

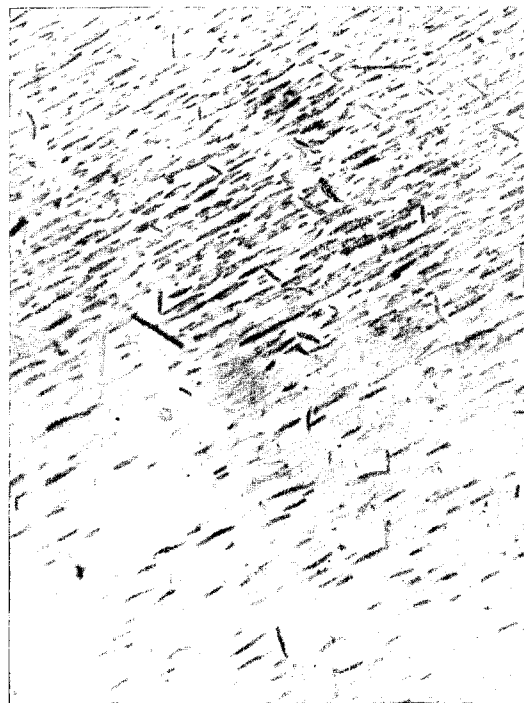
## PHOTOEPITAXY IN SEMICONDUCTORS

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We have performed a number of experiments on the crystallization of anthraquinone on the surface of single-crystal germanium. We established that the illumination in the region of the intrinsic photosensitivity of the semiconductor influences the oriented crystallization of the anthraquinone.

The anthraquinone was crystallized from the gas phase in accordance with a previously described procedure (see, e.g., [1]). The light passed through the semiconductor and was focused on the crystallization surface. It was possible to focus on the semiconductor surface images in the form of a raster or bands. The time of illumination during the crystallization process and the spectral composition of the light could be varied in a wide range. The crystallization was on n-Ge plates with resistivity  $\sim 40$  Ohm-cm, having an orientation (211). Before the crystallization, the germanium plates were edged with a polishing etchant. In darkness, we obtained oriented crystallization of the anthraquinone on the germanium in the form of a two-dimensional needle-like texture. Illumination influenced the crystallization, changing both the density of the crystals and the orientation. It was convenient to observe the influence of the illumination by projecting the images on the surface of the germanium during the crystallization process. After the end of the crystallization, the optical image turned out to be decorated with anthraquinone crystallites, and the image could be observed in reflected light. Investigation of the spectral dependence of the effect has shown that the influence of the illumination on the crystallization takes place in the region of the intrinsic photosensitivity of the germanium.

It was observed simultaneously that illumination influences the oriented crystallization of the anthraquinone in such a broad-band dielectric as mica. In this case, however, the "photosensitivity" took place only in the blue region of the spectrum, where anthraquinone is photoconductive. The role of the photosensitivity of the anthraquinone was confirmed also by the following experiment. At first the anthraquinone was crystallized in the mica in darkness. After this, the crystallization was stopped and the image on the mica was exposed in the blue region. Turning off the light was followed by a repeated crystallization of the anthraquinone, which decorated the optical image. Of course, under the same conditions the preliminary illumination of "pure" mica did not influence the subsequent crystallization of the anthraquinone.



Microphotograph of the photo-epitaxy section, 400x.

The figure shows a microphotograph of the optical image decorated on mica by anthraquinone crystals. The upper half of the photograph corresponds to the section of the mica which was not illuminated during the time of

crystallization of the anthraquinone, and the lower corresponds to the illuminated section. Observation and photography were carried out in a polarization microscope in reflected polarized light. It is seen from the microphotograph that the illumination, without changing the direction of the texture axis (in both cases we have a uniaxial needle-like texture), changes the orientation of the crystals and decreases somewhat their concentration. Needle-like anthraquinone crystals on the illuminated section are turned through a certain angle around the texture axis compared with the crystals on the illuminated section. It is possible that what we have here is not a rotation but a change in the morphology of the faces of the [001] belt. This is seen from the fact that the extinction angle for both groups of crystals, when observed through an analyzer, turned out to be different. At the same time, when the crystals are observed in transmitted polarized light, the extinction angle is the same, since the optical indicatrices of the crystals are parallel. This, in particular, explains why the obtained images were more contrasty in reflected light than in transmitted light. Similar observations were performed also for images obtained on germanium.

We call attention to the analogy between the photoepitaxy on semiconductors, described above, and a phenomenon called by us earlier sensitized photolysis on semiconductors [2]. Apparently the change of the crystallization-center density is connected with optical charge exchange on the surface centers of the semiconductor, and the change of the orientation of the crystals is connected with the structure of the charge-exchanging centers. At any rate, this mechanism agrees with the recent notions concerning the role of charge centers in epitaxy [1]. The epitaxy phenomenon apparently has a general character and, in principle, should be observed for all semiconductors on the surface of which oriented crystallization takes place.

- [1] G.I. Distler and V.G. Obrovov, Dokl. Akad. Nauk SSSR 3, 584 (1970) [sic°].  
[2] A.D. Sablin-Yavorskii and V.M. Fridkin, ZhNiPFiK (Journal of Applied and Scientific Still and Motion Picture Photography) 14, 6, 458 (1969).

#### CONNECTION BETWEEN CHARGE TRANSFER AND LASER SECOND HARMONIC GENERATION

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Several recent communications reported observation of intense second-harmonic generation of neodymium-laser emission in molecular crystals [1 - 3]. The choice of substances used for frequency doubling was in effect accidental. We report in this paper observation of a connection between the effective second-harmonic generation and the nature of the electronic transitions of the molecules. The observed connection enables us to estimate qualitatively the nonlinear properties of molecular crystals, by starting from the structure of its component molecules.

It is known that in order to obtain effective transformation it is necessary to match the phases of the first and second harmonics of the radiation and to have a sufficiently large nonlinear susceptibility,  $\chi^{NL}(2\omega)$  [4].

$\chi^{NL}(2\omega)$  differs from zero only when the crystals have no symmetry center [1]. By virtue of the resonant character of this susceptibility, the largest contribution of  $\chi^{NL}(2\omega)$  is made by the allowed electronic transition closest to the frequency  $2\omega$ . We can therefore confine ourselves in the analysis of frequency doubling to consideration of a two-level system.