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Light-induced oxidation and band-edge shifts in thermally evaporated films of germanium chalcogenide glasses

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Films of amorphous $GeSe_2$, $GeSe_3$, and GeS_2 have been deposited at various angles of incidence onto appropriate substrates and the nature of the photoinduced oxidation (as monitored by the Ge—O peak at $\sim 800\ cm^{-1}$ in the infrared absorption spectrum) and optical-absorption band-edge shifts has been studied. We have identified several processes which occur on illumination and which are manifested as shifts in the optical absorption. All normally deposited films exhibit bleaching, whether or not illumination takes place in air. This behavior is ascribed to a photoinduced reconstruction of the network, resulting in a more chemically ordered structure. Although GeS_2 films exhibit photobleaching irrespective of the angle of incidence, selenide films can show photodarkening, particularly in the case of obliquely evaporated films. Illumination of the films in air invariably produces a larger change in the saturation value of the optical-absorption shift (irrespective of its sign), but this can lead to a crossover behavior from bleaching to darkening for small illumination doses. The photo-oxidation which occurs on illumination in air would be expected to lead to increased bleaching. However, the photodarkening which occurs in obliquely deposited selenide films cannot be understood in this way and, although not fully understood, this behavior may be related to the greater facility for photodensification (void collapse) exhibited by selenide films compared with sulfide films.

I. INTRODUCTION

Amorphous semiconductors containing appreciable proportions of the chalcogens Se and S (e.g., Ge-Se or Ge-S alloys) exhibit a variety of changes on illumination with band-gap light (or other ionizing radiation). Such changes may be reversible (on annealing at the glass transition temperature) or irreversible. Several mechanisms have been proposed for the reversible changes;[1-3] these mechanisms explain the photoeffects in terms of intermolecular and intramolecular bond breaking and lattice distortion. The dominant mechanism seems to be a sensitive function of the composition of the glass.[3]

Irreversible changes, which are most easily seen in as-deposited (and, particularly, obliquely deposited) films, have also been explained in terms of bond-breaking models similar to those mentioned above.[4] Recently, however, the role of oxygen in these irreversible effects has been highlighted. Tanaka, Kasanuki, and Odajima[5] have observed that the magnitude of the photoinduced shift in the absorption edge of normally deposited films of GeS_2 is strongly dependent on the ambient oxygen pressure. They have suggested that if the oxygen pressure could be lowered sufficiently then the bleaching phenomena would disappear. Tanaka, Kasanuki, and Odajima[5] also observed the appearance of an absorption band in the infrared (ir) absorption spectrum, on illumination in air, at $800\ cm^{-1}$ which they associate with a Ge—O stretching mode.

Tichy *et al.*[6,7] have performed further experiments on normally deposited films of $Ge_{30}S_{70}$, and studied the development of features in the ir absorption spectra at $\sim 800\ cm^{-1}$ upon illumination in a variety of atmospheres, and related this to the shift in the optical-absorption edge. They have observed three bands in the ir spectra at 870, 820, and $800\ cm^{-1}$. The first of these corresponds to the dominant mode seen in GeO_2 bulk glass.[8] The other features are thought to be Ge—O stretches in $S_{3-x}O_x$—Ge—O—Ge—O_xS_{3-x} clusters. As x increases from 0 to 3 the "local electronegativity" of the Ge atom increases, and this causes a decrease in the bond strength of the central Ge—O bond in the cluster (because more electrons are withdrawn from the central Ge—O bond), causing a shift in the vibrational frequency to lower wave numbers.

Tichy *et al.*[6,7] have also observed that, on annealing as-deposited films in a vacuum of 10^{-4} torr, no Ge-O peak is seen. In addition, the main chalcogenide stretch peak is seen to increase, indicating an increase in the Ge—Se (Ge—S) bond density. Because of this behavior they attributed different mechanisms to the thermally and optically induced bleaching, ascribing the former to an increase in chemical order, and the latter to the replacement of Ge—Ge bonds (states in the gap), by Ge—O bonds (states outside the gap).

Harshavardhan and Krishna,[9] in addition, have invoked surface photo-oxidation to explain the photothermal ablation that they have observed in obliquely deposited films of $GeSe_3$.

In this paper we present the results of our own uv-visible and ir absorption measurements on films of amorphous $GeSe_2$, $GeSe_3$, and GeS_2, deposited at various angles of deposition, and discuss them with respect to the mechanism of photo-oxidation within these films. The paper is divided into six parts. Sections II and III present the experimental procedures and results of the ir and uv-visible experiments, respectively. Section IV is a summary of the major experimental findings of Secs. II and III. In Sec. V some kinetic data are given, and in Sec. VI the results are discussed and the nature of the photooxidation is considered.

II. ir ABSORPTION EXPERIMENTS

A. Experiment

The films used were made by thermal evaporation of the bulk glassy alloys $GeSe_2$, $GeSe_3$, and GeS_2, with use of a jig which enabled samples to be deposited simultaneously at various angles of incidence (0°–80°) and having approximately the same thickness (in this case 1–2 μm) onto single-crystal silicon substrates. The composition of the films (from EDAX measurements) was found to be $GeSe_{1.9}$, $GeSe_{2.6}$, and $GeS_{1.9}$, respectively. (Further details of sample preparation and characterization can be found in Ref. 10.) ir spectra were recorded using a Perkin-Elmer 599 two-beam spectrometer (range 200–4000 cm^{-1}).

Since it was not possible to purge the spectrometer with dry argon, or to evacuate it, the spectra recorded at low (200–300 cm^{-1}) wave numbers were a little noisy because of absorption by water vapor in the air. The samples were held in position with a sample holder which ensured that the same part of the sample was in the beam each time a spectrum was recorded. For illumination the sample and sample holder were removed from the spectrometer and then illuminated with light from a Xe arc lamp, passed through an ir-cut filter, a neutral density filter, and a water filter, producing an intensity of 100 mW/cm^2 on the sample. The changes in the ir spectra with time were recorded for films of $GeSe_2$, $GeSe_3$, and GeS_2 deposited at 80°, 70°, and 0°. Measurements were also made of the absorption spectra of the Si substrates. In addition spectra of weighted amounts of the bulk glasses $GeSe_2$, GeS_2, and GeO_2, dispersed in CsI pellets, were taken in order to assess the relative strengths of the absorption bands [see Figs. 1(a)–1(c)].

In order to check that the oxidation was a light-induced effect, the ir spectra of obliquely deposited films left in the atmosphere for approximately the duration of the "kinetic" experiments (i.e., ~1 d) were measured for all the films studied, before and after exposure to the atmosphere. No peak at ~800 cm^{-1} was seen to develop. Upon subsequent illumination, however, such a peak appeared in the ir spectra, thus showing that the films had not been "passivated" by this treatment.

