Transient responses of photodarkening and photoinduced volume change in amorphous chalcogenide films

K. SHIMAKAWA[*], Y. IKEDA

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

To understand the dynamics and correlations between photodarkening (PD) and photoinduced volume changes (PVC) in chalcogenide glasses, we built up a *in-situ* simultaneous PD and PVC measuring system based on computer analyzed spectroscope and phase-shifting interferometer (PSI). This new system provides us the records of both PD and PVC during illumination with common time axis. We have found that significant transient components of PD and PVC exist only during illumination. It is also found that the PVC reaches equilibrium faster than the PD.

1. Introduction

One of the interesting phenomena observed in chalcogenide glasses is the photodarkening (PD). To understand the mechanisms many researchers have been involved in this topic for the last three decades [1-5]. In spite of great efforts, overall features of PD are still not clear. The volume changes, on the other hand, have been observed by photoillumination (photoinduced volume change (PVC)). It is naturally believed that PVC is directly related to PD, i.e. there is one-to-one relation between PD and PVC. In the present memorial article of celebration of 95 years of Professor Grigorovici, we briefly review the current understanding of PD and PVC, based on our recent studies.

The correlations between PD and PVC have been reported in recent years [6-8]. However, PD and PVC were measured individually in all previous experimental works [6-13] in which the *time evolution* of PD or PVC has been discussed in details. 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 a real-time computer analyzed spectroscope to measure the PD, and put them together as the *in-situ* simultaneous PD and PVC measuring system [14]. The surface height map of the sample and the spectroscopic analysis data of the transmission are obtained in every 1/4 seconds at maximum.

We have found that the time evolution of PVC seems to be different from that of PD. It is therefore expected that there is no one-to-one correlation between PD and PVC, which is contrary to the expectations of most researchers in this field [2].

2. Experimental

Fig. 1 shows the *in-situ* measurement system of PVC and PD. The phase-shifting interferometer (PSI) is employed to measure the PVC [13]. 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. The details of the height evaluation method is described elsewhere [13,15].
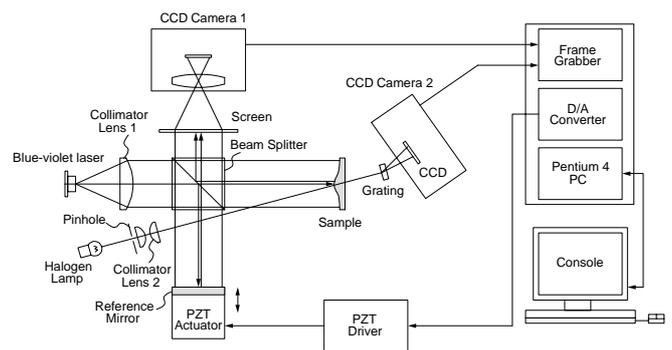
Fig. 1. In-situ simultaneous measuring system of PD and PVC based on the combination of phase - shifting interferometer and computer controlled spectroscope.

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. 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, and the spectrum of transmission is obtained every 1/4 second, which is synchronized with the measurement of the surface height. The photograph of the present system is shown in Fig. 2.
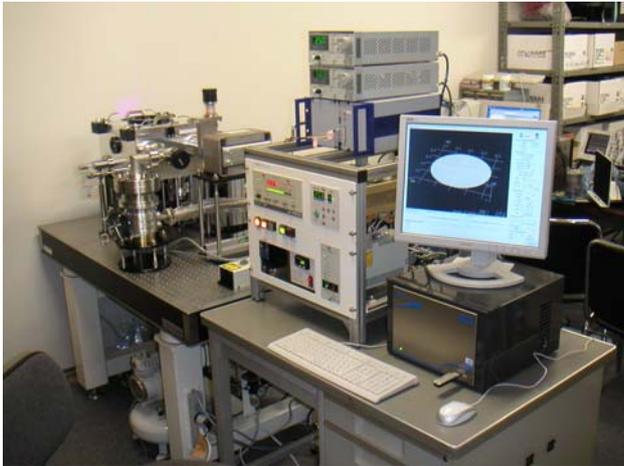
Fig. 2. Photograph of the present system. The system is now commercially available from YM systems Inc. Kyoto, Japan.

