

J. WOJAS, B. SEROCZYŃSKA-WOJAS

**Application of Photoelectron Spectroscopy to Study the Surface States on  
GaAs Single Crystals**

1. Introduction

In Ballantyne's photoemission theory [1] an influence of spectral properties of the clean surface and the bulk of semiconductors is enhanced in equations for photoemission yield, by taking into account  $\alpha(h\nu)$  and  $\delta_2(h\nu)$  dependences. According to the data from that paper [1], a photoelectron emission mechanism for the most of the crystalline semiconductors relies on the nondirect electron transitions<sup>1</sup>, especially at excitation by photons having energies near the thresh-

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<sup>1</sup> They are not identical to the indirect transitions.

hold energies  $h\nu_t$  of photoemission.

In the case of nondirect transitions the quantum yield equation has the form

$$Y \approx \frac{\alpha(h\nu)}{\epsilon_2(h\nu)} \frac{1}{(h\nu)^2} (h\nu - h\nu_t)^3 \quad / 1 /$$

where  $\alpha(h\nu)$  is the spectral absorption coefficient of light and  $\epsilon_2(h\nu)$  is the modulus of imaginary component of dielectric constant function.

The most valuable studies of photoemission from semiconductors of diamond structure are performed for single crystals with oriented surfaces: (100), (110) and (111). Since it is not apparent, that the distributions of the reflection coefficient  $R(h\nu)$  and the ultraviolet absorption for the mentioned above surfaces should be identical, one can suppose, that the optical properties of the studied samples in the above mentioned directions will influence on the obtained distributions  $Y(h\nu)$  and their derivatives.

The authors have studied the spectrum of  $R(h\nu)$  for (100) and (111A) surfaces of GaAs single crystals<sup>1</sup> and have calculated the appropriate  $\alpha(h\nu)$  distributions. Using the Ballantyne's function described by the relation / 1 /, were determined the "theoretical" quantum yield distributions for the mentioned above three types of GaAs surfaces and then derivatives of distributions  $Y'(h\nu)$  were compared with respective derivatives of experimentally measured yield functions from real GaAs surfaces, which have been the object of the preceding

<sup>1</sup>  $R(h\nu)$  distribution for (110) surface of GaAs was taken from the paper [2]. The above mentioned  $R(h\nu)$  distributions are presented in Fig.1.

