

***IN-SITU* SIMULTANEOUS MEASUREMENTS OF PHOTOINDUCED VOLUME AND BANDGAP CHANGES IN AMORPHOUS As₂Se₃ FILMS**

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In-situ simultaneous measurements of photodarkening (PD) and photoinduced volume changes (PVC) of amorphous As₂Se₃ films have been performed with a newly developed system based on a computer controlled spectroscope and a phase-shifting interferometer (PSI). This new system provides us records of both PD and PVC in chalcogenide glasses during and after illumination with a common time axis. We have observed that the PVC saturates faster than the PD in *a*-As₂Se₃ films.

Keywords: Chalcogenide glasses, Photoinduced volume change, Photodarkening

1. Introduction

Although photodarkening (PD) and photoinduced volume changes (PVC) are well known phenomena in amorphous chalcogenides, the mechanisms of these phenomena are still not clear. The correlations between PD and PVC have been reported in recent years [1,2]. However, PD and PVC were measured individually in all previous experimental works. To understand the dynamics and correlations of PD and PVC in chalcogenide glasses, *in-situ* simultaneous measurements are required, since they will provide the important information about the time evolution of the changes. We have developed a real-time *in-situ* surface height measuring system based on phase-shifting interferometer (PSI) and performed the *in-situ* measurements of PVC in chalcogenide glasses [3]. This newer technique overcomes the drawbacks of conventional thickness measuring systems based on the spectral analysis of interference fringes [4,5].

We report a real-time computer controlled spectroscope to measure the PD and put these two components together as an *in-situ* simultaneous PD and PVC measuring system. The surface height map of the sample and the spectroscopic analysis of the transmission data are obtained at a maximum rate of every 1/4 second. We have found that the time evolution of PVC seems to be different from that of PD [6].

2. Experimental

2.1 Sample preparation

The films of *a*-As₂Se₃ (thickness, $d \sim 500$ nm) were deposited onto sapphire substrates (13 mm in diameter and 0.5 mm in thickness) by the conventional thermal evaporation method in vacuum ($\sim 1 \times 10^{-6}$ Torr) at room temperature. The films were deposited at normal incidence to the substrate (so-called flat deposition), and were annealed below the glass transition temperature

(433 K). The samples were mounted onto an aluminum block to reduce the temperature rise during illumination.

2.2 In-situ measurement system

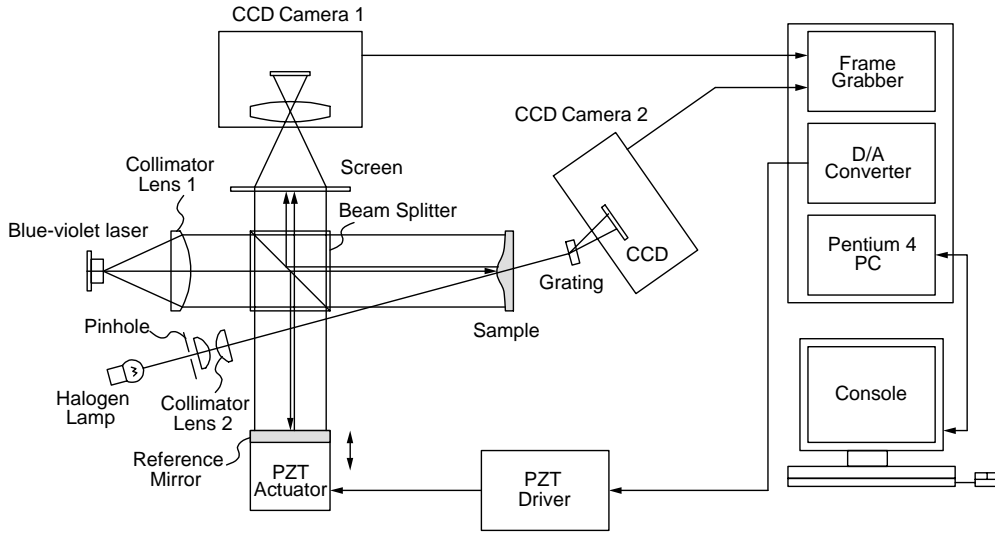


Fig. 1. In-situ simultaneous measuring system of PD and PVC based on the combination of phase-shifting interferometer and computer controlled spectroscope.

