Observation of three-photon absorption and saturation of two-photon absorption in amorphous nanolayered Se/As_2S_3 thin film structures

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We have studied the nonlinear optical properties of nanolayered Se/As_2S_3 film with a modulation period of 10 nm and a total thickness of 1.15 μm at two [1064 nm (8 ns) and 800 nm (20 ps)] wavelengths using the standard *Z*-scan technique. Three-photon absorption was observed at off-resonant excitation and saturation of two-photon absorption at quasiresonant excitation. The observation of the saturation of two-photon absorption is because the pulse duration is shorter than the thermalization time of the photocreated carriers in their bands and three-photon absorption is due to high excitation irradiance. © *2007 American Institute of Physics*.
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The nonlinear optical properties of glasses have recently become the focus of growing scientific and technological interest.[1–3] Moreover, glasses have several advantages such as easy handling, easy fabrication of optical waveguides, excellent homogeneity, and low cost over inorganic crystals and organic materials. In particular, chalcogenide glasses have emerged as promising candidates due to their large optical nonlinearity and subpicosecond response time. Recently chalcogenide glasses were prepared in the form of high quality multilayers with nanomodulation and established the possibilities for tailoring the optical properties.[4] These amorphous nanolayered chalcogenide structures (ANC) are similar to the crystalline superlattices, but it is difficult to imagine such structures as ideal crystalline superlattices produced by molecular beam epitaxy. But the ANCs can be considered as well correlated layers with good periodicity, smooth interface, and good surface roughness. Traditional spectroscopic studies such as optical absorption, photoluminescence, and x-ray photoelectron spectroscopy on ANCs indicate that these materials can be used in micro- and optoelectronics.[4,5] However, there are not many reports about the nonlinear optical properties of the ANCs despite the considerable interests in photoinduced phenomena.[6] In this article we report the optical and nonlinear optical absorption of amorphous nanomultilayered Se/As_2S_3 film on a glass substrate prepared by the conventional thermal evaporation technique. The nonlinear optical absorption was measured at two [1064 nm (8 ns) and 800 nm (20 ps)] wavelengths using the standard *Z*-scan technique.

Nanolayered Se/As_2S_3 films were prepared by the cyclic thermal evaporation technique from bulk (powdered) Se and As_2S_3. Deposition rates were 2–10 nm/s in a vacuum of 5×10^{-4} Pa. Periodicity was monitored by the low angle x-ray diffraction method. The modulation period was kept at 10 nm (sublayer thickness of As_2S_3=6 nm and Se=4 nm) and the total thickness of the film was 1.15 μm. We have used a Bruker Optics IFS 66v/s Fourier-transform infrared spectrometer to obtain the absorption spectrum in the wavelength range from 400 to 1200 nm. A standard *Z*-scan setup was used for the determination of nonlinear absorption. The experimental setup was the same as described by Sheik-Bahae *et al.*[7] The samples were moved along the *Z* axis by a micrometer stage having a resolution of 5 μm. In our experimental setup, a Nd-yttrium-aluminum-garnet laser (Quanta Ray) producing 8 ns pulses was used for excitation at 1064 nm, and a Ti:Sapphire laser system (TSA-10 Spectra Physics) was used for excitation at 800 nm. The nominal input pulse width (full width at half maximum) of this chirped amplifier laser is 100 fs, but we used a longer pulse of 20 ps, obtained by changing the femtosecond compressor grating with a picosecond compressor grating. The pulse width was calculated using autocorrelation traces obtained from second harmonic generation in a thin BBO crystal. Two pyroelectric energy probes were used as detectors, of which one monitored the transmitted energy, while the other monitored input laser energy. The laser was run in the single-shot mode and the repetition rate was approximately 1 Hz. After the experiment, the normalized transmittance of the sample as a function of input laser fluence was calculated from the *Z*-scan data. Precautions were made to avoid the sample damage. At peak input, the input energy was in the order of a few microjoules. The repetition rate was also controlled (<1 Hz) to avoid any damage that may occur due to sample heating. We repeated the experiment at the same spot and the results were reproducible.

