Vol. A51 (1977) *ACTA PHYSICA POLONICA* No 1

A STUDY OF THE PHOTOELECTRIC PROPERTIES AND WORK FUNCTIONS OF THE (111*A*) AND (111*B*) SURFACES OF GaAs SINGLE CRYSTALS*

By J. Wojas

Department of Physics, Olsztyn Higher Pedagogical School**

(Received June 3, 1975; Revised version received February 10, 1976)

In this work the quantum yield spectra, photoelectron energy distributions and work functions of ten etched and vacuum-heated *n*-type GaAs samples with (111*A*) and (111*B*) surfaces have been determined. There are certain differences in the shape of the distributions and in the photoelectric thresholds of the two types of surfaces. The values of $h\nu_t$ obtained by extrapolation of the straight lines $\sqrt[3]{Y(h\nu)}$ are 4.7 eV for (111*A*) and 4.4 eV for (111*B*), respectively. The work functions of the samples have been obtained from photoemissive measurements in high vacuum and by Kelvin's method. On the basis of these measurements the author proposes an energy models for the (111*A*) and (111*B*) surfaces of *n*-type GaAs.

1. *Introduction*

The physical properties of exposed GaAs surfaces with low indices were analysed by measuring LEED and work functions after the samples had been covered with a layer of Na [1] or Cs_2O-Cs [2]. In this work, the photoelectric properties of (111*A*) and (111*B*) surfaces were examined after etching them and then heating in high vacuum at 400°C and 550°C. The microscope patterns of those surfaces were such as described in [3]. Also, the work functions of these surfaces were measured by two methods, and their UV reflectivities were determined.

2. *Experimental*

Ten GaAs *n*-type samples were studied whose exposed surfaces were of the (111*A*) and (111*B*) type, so that their properties under the same vacuum conditions could be compared. The electron concentration of the samples ranged from 6.10^{16} to 5.10^{17} cm^{-3}. After etching the samples were quickly placed in the vacuum apparatus. Measurements of the photoemissive characteristics were made at a pressure of $(10^{-8} \div 10^{-9})$ Tr. The

---

* This work has been supported by the Institute of Physics of the Polish Academy of Sciences.

** Address: Zakład Fizyki, Wyższa Szkoła Pedagogiczna, Żołnierska 14, 10-561 Olsztyn, Poland.

absolute quantum yield of the tested samples was measured within the photon excitation range (4.2÷5.8) eV. The energy distributions of the photoelectrons emitted were determined by measuring the current-voltage characteristics in the field of a spherical capacitor. In this work, over 100 photoelectron energy distributions $N(E) = f(E)$ were obtained — i. e. 5 or 6 distributions for a given surface of each sample at various $h\nu$ values of the photons concerned.

3. *Results*

The quantum yields obtained experimentally were used to determine the photoelectric thresholds $h\nu_t$ (Figs. 1 and 2).

The extrapolations of the yield curves were made by fitting the function below to the