As shown in Fig. 1, the phase-shifting interferometer (PSI) is employed to measure the PVC [3]. A blue-violet laser (wavelength, $\lambda \sim 405$ nm) is used to improve the accuracy and to avoid multiple reflections in the films. The reference mirror is driven by a PZT actuator with a step of $\lambda/8$ (i.e. $\lambda/4$ of optical path length) directed along the light beam axis to shift the phase of the interference fringes. The interference fringes reflect the surface height variation of the sample. A set of seven images of phase-shifted interference fringes are obtained by the frame grabber to calculate the surface height. We employ the seven-frame method [7] to improve the accuracy by reducing the effects of mechanical vibration, and optical and electronic noises. The surface height is given at every point (pixel) as

$$h(x, y) = \frac{\lambda}{4\pi} \tan^{-1} \left[\frac{7\{I_2(x, y) - I_4(x, y)\} - \{I_0(x, y) - I_6(x, y)\}}{8I_3(x, y) - 4\{I_1(x, y) - I_5(x, y)\}} \right] \quad (1)$$

where $I_n(x, y)$ is the intensity of point x, y in frame n ($n = 0, 1, \dots, 6$), and λ is the wavelength of the probe light. To improve the accuracy, the surface height variations from the initial state are obtained by canceling the initial surface height. The surface height variations Δh are given as

$$\Delta h(x, y, t) = h(x, y, t) - h(x, y, 0) \quad (2)$$

where $h(x, y, t)$ is the surface height of point x, y at time t , $h(x, y, 0)$ the initial surface height of point x, y . With this method, the surface height profile can be obtained every 1/4 second with ± 10 Å in accuracy.

To measure the PD, a computer controlled spectroscope is employed. A small probe light beam (~ 0.5 mm in diameter) that is produced by a halogen lamp passes through a pinhole and a collimator lens 2, and is incident on the center of the photodarkened area (See Fig. 1). Some of the probe light is absorbed by the films, some is reflected on the surface and some is transmitted. The

transmitted probe light is decomposed into a spectrum by the grating. The spectrum is directly projected onto the surface of a CCD chip in CCD camera 2 (See Fig. 1). The correlation between the spectrum at wavelength λ and the position of the pixel in the CCD camera $x(\lambda)$ is given as

$$x(\lambda) \approx \frac{z\lambda}{D} + B \quad (3)$$

where z is the distance between the grating and the surface of the CCD chip, D is the grating period, and B is the offset due to the arrangement. The offset B is obtained by an initial calibration. The spectrum of transmission is obtained every 1/4 second, and is synchronized with the measurement of the surface height. The change of the absorption coefficient $\Delta\alpha$ at the wavelength λ is defined as

$$\Delta\alpha(t) = \frac{\log T(0) - \log T(t)}{d} \quad (4)$$

where $T(0)$ and $T(t)$ are the transmission at the wavelength λ in the initial state and at time t , respectively, and d is the thickness of the film. As $\Delta\alpha$ is obtained for any wavelength, the change in bandgap using the Tauc plot is also possible to estimate.

The power densities of the illumination, the probe laser for the interferometer (PVC), and the probe light for the optical absorption spectroscope (PD), were 100 mW/cm^2 , 1.2 mW/cm^2 , and $0.4 \text{ }\mu\text{W/cm}^2$, respectively. Therefore, we can ignore the effect of the probe light on the sample, because the power densities of the probe lights are much smaller than the illumination power density.

The expanded probe laser beam ($\sim 10 \text{ mm}$ in diameter) for the interferometer is incident normal to the sample. The sample is illuminated with the collimated solid state laser (wavelength, $\lambda = 635 \text{ nm}$) at an incident angle of 15 degrees with a 2 mm beam spot diameter. The probe light beam for the spectroscope is pointed at the center of the illumination spot at an incident angle of 15 degrees from the opposite side. The measurements were done at room temperature in air.