Cross-sectional transmission electron microscopy (TEM) was used to investigate the periodicity and the quality of interfaces. TEM picture of the sample showed good periodicity; As_2S_3 and Se correspond to white and dark regions, respectively, (Fig. 1) with a rather smooth interface. Surface geometry analysis made with atomic force microscopy

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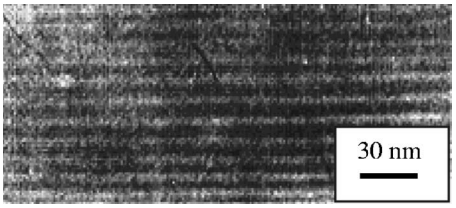

FIG. 1. Cross-sectional transmission electron micrograph (white and dark regions correspond to As_2S_3 and Se, respectively).

(AFM) showed that the surface roughness of the as deposited sample is around 0.5–1 nm (Fig. 2).

The absorption spectra of nanolayered Se/As_2S_3 is shown in Fig. 3. The optical absorption edge was measured and the results were interpreted based on the model of effective optical media.[4] According to this model, narrow band gap "well" layers determine the absorption whereas the contribution from the wide band gap "barrier" layers is small. The effective optical band gap of our samples were determined using the equation

$$(\alpha h\nu)^{1/2} = B^{1/2}(h\nu - E_g), \tag{1}$$

where α, h, ν, E_g, and $B^{1/2}$ are absorption coefficient, Planck's constant, frequency, optical band gap, and a constant, respectively. Equation (1) is valid for a number of amorphous materials in the spectral region of large $\alpha(10^4 \leq \alpha \leq 10^5\ \text{cm}^{-1})$, i.e., Tauc region. Se well layers determine the optical band gap in our sample. Plotting the dependence of $(\alpha h\nu)^{1/2}$ on photon energy will give a straight line and the y intercept gives the value of the optical band gap [Fig. 3 (inset)]. The best fit to Eq. (1) shows that the optical band gap is at 2.19 eV.

Nanolayered Se/As_2S_3 show three-photon absorption at 1064 nm [Fig. 4(a)]. The attenuation of a beam experiencing the three-photon absorption is given by[8]

$$\frac{dI}{dz} = -\alpha_0 I - \gamma I^3, \tag{2}$$

where I, z, α_0, and γ represents the intensity, distance, linear absorption coefficient, and three-photon absorption coefficient, respectively. Equation (2) can be easily solved and the net transmission T, of the sample for a pulsed Gaussian beam is described by the equation

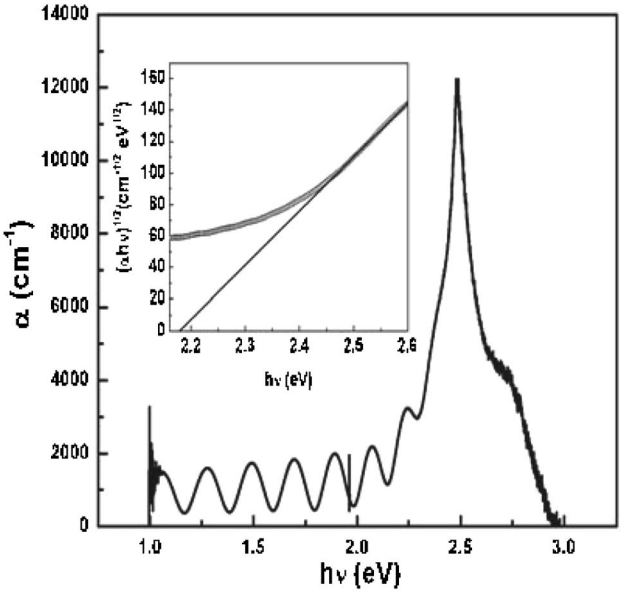

FIG. 3. Optical absorption Spectra of nanolayered Se/As_2S_3 film.

$$T = [(1-R)^2 \exp(-\alpha_0 L)/\sqrt{\pi} P_0] \int_{-\infty}^{+\infty} \{\ln[\sqrt{1 + P_0^2 \exp(-2t^2)} + P_0 \exp(-t^2)]\} dt, \tag{3}$$

