Appl. Phys. B 59, 639–643 (1994)

Applied Physics B Lasers and Optics

A phototermal experiment interpreted as evidence of electron-hole self-ordering in As-S chalcogenide glasses

B. P. Antonyuk[2], M. Bertolotti[1], S. A. Kiselev[2], G. L. Liakhou[3], A. A. Popescu[4], C. Sibilia[4]

[1] Department of Energetics, University of Rome I, Via A. Scarpa 14–16, I-00161 Rome, Italy
(Fax: +39-6/4424-0183)
[2] Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitsk, Moscow Region, Russia
[3] Technical University of Moldavia, Shtefan Cel Mare Str. 168, 277012 Kishinev, Moldavia
[4] Institute of Applied Physics, Academy of Sciences of Moldavia, 277028 Kishinev, Moldavia

Received in revised form 4 November 1993/Accepted 19 May 1994

Abstract. The photodeflection method has been applied to detect optically induced changes of the refractive index due to self-organization of electrons and holes, trapped in the disordered structure of a chalcogenide glass of the As-S type.

PACS: 78.66, 71.55, 42.60

The photodeflection method [1] was originally designed as a spectroscopic method to measure very small absorption coefficients. It was also shown that the method allows thermal measurements giving the thermal diffusion length [2–4]. Many other applications were also considered ranging from the measurement of carrier diffusion in semiconductors [5] to, for example, the determination of changes of the refractive index under intense laser pumping [6]. In this last application only thermal changes could be measured at first, due to the difficulties to detect angular changes of the probe beam on the short-time scale needed to put into evidence electronic contributions to the refractive index changes.

Quite recently, however, the method has been successfully applied to detect slow refractive index changes of electronic origin in semiconductor-doped glasses under quasi cw laser pumping and the competition of this change with the thermal change [7]. This has been possible thanks to the role played by traps in the electron relaxation in these materials.

Here, we want to show another case in which the method has been applied to detect the changes of the refractive index due to self-organization of electrons and holes trapped in the disordered structure of a chalcogenide glass of the As-S type under the influence of a HeNe probe beam.

The theory of self-ordering of carriers in these materials has been discussed in [8]; we report here on a photodeflection experiment which puts it into evidence. Further experimental evidence for this self-ordering has recently been obtained looking at the spectral properties of noise of the time fluctuations of the changes produced by it [9].

Self-organization of electrons and holes in an ordered structure under illumination has recently been proposed by one of the authors of the present paper as an explanation for second-harmonic generation in optical fibers [10, 11]. Excitation and decay of a Ge center has been shown to depend on the space distribution of already excited centers, and this correlation results in the creation of a long-lived polarized ordered structure which is able to produce effective second-harmonic radiation in optical fibers.

A similar phenomenon can occur in chalcogenide glasses of the As-S type under weak pumping with light having band-gap energy.

In these materials, under weak HeNe laser pumping, a change of the refractive index, which needs a long time exposure (hours) and lives for a long time (longer than a few days) after the laser is switched off, can be produced as a result of spatial electron-hole ordering.

The main feature of the theoretical model is the existence of trapped electron and hole states resulting in slow relaxation and recombination, and the dependence of generation and recombination rates in a given trap on the space distribution of trapped electrons and holes. This dependence results in spatial electron-hole ordering; the ordered state is long livied and gives a contribution to the refractive index. If an electron (a hole) occupies a trap, a static electric field is created in the vicinity of this trap, and the next electron (hole) is subjected to this field. The occupation rate of a given trap depends on the value of the electric field in the trap and, hence, on the distribution of electrons and holes in space. A large electric field spoils a trap, and each new electron and hole cannot be trapped in regions where the electric field is too strong.

If an electron localized in a trap α recombines with a hole localized in a trap β, the rate of recombination is proportional to the square of the localized wave function overlap integral and decreases exponentially with the distance between the traps. Short distance pairs recombine rapidly and structures with large electron-hole dis-

tances survive. This dependence of generation and decay rates on the particle distribution in space results in spatial ordering of the particles (self organization) [8, 10, 11]. The ordering is governed by the ratio of the generation rate (proportional to the light power) to the decay rate. The decay rate of an ordered structure tends to zero by increasing the electron-hole distance and this is the reason why ordered structures appear at weak irradiation and are living long after the light is switched off.

