

The kinetics of photo-induced dichroism in thin films of amorphous arsenic triselenide

Robert E. Johanson · Matthew Kowalyshen ·
Daniel DeForrest · K. Shimakawa · S. O. Kasap

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Abstract We have measured the dichroism in amorphous As_2Se_3 films induced by a polarized pump beam of near bandgap light. The total induced dichroism saturates at a value that depends linearly on sample thickness—the relative change in the absorption coefficient is about 0.2%. We fit the time dependence of the induced dichroism to a stretched exponential function of the form $\exp(-(t/\tau)^\beta)$ and find that the time constant (τ) depends inversely on the pump-beam intensity and the stretching exponent (β) is in the range 0.5–0.6 depending on thickness but relatively independent of the intensity. A dc electric field had no effect on the induced dichroism. The addition of a small amount of iodine (0.1%) increased τ in some but not all samples.

1 Introduction

A glass is usually isotropic. The lack of any long-range order results in a random averaging over all orientations of possible microstructure. Lacking any preferred direction (providing one was not impressed during formation of the glass, for example by an external electric field), any macroscopic property can not depend on orientation and thus

must be isotropic. Of particular interest for this paper, a glass should not exhibit either birefringence or dichroism. However, anisotropy can be induced in certain glasses by polarized light with a photon energy near the bandgap [1, 2] (see also recent reviews by Tanaka, and Lyubin and Klebanov and references therein [3, 4]). Typically, the material will bleach—the absorption coefficient will decrease—but only for light polarized the same as the inducing beam resulting in dichroism. The index of refraction might also change resulting in birefringence.

A useful framework for these effects was put forward by Fritzsche [5]. He noted that although a glass is initially overall isotropic, small regions called micro-volumes can be highly anisotropic especially for glasses that are composed of rings or chains of atoms. The micro-volumes can preferentially absorb light with a certain polarization and the recombination event can induce local structural changes; if the new structure preferentially absorbs a different polarization then dichroism results. One can think of this process as a kind of optical pumping where the micro-volumes are altered preferentially toward states that weakly absorb the applied polarization. Three conditions must be met by the material: there must be sufficient freedom to allow the micro-volumes to change to a different yet stable structure, the electron-hole recombination must occur within the absorbing micro-volume with high probability, and a low-energy pathway must exist between stable configurations. Chalcogenide glasses fulfill these conditions, and in particular amorphous arsenic triselenide (a- As_2Se_3) has been the paradigm for these effects.

The purpose of this work is to carefully measure the kinetics of the photo-induced dichroism in a- As_2Se_3 . The time-dependence of the dichroism follows a stretched exponential [6–8] and careful measurements of the stretched exponential parameters can provide guidance for

R. E. Johanson (✉) · M. Kowalyshen · D. DeForrest ·
S. O. Kasap
Department of Electrical and Computer Engineering, University
of Saskatchewan, Saskatoon, SK, Canada S7N 5A9
e-mail: robert.johanson@usask.ca

K. Shimakawa
Department of Electrical and Electronic Engineering, Gifu
University, Gifu 501-1193, Japan

microscopic models. We also look for changes in the kinetics with the addition of iodine and by applying an electric field. Note that although we interpret our results in terms of dichroism, we do not independently measure the real and imaginary parts of the index of refraction; some birefringence might be present.

2 Experimental details

Our apparatus is similar to that used by other researchers [3]. A HeNe laser supplies the pump beam that induces the dichroism; the beam passes through a polarizer that can be rotated by 90° and a neutral density filter. The spot on the sample is about 2 mm in diameter and has a maximum intensity of 1.2 mW/mm^2 . The probe beam is derived from an array of nineteen red LEDs (peak wavelength of 635 nm). The use of LEDs avoids the interference patterns at the detector that can occur when using lasers. The probe beam passes through a polarizer rotating at a frequency f and is then focused onto the sample producing a spot of about 1 mm in diameter. After the sample, the beam is focused onto a pin diode photodetector, and a lock-in amplifier extracts the $2f$ signal; the $2f$ signal is proportional to the dichroism of the sample. Any residual polarization of the probe beam (which also produces a $2f$ signal) is measured and removed during analysis. An experimental run consists of first photo-darkening the sample and then exposing the sample to the pump beam while the $2f$ signal is recorded. Once the dichroism saturates, the polarization of the pump beam is rotated by 90° , and again the signal is recorded until saturation. The process is repeated four or more times. The analysis extracts the anisotropy factor A from the data

