

## Millisecond kinetics of photoinduced changes in the optical parameters of a-As<sub>2</sub>S<sub>3</sub> films

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We report the kinetics of photoinduced changes in absorption coefficient, optical band gap, and refractive index of a-As<sub>2</sub>S<sub>3</sub> films by measuring the time evolution of complete transmission spectrum between 400 and 800 nm at every 10 milliseconds. The wavelength dependence of the time constants invalidates previously assumed parallel shift of the absorption edge, and provides a better description of photodarkening and other photoinduced effects. The time evolution of the absorption coefficient and optical band gap is significantly faster than that of the refractive index. The time constants of the reversible, transient part of the changes are also wavelength dependent. We use the photon-assisted site switching model and defects around *S* atoms to explain the observed changes.

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The photodarkening (PD) of amorphous chalcogenide films, i.e., the increase in absorption coefficient and the decrease in the optical band gap with illumination is a well studied phenomenon, which has both scientific and technological importance.<sup>1,2</sup> Although changes in optical properties have been investigated by various researchers over the years, most of these studies were conducted *ex situ*, i.e., after switching off the illumination, thus providing information about the metastable changes (see for example Refs. 1 and 3). *In situ* changes in absorption coefficient were also measured, but at a fixed wavelength.<sup>4</sup> Such *in situ* experiments gave insight into the kinetics of photodarkening, most significantly that the total change during illumination consisted of a *transient* and a *metastable* part. The transient part decayed once the illumination was switched off, leaving only the metastable part that could be reversed by annealing near the glass transition temperature. The changes in absorption coefficient were explained satisfactorily using the *photon-assisted site switching* model, where a percolative growth of photon-assisted site switching of clusters of atomic sites at ground states was proposed to switch to photo darkened sites by illumination, and the fraction of PD occurrence was expressed by a stretched exponential function.<sup>4</sup> However, as the measurements were performed at a single wavelength, the wavelength dependence of changes in optical properties could not be determined. Then it was generally assumed that photodarkening resulted from a parallel shift of the absorption edge.<sup>1,3</sup> This basic assumption of the parallel shift of absorption edge meant that the measurements at a single wavelength could be extended to other wavelengths, but it has not been verified thus far. The collection of the whole spectrum under *in situ* conditions will validate this important assumption as well as help understand the nature and kinetics of the changes in the optical band gap and the refractive index of the chalcogenide glass films.

In the present work, we report *in situ* changes in transmission spectra recorded over the 400 to 800 nm wavelength ( $\lambda$ ) range, and also at fixed wavelengths to understand the changes in absorption coefficient ( $\alpha$ ), refractive index ( $n$ ), and optical band gap ( $E_g$ ). The spectra are collected after every 10 milliseconds. The time constants are derived for the

rise and decay of  $\alpha$ ,  $n$ , and  $E_g$  as the pump laser is turned on and off.

Thin films of a-As<sub>2</sub>S<sub>3</sub> (thickness: 1.0  $\mu\text{m}$ ) were deposited by thermal evaporation of commercial bulk glass (5N purity) in a vacuum of  $\sim 1 \times 10^{-6}$  Torr onto Schott borofloat glass substrates. The optical transmission was measured using a fiber optic spectrometer, which has the ability of collecting a spectrum in a minimum time of 2 ms. It uses a visible white light source with various wavelength filters. The light is detected by an ultrafast CCD camera and the data are transferred to a computer.