The relative index variation produced by the beam is of the order of the relative concentration of excited electrons [7], which is small due to their fast relaxation.

In this paper we wish to discuss a photodeflection experiment in which the deflection of a HeNe laser probe beam shows a complex behaviour which is interpreted as being produced by the formation of a channel with a space gradient of the refractive index due to the process of self-organisation induced by the HeNe probe beam.

1 Experimental setup

The experimental setup is shown in Fig. 1a. The Ar^+ laser beam ($\lambda = 488$ nm), used as the pump beam, is expanded by a diverging lens L_1 up to a spot size of 3 mm. The mechanical chopper MD modulates the intensity of the pump beam or is used as a shutter.

The pump power on the sample is varied up to 0.25 W/cm^2. The sample S is a parallelepiped of As_2S_5 of $4 \times 4 \times 6$ mm^3 with an absorption coefficient at the Ar^+ wavelength of $\approx 10^4$ cm^{-1} (optical absorption length ≈ 1 μm).

The probe beam is a HeNe laser with $\lambda = 633$ nm focused by lens L_2 to a spot size of 100 μm on the sample which can be shifted along the direction $\pm z$ shown in Fig. 1. The absorption coefficient of the sample at $\lambda = 633$ nm is 4.5 cm^{-1}.

The deflection angle of the probe beam is detected by a position sensor PS, whose output is observed on the oscilloscope O, and recorded on the plotter P.

The sample is mounted on a micrometer translator to move it along the $\pm z$-direction. Changing the sample position along z, the distance between the probe beam and the Ar^+-laser-heated surface of the sample is changed. The position sensor is biased in such a way that a deflection of the probe beam towards the sample surface (positive z direction) gives a positive signal output from the position sensor.

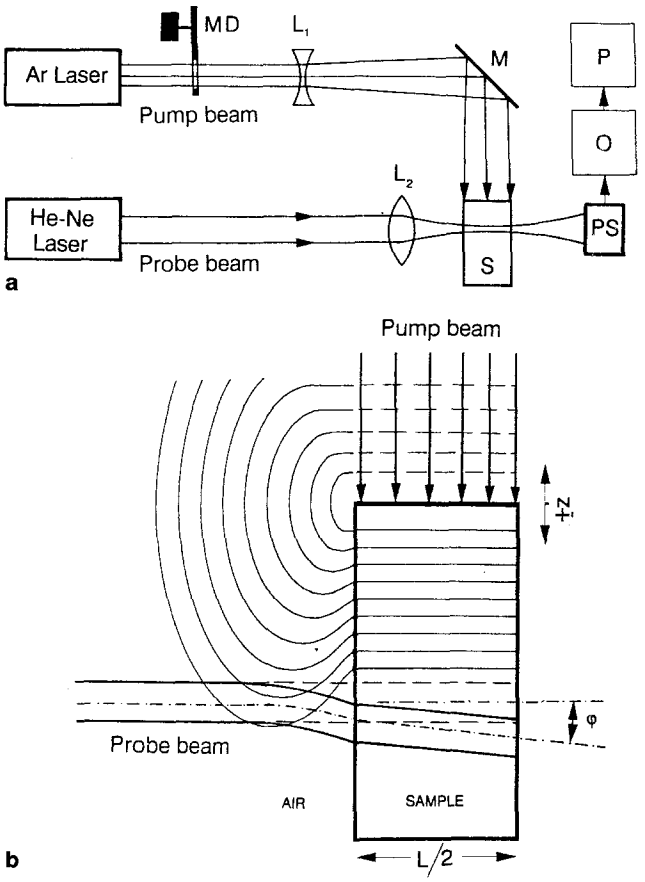

Fig. 1a, b. Experimental setup. **a** Schematic diagram of experimental apparatus. *MD:* mechanical modulator; L_1: concave lens; L_2: convex lens; *M:* mirror; *S:* sample; *PS:* position sensor; *O:* oscilloscope; *P:* plotter. **b** Probe beam deflection