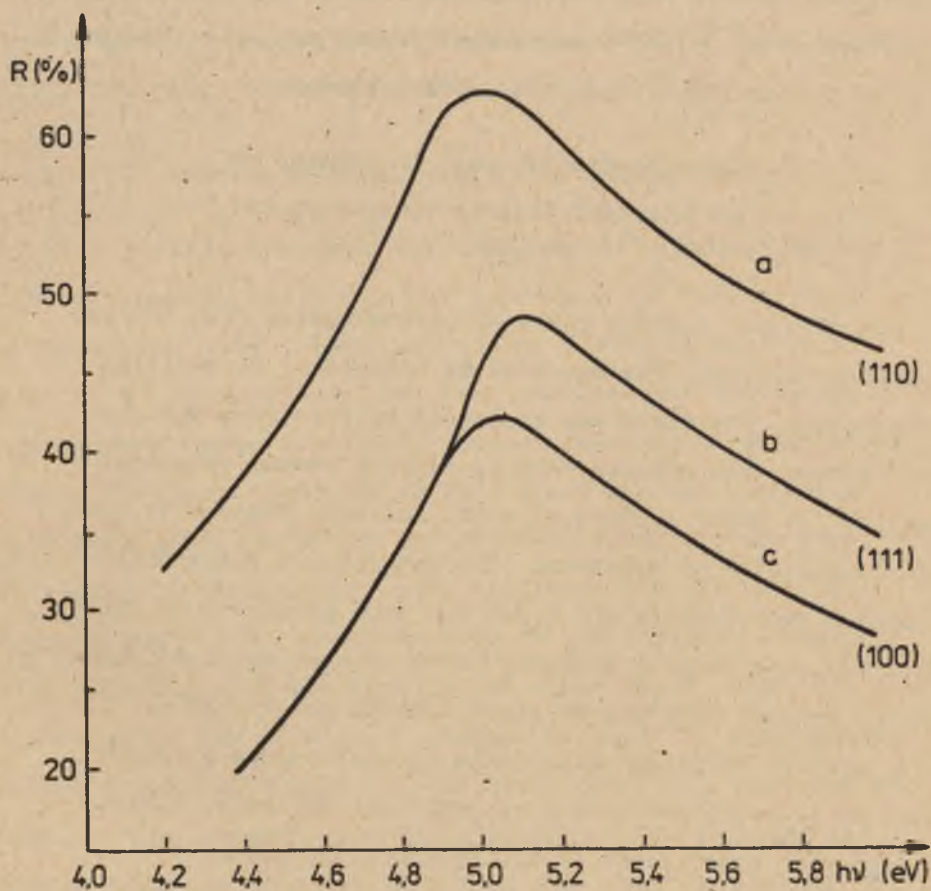


Fig. 1 Reflectivity characteristics for three oriented GaAs surfaces. The curves b and c are obtained experimentally in Institute of Physics of Jagiellonian University. The curve a from data of Phillip and Ehrenreich [2].



papers, i.e. [3] and [4]. The comparison was performed, among others, in order to find the influence of the real surfaces on the course of  $Y(h\nu)$  characteristics and probable occurrence of photoemission from the surface states.

## 2. The experimental part of studies on the spectral distributions of yield $Y(h\nu)$ .

The absolute quantum yield of photoemission from the oriented GaAs crystals was measured as a function of exciting photon energy. The yield was expressed by electrons per absorbed photon. The samples were located in vacuum spherical capacitor the inner surface of which has been covered by conducting collector of electrons. The optical and electrical set up for measurements of  $Y(h\nu)$  has been presented in the paper [3]. A spherical symmetry of the measuring capacitor with the maximal limiting of glass outlets and the metal parts, enabled to detect all of the photoelectrons emitted. In the same vacuum set were also performed the other characteristics of photocurrent in the spherical retarding field. This method has been first used in Poland by Subotowicz [5].

Preparation of the investigated samples to measure the quantum yield relied on the initial polishing the surface using the fine alundum powder to obtain the mirror-like surface, then on etching with few percentage solution of bromine in methanol /EM/ and annealing the crystals in vacuum rising gradually temperature up to  $380^{\circ}\text{C}$ . According to informations from the literature and the results from the Auger effect measurement [6], such treatments of crystals create

on the III-V semiconductors the real surfaces of the moderate cleanness degree. After termination of the technological process, the pressure in the set up was about  $10^{-8}$  Tr, which was afterwards bettered to obtain  $1 + 5 \cdot 10^{-9}$  Tr.

### 3. Results of measurements and calculations

As it was mentioned, the spectrum distributions of the absolute quantum yield has been performed for GaAs of three orientations (100), (110) and (111A); several samples of each of the orientations have been examined and the averaged curves were drawn. The derivatives of these averaged distributions  $Y'(h\nu)$  are presented in Figs 2 + 4 and the comparison with calculated, respective Ballantyne's functions are made. Of course, initially have been calculated the "theoretical"  $Y(h\nu)$  distributions according with the Ballantyne's relation [1], by using the experimental values of  $\alpha$ ,  $R$ , and  $\epsilon_2$  and assuming the threshold energies  $h\nu_0$  as the experimental values determined for the (100), (110) and (111A) surfaces of GaAs. It was assumed, that distributions  $Y(h\nu)$  obtained in this way, illustrates the yields of the ideal GaAs structures, in the case when onto the surfaces the chemically nonactive films were deposited, causing the lowering of the photoelectric thresholds only. Since the real values of the threshold energies for the cleaved in vacuum or repeatedly cleaned surfaces of GaAs were found to be 5.47 eV and 5.39 eV [7, 8].

By comparing the presented in Figs 2 + 4 data, the attention was directed to the location of peaks and shoulders on the  $Y'(h\nu)$  distribution curves and to the discrepancies