The change of the absorption coefficient $\Delta\alpha$ at the wavelength λ is defined as

$$\Delta\alpha(t) = \frac{\log T(0) - \log T(t)}{d} \qquad (1)$$

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 μW/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 films of a-As$_2$Se$_3$ (thickness, $d \sim 500$ nm) were deposited onto sapphire substrates by the conventional thermal evaporation method in vacuum ($\sim 1\times10^{-6}$ 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). Sapphire substrates (13 mm in diameter and 0.5 mm in thickness) were used to minimize temperature rise, and those substrates were mounted onto an aluminum block to reduce the temperature rise during illumination.

3. Experimental results and discussion

Before showing the results of simultaneous measurement of PD and PVC, we will show the time evolution of PD [11] and PVC [13], as shown in Figs. 3 and 4 respectively, which have been independently measured in As$_2$Se$_3$. Fig. 3 shows the initial kinetics of $\Delta\alpha$. $\Delta\alpha$ increases and decreases very rapidly when the illumination is switched on and off, but in neither case does it return the original value, i.e. the metastable photodarkening is accumulated with each successive illumination. The total increase in $\Delta\alpha$, during illumination, is the sum of the transient and the metastable PD. The transient parts of the changes are found to be nearly 60% and 30 % of the total changes induced during illumination at 300 and 50 K, respectively. The cycling was repeated many times after the metastable state was reached, and every illumination confirmed the occurrence of only the transient PD. Fig. 4 shows the photoinduced volume expansion (PVE: increase of surface height) is observed during and after illumination in a-As$_2$Se$_3$ films. Transient PVE [13] must be involved during illumination, since after illumination is cut off, a slight decrease of the surface height is observed. Remaining increase of surface height after cut off the illumination is so called metastable PVE [1].
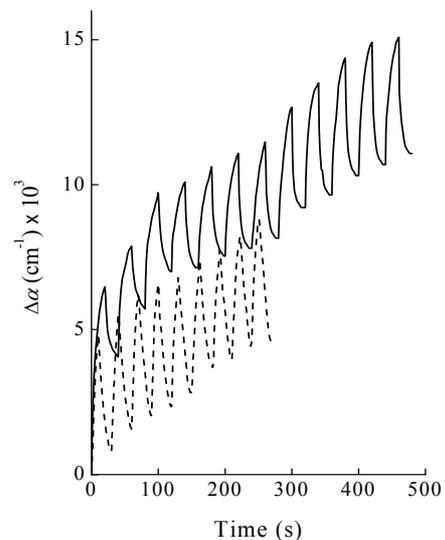
Fig. 3. $\Delta\alpha$ with time for short-duration illumination for a-As$_2$Se$_3$ films at 50 (solid line) and 300 K (dashed line).
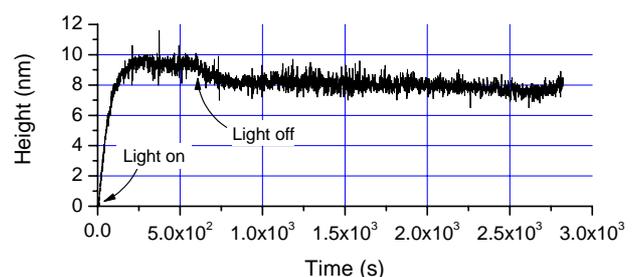
Fig. 4. Time evolution of the surface height for a-As$_2$Se$_3$ films.

These PD and PVC measurements, however, have been performed independently and hence one-to-one correspondence between PD and PVC is still not clear. We, hence, go to the simultaneous measurement of time evolutions of both the PVC and PD in a-As$_2$Se$_3$ film (sapphire substrate). The surface height maps that are obtained by the surface height measuring system described in the previous section are shown in Fig. 4. 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.

