Real-time in situ measurements of photoinduced volume changes in chalcogenide glasses

Y. Ikeda a,b,*, K. Shimakawa a

a Department of Electrical and Electronic Engineering, Gifu University, Gifu 501-1193, Japan
b CEO, YM Systems, Inc., Kyoto 615-8027, Japan

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Abstract

To understand the dynamics of photoinduced volume changes in chalcogenide glasses, we developed the real-time in situ surface height measuring system based on optoelectronic and image processing technologies. This new method provides us a record of in situ volume changes in chalcogenide glasses during illumination.

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1. Introduction

Photoinduced volume changes (PVC) are well known phenomena in amorphous chalcogenides. The correlations between PVC and photoinduced bandgap shift (photodarkening: PD and photobleaching: PB) have been reported in recent years [1,2]. However, in most of studies, PVC has been measured only after illumination [1,2]. To understand the dynamics of PVC in chalcogenide glasses, in situ measurements are required, since they will provide important information about the time evolution of the changes.

The recent in situ measurements we performed [3,4], however, are primitive, and it is hard to measure the evolution of PVC over a short-time interval. In addition, the spectral analysis of interference fringes is used in this method and hence inaccuracy is involved due to a change in refractive index [5].

In the present study, we propose a new technique that overcomes the above-mentioned drawback, i.e. a real-time in situ surface height measuring system, in which a Twyman–Green interferometer [6], fringe phase-shifting method and image analysis technologies [7,8] are employed. The surface height map of the sample is obtained every 1/4 s with ±10 Å accuracy.

2. Experimental

2.1. Sample preparation

The films of a-Se, a-As$_2$Se$_3$, a-As$_2$S$_3$ and a-GeSe$_2$ (thickness, $d \sim 500 \mu m$) were prepared onto Si substrates by conventional thermal evaporation method in vacuum ($\sim 1 \times 10^{-6}$ Torr) at room temperature. Note that Si substrates were used to minimize the temperature rise during illumination. A group of films was deposited with an angle of 80° between the normal to the substrate and the direction of the incidence of the evaporated atoms, and was left as deposited. We call this group of samples obliquely deposited ones. Another group of films was deposited at normal incidence to the substrate, and was annealed below the glass transition temperatures (433 K, 2 h for a-As$_2$Se$_3$, 463 K, 2 h for a-As$_2$S$_3$, 300 K, 12 h for a-Se). We call this group of samples flatly deposited ones. The experimental arrangement is shown in Fig. 1(b). The samples were illuminated with the appropriate laser at 30° in incident angle, in air at room temperature.
2.2. In situ measurement system

As shown in Fig. 1(a), the optical system is based on the well-known Twyman–Green interferometer. The collimated laser beam for the probe light is split into two beams by the beam splitter. One of the light beams goes to the sample. The beam reflects on the surface of the sample and returns back to the beam splitter. The height variation of the surface affects the light path length and hence it creates a variation of the wavefront of the beam. Another beam reflects at the precise plane surface of reference mirror and returns back to the beam splitter with a flat wavefront. These two beams mix at the beam splitter and make the interference fringes that reflect the surface variations of the sample onto the screen.

However, the variations of the fringes are not big enough to measure a change of thickness by a conventional fringe analysis method. The order of the changes of thickness will be only a few nanometers, while the accuracy of fringe analysis method is \( \lambda/20 \) (more than 20 nm when we use 410-nm probe light) [6]. To solve this problem, a phase-shift method is employed as described below.

The reference mirror is driven by the PZT actuator with steps of \( \lambda/8 \) directed along the light beam axis. The shift of the reference mirror causes the phase shift of \( \pi/2(= \lambda/4) \) steps of fringes on the screen. In principle, four steps in the movement of reference mirror are required and the images of the fringes are put into the PC memory, by using a CCD camera and a frame grabber circuit. The PZT actuator has a precise electrical capacitive gap gauge and a feedback control circuit, which avoids the positioning errors caused by using a piezoelectric crystal. The wavelength (410 nm) of laser probe light was selected to minimize the reflection on the interface between the film and the substrate in the present material systems. The power density of probe light on the samples is less than 5 mW/cm², which avoids damage of samples. A processing system is used to control the PZT actuator and to calculate the phase shift producing a surface height maps.

