

Photoinduced Change of Thermophysical Properties of Chalcogenide As_2S_3 Thin Films¹

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The reversible photoinduced change exhibited by amorphous chalcogenide glasses has been extensively studied recently, partly as an interesting subject for fundamental research in the field of disordered solids and partly due to potential applications in optoelectronics such as photoresists, optical memories, optoelectronic circuits, etc. The illumination of many amorphous chalcogenides changes their internal and/or surface structure while preserving their amorphous state. In this study, amorphous arsenic trisulfide (As_2S_3) thin film samples whose thickness is $5\ \mu\text{m}$ were prepared on silicon wafers by thermal evaporation, and their thermal diffusivity and thermal conductivity were measured by photoacoustic spectroscopy and a 3ω method, respectively. These measurements were repeated after illumination by an Ar^+ laser beam whose photon energy E_g is consistent with the energy band gap of As_2S_3 . The results show that the thermal diffusivity and thermal conductivity increase by about 50% and 14–15%, respectively, by the photoinduced darkening, and this can be explained by the rearrangement of atoms and thermal expansion of the film.

KEY WORDS: arsenic trisulfide; photoacoustic method; photodarkening; thermal conductivity; thermal diffusivity; thin film; three omega method.

1. INTRODUCTION

Recent progress in the study of amorphous chalcogenide materials has led to increasing attention for the understanding of their structures and

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various properties at the microscopic level. Among many chalcogenide materials, arsenic trisulfide (As_2S_3) is technically important because of its good transparency in the 0.7–11 μm wavelength range and excellent resistance against devitrification, moisture, and corrosion [1–3].

As_2S_3 exhibits a wide variety of photoinduced phenomena that enable it to be used for optical imaging or as a storage medium and more recently, for various electronic devices, including electrooptic information storage devices and optical mass memories [4].

The reversible photoinduced darkening, which is one of the various photoinduced effects that occur in this material, is produced by the red shift of the optical gap E_g [5] and induces a large change in the optical [6, 7], chemical [8], and thermal properties [9]; however, compared to other properties, the thermal properties have not been widely studied until now.

In this study, amorphous As_2S_3 thin film samples, whose thickness is 5 μm , were prepared on silicon wafers by thermal evaporation, and their thermal diffusivity and thermal conductivity were measured by photoacoustic (PA) spectroscopy [10–12] and a 3ω method [13], respectively. These measurements were repeated after illumination by an Ar^+ laser beam ($\lambda = 514.5 \text{ nm}$) whose photon energy E_g is consistent with the energy band gap of As_2S_3 . The experimental results were analyzed and explained by the photoinduced structural changes.

2. PRINCIPLES OF MEASUREMENT

2.1. Photoacoustic Spectroscopy

There are two kinds of modes in PA measurements, namely, front surface excitation (FSE) and rear surface excitation (RSE). In general, the PA signal from the RSE mode is weaker than that from FSE; therefore, especially for the case of a thin film sample which requires high frequency modulation, FSE is more sensitive than RSE.

For the FSE mode of an opaque film on a backing material, the expressions for the amplitude variation of the PA signal can be derived from the Rosencwaig–Gersho (R–G) theory as follows [10–12];

$$A_{\text{fs}} = \frac{A_o}{2Y^2} \left[\frac{\{(1+g)e^Y + (1-g)e^{-Y}\}^2 \cos^2 Y + \{(1+g)e^Y - (1-g)e^{-Y}\}^2 \sin^2 Y}{\{(1+g)e^Y - (1-g)e^{-Y}\}^2 \cos^2 Y + \{(1+g)e^Y + (1-g)e^{-Y}\}^2 \sin^2 Y} \right]^{1/2} \quad (1)$$

where

$$g = \varepsilon_b / \varepsilon_f \quad (\text{subscripts } b \text{ and } f \text{ refer to backing material and film sample}) \quad (2)$$

$$\varepsilon_i = \lambda_i / \sqrt{\alpha_i} \quad (\lambda_i = \text{thermal conductivity, } \alpha_i = \text{thermal diffusivity}) \quad (3)$$

$$Y = \sqrt{\pi f / f_c} \quad (f = \text{modulation frequency}) \quad (4)$$

$$f_c = \alpha_f / t_f^2 \quad (t_f = \text{thickness of film sample}) \quad (5)$$

where A_0 is the amplitude constant which is independent of modulation frequency, ε_i is the thermal effusivity, f_c is the characteristic frequency of the sample, and g is the effusivity ratio of backing to sample.

