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**SURFACE PHOTOVOLTAGE SPECTROSCOPY  
OF REAL n-TYPE GaAs(110) SURFACES**

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**SURFACE PHOTOVOLTAGE SPECTROSCOPY  
OF REAL *n*-TYPE GaAs(110) SURFACES \***

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**ABSTRACT**

*N*-type GaAs single crystals cut parallel to the (110) plane and doped with phosphorus by ion beam implantation were used in the present study. Temperature dependence of the bulk electrical conductivity showed two distinct activated regions with activation energies  $E_{t1} = 0.75 \pm 0.04$  eV, and  $E_{t2} = 0.12 \pm 0.04$  eV. The first activation energy is probably that of deep phosphorous impurities, while the second was related to long range disorder in the sample near room temperature. Surface photovoltage studies at room temperature were carried out at atmospheric pressure and in vacuum for etched and unetched samples. For *n*-type GaAs etched surface, the experimentally observed surface states were not found to change their positions by changing the pressure. But in the case of etched samples the surface states showed some redistribution under vacuum. The time constants for the initial rise and fall of CPD by illumination and after switching it off,  $\tau_1$  and  $\tau_2$ , respectively, were found to depend on the illumination intensity and photon energy. Their values range between 4 and 15 s.

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**1. INTRODUCTION**

GaAs is an important direct gap III-V semiconductor from the applied point of view. Its high electron mobility and relatively wide gap (1.5 eV at 300K) make it particularly suitable for use in devices working at high frequencies and temperatures. However, its performance in such devices is strongly dependent on its surface conditions, especially when it is brought in contact with an electrolyte, a metal or another semiconductor.

Studies of the GaAs surfaces were concentrated mainly on the (110) clean surfaces<sup>1)-5)</sup> due to the ease of cleavage in this direction. But other surfaces were also investigated either in the real state<sup>6),7)</sup>, or after cleaning by ion beam bombardment followed by annealing<sup>8)</sup>.

Surface photovoltage spectroscopy (SPS) has been successfully employed for studying the surface states of many semiconductors<sup>9)-13)</sup>. This method is based on the observation of the step-like changes in the spectral distribution of surface photovoltage, related to transitions between surface states and the conduction band or valence band.

This work aims at studying the room-temperature real (110) surface states of *n*-type GaAs at atmospheric pressure and low vacuum, as well as the effect of surface etching on these states using the SPS technique.

**2. EXPERIMENTAL**

The *n*-type GaAs single crystals used in this work were obtained from the institute LAMEL, Bologna, Italy. The crystals were cut parallel to the (110) plane and doped with phosphorous using the ion beam implantation technique at a dose of  $1 \times 10^{15}$  cm<sup>-2</sup> and an energy of 200 KeV, followed by annealing at 900°C for 5 min. in continuous flow of nitrogen gas.

Prior to the measurements, the samples were mechanically polished using fine alumina powder ( $\sim 0.5 \mu\text{m}$ ) to obtain parallel flat surfaces, after which they were etched in a 1:1 mixture of HCl and HNO<sub>3</sub> for a few minutes at about 100°C. It is worthwhile to mention that the electric contacts to the samples were ohmic up to  $\pm 100$  V.

Surface photovoltage measurements were carried out using a voltage modulation method (14). Here the surface photovoltage was measured using a vibrating reed detector as the change of the steady state contact potential difference (CPD) with respect to a gold-plated phosphor-bronze electrode, in going from dark to illumination conditions. Details of the experimental procedure can be found elsewhere<sup>14),15)</sup>.

The contact potential difference (CPD) was measured as a function of the incident photon energy  $h\nu$ ; the zero point being taken as that value of CPD in dark conditions. SPS spectra were scanned from lower to higher photon energies. Changes in the slope  $\frac{d(\Delta\text{CPD})}{d(h\nu)}$  with photon energy

$h\nu$  will thus correspond to the onsets of electronic transitions, which either populate or depopulate the surface energy states.

An increasing feature of the slope starting at an energy  $E_0 = h\nu_0$  corresponds to an electronic transition from a state  $E_0$  below the conduction band minimum (CBM). Conversely, a decreasing feature of the slope starting at an energy  $E_1 = h\nu_1$  corresponds to an electronic transition to a surface state  $E_1$  above the valence and maximum (VBM).

### 3. RESULTS AND DISCUSSIONS

Fig.1 shows the dependence of the bulk conductivity  $\sigma$  of *GaAs* on temperature  $T$ . As shown, the conductivity increases with temperature, and one can distinguish two linear regions, the activation energies for which are  $Et_1 = 0.75 \text{ eV}$  and  $Et_2 = 0.12 \pm 0.04 \text{ eV}$  respectively.

The activation energy  $Et_1$  is probably that of deep donors, which might be the phosphorous impurity implanted in the samples.  $Et_2$  may be attributed to the long-range disorder resulting from inhomogeneous distribution of ionized impurities in *GaAs* near room temperature (16).

