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Impurity Photovoltaic Effect in *p-i-n* Structures of Undoped GaAs

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Abstract—Photo-emf in the range $h\nu = 0.76 - 1.35$ eV was found in p-i-n structures produced from undoped GaAs crystals with known parameters; the current sensitivities in the impurity and intrinsic ($h\nu > 1.35$ eV) regions were comparable. It was proven that the impurity photovoltaic effect results from EL2 and EL3 structural defects creating deep donor levels in the forbidden zone. Calculations were performed that justified the possibility of observing this effect on the investigated structures.

Key words: semiinsulating GaAs, impurity photovoltaic effect, deep levels, *p-i-n* structures.

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INTRODUCTION

The main objective of solar power engineering is the conversion of solar energy into electricity. The best materials for the manufacture of solar cells (solar cells) are Si and GaAs [1]. In modern solar cells, the short-circuit current J determining their efficiency is caused by transitions in the region of intrinsic absorption. The question of improving the efficiency using the impurity photovoltaic (IPV) effect [2] has been discussed in the press since 1960. The presence of impurity levels in the midgap allows one to use the generation of nonequilibrium carriers from them the to *c*- and ν-zones, which maximizes the spectral region of absorption and increases the signal J under illumination of a photocell by sunlight. However, subsequent theoretical work has shown that the introduction of such impurities leads to an increase in nonradiative recombination and decrease in efficiency [3–5]. Nevertheless, the possibility of using these levels has been the subject of theoretical research up until the present [6]. According to the calculations of the authors [7], doping of silicon solar cells with an In impurity, creating an acceptor level of (E_v – 0.157 eV), can lead to an increase in efficiency by 1–2%. The IPV effect has been experimentally observed on Si and Ge structures several times, but the question of improving the efficiency of solar cells by using it remains open [7–9].

In this work experiments were performed on *p-i-n* structures produced from undoped single crystals of semi-insulating *n*-GaAs with known parameters. These structures were designed for detecting solar neutrinos. We observed the IPV effect on them for the first time in the range of photon energy $h\nu = 0.76 - 1.35$ eV [10]. The purpose of this work is to determine what levels in GaAs are responsible for the appearance of the IPV effect and analyze the conditions of its observation on the studied *p-i-n* structures.

METHODS AND SAMPLES

Measurements of the J_sc spectra and photoconductivity were performed at 300 K in the range $h\nu = 0.5 - 1.6$ eV. Monochromatic light fell on the structure from the side of the *p*-layer. The light source was an IKS-21 spectrograph, in which, in order to increase the intensity of light, the globar was replaced with a cinema lamp; the modulation frequency was 146 Hz. All spectra were normalized on the number of quanta.

The structure had the following parameters: a thickness of the *i*-area of $d_i \approx 400$ microns, a thickness of highly doped *p*- and *n*-layers $d_{p,\,n}$ of 3 microns, the size of the reception area was 4×4 mm^2.

Single crystals of n-GaAs were grown by the Czochralski method with the atomic fraction of arsenic in the flux $X_\text{As} = 0.495$, 0.492, 0.484, 0.461 for the samples (and then the structures) *1–4*, respectively. The concentration of EL2 point defects (an antisite As_Ga defect), which created a donor level (E_C – 0.78 eV) in the forbidden zone, was $N_2 = (1.6, 1.4, 1.3, 0.84) \times 10^{16}$ cm^{-3}. The concentration of the main background impurities was an order less. The ionized centers EL2$^+$ and the neutral centers EL2^0 are the most effective centers for capturing electrons and holes, respectively [10, 11]. A decrease in X_As and N_2 did not lead to the expected increase in the lifetime of electrons τ_n and holes τ_p because of the increasing concentration of other intrin-

