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ANOMALOUS PROPERTIES OF *n*-InSe/*n*-ZnTe (THIN FILM) HETEROJUNCTION*

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D. C. current-voltage characteristics of the *n*-InSe/*p*-ZnTe heterojunction have been measured in the dark at different temperatures. The model of long-time relaxation and frozen conductivity has been applied in order to explain the anomalous behaviour of forward bias current as a function of temperature.

1. *Introduction*

In systematic studies to form a suitable potential barrier on layered hexagonal indium monoselenide (InSe) as a potentially interesting solar cell material, the authors applied several techniques and methods such as Schottky barrier$^{1)}$, ion implanted junctions and heterojunctions$^{2)}$. Research is concentrated on heterojunctions with CdTe and ZnTe, not reported previously in the literature, in an attempt to obtain low resistivity *p*- and *n*- sides of the junction and matching thermal coefficients of expansion.

In the course of investigation of the InSe/ZnTe heterojunction, an unusual behaviour in the current-voltage characteristics at low temperatures has been observed. In this paper a hypothetical model of extended potential barrier has been proposed in order to explain frozen conductivity and long-time relaxation effects.

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2. *Experimental*

Freshly cleaved single crystal platelets of undoped InSe with *n*-type electrical conductivity and hexagonal crystal lattice, with good cleavage property parallel to the (001) crystal planes, the properties of which have been described previously[2,3], have been used as a substrate for ZnTe thin film deposition by vacuum thermal evaporation from the molybdenum boat at a pressure of 1.33×10^{-4} Pa and the substrate temperature of 390 K. The area of the junction has been 5 mm^2. The films of ZnTe have shown *p*-type conductivity with the electrical resistivity of 2×10^4 Ωcm and the hole concentration of $\sim 10^{12}$ cm^{-3} at room temperature.

X-ray diffraction analysis (counter diffractometer) of the thin films of ZnTe has revealed that they were polycrystalline. The diffraction patterns have been interpreted in terms of a cubic, sphalerite-type, structure with the unit-cell parameter $a = 0.6103$ nm (at 298 K). The crystallites of ZnTe exhibited strong preferred orientation with their (111) crystal lattice planes parallel to the substrate (the dominant 111 diffraction line and some weak lines such as 220, 311, 222, 400). The electrical resistivity of InSe platelets was about 300 Ωcm in the direction parallel to their *c*-axis [normally to the (001) planes], and the electron concentration was $\cong 5 \times 10^{15}$ cm^{-3}.

The thickenss of the ZnTe thin films has been of the order of 0.5 μm, and the thickness of the single crystal InSe platelets has been few tenths of milimeter. Soldered indium proved to be a good ohmic contact to InSe. Silver colloidal paste (Acheson Colloiden B. U., Scheemde, Holland) was used as an ohmic contact to ZnTe. The forbidden energy gap of InSe at 300 K is 1.2 eV[4], while the energy gap of ZnTe is 2.26 eV at room temperature[5].

The samples were mounted in a cryostat for electrical measurements.

3. *Results and discussion*

Fig. 1 shows typical forward and reverse bias current-voltage characteristics, *I* vs. *U*, for an *n*-InSe/*p*-ZnTe heterojunction measured in the dark at different temperatures between 100 K and 350 K. The forward bias characteristics can be divided into two parts, a low-voltage and a high-voltage part. The transition voltage between these two parts decreases with the increase of temperature. The curves are approximately parallel in both regions. Fitting the characteristics to an expression of the form as

$$I_F = I_0(T) \exp(AU_F) \tag{1}$$

gives the value $A_1 = 4.35$ V^{-1} in the low-voltage region (i. e. for voltages $U < 0.4$ V at room temperature), and $A_2 = 1.1$ V^{-1} at higher voltages.

Fig. 2 represents semilogarithmic plots of I_F/U_F (forward current to forward voltage ratio) against the temperature at various forward bias voltages, U_F. All measurements have been performed in the dark. The curves show anomalous thermal quenching below 200 K for forward bias voltages $U_F > 0.3$ V. The temperature of the beginning of thermal quenching decreases with increasing forward bias voltage.

