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Space charge limited currents in β-ZnP$_2$ layers with hole conductivity

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We have studied space charge limited currents (SCLC) in thin β-ZnP$_2$ layers under visible light illumination. When the cathode is illuminated, the electric field strength drops down to zero values. However without illumination the electric fields strength at crystal boundary is sufficient to form microplasmas and to destruct the crystal. Our simulations agree with experiments when in addition to the standard theory of SLCS we also add recombination processes with deep donor level.

Keywords: space charge limited Currents (SCLC), β-ZnP$_2$ (monoclinic zinc diphosphide), microplasmas, trap filling limit (UTFL), photoexcitation, stark effect.

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1. Introduction

Monoclinic zinc diphosphide (β-ZnP$_2$) is known as a material for solar converters [1,2], for polarization sensitive photodetectors [3,4], and for other optoelectronic devices [5,6]. Low symmetry of β-ZnP$_2$ crystals leads to polarized optical transitions in singlet and triplet exciton states [7], to a significant dichroism (when light propagates in certain crystal directions), to long-term relaxation of conductivity, and to memory effects at low temperatures [8]. In addition, point defects in the energy band significantly affect electrical and opto-electrical properties of crystals [9]. However the lack of knowledge and insufficient understanding of process in of β-ZnP$_2$ doesn't let to realize commercial electronic and optoelectronic devices exploiting these unique features.

In this paper we study space charge limited currents (SCLC) and distribution of the electrical field in thin β-ZnP$_2$ crystals with hole conductivity. The study could have an application in the physics of interfaces, in photoelectron emission devices and in the control of structural properties of materials [10–13].

2. Experiments

Bulk ZnP$_2$ crystals and films were obtained by a CVD (gas transport method) in a two-zone furnace. For undoped β-ZnP$_2$ crystals, the intrinsic defects define the type of conductivity and free charge carriers concentration. The variation of CVD parameters (phosphorus pressure, temperature) let to adjust electro-physical properties of ZnP$_2$ crystals (within a certain limitation). The studies were carried out on undoped ZnP$_2$ crystals with hole concentration within a range of $10^{14}-10^{17}\,\text{cm}^{-3}$ (300 K). Contacts to the crystals were deposited by thermal sputtering of metals or by magnetron sputtering of ITO on the {100} plane of semiconductor wafers after polish etching. Monoclinic ZnP$_2$ *p*-type crystal doesn't form a barrier layer with metals and ITO films, which is in favor for our study. The reflection spectra were measured in polarized light with a beam incidence close to normal and the orientation of the light polarization vector $E \parallel C$, where C is the crystallographic axis of the crystal.

3. Result of experiments

Figure 1 shows current-voltage characteristic (I-V) of ITO-(β)-ZnP$_2$-ITO thin-film structures at several temperatures. At $T \geq 77\,\text{K}$ temperature, I-V characteristic demonstrates several regions: with $I \sim U$, with $I \sim U^2$ dependencies. Also at high voltages (U_{tfl}) we can observe a transition region related to trap filling. An analysis of reflection spectrum (reflectivity is sensitive to the near the surface states) near exciton band at nitrogen temperature shows that the spectrum depends on the polarity of applied voltage: with the positive polarity of the voltage, the exciton reflection spectra are preserved, while with the negative voltage, a Stark red shift of the spectrum occurs and exciton resonances are broaden.

In case of monopolar injection of holes from the electrodes into a semiconductor film the behavior of the I-V characteristics and exciton reflection spectra indicate that the current is limited by the space charge of deep traps. In the absence of illumination, the I-V characteristics could be described by a simple SCLC model with monopolar injection [14,15].

The region where I-V characteristics sharply increases can give us an estimation of traps concentration: $U_{\text{cft}} = 0.9 \cdot 10^{-6} \cdot \frac{L^2 N_t}{\varepsilon}$ where L is the thickness of crystal, N_t is the concentration of traps for majority charge carriers, ε is the semiconductor dielectric constant. The estimation gives us $N_t = 2.3 \cdot 10^{21}\,\text{m}^{-3}$.