2.2. 3 ω Method

The 3ω method for the thermal conductivity measurement of thin films uses a single metal-line as both the heater and thermometer. An AC driving current at angular frequency ω heats the surface of the dielectric film at a frequency 2ω . Since the resistance of a pure metal increases with temperature, these temperature oscillations also produce an oscillation of the electrical resistance at a frequency of 2ω . Consequently, the voltage drop across the metal-line has a small component at 3ω that can be used to measure the temperature oscillations and therefore the thermal response of the dielectric film and substrate [13].

Because the dielectric film is thin, the through-plane heat transport in the dielectric layer simply adds a frequency independent ΔT_f to the thermal response of the Si substrate ΔT_{si} . The slope of ΔT vs. $\ln(\omega)$ yields the thermal conductivity of the Si substrate λ_{si} . For completeness, the thermal conductivity of the silicon substrate was used in conjunction with literature values for the specific heat of Si and the width of the metal-line, which allows us to calculate the expected thermal response of the substrate. Then, $\Delta T_f = \Delta T - \Delta T_{\text{si}}$. For the semiconducting silicon substrate used in this work, however, the bare substrate thermal response must be calculated.

Since the film thickness t_f studied in this work is far smaller than the width of the heater $2b$, heat flow in the dielectric layer is one-dimensional and the apparent thermal conductivity of the layer can be found using [13]

$$\Delta T_f = \frac{P t_f}{b \lambda_f} \quad (6)$$

where P is the amplitude of the heater power per unit length.

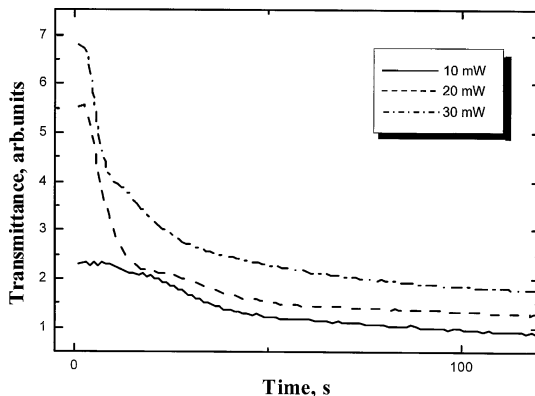


Fig. 1. Time-dependent transmittance in an amorphous As_2S_3 thin film for three incident laser powers.

3. EXPERIMENT

The experiments were carried out with $5\text{ }\mu\text{m}$ thick films prepared by vacuum condensation of high purity amorphous As_2S_3 in a standard vacuum unit with an oil diffusion pump, maintaining a residual pressure on the order of 3×10^{-5} torr. The mean deposition rate was about $0.5\text{ nm}\cdot\text{s}^{-1}$. The Ta crucible was used as an evaporation source, and the silicon (1,1,1) wafer was used as a substrate. The fresh film was photodarkened by 50 min illumination of Ar^+ laser beam whose power and diameter were 130 mW and 10 mm, respectively.

Figure 1 shows the time-dependent transmittance in a fresh As_2S_3 thin film sample for three incident laser powers of 10, 20, and 30 mW. As the incident power becomes higher, the amount of transmittance change increases because the photodarkening was produced gradually on increasing the power. The photodarkened sample was recovered by annealing at about 180°C for 2 h, therefore it is called a “reversible photodarkening.”

The experimental setup for PA thermal diffusivity is shown in Fig. 2. The heating beam from an Ar^+ laser is absorbed by the sample placed in the PA cell. The beam is modulated by an acoustooptic modulator (AOM) whose modulation frequency can be varied from a few Hz to a few MHz. The beam size on the sample surface is fixed by a condensing lens and iris to be 10 mm. For detection of the PA signal, we used a half-inch microphone (B&K 2639) whose sensitivity is $40\text{ mV}\cdot\text{Pa}^{-1}$ in series with an amplifier. A dual-phase lock-in amplifier (EG&G 5302) was used to analyze the phase and amplitude of the signal. Figure 2 also shows the design of the PA cell. To minimize stray effects and other background noise, the

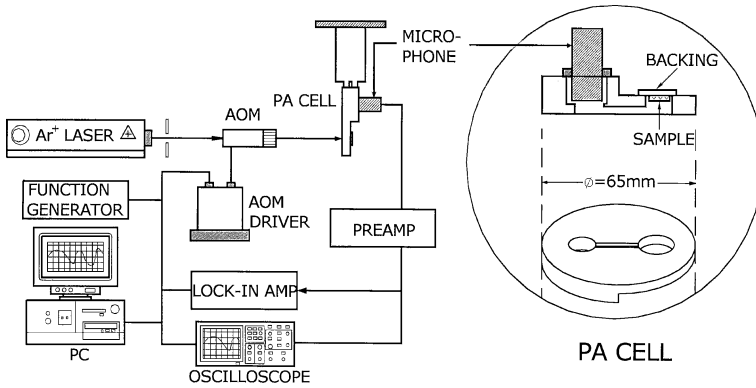


Fig. 2. Schematic diagram of the experimental setup of the PA spectroscopic method and the design of a PA cell.

