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To cite this version:
J. Hajtó, Füstöss-Wégner. LASER INDUCED OSCILLATORY PHENOMENA IN a-GeSe2 FILMS. Journal de Physique Colloques, 1981, 42 (C4), pp.C4-313-C4-316. <10.1051/jphyscol:1981466>. <jpa-00220923>

HAL Id: jpa-00220923
https://hal.archives-ouvertes.fr/jpa-00220923
Submitted on 1 Jan 1981

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LASER INDUCED OSCILLATORY PHENOMENA IN a-GeSe₂ FILMS

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Abstract. - Studying the optical and photoelectric properties of 5 μ to 10 μ thick GeSe₂ amorphous films under the influence of focussed continuous He-Ne laser beams (just below band gap laser light of wavelength λ = 6328 Å) a region of medium intensity (1.4 to 2.7 kW/cm²) is found where low frequency (3 to 50 Hz) oscillations in the absorption coefficient and the photocurrent sets in. To date, this seems to be the only amorphous semiconductor in which a constant input evokes an oscillatory response, which is obviously a far from equilibrium phenomenon. The experimental optical data are compared with the microscopic model of cooperative charge disproportionation of defect centers described by P.Fazekas to explain the first cycle of oscillation which is a sudden switch from the transparent to the dark state. The simultaneous change in photocurrent is also discussed.

1. Introduction. - The oscillatory behaviour of the transmittance and reflectance of amorphous GeSe₂ films illuminated by a continuous He-Ne laser beam was reported in several recent communications [1-3]. Oscillation can be observed when the intensity of the focussed laser beam lies in a certain range which is 1.4-2.7 kW/cm² for a 6.4 μ thick film for example. The oscillation of the optical properties is accompanied with a simultaneous oscillation of the photocurrents [4]. A microscopic model was suggested by P.Fazekas [5] to describe the first step of the oscillation which is a sudden switch from a transparent to a dark state. It is argued [5] that the evaporated GeSe₂ films contain unusually high density of defects, and this gives rise to cooperative behaviour, due to both interdefect Coulomb, and laser induced interactions. The zero temperature phase diagram of a model Hamiltonian was calculated and above a threshold photon density a laser induced partially charge-ordered phase was found. The switching to the dark state was interpreted as a transition into this phase. This paper is concerned with the investigation of optical (frequency depence) and electrooptic (photocurrent measurements) properties of vacuum evaporated GeSe₂ films under the influence of continuous laser irradiation. We describe further experimental details of the previously reported oscillation behaviour of the material and compare the results with the qualitative predictions of the Fazekas model.

2. Experimental. - GeSe₂ films were vacuum evaporated onto silica or mica substrates were measured by quartz crystal monitor and later checked by Talystep. A continuous beam of 30 mW output power He-Ne laser (λ = 6328 Å) was focussed on the layers to a spot diameter of 20-350 μ. The incident light intensity could be varied by a polarizer, the reflected and transmitted signals were displayed on a storage oscilloscope. The photocurrent measurements were made on surface type samples prepared by vacuum evaporation of coplanar gold electrodes onto mica or glass substrates.

The steady state photocurrent (under continuous laser irradiation) was measured by an electrometer or amplified and displayed on a storage oscilloscope. In this way simultaneous measurements of the transmittance, reflectance, and photocurrent pulsations could be performed during the light absorption oscillation.
To obtain the light absorption spectra during the oscillation, a continuous tunable dye laser was focused on the same spot as the He-Ne laser. The intensity of the measuring dye laser beam was kept on a low value not to influence the oscillation processes. In this optical arrangement the He-Ne laser was used for high power illumination and the tunable dye laser served as a light source for absorption measurements. The absorption spectra were calculated from the measured transmission and reflection during the oscillation using the method of Brattain and Briggs [6].

3. Results and discussion.

3/a Light absorption measurements

From $a = 10^2 \text{cm}^{-1}$ to $a = 10^4 \text{cm}^{-1}$ the optical absorption coefficient varies exponentially with the photon energy according to the equation $a = a_0 \exp(-\hbar \nu)$ (Urbach edge). The smaller value of the slope of the observed exponential adsorption edge ($\Gamma = 8.7 \text{ eV}^{-1}$ for the as deposited films and $\Gamma = 15.3 \text{ eV}^{-1}$ for the bulk glass) indicates higher concentration of defects in the as deposited films than in the bulk glass form, i.e. the decrease of the slope of the Urbach edge is due to the increase of internal electric fields created by charged impurities of the material [7].

Absorption oscillation can be observed when the amorphous GeSe$_2$ films are illuminated by a continuous He-Ne laser beam with incident light intensity of 1.4-2.7 kW/cm$^2$ for a 6.4 $\mu$m thick film for example. We measured the changes of absorption edge during the oscillation induced by He-Ne laser at an incident laser power density of 2.7 kW/cm$^2$. (Maximum laser power density at which oscillation can be observed for 6 $\mu$m thick films.) The absorption edge has two characteristic positions during the oscillation. First the edge shifts to lower photon energies (line 1 in Fig. 1) with a slope ($\Gamma = 5.7 \text{ eV}^{-1}$) smaller than for the as deposited material and after turns back to higher photon energies (line 3 in Fig. 1), with a slope ($\Gamma = 9.1 \text{ eV}^{-1}$) about the same as for the as deposited edges (line 1 and line 3 in Fig. 1) represent metastable states of the material and exist only under the influence of intense He-Ne laser irradiation. The absorption edge shifts to the stable photobleached state (line 4 in Fig. 1) independent of the momentary state of the oscillation, when the exciting laser is switched off. The "amplitude" of oscillation (shaded area in Fig. 1) becomes more marked as the measuring light energy is lowered from the band gap suggesting

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**Fig. 1:**

Optical absorption edges of a-GeSe$_2$ films.