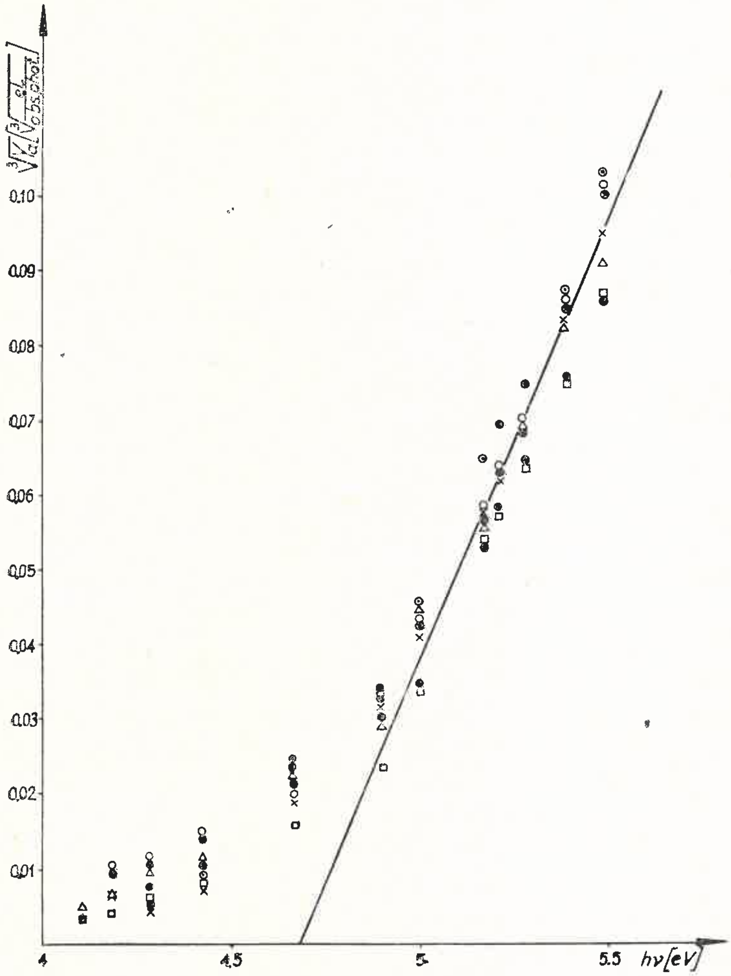

Fig. 1. Quantum yield vs photon energy for the vacuum heated (111*A*) surfaces of *n*-type GaAs (averaged curve for 7 samples)

experimental data obtained (according to [4], [5] and others):

$$Y = k(h\nu - h\nu_t)^3, \tag{1}$$

where k is a constant.

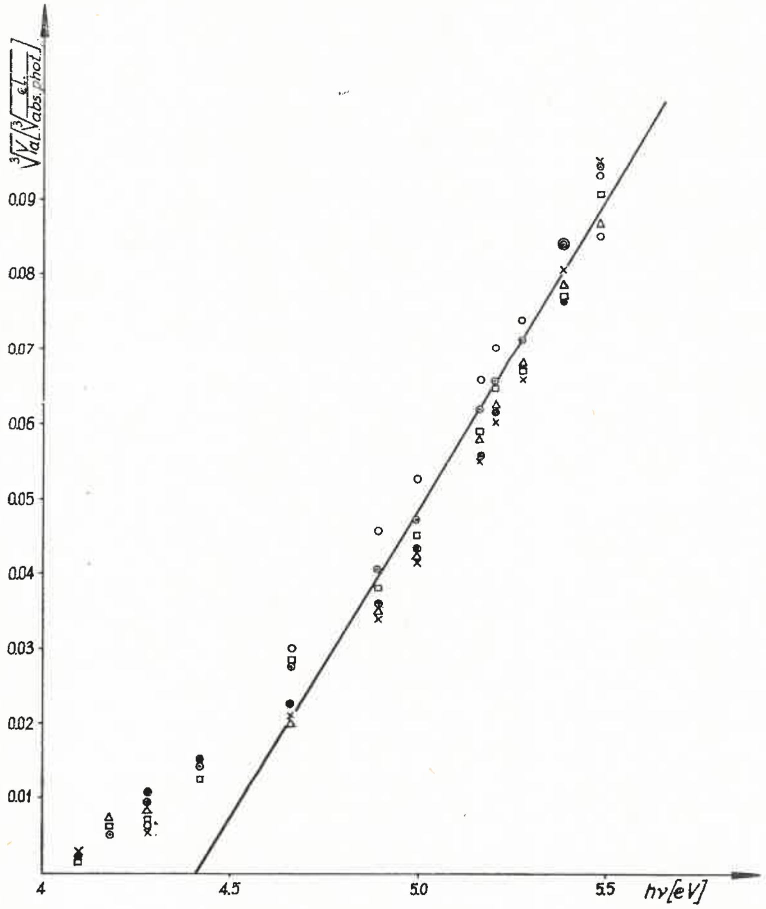

Fig. 2. Quantum yield vs photon energy for the vacuum heated (111B) surfaces of n-type GaAs (averaged curve for 6 samples)

From such yield distributions the values of $h\nu_t$ were estimated; they were assumed to be the energy positions of the tops of the valence bands at the (111A) and (111B) surfaces of the samples studied (Table I).

In general, the distributions exhibit the following characteristic features:

a. single maxima and overlapping low-energy slopes, the latter feature being characteristic of the valence band emission;
b. the maxima of the electron distributions from the (111A) and (111B) surfaces exhibit a minimal shift, but the distributions from (111A) have a longish high-energy tail and are wider than the (111B) distributions by approximately 0.3 eV.