3. Experimental results and discussion

The time evolutions of both the PVC and PD in $a\text{-As}_2\text{Se}_3$ film, and the surface height maps that is obtained by the surface height measuring system described in the previous section are shown in Fig. 2. The surface height increased by 8.5 nm ($\Delta d/d \approx 1.7 \%$) after 1200 seconds of illumination and reached an equilibrium state, while the change in the optical absorption is still taking place. When the illumination was turned off (after illumination of 1500 s), the surface height and $\Delta\alpha$ decreased around 1 nm and 500 cm^{-1} , respectively, from those values just before stopping the illumination.

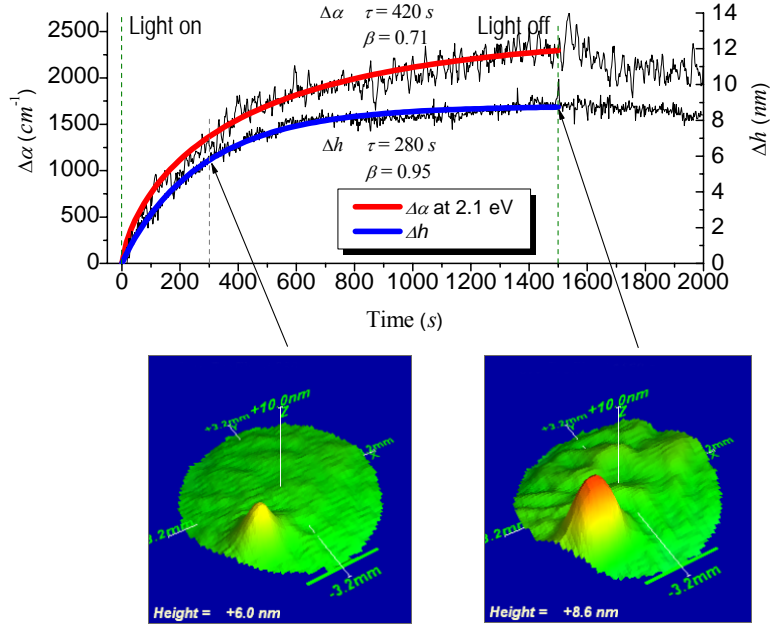


Fig. 2. Time evolution of the $\Delta\alpha$ and Δh for a -As₂Se₃ film ($\lambda = 635$ nm, 100 mW/cm²), and height maps at 300 s and 1500 s after illumination starts.

As shown in Fig. 2, PD and photoinduced volume expansion (PVE: increase of surface height) are observed during and after illumination. Transient PD and transient PVE [8] must be involved during illumination, since after stopping illumination, slight decreases of $\Delta\alpha$ and Δh are observed. The remaining increases of $\Delta\alpha$ and Δh after the cut off of illumination are the so-called metastable PD and metastable PVE [8], respectively. We analyze the PD and PVC during the illumination by nonlinear fitting using the Marquardt-Levenberg algorithm [9]. Both the PD and PVE are presented by the following stretched exponential function:

$$y = A \left[1 - \exp \left\{ - \left(\frac{t}{\tau} \right)^\beta \right\} \right] \quad (5)$$

where y is the measured value ($\Delta\alpha$ or Δh) at time t , and A is a constant (equal to the total amount of change), τ and β are, the effective reaction time and the dispersion parameter, respectively.

As shown in Fig. 2, the time evolution of Δh is very close to an exponential function (β is close to 1), while the change in $\Delta\alpha$ at 2.1 eV is given by a typical stretched exponential function ($\beta = 0.71$). The effective reaction time τ for Δh and $\Delta\alpha$ are 280 s and 420 s, respectively: This behavior indicates that $\Delta\alpha$ continues to change (increase) even after the changes in Δh saturate. The above results suggest that there is no one-to-one correspondence between PD and PVE as pointed out in an earlier work [10].

It is of interest to observe the dependence of photon energy of the probe light on $\Delta\alpha$. Fig. 3 shows the time evolution of $\Delta\alpha$ at 1.85 eV, 2.0 eV, 2.1 eV and 2.21 eV of probe light. The magnitude of $\Delta\alpha$ is greater at higher photon energies and is represented by a stretched exponential function.