where L and R are the sample thickness and surface reflectivity, respectively. P_0 is given by $[2\gamma(1-R)^2 I_0^2 L_{\text{eff}}]^{1/2}$, where L_{eff} is given by $[1-\exp(-2\alpha_0 L)]/2\alpha_0$. The integration over the time in Eq. (3) includes the temporal variation of the Gaussian pulse. A three-photon absorption coefficient of 5×10^{-20} m^3/W^2 gave a good fit to the open aperture Z-scan data. The ratio of photon energy at wavelength of 1064 nm to the band gap (2.19 eV) for nanolayered Se/As_2S_3 is 1.8. Two-photon absorption is thus expected at this wavelength, but a three-photon absorption coefficient gave a good fit to the experimental open aperture Z-scan data. We used a peak input irradiance of 5.8×10^{12} W/m^2 for irradiation and at these large irradiance levels the nanolayered Se/As_2S_3 film will favor for higher order multiphoton absorption process. Smektala *et al.*[9] observed a fifth order nonlinearity in As_2S_3 and As_2Se_3 glasses when 1064 nm radiation intensity was increased from 2×10^{12} W/m^2 to 2×10^{13} W/m^2. More-

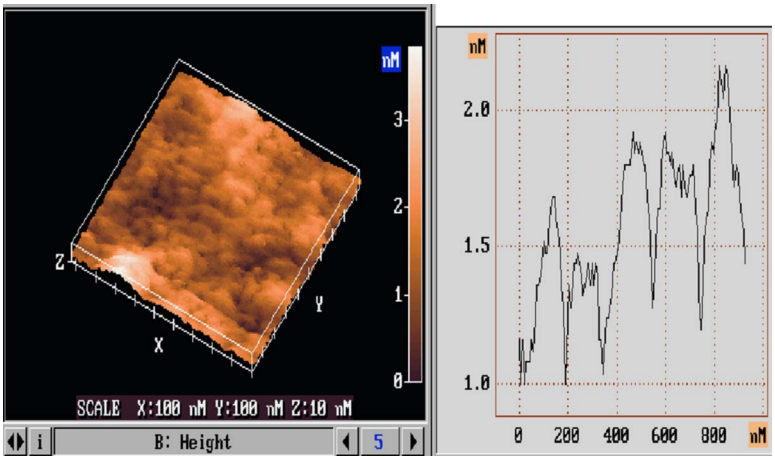

FIG. 2. AFM picture of the right-cross section surface of Se/As_2S_3.

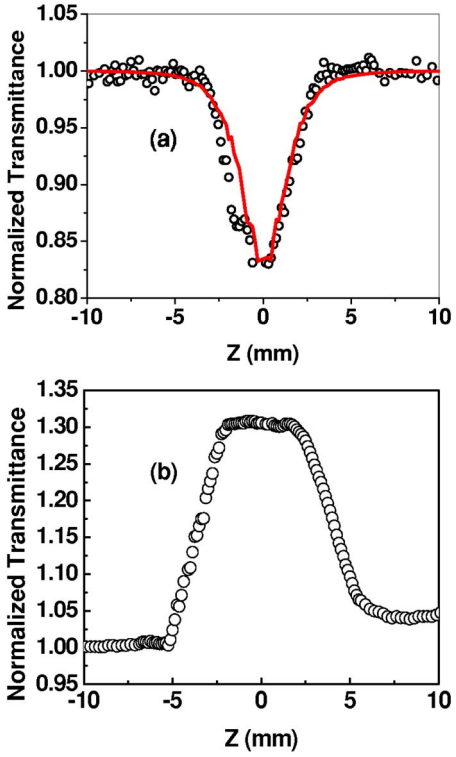

FIG. 4. Normalized transmittance as a function of position in open aperture *Z*-scan at (a) 1064 nm with a pulse width of 8 ns, where hollow circles represent the experimental data and the solid line shows the theoretical fit (accounted for the energy fluctuations of the laser in the simulations) and (b) 800 nm with a pulse width of 20 ps.

over, for semiconductors and dielectric materials the two-photon absorption coefficient is maximum for $x=0.7$, where $x=\lambda_{\text{band gap}}/\lambda_{\text{laser}}$ in which $\lambda_{\text{band gap}}$ and λ_{laser} are wavelengths that correspond to the optical band gap and the excitation wavelength.[10] Two-photon absorption coefficient continuously decreases when the band gap wavelength moves away from the laser wavelength, from $x=0.7$ to $x=0.5$, where the absorption is minimum. The x value for nanolayered Se/As_2S_3 film at 1064 nm is 0.53 and therefore the probability for the two-photon absorption is minimum. We assume that at these large irradiance levels the nanolayered Se/As_2S_3 film will favor higher order three-photon absorption than two-photon absorption.

