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DIRECT CONVERSION OF SOLAR ENERGY TO ELECTRIC ENERGY

Extrinsic Thermal Voltaic Effect in Photothermal Elements

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Abstract—We have studied the peculiarities of the extrinsic thermal voltaic effect and the possibility of reducing the optimal temperature for using photothermal elements and selecting the impurities for conducting preliminary experimental surveys on this subject.

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INTRODUCTION

The development of the photovoltaic and large-scale production of solar elements has shown that the elaboration of more efficient semiconducting converters of radiation and heat energy into electric energy is a long-term priority task of renewable power generation. It should be noted that high-efficiency multijunction solar elements (SEs) [1] are still not widely used due to their high cost. A significant increase in the efficiency of one-junction SEs significantly reduces the costs connected with the area of the semiconducting photoelectric converters and the cost of energy generated thereby. One of the approaches in this direction was to evaluate the extrinsic thermal voltaic effect [2–4], which enables the absorption of photons with energies less than the width of the band gap of the semiconductor (E_g), and would exceed the efficiency of the element. However, until now, it has not been possible to experimentally observe the extrinsic thermal voltaic effect. The peculiarities and perspectives of using the extrinsic thermal voltaic effect of semiconducting structures were reviewed in [5]. The main reason that prevents the extrinsic thermal voltaic effects from being implemented is that their concentration is almost three orders lower than the concentration of the basic semiconductor atoms, which is why the absorption of the photons by deep-level impurities will be insignificant. In [6, 7], an attempt was made to substantiate the idea on the photothermal elements on based on narrow-bandgap semiconductors in which the photo- and thermogeneration of electron–hole pairs occur which separation by the p–n transition creates photothermal electron–hole structures. It should be specially noted that, to separate thermogenerated electron–hole pairs with concentration n, the presence of the temperature gradient is necessary to determine the gradient n_i in the p and n layers of the photothermal element. In existing thermal $Bi_2Te_{1-x}Se_x$ elements with a branch length of 5 mm and $\Delta T = 200$°C, the average temperature gradient is 400 deg/cm. In photothermal elements with a thickness of the p and n layers of ~1 μm and a rear ohmic contact with a thickness of ~10 μm due to the convection heat loss and heat radiation of the front and rear surfaces at $\Delta T = 0.1$°C, the temperature gradient is 1000 deg/cm and, at $\Delta T = 1$°C, it is 10000 deg/cm, which allows for the appearance of a barrier thermal electron–hole structure that significantly exceeds the barrier thermal electron–hole structure of the thermal element $Bi_2Te_{1-x}Se_x$. At this intensity of the incident radiation, the concentration of the photogenerated electron–hole pairs does not depend on the temperature or its gradient for these elements. The heating of the element due to the excess energy of the photocarrier transform it into the energy of the thermogenerated electron–hole pairs. Thus, the photothermal element may be more efficient than the existing one-junction SE. The high temperature of the photothermal elements action may decrease the terms of their operation.

In this respect, this message is devoted to discussing the possibility of reducing the operating temperature of the photothermal element due to the extrinsic thermal voltaic effect.

CONCENTRATION OF INTRINSIC CARRIERS AND HOT ATOMS

The distribution of the number of crystal atoms by energies complies with the Bose statistics and is expressed by a curve with a maximum value that corresponds to an energy equal of $3\,kT/2$. The volume concentration of the atoms in Ge, Si, GaAs, InAs, and InSb crystals is approximately $3–4 \times 10^{22}$ cm^{-3}. The excess energy of atoms with energy (E_h) greater than $3\,kT/2$ will be specified by ΔE_h. At $\Delta E_h > 3\,kT/5$, these atoms are called "hot." It is possible to use data on the concentrations of the intrinsic carriers of the semiconductors n at different temperatures to approximately evaluate the concentration of hot atoms N_h based on their energies; n_i represents the concentration of the thermogenerated electron–hole pairs conditioned by hot atoms with an excess energy of $\Delta E_h > E_g$. The distribution of the hot atoms by energies at different temperatures is proposed in Fig. 1. It is possible to approx-