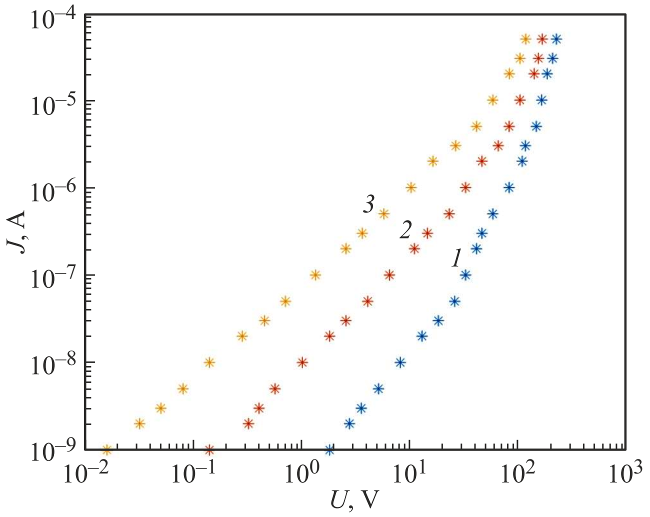

Figure 1. I-V characteristics for ZnP_2 crystals at temperatures T, K: *1* — 87, *2* — 119, *3* — 182.

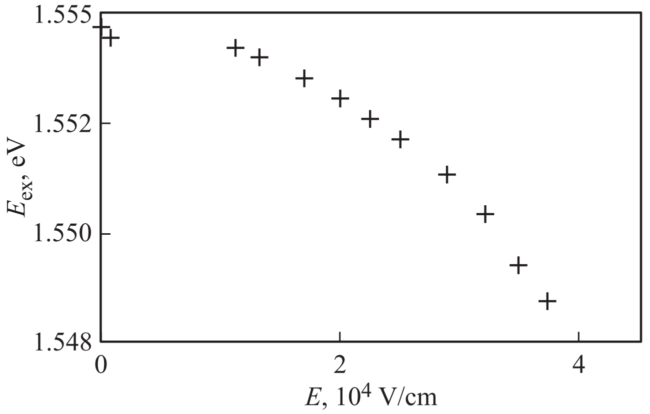

Figure 2. The dependence of the exciton absorption band $C_{n=1}$ shift on the electrical field strength.

Illumination of the structure by light with photon energy $\hbar\omega > E_g$ leads to a significant change in the resistance of thin-film structures, while metal-semiconductor structures on a bulk crystal are not photosensitive and have a linear I-V characteristics. To construct a model that describes the current flow limited by a space charge, we have to know the amplitude of the electric fields at the boundaries.

Exciton light reflection spectra could work as a detector of electric field strength and surface states. Studies of the influence of electric field strength on the exciton reflections spectra are possible on sufficiently thin crystals due to the large values of the absorption coefficient in the exciton band. The influence of the electric field on the exciton reflection and absorption spectra of light was carried out in [16–18]. It should be noted that in these works the optical spectra were measured in an inhomogeneous field of the Schottky barrier. The accuracy of the measurements is limited by the inhomogeneity of the near-surface regions, deep traps and surface states. At the same time in semiconductors with ohmic contacts the maximum strength of an electric field is limited by the conductivity of crystals. In highly resistance crystals the distribution of electric field is also inhomogeneous due to SCLC effect. The measurements of optical spectra in capacitor structures give just an estimation of the electric field strength.

Parameters for our SCLC model with photoexcitation have been taken from [16–18]. Figure 2 shows the dependence of $n = 1C$ series band shift of exciton absorption spectrum on the electric field strength. The data of the band shift on the electric field strength for ITO-ZnP_2-ITO structures are taken from [16].

Surface photo voltage in the studied structures did not exceed 1 mV at any level of illumination.

4. Theoretical model and discussion

To describe the observed experimental results, we propose a model which describes ZnP_2 crystals as a semiconductor with deep impurity levels. It was assumed that the semiconductor has p-type conductivity (the concentration of acceptors exceeds the concentration of donors).

In a thermodynamically equilibrium conditions in a nondegenerate semiconductor the concentrations of holes, electrons, ionized acceptors, and donors have a relationship to the chemical potential μ [18,19]:

$$p = N_v \exp\left(\frac{E_v - \mu}{kT}\right), \tag{1}$$

$$n = N_c \exp\left(\frac{\mu - E_c}{kT}\right), \tag{2}$$

$$N_a^- = N_a \frac{1}{g_a \exp\left(\frac{E_a - \mu}{kT}\right) + 1}, \tag{3}$$

$$N_d^+ = N_d \frac{1}{g_d \exp\left(\frac{\mu - E_d}{kT}\right) + 1}, \tag{4}$$

where N_c, N_v, N_a, N_d is the effective density of states in the conduction band, valence band, acceptor impurity concentration and donor impurity concentration, respectively; g_a, g_d are the degeneracy factor of the acceptor and donor levels, respectively (in numerical calculations, these parameters were set to 2); k, T is the Boltzmann constant and temperature.