B. Results (illumination in air)

Spectra of the 0° films showing the difference in absorption before and after illumination are shown in Fig. 2 for $GeSe_2$, $GeSe_3$, and GeS_2. In contrast to the data of Tanaka, Kasanuki, and Odajima[5] and Tichy *et al.*[6,7] no significant peaks at ~800 cm^{-1} were observed. A small increase in the main chalcogenide stretch peak was noticed, however, indicating an increase in the density of

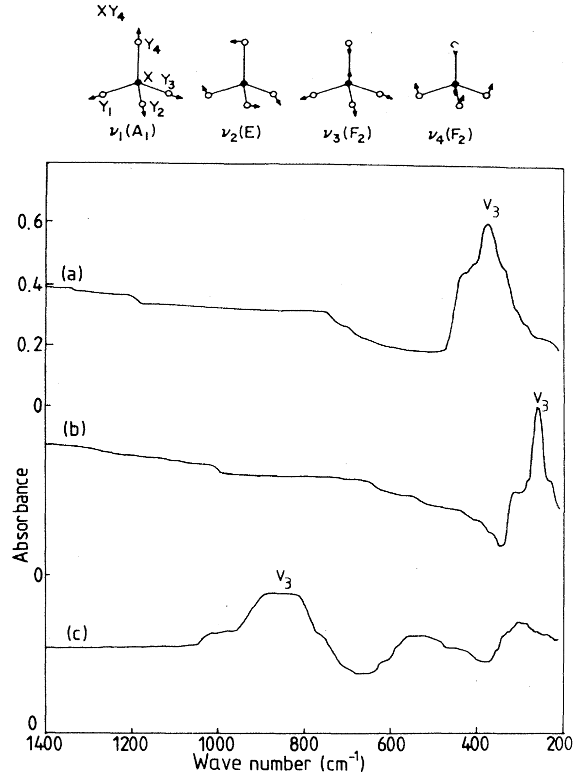

FIG. 1. ir absorbance spectra of bulk glasses: (a) GeS_2; (b) $GeSe_2$; (c) GeO_2. Here absorbance is defined as −log(transmission). The molecularlike modes characteristic of XY_4 tetrahedra in XY_2 glasses (X=Ge; Y=S,Se) are also indicated.

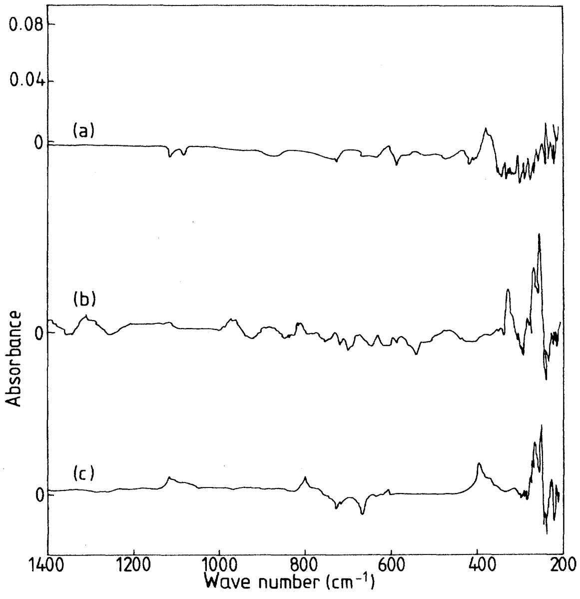

FIG. 2. ir difference spectra (after−before illumination in air) for normally deposited (0°) films of (a) a-GeS_2 (dose 200); (b) a-$GeSe_2$ (dose 250); (c) a-$GeSe_3$ (dose 180) (where the units of illumination dose are 100 mW min cm^{-2}).

Ge—Se (Ge—S) bonds.

The situation for the obliquely deposited films is rather different and some of the data is presented in Figs. 3(a) and 3(b). The difference spectra show a wealth of features; we were not able to assign modes to many of the absorption bands observed. In describing the data we will concentrate on two regions in the spectra; 700–1100 cm^{-1}, the region containing the Ge—O stretch frequencies and 200–450 cm^{-1}, the region containing the main chalcogenide stretch frequencies.

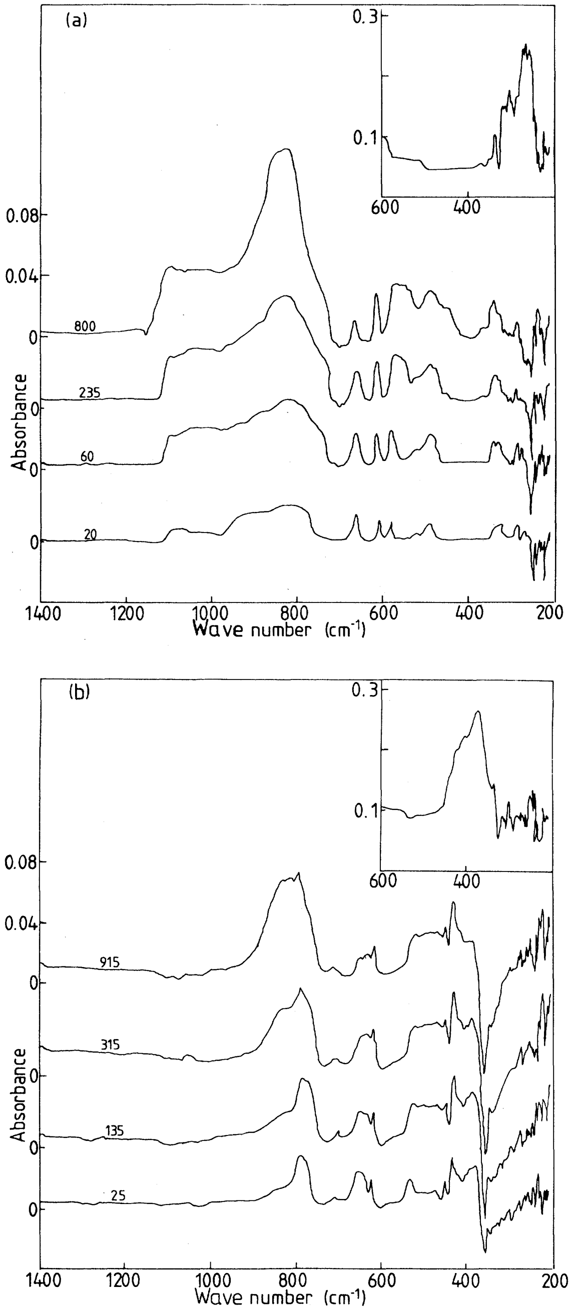

FIG. 3. Evolution of ir difference spectra (after—before illumination in air) with doses (in units of 100 mW min cm^{-2}) for (a) an 80° film of a-GeSe_2; (b) an 80° film of a-GeS_2. In each case, the inset shows the ir absorbance in the region of the main chalcogenide stretch frequency.

The GeSe_2 80° films show a large feature in the range 750–1100 cm^{-1} [see Fig. 3(a)] which consists of a main peak at 830 cm^{-1} with a shoulder at lower wave numbers and a broad band centered at 1050 cm^{-1}. These features seem to grow and saturate concurrently. The 200–400-cm^{-1} region shows a slight decrease ($\sim 5\%$), indicating that there is a slight decrease in the number of Ge—Se bonds. The 70° films do not show the band at 1050 cm^{-1}, but they do show a band at 790 cm^{-1} which saturates after 135 min, and another peak at 830 cm^{-1} which seems to start to grow once the peak at 790 cm^{-1} has been saturated. The 200–400-cm^{-1} region again shows a slight decrease in absorption ($\sim 5\%$).

The GeSe_3 80° films, by contrast with those of GeSe_2, show much less absorption in the 800-cm^{-1} region, and a large, unidentified decrease in absorption at 670 cm^{-1}. The absorption band at 830 cm^{-1} is more pronounced in the 70° films of GeSe_3; in addition there is no decrease in absorption at 670 cm^{-1}. Neither film shows much change in absorption in the region 200–400 cm^{-1}.

The GeS_2 80° film [see Fig. 3(b)] shows a feature at 800 cm^{-1} which first appears on illumination and is then incorporated into the growing peak at 840 cm^{-1}. In 70° films of GeS_2 two peaks are seen, one at 700 cm^{-1}, which saturates after 100 min, and one at 830 cm^{-1}. We notice in both types of GeS_2 film a decrease of $\sim 35\%$ in the Ge-S absorption band centered at 370 cm^{-1}.

The areas under the Ge-O absorbance peaks (700–1150 cm^{-1} for the 80° films of GeSe_2, 700–1000 cm^{-1} for the 70° film of GeSe_2, 750–950 cm^{-1} for the 80° film of GeS_2, and 750–1000 cm^{-1} for the other films), normalized to the area under the main chalcogenide stretch for the as-deposited film (200–400 cm^{-1} for films of GeSe_2 and GeSe_3, and 200–500 cm^{-1} for films of GeS_2) are shown in Figs. 4(a)–4(c) as a function of illumination dose.