The effect of light intensity on  $\Delta CPD$  of *n-GaAs* single crystals at a wavelength  $\lambda = 0.76 \mu\text{m}$  is illustrated in Fig. 2. It is clear from this figure that  $\Delta CPD$  saturates at a light intensity near  $2 \mu\text{W}/\text{cm}^2$ , which is typical for most of the wavelengths used. Accordingly the SPS of the investigated sample were scanned in the saturation region of  $\Delta CPD$ .

The room temperature surface photovoltage spectra of *n-type GaAs* (110) real surfaces at atmospheric pressure and under vacuum ( $\sim 10^{-3}$  Torr) are illustrated in Figs.3 and 4, respectively. Analyzing these spectra as described before, various surface states could be defined and represented in Table 1.

Results concerning the surface states of real *n-GaAs* surfaces make more confusion than those of clean surfaces because of the greater uncertainty regarding the nature of the surface involved. All the electronic surface features detected by SPS for etched and unetched *n-GaAs* (110) surfaces within and outside the energy gap can be correlated to intrinsic and extrinsic surface states.

It has been previously reported that cleaned *GaAs*(110) surfaces have no intrinsic surface states within the energy gap<sup>(17),(18)</sup>. Surface states outside the energy gap (below VBM and above CBM) may be attributed to foreign adsorbed atoms and molecules, e.g. oxygen, hydrogen, carbon dioxide, nitrogen, oxides of both *Ga* and *As*, complexes, and to dangling bonds at the surface. Surface states band close to CBM being *Ga*-derived, has been detected by low energy loss spectroscopy (19), and photoemission partial yield spectroscopy (20), which is similar to the surface states observed in our results near 1.32, 1.4 eV measured from the VBM. Meanwhile, low energy electron diffraction measurements (21) have revealed that *GaAs* (110) surface has *As* atoms displaced outwards the surface and *Ga* atoms inward in such a way that no nearest neighbour bond lengths are altered. The relative displacement of the cation and the anion within the outermost layer

defines a rotation angle " $\omega$ " which is generally defined by two independent sets of displacements for the cations and the anions. Its value determines the average atomic force.

It can be observed from Table 1 that the transition states  $E_0$  for etched samples occur at 1.3; 1.59; 2.07; 2.38 and 2.95 eV at atmospheric pressure as well as under vacuum ( $\sim 10^{-3}$  Torr). In addition, the transition states  $E_1$  at 1.24; 1.4 eV for the etched samples do not shift as a result of evacuation, while the states  $E_1 = 1.55$  and 2.28 eV are shifted to 1.5 and 2.38 eV respectively.

Regarding the surface structure of *GaAs* proposed by Berkovits et al (23), *GaAs* (110) surface plane possesses a relatively low symmetry. The bulk atoms lying in the (110) plane, form a kind of zig-zag chains aligned along the  $(\bar{1}10)$  with transverse displacement along the (001) direction. Accordingly the shift observed in the energy states  $E_1 = 1.55$  and 2.28 eV respectively may be attributed to a change of the rotation angle  $\omega$ , such a change is believed to be due to partial desorption of foreign atoms, forming complexes with the *As* atoms coming out of the surface plane (24), since the adsorption of foreign atoms produce considerable change in the optical spectra of surfaces and leads to shifts of spectral bands and appearance of new bands.

Moreover, the energy state observed here at  $E_0 = 2.7 \text{ eV}$  for unetched sample at atmospheric pressure is not likely believed that surface state at 2.83 or 2.62 eV observed previously on cleaned (110) *GaAs* surface (23), which disappear upon oxidation of the surface. Accordingly, this state ( $E_1 = 2.7 \text{ eV}$ ) may be related to oxygen adsorption, or oxygen complex compounds at the surface. Besides, the surface state at  $E_0 = 2.9$  and 3.1 eV observed in the present work are in excellent agreement with the results previously obtained by other investigators<sup>(25),(26)</sup>. The energy state at 0.7 eV below conduction band minimum previously detected<sup>(27),(28)</sup>, and which was attributed to the polar surface nature of *n-type GaAs* is not observed in our measurements. This may be due to the fact that the presence of *P* as a dopant in our samples masks this polar effect.

Empty surface states are detected in present measurements at  $\approx 0.7 \text{ eV}$  above the CBM, which were found before by Dose et al.<sup>(5)</sup>. While the surface states at -1.47 and -1.67 observed in unetched surfaces in this work are near to the values of surface states at -1.36 -1.52 eV (28), and the experimental values at -1.4; -1.6 eV (2).

Fig. 5 represents the energy band diagrams of *n-type GaAs* under different surface and pressure conditions, and illustrating the detected surface states and the corresponding transitions. It can be observed from Table 1 and Fig. 5 that except for a few shallow surface states near the CBM or VBM, there are no deep lying surface states within the forbidden energy gap of *GaAs*.