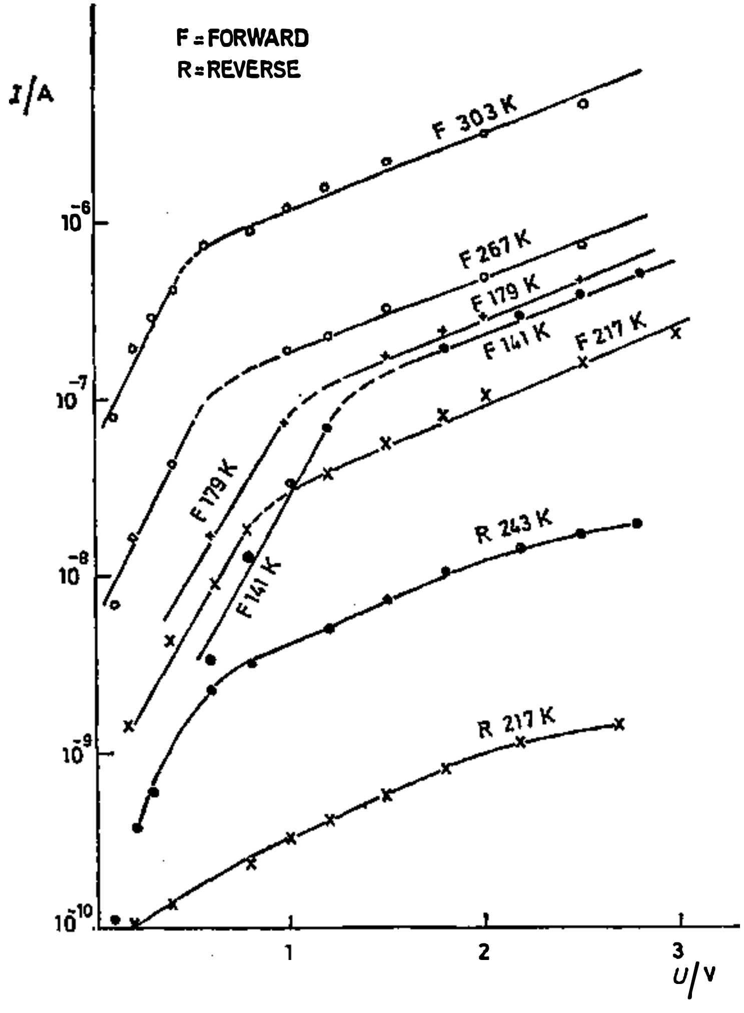

Fig. 1. Current-voltage, I vs. U, characteristics of an n-InSe/p-ZnTe heterojunction measured in the dark at different temperatures.

It is important to notice that the same shape of the curves as seen in Fig. 2 has been preserved while keeping the sample in the dark during successive heating-cooling cycles and I_F vs. T measurements with parameter $U_F = 0.8$ V are shown in Fig. 3; the sample has been first heated from 110 K to 240 K, then cooled back to 110 K and heated again from 110 K to 350 K.

The reverse bias current-voltage characteristics, I_R vs. U_R, of the n-InSe/p-ZnTe heterojunction at various temperatures are presented in Fig. 4. The experimental data can be fitted to the following equation:

$$I_R = B(T) \exp[-C(U_D - U_R)^{-1/2}] \tag{2}$$

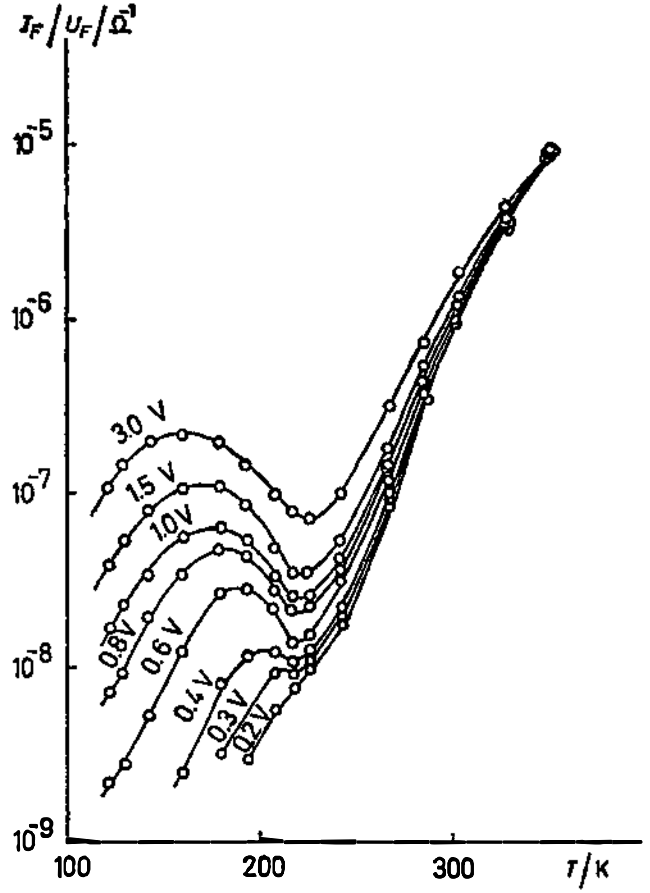

Fig. 2. Conductance (forward current to forward voltage ratio) vs. temperature, I_F/U_F vs. T, curves measured in the dark at various forward voltages.

where U_D is the diffusion potential, and C, a constant independent of temperature, is equal to 5.25 V^{-1}. The diffusion potential U_D of this heterojunction has been estimated by extrapolating the linear forward characteristic to the point where the current equals zero$^{6)}$ and it was found to be equal to 0.7 V, the value somewhat lower than the calculated one, 1.1 V, based on the electron affinities* and the positions of the Fermi levels in ZnTe and InSe energy gaps.

The behaviour of both forward and reverse bias characteristics which are expressed by Eqs. (1) and (2), with the slopes A and C independent of temperature, is indicative of tunnel currents.$^{6)}$

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* The electron affinities of InSe and ZnTe at room temperature are 4.0 eV and 3.53 eV (Ref. 12), respectively.

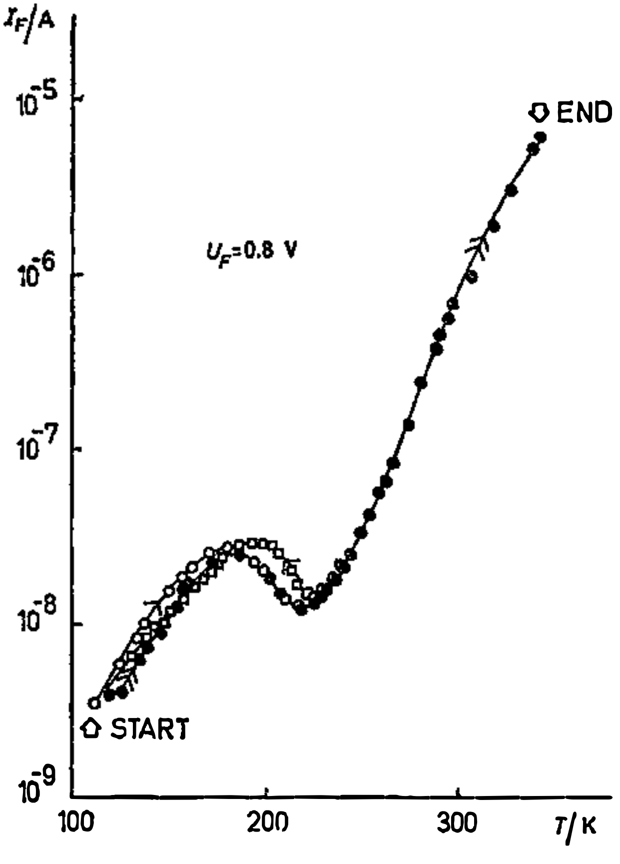

Fig. 3. Forward current vs. temperature, I_F vs. T, at 0.8 V forward bias during heating-cooling cycles, in the dark.

In order to elucidate the unusual behaviour of I_F vs. T or I_F/U_F vs. T dependences (Figs. 2 and 3), the model of long-time relaxation (LTR) and frozen conductivity (FC)$^{7)-9)}$ has been applied.