The samples were illuminated at room temperature with an argon ion laser of energy,  $h\nu=2.54$  eV, intensity = 25 mW/cm<sup>2</sup>, and a light spot of 4 mm diameter on the film. The diameter of the relatively weak probing white light spot from the spectrometer was 2 mm. The two beams were directed such that they crossed each other at the sample with the Ar<sup>+</sup> laser spot completely overlapping the light spot from the spectrometer. It should be noted here that such a small exciting laser intensity and large beam spot on the sample would result in a relatively small temperature increase during illumination.<sup>5</sup> So, the observed changes are not due to temperature rise but mainly due to photoeffects. Simultaneously with the full spectrum, transmission signals were also recorded at fixed wavelengths of 450, 460, 470, 480, 490, and 500 nm, using different channels of the spectrometer, to measure the changes in optical characteristics at and around the band gap of the films. The change in absorption coefficient,  $\Delta\alpha$ , at these fixed wavelengths was calculated from  $\Delta\alpha = (-1/d)\ln(T/T_0)$ , where  $T/T_0$  is the transmitted signal relative to that of the initial signal (i.e., the signal measured before Ar<sup>+</sup> laser is switched on).<sup>4</sup> There might be a change in reflection due to the change in refractive index during illumination (to be discussed later), but its magnitude would be too small to affect the measurements of absorption coefficient significantly. It should be noted that the illumination also causes an increase in the thickness ( $d$ ) of the films, which may influence the changes in absorption coefficient. However, for the present calculations, we assume  $d$  to remain constant as the changes in  $d$  by illumination are small ( $\leq 5\%$  at room temperature for a-As<sub>2</sub>S<sub>3</sub> films<sup>6</sup>) compared to

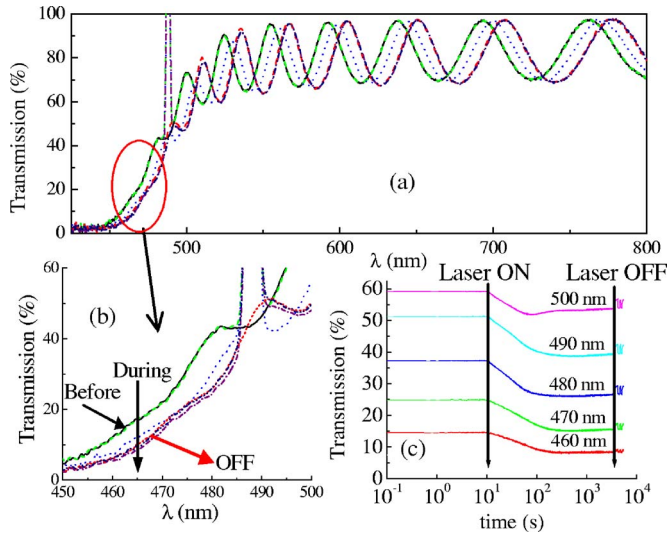


FIG. 1. (Color online) (a) Transmission spectra for a-As<sub>2</sub>S<sub>3</sub> films before (—), during (at  $t=1$  sec (- - - -), 60 sec (•••••), 3600 sec (- • - • - •) and after illumination (•••••). The spectrum before switching off the illumination (- • - • -) is recovered when the exciting laser is switched on again (•••••). (b) Expanded part of the spectra between 450 and 500 nm and (c) variation of transmission as a function of time at the indicated wavelengths.

the changes in absorption coefficient. In any case, an increase in  $d$  will result in a decrease in absorption coefficient, which is opposite to that observed in PD ( $\Delta\alpha$  increases in PD).

Figure 1(a) shows the full transmission spectra for a-As<sub>2</sub>S<sub>3</sub> films at different illumination times; Fig. 1(b) is an expanded view of the absorption edge region between 450 and 500 nm. Figure 1(c) shows the time variation of the transmitted signals at  $\lambda=450, 460, 470, 480, 490,$  and 500 nm. First we discuss the full transmission spectra in Fig. 1(a) obtained before, during, and after illumination. Before the excitation laser is switched on, there is no change in the transmission spectra due to exposure to the white light probe beam. When the exciting laser is switched on, the spectra, which consist of absorption edge and interference fringes, shift to longer wavelengths with time. Note the spike observed at around 488 nm in the spectra is the signal from the exciting source. After the laser is switched off, the transmission spectrum recovers slightly (blueshift). When the illumination is switched on subsequently, there is again a redshift of the transmission spectrum with the transmitted signal reaching the values before the illumination was switched off. This observation indicates the existence of a reversible *transient part* of the changes which decays and vanishes when the illumination is switched off. The permanent shift of spectrum after the illumination is switched off indicates the *metastable change*, which persists till the sample is annealed near the glass transition temperature. We repeated the on and off cycles many times and the red shift (with illumination on) and the blueshift (with illumination off) were observed with each cycle; the magnitude of the transient shift was always the same.