among them. To complete the picture the respective valu-

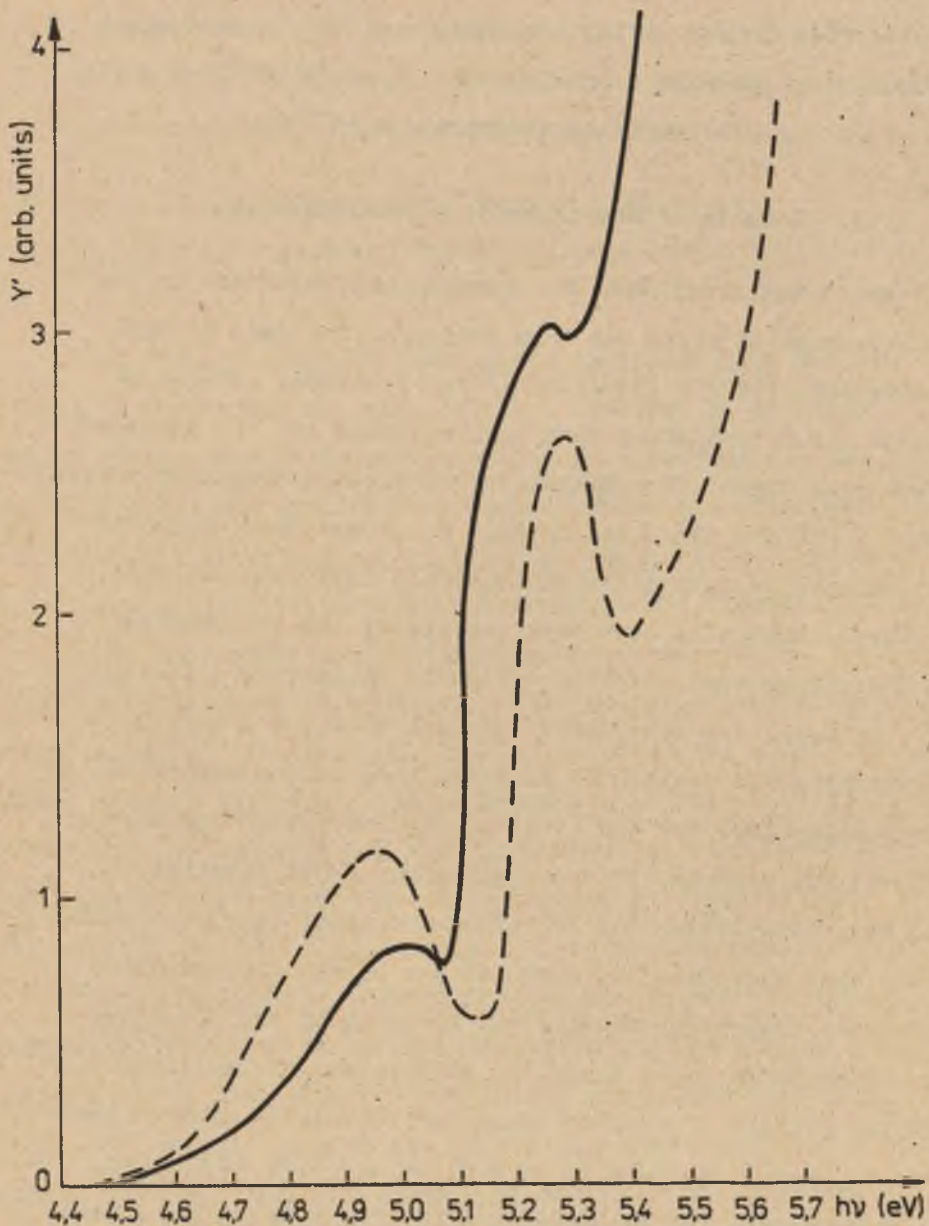


Fig. 2 Comparison of  $Y'(h\nu)$  distribution for real (110) surface GaAs, which is obtained from experimental data with the respective, derivative of Ballantyne's theoretical function for nondirect transitions /the dashed line/.