C. Discussion (illumination in air)

Initially it was hoped that the area under the peak at 800 cm^{-1} would give *quantitative* information concerning the amount of oxygen absorbed; however, calculations which used the absorbances of the bulk glasses as standards (see Fig. 1) predicted that, for the 80° GeSe_2 film, $\sim 50\%$ of the film would have to convert to GeO_2 to account for the size of the peak seen. This is clearly incompatible with the small ($\sim 5\%$) decrease in the main chalcogenide band. We suggest that the reason for the enhanced absorption of this mode is due to it being a surface mode. It has been pointed out by Galeener[11] that because of the wide Ge—O—Ge bond angle (130°) in bulk glassy GeO_2 the modes are strongly coupled and so ir absorption spectra do not show the sharp molecular modes observed in Ge-Se and Ge-S glasses. If the oxygen is incorporated on the surface of the films then the Ge-O modes will be less strongly coupled and so would appear sharper and more strongly absorbing. The much smaller *accessible* surface areas of normally deposited films, compared with obliquely deposited (porous) films probably explains why no peaks are seen in the 800-cm^{-1} region, on illumination, in the case of normally deposited films.

An experiment was performed to investigate the effect of illuminating the films in vacuum. An evacuable cell was constructed with quartz windows so that uv, but not ir, absorption measurements could be made without removing the sample from the cell. Having recorded the spectrum of an 80° film (the 0° films show no peak at 800 cm^{-1} on illumination in air and so the effect of illumination in a vacuum was not studied), the sample was placed in the cell which was pumped overnight at a pressure of 10^{-4} torr. The cell was then sealed, and illuminated with light from a Xe arc lamp, passed through ir-cut and water filters and with an intensity of 200 mW/cm^2 on the sample, for about four hours. After this the sample was removed, and the ir absorption measured. The difference in absorption, before and after illumination, is shown in Figs. 5(a)–5(c), for films of $GeSe_2$, $GeSe_3$, and GeS_2.

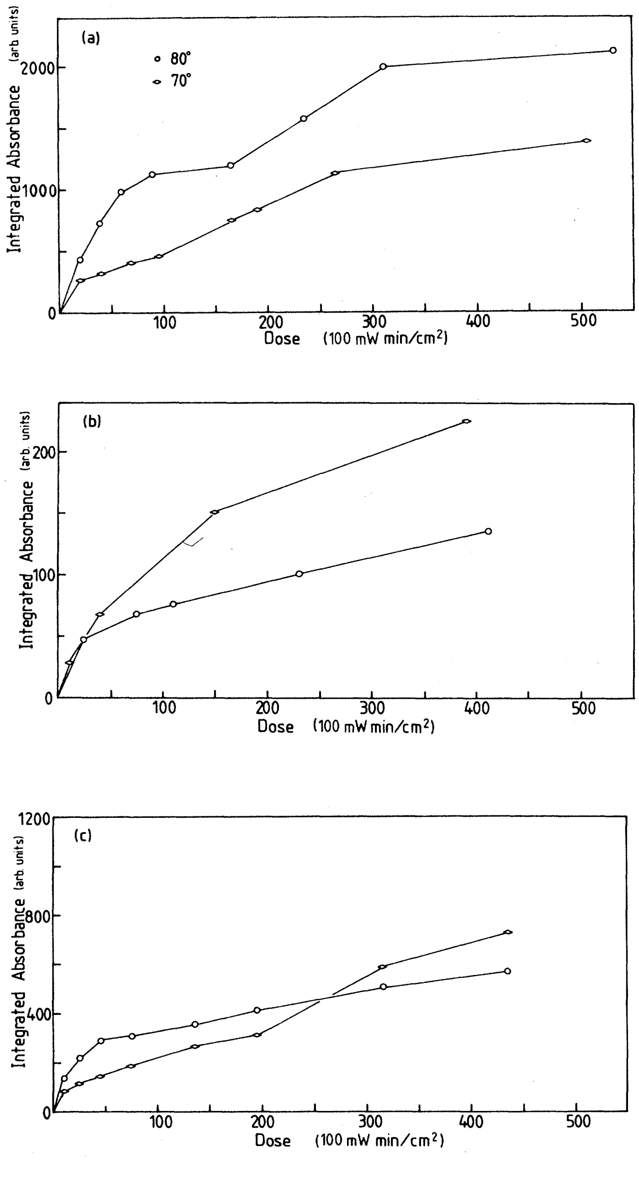

FIG. 4. Evolution with illumination dose of the area under the Ge—O stretch peak seen in the ir spectra at ~ 800 cm^{-1}, normalized by the area under the main chalcogenide stretch peak for films deposited at various angles for (a) a-$GeSe_2$; (b) a-$GeSe_3$; (c) a-GeS_2.

In all cases the size of the peak at 800 cm^{-1} is much smaller than when the sample has been illuminated in air [see Figs. 3(a) and 3(b)]. This adds further weight to the identification of this feature as a Ge-O mode. Further evidence that the peak is associated with a Ge—O stretch was provided by Auger depth-profiling experiments on some films of $GeSe_3$. Auger spectroscopy is more sensitive to the presence of elements of low atomic number than EDAX, and so allows the oxygen content to be monitored. Unfortunately, sensitivity factors were not known for Ge, Se, and O, and so it was not possible to calculate the absolute amount of oxygen present in the films. The data obtained (with oxygen content in arbitrary units) are shown in Fig. 6. They show that upon illumination (using a Xe arc, passed through ir-cut and water filters; 20 min at 200 mW/cm^2) the oxygen content increases throughout the depth of the 80° film. On illumination of a normally deposited film, there is only oxidation of the uppermost region of the film; the oxygen content of the "bulk" of the film remains the same (to the accuracy of the experiment). It should also be noted that the films appear to contain a certain amount of oxygen in the as-deposited state. Since the experiments were carried out in a chamber evacuated to a base pressure of $< 10^{-7}$ mbar, it is thought to be unlikely that the oxygen signal is due to contamination from the chamber, and must thus be an intrinsic feature of the films when prepared in this manner. (The oxygen may have been in-

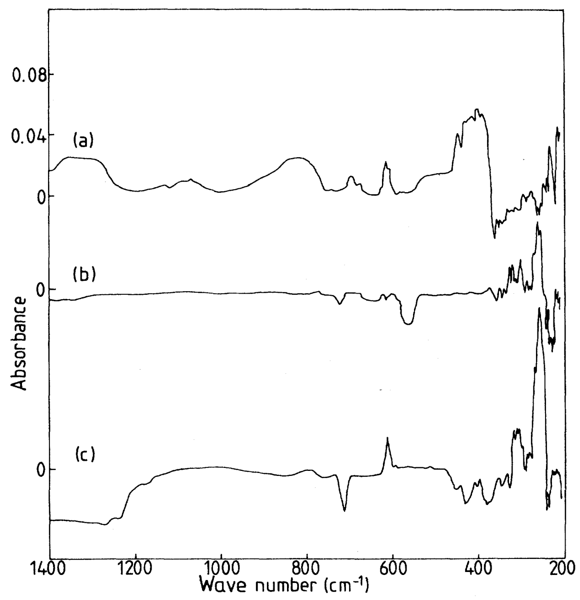

FIG. 5. ir difference spectra (after—before illumination *in vacuo*) for 80°-deposited films of (a) a-GeS_2 (dose 480); (b) a-$GeSe_2$ (dose 385); (c) a-$GeSe_3$ (dose 385) (where the units of illumination dose are 100 mW min cm^{-2}).