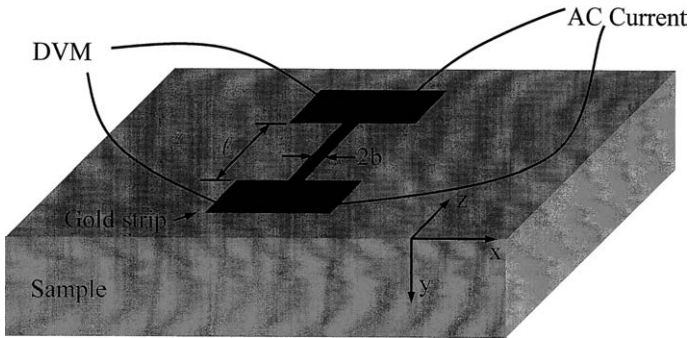


Fig. 3. Shape of a prepared As_2S_3 thin film sample for the measurement of thermal conductivity.

cell was made of plexiglass, whose absorption is negligible. There are two chambers in the cell, one for the sample and the other for the microphone. The two chambers are connected by a narrow channel. The amplitude of the PA signal was measured by changing the modulation frequency of AOM from a few Hz to 5 kHz.

The sample geometry for the 3ω method is shown in Fig. 3. A narrow gold metal strip and the rectangular pads are evaporated onto the sample through a stainless steel mask, and the lead lines are electrically connected to the pads. The samples are mounted in the sample holder using low temperature epoxy, and lead lines are connected to the pads using silver paste. Then, the metal strip is connected by a four-probe type to the current and voltage lead lines. The width of the heater pattern is about $60\ \mu\text{m}$, and its

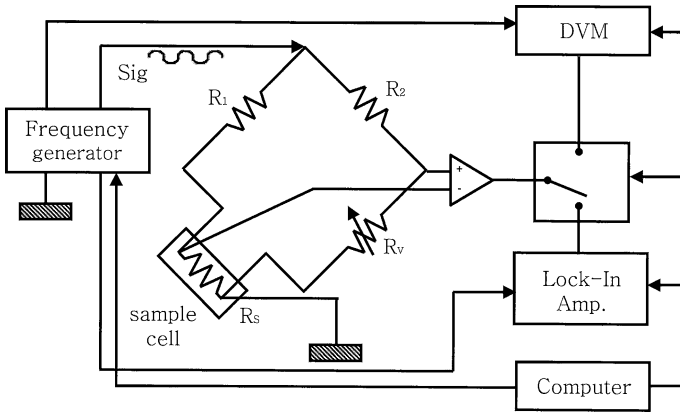


Fig. 4. Schematic of 3ω apparatus for thermal conductivity measurements.

length is 4 mm. Gold is preferred as a heating element because it is not susceptible to oxidation and has suitable electrical resistivity as a heater and temperature sensor.

The measurement circuit is shown in Fig. 4. Since the ω component of the AC voltage at the heater causes a spurious signal at the lock-in amplifier, a Wheatstone bridge is used. R_1 and R_2 are fixed resistances, R_v and R_s are the rheostat resistance and resistance of the gold pattern, respectively. Since R_2 and R_v are a few tens of $k\Omega$ and R_1 and R_s are a few tens of Ω , most of the current flows through R_1 and R_s . In the experimental apparatus, to balance the bridge circuit, we adjusted the value of R_v to suppress the signal at ω and then to separate only the 3ω component of the voltage signal. Using a lock-in amplifier, the amplitude and phase of the 3ω signal voltage were measured through the third harmonic mixer in the lock-in amplifier. The apparatus was controlled by a GPIB card and a LabView control program.

