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PHOTOEMISSIVE PROPERTIES AND PHOTOELECTRIC TRESHOLDS OF ORIENTED InAs SINGLE CRYSTALS*

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Photoemission from about 20 InAs surfaces, most of them having the orientation (110), was examined at photon energies between 4.0 and 5.8 eV. The *n*-type InAs samples were etched and then purified by vacuum heating. The absolute yield spectra and energy distributions of photoelectrons were obtained for various values of $h\nu$. The following surface parameters were determined: photoelectric thresholds, work function and electron affinity. Photoelctric thresholds were determined using a new method of extrapolating the function $Y\left(\frac{\partial Y}{\partial h\nu}\right)^{-1}$ to the point of intersection with the energy axis. Two averaged values of $h\nu_t$ were obtained: 4.33 eV and 5.03 eV. These values were ascribed to the respective optical transitions. Another method, involving the use of electron energy distributions $N(E)$, was used to confirm the value for the lower threshold obtained in this work and the value for cleaved (110) InAs surfaces. An energy model for *n*-type (110) InAs surfaces is proposed.

1. *Introduction*

The external photoelectric effect in InAs has been studied on a fairly limited scale for clean (110) surfaces of *n*-type crystals [1], and, on a wider scale, for surfaces covered with various amounts of Cs [2].

Comparison of the results presented in the two papers mentioned above reveals considerable discrepancies between the respective experimental curves and between the structures of the surface layers examined, which are consequences of the different surface treatments used. One of the aims of this work was to elucidate the effect of the thermal vacuum treatment of InAs single crystals on their photoemission characteristics and on the photoelectric parameters of the (110) InAs surface as compared with surfaces cleaved in high vacuum. In the discussion of the results, use is made of some optical data on InAs and its energy band model as presented in [3–5].

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2. *Experimental results*

Six InAs samples with the orientation (110) and two samples with the orientation (111) were examined. All the samples were "two-sided" and were obtained from n-type crystal with $n_e \cong 1.10^{17}$ cm^{-3}. The samples were etched and then heated in high vacuum at 350°–400° C. According to the literature [6], this kind of treatment of certain III–V semiconductors gives surfaces with sufficient initial purity. During the photoemission measurements the vacuum in the glass capacitor was of order of 10^{-8} Tr. The other details of the procedure are given in [7, 8]. Two types of experimental curves were obtained: photoelectric quantum yield spectra and the energy distributions of emitted electrons $N = f(E)$ at different photon energies. The energy distributions were obtained by differentiation of the current-voltage characteristics which were also used to determine the collector-emitter CPD.

The experimental material comprises more than 10 yield spectra $Y(h\nu)$ and more than 50 energy distributions $N(E)$.

3. *Discussion*

2.1. Absolute quantum yields

There was some difficulty in estimating the photoelectric thresholds from the curves $Y\left[\frac{\text{el.}}{\text{abs. photon}}\right] = f(h\nu)$. Gobeli and Allen [1] assumed that near the thresholds region the yield of InAs and some other III–V compounds is given by

$$Y = k(h\nu - h\nu_t)^m, \tag{1}$$

where k — is constant within a fairly narrow photon energy interval.

The value of m was equal to $3 \pm \frac{1}{2}$, which led the authors to conclusion that the optical transitions in the photoemission process are indirect. The lower photoelectric threshold $h\nu_t$ was estimated by extrapolation of the straight line $\sqrt[3]{Y} = k_1 \cdot h\nu$ to the point of intersection with the energy axis. A similar procedure is mentioned in another work [9] containing data on InAs and InP.

It has been shown experimentally that most of the methods of semiconductor surface treatment used in practice result in surfaces with lower values of such parameters as $h\nu_t$, φ or χ_s than is the case with atomically clean surfaces. For example, a considerable drop in these parameters is observed when InAs surfaces are covered with Cs [2]. Considerable changes have also been observed after heating oriented GaAs single crystals in vacuum [8].