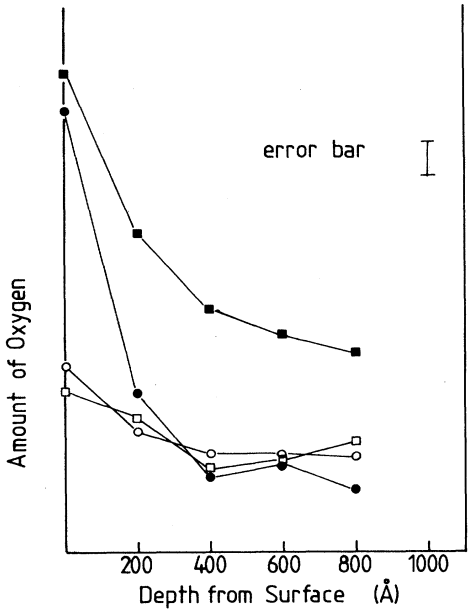

FIG. 6. Oxygen content of films of a-GeSe$_3$ deposited at various angles (in arbitrary units) measured by Auger depth profiling. The data points refer to ○, 0°, before illumination; ●, 0°, after illumination; □, 80°, before illumination; ■, 80°, after illumination.

corporated when the bulk glass was ground up prior to evaporation, or may have been absorbed after deposition when the films were transferred from a bell jar to a desiccator.)

III. uv-VISIBLE ABSORPTION EXPERIMENTS

In order to complement the ir studies reported in the preceding section, the shift of the uv-visible absorption spectra with illumination was studied for all the films mentioned so far, both in air and under vacuum ($\sim 10^{-4}$ torr).

The optical-absorption spectra of amorphous semiconductors can be described in a number of ways. If we assume that the density of states just beyond the valence-band mobility edge is parabolic, then the band-to-band absorption should have the following form:[12]

$$h\nu\alpha(\nu)=\text{const}\times(h\nu-E_0)^2 , \tag{1}$$

where E_0 is the energy band gap between the mobility edges in the valence and conduction bands. When considering the absorption arising from transitions between band-tail states we find that Urbach behavior[13] is generally obeyed, i.e.,

$$\alpha(\nu)=\text{const}\times[-(E_e-h\nu)/F] , \tag{2}$$

where F is a constant depending on the temperature and the nature of the sample. E_e is an energy of the order E_0, and may be considered as an effective band gap.

In order to calculate the absorption we need to measure both the transmission (T) and reflectance (R) spectra for the sample. The absorption coefficient for the case where TR is small compared with $(1-R)^2$, is given by the following relationship:

$$\alpha=d^{-1}\ln[(1-R)^2/T] . \tag{3}$$

In studies by Rajagopalan *et al.*[14] of the effect of illumination on the uv absorption of GeSe$_3$ films, deposited at a variety of angles (~ 0.4 μm thick), the percentage transmission at a given wavelength was plotted versus time of illumination. This can lead to spurious results because of interference effects. For example, photocontraction, or a light-induced change in the refractive index would cause the interference pattern to shift: this would lead to a change in transmission at a particular wavelength without there being, necessarily, a change in absorption.

Instead of using this method, the shift in the wavelength at which the films were 10% transmitting [$\lambda(T=10\%)$] was measured. Interference effects are negligible in this region, and for films less than 0.5 μm thick this corresponds to a value of $\alpha > 5\times10^4$ cm^{-1}. At values of α above 10^4 cm^{-1} it has been observed that Urbach behavior is no longer obeyed in a variety of amorphous chalcogenides.[1,15] We are thus looking predominantly at transitions across the band gap.

A. Experiment

Films of amorphous GeSe$_2$, GeSe$_3$ and GeS$_2$ were deposited at angles of 0°, 50°, 70°, and 80° with thicknesses 0.4 μm, onto glass microscope slides which had been prepared as described in Ref. 10. uv spectra were recorded over the range 300–750 nm using a Pye-Unicam SP8-100 twin-beam spectrometer (it was only possible to measure uv transmission with this machine). Samples were illuminated, in air, by light from a Xe arc lamp, passed through a heat-cut filter, a water filter, and a fiber optic coupler with an intensity at the sample of 100 mW/cm^2.

In order to illuminate the samples it was necessary to remove them from the spectrometer. A sample holder was used, however, which ensured that the samples were located in the same place each time, and it was noted that this caused changes in the value of $\lambda(T=10\%)$ of ±1 nm [slightly greater than the error due to backlash in the monochromator drive (±0.5 nm)].

B. Results (illumination in air)

Transmission spectra for unilluminated normally deposited and obliquely deposited (80°) films of amorphous GeSe$_2$ are shown in Fig. 7. Two features are immediately apparent: the value of $\lambda(T=10\%)$ shifts to shorter wavelengths with increasing angles of deposition (the films are of nominally equal thickness) and, in the nonabsorbing long-wavelength region, whereas the normally deposited film shows strong interference fringes, the 80° film shows none. This is because, while the normally deposited films are smooth, the 80° films are rough (on the scale of the wavelength of light) due to their columnar structure and scatter light in a nonspecular manner: thus no fringes are seen.

Plots of the shift in $\lambda(T=10\%)$ with "dose" for films

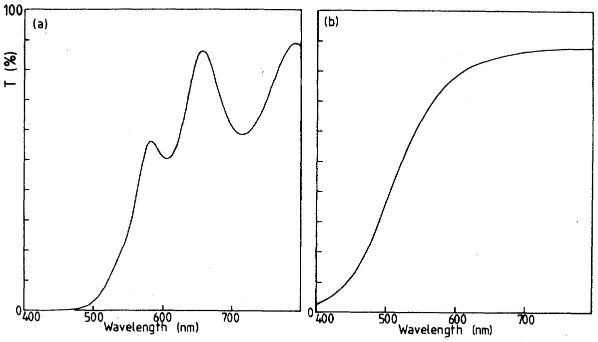

FIG. 7. Optical transmission spectra for films of unilluminated a-GeSe$_2$ deposited at angles (a) 0°; (b) 80°.

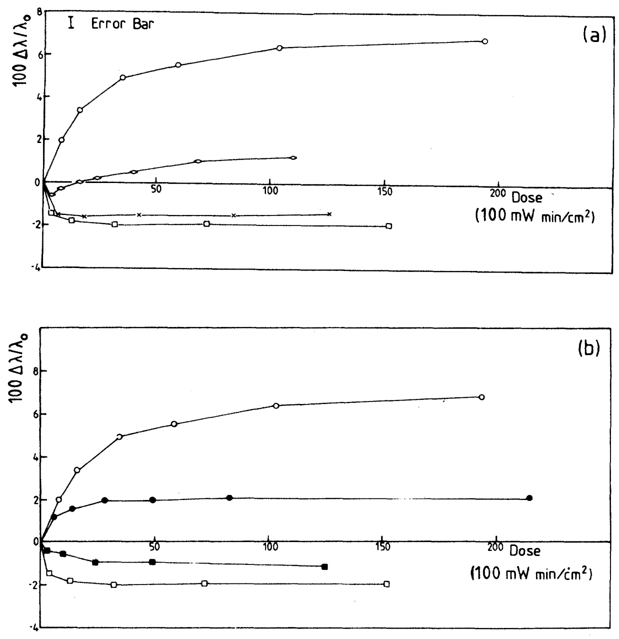

FIG. 9. Optical-absorption changes [shift in $\lambda(T=10\%)$] on illumination under different conditions for films of a-GeSe$_3$ deposited at various angles (key as in Fig. 8).

of GeSe$_2$, GeSe$_3$, and GeS$_2$, deposited at angles of 0°, 50°, 70°, and 80° are shown in Figs. 8–10. In the case of GeS$_2$ films (Fig. 8), we see bleaching at all angles of deposition. The magnitude of the bleaching varies with angle of deposition, 80° films showing the largest bleaching. The rate of bleaching was similar for all angles of deposition.

