Origin of Anomalous Photoinduced Transformations in Amorphous Ge-Based Chalcogenide Thin Films

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Anomalous photoinduced transformations in amorphous Ge-based chalcogenide thin films are established as being due to photochemical modification of the surfaces, by photoemission studies. Mass measurements indicate that the giant thickness reduction on irradiation is predominantly due to the loss of material as a result of photogenerated volatile high-vapor-pressure oxide fractions on the surface. This extrinsic contribution contradicts the models of the phenomenon proposed so far, which are based purely on intrinsic structural transformations.

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Anomalous photoinduced transformations in amorphous Ge-based chalcogenide thin films have been reported by various investigators.[1-3] When irradiated with photons of energy comparable to the band gap, the films undergo a giant photostructural transformation which manifests as a thickness contraction of up to 12% (for the typical case of $Ge_{25}Se_{75}$) accompanied by significant changes in band gap, refractive index, and chemical dissolution rates. All these giant effects have been found only in vacuum-deposited films, the deposition angle being 80°. Of all the photoinduced effects, the giant thickness contraction has been considered[3] as the most prominent signature of the underlying gross structural transformation. Three different approaches have been proposed to interpret this phenomenon. (1) Singh *et al.* have proposed[1] a qualitative explanation in terms of a strain-induced mechanical collapse of the low-density columnar structure due to the interaction of the photogenerated carriers with charged dangling bonds[4,5] of the chalcogenide network. (2) Phillips and Cohen have constructed[6] molecular models to explain whisker formation (columnar structure) and hence the giant photocontraction. According to these authors, the thickness contraction takes place because of the topologically critical nature of the kinetics of the growth and structure of the inherently unstable noncrystalline helical whiskers. (3) Based on small-angle neutron-scattering studies, Elliott *et al.* have suggested[7,8] that as-deposited films consist of anisotropic ellipsoidal voids and the giant photocontraction is a result of reconstruction of the structure across the voids involving the chalcogen atoms. Their scanning-electron-microscope data[8] show that the columnar microstructure is retained even after photoirradiation, contradicting the explanations of the phenomenon put forward in Refs. 1 and 2.

In view of these conflicting, yet seemingly convincing interpretations, the actual physical process underlying the giant photoinduced effects remains unknown. The primary objective of this Letter is to establish the origin of these effects unambiguously, based on our recent photoemission data on Ge-based chalcogenide thin films. In addition to the intrinsic structural changes (defined as purely structural modifications of the molecular network) which contribute to the reversible part of the phenomenon, we observe an extrinsic contribution (defined as those changes resulting from the chemical modification of the surface) which is responsible for the giant irreversible part of the phenomenon. We have been able to fit the observed effects in the framework of a simple model of the phenomenon. This Letter reports the first results of such investigations.

Bulk glasses of $Ge_{25}X_{75}$ (X=S, Se, and Te) were prepared by melt quenching. The experimental details for the oblique deposition of the films, and photoemission studies have been described elsewhere.[2,9] A 125-W mercury vapor lamp at an intensity of 55 mW/cm^2 was used to irradiate the films in air as well as in vacuum $\sim 10^{-6}$ Torr. A quart-crystal oscillator was used to monitor the mass of the films during irradiation.

Large changes (decrease) in mass have been observed when 80°-deposited $Ge_{25}Se_{75}$ films are irradiated in air. Figure 1, curve *a*, depicts the fractional changes occurring in the mass of such films as a function of exposure time. The most remarkable feature of this figure is that a comparison of it with Fig. 1, curve *b*, clearly indicates that the observed thickness reduction is related to the decrease in the mass of the films. Note that there is no mass change on further irradiation when 10.5% of the total mass has been lost (Fig. 1, curve *a*). The major contribution to the maximum thickness reduction of 12% (Fig. 1, curve *b*) is therefore due to the loss of material from the film surface. 0°-deposited films, on the other hand, do not show any changes in mass on exposure (Fig. 1, curve *c*) while they exhibit a thickness contraction of 1% (Fig. 1, curve *d*) suggesting an intrinsic structural change in contrast to the extrinsic origin (mass loss) of the giant thickness reduction in 80°-deposited films.