2 Experimental results

Figure 2 shows the time behavior of the deflection signal $\delta V/V_0$ given as the change in voltage of the position sensor over its continuous bias, for several distances z of the probe beam from the Ar^+-laser-illuminated sample surface. The pump beam is switched on at $t = 0$ and the switch-off time is marked with a filled square on the curve. One sees that for $z = -0.5$ mm (curve 1) $\delta V/V_0$ increases, starting from $t = 0$, and reaches saturation at $t \cong 2$ s. After switching off the Ar^+ pump beam, $\delta V/V_0$ decreases rapidly.

For larger values of z (curves 2–4, Fig. 2) a more complex time behaviour is obtained. Near $t = 0$ there is a negative signal, and when the Ar^+ laser is switched off,

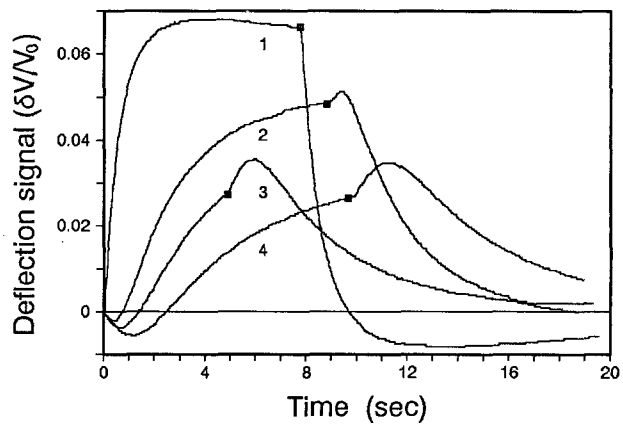

Fig. 2. Time dependence of the probe-beam deflection as a function of the distance z of the propagating beam from the illuminated sample surface: (*1*) $z = -0.5$ mm; (*2*) $z = -1$ mm; (*3*) $z = -1.25$ mm; (*4*) $z = -1.5$ mm

the deflection first continues to increase with a greater slope, and then decreases.

For $z = -0.5$ mm the deflection signal is positive and varies slowly according to heating and cooling of the sample. Obviously this is the ordinary photothermal deflection, corresponding to the positive contribution of a change Δn_T of the refractive index due to an increase of temperature (the probe beam deflects in the direction where the temperature T is highest)

$$\Delta n_T = \frac{dn}{dT}\Delta T,$$

where ΔT is the temperature increase, being $dn/dT > 0$ in chalcogenide.

For $|z| \geq 1$ mm (curves 2–4) the initial negative part is faster in time than the thermal one (we will indicate this part by the term kink). Here, we shall show that this negative part has a complex explanation which eventually involves a change Δn_e of the refractive index produced by an electronic contribution, and the total variation of the refractive index consist of two independent parts

$$\Delta n = \Delta n_T + \Delta n_e.$$

Note an important peculiarity: the negative response shown in Fig. 2 is observed when the probe beam propagates at a depth ≥ 1 mm below the pumped surface: much deeper than the absorption length (≈ 1 μm) of the pump beam. We have here the existence of an electronic response far from the pump beam. Measurements show an approximately linear dependence of the negative signal on the pump power (Fig. 3a) and does not depend on the probe-beam power (Fig. 3b). In Fig. 3 the power dependence of down-kinks is presented. It is difficult to select $\delta V/V_0$ from the up-kinks, because of a larger photothermal contribution.

We were not able to find a mechanism of long-range (≥ 1 mm) influence of the pump beam on the electrons in the region of the probe beam. Indeed, electrons and holes generated by pumping, cannot propagate along this distance; if pumping separates charges in space, the resulting electric field, due to the planar geometry, exists only in the region of the separation, and vanishes in the region of the probe beam.