In case of $kT \ll E_g$ and $N_d < N_a$, the donors are completely ionized and the concentration of ionized acceptors is equal to

$$p_0 + N_d^+ = N_a^-, \tag{5}$$

the following equation conjugates the equilibrium concentration of holes (p_0) and the concentration of impurity centers:

$$\frac{N_a^-}{N_a} = \frac{p_0 + N_d}{N_a} = \frac{1}{1 + g_a \frac{p_0}{N_v} \exp\left(\frac{E_a}{kT}\right)}, \tag{6}$$

where E_a is the depth of acceptor levels.

In general case, the equation (6) is quadratic with respect to the hole concentration, but due to the cumbersomeness of the expressions, we do not present the analytical solution here. However, at low temperatures, when $kT \ll E_a$, the expression (6) can be linearized:

$$p_0 = N_v \left(\frac{\frac{N_a}{N_d^+} - 1}{2} \right) \exp\left(-\frac{E_a}{kT} \right). \tag{7}$$

In case of holes injection from a metal (or ITO) contact into a semiconductor, when the electrical neutrality condition is not satisfied, the equation (6) can be rewritten:

$$\frac{N_a}{N_a^-} = g_a \frac{p_0 + \Delta p}{N_v} \exp\left(\frac{E_a}{kT} \right) + 1. \tag{8}$$

The equation relating the concentration of ionized acceptors (ΔN_a^-) and a nonequilibrium holes concentration has the following form:

$$\Delta N_a^- = -\frac{g_a N_d^+ \Delta p \exp\left(\frac{E_a}{kT}\right)}{\frac{N_a N_v}{N_d} + g_a \Delta p \exp\left(\frac{E_a}{kT}\right)}, \tag{9}$$

where $\Delta p = p - p_o$ are the changes hole concentration.

In case of photo excitation of electrons and holes, the system is not in a thermodynamic equilibrium. In this case, however, it can be described by quasi-chemical potentials for electrons and for holes separately [20,21].

In this case, equation (6) for electrons can be rewritten

$$\frac{N_d^+}{N_d} = \frac{1}{1 + \frac{g_a \Delta n}{N_c} \exp\left(\frac{E_a}{kT}\right)}, \tag{10}$$

where Δn is the concentration of injected electrons.

For the concentration of ionized donors we can write:

$$\Delta N_d^+ = -N_d \frac{g_d \frac{\Delta n}{N_c} \exp\left(\frac{E_d}{kT}\right)}{g_d \frac{\Delta n}{N_c} \exp\left(\frac{E_d}{kT}\right) + 1}, \tag{11}$$

where E_d is the depth of donor levels.

Gauss law connects electric field strength, additionally injected charged carriers (electrons and holes) and ionized acceptors and donors:

$$\frac{\varepsilon\varepsilon_0}{e} \frac{dE}{dx} = \Delta p - \Delta n - \Delta N_a^- + \Delta N_d^+, \tag{12}$$

where ε is the relative dielectric constant of the crystal, ε_0 is the dielectric constant of vacuum.

Taking into account recombination, optical generation of charge carriers and the continuity equation, the change in the concentration of holes and electrons could defined by the following relations:

$$\frac{dp}{dt} = -\frac{\Delta n(\Delta p + p_0)}{\gamma} + gI(x) - \frac{1}{e}\frac{dj_p}{dx}, \tag{13}$$

$$\frac{dn}{dt} = -\frac{\Delta n(\Delta p + p_0)}{\gamma} + gI(x) + \frac{1}{e}\frac{dj_n}{dx}, \tag{14}$$

where γ is the charge carrier recombination constant, $gI(x)$ is the rate of optical generation; e is the electron charge; j_p, j_n is the hole and electron current, respectively; x, t are spatial and temporal coordinates.

In a quasi-stationary case:

$$\frac{dp}{dt} = 0 \quad \text{and} \quad \frac{dn}{dt} = 0. \tag{15}$$

For a complete description of the system, we have to provide additional equations: Ohm's law for holes and electrons and the equation relating the electric field strength and the voltage U applied to the structure:

$$j_p = e(\Delta p + p_0)\mu_p E, \tag{16}$$

$$j_n = -e\Delta n \mu_n E, \tag{17}$$

$$U = \int_0^L E(x)dx, \tag{18}$$

where μ_p, μ_n are the mobility of holes and electrons; L is the crystal thickness.

The system of equations (6), (12)−(18) describes the distribution of the electric field in a semiconductor with deep impurity centers. The equations take into account charge carrier injection from the electrodes and photo generation of charge carrier under illumination. In general, the system of nonlinear differential equations cannot be integrated analytically; therefore, here we present the results of numerical simulations and compare these results with experimental data. In our calculations we applied parameters corresponding to the experiment (such as sample geometry, temperature, etc) and also use data from the literature (recombination constants, effective masses of charge carriers, mobilities) [22–23]. The impurity centers depths were a variable parameter. It has been adjusted to fit experimental data and simulation results.