The effect of etching on the surface properties of *n-GaAs* (110) surfaces can be visualized by comparing the band diagrams shown in Figs.5a and b at atmospheric pressure and Figs.5c and d under vacuum.

Electronic surface properties of ultra-high vacuum cleared *GaAs* have been studied using combined CPD and photoemission measurements (17). These authors reported an empty surface state band whose edge lies at 1.4 eV from the VBM, which is similar to the state  $E_1 = 1.4 \text{ eV}$  in

etched real surface observed in our measurements, which is likely believed due to lattice imperfections at the surface or to Ga empty dangling-bond state (22).

The effect of vacuum on the surface states on GaAs (110) surface, can be seen through comparing Figs.5a and 5c for unetched samples, and 5b and 5d for etched surfaces. Under atmospheric pressure, it is expected that oxygen is the most important atomic species which may be adsorbed on the GaAs surface. Exposure of real (110) GaAs surfaces to air or oxygen causes the formation of oxidation products such as  $Ga_2O_3$ ,  $As_2O_3$  and  $As_2O_5$  as observed before using ESKA technique for surface analysis<sup>28),30)</sup>. So adsorption of oxygen at the GaAs (110) surface may produce the surface state at 1.7 eV above VBM observed in the present work. In addition oxygen adsorption induces CPD and SPV variations, and leads if the exposure is high enough to the pinning of the Fermi level  $E_F$ , hence to a variation in the work function  $\phi$ , which produces the shifts observed in the energy of surface states in changing from atmospheric pressure to vacuum condition (compare e.g. Figs.5b and 5d). Ismail et al. (31) considered that the change in the measured work function  $\phi$  along the surface, results essentially from a modification of the surface barrier potential  $V_S$ .

An example of the room temperature surface photovoltage transient curves for unetched GaAs (110) surfaces at atmospheric pressure is illustrated in Fig. 6. As may be observed, the shape of the growth and decay curves vary with the excitation wavelength. At short wavelengths (up to  $0.6\mu m$ ) the behaviour is normal and has exponential variation of CPD with time along the growth and decay curves, having time constants in the range 4.15 s. For long wavelengths (in the near IR, e.g. at  $\lambda = 0.92\mu m$ ), the transient curves show positive spikes observed spontaneously after switching the light on or off, which have time constants ranging from fractions to few seconds. These transients are accompanied by an increase of  $\Delta CPD$ , and hence a decrease in the surface barrier  $V_S$ , which may be attributed to depopulation of surface states. The depopulation process after switching the light on in the spike region, may be due to redistribution of charge carriers between surface states and conduction band or bulk states in a manner similar to IR quenching of photoconductivity.

The time constants for the initial rise (at  $t = 0$ ) and fall of CPD;  $\tau_1$  and  $\tau_2$  respectively, correspond to the charging and discharging, time constants of the space charge layer capacitor.

#### 4. CONCLUSIONS

The results of the experiments have shown the explicit influence of the surface condition, and pressure on the surface photovoltage, and the surface states distribution on real GaAs (110) surfaces. Unlike the results of Germanova et al.<sup>10)</sup> on SPV of real (100)  $n$ -conductive and semi-insulating GaAs surfaces, treated with preepitaxial procedures, which showed that (100) real surfaces has sub-band gap surface states, our results showed that, except of shallow surface states near the CBM, VBM, the energy gap of GaAs, phosphor doped, has no sub-band gap surface states

on the (110) surface. Due to lack of information and surface studies on real GaAs (110) surfaces for better comparison with our results. The informations we give in this work are pioneer in this respect. However, a complete analysis of the results needs more investigations using other surface analysis techniques, to detect the nature of the adsorbed species on such real surfaces.

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**Table I**

Summary of the surface energy states on n-GaAs (110) real surfaces detected by SPS in this work

section	type	$E_0 = E_{cs} - E_{ss}(eV)$		$E_1 = E_{ss} - E_{vs}(eV)$	
		$+ved(\Delta CPD)/d(h\nu)$		$-ved(\Delta CPD)/d(h\nu)$	
		unetched	etched	unetched	etched
A	n-type	1.32	1.30	1.20	1.24
	sample F1	1.95	1.59	1.42	1.41
	in air		2.07	1.55	1.44
			2.74	2.38	1.77
				2.95	2.28
B{		1.24	1.32	1.32	1.24
		1.41	1.59	1.65	1.41
	n-type	1.75	2.07	2.38	1.70
	sample F1	3.10	2.38		
	in vacuum		2.95		
in vacuum		1.24		1.62	
	sample F2	1.80		2.38	
		2.90			

The accuracy for the determination of the energy transitions is  $\pm 0.04 eV$

$E_{ss}$  : Surface state

$E_{cs}$  : Conduction band edge at the surface

$E_{vs}$  : Valence band maximum at the surface

**Figure Captions**

Fig. 1  $\ln\sigma$  (conductivity) versus  $1/T$  for n-type phosphor doped GaAs.