Amazingly, when irradiated in vacuum $\sim 10^{-6}$ Torr,

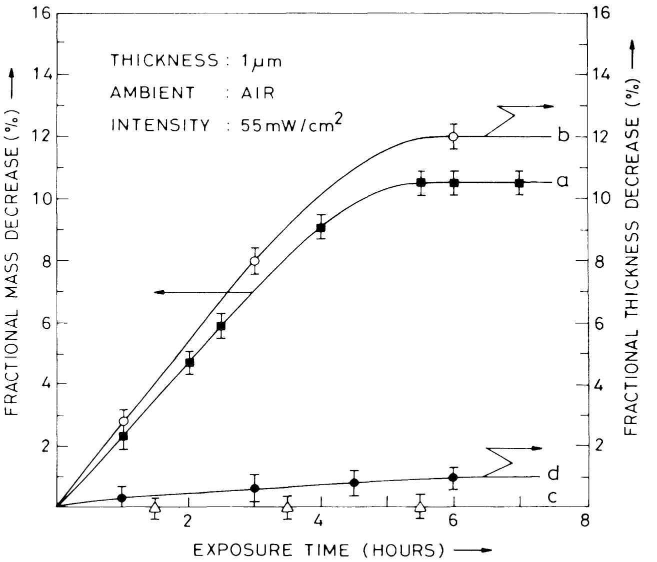

FIG. 1. Fractional mass and thickness decrease as a function of exposure time, for $Ge_{25}Se_{75}$ films, photoirradiated in air.

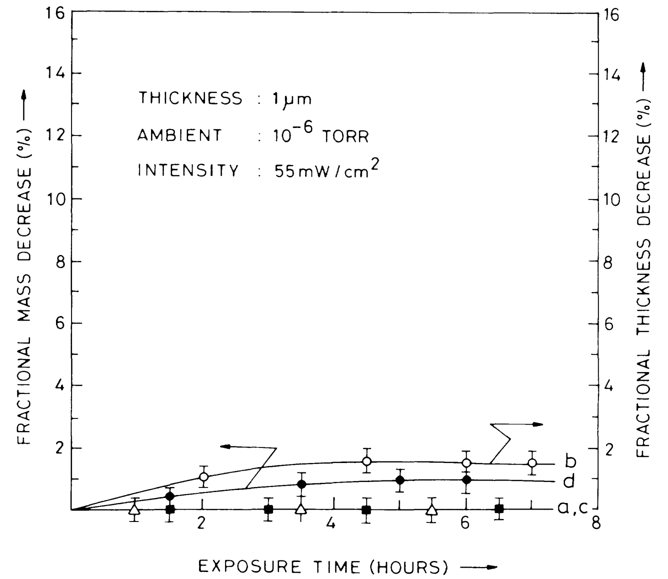

FIG. 2. Fractional mass and thickness decrease as a function of exposure time, for $Ge_{25}Se_{75}$ films, photoirradiated in vacuum of ~10^{-6} Torr.

the 80°-deposited films do not show any giant thickness reduction or mass loss. Only a small thickness contraction of 1.5% (Fig. 2) which is comparable to the intrinsic change observed in 0°-deposited films, is present. For 0°-deposited films, however, there is no discernible difference between the magnitude of thickness contraction on exposure in air (Fig. 1, curve *d*) and in vacuum (Fig. 2, curve *d*). This dependence of the giant thickness reduction and accompanying mass loss on ambient pressure raises serious objections against the validity of the earlier proposed models.[1,6-8] $Ge_{25}S_{75}$ films show similar behavior (Table I). The absence of any effect in $Ge_{25}Te_{75}$ films deserves special mention, a point to which we shall return later.

We chose photoemission studies to probe the surface chemistry of the films undergoing such gross transformations. Figure 3 shows our x-ray photoelectron spectroscopy (XPS) results indicating phenomenal chemical modification of the surface *s* after irradiation. The $S(2p)$ core level at 162 eV in Fig. 3(a) is absent after irradiation, indicating the absence of sulfer on the surface of the irradiated $Ge_{25}S_{75}$ film. Similarly, in $Ge_{25}Se_{75}$ films the $Se(3d)$ core level [Fig. 3(b)] shifts, on irradiation, from 55.1 to 55.6 eV with a drastic decrease in the peak intensity indicating (i) formation of SeO_x phases and (ii) significant reduction of Se concentration, on the surface. Our x-ray-initiated Auger-electron spectroscopy (XAES) studies also indicate that the peak in L_3VV region of Se shifts by 5.5 eV, confirming the formation of SeO_x.[9] The $Ge(2p_{3/2})$ core level at 1220.0 eV in $Ge_{25}S_{75}$ films [Fig. 3(c), curve *A*] similarly shifts to 1221.0 eV after irradiation indicating the formation of GeO_2 phase[10] [Fig. 3(c), curve *B*]. The $Ge(2p_{3/2})$ core levels at 1219.1 and 1220.0 eV in $Ge_{25}Se_{75}$ film [Fig. 3(c), curve *C*] shift to 1220.1 eV [Fig. 3(c), curve *D*] after irradiation indicating the formation of GeO.[11] The nature of photochemical reactions leading to the surface modification of these obliquely deposited films is presented in Table II. While in $Ge_{25}S_{75}$ films photo-oxidation leads to GeO_2 formation as indicated by $Ge(L_3VV)$, in $Ge_{25}Se_{75}$ and $Ge_{25}Te_{75}$ films the GeO phase is clearly seen (Table II).