Next, let us examine the change in transmission at fixed

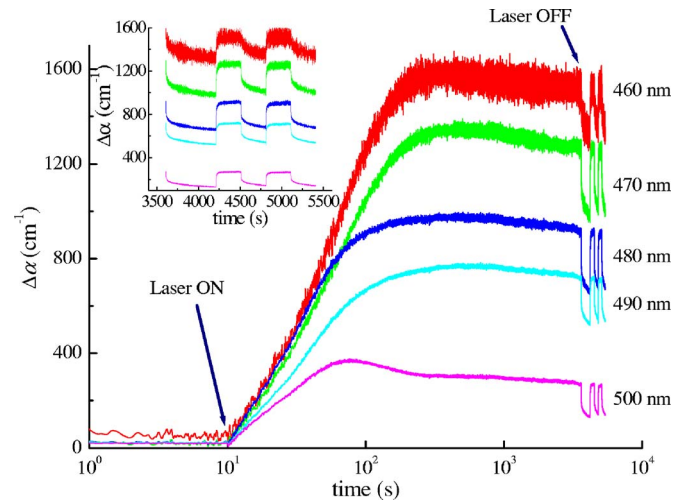


FIG. 2. (Color online) Variation of absorption coefficient with time at indicated wavelengths. The laser ON and OFF states are indicated in the figure. Inset shows the decay and rise of the transient part of the changes on linear time scale when the exciting laser is switched off and on repeatedly.

wavelengths as a function of time [Fig. 1(c)]. Initially, when the exciting laser is off, we see no changes in the transmission intensity (flat part for each wavelength till  $t=10$  sec in Fig. 1) at all the measured wavelengths, indicating no visible effect on the films due to the white light from the spectrometer source. When the excitation light (Ar<sup>+</sup> laser) is switched on, the transmission at each wavelength starts to decrease. Note that the pump laser is switched on after recording the data in “dark” for the first 10 sec. The data before and during laser illumination are collected every 10 milliseconds. The transmission continuously decreases with time during illumination approaching a plateau, followed by a slight increase. When the excitation light is switched off, an increase in the transmission is observed which reaches a constant value quite quickly, but does not reach the initial value before illumination. This portion is the *transient part* of the total changes induced by illumination, and the portion remaining after the illumination is the usually observed *metastable part* of the changes. When the illumination is switched on again, the transient part reappears with the maximum transmission reaching the same value as the saturated value in the first illumination.

Figure 2 shows the time evolution of  $\Delta\alpha$  calculated from the changes in transmission at various wavelengths in the absorption edge region [Fig. 1(c)] and the inset shows the decay/growth of the reversible, transient part with successive off/on cycles. During illumination,  $\Delta\alpha$  increases continuously at all the wavelengths before saturating. When the laser is switched off,  $\Delta\alpha$  decreases, reaching a plateau. The decrease is the *transient part* of changes induced by illumination and the saturated change is the *metastable part*. Repeated off/on cycles induces only the transient part of the changes in absorption coefficient.

To explain the behavior of the observed changes, during and after illumination, and to understand the dynamics of the changes, we consider the films to contain clusters of atoms initially at the ground state, which act as potential sites for

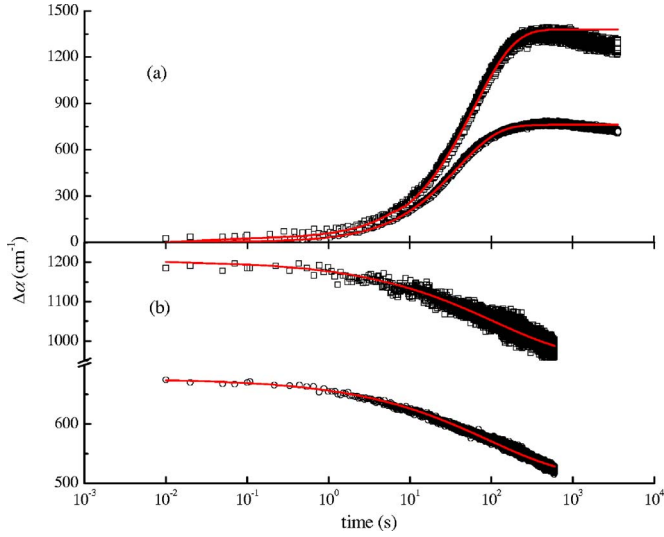


FIG. 3. (Color online) Fitting of Eq. (1) to the rise of changes in absorption coefficient (top) at 490 (squares) and 470 nm (circles). The bottom figure shows the fitting of Eq. (2) to the decay of the transient part at 490 (squares) and 470 nm (circles).