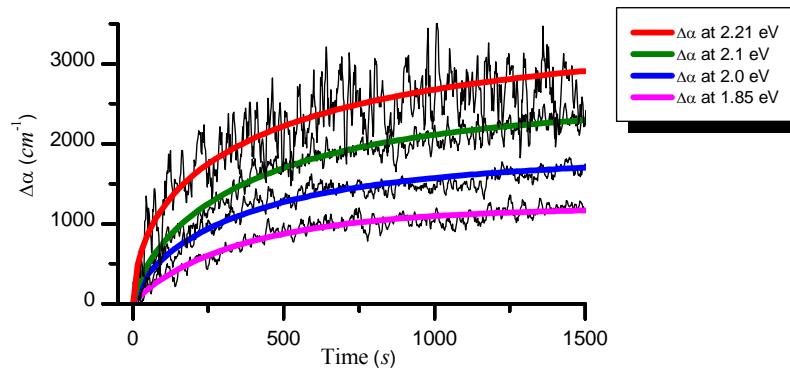


Fig. 3. Time evolution of the $\Delta\alpha$ at various light energies for $a\text{-As}_2\text{Se}_3$ film.

The time evolution of $\Delta\alpha$ depends on the photon energy of the probe light. The higher energy probe light monitors the higher energy optical absorption region. The fact that $\Delta\alpha$ is greater at higher photon energies seems to be a natural consequence, since the initial optical absorption at higher energies is greater than that at lower energies. Of particular interest are the parameters τ and β which appear in the stretched exponential function. The effective reaction time τ in the higher energy optical absorption region is greater than that for the lower energy absorption region. The PD seems to take place more slowly in the higher energy region compared to the lower energy region (i.e. there is no parallel shift of α vs. $h\nu$ in the optical absorption). The Tauc plots in Fig. 4 show that density of the plot lines in after time progress is higher in lower energy part than that in higher energy part (see inserted figures). Probably, the effects of photoinduced defect creations [8] can be involved in the optical absorption in lower energies. Details are not clear at present.

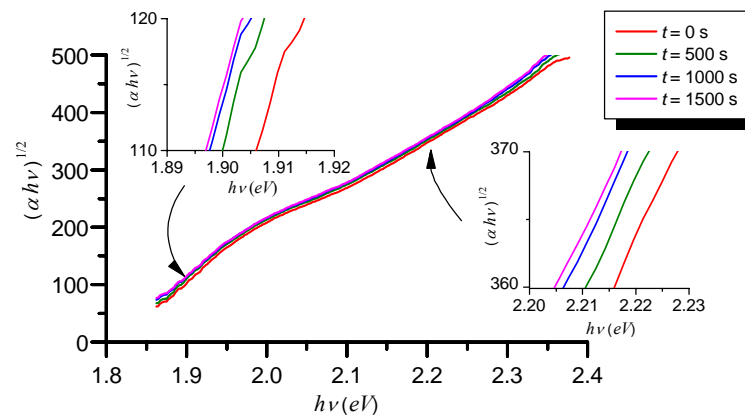


Fig. 4. Time evolution of Tauc plots for $a\text{-As}_2\text{Se}_3$ film.

Finally, we discuss the effect of heating on PD and PVE. According to a thermal simulation using the finite element method, the temperature rise in the present illumination conditions is estimated to be up to 2 degrees in the center of the illumination spot. This relatively low temperature rise is attributed to the heat sinking effect of the sapphire substrate and the aluminum block. Therefore any effect of temperature on PD and PVE can be ignored.

5. Conclusions

An *in-situ* system for the simultaneous measurement of PD and PVC in amorphous chalcogenides has been established. Through the simultaneous measurements of the time evolution of PD and PVC in *a*-As₂Se₃ films, we have found the differences in the growth kinetics for PD and PVC. Differences in both the effective reaction times and the dispersion parameters for PD and PVC suggest that the origins of PD and PVC are not the same. An interference effect between the film surface and the interface between the film and the substrate, as well as defect absorption, should be taken into account in the low energy region of the probe light. In addition, as the illumination was made in air, some photoinduced oxidation may also take place [11]. A measurement in a cryostat is desirable, which will be performed in a next step of the present work.

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