TABLE I. Photoinduced fractional mass decrease and relevant structural parameters of Ge-based chalcogenide films.

Chalcogenide system	Fractional mass decrease (%) 0°	80°	Fractional thickness decrease (%) 0°	80°	Density deficit (%) 0°	80°	Band-gap change (%) 0°	80°	Refractive index change (%) 0°	80°	Extinction coefficient change (%) 0°	80°
$Ge_{25}S_{75}$	0	18	1	19	1.5	27	2.4	10	2.8	8	7	30
$Ge_{25}Se_{75}$	0	10.5	~1	12	2	16	1.5	6	1.2	3.5	4	20
$Ge_{25}Te_{75}$	0	0	0	0	1	6	<1	<1	<1	<1	<1	<1

TABLE II. Core-level binding energies in electron volts.

System	Ge($2p_{3/2}$)	Ge(L_3VV)	Te($3d_{5/2}$)	Te($3d_{3/2}$)	O($1s$)	Se($3d$)	S($2p$)	Oxidation state
Ge	1217.6	1145.8	⋯	⋯	⋯	⋯	⋯	Ge^0
S	⋯	⋯	⋯	⋯	⋯	⋯	165	S^0
$Ge_{25}S_{75}$ (unirradiated)	1220.0	1140.2	⋯	⋯	⋯	⋯	162	⋯
$Ge_{25}S_{75}$ (irradiated)	1221.0	1137.8	⋯	⋯	532.4	⋯	⋯	GeO_2
Se	⋯	⋯	⋯	⋯	⋯	57.1	⋯	Se^0
$Ge_{25}Se_{75}$	1219.1	1143.6	⋯	⋯	530.8	55.1	⋯	GeO (traces)
(unirradiated)	1220.0	1139.6						
$Ge_{25}Se_{75}$ (irradiated)	1220.1	1139.6	⋯	⋯	530.8	55.6	⋯	GeO, SeO_x ($x \simeq 2$)
Te	⋯	⋯	573.0	⋯	⋯	⋯	⋯	Te^0
$Ge_{25}Te_{75}$	1218.2	1145.0	572.3	582.2				
(unirradiated)		1139.8	575.6	585.7	531.2	⋯	⋯	GeO, TeO_2 (traces)
$Ge_{25}Te_{75}$ (irradiated)	1220.2	1139.8	575.6	585.7	531.2	⋯	⋯	GeO, TeO_2

From the above data, we conclude the following. In obliquely deposited $Ge_{25}S_{75}$ and $Ge_{25}Se_{75}$ films, irradiation in air leads to chemical modification of the surfaces as a result of the formation of oxides of the types GeO, GeO_2, SeO_x, and SO_x ($x \simeq 2$) on the surface. The surface of the $Ge_{25}S_{75}$ films is totally depleted of the oxides of sulphur because of their large vapor pressure at room temperature,[12,13] resulting in the observed loss in the mass (Table I). The lower mass loss and hence lower thickness reduction in $Ge_{25}Se_{75}$ films compared to $Ge_{25}S_{75}$ films is due to the lower vapor pressure of the oxides of Se at room temperature,[12,13] as a result of which these oxides are partly retained on the surface.

The irreversible photoinduced changes are absent in $Ge_{25}Te_{75}$ films in conformity with our mass measurements (Table I), which indicate no measurable mass loss on irradiation. The XPS results explain this behavior. The core-level energies of Te($3d_{5/2}$) and Te($3d_{3/2}$) at 572.3 and 582.2 eV, respectively (Fig. 4, curve a), shift to 575.6 and 585.7 eV after irradiation (Fig. 4, curve b), indicating the formation of TeO_2 phase.[14] Also, there are no significant changes in the peak intensities of either Te($3d_{5/2}$) or Te($3d_{3/2}$) levels, which indicates that there is no observable loss of Te from the surface. Te gets photo-oxidized to TeO_2 and because of its very low vapor pressure[12,13] is retained on the surface.

