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PHYSICS

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THE INFLUENCE OF THE CRYSTALLINE PHASE IN AMORPHOUS SELENIUM ON THE SIGN OF DARK AND LIGHT CHARGE CARRIERS

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The question of the sign of light and dark charge carriers in layers of amorphous selenium, which are of great interest for electrophotography and for vidicon tubes with photoconducting targets, has not yet been finally resolved: in various works either a hole sign ($^{1-6}$) or an electron sign ($^{5-7}$) of the light carriers has been found. In the present work, in order to study the sign of the charge carriers in layers of amorphous selenium, we used a new method (^{5,6}), which, unlike existing methods (^{8}), makes it possible to determine in high-resistance semiconductor layers the predominant sign of the dark and light carriers, i.e., the carriers having a large value of $\mu\tau$, where μ is the drift mobility and τ is the lifetime, even when the mobility is small.

1. The method is based on the possibility of obtaining a controlled bending of the bands over a considerable part, or even over the entire thickness, of a high-resistance semiconductor layer on a conducting substrate by depositing on its surface an ionic charge of one sign or another. The sign of the dark and light charge carriers is determined from the shape of the curves of dark and light relaxation of the potential of the double layer created by the ionic charge and the screening charge (^{6}). When the sign of the ionic charge coincides with the sign of the dark carriers, the latter are removed from the layer, which leads to an increase in resistance. Therefore the rate of potential relaxation, which depends on the resistance, when the sign of the surface charge coincides with the sign of the dark carriers, will be smaller than in the case of opposite signs. The sign of the light charge carriers is determined by comparing the rate of light relaxation of the layer potential for a definite sign of the carriers passing through it. The higher relaxation rate corresponds to the passage through the layer of carriers with the larger value of $\mu\tau$. The sign of the carriers passing through the

Figure 1: curves of relative dark potential versus time

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layer was changed by exposing the layers, from opposite sides—from the side of the surface ionic charge and from the side of the screening charge—to strongly absorbed light of $\lambda = 436$ mμ, whose penetration depth is much smaller than the layer thickness (6). In this case the depth of penetration of the field was equal to the thickness of the layer, which was specially checked. The amount of energy absorbed in the layer (illumination about 1 erg/sec $\cdot$ cm^2) during exposure from different sides was kept constant.

Amorphous selenium layers were prepared by vacuum evaporation at 10^{-4} mm Hg of selenium of the "reagent-grade" brand with a purity of 99.7% and B_4 with a purity of 99.9999% onto glass substrates coated with a semitransparent conducting layer of tin dioxide and held at temperatures from 20 to 70°. Some of these layers were subjected to subsequent heat treatment in air at a temperature of 70° for 2 hours.

2. As studies under an MIK-1 microscope at a magnification of 600× showed, selenium layers deposited on substrates with a temperature of about 20° are amorphous, and no structure is detected in them. After thermal treatment, these layers, as well as layers deposited on substrates at a higher temperature, show under the microscope the formation of individual microcrystallites of size on the order of 0.5-1 μ, embedded in an amorphous medium at distances of several microns from one another.

3. Typical curves of the dark relaxation of the potential of amorphous layers containing no crystalline phase are shown in Fig. 1a. It is seen from the figure that the relaxation rate is significantly smaller when a negative charge is deposited on the surface, which indicates the predominance of electronic conductivity over hole conductivity. A different result is obtained for amorphous layers with inclusions of the crystalline phase (Fig. 1b). In this case the relaxation rate is smaller when a positive charge is deposited, i.e., the appearance of the crystalline phase changes the sign of the dark carriers in amorphous selenium from electronic to hole.

Fig. 1. Dependence of the relative dark potential $V/V_{\max}$ of different sign on time for amorphous selenium layers without inclusion of the crystalline phase (a) and with inclusion (b).

4. Typical curves of the light relaxation of the potential of amorphous selenium layers containing no crystalline phase are shown in Fig. 2a and b. It is seen from Fig. 2a that, when a negative charge is deposited, the relaxation rate under exposure from the side of this charge, when electrons pass through the layer, is greater than under exposure from the side of the shielding charge, when holes pass through the layer. When a positive ionic charge is deposited, the potential relaxation rate is also greater in the case

of electrons passing through the layer, i.e., electrons are the predominant light charge carriers in these layers. The drift distance of electrons and holes is several microns, so that when the layer thickness is decreased from 9 to 5 μ the linear portions of the light-potential-relaxation curves under exposure from different sides coincide (Fig. 2b), i.e., the drift distance of carriers of both signs becomes comparable with the layer thickness.

Investigation of the sign of the light carriers of the above-mentioned layers by the sign of the diffusion photo-emf(9–11) confirms the predominantly electronic type of light charge carriers.

Typical curves of the light relaxation of the potential of amorphous selenium layers with inclusions of the crystalline phase are shown in Fig. 2c. Comparison of the curves shows that the appearance of the crystalline phase in amorphous selenium, in full agreement with the change in the sign of the dark carriers, also leads to a change in the sign of the light charge carriers from electronic to hole. The value of $\mu\tau$ for holes in these layers considerably exceeds $\mu\tau$ for electrons, and the potential relaxation rate is substantially different at layer thicknesses of only 3 μ, whereas for amorphous selenium layers containing no crystalline phase no difference is observed in the potential relaxation rate even at thicknesses of 5 μ.

Investigation of the sign of the carriers in the indicated layers by the sign of the photo-emf also gives a hole type of carriers, and the magnitude of the photo-emf in amorph-

selenium layers with inclusions of the crystalline phase increases by approximately an order of magnitude.

5. The totality of the results presented above indicates the influence of the crystalline phase in amorphous selenium layers on the sign of their dark and light charge carriers. The previously obtained data on the hole type of light carriers in layers of amorphous selenium (1) apparently pertain to amorphous selenium with inclusions of the crystalline phase. This is all the more probable because amorphous selenium is a thermodynamically unstable system and undergoes recrystallization already at room temperature (12).

At the same time, apparently, one cannot judge the predominant sign of the charge carriers in amorphous selenium solely from the magnitude of carrier mobility. A comparison of the data on the higher mobility of holes in amorphous selenium layers, obtained in (2–4), with the results of the present work makes it possible to suppose that in layers of amorphous selenium not containing the crystalline phase, a rare case is realized in which the mobility of holes is greater than the mobility of electrons, while the lifetime, conversely, is considerably greater for electrons than for holes. The latter leads to the fact that, despite the large magnitude of the hole mobility, the value $\mu\tau$, which determines the predominant sign of the carriers, is greater for electrons. The dark and light conductivity of these layers is mixed, with an electronic predominance. When the

Fig. 2

Figure 2: Fig. 2

crystalline phase appears in amorphous selenium, the ratio between the electron and hole components of the current changes, and hole conductivity begins to predominate. As may be supposed from the increase in the photo-emf and from the circumstance that the mobility of holes in amorphous (2) and crystalline (13,14) selenium practically coincides, the increase in hole conductivity is due to an increase in the lifetime of holes.

Fig. 2. Dependence of the relative potential $V/V_{\max}$ on the amount of illumination Et upon exposure from the side of the ionic charge (1) and the screening charge (2). *a*—for amorphous selenium layers 9 μ thick, containing no crystalline phase; *b*—for the same layers 5 μ thick; *c*—for amorphous selenium layers 3 μ thick with inclusions of the crystalline phase.

Thus, the results obtained in the present work show that amorphous selenium layers possess predominantly electronic dark and light conductivity, which, upon the appearance of the crystalline phase in amorphous selenium, changes to hole conductivity.

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