ Å) and used as the second heterojunction component.

2. Experimental details

n-InSe single crystals were grown by Bridgman method, from their chemically pure component elements, in stoichiometric proportions. The charge carrier concentration and mobility along the C_6 optical axis were $n=8\times10^{14}$ cm^3 and $\mu=(6\text{–}7)\times10^2$ $cm^2\,V^{-1}\,s^{-1}$, while the electric resistivity was $\rho=3.0\text{–}3.2$ Ω cm at $T=300$ K. In order to obtain *p*-InSe crystals, Cd doping (with concentrations of 0.1–1.0 at.%) of melt has been performed. From bulk *p*-InSe crystals with the resistivity of 1.25 Ω cm along the C_6 axis, plan-parallel plates of 10–20 μm in thickness and surface area of 0.4–0.6 cm^2 have been split, by cleavage perpendicular to the C_6 axis. Thin In films, vacuum thermally evaporated, were used as electrodes in electric measurements on InSe crystals.

Onto freshly cleaved surface of InSe:Cd (0.5 at.%) plates, with the thickness of 18–20 μm, In_2O_3 films have been grown by thermal treatment in normal open-air atmosphere at 450–460 °C, with durations of 0.10 h, 0.25 h and 0.35 h. Thickness of In_2O_3 films, determined by the ellipsometric method [14] was of 8, 21 and 56 nm, respectively. Afterwards, onto In_2O_3 film surface a Zn:Al film, 300–400 nm thick, was thermally vacuum evaporated from a Zn:Al (1.5 at.%) source. A thin In film ($d\approx500$ nm) was then deposited by the same method onto the outer surface of InSe:Cd. Thin Zn:Al and In films were also obtained under the same technological conditions,

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onto separate quartz substrates. Further, Zn:Al/In_2O_3/InSe:Cd/In, Zn:Al and In samples on SiO_2 substrates have been heat-treated, in open air, at 460 °C, for 1 h.

As a result of thermal treatment, ZnO:Al/In_2O_3/InSe:Cd/In structures, as well as ZnO:Al and In_2O_3 thin films, optically transparent in the visible region, have been obtained. By electric conductivity and Hall effect measurements, electron concentration and mobility in ZnO:Al films were found as 8×10^{19} cm^{-3} and 210 cm^2 V^{-1} s^{-1}. Optical transmittance of ZnO:Al and In_2O_3 films (at the wavelength of 400 nm, of 68% and 85%, respectively) was measured by a UV–Vis Cary 100 spectrophotometer (Varian Inc.), while that of InSe:Cd layers, with a FTIR JASCO 6300R spectrophotometer.

The spectral characteristics of photocurrent through Zn:Al/In_2O_3/InSe:Cd structures have been investigated with a spectrometric installation based on a MDR-2 type monochromator with 1200 and 600 mm^{-1} diffraction gratings, using a Xe-arc lamp of DKCS-250 type (120 W) as a light source. The energy of incident beam was measured with a Vth-1 type thermoelement with quartz window.

3. Results and discussions

Fig. 1 shows absorption spectra of single crystalline InSe, InSe:Cd (0.1 at.%) and InSe:Cd (0.5 at.%) layers. Fundamental absorption edge of InSe is determined by indirect optical transitions. The low intensity maximum at 1.30 eV (curve 1) is the result of direct, $n=1$ exciton absorption. Cd doping of InSe crystals (curves 2 and 3) leads to slight blue shift of the absorption edge, which was also found for other dopants: Er, Ho, and Sn [15–17]. Besides, doped InSe crystals display an attenuated absorption in the region of the excitonic band, as well as an increased absorption coefficient in the depth of the fundamental absorption band, with respect to undoped InSe. In the domain of band-to-band transitions ($h\nu \geq 1.30$ eV), the absorption coefficient increases monotonically up to 6×10^4 cm^{-1} at a photon energy of 2.70 eV. An increase of Cd concentration from 0.1 at.% to 0.5 at.% practically doesn't affect the structure of the absorption spectrum, in the energy range 0.90–2.70 eV.

Both undoped and Cd-doped InSe single crystals show high photosensitivity in the photon energy range between 1 and 4–5 eV [Fig. 2(a)]. The rapid increase of photosensitivity in the energy domain 0.95–1.25 eV is determined by the rise of the absorption coefficient in the vicinity of the fundamental absorption edge. Moreover, an overall photosensitivity increase actually takes place over the entire energy range examined, 1–5 eV.