1 - dark state of oscillation,
2 - as deposited films,
3 - bright state of oscillation
4 - photobleached state,
5 - bulk glass

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Since the images are not provided, the diagram is described as follows:

- **Fig. 1:**
  - Optical absorption edges of a-GeSe$_2$ films.
  - 1 - dark state of oscillation,
  - 2 - as deposited films,
  - 3 - bright state of oscillation
  - 4 - photobleached state,
  - 5 - bulk glass

The diagram shows the absorption edge transitions during the oscillation process.
that the relevant optical transitions are between localised states according to the phase transition model [5] for the laser induced switching. Evaporated a-GeSe$_2$ films in contrast to bulk samples are likely contain large defect concentration according to the low value of the slope of the absorption edge, and to the temperature dependence of the steady state photocurrent.

The shifts in the absorption edge can be associated with either changes in the charge state or concentration of defects [7] or with changes in temperature (according to the temperature dependence of the Urbach tail).

3/b Photocurrent measurements

Temperature dependence of dark current $I_d$ (curve 1) and photocurrent $I_{ph}$ (curves 3, 4, 5 and 6) for different photoexcitation intensities in GeSe$_2$ films are shown in Fig. 2. The photocurrent measurements were completed by photocurrent-intensity characteristics as it can be seen in Fig. 3.

As compared to the general form of temperature and intensity dependence of photocurrent observed for different chalcogenides, these curves show two anomalies. First of all the photocurrent rises with increasing temperature up to 500 K independently of magnitude of the dark current. Secondly, the photocurrent $I_{ph}$ is proportional to the intensity $F$ at "low"-temperature range and the exponent $\gamma$ in relation $I_{ph} \sim F^\gamma$ is about 0.6 at elevated temperatures.

Above 380 K the mechanism of dark conduction may be a charge carrier transport by carriers excited beyond the mobility edge into extended states. The activation energy for dark current (1.1-1.3 eV) will be the sum of the energy $E_1$ to form a D$^0$ centre and of the energy $\varepsilon$ required to take a hole from a D$^0$ centre into the valence band. Below 380 K we can assume hopping conduction according to the "tail" observed in log $I_d$ versus $1/T$ plot. The shape of dark current curves were the same whether the surface type (curve 1 in Fig. 2) or the sandwich type (curve 2 in Fig. 2) samples were investigated.) The activation energy of charge carrier motion is the energy $E_1$ (i.e. the energy of a D$^0$ centre's formation) and an energy $W$ representing the hopping activation energy of charge carriers in the D$^0$ D$^+$ D$^-$ system.

The photocurrent is controlled, on the one hand, by the recombination for which the rate-determining step is the 2D$^-$ +D$^+$ + D rela-

The photodiode is, on the other hand, by the drifts mobility which depends on filling of charged centres D$^+$ and D$^-$ . The drift mobility, which is trap limited above 380 K, is activated with an energy $\varepsilon$ and the photocurrent will be proportional to it in this temperature range ($\Delta E = 0.8$ eV). The fact that the recombination with thermally excited charge carriers does not become dominant up to 500 K($\gamma = 0.60$) indicates the unusually high concentration of defects D$^0$ in the films. This is in a good agreement with
the ESR measurements which show high defect concentrations \((D^0 \sim 5 \cdot 10^{18} - 10^{21}/\text{cm}^3)\) as in as deposited as in photobleached conditions of evaporated GeSe\(_2\) layers (M. Erős–Gécseg private communications). In the low temperature region a transition to monomolecular recombination kinetics is observed \((\gamma < 0.9)\) and it seems that the role of the different traps increases too. It can be seen that the slope of lines 3, 4, 5 and 6 in Fig. 2 varies with the light intensities, i.e. the activation energy depends on the filling of traps. As it was previously established the oscillation of transmittance was accompanied with a simultaneous oscillation of the photocurrent signal. With synchronous measurements of the transmittance, the reflection and the photocurrent we could estimate the change of the absorption (the number of photons absorbed per second in the sample) and the photocurrent when the as deposited sample was photobleached and during the oscillation. While the ratio of absorption in the as deposited state \((A_{\text{as}})\) to the absorption in photobleached one \((A_{\text{phb}})\) is

\[
\frac{A_{\text{as}}}{A_{\text{phb}}} = 1.2,
\]

the ratio of adequate photocurrents shows a higher value;

\[
\frac{I_{\text{as}}}{I_{\text{phb}}} = 1.7.
\]

During the oscillation the absorption ratio of 1.9 \(\frac{I_{\text{d}}}{I_{\text{tr}}} = 1.9\), where \(I_d\) the absorption in the dark and \(I_{\text{tr}}\) in the more transparent state) attend upon a ratio of 2.9 in photocurrents; the change of photocurrent is not proportional to the change of absorption. It seems that the formation of defects \(D^0\) is followed by a change in the recombination process of/and in the charge carrier mobility.

References