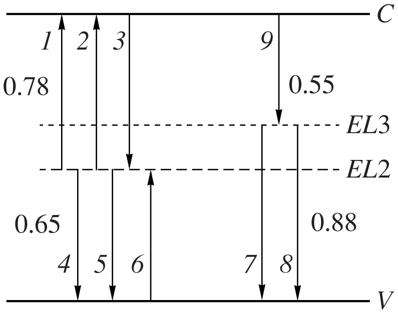

Fig. 1. The scheme of the possible transitions in semi-insulating GaAs with the two types of structural defects, EL2 and EL3

sic defects, in particular, Ga_{As} (the acceptor level ($E_\nu - 0.075$ eV)) and Ga–O–Ga (the donor level ($E_C - 0.55$ eV), the EL3 centers) [10–13]. The concentrations of the ionized centers $EL2^+$ and $EL3^+$ for samples 1–4 were $N_2^+ = (1.5, 3.0, 3.0, 2.6) \times 10^{15}$ cm^{-3} and $N_3^+ = (0.1, 1.7, 2.0, 2.6) \times 10^{15}$ cm^{-3}, respectively. The Fermi level lies near the EL2 level, therefore the concentration of $EL3^0$ centers $N_3^0 \approx 0$. It was shown that the absorption coefficient α in the range $h\nu = 0.65 - 1.35$ eV is determined by the centers $EL2^0$, $EL2^+$ and $EL3^+$ [10]:

$$\alpha(h\nu) = \sigma_{n2}(h\nu)N_2^0 + \sigma_{p2}(h\nu)N_2^+ + \sigma_{p3}(h\nu)N_3^+.$$

Here N_2^0 is the concentration of the neutral $EL2^0$ centers, $N_2 = N_2^0 + N_2^+$; σ_{n2}, σ_{p2}, σ_{p3} are photoionization cross sections for the EL2, EL3 centers for electrons and holes.

Figure 1 shows the band structure of the investigated GaAs and possible transitions between the *c*-, ν-zones and the levels EL2 and EL3.

EXPERIMENTAL RESULTS AND DISCUSSION

The J_{sc} spectra for the structures 1 (curve *1*) and 4 (curve *2*) are shown in Fig. 2. We see that in the interval $h\nu = 0.76–1.35$ eV photo-emf is observed, and the current sensitivities in the region of the impurity and intrinsic ($h\nu > 1.35$ eV) absorption are comparable. For all the structures at $h\nu = 1.2$ eV and the light intensity $I \approx 10^{12}$ photons/(cm^2 s) the values of variables entering J_{sc} were in the range $\approx(0.33–1) \times 10^{-7}$ A/cm^2.

Figure 2 also shows the photoabsorption spectra of structures 1 and 4 measured at 4 V (curves *3* and *4*). The structure becomes a normal photoresistor if a forward voltage is applied, removing the space charge of the *p-i* and *i*-n barriers. In fact, the photoabsorption signal increased linearly with the increase in voltage from 1 to 10 V, and the form of the spectrum remained. For ease of examination, the curves *1–4* were arbitrarily shifted along the ordinate axis. The figure also shows the spectra of the absorption coefficients α for samples 1 and 4 (curves *5* and *6*) and the photoionization cross sections σ_{p2}, σ_{n2}, σ_{p3} (curves *7–9*) taken from [10, 14].

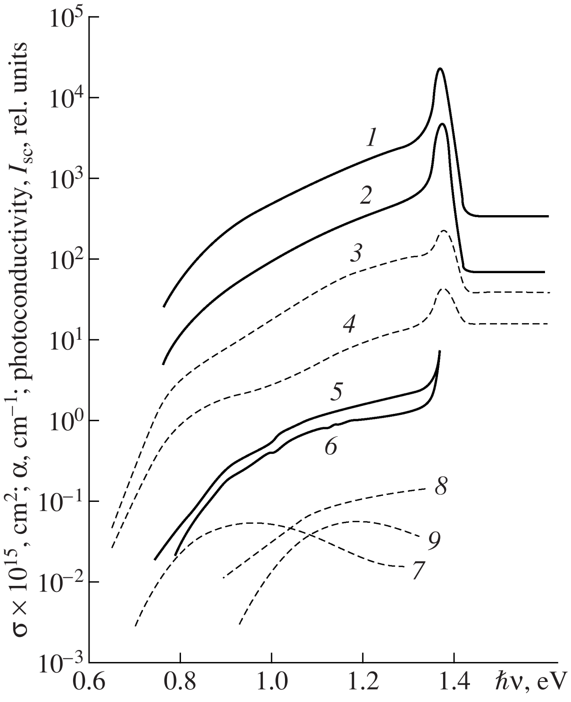

Fig. 2. The spectra *J* (*1* and *2*), photoconductivity (*3* and *4*), α (*5* and *6*), σ_{p2} (*7*), σ_{n2} (*8*) and σ_{p3} (*9*) of the samples (structures) 1 (*1, 3,* and *5*) and 4 (*2, 4,* and *6*) of semi-insulating GaAs