Figure 3 shows the I-V characteristics obtained by numerical calculations of equations (1)−(17).

The comparison of experimental I-V characteristics (Figures 2, 3) with the numerical one demonstrates the agreement of theoretical model with experiments. At low hole currents injected from anode, the I-V characteristic is linear, i.e. it obeys Ohm's law. An increase in the temperature leads to increase in the conductivity. This increase is associated with the ejection of charge carriers (holes) from the deep centers. Complete ionization of acceptors is achieved at temperatures > 200 K.

With holes injection currents increase (at a certain threshold voltage applied to the structure) an abrupt increase in the differential conductivity is observed, especially at low temperatures. This behavior is associated with the complete filling of traps (acceptors) and it has been described earlier in [24]. However, in a classical SCLC model a quadratic dependence of the I-V characteristic is followed by a complete trap filling. In contrast, in our case, this region of

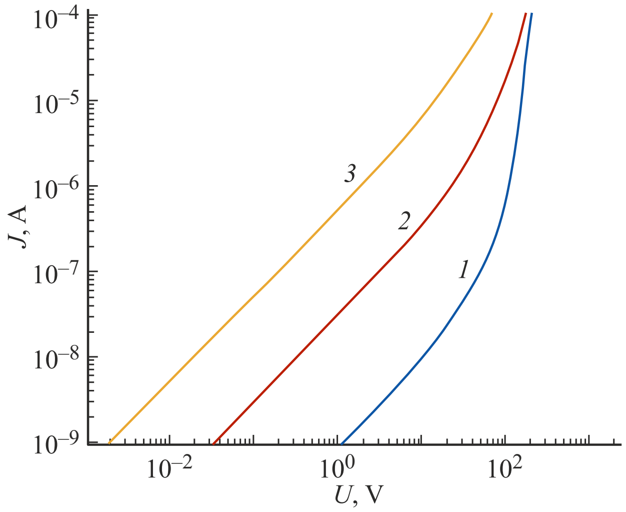

Figure 3. Calculated I-V characteristics for a ITO-ZnP_2-ITO structure at temperatures T K: *1* — 87, *2* — 119, *3* — 182.

I-V characteristic is linear, which agrees with experimental data.

It is interesting to note that, in the trap saturation region, the temperature dependence of the current is practically absent, and all I-V curves merge. At high injection currents, the I-V characteristic acquires a classical quadratic law. Experimentally this region was not investigated, due to the electrical break down of films near the periphery of studied structures. At high voltages, conductive film was completely evaporated and the structure was covered with pits. This indicates on the current filamentation and microplasma formation. After the breakdown, the conductivity of samples has increased by a several orders of magnitude. In the absence of current control, an explosive destruction of crystals occurs when applied voltage is close to the U_{TFL}.

Our model also makes it possible to study the processes upon optical generation of charge carriers in the ZnP_2 crystals. In the simulation, the cathode was illuminated with 632.8 nm light (fundamental absorption region). Optical pumping level has been varied in a wide range from microwatts to watts per square centimeter. The calculation shows that at relatively low levels of illumination ($100\,\text{mW/cm}^2$), the electric field at the cathode decreases significantly, turning almost to zero. As the optical pumping increases, the field inside the crystal increases too (Figure 4). We would like to note that this effect occur only when deep donor centers are taken into account. The effect is associated with donor saturation.

I-V characteristic of the structure at different cathode illumination levels does not contain any significant features (Figure 5). The effect of optical pumping of the cathode is equal to an increase in the temperature, which could be revealed by an increase in conductivity in the linear region of the CVC.

In our model the diffusion of charge carriers was not taken into account. Comparison of numerical calculation results with experiment shows that the role of diffusion is insignificant. It is possible, that in the region of maximum electric field strengths (at the cathode), the mobility and other kinetic parameters of the material are a function of electric fields. Taking these factors into account would require adjusting of our model.