In the present work the decrease in $h\nu_t$ as compared with the values given in [1] and [9] resulted in extended threshold parts of the yield distributions. Therefore, in describing the function $Y(h\nu)$ in the threshold region the author of this work did not assume that $m = 3$. Instead, another method was used from which the following formula was derived:

$$\frac{Y}{Y'} = \frac{h\nu - h\nu_t}{m}. \tag{2}$$

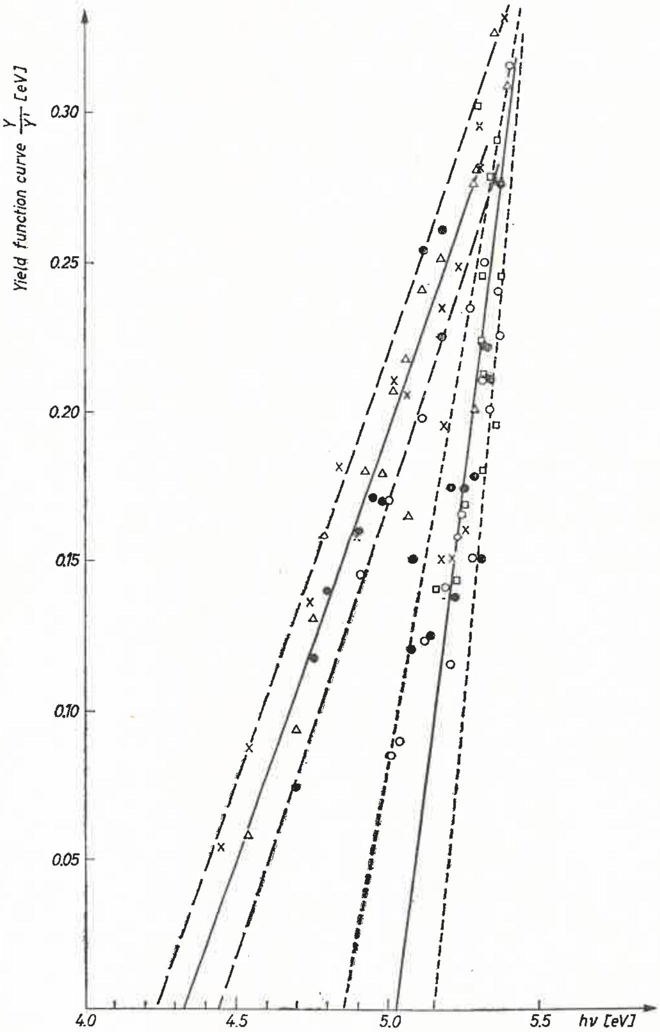

Fig. 1. Quotient of absolute quantum yield and its derivative for *n*-type InAs single crystals vs photon energy. The points for each sample are marked differently; spread intervals are demarcated with dashed lines

For $h\nu$ intervals in which the values of m are constant the $\frac{Y}{Y'} = f(h\nu)$ diagram consist of straight lines which can be used to determine the threshold energy and the parameter m. Fig. 1 shows several values of $\frac{Y}{Y'}$ computed from the results of quantum yield measurements in several InAs single crystals with the orientation (110). Extrapolation of these straight lines gives the following threshold energies: $h\nu_{t_1} = 4.33$ eV and $h\nu_{t_2} = 5.03$ eV. An attempt was made to relate the $h\nu_t$ values with respective optical transitions. The experimentally determined thresholds can be attributed to the highly probable transitions which are realized by the lowest photon energies in the centre of the Brillouin zone and at its boundary in the direction [110]. Of course, only transition to levels with energies $\geqslant E_{vac}$ can be involved. In the centre, the transition $\Gamma_{15v}-\Gamma_{15c}$ (Fig. 2) of 4.36 eV [4] is highly probable. This value corresponds to the threshold $h\nu_{t_1} = 4.33$ eV. It is at this distance that the vacuum level of the heated InAs samples has been marked in Fig. 2. The level E_{vac} corresponds to the point Γ_{15c} and, significantly, runs close to the point K_{1c}. These observations lead to the following interpretation of the function $\frac{Y}{Y'}(h\nu)$ presented in Fig. 1. The left-hand side of the straight line corresponds to emission from the higher part of valence bands to the parabolic *p*-conduction band. From the slope of this part one