Fig. 2 Effect of light intensity  $I$  ( $\mu W cm^{-2}$ ) on the CPD at a wavelength  $\lambda = 0.76 \mu m$  on (110) n-GaAs surface.

Fig. 3 SPS for n-type GaAs (110) surface at 300 K, curve (1) for unetched surfaces, curve (2) for etched surface both at atmospheric pressure.

Fig. 4 SPS for n-type GaAs(110) surface, at 300K, curve (1) and curve (2) for unetched surface; of two different samples; (3) after etching sample of curve (1).

Fig. 5 Energy band diagrams of n-type GaAs (110) surfaces at 300K; a) unetched at atmospheric pressure; b) etched at atmospheric pressure; c) unetched under vacuum ( $10^{-3}$  torr); d) etched under vacuum ( $10^{-3}$  Torr).  $E_c, E_v$  bulk CBM, VBM respectively,  $E_{cs}, E_{vs}$  the corresponding CBM, VBM at the surface,  $E_{VS} = 0 eV$   $E_F$  is the Fermi level.

Fig. 6 Surface photovoltage transient curves for unetched n-type GaAs (110) surface at two different wavelengths and constant light intensity  $I = 6 \mu W cm^{-2}$ ,  $T = 300 K$

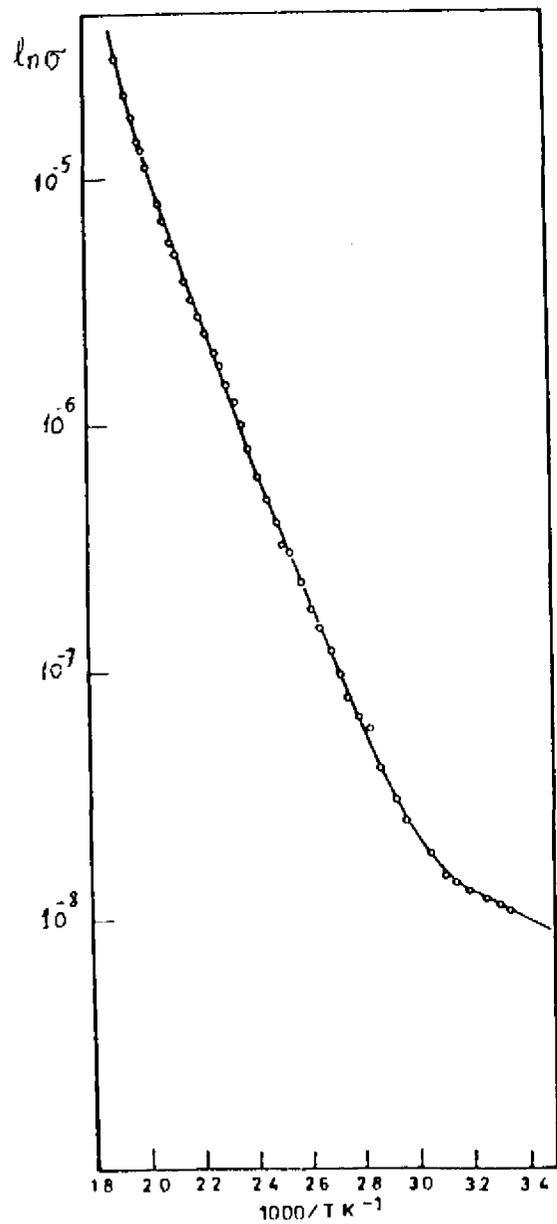


Fig.1  
-11-

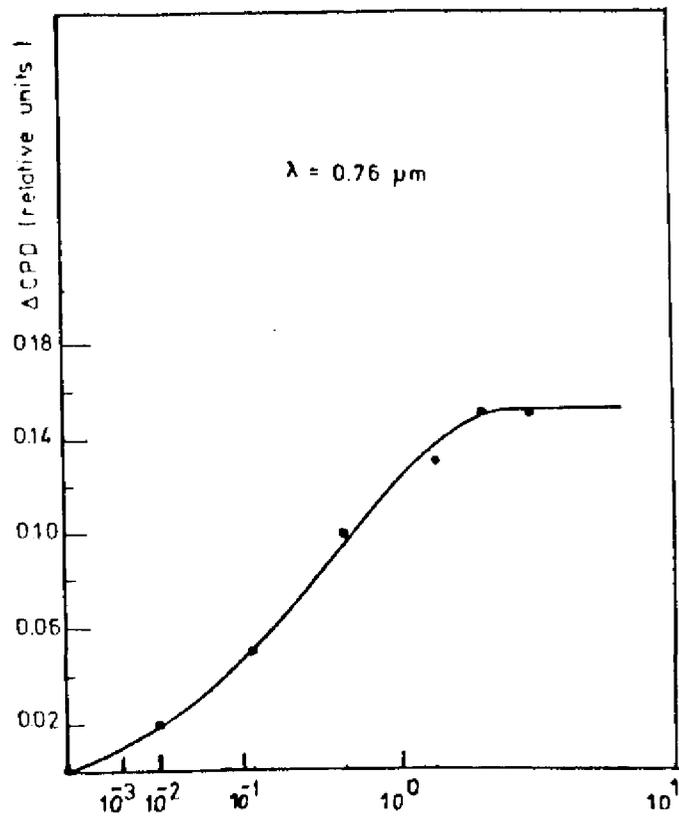


Fig.2.