$$A = 2 \frac{I_{//} - I_{\perp}}{I_{//} + I_{\perp}} \quad (1)$$

where $I_{//}$ and I_{\perp} are the transmitted intensities for probe light with polarization along and perpendicular to the pump beam's initial polarization. For $|A| \ll 1$,

$$A \approx (\alpha_{\perp} - \alpha_{//})d \quad (2)$$

where α is the absorption coefficient for light polarized in the indicated direction and d is the sample thickness. The time dependence of A is fit to a stretched exponential function

$$A(t) = A_{\text{sat}} + (A_{\text{init}} - A_{\text{sat}})e^{-(t/\tau)^{\beta}} \quad (3)$$

where $A_{\text{init}} = A(0)$ (any change to the pump beam defines $t = 0$), and the three fitting parameters are $A_{\text{sat}} = A(\infty)$ the

saturated anisotropy, τ the time constant, and β the stretching exponent. A stretched exponential is required as a simple exponential does not fit well to the data as shown in Fig. 1.

The samples used in this study are evaporated a-As₂Se₃ with a composition close to stoichiometry. The five samples have thicknesses ranging from 0.25 μm to 1.93 μm . Four additional samples are doped with 0.1% iodine and have thicknesses from 0.55 μm to 1.78 μm . A single sample of a-As₂Se₃ (prepared at Gifu University) has transparent indium-tin-oxide electrodes in a sandwich geometry so that a dc electric field can be applied transverse to the substrate.

3 Results and discussion

Starting from zero anisotropy, near saturation is attained after about 10 min of illumination with a pump beam intensity of 1.2 mW/mm^2 (Fig. 1). Rotating the polarization of the pump light by 90° reverses the dichroism so that A saturates to a negative value with the same time scale. The reversals can be repeated scores of times without any sign of fatiguing. For each reversal, we fit the data to Eq. 3 and obtain the three fitting parameters. Statistics over all the reversals provide an estimate of the errors in the parameters.

We first discuss the effects of pump light intensity $I_{\text{pump}} \cdot A_{\text{sat}}$ does not vary with I_{pump} ; the implication is that thermal relaxation is much slower than the inducing process. Within the model described above, the level of dichroism is determined by an equilibrium with thermally

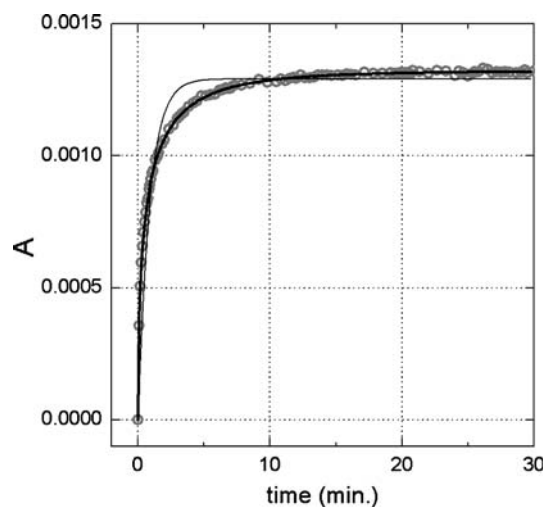


Fig. 1 Typical time dependence of the anisotropy factor A . A stretched exponential function (thick line) gives a very good fit to the data (circles). The best fit using a simple exponential function (thin line) deviates significantly from the data

driven structural changes which tend to randomize the micro-volumes. If the thermal relaxation rate were comparable or larger than the inducing rate then increasing I_{pump} would push the equilibrium toward greater dichroism. The failure to observe any dependence on I_{pump} implies that A_{sat} is instead limited by the total number of suitable micro-volumes. The rate $(1/\tau)$ depends linearly on I_{pump} (Fig. 2), not a surprising result from which we infer that the structural changes produced by recombination events are independent of each other. Our maximum I_{pump} is not very large and non-linear effects might occur for larger I_{pump} . Finally, β is mostly independent of I_{pump} although Fig. 3 shows a small increase for the smaller values of I_{pump} . The significance of β for a microscopic model is not obvious. It might be a measure of the distribution of energy barriers for structural reconfiguration; a single energy barrier produces a simple exponential time dependence. If correct then β is determined by the material's structure and should not depend on I_{pump} . We note that the values we find, 0.5–0.6, are about 0.2 less than other researchers have observed on similar material but thicker samples [9].