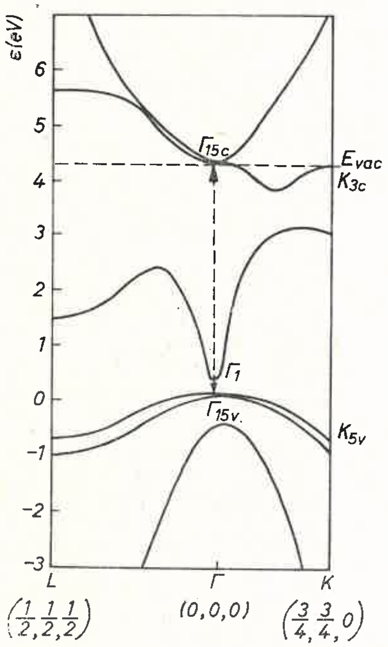

Fig. 2. Energy-band diagram for InAs after [4]. The line marked E_{vac} shows the vacuum level for the samples

obtains $m = 3.5$ which means [according to [1]] that indirect transitions are dominant. The emitted electrons have energies corresponding to the lowest part of the conduction band mentioned above. The value $h\nu_{t_2} = 5.03$ eV, obtained by extrapolation of the other part of the function $\frac{Y}{Y'}(h\nu)$ is in good agreement with the transition $K_{2v}-K_{1c}$, the energy of which, as determined from Fig. 2 is equal to 5.06 eV. It is a probable transition at the boundary of the Brillouin zone in the direction [110]. The parameter m of the higher straight-line section is almost equal to 1 which should correspond to direct transitions.

The yield spectra from cleaved (110) InAs surfaces [1] also exhibit two photoelectric thresholds with higher values of $h\nu_t$ resulting from the higher position of the vacuum level. The higher threshold — 5.58 eV — is in good agreement with a direct transition from the point K_{2v} to the vacuum level. Data presented in [2] indicate that the lower threshold for this surface is approximately 4.9 eV, which corresponds to the transition $\Gamma_{15v}-E_{vac}$ on a cleaved InAs surface. Comparison of these values with Fig. 1 leads to the conclusion, that for both types of (110) surfaces (heated and cleaved in vacuum) the two lower photoemission thresholds correspond to the same two optical transitions in the 1 st Brillouin zone. The thresholds obtained in the present work are consistently lower, by approximately 0.6 eV than for atomically clean surfaces.

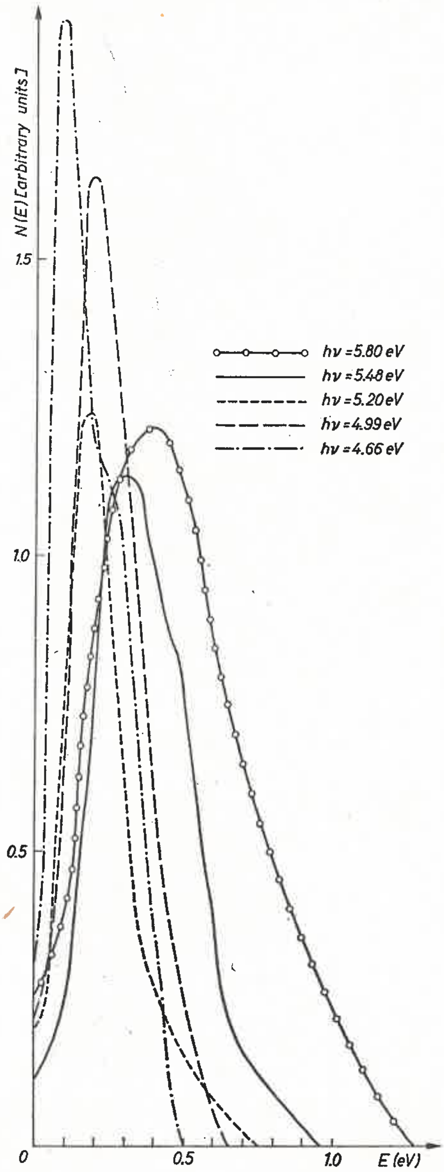

Fig. 3. Averaged photoelectron energy distributions for (110) n-type InAs surfaces

2.2. Energy distributions of photoelectrons

Fig. 3 shows several "averaged" energy distributions of photoelectrons emitted from the (110) InAs surface. Each averaged curve, for a given $h\nu$, has been obtained by combining at least four distribution from different samples.