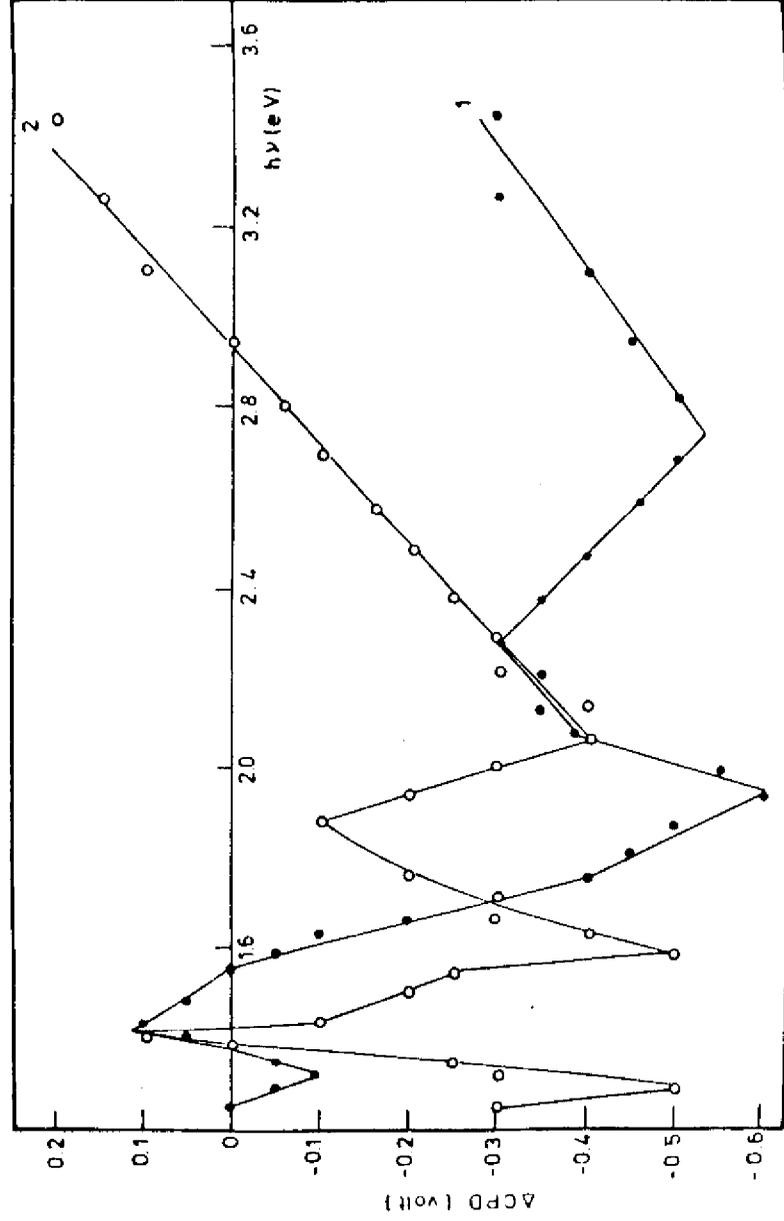


FIG. 3

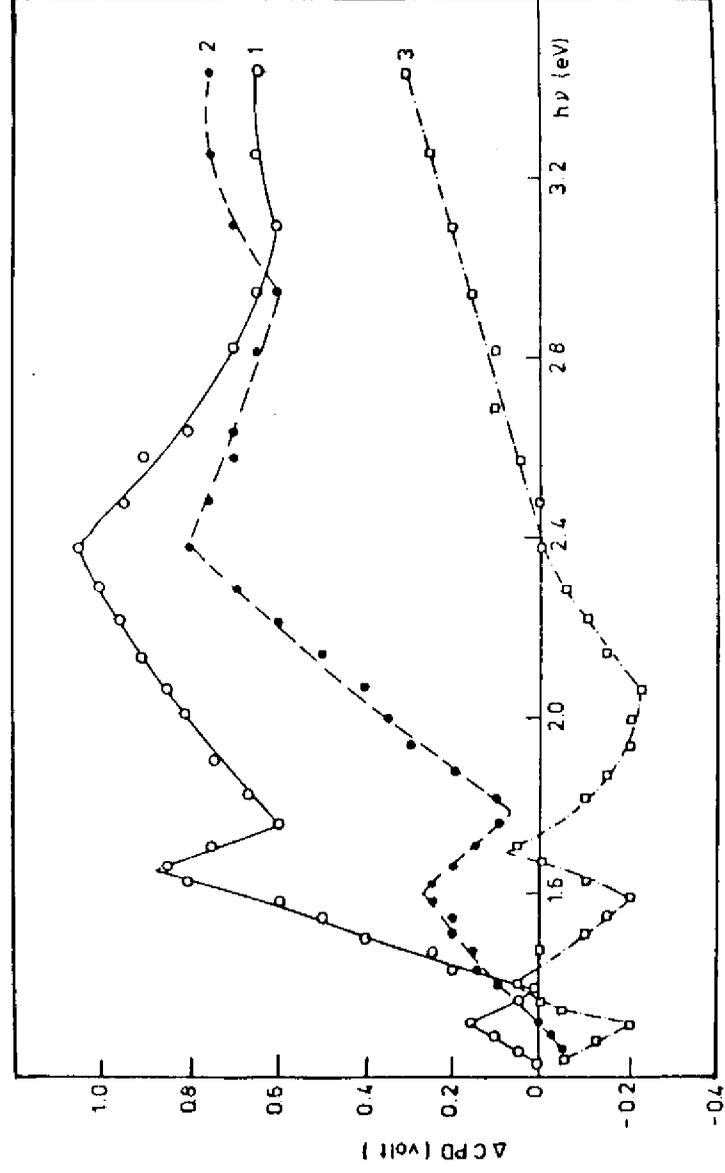


Fig. 4