Next we discuss variations with thickness. As expected from Eq. 2, A_{sat} depends linearly on sample thickness; the slope gives $(\alpha_{\perp} - \alpha_{\parallel}) \approx 48 \text{ cm}^{-1}$. Since at the probe wavelengths $1/\alpha \sim 0.5 \mu\text{m}$, the maximum relative change in the absorption coefficient amounts to about 2×10^{-3} . Both β and the rate decrease with increasing sample thickness (Figs. 4 and 5). The rate decreases because the light intensity of the pump beam falls off with depth in the material and thus the rate also decreases with depth. The observed rate is an average over the thickness of the sample; so the thicker the sample, the lower the average. A more sophisticated analysis that can take the attenuation

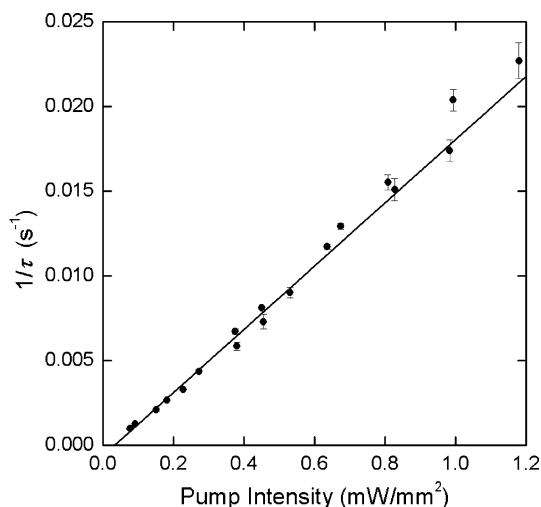


Fig. 2 The dependence of the rate for inducing dichroism ($1/\tau$) on pump light intensity. The line is the linear regression

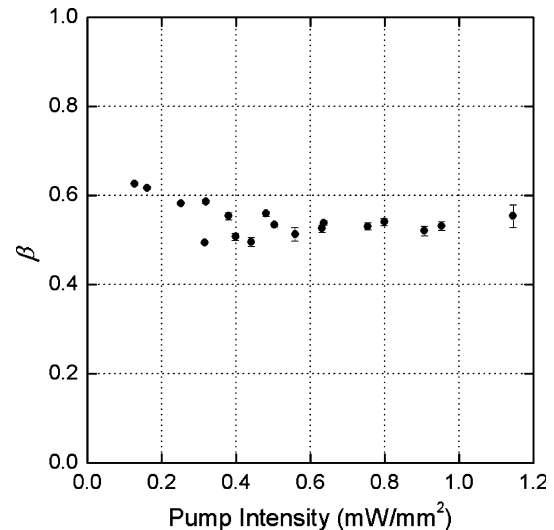


Fig. 3 The dependence of the stretching exponent β on pump light intensity

into account and provide parameters for an idealized infinitely thin sample will be the subject of a future paper. However, the stretched-exponential parameters quoted here are of use in showing trends and providing a means to compare results on samples with similar thicknesses. The decrease in β can not be explained by the same mechanism since β depends only weakly on intensity and requires further study.

The sample with transparent electrodes allows us to apply an electric field while the pump light induces the dichroism. According to the model of Fritzsche, polarized light is effective in inducing anisotropy only if the recombination of the electron and hole takes place in the same micro-volume responsible for absorbing the photon.

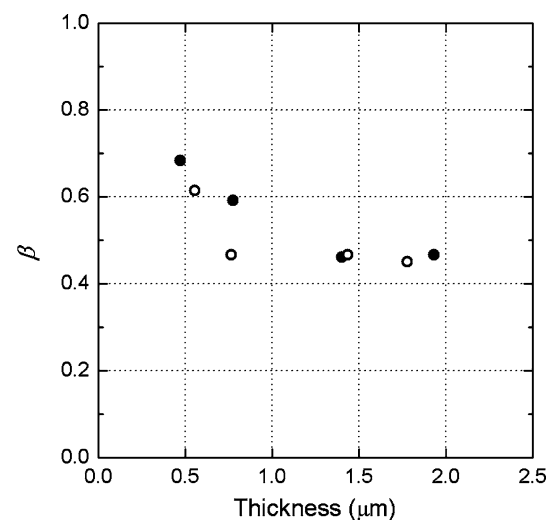


Fig. 4 The dependence of the stretching exponent β on sample thickness for a-AsSe (closed circles) and a-AsSe doped with 0.1% iodine (open circles)