The GeSe$_3$ films (Fig. 9) show behavior similar to that reported by Rajagopalan *et al*;[14] normally deposited films bleach, obliquely deposited films darken, and in addition the bleaching of normally deposited films occurs more rapidly than the darkening of the obliquely deposited films. There are, however, some differences between our results and those of Rajagopalan *et al.*,[14] viz., the "crossover" from bleaching to darkening occurs for 65°

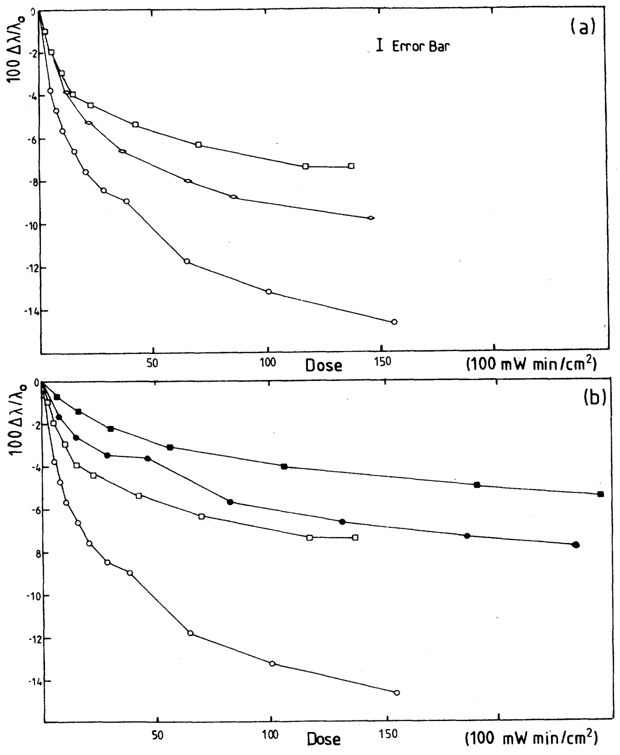

FIG. 8. Optical-absorption changes [shift of $\lambda(T=10\%)$] on illumination under different conditions for films of a-GeS$_2$ deposited at various angles (○, 80°, illuminated in air; ◇, 70°, illuminated in air; ×, 50°, illuminated in air; □, 0°, illuminated in air; ●, 80°, illuminated *in vacuo*; ■, 0°, illuminated *in vacuo*).

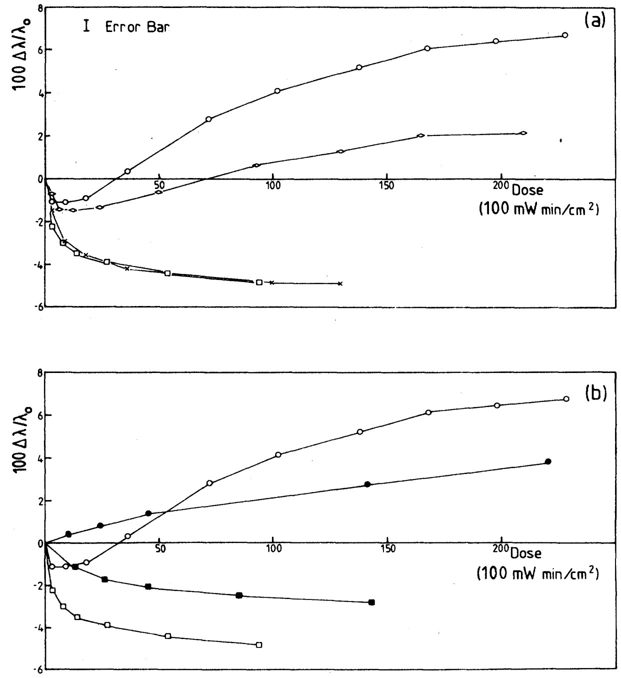

FIG. 10. Optical-absorption changes [shift in $\lambda(T=10\%)$] on illumination under different conditions for films of a-GeSe$_2$ deposited at various angles (key as in Fig. 8).

films in our experiments compared with 50° for those of Rajagopalan *et al.* We also observe an initial bleaching followed by darkening on illumination of 70° films, suggesting that there are two effects occurring when these films are illuminated in air.

Films of $GeSe_2$ (Fig. 10) show similar behavior to those of $GeSe_3$, in that normally deposited films bleach and obliquely deposited films darken, and the rate of bleaching is faster than the rate of darkening. The magnitude of the bleaching is greater for films of $GeSe_2$ than for those of $GeSe_3$. In addition, all films show an initial bleaching on illumination. We also note that the time to saturate the darkening or bleaching is longer for films of $GeSe_2$ than for films of $GeSe_3$, for a given film.

Plots of $[h\nu\alpha(\nu)]^{1/2}$ versus $h\nu$, presented by Tichy *et al.*[6] show that the photobleaching in a-GeS_2 films involves a shift in the band gap, as well as changes in the Urbach tail.[16] In order to see whether this was the case in obliquely deposited films as well, measurements of the uv transmission and reflectance of 0° and 80° films of GeS_2 and $GeSe_2$ were performed using a Perkin-Elmer 330 spectrometer with an integrating sphere attachment. Considering the data in the wavelength range for which $T < 15\%$ (to minimize interference effects) the absorption of the films was calculated using Eq. (3). Plots of $[h\nu\alpha(\nu)]^{1/2}$ versus $h\nu$ are seen to be linear [see Figs. 11(a) and 11(b)], and from the intercepts of these plots the band gaps of the films have been calculated, both before and after illumination (for 1 h, with light from a Xe arc lamp, passed through ir-cut and water filters, at an intensity of 200 mW/cm^2) (see Table I).

While these data show that the photobleaching or photodarkening is associated with an increase or decrease, respectively, in the band gap, the band gap in the films is always less than that of the bulk (3.15 eV for GeS_2, 2.20 eV for $GeSe_2$.[1])

C. Results (illumination in vacuum)

The effect of oxygen (air) upon the shifts in $\lambda(T=10\%)$ seen in these films was investigated. Films were placed in a specially constructed cell, which allowed illumination and measurement of the uv absorption of the films without breaking vacuum. The cell was evacuated overnight at a pressure of 10^{-4} torr. The films were illuminated with light from a Xe arc lamp, passed through ir-cut and water filters, producing an intensity at the sample of 100 mW/cm^2. Again it was necessary to remove the cell from the spectrometer to perform the illumination; however, the cell could be replaced accurately in the spectrometer, resulting in errors in the position of $\lambda(T=10\%)$ of only ±1 nm.

Plots showing the shift of $\lambda(T=10\%)$ with illumination are shown in Figs. 8(b), 9(b), and 10(b). We notice that for GeS_2, the bleaching seen in the films illuminated in vacuum is less than for those illuminated in air, in agreement with Tichy *et al.*[6] and Tanaka, Kasanuki, and Odajima[5]. For films of $GeSe_2$ and $GeSe_3$, we note that the bleaching in the normally deposited films is reduced, and the darkening in the 80° films is also reduced when we illuminate in vacuum.