The estimated spread of high-energy ends of distributions $N(E)$ amounts to ± 0.05 eV. The distributions obtained in the present work were compared with those obtained from GaAs single crystals subjected to a similar surface treatment [8] and with the results presented in [1]. The electron distributions (Fig. 3) are tall and "narrow" (small widths

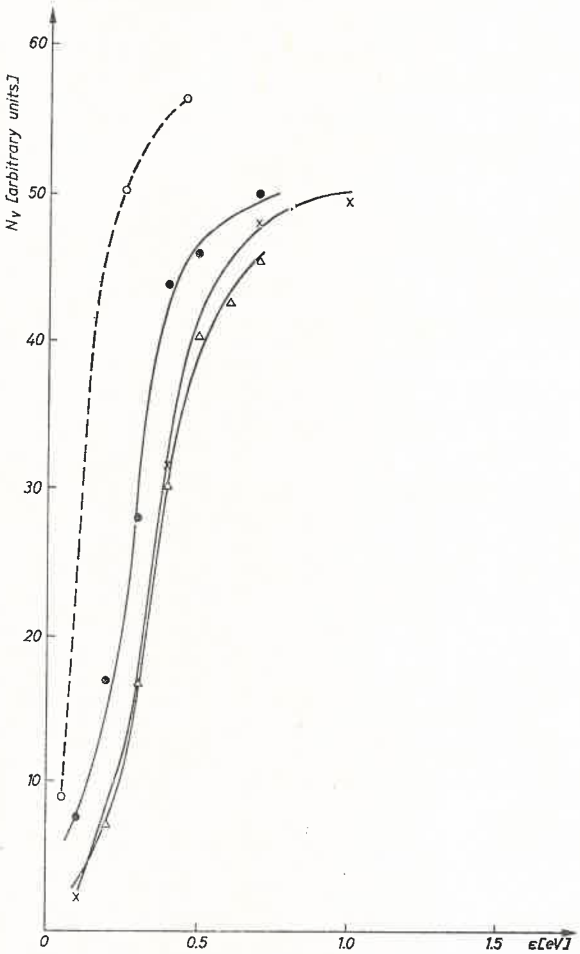

Fig. 4. Density of states vs energy ε in the emitting electron band for several InAs samples. Points of the dashed curve were calculated by the author from data given in [1]

of the kinetic energy spectrum — ΔE) with sharp peaks; in particular, they differ from the wider and "blurred" distributions from InSb, GaSb and Ge. The distributions from InAs exhibit two interesting features:

(a) linear increase in width ΔE of the distributions with rising $h\nu$ — this will be discussed later on,

(b) slight but distinct shifting of the peaks to the right with rising $h\nu$.

In the work of Gobeli and Allen [1] this shift amounted to about 0.2 eV for a 0.64 eV increase in photon $h\nu$. This can be explained by the bending observed in the distributions of the density of states in the upper parts of the valence bands (Fig. 4)[1]. For photon energies from 5.2 to 5.8 eV the peaks of the $N(E)$ distributions lie at distances from 0.6 to 0.8 eV from the high-energy ends — i. e. approximately, from the top of the valence band. For the same photon energies the curves shown in Fig. 4 reach a plateau.

The good time repeatability of the distributions as well as the lack of "blurring" of their tails confirm that the heated surfaces were stable, i. e. that the cleaning process was efficient.