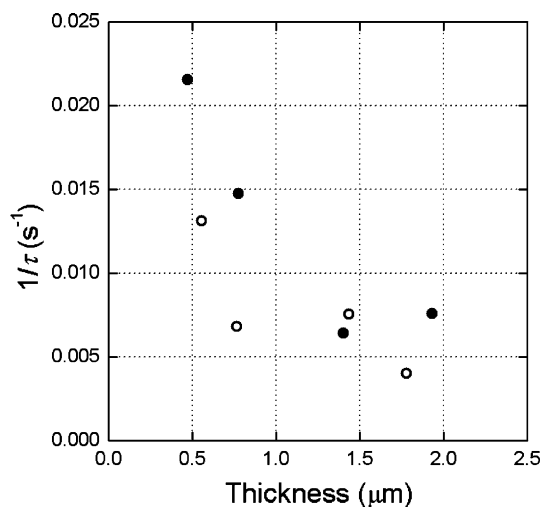


Fig. 5 The dependence of the rate ($1/\tau$) on sample thickness for a-AsSe (closed circles) and a-AsSe doped with 0.1% iodine (open circles)

Table 1 Comparison of the stretched exponential fitting parameters obtained with and without an applied transverse electric field. The errors are statistical over four measurements

	A_{sat}	τ (s)	β
No field	0.0112 ± 0.0002	367 ± 10	0.35 ± 0.1
5 V/ μm	0.0108 ± 0.0002	335 ± 50	0.35 ± 0.3

If the electron or hole recombines in a different micro-volume then the resulting changes to the structure are uncorrelated with the particular structure that preferentially absorbs the incident polarization. A sufficiently strong electric field should break the exciton and drift either electron or hole or both away from the absorbing site and hence reduce the efficiency of producing the dichroism. We expect τ to increase with electric field and perhaps β to decrease stretching out the curve. The results do not agree with our expectations. The kinetics with and without a transverse electric field of 5 V/ μm did not change; the fitting parameters are listed in Table 1. We must emphasize that this result is preliminary and more data is required, especially at higher fields, before any conclusions can be reached regarding the models.

Adding small quantities of iodine affects charge transport in a-As₂Se₃; in particular, the hole mobility increases significantly [10]. Should the electron-hole pair separate, a more mobile hole would be more likely to diffuse away from the absorbing micro-volume leading to a decrease in

the rate. The effect of iodine on the structure is not known. As a halogen, iodine forms a single bond and thus should reduce the average coordination number of the glass perhaps making for easier structural rearrangements. The data show that adding 0.1% iodine has no substantial effect on A_{sat} or β (Fig. 4). Adding iodine decreased the rate significantly for three of the four samples compared to undoped a-As₂Se₃ of similar thickness but not the fourth sample (Fig. 5).

4 Conclusions

Measurements of the kinetics of photo-induced dichroism in a-As₂Se₃ can be used to constrain models of the phenomenon. In particular, any model must account for the stretched exponential time dependence and why β is in the range 0.5–0.65 independent of light intensity and only slightly dependent on sample thickness. We find no non-linear effects and that thermal relaxation is unimportant over the range of light intensity studied. We did not find any effect of an external electric field; measurements at larger fields will test the importance of geminate recombination for photo-induced dichroism. Doping with 0.1% iodine produced an increase in τ in some samples consistent with the increase in hole mobility.

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References

1. V.G. Zhdanov, V.K. Malinovskii, Sov. Tech. Phys. Lett. **3**, 943 (1977)
2. V.G. Zhdanov, B.T. Kolomiets, V.M. Lyubin, V.K. Malinovskii, Phys. Status Solidi A **52**, 621 (1979)
3. K. Tanaka, ch. 4 in *Handbook of Advanced Electronics and Photonic Materials and Devices*, vol. 5, ed. by H.S. Nalwa (Academic Press, 2001)
4. V.M. Lyubin, M.L. Klebanov, ch. 6 in *Photo-Induced Metastability in Amorphous Semiconductors*, ed. by A.V. Kolobov (Wiley-VCH Verlag & Co., 2003)
5. H. Fritzsche, Phys. Rev. B **52**, 15854 (1995)
6. V.K. Tikhomirov, G.J. Adriaenssens, Phys. Rev. B **55**, R660 (1997)
7. P. Hertogen, Ph.D. thesis (Katholie University Leuven, 2000)
8. P. Hertogen, G.J. Adriaenssens, J. Non-Cryst. Solids **266**, 948 (2000)
9. P. Hertogen, V.K. Tikhomirov, G.J. Adriaenssens, J. Non-Cryst. Solids **256–257**, 343 (1999)
10. G. Pfister, A.R. Melnyk, M.E. Scharfe, Solid State Comm. **21**, 907 (1977)