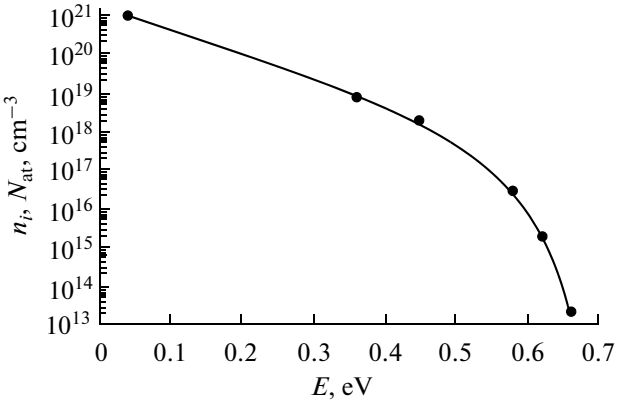

Fig. 1. Distribution of hot atoms based on energy.

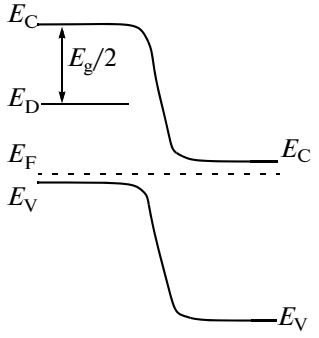

Fig. 2. Diagram of transition of p–n energy zones with donor impurity at an activation energy $E_D = E_g/2$.

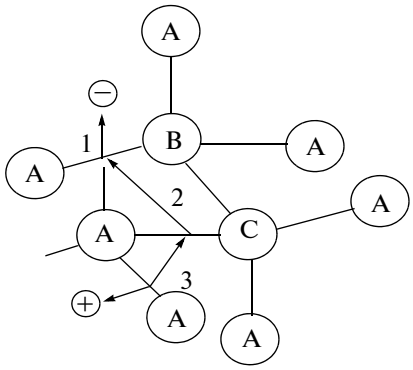

Fig. 3. Energy band diagram of solid solution $(A_2)_{1-x}(BC)_x$. Thermogeneration of electron–hole pairs as a result of electron transition with the participation of donor (E_D) levels of A–B and A–C interatomic bonds. 1, 2, 3 are numbers of the sequence of the electron transitions.

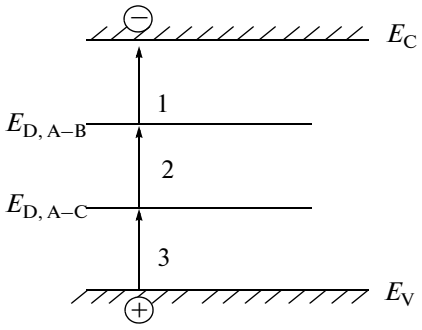

Fig. 4. Space configuration of tetrahedral bonds of solid solution $(A_2)_{1-x}(BC)_x$. Electron transitions 1, 2, 3 are shown in Fig. 3.

imately estimate the concentration of the thermogenerated pairs with the participation of impurities with an activation energy of $E_g/2$ (Fig. 2). For the case of donor impurities, the diagram of the energy zones of the p–n transition based on a semiconductor with E_g = 0.4 eV is shown in Fig. 2. At an ionization energy of the donor impurities of $E_g/2 = 0.2$ eV, the concentration of the hot atoms is 8×10^{19} cm^{-3}, which is 1.5 orders of magnitudegreater than $n_i = 4 \times 10^{18}$ cm^{-3}. At a concentration of hot atoms of 8×10^{19} cm^{-3}, the distance between the hot atoms is about 3–4 nm, since, in order to generate one electron–hole pair involving the collision of the impurity atom with two hot atoms is required. Since the rate of energy transition of hot atoms is equal to the speed of sound in a semiconducting crystal, for the energy transition of a hot atom at a distance of 3–4 nm × (10^{-11} to 10^{-12}) s, the thermogeneration of electron–hole pairs must occur with the participation of impurities. During thermogeneration n, all crystal atoms with a concentration of 10^{22} cm^{-3} participate, which is an order of magnitude greater than the concentration of the impurities. However, as a result of the transition from the valence band to the conducting band, the concentration of hot atoms generate electron–hole vapors.

