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JOURNAL DE PHYSIQUE Colloque C2, supplément au n° 4, Tome 33, Avril 1972, page C2-127

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Résumé. — L'étude de la distribution spectrale de la photoconductivité dans les monocristaux de $BaTiO_3$ et SbSI révèle deux maxima.

Le maximum vers les grandes longueurs d'onde est dû, comme d'habitude, à la photoconductivité intrinsèque d'un ferroélectrique et son énergie correspond au gap Eg ($Eg = 2$ eV pour SbSI et $Eg = 3$ eV pour $BaTiO_3$ à la température ambiante).

Le maximum aux courtes longueurs d'onde, observé pour la première fois dans ce travail, est dû à la couche de surface du ferroélectrique qui pourrait être décrite par le modèle de Schottky. La photoconductivité eytrinsèque dépend de l'effet du champ électrique intense dans la couche de surface sur le rendement quantique, et sur le temps de vie des porteurs hors d'équilibre.

Abstract. — The study of the spectral distribution of photoconductivity in $BaTiO_3$ and SbSI single crystals reveals two maxima. The long-wave maximum, as usual, is due to the intrinsic photoconductivity of a ferroelectric and its energy corresponds to the energy gap Eg ($Eg = 2$ eV for SbSI and $Eg = 3$ eV for $BaTiO_3$ at room temperature). The short-wave one, which was for the first time observed in the present work is due to the surface layer of the ferroelectric which could be described by the Schottky model. The extrinsic photoconductivity is conditioned by the effect of a strong electric field in the surface layer on the quantum yield and the life-time of nonequilibrium carriers.

The ferroelectrics-semiconductors $A^V B^{VI} C^{VII}$, $BaTiO_3$, $SrTiO_3$ show maximum of intrinsic photoconductivity, located near the adsorption edge [1], [2], [3], [4]. On the other hand photoconductivity in the short-wave region was found in $BaTiO_3$ and SbSI. This was due to the generation of non-equilibrium carriers in the Schottky barrier region appearing in the case of contact of metal with a ferroelectric [5], [6]. However it is quite evident, that ferroelectrics-semiconductors should exhibit one more special type of extrinsic photoconductivity conditioned by the existence in ferroelectric crystals of the so-called screening surface layers (Känzig layers) [7], [8], [9], [10], [11], [12]. The surface layer of a ferroelectric similar to the Schottky barrier should condition the extrinsic photoconductivity in the region of strong absorption of crystal. This phenomenon was discovered and investigated in the present work.

Measurements were made with non-reduced $BaTiO_3$ single crystals grown by Remeika method and SbSI single crystals grown from the vapour phase. For $BaTiO_3$ single crystals spectral distribution studies were made both of the longitudinal and transverse photoconductivity. Longitudinal photoconductivity was measured along c-axis, for what purpose gold semi-transparent electrodes were evaporated on the (001) faces, and illumination was effected through these electrodes. The spectral distribution of longitudinal photoconductivity in $BaTiO_3$ possesses one maximum at $\lambda \simeq 360$ nm. The intrinsic photoconductivity of the crystals appeared very low and did not show maximum or any other peculiarities at the intrinsic absorption edge, i. e. at $\lambda \simeq 400$ nm. When measuring the longitudinal photoconductivity extrinsic photoconductivity of $BaTiO_3$ in the region of strong absorption may be related with the Schottky barrier, as expected earlier [5]. Therefore spectral distribution of transverse photoconductivity of $BaTiO_3$ was measured simultaneously. For this purpose barium titanate plates were electroded in the form of strips. Thus, an electric field was applied in the [100] direction, and illumination was performed with a light slit in the [001], the electrodes being nonilluminated. In figure 1 there is given the spectral distribution of transverse photoconductivity of $BaTiO_3$ revealing one extrinsic maximum at $\lambda \simeq 360$ nm (curve 2). The maximum did not depend on applied field and material of the contacts. The illumination of the contacts did not influence on the short wave maximum and did not lead to the appearing of any maxima in the spectral distribution of the photoconductivity. Figure 1 shows the spectral distribution of the absorption coefficient of $BaTiO_3$ (curve 1) taken from [13]. The maximum of the extrinsic photoconductivity is seen from figure 1 to correspond to the effective surface layer $\simeq 10^{-4}$ cm, which coincides of the order of the value with depth of surface screening layer in $BaTiO_3$ [7], [10].

