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Two-photon absorption spectroscopy of As$_2$S$_3$ glass

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Spectral dependence of two-photon absorption in a chalcogenide glass, As$_2$S$_3$, has been studied using a tunable light source. The result shows that two-photon and two-step absorptions occur, and the two-photon absorption spectrum appears to be exponential. These results and roles of nonlinear processes in photoinduced phenomena are discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1433908]

Nonlinear optical phenomena in solids continue to attract wide interest. For instance, extensive studies have been reported for two-photon absorption in crystalline semiconductors, which give a base for creating optical functional devices.[1] For oxide glasses, recent developments of femtosecond-pulse lasers lead to discoveries of many phenomena which seem to be triggered by multiphoton absorption processes (see, for instance, Ref. 2). On the other hand, for chalcogenide glasses, despite considerable interests in photoinduced phenomena,[3] studies on nonlinear phenomena are relatively limited.[4] Most experiments have been carried out at selected wavelengths,[4–14] and spectroscopic studies are a few.[15–17] In addition, reliability and interpretation of the results remain to be studied.

We note that the chalcogenide glass exhibits a characteristic one-photon absorption spectrum. That is, the absorption edge consists of three functional curves, i.e., a square-root dependence ($\alpha \geq 10^3$ cm^{-1}), the so-called Urbach edge ($10^3 \geq \alpha \geq 10^0$ cm^{-1}), and an exponential weak-absorption tail (10^0 cm$^{-1} \geq \alpha$), the origins of these features being still controversial.[3] Specifically, it is important to recognize that the weak-absorption tail limits optical transparency of chalcogenide glasses;[18] a marked attenuation, 50 dB/km, in highly purified As$_2$S$_3$ optical fibers[19] being contrastive to small attenuation in oxide [0.2 dB/km in SiO$_2$ (Ref. 20)] and halide (0.5 dB/km in ZrF$_4$-based[21]) glasses. Needlessly, such midgap absorption does not exist in ideal single crystalline semiconductors.[1]

It is therefore valuable to study two-photon processes in chalcogenide glasses with several reasons. The first is to evaluate the roles of two-photon and two-step absorption, i.e., simultaneous and consecutive absorption processes. The residual absorption, mentioned above, may enhance probabilities of two-step absorption[22] and/or resonant two-photon absorption.[23] The second is to examine the role of these nonlinear absorption processes in such phenomena as photoinduced changes by low energy photons.[24,25] Photoinduced changes induced by near-infrared light cannot straightforwardly be ascribed to two-photon absorption, because one-photon absorption occurs in the weak-absorption tail. Third, if the nonlinear absorption is governed by the two-photon process, the spectrum may provide new insight into the optical absorption in chalcogenide glasses, since the two-

photon transition has a different selection rule from that of one-photon transitions.[1]

Among many chalcogenide glasses, we select As$_2$S$_3$ for this investigation. The glass is known to provide reproducible properties, which may be due to the average coordination number of 2.4 (Ref. 3) and to the existence of only one kind crystalline form [Se and GeS(Se)$_2$ possess several kinds]. In addition, high-purity ingots are now available, which is important to obtain an intrinsic one-photon spectrum, which is needed for evaluation of two-photon spectra. The optical gap E_g is ~2.4 eV,[3] being appropriate for optical experiments.

A high-purity ingot of As$_2$S$_3$ glass, which was prepared for producing optical fibers,[19] was employed. Sliced samples were polished to thicknesses of 0.05–5 cm. Then, optical transmittances of these samples were measured as a function of light intensity at room temperature and photon energies of 1–2 eV using an optical parametric oscillator (GWU, C355), which was pumped by a beam from a frequency-tripled YAG laser (Continuum, Surelite I), and a joule meter (Gentec, ED-200). Pulsed light had a width and a repetition of 5 ns and 5 Hz and the intensity was varied using neutral-density filters. The light beam was focused using a lens with a focal distance of 30 cm, and at the sample position the diameter was ~0.5 mm. Pulse shape of light transmitted through a sample was monitored using a Si pin detector with a response time of ~2 ns.