4. RESULTS AND DISCUSSION

Figure 5 shows the measured amplitude variation of the PA signal for fresh and photo-darkened As_2S_3 film samples by changing the modulation frequency from a few Hz to 5 kHz. As the modulation frequency increases, the signal increases to about 600 Hz, and after that point, it decreases rapidly. The peak near 600 Hz is due to the Helmholtz resonance, and it does not affect the measurement of the thermal diffusivity because f_c is far from that frequency. The amplitude of the signal from the photodarkened

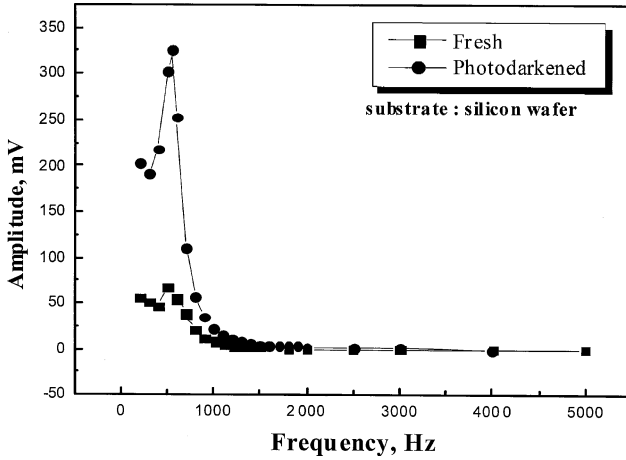


Fig. 5. Amplitude variation of the PA signal as a function of modulation frequency.

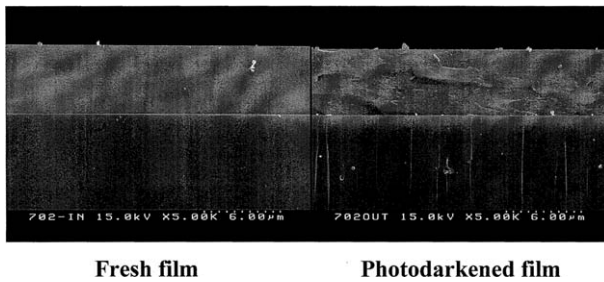


Fig. 6. Cross-sectional micrographs of fresh and a photodarkened As₂S₃ thin films coated on a silicon substrate.

sample is slightly larger than that from the fresh sample. The phase of the PA signal was unstable, therefore, we did not record it.

The measured amplitudes were analyzed using three-parameter (f_c , g , and A_0) estimation. The estimated f_c values for fresh and photodarkened samples were 2065 and 3092 Hz, respectively, and the calculated thermal diffusivities using Eq. (5) with a film thickness of 5 μm were 5.16×10^{-4} and $7.62 \times 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$, respectively. This means that the thermal diffusivity increased by about 50% by the photodarkening.

Figure 6 shows cross-sectional micrographs of fresh and photodarkened As₂S₃ thin films coated on the silicon substrate. The grains in fresh film are small and uniform; however, the grain size becomes larger by the photodarkening. By the photodarkening, the film changes from a

Table I. Measured Thermal Conductivities of Fresh and Photodarkened As₂S₃ Thin Films

Temperature	Thermal Conductivity (W·m ⁻¹ ·K ⁻¹)	
	Fresh Film	Photodarkened Film
Room Temperature	0.206 ± 0.009	0.239 ± 0.011
130°C	0.275 ± 0.015	0.316 ± 0.019

homogeneous to an inhomogeneous state and from a stable to an unstable state. Up to now, a variety of models have been proposed to explain this behavior; however, most of them are speculative [14]. In common with these models, it can be explained that during photodarkening, the incident photons can excite electrons not only from lone-pair states but also from bonding states; therefore, some rearrangement of the atoms in the sample may take place within a short-range order and the atomic configuration of the system reaches a new state. Therefore, the increase of thermal diffusivity by photodarkening can be explained qualitatively.

Table I shows the measured thermal conductivity of the fresh and photodarkened samples at room temperature and at 130°C in the frequency range from 200–850 Hz. At both temperatures, the thermal conductivity increased by about 14–15% by the photodarkening; however, the increase is small compared to that for the thermal diffusivity. This can be explained by the relation between the thermal conductivity (λ_f) and thermal diffusivity (α_f) of the thin film; $\lambda_f = \alpha_f c_p \rho_f$, where ρ_f and c_p are the density and heat capacity, respectively, of the thin film. The photo-illumination always increases the thickness of As-based chalcogenide glass [15, 16]; therefore, by this thermal expansion, ρ_f decreases and the amount of thermal conductivity increase is reduced, if c_p is a constant. The thermal conductivities at 130°C are larger than the room temperature values. This trend is common in most semiconducting materials.

5. CONCLUSIONS

Before and after photodarkening, the thermal diffusivity and thermal conductivity of an amorphous As₂S₃ thin film coated on a silicon substrate were measured by PA spectroscopy and the 3ω method, respectively. The obtained result shows that after photodarkening, the thermal diffusivity and thermal conductivity increased by about 50% and 14–15%, respectively, and this can be explained by the rearrangement of atoms and thermal expansion of the film [16].

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