KINETICS OF THE PHASE TRANSITION FROM THE AMORPHOUS TO THE POLYCRYSTALLINE STATE IN SEMICONDUCTORS

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Submitted 19 November 1971
ZhETF Pis. Red. 15, No. 1, 21 - 24 (5 January 1972)

A study of the phase transition (PT) from the amorphous to the polycrystalline state in solids is quite vital in connection with research on switching and "memory" effects [1, 2] in amorphous semiconductors. In particular, to establish whether the effect of reversible switching can be due to this PT [3, 4], it is necessary to investigate the kinetics of the latter.

We have investigated the kinetics of such a phase transition in amorphous GeTe films 10^{-5} cm thick, obtained by thermal sputtering in vacuum, and observed also switching and "memory" effects in such films. To investigate the indicated PT under conditions close to those under which these phenomena take place, the transition was stimulated by heating the films with powerful light pulses [5], at a rate 10^6 deg/sec. Investigations have shown that such a rate corresponds to the rate of heating of amorphous matter by current when switched with "memory" in identical GeTe film. The radiation source was a gas-discharge flash lamp with a spectrum in the wavelength interval 0.2 - 0.8 μ.

Owing to the generation of free carriers by the light, the PT occurred with increased carrier density (as did the switching effect, in the case of which the carriers were injected from contacts). This may be of importance for the kinetics of the PT from the amorphous to the polycrystalline state [5, 6].

The PT kinetics was observed by a microwave contactless method [7], in which the changes of the conductivity (σ) of the substance, which is one of the most structure-sensitive parameters of a solid, were measured. The films were exposed to a light flash in an evacuated waveguide, and the changes of σ were revealed by the changes of the absorption, in the film, of microwave power of low amplitude propagating through this waveguide.

Figure 1 (top) shows an oscillogram of the change of the microwave power absorbed by an amorphous GeTe film exposed to a powerful light flash from a gas-discharge lamp. The lower oscillogram shows the time variation of the light flux passing through the film. As seen from the figure, the PT begins at a definite stage of heating of the amorphous GeTe and occurs after 100 μsec. The conductivity σ of the substance is irreversibly increased thereby by several order of magnitude.

Fig. 1

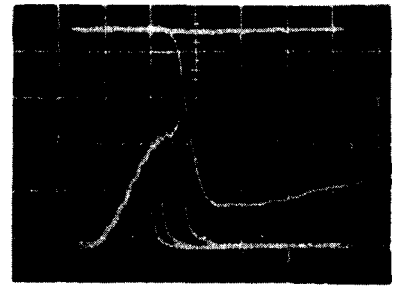

Fig. 2

Fig. 1. Change of microwave signal (top) and light flux (bottom) passing through a film of amorphous GeTe following an amorphous-polycrystalline phase transition. Sweep rate 200 μsec/div.

Fig. 2. The same as in Fig. 1 for three light flashes of different duration. Sweep rate 200 μsec/div.

Electron-microscope and electro-diffraction investigations have shown that the film has a polycrystalline structure after the irradiation, the crystallites produced in it having an average dimension 10^{-3} cm (the dimension of the correlation region in the initial amorphous substance was of the order of 10^{-7} cm). Repeated irradiations did not change the structure of the polycrystalline films.

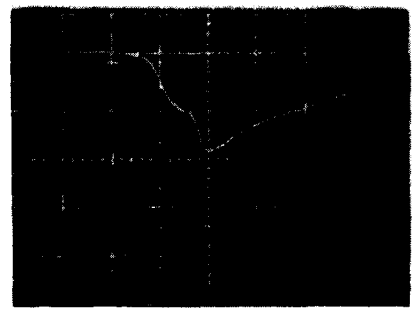

Fig. 3. Variation of microwave film passing through an amorphous Ge film in an amorphous - polycrystalline - liquid phase transition. Sweep rate 100 μsec/div.