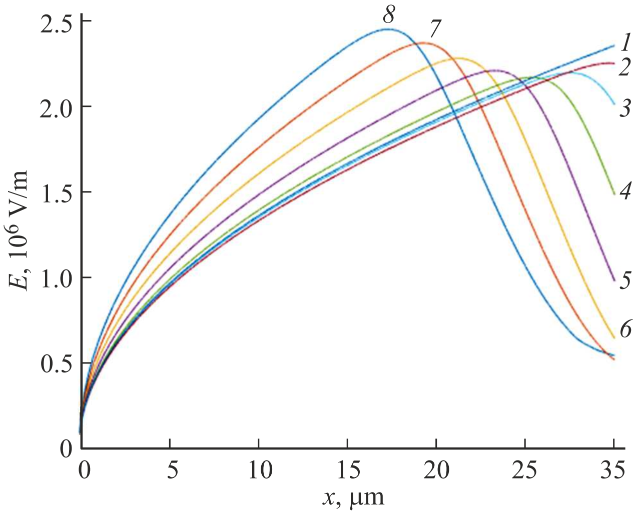

Figure 4. The distribution of the electric field along the crystal depending on the level of illumination of the cathode I, mW/cm^2: *1* — 0, *2* — 0.001, *3* — 0.01, *4* — 0.1, *5* — 1, *6* — 10, *7* — 100, *8* — 1000. (Calculation parameters: $T = 87\,\text{K}$, $E_g = 1.6\,\text{eV}$, $\mu_p = 65\,\text{cm}^2/\text{Vs}$, $\mu_n = 150\,\text{cm}^2/\text{Vs}$, $L = 30\,\mu\text{m}$, $m_e = 0.57m_0$, $m_h = 2.5m_0$, $\varepsilon = 12$, $\gamma = 10^{-7}\,\text{cm}^3\text{s}$, $N_a = 2 \cdot 10^{13}\,\text{cm}^{-3}$, $N_d = 1.9 \cdot 10^{13}\,\text{cm}^{-3}$, $E_a = 0.18\,\text{eV}$, $Ed = 0.3\,\text{eV}$, light absorption coefficient $10^4\,\text{cm}^{-1}$), applied voltage on the structure 45 V.

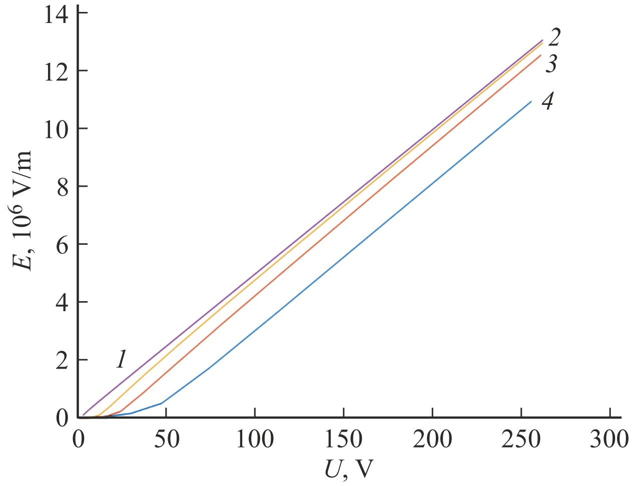

Figure 5. Dependence of electric field strength at the cathode on the applied voltage. Cathode illumination levels I, mW/cm^2: *1* — 0, *2* — 0.001, *3* — 0.01, *4* — 1 (Calculation parameters: $T = 87\,\text{K}$, $E_g = 1.6\,\text{eV}$, $\mu_p = 65\,\text{cm}^2/\text{Vs}$, $mu_n = 150\,\text{cm}^2/\text{Vs}$, $L = 30\,\mu\text{m}$, $m_e = 0.57m_0$, $m_h = 2.5m_0$, $\varepsilon = 12$, $\gamma = 10^{-7}\,\text{cm}^3\text{s}$, $N_a = 2 \cdot 10^{13}\,\text{cm}^{-3}$, $N_d = 1.9 \cdot 10^{13}\,\text{cm}^{-3}$, $E_a = 0.18\,\text{eV}$, $E_d = 0.3\,\text{eV}$, light absorption coefficient $10^4\,\text{cm}^{-1}$).

In conclusion we would like to note that unique properties of monoclinic zinc diphosphide (and a possibility of monopolar injection of holes in metal-ITO-ZnP$_2$ structures, pronounced exciton reflection of light) make it possible to study in detail SCLC phenomenon in thin film semiconductors under light illumination.

5. Conclusion

Our experiments directly show that in monoclinic zinc diphosphide films with hole conductivity, under monopolar injection of holes, the electric field changes from zero values at the anode to the maximum values at the cathode. It is shown that at U_{TFL} the electric field strength reaches the limit values, leading to the formation of microplasmas and the destruction of the crystal. Illumination can decrease the electric field strength from the maximum values to zero in the near-surface region at the cathode.

Proposed model describes the evolution of the electric field strength in crystals with SCLC under visible light illumination. Simulations show that our model is consistent with experimental data.

Conflict of interest

The authors declare that they have no conflict of interest.

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