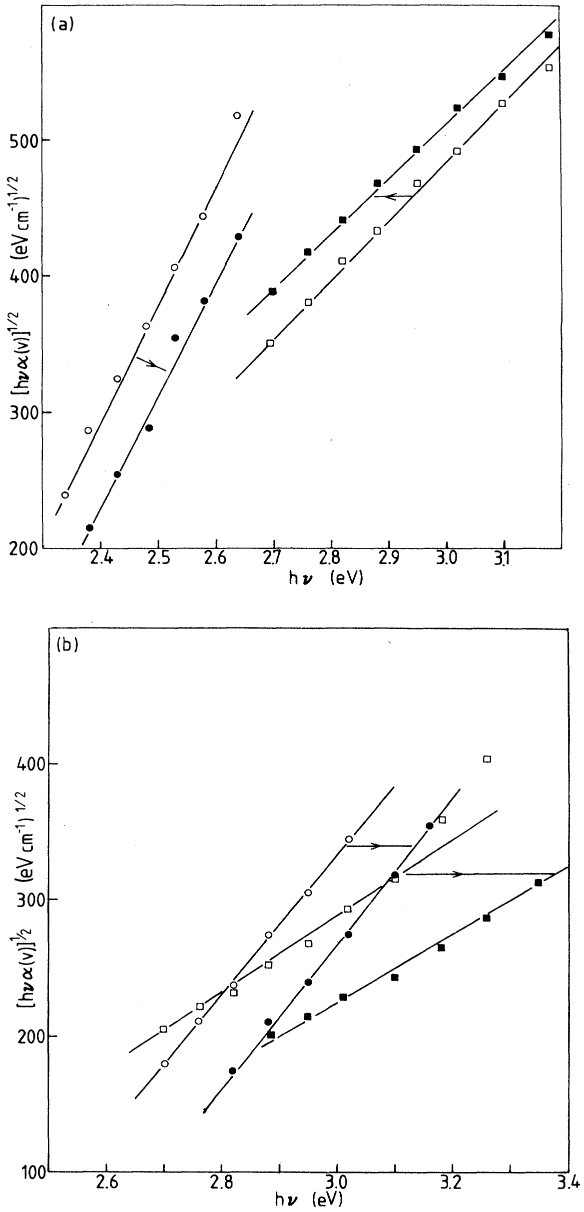

FIG. 11. Plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for films deposited at various angles before and after illumination for (a) a-$GeSe_2$; (b) a-GeS_2 (○, 5°, before illumination; ●, 5°, after illumination; □, 80°, before illumination; ■, 80°, after illumination).

TABLE I. Optical properties of chalcogenide films before and after illumination.

Film (angle of deposition)	Band gap (eV) as-deposited	Band gap (eV) after illumination
$GeSe_2$ 0°	2.06±0.01	2.13±0.01
$GeSe_2$ 70°	1.99±0.02	2.02±0.02
$GeSe_2$ 80°	1.84±0.04	1.69±0.04
GeS_2 0°	2.35±0.01	2.47±0.01
GeS_2 80°	1.98±0.10	2.14±0.10

This behavior places constraints on any model that tries to explain the light-induced edge shifts seen in these materials. Because of the absence of a peak at ~800 cm^{-1} in the ir absorption spectra of normally deposited films of GeS_2, $GeSe_2$, and $GeSe_3$, upon illumination, it is tempting to attribute the bleaching observed in the normally deposited films of GeS_2 (and hence normally deposited films of $GeSe_2$ and $GeSe_3$), to a light-induced chemical ordering, as suggested by Tichy *et al.*[6] to account for the bleaching upon *annealing*. The bleaching of the 80° films of GeS_2 is then explained by the incorporation of oxygen.

The strong dependence of the bleaching in normally-deposited films (which show no Ge—O stretch upon illumination) on air (oxygen) pressure, however, show that in some way incorporation of oxygen with illumination is occurring. The inability to detect a peak at ~800 cm^{-1}, after illumination, does not necessarily signify that oxygen does not play a role in the light-induced bleaching.

The explanation of the light-induced shifts in the absorption of obliquely deposited films in terms of Ge—O bonds replacing Ge—Ge bonds, removing states from the gap, and thereby increasing the band gap[6] is clearly too naive, since films of $GeSe_2$ and $GeSe_3$ [which show peaks at ~800 cm^{-1} after illumination in air, and for which the shift in $\lambda(T=10\%)$ shows a strong dependence on air (oxygen) pressure], actually *darken* upon illumination.

IV. SUMMARY OF THE MAJOR RESULTS OF THE ir AND uv ABSORPTION EXPERIMENTS

An explanation of these phenomena will be suggested in Sec. V. The major experimental findings of these studies of the changes in the ir and uv absorption spectra of these films may be summarized as follows.

(1) On illumination, obliquely deposited (porous) films of $GeSe_2$ and $GeSe_3$ (as well as those of GeS_2) develop features in their ir absorption spectra at ~800 cm^{-1}.

(2) No absorption band at ~800 cm^{-1} is seen on illumination of normally deposited films.

(3) The features at ~800 cm^{-1} are identified with a Ge—O stretching frequency, both from comparison with modes in the bulk glass (GeO_2) and from the dependence of the peak height on air (oxygen) pressure during illumination.

(4) Bleaching on illumination was observed for GeS_2 films at all angles of deposition, and in normally deposited films of $GeSe_2$ and $GeSe_3$. Darkening on illumination was seen in obliquely (70° and 80°) deposited films of $GeSe_2$ and $GeSe_3$, in agreement with previous work.[14]

(5) In the selenide films the darkening (of obliquely deposited films) takes longer to saturate than the bleaching (of normally deposited films).

(6) The band gaps of the as-deposited films (in all cases) are substantially less than those of the corresponding bulk glasses.

(7) The magnitude of both bleaching and darkening (where appropriate) is diminished, in all films, by reducing the air pressure.

V. KINETIC STUDIES

In addition to the spectroscopic aspects of the ir and visible absorption measurements outlined in Secs. II and III, we have also investigated such measurements kinetically, as well as those of small-angle x-ray scattering (SAXS), as a function of illumination dose.[10,17,18] The pronounced change observed in the SAXS intensity with illumination[17–19] is direct evidence for the occurrence of gross structural changes caused by optical irradiation; such behavior has been interpreted[19] in terms of photoinduced void collapse leading to photocontraction.[14] There is also some evidence for photoinduced structural changes at a more microscopic level from both extended x-ray-absorption fine structure (EXAFS) measurements[10] and from investigations of the first sharp diffraction peak in the x-ray diffraction pattern,[20] although neither of these could be quantified. However, the absence of any change in the nearest-neighbor bond length on illumination, as monitored by EXAFS,[10] is indicative that photocontraction effects do not arise from this effect. The interest in performing kinetic experiments is to examine thereby whether there is any direct correspondence for a given film (e.g., a-$GeSe_3$) between the observed structural changes and other photoinduced phenomena, such as photodarkening or photobleaching and photo-oxidation, with the aim of placing the understanding of these phenomena on a microscopic (structural) footing.

Some results for the change in void volume with illumination dose for a-$GeSe_3$ films deduced from time-resolved SAXS experiments,[17,18] performed using a Kratky camera and a laboratory x-ray generator, are reproduced in Fig. 12. A suitably normalized volume is plotted in Fig. 12, namely, $\bar{V}=(V-V_f)/(V_0-V_f)$, where V is the total void volume inferred from the SAXS data after illumination time t, V_0 is that observed before illumination, and V_f is that after cessation of illumination when the photoinduced structural change had saturated. It can be seen from Fig. 12 that for a given film composition, a universal behavior for the dose dependence of $\bar{V}$ is observed, irrespective of the initial angle of deposition of the films, and whether the scattering is mea-

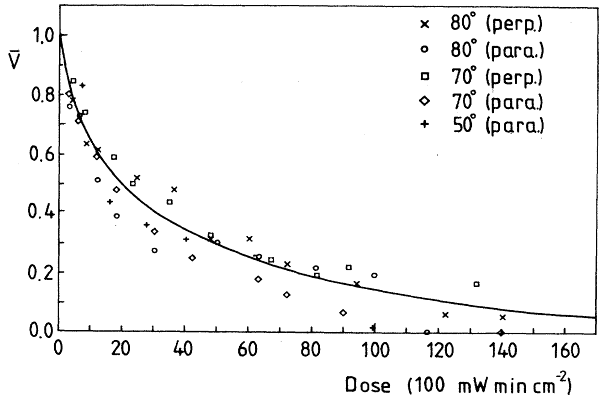

FIG. 12. Evolution with illumination dose of normalized void volume as measured by SAXS (both parallel and perpendicular to the major scattering axis) for films of a-$GeSe_3$ deposited at various angles. The solid line is a theoretical fit (see text).

sured parallel or perpendicular to the major scattering axis (i.e., incorporating scattering contributions from both the minor and major axes of the voids, respectively); in other words, the kinetics are independent of the initial void volume.