From Fig. 2 we see that the spectra of photoabsorption and *J* are generally similar to the form of the spectrum α. For all structures $\alpha d_i \ll 1$ at $h\nu < 1.35$ eV, so the spectral changes of photoabsorption reflect changes in α and $h\nu$. In fact, thresholds of photoabsorption spectra, in agreement with Fig. 1, were observed at $h\nu = 0.64$ eV (curves *3* and *4*). The behavior of the photoabsorption spectrum in the range $h\nu = 0.7 - 0.85$ eV reflected the spectral behavior of σ_{p2} (curve *7*). The generation of electrons and holes from the centers $EL2^0$ and $EL3^+$, respectively, leads to an increase in the photoabsorption signal at $h\nu > 0.85$ eV, reflecting changes of α and $h\nu$ (curves *5* and *6*).

We know that for the appearance of the J_{sc} excitation must be bipolar. Taking into account the position of the EL2 level we expected to observe J_{sc} signals at $h\nu \geq 0.78$ eV. In fact, the thresholds of spectra were observed at $h\nu = 0.76$ eV (curves *1* and *2*). For the *i-p* barrier in the *i*-region the minority carriers are holes, so their photoionization from the centers $EL2^+$ and $EL3^+$ must determine the form of the J_{sc} spectrum. For the *i-n* barrier in the *i*-region, the minority carriers are electrons and their generation from the centers $EL2^0$ substantially increased the signal J_{sc}. As a result, the dependence of J_{sc} on $h\nu$ (as well as photoabsorption and α)

reflects the photoionization of electrons and holes from the centers $EL2^0$, $EL2^+$ and $EL3^+$.

For the structures 1–4 the values of the diffusion lengths in the *i*-region are $L_n \leq 6$ microns and $L_n \leq 1.2$ microns, i.e., collection of minority carriers in the impurity absorption region by *i-p* and *i-n* junctions is already complete at $d_i \approx 10$ microns. Collection of minority carriers in the intrinsic absorption region is limited by the quantities $d_i = 400$ microns and $d_p = 3$ microns. For example, at $h\nu \geq 1.39$ eV, $\alpha \geq 100\ \mathrm{cm}^{-1}$ [15], $\alpha d_i \geq 4$ and the contribution of the *i-n* junction stops, J_{sc} drops (curves *1* and *2*). If $h\nu \geq 1.43$ eV, $\alpha \approx 10^4\ \mathrm{cm}^{-1}$, $\alpha d_p \approx 3$, all light is absorbed in the *p*-layer and electrons are dragged to the area of space charge only from the side of the *p*-layer.

EVALUATION OF THE CONCENTRATIONS OF NONEQUILIBRIUM ELECTRONS AND HOLES IN THE IMPURITY ABSORPTION REGION

For the appearance of a stationary photo-emf on a barrier layer the generation of minority charge carriers is necessary [8]. In the *i*-region at the distance $\leq L_p$ from the *i-p* junction these are holes, i.e. $J_{sc} \sim \Delta p$ and at the distance $\leq L_n$ from the *i-n* junction they are electrons, i.e. $J_{sc} \sim \Delta n$. Our task is to find the relation between nonequilibrium concentrations Δn and Δp and the parameters of impurity centers and estimate the degree of bipolarity $\Delta n/\Delta p$ (for the *i-p* junction) and $\Delta p/\Delta n$ (for the *i-n* junction), because it determines the possibility of observing the IPV effect [8]. Typically, in the region of intrinsic absorption $\Delta n/\Delta p \approx 1$.