Here, we explain briefly the principle of the in situ surface height measuring system. Let us consider the
height of any point on the surface of sample as \( h(x, y) \).
The intensity of the corresponding point on the screen \( I(x, y) \) is obtained as
\[
I(x, y) = A_0 \exp \left[ i \left( \omega t + 4\pi \frac{p}{\lambda} \right) \right] + A_1 \exp \left[ i \left( \omega t + 4\pi \frac{h(x, y)}{\lambda} \right) \right]^2,
\]
where \( A_0 \) and \( A_1 \) are the amplitude of wave, \( \omega \) the angular velocity, \( t \) the time, \( p \) the position of reference mirror, and \( h(x, y) \) the surface height of the sample. 
Assume that \( I_0(x, y) \) is the intensity in case the position of reference mirror is \( p_n \) (\( n = 0, 1, 2, 3 \)) and \( p_n = 0, \frac{\lambda}{4}, \frac{\lambda}{2}, \frac{3\lambda}{4} \), the surface height \( h(x, y) \) is obtained as
\[
h(x, y) = \frac{\lambda}{4\pi} \tan^{-1} \left[ \frac{I_2(x, y) - I_0(x, y)}{I_1(x, y) - I_3(x, y)} \right].
\]
Practically, a seven-frame algorithm [8], instead of a four step movement of reference mirror mentioned above, was employed to improve the accuracy by reducing the effect of mechanical vibration, optical and electronic noises, and miscalibration of phase-shifting. The height \( h(x, y) \) is given as
\[
h(x, y) = \frac{\lambda}{4\pi} \tan^{-1} \left[ \frac{7 \{ I_2(x, y) - I_4(x, y) \} - \{ I_0(x, y) - I_6(x, y) \}}{8 I_3(x, y) - 4 \{ I_1(x, y) - I_5(x, y) \} } \right].
\]
As described above, the phase-shift method made it possible for interferometer to measure the PVC with high accuracy.

3. Experimental results

Fig. 2(a) shows an example of surface height map for the flatly deposited a-As_2Se_3 films (Si substrate) that is obtained by the measuring system described in the previous section. The time evolution of the changes in flatly and obliquely deposited a-As_2Se_3 is shown in Fig. 2(b) and (c), respectively. In flatly deposited a-As_2Se_3 film, the surface height increased by 10 nm (\( \Delta d/d \approx 2\% \)) in 200 s of illumination of laser (532 nm in wave length and 91 mW/cm^2 of power density). After 600 s, we turned off the illumination. The surface height started decreasing and settled in 200 s at 2 nm less than the height before light off. In the case of the obliquely deposited a-As_2Se_3 film, the surface height decreased by 12 nm (\( \Delta d/d \approx 2.4\% \)) in \( 3 \times 10^4 \) s. Similar results have also been obtained in both obliquely deposited a-As_2S_3 and a-GeSe_2 films (Si substrate).

Fig. 3 shows the time evolution of surface height in flatly deposited a-Se onto Si substrate. The height increased rapidly by 2.5 nm (\( \Delta d/d \approx 0.5\% \)) with illumination (\( \lambda = 532 \) nm, 91 mW/cm^2). As soon as the light was turned off after 800 s of illumination, the height decreased by 2 nm and then gradually decreased to the original height in 200 s.
4. Discussion

Let us discuss the height variations with the illumination. In flatly deposited a-As$_2$Se$_3$ films, as shown in Fig. 2(b), photoinduced volume expansion (PVE: increase of surface height) is observed during and after illumination. Transient PVE [9] must be involved during illumination, since after illumination is cut off, a slight decrease of the surface height is observed. The remaining increase of surface height after cut off of the illumination is the so-called metastable PVE [9]. In obliquely deposited a-As$_2$Se$_3$ films, as shown in Fig. 2(c), the surface height increases a little when turning the light on and then decreases with time. The PVE might have been eclipsed by photoinduced volume contraction, and hence the height decreases with time. This volume contraction can be interpreted as void collapsing, since many voids are involved in obliquely deposited films, which consist of columnar structure with much free space [10]. As the illumination was made in air, some oxidation may also occur [11].

In the a-Se films, as shown in Fig. 3, the behaviors are similar to those observed in a-As$_2$Se$_3$ films. Note, however, that the transient PVE in a-Se is much bigger than that in a-As$_2$Se$_3$. Note also that the transient photodarkening has been reported to be larger in a-Se than in a-As$_2$Se$_3$ [12].

5. Conclusions

We have developed the in situ surface height measuring system and have confirmed that it has good repeatable accuracy to measure the photoinduced volume changes (changes in the surface height). We have reported the transient and metastable volume expansion in flatly deposited a-As$_2$Se$_3$ and a-Se films. The same behaviors are observed in a-As$_2$S$_3$ and a-GeSe$_2$ as well. By prolonged illumination on obliquely deposited a-As$_2$Se$_3$, a-As$_2$S$_3$ and a-GeSe$_2$, volume contraction has been observed. This can be due to void collapsing in obliquely deposited films. A temperature rise may be involved during illumination, and the effect of it should be discussed more carefully in a future publication.

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References