LONG-TERM CHANGES IN THE SURFACE POTENTIAL
OF CdGeP₂ SINGLE CRYSTALS UNDER ILLUMINATION

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A study is made of the variation in the surface potential \( \Delta V_c \) of p-type CdGeP₂单 crystals during and after illumination. The sign of \( \Delta V_c \) corresponds to the increase of the work function of the semiconductor surface under illumination. Together with a sharp variation of \( \Delta V_c \), a long-term component is observed whose value increases with the increase of the light intensity and the time of exposure of the specimens to light. Slow changes are explained by the presence on the semiconductor surface of an amorphous film, which impedes the electron exchange of the semiconductor with surface states. A model is proposed and a calculation carried out for the long-term kinetics in the small-signal approximation.

The compound CdGeP₂ belongs to the group of ternary diamondlike semiconductors of type \( \text{A}^3\text{B}^4\text{C}_2 \) interest in which is associated with a number of properties which are very valuable as regards practical applications [1]. Multilateral investigations of these materials should, of course, also include study of their surface properties. The absence of data in the literature has stimulated interest in such investigations.

In the present work, we investigated the variation of the surface potential of CdGeP₂ single crystals produced by light. The measurements were carried out using p-type specimens with bulk hole concentration \( p = 1.7 \times 10^{12} \text{ cm}^{-3} \) by the dynamic capacitor method. The usual method of measuring the contact potential difference was augmented by a self-recording system using an automatic pen. The setting time of the system, which was based on an \( \text{EFP-09 MZ potentiometer} \), was 10 sec. The illumination was produced by undecomposed light from a 500-W incandescent lamp. The maximum illumination of the surface of the specimen was \( \sim 5 \times 10^3 \text{ lux} \).

TREATMENT OF THE SURFACE

In view of the absence of published data on a method of chemical polishing of the compound CdGeP₂, it became necessary to select a polishing etchant. Good results were obtained using a 10% solution of bromine in ethylene glycol as the etchant (the rate of etching was 15–30 \( \mu \text{m} \)/h at room temperature). The quality of the surface was monitored using fast-electron diffraction. In the diffraction picture obtained after mechanical processing of the surface (grinding and polishing) Debye half-rings were observed with a fairly strong background, which is evidence of the presence on the surface of a polycrystalline layer (mean particle size \( \sim 10^{-6} \text{ cm} \)). Etching for 30 min led to the removal of the polycrystalline layer and the exposure of a block-structure, which
is attested by the appearance of a network of Kikuchi lines. As a result of a second 30-min etching of the specimen, the network of point reflections vanished from its electron-diffraction pattern and the sharpness of the Kikuchi lines increased, which was a proof of the high perfection of the surface structure (Fig. 1). However, the presence of weak diffuse rings in the electron-diffraction pattern forces us to postulate the presence on the surface of the specimens of an amorphous, evidently oxide, film. An attempt was made to remove the amorphous film from the CdGeP\(_2\) surface by heating in vacuo (~5\(\times\)10\(^{-9}\) torr). The state of the surface was monitored using low-energy electron diffraction (10-200 eV). However, it was not possible to remove the amorphous film by prolonged heating at 300°C; this was confirmed by subsequent investigation of the given specimen using fast-electron diffraction.

**RESULTS**

Figure 2 gives the kinetics of the change in the surface potential \(\Delta V_0\), with maximum intensity of illumination (curve 1) and after switching off the light (curve 1'). The sign \(\Delta V_0\) corresponds to an increase in the work function of the semiconductor surface in light. A special feature of the kinetics is the presence of fast \(\Delta V_0^f\) (t < 10 sec) and long-term \(\Delta V_0^s\) components of \(\Delta V_0\), while in light the value of \(\Delta V_0^f\) is greater than after the light is switched off. It must be noted that measurements carried out in air and in vacuo (~5\(\times\)10\(^{-9}\) torr) gave identical results.

Investigation of the kinetics of \(\Delta V_0\) at different temperatures in the range from 20 to 100°C showed that \(\Delta V_0^f\) decreases as the temperature rises, while \(\Delta V_0^s\) is only very slightly dependent on the temperature.

In order to simplify the theoretical calculation of the kinetics and to compare the experimental results with the theory, measurements were made at a weak level of illumination and a comparatively short exposure time, when \(\Delta V_0^s << kT/q\) (\(k\) is Boltzmann's constant, \(T\) is the absolute temperature, \(q\) is the charge on an electron). The corresponding curves for three different levels of illumination are given in Fig. 3. From the figure it is seen that as the intensity of the light increases, so does the gradient \(\Delta V_0/\Delta t\) in the presence of light, while in the region of relaxation (curves 1'-3') it is practically independent of the level of illumination.

**DISCUSSION OF RESULTS**

It is known [2] that the main reason for the change in surface potential under illumination is the change in the surface flexure of the zones \(Y_S\) due, first of all, to the appearance of photocarriers in the surface layer of bulk charge, secondly, to their capture on the surface states. The Dember emf may also introduce a definite contribution to the surface photoemf. The fast component \(\Delta V_0^f\) which we observed may also be conditioned by the first of these causes and also by capture on fast surface states. A detailed analysis of the fast process lies outside the framework of the present article. We note only that in our case the contribution of the Dember emf cannot be dominant, since its sign is opposite the sign of the observed change in the surface potential.

The long-term component \(\Delta V_0^s\) is connected with the slow variation of the surface charge \(Q_{SS}\) during illumination.

The absence of any effect of the pressure of the ambient medium on the kinetics of \(\Delta V_0\) allows photodesorption to be excluded from our consideration as a possible mechanism of this phenomenon.