photodarkening and related changes. The potential sites are most likely the chalcogen atom ( $S$  in the present case) sites, because *in situ* extended x-ray absorption fine structure (EXAFS) results indicate significantly larger transient and metastable photoinduced changes around the chalcogen atom.<sup>7,8</sup> These particular sites undergo *photon-assisted site switching*<sup>4</sup> (PASS) under illumination forming photodarkened sites, which have higher energy than the original state. The rate of growth of the number,  $N$ , of these clusters with time (or number of absorbed photons) can be written as

$$\frac{dN}{dt} = k_p(N_T - N) - k_r N,$$

where  $N_T$  is the total number of clusters and  $k_p$  and  $k_r$  are the reaction rates for promotion (to the higher energy transformed state) and recovery to the initial state, respectively. Their time dependence is assumed to follow  $k_p = At^{\beta-1}$  and  $k_r = Bt^{\beta-1}$ , where  $A$  and  $B$  are temperature- and intensity-dependent constants and  $\beta$  is the dispersion parameter ( $0 \leq \beta \leq 1$ ) to be used in the fitting procedure.  $N$  is then given as  $N = N_S [1 - \exp\{- (t/\tau)^\beta\}]$ , where  $N_S = AN_T / (A + B)$  and  $\tau = [\beta / (A + B)]^{1/\beta}$  are the saturated number of transformed sites and the effective time constant, respectively. The expression defining the increase of absorption coefficient with time can then be written as

$$\Delta\alpha_r = \Delta\alpha_{Sr} \left[ 1 - \exp\left\{- \left(\frac{t}{\tau_r}\right)^{\beta_r}\right\}\right], \quad (1)$$

where the subscript  $r$  refers to the rise component. This type of stretched exponential first introduced by Kohlrausch in 1847,<sup>9</sup> has been widely used to describe the kinetics of changes in amorphous semiconductors and other complex systems.<sup>1,10-12</sup>

Figure 3 shows the time dependence of total changes in  $\Delta\alpha$  when the excitation illumination is switched on and the

TABLE I. Fitting parameters obtained from fitting Eqs. (1) and (2) to the calculated rise and fall of the absorption coefficient at different wavelengths. The subscript  $r$  and  $d$  refer to rise and decay, respectively.

$\lambda$ (nm)	$\tau_r$ (sec)	$\beta_r$	$\tau_d$ (sec)	$\beta_d$	$\Delta\alpha_{Sr}$ ( $\text{cm}^{-1}$ )	$\Delta\alpha_{Sd}$ ( $\text{cm}^{-1}$ )
470	61.5	0.87	105.66	0.45	1380	960
480	48.02	0.87	98.46	0.45	950	645
490	34.48	0.87	93.03	0.45	760	512
500	10.10	0.87	62.50	0.45	310	128