Let us consider the possible transitions in GaAs with the EL2 level (sample 1, $N_3 \approx 0$), Fig. 1. From the level the optical (transitions 1 and 4) and thermal (2 and 5) generation of electrons and holes in the *c*- and ν-zones occurs as well as their capture on the level (3 and 6). In a stationary state the system is described by the equations:

$$\sigma_{n2}(N_2^0 - \Delta N)I - \gamma_{n2}(N_2^+ + \Delta N)(n_0 + \Delta n)$$
$$+ \gamma_{n2}(N_2^0 - \Delta N)N_{cM} = 0$$
$$\sigma_{p2}(N_2^+ + \Delta N)I - \gamma_{p2}(N_2^0 - \Delta N)(p_0 + \Delta p)$$
$$+ \gamma_{p2}(N_2^+ + \Delta N)P_{\nu M} = 0$$
$$\Delta n - \Delta N = \Delta p$$

Here $(n_0 + \Delta n)$, $(p_0 + \Delta p)$, $(N_2^0 - \Delta N)$, $(N_2^+ + \Delta N)$ are total concentrations of electrons in the *c*-zone, holes in the ν-zone and electrons and holes on the impurity level; $\gamma_{n2} = 1/(N_2^+ \tau_n)$, $\gamma_{p2} = 1/(N_2^0 \tau_p)$ are the coefficients of electron and hole capture by the EL2 level; $N_{cM} = N_c \exp(-\Delta E_{Mc}/kT)$, $P_{\nu M} = P_\nu \exp(-\Delta E_{M\nu}/kT)$ are the reduced densities of states in the *c*- and ν-zones, ΔE_{Mc}, $\Delta E_{M\nu}$ are the energy distances from the impurity level to the corresponding zone.

In our case at $I \approx 10^{12}$ photons/(cm^2 s) the equilibrium level filling does not change i.e. $\Delta N \ll N_2^0, N_2^+$. Thus, we have [8]:

$$\Delta n = I(A_n + B)/(1 + C),$$
$$\Delta p = I(A_p + B)/(1 + C),$$

where $A_n = \sigma_{n2}N_2^0/(N_2^+\gamma_{n2})$, $A_p = \sigma_{p2}N_2^+/(N_2^0\gamma_{p2})$, $B = (\sigma_{n2}\gamma_{n2}^{-1}P_{\nu M} + \sigma_{p2}\gamma_{p2}^{-1}N_{cM})N_2/(N_2^+N_2^0)$; $C = N_2[N_{cM}(N_2^+)^{-2} + P_{\nu M}(N_2^0)^{-2}]$.

For the sample 1 $n_0 = 1.4 \times 10^7\ \mathrm{cm}^{-3}$, $\mu_n = 8040\ \mathrm{cm}^2/(\mathrm{V\ s})$, $\tau_n = 1.8 \times 10^{-9}$ s, $\tau_p = 1.4 \times 10^{-9}$ s [12, 16]; $N_{cM} = 1.3 \times 10^5\ \mathrm{cm}^{-3}$, $P_{\nu M} = 1.5 \times 10^8\ \mathrm{cm}^{-3}$ [17]; $\gamma_{n2} = 3.7 \times 10^{-7}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, $\gamma_{p2} = 5.1 \times 10^{-8}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$; $\sigma_{n2}(h\nu)$ and $\sigma_{p2}(h\nu)$ are shown in Fig. 2. At these values of parameters we have $B \ll A_n, A_p$ and $C \ll 1$, therefore

$$\Delta n = I\sigma_{n2}N_2^0/\gamma_{n2}N_2^+; \quad \Delta p = I\sigma_{p2}N_2^+/\gamma_{p2}N_2^0. \quad (1)$$

Availability of the centers $EL3^+$ in GaAs leads to the optical and thermal generation of holes from them (transitions 7 and 8, see Fig. 1) and electron capture (transition 9), i.e., for electrons the number of recombination centers $(N_2^+ + N_3^+)$ increased. In this case, inequalities similar to the above hold, and taking into account that $\gamma_{n2} \approx \gamma_{n3}$ [18] we have:

$$\begin{aligned}\Delta n &= I\sigma_{n2}N_2^0/\gamma_{n2}(N_2^+ + N_3^+);\\ \Delta p &= I(\sigma_{p2}N_2^+ + \sigma_{p3}N_3^+)/\gamma_{p2}N_2^0.\end{aligned} \quad (2)$$

We see that Δn and Δp are proportional to I, as observed in the experiment: the dependence of J_{sc} on I in the range $h\nu = 0.9$–1.35 eV was linear.