As shown in Fig. 5, PD and photoinduced volume expansion (PVE: increase of surface height) are observed during and after illumination. Transient PD and transient PVE [13,14] 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 [13,14], respectively. We analyze the PD and PVC during the illumination by nonlinear fitting. Both the PD and PVE are presented by the following stretched exponential function:

$$y = A\left[1 - \exp\left\{-\left(\frac{t}{\tau}\right)^\beta\right\}\right] \qquad (2)$$

where A, τ and β are the effective reaction time and the dispersion parameter, respectively, t is the time, and y is the measured value ($\Delta\alpha$ or Δh) at time t.
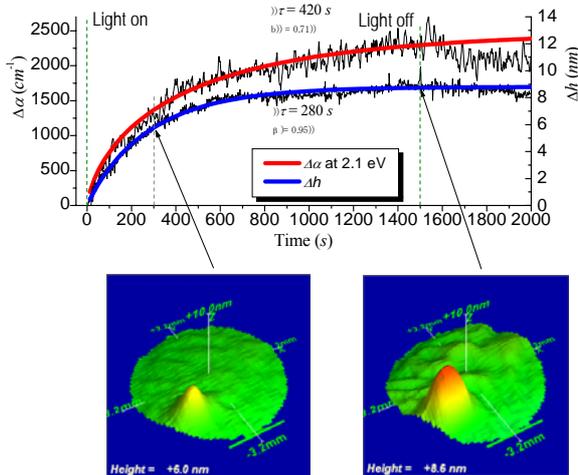
Fig. 5. Time evolution of the $\Delta\alpha$ and Δh for a-As$_2$Se$_3$ film (λ = 635 nm, 100 mW/cm^2), and height maps at 300 s and 1500 s after illumination starts.

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 (β = 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 [6].

It is of interest to observe the dependence of photon energy of the probe light on $\Delta\alpha$. Fig. 6 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. 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 is a natural consequence, since the initial optical absorption at higher energies, before PD is greater than that at lower energies. Of particular interest are the parameters τ and β which appear in the stretched exponential function, which are tabulated in the table.
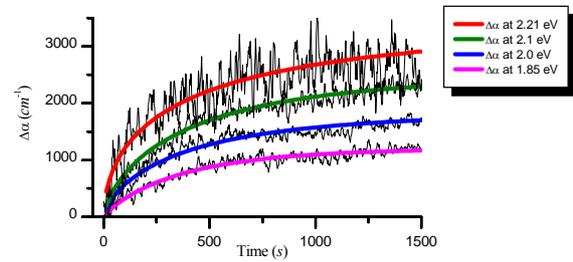
Fig. 6. Time evolution of the $\Delta\alpha$ at various light energies for a-As$_2$Se$_3$ film.

Table. Parameters appeared in a stretched exponential function of eq.(2).

	2.21 eV	2.10 eV	2.00 eV	1.85 eV
τ(s)	480	420	377	374
β	0.55	0.71	0.86	0.89

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 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 similar results have been also reported for the PD excited by a short light pulse in a-As$_2$Se$_3$ [16].

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.

Before summarizing the results, we should state some of interesting results recently reported. The time scale we

discussed here was a scale of "hours". Interestingly, transient PD is recently observed in nano- and microsecond domain in a-As$_2$Se$_3$ [16]. This fast response of PD is also observed in *liquid* As$_2$Se$_3$ [17]. Note, however, that the PD induced in nano- and microsecond domain in liquid As$_2$Se$_3$ disappears after excitation. In liquid states, therefore, the lifetime of PD is up to microseconds. Further detailed study of this time range may yield more detailed information for understanding the dynamics of photoinduced PD and PVC.

There are principally three kinds of model on PD and PVC in amorphous chalcogenides: the bond-twisting [18], bond-breaking [19,20], and macroscopic electronic charging models [21,22]. To understand the microscopic origin of PD or PVC, several theoretical approaches have been proposed: One is a time-dependent density-functional response theory [23] and the other is a molecular dynamics simulation study [24-27]. Concerning the dynamics of PVC in a-Se films, the results from a recent molecular dynamics simulation is of interest, suggesting the importance of bond-breaking and subsequent bond-alternation [25-27]. There is a suggestion that PVC in the CW excitation occurs with an oscillation (time range around 160 s) [28]. This suggestion is of interest and we will examine "oscillation" in transient response of PD and PVC.

5. Conclusions

We have developed an *in-situ* system for the simultaneous measurement of PD and PVC in amorphous chalcogenides. Simultaneous measurements of the time evolution of PD and PVC in *a*-As$_2$Se$_3$, show that the growth is represented by a stretched exponential function. 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. The subject of PD and PVC found in amorphous chalcogenides is still "charming" for us and, of course, for many researchers. Can we expect "harvest" (e.g. commercial applications) from the PD or PVC in the near future? No one can reply to this question.