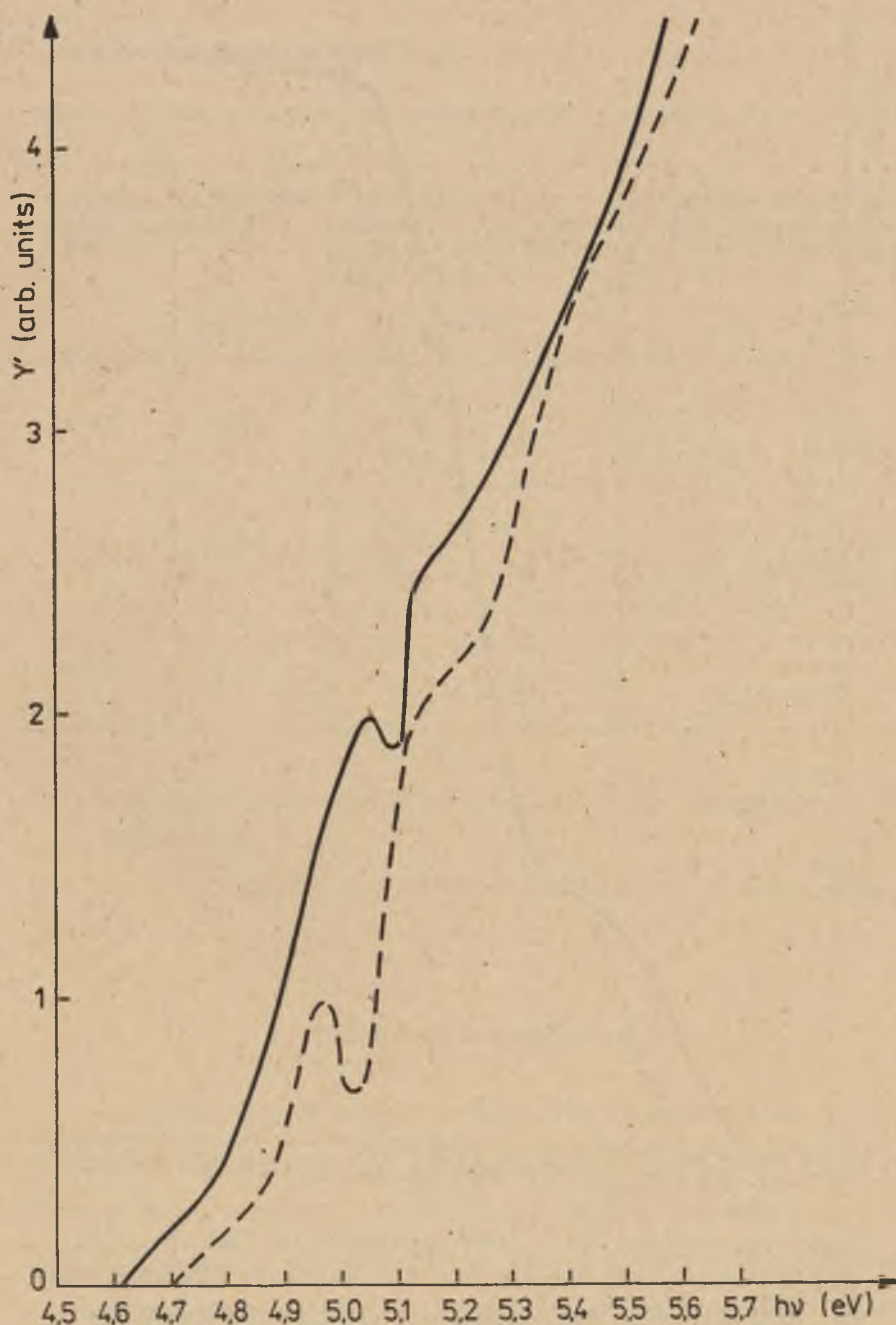


Fig. 3 Comparison of  $Y'(h\nu)$  distribution for real (100) surface GaAs /from experimental data/ with the respective, derivative of Ballantyne's function for nondirect transitions /the dashed line/