decay of transient part when illumination is switched off at two fixed wavelengths of 470 and 490 nm. The theoretical curves shown in Fig. 3(a) are based on Eq. (1). We have fitted the data for the entire wavelengths studied but in the figure we show only the fitting for these two wavelengths. The essential features of the experimental data, namely a slow initial rise in the absorption coefficient followed by the rapid increase towards saturation are reproduced. However, the slight decrease in the absorption coefficient after reaching the maximum is not predicted by the theory. This discrepancy may be due to the decrease in the penetration depth with increasing absorption coefficient. As penetration depth decreases, the total contribution of the bulk to PD decreases. Also, the kinetics of change in thickness, which is different than the kinetics of photodarkening may affect the overall changes.<sup>13,14</sup> The fitting of Eq. (1) to the rise of absorption coefficient at different wavelengths gives the effective rise time ( $\tau_r$ ) and the dispersion parameter ( $\beta_r$ ), as listed in Table I. We find that  $\beta_r$  is wavelength independent, whereas  $\tau_r$  decreases with increasing  $\lambda$ . The other fitting parameter,  $\Delta\alpha_{Sr}$ , the saturated change in the rise of the absorption coefficient, is also wavelength dependent and decreases with increasing wavelength. The variation of the time constants with wavelength contradicts the usually assumed parallel shift of the absorption edge with illumination. Note that previously a parallel shift was suggested from the metastable changes of the absorption coefficient at room temperature,<sup>1</sup> but the nature of the shift during illumination was not determined (a nonparallel shift was reported in the metastable changes in  $\alpha$  when illumination was done at low temperatures<sup>1,15</sup>). A parallel shift of the absorption edge was also assumed in previous *in situ* measurements of  $\alpha$  at a fixed wavelength. Clearly, a fully accurate description of photoinduced changes in optical properties could not have emerged from such measurements.

The decay of the transient part, once the illumination is switched off, is shown in Fig. 3(b) for the absorption coefficient at  $\alpha=470$  and 490 nm. The logarithmic scale is adjusted to show the starting time when the exciting laser is switched off. The decay can be described by a stretched exponential function<sup>4</sup>

$$\Delta\alpha = C \left[ \exp\left\{- \left(\frac{t}{\tau_d}\right)^{\beta_d}\right\}\right] + \Delta\alpha_{Sd}, \quad (2)$$

where  $t$  is the time after the illumination is switched off,  $\tau_d$  is the effective decay time constant,  $\beta_d$  is the dispersion param-

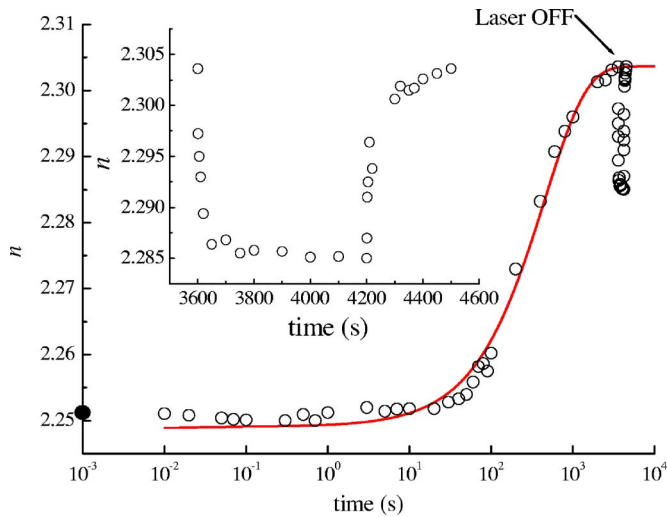


FIG. 4. (Color online) Time variation of the changes in refractive index ( $n$ ) at 633 nm during and after illumination. The solid line is theoretical fit. The solid black circle shows the refractive index before the exciting laser is switched on. Inset shows the decay and the rise of the transient part of the changes on linear time scale when the exciting laser is switched off and on.

eter ( $0 \leq \beta_d \leq 1$ ) and  $\Delta\alpha_{sd}$  is the persistent value of  $\Delta\alpha$  (i.e., the metastable part of the changes).  $C$  is a temperature-dependent quantity (equal to the maximum transient changes). The solid lines in Fig. 3(b), which are generated using Eq. (2), show reasonable fitting to the experimental data. The fitting parameters are listed in Table I.  $\tau_d$  decreases with increasing wavelength (similar to  $\tau_r$ ) indicating that the decay of the transient part depends on the wavelength probed. By comparison,  $\beta_d$  is wavelength independent, similar to the dispersion parameter for the rise in absorption coefficient during illumination. The fact that  $\beta_r > \beta_d$  suggests that during illumination the films are less dispersive in nature than subsequent to illumination. As both  $\beta$ 's remain independent of  $\lambda$ , the dispersion of relaxation appears to be a basic material characteristic. The fitting of Eqs. (1) and (2) to the data from different on/off cycles of illumination gives same values of the fitting parameters, thus indicating that the kinetics of the transient part do not change once the saturation is reached.