TABLE I

Photoelectric parameters and work functions of (111) surfaces of *n*-type GaAs samples

	Type of surface	
Measured values	(111*A*)	(111*B*)
$h\nu_t$ [eV]	4.7	4.4
φ [eV] (from photoemissive characteristics in high vacuum)	4.1	4.3
φ [eV] (by the Kelvin method, in air atmosphere)	4.5÷4.65	
Surface electron affinity $\mathcal{K}_S$ [eV]	3.3	3.0

The occurrence of elongated high-energy tails in the photoelectron energy distributions is caused by above-threshold emission from the surfaces studied. The high-energy parts of the photoelectron distributions associated with above-threshold emission, mainly originating from the surface states in the band gap, were separated by the method applied by Wojas [6] for other GaAs surfaces. The longer tails of the distributions from the "gallium" surfaces are evidence of the fact that the bands of emitting states at these surfaces are wider. Using the method of Kindig and Spicer [7] the author has calculated and compared the density-of-state distributions of the emitting bands (Figs. 3 and 4). In the opinion of the author the small maxima near the peaks of the emitting bands originate from additional, filled energy levels overlapping with the valence bands. Apart from surface states, levels near to the surface might also be involved in this process. The full region of bending of the energy bands does not contribute to the process of photoemission because its thickness in the samples investigated is several times greater than the geometric depth of photoemission. On comparing Figs. 3 and 4, it is seen that the small maximum of the curve obtained from (111*A*) surfaces is wider and more distinct. This, and the differences in the energy distributions $N(E)$, is connected with the properties of the two types of (111) surfaces. In general, surfaces of the A^{III} types are less active chemically [8], as can be inferred, among other things, from their microscope pictures after etching. The gallium surface of GaAs samples is characterized by a smaller adsorption of O and O_2 than the arsenic one; the respective sticking probabilities of O_2 are equal to 10^{-5} and 10^{-4} [9]. The greater extent of electron capture by oxygen atoms in the case of (111*B*) surfaces results in a narrowing and weakening of the small maximum of Fig. 4.

In order to examine emission from surface states more fully, photocurrent characteristics were obtained at such a photon energy ($h\nu = 4.66$ eV) at which surface state

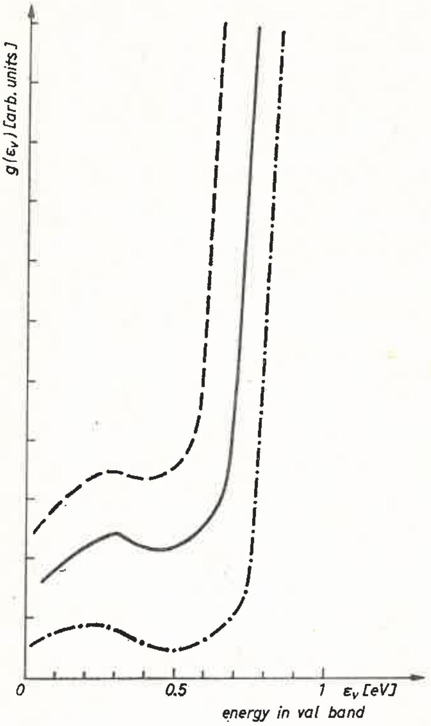

Fig. 3

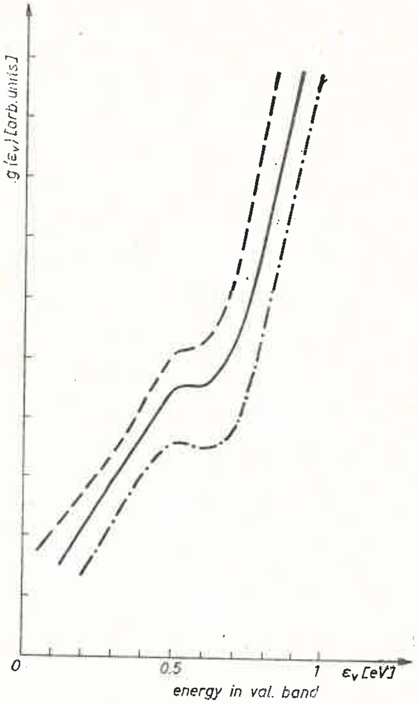

Fig. 4

Fig. 3. Valence-band density of states in (111*A*) surface layer of *n*-type GaAs (dashed lines delimit curve--spread intervals)