The dependences $\Delta n(h\nu)$ and $\Delta p(h\nu)$ calculated according to formulas (1) and (2) for the structures 1–4 are shown in Fig. 3. Comparison of the experimental and calculated curves shows that for all structures the form of spectra J_{sc} and Δn are identical (see Figs. 2 and 3). For structure 1 this could be expected, since $\Delta n > \Delta p$ (Fig. 3, curves *1* and *2*) and $L_n = 5L_p$, so the *i-n* junction makes the main contribution to J_{sc}, i.e., $J(h\nu) \sim \Delta n(h\nu)$. In the range $h\nu = 0.9$–1.35 eV the value $\Delta p/\Delta n$ determining the possibility of observing the IPV effect varies from ≈0.33 to 0.01, and $\Delta n/\Delta p$ varies from ≈3 to 100. For structure 4, in contrast with structure 1, (structures 2 and 3 are an intermediate case) Δn is an order less and $\Delta p > \Delta n$ (curves *7* and *8*), therefore a noticeable contribution to the photocurrent from the *i-p* junction was expected. Indeed, the absolute values of J for the structure of 4 are 3 times higher than those for structure 1 (see Fig. 4), but the spectrum still reflects the behavior of $\Delta n(h\nu)$. For structure 4 the degree of bipolarity $\Delta p/\Delta n$ changes from ≈11 to 1.1, and $\Delta n/\Delta p$ changes from ≈0.09 to 0.9, i.e., conditions for observ-

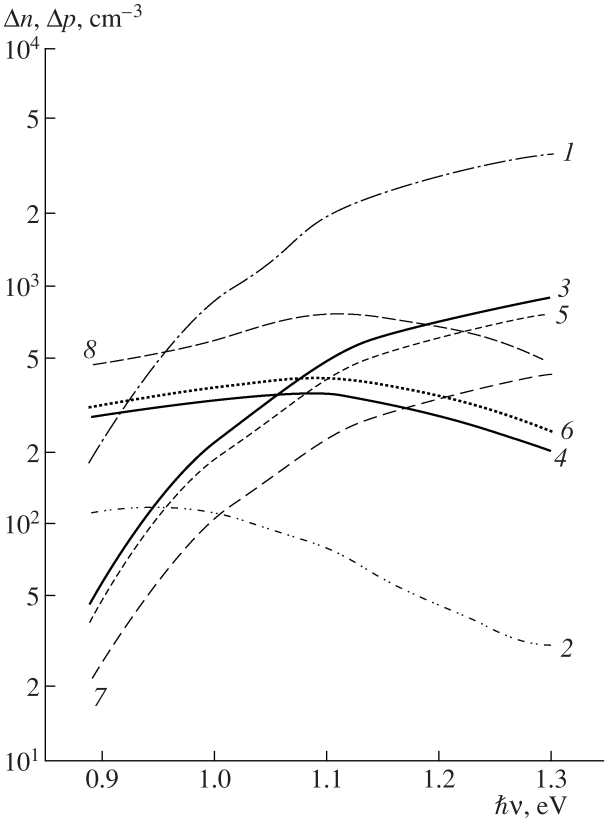

Fig. 3. The spectral dependence of the nonequilibrium concentration of electrons Δn (*1, 3, 5,* and *7*) and holes Δp (*2, 4, 6*, and *8*) for the structures 1 (*1* and *2*), 2 (*3* and *4*), 3 (*5* and *6*) and 4 (*7* and *8*)

ing the IPV effect are better than those for structure 1. Apparently, the relationships between Δn and Δp, $\Delta p/\Delta n$ and $\Delta n/\Delta p$ for each structure are such, that the forms of the resulting spectra J_{sc} and Δn are identical.

Thus, the IPV effect observed in *p-i-n* structures is caused by intrinsic structural defects of GaAs, with the EL2 and EL3 centers creating levels near the midgap. The performed calculations showed that for the investigated structures the probability of appearance of minority carriers in the impurity excitation is rather large, and the degree of bipolarity for *i-n* and *i-p* junctions is low, which gives the possibility of experimental observation of the IPV effect.