The monotonic increase of the photosensitivity (photocurrent per absorbed photon) with absorption coefficient (Fig. 1, curve 1) indicates a low surface-state density of InSe samples. At the same time, photosensitivity of InSe:Cd (0.5 at.%) crystals [Fig. 2(a), curve 2] displays a slight diminution with increasing energy. This tendency is further amplified for higher doping levels, up to 1.0 at.% [Fig. 2(a), curve 3]. The photocurrent decrease with the increase of the absorption coefficient serves as a criterion for the existence of surface states, by means of which the nonequilibrium charge carriers intensely recombine. Therefore, one can admit that a part of dopant atoms is localized at the surface of stratified packages and may generate new chemical bonds between neighbor packages, as well as structural defects at the outer sample surface.

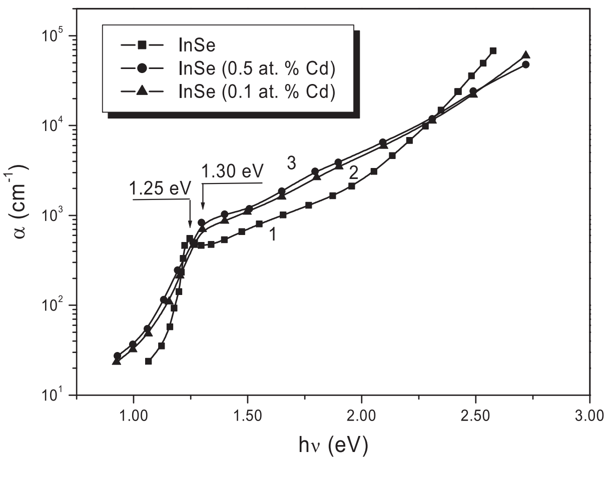

Fig. 1. Spectral distribution of the absorption coefficient for undoped (curve 1) and Cd-doped: 0.1 at.% (curve 2) and 0.5 at.% (curve 3) InSe films, at $T=293$ K.

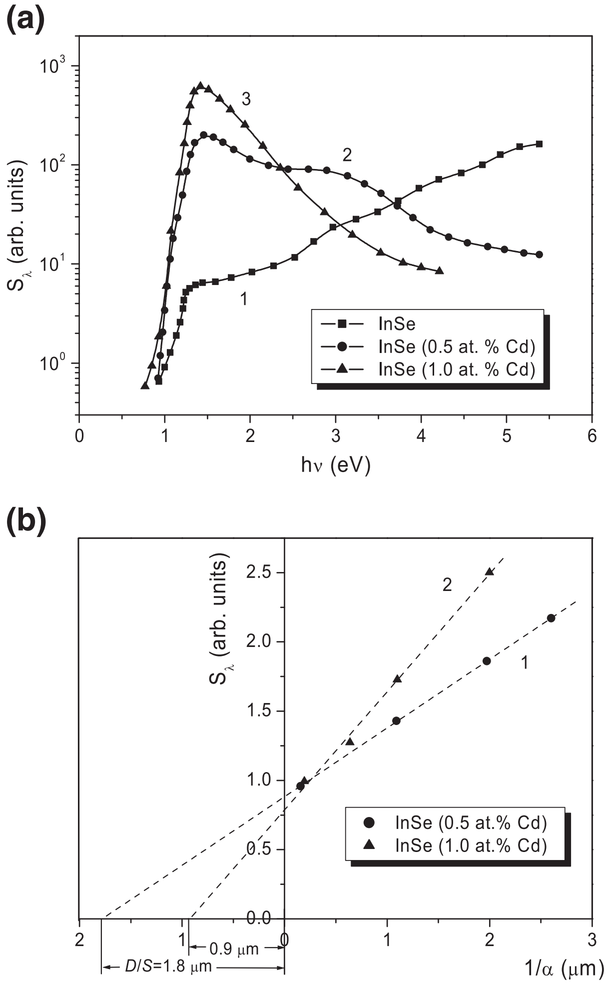

Fig. 2. (a) Spectral characteristics of photocurrent in undoped (curve 1), and Cd-doped: 0.5 at.% (curve 2) and 1.0 at.% (curve 3) InSe crystals, at $T=293$ K. (b) Determining ratio of the ambipolar diffusion coefficient and recombination rate at the surface of Cd-doped InSe crystal samples: 0.5 at.% (curve 1) and 1.0 at.% (curve 2).

For a sample with a thickness d much larger than the mean free path of charge carriers, L ($d \gg L$) and high absorption coefficient, α ($1/\alpha \ll d$), the photosensitivity (S_λ) is given by [18]

$$S_\lambda = 1 + \frac{S}{D}\frac{L}{1+\alpha L}, \qquad (1)$$

where S denotes the surface recombination rate and D is the ambipolar diffusion coefficient. In the high absorption region ($\alpha \gg 1/L$), the photosensitivity may be expressed as

$$S_\lambda = 1 + \frac{S}{D}\frac{1}{\alpha}. \qquad (2)$$