The general form of the data shown in Fig. 12 is suggestive of first-order kinetics, but a single exponential function could not be fitted to the data. However, a good fit was achieved (see Fig. 12) by using *two* exponential functions, i.e., by assuming that two independent first-order processes are operative, viz.,

$$\bar{V}=a_1\exp(-\alpha_1 d)+a_2\exp(-\alpha_2 d)\ , \qquad (4)$$

where $a_1+a_2=1$, and d is the dose (proportional to time). The first of these functions is significant only at very low doses whereas the other is dominant otherwise; the time (dose) constants characteristic of the two exponentials for the data shown in Fig. 12 are in the ratio of approximately $\alpha_1/\alpha_2 \simeq 9$, and the relative magnitude of each process is correspondingly $a_1/a_2 \simeq 0.7$. (Qualitatively similar results were obtained from synchrotron SAXS results, although the data were more noisy.)

Kinetic experiments monitoring the dose (time) dependence of the Ge—O stretching (800 cm^{-1}) ir peak have also been carried out.[10,18] The integrated ir absorption of this, normalized to the area under the main Ge—Se stretching mode ir peak, is shown as a function of illumination dose in Fig. 13 for an 80°-deposited *a*-$GeSe_3$ film. Once more, the data could not be fitted by a single exponential function of the form $[1-\exp(-\alpha D)]$, characteristic of a single first-order (growth) process; instead, two such functions had to be employed, as in Eq. (4), indicating that *two* independent first-order processes might be responsible for the photooxidation process. However, the long-time (dose) term was characterized by a time constant α_2 approximately one-third of that obtained for the photodensification process (i.e., from SAXS). The value of the other time (dose) constant α_1 was difficult to obtain precisely from the fitting procedure since the short-time term was present only in a relative small proportion ($a_1/a_2 \simeq 0.25$); however, it appeared to be of the same order of magnitude as for the corresponding term for photodensification.

Finally, the kinetics of photoinduced optical changes will be discussed. As seen from Figs. 8–10, the behavior is in general rather complex, depending on the composition and the initial angle of deposition of the film amongst other parameters. We have not yet fully analyzed all these data,[17,18] and so for simplicity we will consider here only data for the same type of film (80°-deposited *a*-$GeSe_3$) whose photostructural and photooxidative kinetics have already been discussed. The data are reproduced in Fig. 14, and the two sets correspond to optical illumination in air and *in vacuo*. As before, we have tried to analyze the kinetics assuming first-order kinetics with either single- or two-exponential contributions. It was found that the *vacuum*-irradiated data could be fitted very well using a *single*-exponential function $(1-e^{-x})$ with the *same* value of time-(dose) constant, α_1, as was found for the short-time behavior in the photodensification (SAXS) studies; this curve is shown in Fig. 14. On the other hand, *two* exponentials, with the *same* time (dose) constants α_1 and α_2 and weight factors a_1 and a_2 as those deduced from the photodensification studies fitted the optical-absorption kinetic data very well without any further adjustment of parameters (see Fig. 14). This is a strong indication that it is likely that the *same* two independent processes control photodensification and photodarkening (in this case), one of which is always present (i.e., even for *in vacuo* illumination) and the other which occurs only for illumination in the presence of air (oxygen). On the other hand, although the role played by oxygen in various photoinduced phenomena is demonstrably important, the kinetic analysis discussed above indicates that a one-to-one correspondence between photo-oxidation and photodarkening does not exist, since the time constants for the two processes are substantially different. It appears, therefore, that photo-oxidation acts somewhat as a "catalyst" for photoinduced phenomena, such as densification and darkening, rather than as a direct agent. A further discussion of the possible role played by oxygen in these pro-

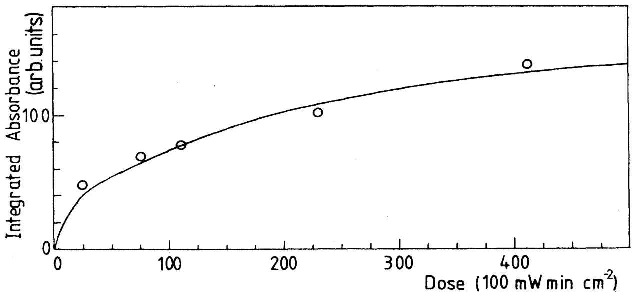

FIG. 13. Evolution with illumination dose of integrated absorption of the Ge-O 800-cm^{-1} ir peak, normalized by the area under the main Ge—Se stretch peak for an 80° *a*-$GeSe_3$ film. The solid line is a theoretical fit (see text).

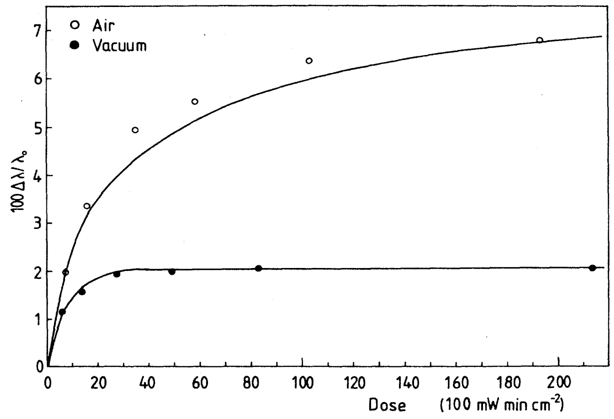

FIG. 14. Evolution with illumination dose of the photodarkening in an 80° *a*-$GeSe_3$ exposed in air and in vacuum. The solid lines are theoretical fits (see text).

cesses is given in Sec. VI.

Finally, some mention should be made here of the assumption made in the above discussion of separate independent first-order processes being responsible for the observed overall nonexponential kinetics. In fact, many time-dependent phenomena exhibit nonexponential temporal decays when it might otherwise be expected that first-order kinetics (single-exponential decays) would be observed. Such behavior has been observed for a number of chemical reactions in condensed phases,[21–23] as well for a wide variety of electrical and mechanical phenomena.[24] Very often, the empirical stretched exponential function

$$\phi(t)=\exp(-t/\tau)^{\beta} \tag{5}$$

describes the temporal decay data rather well. A complete theoretical understanding of the origin of Eq. (5) is still wanting, although several models, based on, for example, hierarchically constrained dynamics[25] or diffusion-controlled processes,[26] have been proposed; however, it has been suggested[27] that a common mathematical framework underlies these seemingly disparate models. An alternative approach is to consider that a distribution of rate constants is responsible for the overall observed nonexponential behavior.[21–23] We have to consider, therefore, whether our kinetic data for various photoinduced phenomena, as shown, for example, in Figs. 12–14, could be better described instead in such a general nonexponential fashion. However, we are of the opinion that, in this case, such a viewpoint is not warranted and that there is physical justification for the assumption of two-independent (first-order) processes being operative (under condition of illumination in air). The reason for this assertion is to be found in Fig. 14, where it is found that one of the exponential functions describing the photoinduced changes occurring in air remains when illumination occurs *in vacuo* (i.e., it is intrinsic), while the other extrinsic term vanishes. This behavior would not necessarily be expected in the general nonexponential picture.