Here, procedures for obtaining β follow the conventional way.[1,23] Light absorption including one- and two-photon(step) processes can be written as

$$dI/dx = -aI - \beta I^2, \tag{1}$$

where a light pulse with peak intensity I is assumed to propagate along the x direction, and α and β are the one-and two-photon(step) absorption coefficients. Solving this equation, taking the light reflection at sample surfaces into account, we obtain

$$1/T = \exp(\alpha L)/(1-R)^2$$
$$+ \beta I_0 [\exp(\alpha L) - 1]/[\alpha(1-R)], \tag{2}$$

where T is the transmittance, L the sample thickness, R the reflectivity, which can be evaluated from the refractive index, and I_0 the incident light intensity. Accordingly, by plotting $1/T$ as a function of I_0, we can evaluate β.
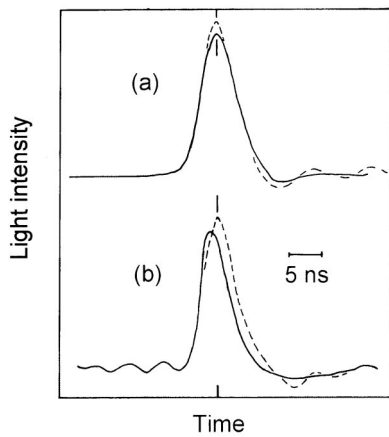

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FIG. 1. Typical shape of light pulses before (dashed) and after (solid) transmitting As_2S_3 samples; (a) is obtained with light of $\hbar\omega = 1.17$ eV and $I_0 = 430$ MW/cm^2 for a 50 mm long sample and (b) is of 2.16 eV and 82 MW/cm^2 for a 4.2 mm sample.
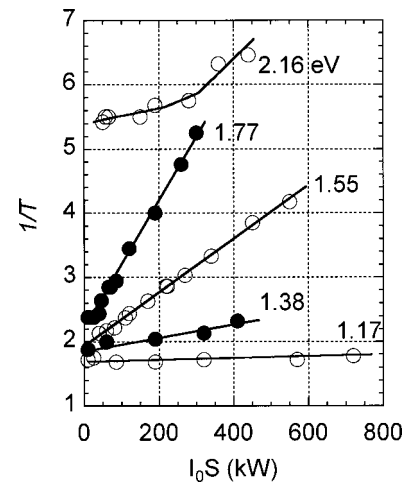

FIG. 2. Inverse of the transmittance T as a function of the peak intensity I_0S (S is the area of light spots) of incident light at the photon energies indicated. The results for 1.17–1.77 eV are obtained using a sample of 50 mm in length and that for 2.16 eV is 0.5 mm.

Equation (2) shows that the accuracy of β is governed by I_0 and α. For I_0 the spatial and temporal shapes of light pulses should be known. In this case, the spatial shape of light spots was evaluated by scanning a pinhole, which was fixed in front of the Si detector. On the other hand, the temporal shape was assumed to be rectangular with a width of 5 ns. The error introduced through these estimations of I_0 was relatively small. In contrast, α smaller than $\sim 1/5$ cm^{-1} ($\hbar\omega \lesssim 1.9$ eV) could not be evaluated accurately, since the longest sample employed in the present experiment was 5 cm. Accordingly, α was evaluated using photothermal deflection spectroscopy,[26] the result being consistent with that reported for As_2S_3 optical fibers.[19]

Figure 1 shows typical light pulses obtained with (a) infrared light ($\hbar\omega = 1.17$ eV and $I_0 = 430$ MW/cm^2) and (b) subgap light (2.16 eV and 82 MW/cm^2). The vertical axes are arbitrary so that only the pulse shape can be compared. We see that no appreciable distortion of pulse shape occurs for the infrared light, while for the subgap light the peak of transmitted pulse occurs earlier by ~ 1 ns than that of the incident pulse. It is mentioned here that the temperature rise by light pulses can be neglected under the present experimental conditions.

Since there exist gap states in chalcogenide glasses, the two-photon (simultaneous) and the two-step (consecutive) absorption can occur. The distinction may be possible when $\sigma(V-G) \neq \sigma(G-C)$, where σ are the absorption cross sections of electronic transitions between the valence band (V), the gap state (G), and the conduction band (C). If the two-step absorption occurs under this condition, the shape of light pulses transmitted through a sample deforms and β depends upon I_0.[22] The results in Fig. 1, therefore, imply that the two-photon absorption is dominant for light with $\hbar\omega \approx E_g/2$, while the two-step absorption becomes effective when $\hbar\omega$ lies in the Urbach-edge region, which extends at $\hbar\omega \approx 1.9$–2.3 eV.[3]

Figure 2 shows some examples of $1/T$ as a function of the peak intensity (I_0S) of incident light. We see that the results, except 2.16 eV, give straight lines. It is also noted that the reproducibility of data at $\hbar\omega \geqslant 2.0$ eV is relatively worse than that of lower energy regions. In some cases, the

data taken upon increasing and decreasing the light intensity have been different. These results are consistent with those in Fig. 1, i.e., the transitions by high energy photons follow the two-step process. For the straight lines, β can be determined using Eq. (2).