Interestingly, such a photo-oxidation process has not been observed for 0°-deposited films. This could be explained as being due to the absence of porosity (which

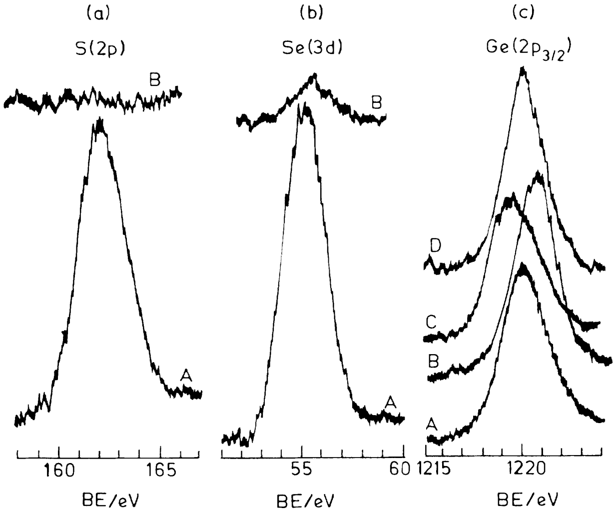

FIG. 3. (a) S($2p$) region of $Ge_{25}S_{75}$ films and (b) Se($3d$) region of $Ge_{25}Se_{75}$ films before (A) and after (B) photoirradiation. (c) Ge($2p_{3/2}$) in $Ge_{25}S_{75}$ films before (A) and after (B) photoirradiation and in $Ge_{25}Se_{75}$ films before (C) and after (D) photoirradiation.

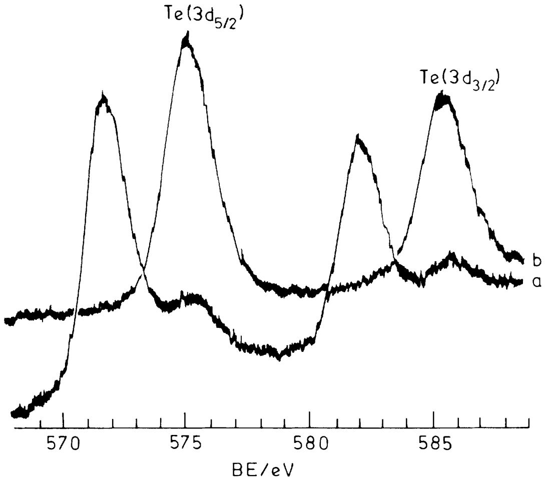

FIG. 4. Te($3d_{5/2}$) and Te($3d_{3/2}$) regions of $Ge_{25}Te_{75}$ films (a) before and (b) after photoirradiation.

results in density deficit) in 0°-deposited films, the density deficit centers[9] being responsible for the active photooxidation processes in 80°-deposited films. A critical examination of the correlation of the observed fractional changes in mass, with fractional changes in thickness and density deficit and the photoinduced variations in various optical parameters (Table I) clearly shows that the low apparent density[9] (porosity) of 80°-deposited films is conducive for such photochemical surface modifications.

Having established that in 80°-deposited films photoirradiation leads to loss of film material associated with the formation of volatile high–vapor-pressure oxide fractions on the surface, the origin of photoinduced giant decrease in thickness of the films is very clear. The XPS and XAES results, however, indicate that the lower-vapor-pressure oxide fractions are retained leading to large chemical modification of the surfaces. The large irreversible changes occurring in refractive index, band gap, and extinction coefficient of these films (Table I) are therefore due to the chemical modification of the surfaces. The small reversible changes in these properties are intrinsic, however, resulting from a purely structural transformation. For instance, the reversible change of $\sim 1.2\%$ in the refractive index for the typical case of $Ge_{25}Se_{75}$ films involves changes in the number of polarizable units per unit volume—similar to those reported for bulk glasses and well-annealed films. The absence of mass loss for films irradiated in vacuum is essentially due to the absence of the "extrinsic" contribution, the observed thickness contraction ($\sim 1.5\%$) being the true "intrinsic" phenomenon (Fig. 2, curve *b*). The anomalous, predominantly irreversible photoinduced transformations in obliquely deposited films are therefore not the true representations of the intrinsic nature of the chalcogenide network as reported in literature,[1,6] but extrinsic in origin.

In conclusion, through detailed XPS and XAES analysis and mass measurements we have established that the giant photoinduced decrease in thickness in obliquely deposted Ge-based chalcogenide films is a direct consequence of the loss of film material from the surface, as a result of photogenerated volatile high–vapor-pressure oxide fractions. The subsequent photochemical modification of the chalcogenide surfaces is shown to be mainly responsible for the concomitant anomalous photoinduced effects, leading to large changes in various structural and optical parameters.

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