Fig. 4. Valence-band density of states in (111*B*) surface layer of *n*-type GaAs (dashed lines delimit curve--spread intervals)

emission is dominant. The obtained distributions $N(E) = f(E)$ for the (111*A*) and (111*B*) surfaces had the widths: 0.7 eV and 0.3 eV, respectively. The Gauss function was then fitted to these distributions. It was found that there was good agreement between experimental and calculated curves. Therefore, the author concludes that the surface states at (111*A*) and (111*B*) occupy the lower part of the energy gap, and exhibit Gaussian density distributions.

4. *Conclusions*

1. In the photon energy range (4.1 ÷ 5.5) eV there is a considerable rise in the quantum yield of photoelectrons from *n*-type (111*A*) and (111*B*) GaAs surfaces. The photoelectric thresholds of these surfaces are shifted with respect to each other by 0.3 eV. At the photon energy $h\nu = 5.5$ eV both values of quantum yield come close to 10^{-3} el./abs. photon, where $Y_{(111A)} > Y_{(111B)}$. The greater rise in quantum yield in the case of type *A* surfaces is explained by the author by stronger scattering of low-energy electrons by these surfaces with a simultaneous widening of the high-energy parts of the electron spectra with rising $h\nu$.

2. No noticeable differences are observed between the quantum yield distributions and the energy distributions $N(E)$ of GaAs samples heated in vacuum at 400°C and 550°C, respectively. Therefore, it can be concluded that the molecular oxygen layer, which is removed by heating at 550°C [9], does not influence the photoemissive properties of (111) GaAs surfaces.

3. In the density-of-state curve obtained from (111*B*) surfaces the small maximum is less marked. This, and some other properties observed by the author (e. g. the values of $h\nu_t$), indicates that (111*B*) surfaces exhibit similar properties to (110) GaAs surfaces.

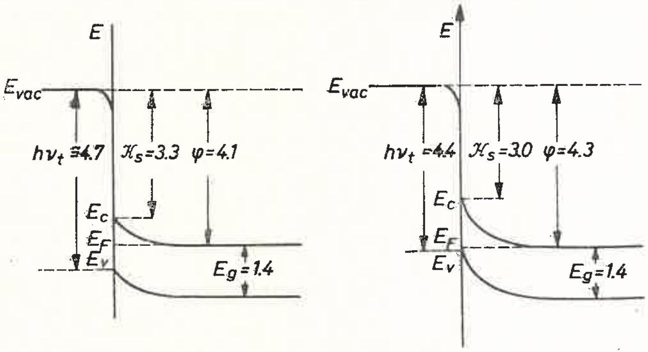

Fig. 5. Energy band diagram for (111*A*) and (111*B*) surfaces of GaAs examinated samples. (All numerical values are in electronovolts)

4. The author proposes energy models of the heated *n*-type (111*A*) and (111*B*) GaAs surfaces (Fig. 5). These models are characterized by similar work functions φ and different band-bending of the energy bands. The smaller bending observed at (111*A*) surfaces is caused by their being covered with Ga atoms.

The author would like to thank Professor M. Subotowicz of the Marie Curie-Skłodowska University for his permission to perform the work function measurements of the GaAs crystals by Kelvin's method, and Dr A. Kisiel of the Jagellonian University for the UV reflectivity measurements.

REFERENCES

[1] J. Chen, *Surf. Sci.* **25**, 305 (1971).
[2] L. James et al., *J. Appl. Phys.* **42**, 4976 (1971).
[3] J. Łagowski et al., *Surf. Sci.* **40**, 216 (1973).
[4] W. Gobeli, F. Allen, *Phys. Rev.* **137**, A245 (1965).
[5] T. Fischer, *Surf. Sci.* **13**, 30 (1969).
[6] J. Wojas, *Acta Phys. Pol.* **A48**, 603 (1975).
[7] N. Kindig, W. Spicer, *Phys. Rev.* **138**, A561 (1965).
[8] J. I. Pankove, *Optical Processes in Semiconductors*, Warsaw 1974.
[9] D. Pretzer, H. Hagstrum, *Surf. Sci.* **4**, 265 (1966).