As a result, we have supposed that the weak HeNe beam produces a long-livied variation of the refractive index depending, in accordance with Fig. 3b, not on the beam power, but on the total beam energy transmitted through the sample. This idea, as we will show below, easily explains Figs. 2 and 3 discussed above and is supported by other experimental results [9]. It has been fully explained in [8].

Starting from this assumption, the observed photodeflection behavior can be explained considering the following facts. The top face of the sample is uniformly illuminated by the Ar^+ pump beam whose dimensions are much larger than the thermal and carrier diffusion lengths. The probe beam is tightly focused (≈ 100 μm), as shown in Fig. 1b. The probe beam starts to move a

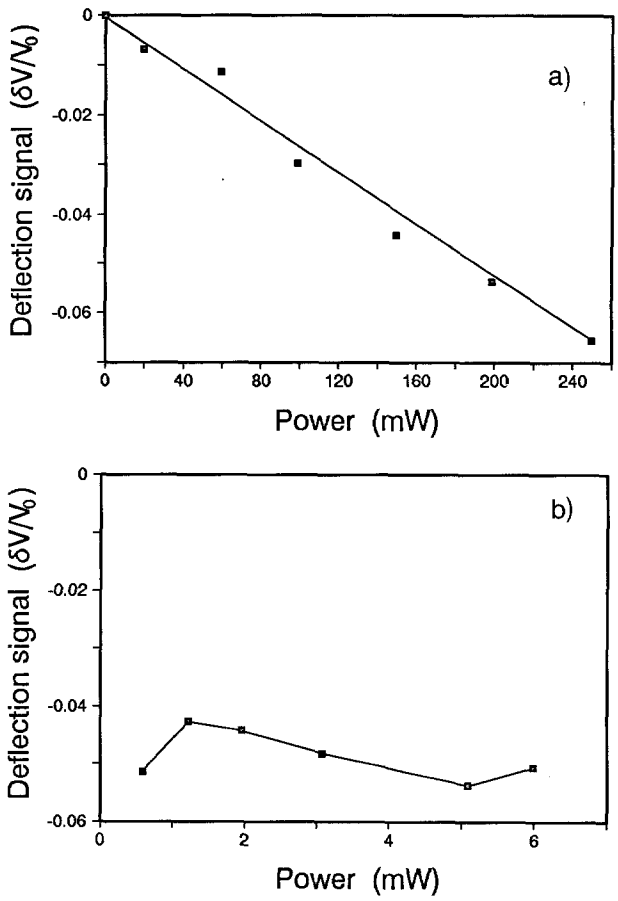

Fig. 3a, b. Dependence of the probe-beam deflection on (**a**) pump power, and (**b**) probe power

$t = 0$ even when the beam is at some distance z below the heated surface. Heat would take a time $t = z^2/8\chi$ (where $\chi = 3 \times 10^{-3}$ cm^2/sec is the thermal diffusivity of the sample) to reach the region where the HeNe beam propagates and therefore, cannot, be responsible for its immediate response.

However, being the thermal diffusivity of air $\chi_a = 0.2$ cm^2/sec, the time the heat needs to reach the depth z laterally to the sample is much shorter. For $z = -1$ mm, for example $t \cong 0.007$ s. With reference to Fig. 1b one may therefore assume that the initial movement of the probe beam is produced by a thermal gradient in the air near to the sample side. In air $dn/dT < 0$, and therefore the deflection angle is in the direction opposide to the one produced by the subsequent slow heating of the sample. A problem arises as far as the magnitude of the negative deflection angle is concerned. In this case, the situation can be accurately analyzed with a one-dimensional theory. The thermal deflection angle φ_T of the illuminated sample surface is given by

$$\varphi_T(z, t) = \frac{L}{n_s}\frac{\partial n_s(z, t)}{\partial z} = \frac{L}{n_s}\frac{\partial n_s}{\partial T_s}\frac{\partial T_s(z, t)}{\partial z}$$

$$= \frac{L}{n_s}\frac{\partial n_s}{\partial T_s}\frac{\partial T_s(0, t)}{\partial z}\exp\left(-\frac{z}{l}\right) = \varphi_T(0, t)\exp\left(-\frac{z}{l}\right), \quad (1)$$