In order to extract more information from the results the dependence of the width ΔE on $h\nu$ was analysed. The diagrams shown on Fig. 5 have been drawn using the results of the present study and those given in [1] and [9]. It is seen that three plots ΔE vs $h\nu$ are linear[2];

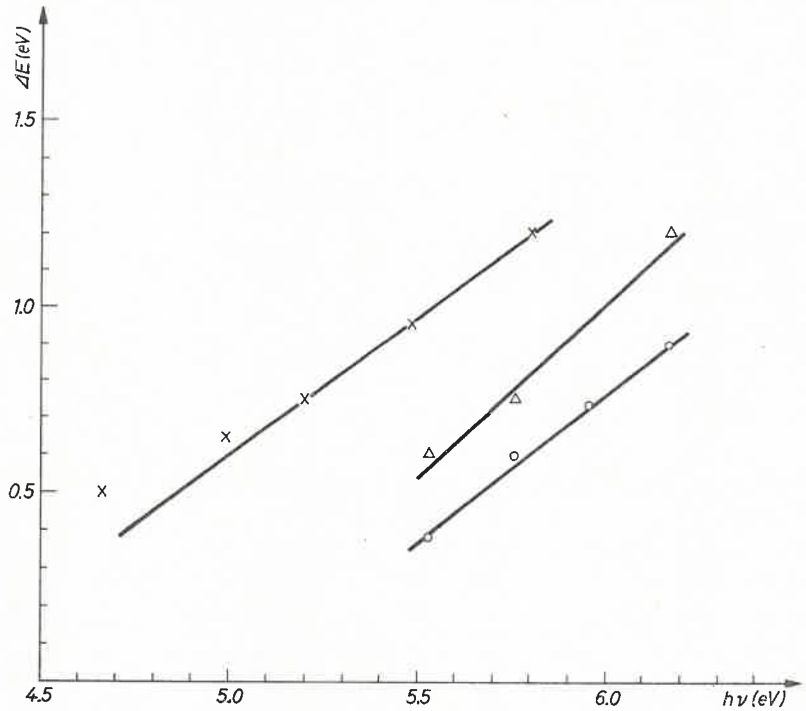

Fig. 5. Width of photoelectron distributions vs the energy of exciting photons for n-type InAs; × — data obtained in the present work, △ — data from [1], ○ — data from [9]

[1] Curves of Fig. 4 have been obtained from the $N(E)$ characteristics and the yield spectra by the method of Kindig and Spicer [10].

[2] In Fig. 5 the lowest point of the author results deviates from the straight line. The value of ΔE at this point has been determined for such a low photon energy that, as a result of the very low valence yield, the value of ΔE is increased by the contribution of the "above-threshold" emission.

this is connected with optical transitions to the conduction bands. If ΔE, which determines the kinetic energy of the fastest electrons, rises proportionally with $h\nu$ then the following relations is satisfied:

$$h\nu - E_{si} = \Delta E, \tag{3}$$

where

$$E_{si} = E_{vac} - E_{\Gamma 15v} = \text{const}, \tag{4}$$

is the electron ionisation energy of the crystal surface.

The linear dependence ΔE on $h\nu$ for InAs means that:

(a) the fastest photoelectrons in each of the distributions $N(E)$ originate from a direct transitions because relation (3) is satisfied for such transitions,

(b) it is possible to estimate the photoelectric threshold $h\nu_{t_1}$ by extrapolation of the straight lines of Fig. 5 to the point of intersection with the $h\nu$ axis.

This extrapolation from data given in [9] and [1] yields $E_{si} = 5.03$ eV and 4.98 eV respectively. These values are distinctly lower than 5.3 eV [1] and are in agreement with the conclusion that can be drawn from the results given in [2].

Extrapolation of the straight line obtained from the results of the present study yields $E_{si} = 4.25$ eV, which is in agreement, within the limits of experimental error, with $h\nu_{t_1} = 4.33$ eV.

The curves $N(E)$ from the (111) InAs surfaces have not been included in this paper because the experimental results are too scanty. However, it can be said that the distributions from these surfaces do not differ much from the curves $N(E)_{(110)}$.