The illuminated *p-i-n* structure can be used both in a mode of photo-emf generation, and a photodiode mode [19]. Figure 4 shows spectra J for structures 1 and 4 (curves *1, 2*, and *3–8*) at different values of the reverse voltage U. It can be seen that with the increasing U signals J noticeably increased, and the form of the spectrum J changed. For the structure 1 (curves *3, 5*, and *7*), where $N_3^+ \approx 0$, U_{rev} was distributed in such a way that a large part of it was in a higher-resistance region of the *i-p* junction (J_{sc} at $h\nu < 0.85$ eV is determined by the *i-p* junction, see Fig. 2). For structure 4 under the similar conditions the form of the J_{inv} spectrum changed insignificantly, apparently because of the presence of the centers $N_3^+ = N_2^+$.

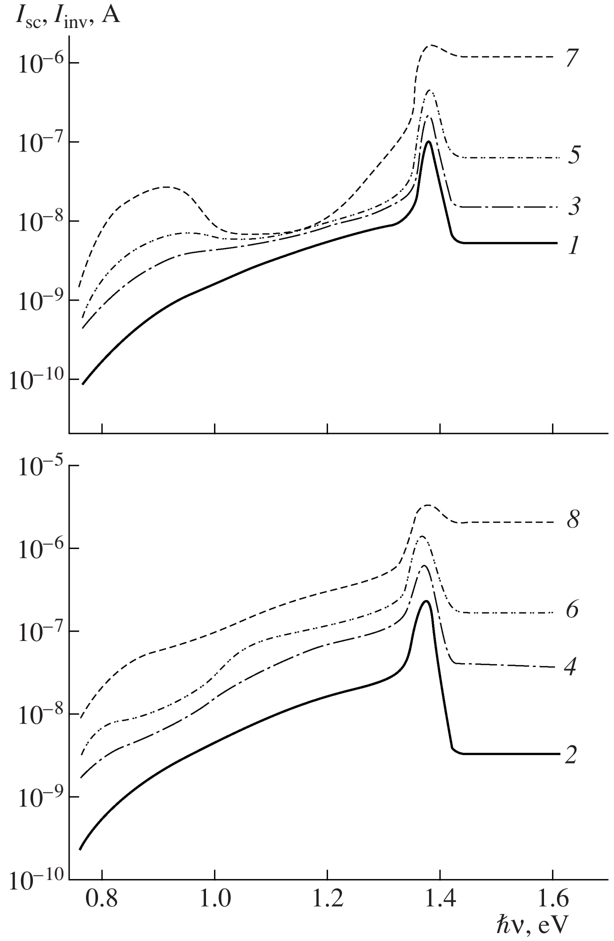

Fig. 4. The spectra J_{sc} (*1, 2*, and *3 – 8*) at U 1 (*3* and *4*), 4 (*5* and *6*), 50 V (*7* and *8*) for structures 1 (*1, 3, 5*, and *7*) and 4 (*2, 4, 6*, and *8*)

For the *i-p* and *i-n* junctions the thickness of layers of the space charge at $U = 0$: d_{ip}, $d_{in} \approx 0.3$, 0.5 microns and L_p, $L_n \le 1.2$, 6 microns i.e., a noticeable proportion of carriers generated by light is absorbed in the space charge regions. This proportion (J) should grow with the increase of U because d_{ip}, $d_{in} \sim (U)^{1/2}$, which was observed in the experiment for all structures.

Thus, if we use GaAs *p-i-n* structures in the photodiode mode their spectral characteristics greatly extend (to the region $h\nu \approx 0.76$–1.35 eV) due to the IPV effect and the photosensitivity increases with the increase in U.

CONCLUSION

For the first time, the investigation of spectra J_{sc} has been performed in the region of impurity absorption on *p-i-n* structures produced from undoped single crystals of semiinsulating GaAs with known parameters. It is shown that the appearance of the impurity photovoltaic effect is caused by intrinsic structural defects (EL2 and EL3 centers) creating donor levels (E_c – 0.78 eV) and (E_c – 0.55 eV), respectively, in the forbidden zone of GaAs. Numerical simulations were performed that justified the possibility of observation of this effect on the investigated structures. It is shown that by using *p-i-n* structures in a mode of photo-emf generation and photodiode mode their spectral characteristics greatly extend to the region of photon energy $h\nu = 0.76$–1.35 eV.

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