For crystals SbSI is most interesting to compare the

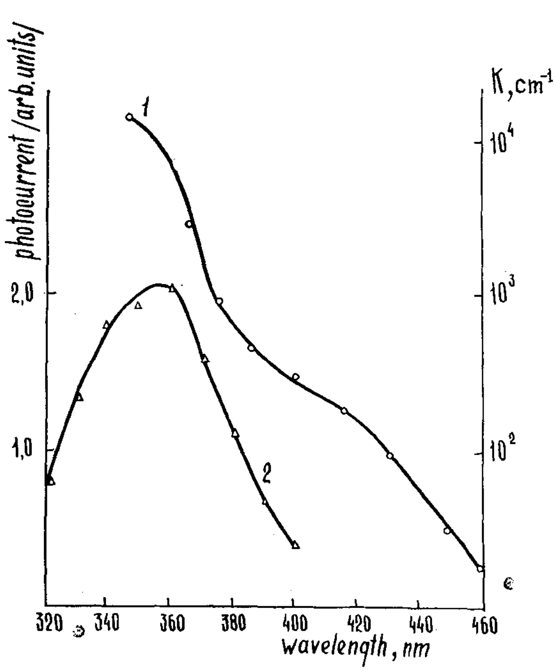

FIG. 1. — Spectral dependence of absorption coefficient (1) [13] and photoconductivity (2) for $BaTiO_3$.

curves of spectral distribution of transverse photoconductivity when illuminating the faces parallel to the [001] direction where by symmetry reasons the screening surface layer is lacking, with the corresponding curves obtained when illuminating the butt-end faces (101), where the screening surface layer is located. Note that for $BaTiO_3$ similar observations are hampered because of the presence of *a*- and *c*-domains. In figure 2 there are given the curves of spectral distribution of transverse photoconductivity of SbSI, produced in the ferroelectric region for a non-polarized

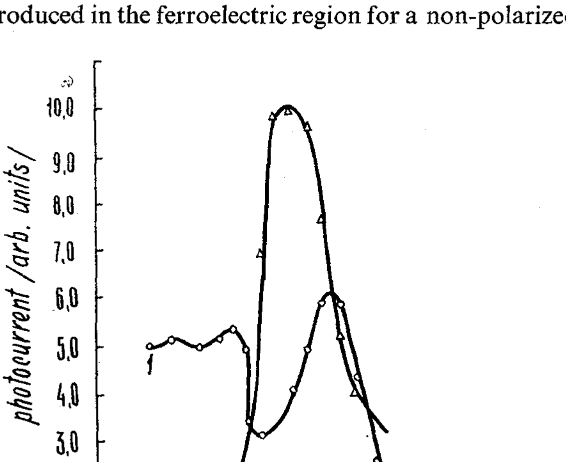

FIG. 2. — Spectral distribution of transverse photoconductivity for SbSI in the ferroelectric region. Curve 1 corresponds to the face (100), curve 2 — to the face (101).

crystal. Curve 1 was obtained when contacts were on face (100), curve 2 — correspondingly on the butt-end face (101). The long-wave maximum of curve 1 corresponds to the intrinsic photoconductivity of SbSI. The shortwave maximum of curve 1 is not always observed and evidently related with the Schottky barrier near the contact. This supposition is favored by the fact that this maximum disappears when darkening the contacts and shifts with applied field. Most notable is the fact of the short-wave shift of maximum in curve 2 with respect to the maximum of intrinsic photoconductivity of curve 1. When in paraelectric region this shift disappears, the position of maxima of curves 1 and 2 coincides and corresponds to the intrinsic photoconductivity of SbSI at measurement temperature. The process of the disappearing of extrinsic photoconductivity in the paraelectric region of SbSI due to the decay of the screening surface layer exhibits kinetics depending on temperature.

Figure 3 illustrates the effect of spontaneous polarization direction on the spectral distribution of extrinsic photoconductivity (curves 2 and 3). Before measuring photoconductivity the ferroelectric was polarized by

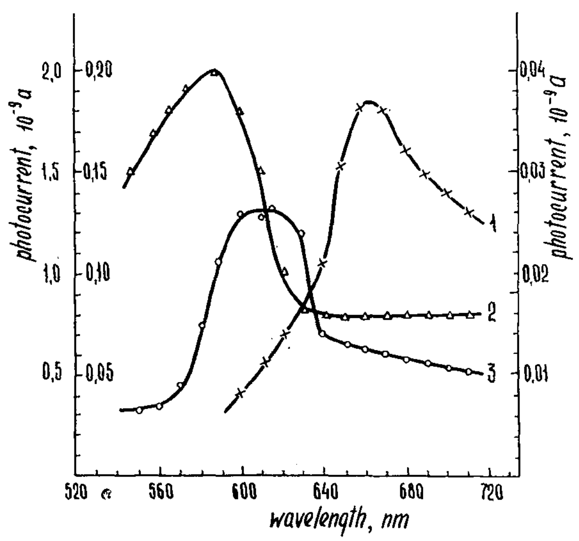

FIG. 3. — Effect of ferroelectric polarization on spectral distribution of transverse photoconductivity for SbSI in the ferroelectric region. Curve 1 corresponds to face (100), curves 2 and 3 — to face (101) ; curve 2 — anode region, curve 3 — cathode region.

applying a dc field higher than the coercitive field ($E = 600$ V/cm) along the ferroelectric *c*-axis. Measurements were performed using two directions of polarization. The spectral distribution of transverse photoconductivity for face (100) does not change when polarizing the crystal and changing the direction of polarization (curve 1). For the butt-end face (101), alternatively, preliminary polarization of the ferroelectric considerably influences the spectral distribution of photoconductivity. This fact additionally verifies the assumption about the role of the screening surface layer.

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