References

[1] K. Shimakawa, A. V. Kolobov, S. R. Elliott, Adv. Phys. **44**, 475 (1995).

[2] K. Shimakawa, Dynamics of Photo-induced Metastability in Amorphous Chalcogenides, edited by A. V. Kolobov (Wiley-VCH GmbH & Co.KGaA, Weinheim, 2003) p.58.

[3] A. V. Kolobov, K. Tanaka, Handbook of Advanced Electronic and Photonic Materials and Devices Vol.**5**, edited by H.S. Nalwa (Academic Press, San Diego, 2001) p.47

[4] Ke. Tanaka, Rev. Solid St. Sci. **4**, 641 (1990).

[5] J. Singh, K. Shimakawa, Advances in Amorphous Semiconductor, (Taylor & Francis, London, 2003) p. 294.

[6] Ke. Tanaka, Phys. Rev. B **57**, 5163 (1998).

[7] Y. Kuzukawa, A. Ganjoo, K. Shimakawa, J. Non-Cryst. Solids **227-230** (1998) 715.

[8] Y. Kuzukawa, A. Ganjoo, K. Shimakawa, Y. Ikeda, Philos. Mag. B **79** (1999) 249.

[9] A. Ganjoo, Y. Ikeda, K. Shimakawa, Appl. Phys. Lett. **74** (1999) 2119.

[10] A. Ganjoo, K. Shimakawa, H. Kamiya, E. A. Davis, and Jai Singh, Phys. Rev., B **62**, R14601 (2000).

[11] A. Ganjoo, K. Shimakawa, K. Kitano, E. A. Davis, J. Non-Cryst. Solids **299-302,** 917 (2002).

[12] M. S. Iovu, S. D. Shutov, M. Popescu, J. Non-Cryst. Solids **299-302,** 924 (2002).

[13] Y. Ikeda, K. Shimakawa, J. Non-Cryst. Solids **338-340,** 539 (2004).

[14] Y. Ikeda, K. Shimakawa, J. Non-Cryst. Solids **352,** 1582 (2006).

[15] Y. Ikeda, K. Shimakawa, Chalcogenide Letters **2,** 127 (2005).

[16] Y. Sakaguchi, K. Tamura, J. Phys. Condens. Matter **18,** L331 (2006).

[17] Y. Sakaguchi, K. Tamura, Dynamics of Photo-induced Metastability in Amorphous Chalcogenides, edited by A.V. Kolobov (Wiley-VCH GmbH & Co.KGaA, Weinheim, 2003) p.199.

[18] Ke. Tanaka, J. Non-Cryst. Solids **35&36** (1983) 1023; Philos. Mag. Lett. **79,** 25 (1999).

[19] S. R. Elliott, J. Non-Cryst. Solids **81** (1986) 71.

[20] A. V. Kolobov, H. Oyanagi, K. Tanaka, Ke. Tanaka, Phys. Rev. B **55,** 726 (1997).

[21] K. Shimakawa, N. Yoshida, A. Ganjoo, A. Kuzukawa, J. Singh, Philos. Mag. Lett. **77**, 153 (1998).

[22] K. Shimakawa, Y. Ikeda, S. Kugler, Fundamental optoelectronic processes in amorphous chalcogenides; Non-Crystalline Materials for Optoelectronics, Ed. G. Lucovsky and M. A. Popescu, INOE Publishing House (2004) pp103-130

[23] T. Uchino, D. C. Clary, S. R. Elliott, Phys. Rev. Lett. **85,** 3305 (2000).

[24] J. Li, D. A. Dorabold, Phys. Rev. Lett. **85,** 2785 (2000).

[25] J. Hegedus, K. Kohary, S. Kugler, K. Shimakawa, J. Non-Cryst. Solids **338-340,** 557 (2004).

[26] J. Hegedus, K. Kohary, D.G. Pettifor, K. Shimakawa, S. Kugler, Phys. Rev. Lett. **95** (2005) 206803.

[27] J. Hegedus, K. Kohary, S. Kugler, J. Non-Cryst. Solids **352,** 1587 (2006).

[28] M. Popescu, private commun.

*Corresponding author: koichi@gifu-u.ac.jp (Ovshinsky Prize, 2003)