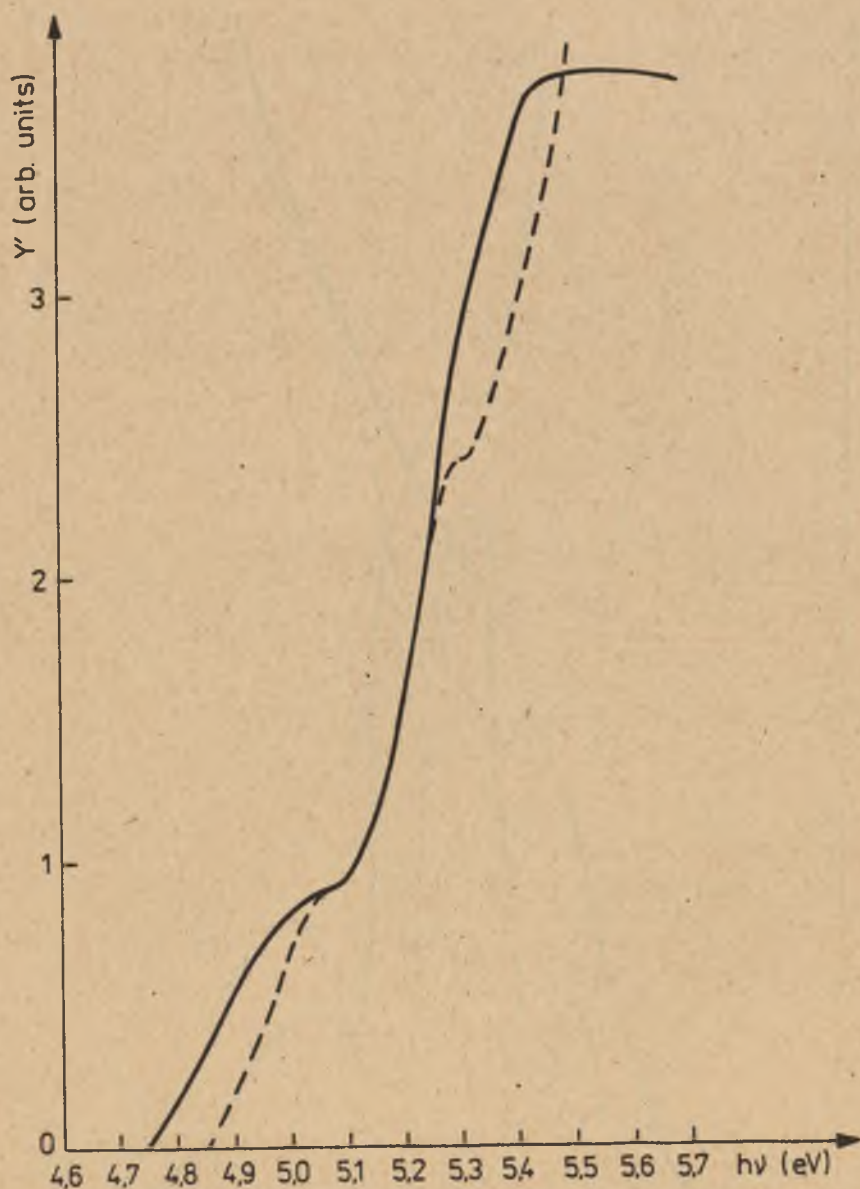


Fig. 4 Comparison of  $Y'(h\nu)$  distribution for real (111) surface GaAs /from experimental data/ with the respective, derivative of Ballantyne's function for nondirect transitions /the dashed line/



es were presented in Table 1.

Table 1. The energies of characteristics points from Figs 2-4

Surface orientation	Threshold energy	Energetic situations of the lower peaks, near the $\mathcal{E}_{V_0}$ point	Energetic situations of the "deep" peaks of the "deep" peaks /in the valence band/
	$h\nu_t$ /eV/	$P_1$ /eV/	$P_2$ /eV/
(111A)	4.70	$P_{1b} = 0.30$ $P_{1d} = 0.30$	$P_{2b} = 0.55$ $P_{2d}$ smoothed
(100)	4.60	$P_{1b} = 0.37$ $P_{1d} = 0.45$	$P_{2b}$ } no peaks, $P_{2d}$ } but plateau 0.55+0.65
(110)	4.45	$P_{1b} = 0.50$ $P_{1d} = 0.55$	$P_{2b} = 0.85$ $P_{2d} = 0.82$

$P_b$  - for calculated distributions,  $P_d$  - for experimental distributions.

The presented values are determined from the valence edge  $\mathcal{E}_{V_0} = 0$ .

#### 4. Results and discussion

The purpose of interduction into Figs 2 + 4 of the calculated distributions  $Y_b(h\nu)$ , reflecting the bulk properties of GaAs crystals, is obtaining of the informations about additional bands connected with the real surfaces of the crystals. Comparison of the mentioned above "theoretical" distri-

tutions for the (110) and (100) surfaces Figs 2 and 3 indicates the small discrepancy between them, especially for the lower photon energies. The lower maximums, connected with the optical properties of the crystals and with the structure of the Ballantyne's function shows the energetic shift of about 0.1 eV in relation to each other which is comparable with the errors originating from calculation and differentiation. Such a good consistence is due, among others, to the consistence of the reflection distribution curves for all investigated surfaces /Fig.1/. The lower values of R for the (100) and (111A) surfaces than for the (110) one indicates the nonideal surface quality after the polishing and etching treatments.