Residual or frozen conductivity is the conductivity persisting in darkness in many semiconductors (for example, in CdS, CdSe, CdTe, ZnS, ZnSe, Sb_2S_3 etc.)$^{8)}$ for a long time at levels close to the photoconductivity level. LTR and FC are related to the macroscopic potential barriers resulting from different kinds of inhomogeneities in semiconductor which consists of low-resistivity (LR) and high-resistivity (HR) regions. Let us consider a semiconductor of *n*-type conductivity. The electric field of such a barrier (see Fig. 5) leads to the separation of, for instance, light-excited charge carriers: electrons are shifted to LR and holes to HR, where they are captured by deep local recombination centres. Nonequilibrium electrons in LR are responsible for the observed photoconductivity; later, in the dark, these electrons have to surmount the potential barrier (so called recombination barrier) in order to recombine with the holes in HR. Small probability of such an activation

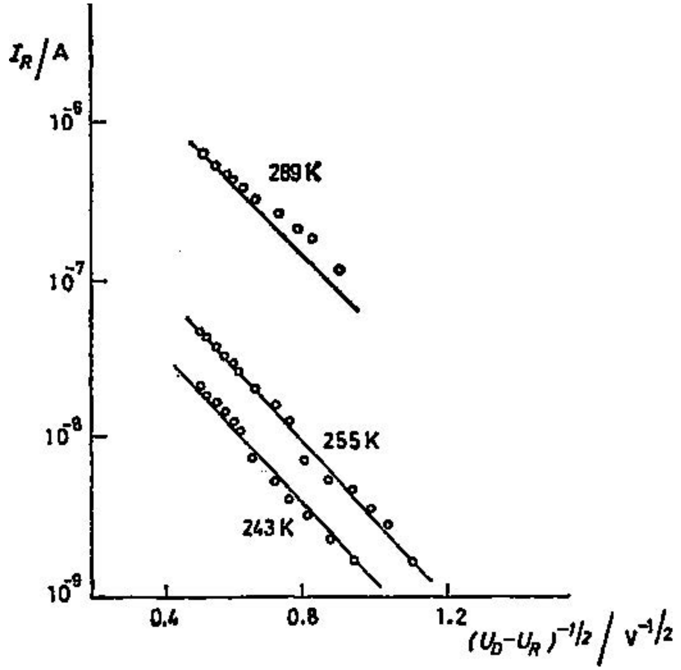

Fig. 4. Reverse current-voltage characteristics, measured in the dark at three different temperatures.

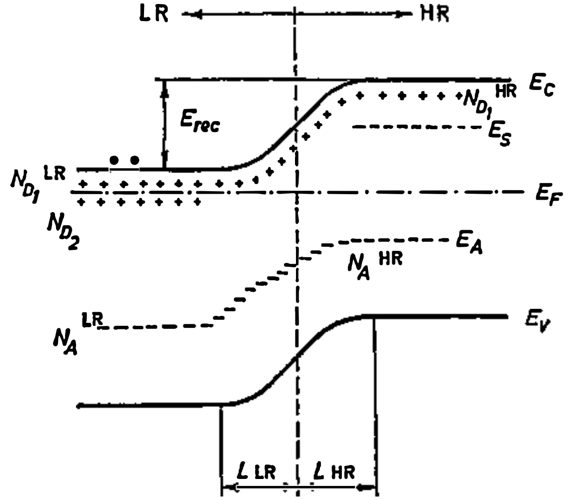

Fig. 5. The energy diagram of the proposed recombination potential barrier in indium monoselenide with high (HR) and low (LR) resistivity regions. E_{rec} — recombination barrier, N_{D1}, N_{D2} — concentrations of donor levels, E_s and E_A — concentration of the acceptor level, E_F — Fermi level; E_c and E_v conduction and valence band edges, respectively, L_{LR} and L_{HR} the barrier widths.

process in wide gap semiconductors with the width of the recombination barrier large enough to prevent tunneling through the barrier, leads to the anomalous long carrier lifetimes. If τ_0 is the relaxation time without barrier, the relaxation time τ in the presence ot barrier of height E_{rcc} becomes:

$$\tau = \tau_0 \exp (E_{rec}/kT). \tag{3}$$

E_{rec} is ordinarily of the order of tenths of electronvolt (eV) (it is smaller than the forbidden energy gap but is greater than conductivity activation energy at low temperature⁸⁾). For example, at 300 K, if $\tau_0 = 10^{-3}$s, then with E_{rec} equal to 0.6 eV, τ is of the order of 10^7 s, long enough for the manifestation of LRT and FC in the course of measurements.

4. *The model of the potential barrier*

The model to be proposed here should explain the following experimental facts:

1. anomalous *thermal quenching* at low temperatures, below 200 K in the dark: a reproducible occurence of the same conductance maximum after several heating and cooling cycles between 100 and 350 K with or without interrupting current during the temperature cycling,
2. the shift of the conductance maxima towards lower temperatures with the increase of the forward bias voltage,
3. the non-existence of similar anomalous *thermal quenching* in the *n*-InSe/*p*-CdTe heterojunctions²⁾.