VI. GENERAL DISCUSSION

In this final part we will discuss the implications of this work with regard to possible mechanisms for the photobleaching or photodarkening and photo-oxidation we have observed. The work presented in Secs. II, III, and IV has demonstrated that oxygen plays a crucial role in the mechanisms of the photobleaching or photodarkening. Any mechanisms describing the irreversible light-induced effects must attempt to define the role of oxygen in these effects. Tichy *et al.*[6] and Tanaka, Kasunuki, and Odajima[5] have explained the bleaching seen upon illumination in air of amorphous films of Ge-S alloys by a model in which Ge—Ge bonds were broken upon illumination and oxidation then occurred producing Ge—O bonds. As we have pointed out in Sec. III C, such a model is unable to explain the photodarkening observed in obliquely deposited Ge-Se films.

Bleaching produced by annealing films of $Ge_{30}S_{70}$ in vacuum has been attributed by Tichy *et al.*[6] to the conversion of homopolar to heteropolar bonds within the films. The role of oxygen was discounted because the ir absorption spectra showed no new features at ~ 800 cm^{-1} after annealing. Our experiments on normally deposited films of $GeSe_2$, $GeSe_3$, and GeS_2, however, show that the edge shift *is* dependent upon ambient oxygen pressure during illumination even when no peak at 800 cm^{-1} is seen in the ir absorption spectra (see Fig. 2). Thus the absence of a peak in the ir absorption spectrum is not *necessarily* an indication that oxygen is not involved in the photobleaching mechanism.

Band gaps have been estimated for bulk Ge-S glasses using mean bond-energy approaches (e.g., Tichy *et al.*[28]). In such an approach the band gap E_g is calculated by

$$E_g=b(E_s-a)\ , \tag{6}$$

where $E_s=\sum_j w_j E_{sj}$, w_j is the relative fraction of j-type bonds, E_{sj} is the bond energy of a j-type bond, and a and b are fitting parameters. This method can be used to estimate the number of Ge—Ge bonds present in the films. Values for the bond energies were taken from Street and Lucovsky,[29] the values being

$$E_{\text{Ge—Ge}}=40.0\ \text{kcal/mol}\ ,$$

$$E_{\text{Ge—S}}=56.3\ \text{kcal/mol}\ ,$$

$$E_{\text{S—S}}=50.0\ \text{kcal/mol}\ ,$$

$$E_{\text{Ge—Se}}=50.7\ \text{kcal/mol}\ ,$$

$$E_{\text{Se—Se}}=42.0\ \text{kcal/mol}\ .$$

Knowing the band gaps of the chemically ordered glasses $GeSe_2$ and GeS_2, we can calculate the values of a and b. With these parameters, we calculate the band gap in a random covalent network (RCN) (the bonding statistics for a RCN are given by Lucovsky *et al.*[30] For GeS_2 a RCN should have a band gap of 2.20 eV, 0.95 eV less than that of the ordered network. To explain the difference between the band gap of the normally deposited film (2.35 eV) and the bulk (presumably chemically ordered) glass, 85% of the atoms in the films would have to obey RCN statistics. In a RCN with composition GeX_2, 33% of the Ge first-nearest neighbors are Ge atoms.

From EXAFS experiments[10] we have been able to place an upper limit of 10% on the number of Ge—Ge bonds present in GeS_2 films. Because of the similarity in the bond length of Ge—Ge and Ge—Se bonds, and the similarity in their backscattering factors, it was not possible to estimate the corresponding maximum number of Ge—Ge bonds occurring in Ge-Se films. We believe that it is not possible therefore to explain the difference between the band gap of the bulk glass and films of GeS_2 by this mean bond-energy approach alone (despite the success of such models in explaining the compositional dependence of the band gap in bulk Ge-S glasses[28]).

Tanaka, Kasunuki, and Odajima[5] concluded that amorphous films of GeS_2, unlike amorphous films of As_2S_3, are intrinsically different from the bulk, although they did not describe the nature of this difference. Obliquely deposited films of Ge-Se and Ge-S glasses *are* intrinsically different from the bulk, in that they have a porous columnar microstructure. Normally deposited films have a much less pronounced columnar microstructure. However, when normally deposited films of $GeSe_2$ are etched in lithographic applications (see Ref. 31, and references therein), the columnar microstructure becomes apparent. The density deficit in normally deposited films of amorphous $GeSe_2$, $GeSe_3$, and GeS_2, has been measured[32] and found to be 2% compared with the bulk glass. It is known that the presence of voids in sputtered films of *a*-Si, *a*-Ge, and *a*-GaAs can reduce the observed band gap.[33] We thus believe that changes in the microstructure, as well as changes in the chemical ordering of these films, are responsible for the observed changes in the band gap.

When considering the light-induced shifts in the absorption edge, we can identify two effects; the first is a bleaching which occurs in normally deposited films of all the compounds studied. For normally deposited films we observe no peak in the ir absorption spectra at ~ 800 cm^{-1} on illumination. The second effect, which we associate with the appearance of a feature at ~ 800 cm^{-1} in the ir spectra, and is most easily observed in 70° and 80° deposited films, can lead to a further bleaching (as in the case of GeS_2 films) or to a darkening of the films (as seen in Ge-Se films). The crossover (from bleaching to darkening) behavior observed in some films leads us to believe that both effects occur in *all* films, but that the relative magnitudes of the effects is controlled by the microstructure of the films.

When illuminating normally deposited films, a small increase in the main chalcogenide stretch peak in the ir absorption spectra is seen (Fig. 2). In addition, we have performed EXAFS measurements which appear to show a small increase in the coordination number of Ge atoms upon illumination of normally deposited films of $GeSe_2$ and GeS_2.[10] These results lead us to propose an oxygen-assisted bond reconstruction (because of the air-pressure dependence of the bleaching of normally deposited films, see Figs. 8(b), 9(b), and 10(b), involving the elimination of some dangling bonds and the conversion of some homopolar to heteropolar bonds.

The second effect, seen most clearly in the obliquely deposited films, is associated with the appearance of a Ge-O absorption feature in the ir spectra. We associate this feature with surface oxidation of the films. The porous, columnar microstructure of the obliquely deposited films presents a much greater accessible surface area than the normally deposited films, thus explaining why the Ge-O absorption peak in the ir spectra is so much bigger in the obliquely deposited films.

There remains, however, a problem: from average bond-energy considerations we would expect oxidation to increase the band gap in both Ge-S and Ge-Se films. Instead of this, in the case of $GeSe_2$ and $GeSe_3$ films deposited at oblique incidence, darkening and a shift of the band gap to lower energies is observed (see Table I). We do not know the cause of this, but make the following suggestions. It is known from our SAXS studies[10] that for a given angle of incidence of the film, Se-containing glasses exhibit larger proportional decreases in void volume than do S-containing glasses. A decrease in the void density might be expected to increase the optical-absorption coefficient,[33] and so if this effect were dominant, photodarkening would be expected. Alternatively, and more speculatively, the oxidation will produce an oxide layer at the surface, and the strain at the oxide-chalcogenide interface may introduce states into the band gap. The overall effect of this oxidation is a balance between bleaching due to the creation of Ge—O bonds and darkening caused by the interfacial strain. Since the mismatch between Ge—Se bond lengths (2.39 Å) and Ge—O bond lengths (1.72 Å) is greater than between Ge—S (2.22 Å) and Ge—O, we would expect the darkening effect to be greater in the Ge-Se films.

VII. CONCLUSIONS

The work presented in this paper has identified two effects which occur on illumination of these amorphous chalcogenide films. One is an oxygen-assisted bond reconstruction which leads to a bleaching in all films. The other is a light-induced surface oxidation which can result in bleaching or darkening, depending on the material. The critical role played by the porous microstructure of these films in the photo bleaching or photodarkening has been highlighted.

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