Additionally, comparison of "theoretical" and experimental  $Y^*(h\nu)$  distributions for three types of the surfaces results in the following observations :

a/ the similar character and the coincidence of  $Y_b^*(h\nu)$  and  $Y_d^*(h\nu)$  distribution maximums is observed at their low energetic regions / up to 0.6 eV from their photoelectric thresholds / 1/.

b/ for the (110) surface the experimental  $Y_d^*(h\nu)$  distribution reflects fairly well the derivative of the Ballantyne's function

c/ the experimental  $Y_d^*(h\nu)$  distributions in the case of (100) and (111A) orientations do not exhibit the further maximums, but diffused hump and plateau respectively for the energies

1/

It was considered the small shifts to the left of the near by threshold intervals on the experimental  $Y_d^*(h\nu)$  distributions which will be discussed below.

higher than 5 eV / Figs 3, and 4 /.

For the purpose of discussion we recollect the kinds of the surface states occurring in the band gap and in the valence bands of the III-V group semiconductors. With regard to the intrinsic states on the surface of these semiconductors in 1970- ties has been elaborated the so called "G-S-C-H" [9, 10] model in which filled by electrons states are attributed to the V group atoms, and the empty states, connected with the III group atoms, seem to be located in the upper part of the band gap. Bands of the filled states appear to be located fairly deep in the valence bands of semiconductors; in the case of GaAs the distance from the valence band maximum is greater than 1 eV. On the real surfaces and in the defected surface layers exist the states resulting from variety of defects and from gas adsorption. For GaAs the bands have been studied by Szuber [11] by the use a method of photoelectron spectroscopy from the real (100) surface. He has found two small and diffused peaks, the lower one /referred to the defect states/ overlaps partially the valence band of GaAs. The quantum yield of this diffused band was found to be about 20% of the valence electrons yield for photon energies near the  $h\nu_0$  value. The other filled surface states are within the band gap of GaAs, which was observed by Szuber [11] and Wojas, specifying the effect as the "above-threshold emission" from GaAs [13].

It is not the subject of this paper to identify the surface levels located in the gap, but theirs presence or absence in the upper regions of the valence bands, with respect



to the threshold energy, which is identical with the location of the valence band maximum. Thus comparing the experimental data with the presented above informations concerning the surface states, it can be firstly concluded, that in the analysed range of energy / about 1.3 eV respectively to  $\epsilon_{V_0}$  / there exist no energetic bands having yields  $\geq 0.1$  of the valence-band emission yield, since are not observed the steep increase of the  $Y_d(h\nu)$  yields and <sup>no</sup> additional / with respect to the "theoretical" distributions / maximums on these curves. This appears to be consistent with the G-S-C-H model, with respect to localization of the intrinsic-state band, the edge of which should be located by 1.35 eV lower than threshold. Conditions of this work enabled to discover the band located so deeply.

Regarding the possible presence of the defect band, can be stated, that the small emission connected with it occurs in Figs 3 and 4 as the convexity in the experimental  $Y_d^*(h\nu)$  distributions very near to the threshold and as the shift of these characteristics to the lower energy region. The rough approximation gives for the GaAs (110) surface [3] that the adding, surface photoemission exceeds the valence-band emission at the exciting photon energy  $h\nu = 4.7$  eV. This effect is not fulfilled for the GaAs (110) surface. Since for the (110) surface of GaAs this effect appears to be small and unmeasurable /Fig.2/ it suggest the defect density to be larger on the polar surfaces of GaAs or the native oxide-films to be thicker on these surfaces.

The second effect, confirming the above statement relies on the considerable discrepancies between the experimental

and "theoretical" distributions for energies  $h\nu > 5.1$  eV for the case of (110) surface and for  $h\nu > 5.3$  eV for the (111A) surface. These anomalies /Figs 3 and 4/ can be explained by considerable scattering of excited photoelectrons in the defected surface layers. Thicknesses of these layers were determined in recently performed ellipsometry studies on the real GaAs and InSb surfaces ; some results will be published [12] . It was found, that after reduction of the surface oxides by polishing and etching of crystals, remain thicker, defected layers on the (100) and (111) surfaces than on the (110) surfaces. However the accurate analysis of the influence of defect levels on the photoemission effect from GaAs requires the further studies to be performed.

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