Figure 3 shows obtained β (solid circles) together with previous results.[5,7–11,15] Except for the results reported by Fork[7] and Nasyrov,[15] the agreement between the present spectrum and the previous data appears to be satisfactory. The reason why the two results markedly deviate from the present and others is not known. Different from the present, these two experiments have been done using the two-beam configuration. In addition, Fork $et\ al.$ examine only 2.03 eV,[7] which is near the optical gap of ~ 2.4 eV, and Nasyrov employs long light pulses (30 ns and 150 μs widths).[15] The two-step absorption may be responsible for these cases. Furthermore, how they evaluate α are not known. In the following, therefore, we neglect these two results.

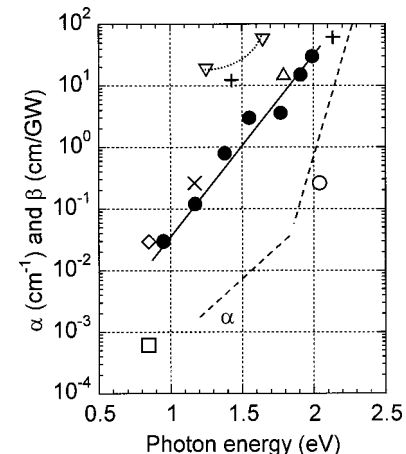Figure 3 shows that β is approximately proportional to

FIG. 3. Spectral dependence of the one- and the two-photon absorption coefficient, α (dashed line) (Ref. 26) and β (solid circles with a solid line). Previous results for β are also shown by symbols: ($\triangle$) Maker and Terhune (Ref. 5); ($\bigcirc$) Fork $et\ al.$ (Ref. 7); ($\times$) Rangel-Rojo $et\ al.$ (Ref. 8); ($+$) Fazio $et\ al.$ (Ref. 9); ($\square$) Asobe $et\ al.$ (Ref. 10); ($\diamond$) Cerqua-Richardson $et\ al.$ (Ref. 11); and ($\triangledown$) Nasyrov (Ref. 15).

$\exp(\hbar\omega/E_\beta)$, where $E_\beta \approx 150$ meV. This energy is roughly the same with the characteristic energy of the weak-absorption tail, 200–300 meV,[3] which appears at around $\hbar\omega \approx 1.5$ eV, the actual shape in the present sample being shown by the dashed line.[26] This approximate coincidence implies that the two-photon absorption process in As_2S_3 is governed by the states which give rise to the absorption tail. The process is probably resonantly enhanced by the states,[23] for which theoretical calculations including transition probabilities remain.

The results in Fig. 3 evaluate the roles of the linear and nonlinear excitation effects in some photoinduced phenomena induced by low-energy photons.[24,25] That is, the one-photon absorption can prevail at $\alpha \gtrsim \beta I_0$ even if $\hbar\omega \approx E_g/2$. The threshold intensity is evaluated at ~ 10 MW/cm^2, which is, very roughly, irrespective of $\hbar\omega$. That is, when the light intensity is smaller than this value, the one-photon excitation of gap states occurs more frequently than the excitation of free carriers by two photons. Carriers excited to gap states may be thermally excited to extended states.[27] Accordingly, unless a square dependence on I_0 was recorded, it could be assumed that one-photon processes are responsible for such photoinduced phenomena.

In summary, it has been demonstrated through careful experiments that the two-photon absorption spectrum of As_2S_3 glass has a form of $\beta \propto \exp(\hbar\omega/E_\beta)$, where $E_\beta \approx 150$ meV. This exponential form implies that the two-photon process is resonantly enhanced by the gap states, which cause the weak-absorption tail. When $I_0 \leqslant 10$ MW/cm^2, one-photon excitation of the gap states occurs more frequently than two-photon excitation of free carriers, and accordingly, the former could be responsible for the photoinduced phenomena induced by subgap photons.

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