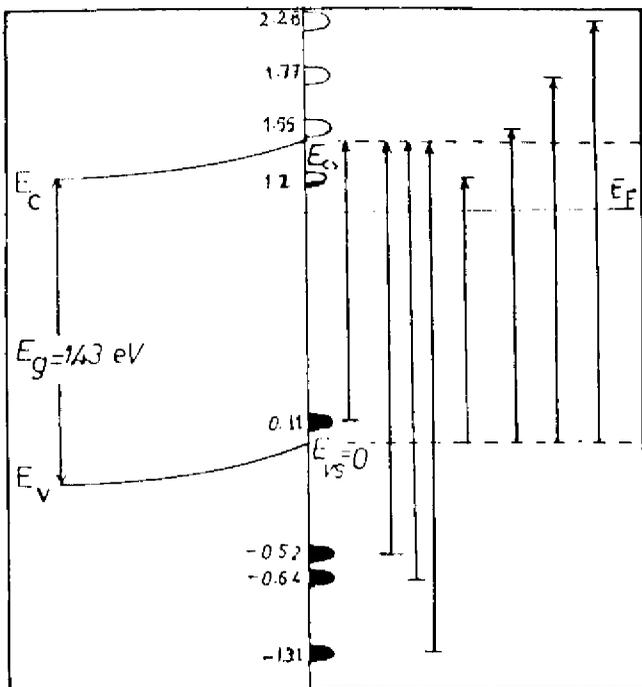


Fig. 5a

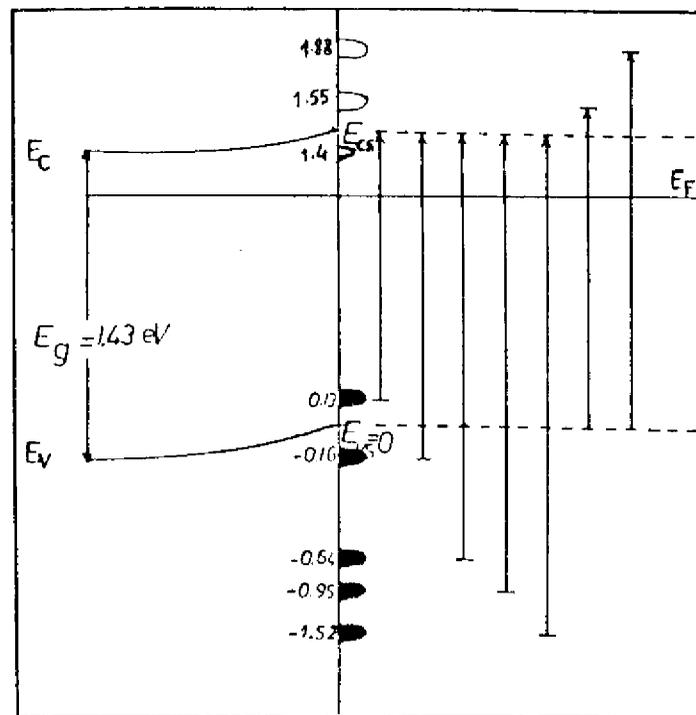


Fig. 5b

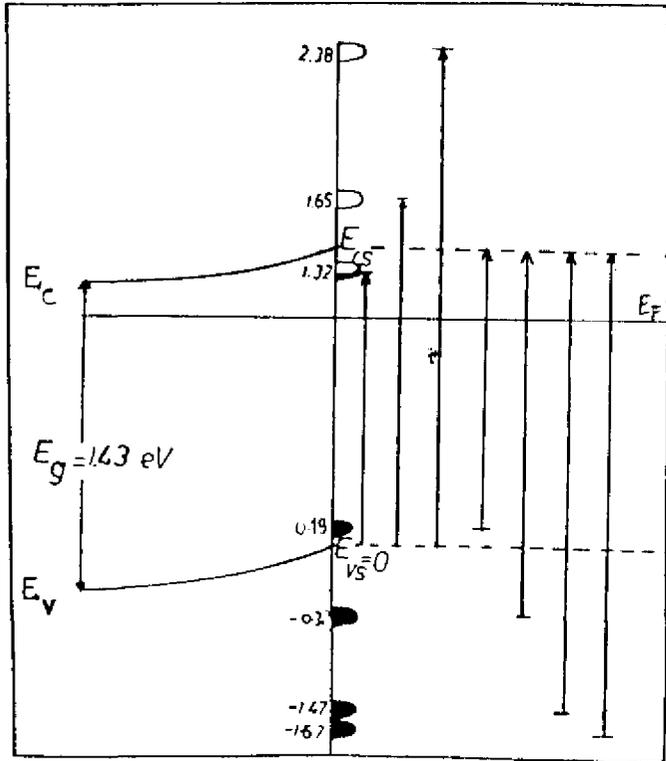