Table 1. Different parameters involved in the curves of Fig. 2. z is the probe-beam depth below the heated surface, t_0 is the time at which the $\varphi_T = \varphi_e$, l is the thermal diffusion length. In column 4 the common value of the moduli of $\varphi_T = \varphi_e$ at $t = t_0$ are given, in column 5, the spatial refractive index gradient dn_e/dz produced by self-organisation in the channel is shown

0	1	2	3	4	5
N°	z [cm]	t_0 [s]	$l=\sqrt{8\chi t_0}$ [cm]	φ_T, φ_e [rad] $\times 10^4$	dn_e/dz [cm^{-1}] $\times 10^4$
1	0.05	–	–	–	–
2	0.1	0.8	0.138	0.84	5.2
3	0.125	1.4	0.183	1.0	6.2
4	0.15	2.4	0.24	1.2	7.5

where L is the horizontal path length in the sample of refractive index n_s, $l=\sqrt{8\chi t}$ and $\varphi_T(0, t)$ is the deflection angle for $z=0$.

Considering the curves of Fig. 2 all the curves referring to z values larger than 0.05 mm, at some time t_0, cross zero again. At this time the negative φ_e and the positive φ_T deflection angle are equal. Using (1), the data of the Fig. 2, and knowing by calibration of the setup that a change $\delta V/V_0 = 10^{-2}$ corresponds to an angular deflection $\varphi = 3 \times 10^{-5}$ rad, Table 1 has been obtained which gives for different values z (column 1) the t_0 values (column 2), the l values (column 3) and the common value $\varphi_T = \varphi_e$ at $t = t_0$ in column 4. In column 5 the space gradient dn_e/dz is also given. One may note that $l \geq z$ in all cases, as must be expected.

An estimate of the change of the incidence angle of the probe beam on the sample side, due to heating of air, is not easy; however, it can be easily inferred that because $dn_a/dT < dn_s/dT$ (by a factor 10 at most) this angle is much smaller than the one it would be in the sample at the same temperature. Moreover, it can easily be estimated that the rise in temperature at a given z-value in the sample is much larger than in air.

One should therefore conclude that $\varphi_e < \varphi_T$, while at t_0 they are equal. The circumstance that in the sample the negative deflection φ_e is much greater than in air can be explained as due to the effect of the spatial refractive-index distribution in the channel, produced by self-organisation. As explained before in the channel $dn_e/dz < 0$ [8] and the beam, entering the channel off-axis, is by this gradient pushed further away, magnifying the initial incidence angle.

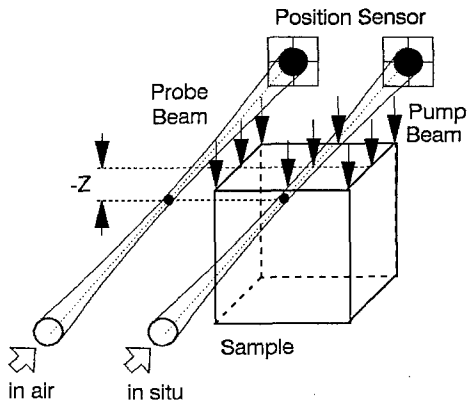

Fig. 4. The experimental arrangement to detect the presence of heating the air near the sample