When the laser wavelength and pulse width was changed to 800 nm and 20 ps, respectively, the sample showed saturable absorption [Fig. 4(b)]. Under the experimental circumstances, an 800 nm laser beam illumination corresponds to the two-photon absorption process because the photon energy of the 800 nm laser is within the range $E_g<2h\nu<2E_g$, where $h\nu=1.55$ eV and $E_g=2.19$ eV. Moreover, the x value for the nanolayered Se/As_2S_3 film at 800 nm is 0.71 and therefore the probability for the two-photon absorption is maximum. But the observed saturation of two-photon absorption may be due to the short pulse duration with high excitation irradiance. The necessary conditions for the saturation of two-photon absorption are the following. First, the duration needed for the creation of photocreated carriers must be shorter than the thermalization time of the photocreated carriers to the bottom of their band in order to reach high values of excited carrier density. Second is the high excitation irradiance, which will remove an appreciable fraction of photocarriers from the ground state. In this case, the dependence of the measured absorption coefficient α on the intensity I of the incident laser is given[11] by

$$\alpha=\frac{\alpha_0}{1+(I/I_s)}, \tag{4}$$

where α_0, I, and I_s are linear absorption coefficient, incident intensity, and a constant known as the saturation intensity. From Eq. (4) it is clear that when the incident intensity exceeds the saturation intensity, the value of the absorption coefficient of the medium decreases. Because of the finite number of excited states in which carriers can be promoted by the two-photon absorption process, its saturation at sufficiently high excitation can be easily predicted for nanolayered Se/As_2S_3 film. This suggests that at 800 nm with an excitation irradiance of 2.6×10^{15} W/m^2 and pulse width of 20 ps, nanolayered Se/As_2S_3 favors a saturation behavior. Moreover, the thermalization times for As_2S_3 and Se from photoluminescence experiments are found to be of the order of $10^{-9}-10^{-12}$ s.[12,13] From this it is clear that the observed saturation of two-photon absorption at 800 nm is mainly due to high excitation intensity and the shorter pulse duration (20 ps), which is less than the thermalization time. Observation of the saturation of two-photon absorption has never been reported for chalcogenide glasses in literature, however, there are reports about this kind of saturation in CdS.[11]

In conclusion, we observed three-photon absorption and saturation of two-photon absorption in nanolayered Se/As_2S_3 film when excited with 1064 nm (8 ns) and 800 nm (20 ps) light pulses, respectively. We assume that the three-photon absorption may be due to the high irradiance used for excitation. Observation of the saturation of two-photon absorption in chalcogenide amorphous multilayers is mainly due to high excitation irradiance and the shorter pulse duration, which is less than the thermalization time.

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[1] K. Ogusu, J. Yamasaki, S. Maeda, M. Kitao, and M. Minakata, Opt. Lett. **29**, 265 (2004).
[2] K. S. Bindra, H. T. Bookey, A. K. Kar, B. S. Wherrett, X. Liu, and A. Jha, Appl. Phys. Lett. **79**, 1939 (2001).
[3] K. Tanaka, Appl. Phys. Lett. **80**, 177 (2002).
[4] M. Malyovanik, S. Ivan, A. Csik, G. A. Langer, D. L. Beke, and S. Kokenyesi, J. Appl. Phys. **93**, 139 (2003).
[5] K. V. Adarsh, K. S. Sangunni, T. Shripathi, S. Kokenyesi, and M. Shipljak, J. Appl. Phys. **99**, 094301 (2006).
[6] R. A. Ganeev, A. I. Ryasnyansky, M. K. Kodirov, and T. Usmanov, J. Opt. A, Pure Appl. Opt. **4**, 446 (2002).
[7] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **26**, 760 (1990).
[8] R. L. Sutherland, *Hand Book of Nonlinear Optics*, 2nd ed. (Marcel Dekker, New York, 2003).
[9] F. Smektala, C. Quemard, V. Couders, and A. Berthelemy, J. Non-Cryst. Solids **274**, 232 (2000).
[10] F. Smektala, C. Quemard, L. Leneindre, J. Lucas, A. Berthelemy, and C. De Angelis, J. Non-Cryst. Solids **239**, 139 (1998).
[11] J. F. Lami, P. Gilliot, and C. Hirlimann, Phys. Rev. Lett. **77**, 1632 (1996).
[12] R. A. Street, Phys. Rev. B **17**, 3984 (1978).
[13] J. Sha and M. A. Bosch, Phys. Rev. Lett. **42**, 1420 (1979).