The PT from the amorphous to the polycrystalline state could be stimulated by light pulses whose intensity and duration (τ) exceeded certain threshold values. Figure 2 shows oscillograms analogous to that of Fig. 1, obtained by irradiating an amorphous GeTe film with three light pulses with increasing τ. The first and second pulses produced no noticeable changes in σ. The PT was stimulated by the third pulse with $\tau > 350$ μsec. Pulses with shorter τ did not stimulate any amorphous-polycrystalline PT even when their intensity was considerably increased, and could only melt and evaporate the GeTe films. At $\tau > 350$ μsec, the PT occurred at a certain light-flash intensity corresponding to heating of the amorphous GeTe to 150°C, as shown by a comparison of similar oscillograms of the temperature dependence of σ of amorphous GeTe films, measured by an analogous microwave method. This corresponds to the temperature of the analogous thermally-stimulated PT in amorphous GeTe films [8]. Another characteristic feature is that, as seen from Fig. 2, the PT continued after the intensity of the optical radiation had dropped, and was probably maintained by the energy released during the PT process.

The amorphous-polycrystalline PT proceeded in similar fashions in films of other substances, e.g., Ge and C [7]. This PT occurred also when amorphous Ge films were heated on a metallic grid through which a current pulse was passed.

The described microwave method was used also to observe PT connected with the appearance of a liquid phase. For example, when amorphous Ge films were exposed to a light flash of sufficient intensity, the appearance of a liquid phase was observed following the phase transition from the amorphous to the polycrystalline state. This was manifest by a two-stage variation of σ of the film (Fig. 3).

The results presented above for GeTe enable us to determine approximately the propagation velocity of the phase-transformation front, which turned out to be of the order of 10 cm/sec under the given conditions.

Switching with "memory" in identical GeTe films was observed when the duration τ of the electric pulse was of the order of 10^{-4} sec and longer. A polycrystalline conducting filament of width on the order of 10^{-2} cm was then produced in the amorphous matter between the electrodes, and consisted of crystallites with approximate dimension 10^{-3} cm. This effect and the kinetics of the amorphous-polycrystalline PT were observed in identical samples under conditions of increased free-carrier density and at a commensurate rate of heating of the substance, i.e., under nearly equal conditions. It can therefore be assumed that the growth rates of the crystallites were of the same order in both cases. Then the needed time for the crystallites making up the polycrystalline "memory" filament to grow until boundaries come in contact should be on the order of 10^{-4} sec, corresponding to the minimum electric-pulse time τ at which switching with "memory" takes place. Such a PT, however, can obviously

not cause reversible switching, the duration of which is of the order of 10^{-10} sec [2].

A comparison of the amorphous-crystalline PT temperatures stimulated in GeTe by thermal and optical radiation indicates that the excess density of the free carriers generated by the light does not change the conditions of this PT significantly.

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TEMPERATURE OSCILLATIONS OF THE THERMAL EXPANSION COEFFICIENT OF A SUPERCONDUCTING CuS FILM

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Submitted 20 September 1971
ZhETF Pis. Red. 15, No. 1, 24 - 26 (5 January 1972)

According to Nedorezov's theory [1], the non-equidistance of the quantum energy levels of the carriers in films should lead to oscillations of the thermodynamic and kinetic quantities as functions of the temperature. This was first confirmed experimentally by observation of a temperature oscillation of the resistivity of semiconducting CuS films 200 and 500 Å thick [2]. For further study of the high-temperature quantum size effect, it was deemed of interest to investigate the thermodynamic properties of this semiconducting film as functions of the temperature.

We present here experimental data on the thermal expansion of a semiconducting CuS film 500 Å thick in the temperature interval from 60 to 300°K, obtained by the double-helix procedure of Lazarev and Sudovtsov [3, 4].

The sample was prepared by evaporating in vacuum ($\sim 10^{-5}$ mm Hg) the compound CuS, with accompanying sulfur enrichment, on the internal surface of a glass helix. To obtain uniform thickness, the glass helix was moved around the evaporator by a special device. The finished sample was annealed in sulfur vapor at 150°C for 5 hours.

The double helix had the following dimensions: height 65, inside diameter 35, turn width 5, thickness 0.8 mm, number of turns 6.

In the experiment we measured the difference between the thermal expansion of the investigated sample and pyrex glass at constant pressure. The rotation of the double helix was registered with a bridge-type measuring circuit, one arm of which was an FSK-6 photoresistor. The dilatometer was calibrated against a standard copper-glass sample [5, 6], and the obtained sensitivity was $(4.0 \pm 0.4) \times 10^{-9}$.