Figure 4 shows the variation of estimated refractive index ( $n$ ) (at 633 nm) and the inset shows the decay and rise of  $n$  when the illumination is switched off (decay) and then switched on again (rise). The refractive index is estimated from the fringes in the full transmission spectra shown in Fig. 1(a) using Swanepoel method.<sup>16</sup> Only a small portion of the data is shown for clarity. When the excitation laser is switched on,  $n$  increases slowly at first, followed by a fast increase, and finally reaches a plateau. When illumination is switched off, there is a decrease followed by a plateau of the calculated  $n$ . This decrease indicates that there exists a reversible *transient part* of the changes in  $n$  during illumination, which vanishes when the illumination is switched off leaving only the *metastable part* of the changes. Switching on the excitation laser subsequently shows only the transient changes as is evident from the figure. Thus, like the changes

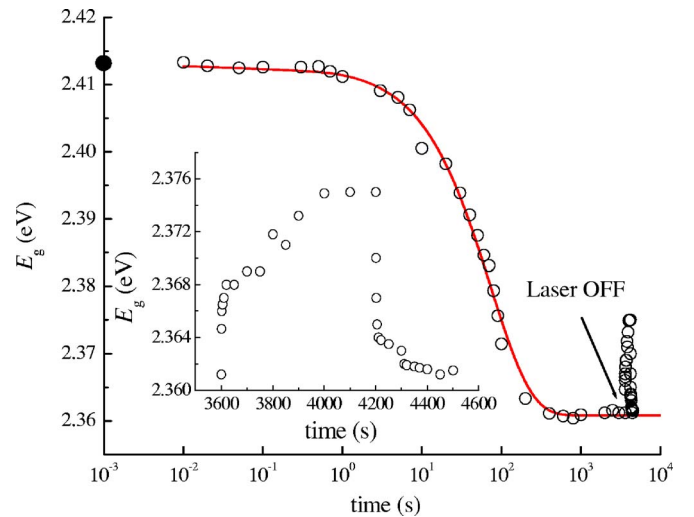


FIG. 5. (Color online) Time variation of the changes in optical band gap ( $E_g$ ) during and after illumination. The solid line is theoretical fit. The solid black circle shows the optical band gap before the exciting laser is switched on. Inset shows the decay and the rise of the transient part of the changes on linear time scale when the exciting laser is switched off and on.

in absorption coefficient, *transient* and *metastable changes* are induced in the refractive index during illumination and only the metastable changes remain after the illumination is switched off.

Figure 5 shows the variation of the optical band gap ( $E_g$ ) as a function of time, during illumination as calculated from the transmission spectra [Fig. 1(a)] using Tauc's relation.<sup>17</sup>  $E_g$  decreases slowly at first before decreasing rapidly and finally settling to a low stable value. On switching off the laser  $E_g$  increases slightly and then saturates at a constant value indicating that during illumination the total changes in  $E_g$  are also composed of a *transient* and a *metastable* part, similar to absorption coefficient and refractive index. On switching the exciting laser on again after the metastable changes have stabilized, one observes only the transient part of the changes in  $E_g$ . Note that in earlier investigations, effect of illumination on  $n$  and  $E_g$  were observed only for the metastable changes, and the time evolution during illumination was not determined (see for example Ref. 1).

To understand the time evolution of refractive index (or the optical band gap), we use the analog of Eqs. (1) and (2) with  $n$  (or  $E_g$ ) replacing  $\Delta\alpha$ . The solid line in Fig. 4 is generated using the modified Eq. (1) for increase of  $n$  and the solid line in Fig. 5 is generated using the modified Eq. (2) for the time variation of  $E_g$  during illumination. The fittings to  $n$  and  $E_g$  give  $\beta=0.87$ , same as for  $\alpha$  above. Although the origin of the dispersion parameter is not fully understood, it appears to be a fundamental characteristic of the glass structure rather than the physical property probed. By comparison, the effective time constants for  $n$  and  $E_g$  are significantly different, viz. 456.3 sec and 73.5 sec, respectively. Note that, during illumination,  $\tau$  for  $n$  is longer (almost by a factor of 6) than the  $\tau$  for  $E_g$  or  $\alpha$ . Since the effective time constant for changes in absorption coefficient is estimated at fixed wavelengths, any comparison with the  $\tau$  for  $n$  is only