2.3. "Above-threshold' emission from InAs

In a previous work [7] the author assumed that the "above-threshold" emission is smaller than the resolution of the energy distributions when

$$\Delta E \cong h\nu - h\nu_t. \tag{5}$$

For distributions from InAs the above equation is satisfied, within the experimental error, for all the photon energies used except for $h\nu = 4.66$ eV. For the distribution obtained for the latter energy (Fig. 3) the "above-threshold" emission is reflected by the "step" on the high-energy shoulder. A rough estimate of the width of the emitting above-threshold states gives a value of 0.15 eV. This corresponds to the energies of the lower half of the energy gap. This emission probably originates from surface states in the energy gap and from levels lying in the surface layer penetrated by the exciting radiation. Compared with GaAs [8], the "above-threshold" photoelectric yield in InAs is considerably smaller.

2.4. Energy model of the InAs surface layer

It results from the foregoing discussion that the direct optical transition $\Gamma_{15v} - E_{vac}$ can be identified with the threshold of valence emission of the InAs samples studied. Therefore, the above energy distance determines the position of the top of the valence bands with respect to the vacuum level. Within the experimental error, the lower threshold $h\nu_{t_1}$

TABLE I

Electron parameters of heated (110) InAs surfaces of InAs n-type

Bulk electron concentration n_e (cm^{-3})	Lower photo-electric threshold $h\nu_{t1}$ (eV)	Work function φ (eV)	Absolute band bending ΔV (eV)	Surface electron affinity χ_s (eV)	Bulk ionisation energy E_i (eV)
$\sim 1.10^{17}$	4.33 ± 0.10	4.30 ± 0.05	0.32	3.98	4.65

corresponds to the Fermi level at the surface (Table I and Fig. 6) — hence the upward bending of the energy band by almost a full width of the band gap. The layer nearest to the surface is strongly p-type. There are reasons to believe that on the surface there is a large density of centres which can trap electrons leaving the space charge region. There-

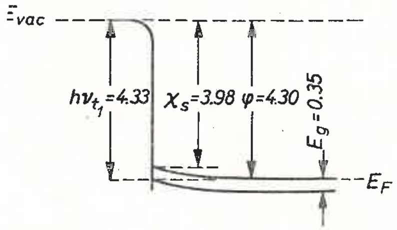

Fig. 6. Energy model of the surface layer of heated (110) n-type InAs single crystal. The numerical values are given in eV

fore, the surface structure of InAs can vary to a large extent, from upward band bending as in [2] and in the present study, to downward band bending and degenerate n-type surface. The latter possibility occurs after covering the surface with monolayer Cs [2] and after making the MOS layer [11].

4. *Conclusions*

1. In this work, the photoelectric yield from n-type InAs single crystals heated in vacuum was investigated. At photon energies from 4.2 to 5.8 eV the yields increase up to $\sim 5 \cdot 10^{-3}$ el./abs. photon. It was assumed that lower photoelectric threshold corresponds to emission from the top of the valence bands; the estimated value of this threshold is (4.33 ± 0.1) eV. Above of this threshold the yield curves $Y(h\nu)$ consist of two parts corresponding to indirect and direct transitions, respectively.

2. The author has observed that the relationship between the width ΔE of the photoelectron energy distributions and the values of $h\nu$ for which these distributions have been obtained is linear for both of the InAs surfaces examined in the present work and atomically clean surfaces [1, 9]. Extrapolation of these straight lines to the intersection with the $h\nu$ axis provides a new way of tentative estimation of the lower photoelectric threshold.

3. The proposed energy model of the (110) surface layer of InAs samples heated in vacuum is similar in quality to the behaviour of the same surface cleaved in high vacuum [2].

Both models involve upward band bending by the whole width of the gap; however, the electron parameters of the surfaces investigated in the present work are consistently lower by 0.6 eV compared to those given in [2].

4. The author's conclusions is that InAs surfaces prepared in this work could be covered with a photoelectrically inactive layer producing the above-mentioned lowering of $h\nu_t$, φ and χ_s. That this layer is not composed of oxides is confirmed by the similar — after allowing for the shifts in photoelectric thresholds — photoelectric yields from heated surfaces and from surfaces cleaved in vacuum.

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