Firstly, we ruled out the possibility that the thin ZnTe layer was responsible for such a behaviour as it has been semi-insulating with the majority carrier concentration (holes) less than 10^{12} cm^{-3} at room temperature. However, LTR and FC effects have been found in InSe, previously¹⁰⁾. Anomalous *thermal quenching* at low temperatures can be explained by the presence of extended (but localized in the islands) recombination potential barriers in InSe, which may be introduced by different mechanisms such as, for example, by generation of dislocations due to plastic deformation and bending, induced in InSe near the InSe/ZnTe interface as a result of their coefficients of thermal expansion mismatches, as it will be shown later.

The model of such a potential barrier is shown in Fig. 5. The high-resistivity (HR) regions are embedded in the low-resistivity (LR) *n*-type unperturbed matrix where normally current flows and which is in contact with the *p*-ZnTe. The HR region contains at least two acceptor levels: the deeper one the charge of which determines the barrier height and the shallow level at energy E_s from the bottom of the conduction band. If E_s is smaller than E_{rec}, the width of the space charge region is large and may contain several Se-In-In-Se layers, while the concentration N_s of these shallow states may be greater than the effective number of states in the conduction band⁸⁾. There are as well at least two donor levels in the upper half of the energy gap in the LR region. In the experiment, before placing the sample in the cryostat and cooling down to the liquid nitrogen temperature, the ambient light excites the additional non-equilibrium carriers which are separated by such potential barriers: electrons participate to the current in the conduction band of the LR region while holes get captured to the top of the valence band in the HR region. This is the origin of LTR and FC effects. As the relaxation times are very long, the recombination barrier height remains constant during the period of measurements, and the observed phenomena are reproducible with time.

By heating the sample from 77 K to higher temperatures, there is additional ionization of electrons from the shallower donor levels in the LR region and forward current or conductance, I_F or I_F/U_F, increases. At high enough temperatures, electrons gain enough energy to surmount the recombination potential barrier and get trapped by the acceptors in the HR region. As they are temporarily removed from the conduction process, the thermal quenching is observed and conductance decreases. At still higher temperatures, the ionization from the deeper donor level and/or release of the trapped carriers in the HR region start to dominate in the conduction process and the conductance increases significantly. The opposite processes dominate during the cooling down from the room temperature. In addition, the thermally generated charge carriers at higher temperatures become additional non-equilibrium carriers at low temperatures after separation by the potential barrier and after their capture by the traps in the HR region. There is an increase in the potential of electrons in the forward bias low resistivity matrix of the *p-n* junction, and this is the reason why the carrier transition over the recombination potential barrier starts at lower temperatures with the increase of the bias, causing the shift of the conductance maxima (as seen in Fig. 2).

It is possible to explain the different behaviour of the *n*-InSe/*p*-ZnTe from the *n*-InSe/*p*-CdTe heterojunction by a mismatch in the thermal coefficients of linear expansion of InSe and ZnTe, and InSe and CdTe, including large stress and strain, in the InSe lattice, close to the heterojunction interface. Namely, the room-temperature values of these coefficients are 5×10^{-6}/°C for CdTe$^{11)}$, 8.3×10^{-6}/°C for ZnTe$^{11)}$ and 6×10^{-6}/°C for the direction perpendicular to the *c*-axis for InSe, i. e. the coefficient of InSe is greater than that of CdTe and lower than that in the case of ZnTe. In the first case (the heterojunction InSe/CdTe) there is a dilatation in the InSe atomic layers parallel and close to the heterojunction interface, and for the InSe/ZnTe heterojunction there is a compression in these layers introducing extended defects with the recombination potential barrier. However, more research is, of course, needed to confirm this hypothesis.

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ANOMALNA SVOJSTVA HETEROSPOJA *n*-InSe/*p*-ZnTe (TANKI SLOJ)

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Izmjerene su istosmjerne strujno-naponske karakteristike heterospoja *n*-InSe/*p*-ZnTe u mraku na različitim temperaturama. Pokušao se primijeniti model dugovremene relaksacije i zamrznute vodljivosti da bi se objasnilo anomalno ponašanje propusne struje u ovisnosti o temperaturi.