Fig. 5c

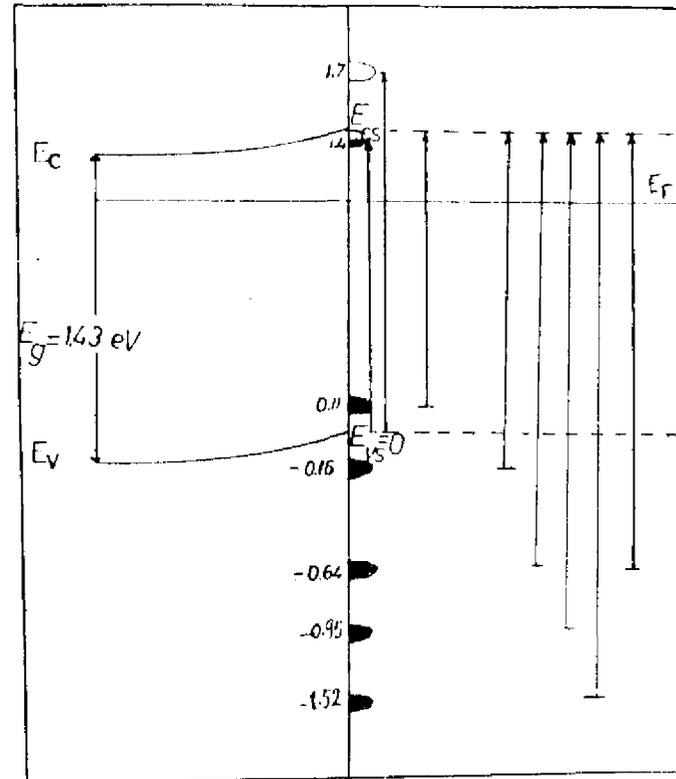


Fig. 5d

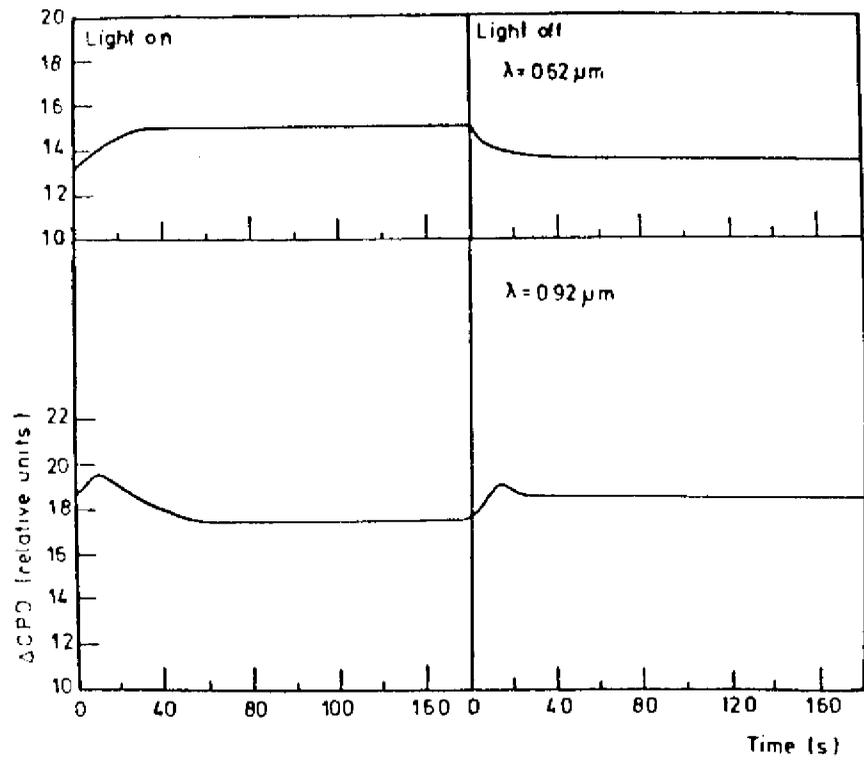