Let us also consider the following case: semiconductor A with $E_g = 0.6$ eV doped with the impurity BC introduces two donor levels with ionization energies of 0.2 and 0.4 eV (Fig. 3) and forms a substitution solid solution $(A_2)_{1-x}(BC)_x$ with $x < 0.01$. The thermal generation of electron–hole pairs occurs in the sequence of transitions 1, 2, 3 (as shown in Figs. 3 and 4) due to the energy of the hot atoms with excess energy of 0.2 eV, which is almost four orders of magnitude greater more than the concentration of hot atoms (10^{15} at cm^{-3}) and has an excess energy E_g, which thermogenerates electron–hole pairs as a result of the band-to-band transition. That is why it is possible to expect that the presence of a significant concentration of deep impurities, especially if they introduce two donor levels located as shown in Fig. 3, may considerably reduce the optimum operating temperature of the photothermal element, since the excess energy of hot atoms is twofold smaller than E_g.

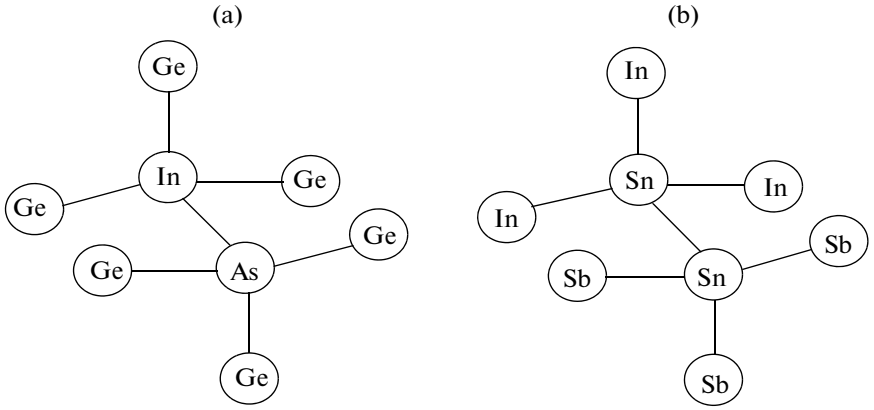

Fig. 5. Space configuration of tetrahedral Ge bonds doped by InAs (a) and InSb (b) doped by Sn_2.

Semiconductor	Impurity	Expected donor levels, eV
Ge	In As, InSb	0.35, 0.2
GaSb	In	0.2
InAs	Sb	0.2
InSb	Sn, HgTe	0.1, 0.1

SELECTION OF SEMICONDUCTING IMPURITIES FOR PHOTOTHERMAL ELEMENTS

To conduct preliminary experimental surveys on carrying out and evaluating the extrinsic thermal voltaic effect, we recommend using Ge, GaSb, InAs, and InSb as the semiconductors. Ge may be doped by InAs and InSb impurities, which form a solid solution $(Ge_2)_{1-x}(InAs)_x$, $(Ge_2)_{1-x}(InSb)_x$, respectively; GaSb may be doped by In impurities, which form the solid solution $Ga_{1-x}In_xSb$; InAs may be doped by Sb impurities, which form the solid solution $In_{1-x}Sb_xAs$; and InSb may be doped by Sn and HgTe impurities, which form the solid solutions $(InSb)_{1-x}(Sn_2)_x$ [8] and $(InSb)_{1-x}(HgTe)_x$. These impurities are isovalent in relatively basic semiconductors and may introduce donor levels located in the band gap according to the width of the band gap of the extrinsic semiconductors.

To illustrate the interatomic bond that conditions the InAs donor levels in Ge and Sn_2 donor levels in InSb, Figs. 5a, 5b present the space configurations of tetrahedral Ge bonds doped by InAs and InSb doped by Sn_2, respectively. The author hopes that the proposed idea will be useful for goal-oriented exploratory studies in the development of extrinsic photothermalvoltaics.

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