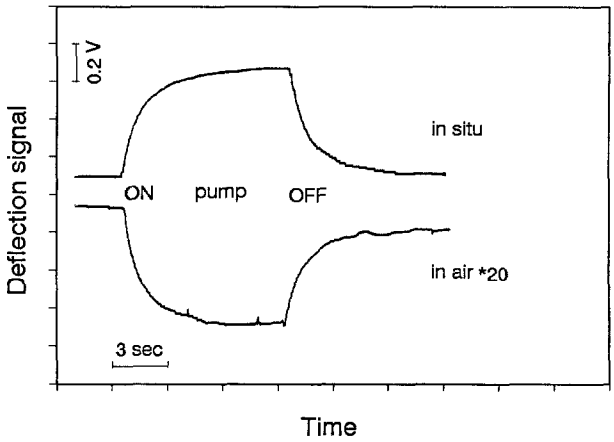

Fig. 5. Time dependence of the probe-beam deflection for the in situ and in air configuration shown in Fig. 4 for $z = -1.5$ mm

By using the experimental data of Table 1, the value of the spatial gradient dn_e/dz can be derived from the relation $\varphi_e = (L/n_s)(dn_e/dz)$, and is given in column 5. The values are in good agreement with results obtained in [8] with a different method.

To test the above presented theory we have performed a very simple experiment looking for the deflection of the probe beam travelling in air next to the sample. The arrangement is shown in Fig. 4. The upper surface covered with a black layer of a glass sample $5 \times 5 \times 10$ mm^3 was fully illuminated with the pump laser. In the in-situ disposition the probe beam traveled in the sample at some depth z below the surface. When the pump beam was switched on a positive (thermal) deflection started which, after switching off the pump beam, decreased to zero (Fig. 5).

Making the probe beam travel in air parallel to the lateral glass surface at the same vertical height z, as shown in Fig. 4, a deflection was obtained which was, however, in the negative direction (Fig. 5), as it does being dn/dT negative in the case of air, and which was about 20 times smaller than in the case of the bulk sample.

This fully confirms the presence of a heated region near the lateral surface of the sample which supports the explanation of the experimental results given in Fig. 2.

3 Conclusion

In this paper it has been shown that the photodeflection method used in the in situ configuration to study As-S glass samples, reveals a complex behaviour. The time behaviour of the signal is the result of heating by the pump beam of both the sample and the nearby air, and

of the creation of a self-ordered channel induced in the sample by the probe beam.

Once the different processes occurring in the experiment have been taken into account one obtains experimental evidence of the existence of the self-ordered channell and one can derive the values of the refractive-index gradient produced by the self-ordering process.

The obtained values are in good agreement with the ones obtained in different experiments [8].

Acknowledgements. We are grateful to the participants of a seminar headed by Prof. V.M. Agranovich for useful discussions.

References

1. W.B. Jackson, N.M. Amer, A.C. Boccara, D. Fournier: Appl. Opt. **20**, 1333 (1981)
2. A.C. Boccara, D. Fournier, J. Badoz: Appl. Phys. Lett. **36**, 133 (1980)
3. G. Suber, M. Bertolotti, C. Sibilia, A. Ferrari, F. Genel-Ricciardiello: J. Therm. Anal. **32**, 1039 (1987)
4. M. Bertolotti, R. Li Voti, G. Liakhou, C. Sibilia: Rev. Sci. Instrum. **64**, 1576 (1993)
5. A. Skumanich, D. Fournier, A.C. Boccara, N.M. Amer: Appl. Phys. Lett. **47**, 402 (1985)
6. M. Bertolotti, A. Ferrari, C. Sibilia, G. Suber, B. Apostol, P. Jani: Appl. Opt. **27**, 1811 (1988)
7. B.P. Antonyuk, M. Bertolotti, E. Fazio, G. Liakhou, C. Sibilia: J. Mod. Opt. **39**, 1965 (1992)
8. B.P. Antonyuk, A.M. Andriesh, M. Bertolotti, S.A. Kiselev, G.L. Liakhou, C. Sibilia: Phys. Rev. B **47**, 10186 (1993)
9. B.P. Antonyuk, S.A. Kiselev, S.F. Musichenko, M. Bertolotti, R. Li Voti, C. Sibilia, G. Liakhou: Phys. Rev. B (submitted)
10. B.P. Antonyuk: Phys. Lett. A **159**, 298 (1991)
11. B.P. Antonyuk, B.E. Stern: Phys. Lett. A **123**, 95 (1987)