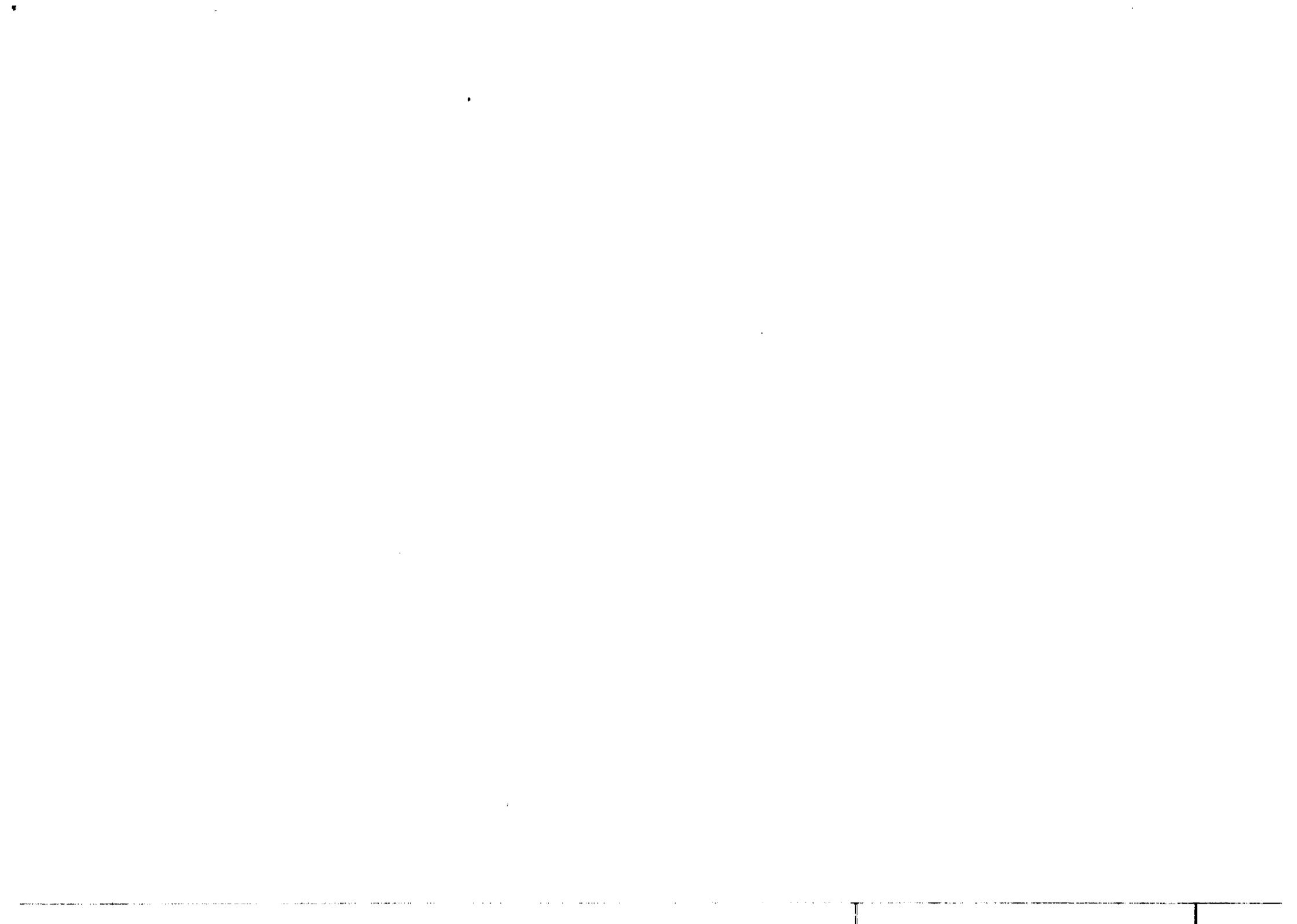


Fig.6



Stampato in proprio nella tipografia  
del Centro Internazionale di Fisica Teorica