approximate. Phenomenologically,  $\alpha$  and  $n$  are related to each other via Kramers-Kronig relation. If only one simple microscopic mechanism determines the changes in both parameters, same time constant is expected to describe their photoinduced changes. The present results show that for a dispersive medium (i.e., for  $\beta < 1$ ), this need not be the case.

The observed slower change in  $n$  than in  $E_g$  suggests an additional mechanism, other than site switching, which contributes to the time dependence of  $n$  during illumination. This additional mechanism delays the onset and saturation and appears as a slower kinetics for the changes in  $n$  (changes in  $n$  start at  $\sim 10$  sec and saturate at  $\sim 3 \times 10^3$  sec as compared to changes in  $\alpha$  and  $E_g$ , which start at  $\sim 2$  sec and saturate at  $\sim 5 \times 10^2$  sec). We suggest that the additional mechanism originates in defect states created during illumination, which significantly affect the behavior of  $n$ , but not of the band gap.

Charged and neutral defect states are shown to increase during illumination in amorphous chalcogenides (see for example Refs. 1 and 2), affecting the transport properties (real<sup>1,18</sup> and imaginary part<sup>19,20</sup> of frequency dependent photoconductivity and dc photoconductivity<sup>1,21,22</sup>). It has been suggested that the change in ac photoconductivity is due to the increase in the density of defect centers and not due to PD (i.e., decrease of  $E_g$ ).<sup>1</sup> Slower kinetics of  $n$  are expected as the generation of defect states is usually a slower process than the changes in absorption coefficient (for comparison, see for example Refs. 4 and 23). Initially, the defect creation is a slow process which increases sharply with increasing number of absorbed photons (time).<sup>23</sup> So at the beginning the contribution of defects to  $n$  is small and the change in  $n$  is dominated by the site switching mechanism that also determines the band gap. With increasing time, site switching contribution approaches a plateau and the contribution of defects begins to dominate the dynamic behavior of  $n$  but at a slower rate. The defect states may also contribute to changes in  $\alpha$  and  $E_g$  during illumination, but apparently the contribution is smaller as compared to that to  $n$ .

The source of refractive index of any material is the elec-

tronic polarization of atoms, ion pairs, or molecular units at a microscopic level,<sup>24</sup> which arises from the shift of the electron cloud in relation to the positive charge center in an electric field. In covalent solids, any distortion of the electronic charge density results in changes in bond polarizability and hence the refractive index.<sup>25</sup> These changes will primarily be around chalcogen ( $S$ ) atom, because in general  $S$  has a larger polarizability than As.<sup>26</sup> Illumination is known to distort bonding configuration in amorphous chalcogenides (see for example Refs. 1 and 2), with larger changes around  $S$  as evident from EXAFS results.<sup>7,8</sup> Therefore, the defects that affect the kinetics of  $n$  are likely to be centered on the chalcogen atoms,  $S$  in the present case.

In summary, we have determined the photoinduced changes in optical transmission as a function of time for the wavelengths between 400–800 nm as well as at a few discrete wavelengths. The total changes in absorption coefficient, refractive index and optical band gap consist of a transient part which vanishes, and a metastable change which persists even after the illumination is switched off. The kinetics of all the changes can be described by the stretched exponential function, which forms the basis of the phenomenological photon assisted site switching model. The evolution of the refractive index kinetics is slower than that of the absorption coefficient or the optical band gap, thus illustrating complex nature of Kramers-Kronig correlation under dynamic conditions. It suggests the existence of another mechanism, which is attributed to the creation of defect states during illumination. From the changes of absorption coefficient, we find the wavelength dependence of the effective time constants. It contradicts the usually assumed parallel shift of absorption coefficient during photodarkening.

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