Preparation and investigation on glasses in the $Te_{46}As_{32}Ge_{10}Si_{12}$ and $Te_{41}As_{37}Ge_{10}Si_{12}$ systems

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Thin films of $Te_{46-x}As_{32+x}Ge_{10}Si_{12}$ ($x = 0, 5$) of different thicknesses are deposited on glass substrate by vacuum evaporation. X-ray diffraction revealed the formation of amorphous films. The value of the optical band gap, E_g, is found to increase with the thickness of the films and with increasing As content. The films are heat treated at different elevated temperatures from 298 to 423 K. The values of E_g are found to decrease with increasing temperature of heat treatment. The band tail, E_e, obey Urbach's empirical relation.

1. Introduction

In recent years there has been a great deal of interest in the study of semiconducting glasses from the point of view of basic physics as well as of device technology. These glasses are used for example as switching, memory elements and optoelectronic device material [1]. Among the amorphous chalcogenide semiconductors, arsenic chalcogenide has been investigated extensively [2–5]. A number of papers [6–10] have appeared in the literature reporting various properties of amorphous alloys belonging to the $A_x^V B_{1-x}^{VI}$ systems, where A is a group V element, such as As, and B is a group VI element, such as Se, Te, S, etc.

Study of the optical absorption spectra has been one of the most productive methods in developing and understanding the structure and energy gap of amorphous non-metallic materials. The absorption coefficients, $\alpha(\omega)$, of the optical absorption show an exponential dependence on photon energy, $\hbar\omega$, and obey Urbach's relation [11]

$$\alpha(\omega) = \alpha_0 \exp \hbar\omega/E_e \qquad (1)$$

where α_0 is a constant, ω is the angular frequency of the incident photon, h is Planck's constant and E_e the band tails' width of the localized states in the band gap. In general it represents the degree of disorder in an amorphous semiconductor [12].

In the high absorption region, $\alpha(\omega)$ was discussed in terms by Davis and Mott [13], whose equation

$$\alpha(\omega) = \beta(\alpha\hbar\omega - E_g)^M/\hbar\omega \qquad (2)$$

where β is a constant, M is a number ($M = 1, 2, 3$) that characterizes the transition process, and E_g is the optical band gap of the material.

The absorption coefficient, $\alpha(\omega)$, can be calculated from the optical absorption spectra using the relation

$$\alpha(\omega) = 2.303A/d \qquad (3)$$

where d is the film thickness and A is the optical absorbance of the film.

The degree of disorder and defects present in the amorphous structure changes due to heat treatment [8]. Thus a study of the variation of E_g as a function of temperature and time of heat treatment may provide a deeper insight into the mechanism of disorder and defect formation in the amorphous chalcogenide.

2. Experimental procedure

The samples were prepared by alloying proper portions of reagent grade arsenic, tellerium, germanium and silicon in the compositions $Te_{46}As_{32}Ge_{10}Si_{12}$ and $Te_{41}As_{37}Ge_{10}Si_{12}$. Bulk glasses of the compositions have been prepared by the well established melt-quenching technique. Appropriate amounts of 99.999% pure constituent elements were taken in an evacuated silica ampoule. The ampoule was then placed in a specially designed oscillation furnace. The sample temperature was raised in steps in order to reduce the vapour pressure of constituent components. At first it was raised from room temperature to the melting point of each element constituently and kept at each temperature for 2 h. Then the temperature was raised to 1000 °C for a long time (45–50 h). The long period of synthesis and rocking of the melt via the oscillations of the furnace ensure homogeneity of the material composition. The molten materials were then rapidly quenched in iced water to obtain a glassy phase sample. The mean rate of cooling in this case was about 300 °C min^{-1}.

Films were then prepared by thermal evaporation technique using a high vacuum plant (BAE 121, Balzar) on well cleaned glass substrates of suitable dimensions.

The $Te_{46-x}As_{32+x}Ge_{10}Si_{12}$ ($x = 0, 5$) system was crushed into small grains. These grains were introduced into a cleaned dry silica boat placed in the electrical spiral heater of the coating unit. The glass substrate was placed at a tangent to a suitable holder (rotated horizontally) with the desired mask. The vacuum chamber was pumped down to 1.3 MPa. The temperature of the chalcogenide grains was then raised in steps according to a certain regime to a temperature above the highest melting point of the constituents (see Table I). Samples with different thicknesses were

TABLE I Evaporation scheme for the considered compositions

Time (min)	2	3	3	3	3	3	3	3	3	3	2	2	2	2	2
Temperature (°C)	160	225	265	315	360	410	470	515	550	590	615	655	690	735	780

prepared under the same evaporation conditions. The substrate temperature was held below 50 °C during deposition. The film thickness was established by Tolansky's method [14] using multiple beam Fizeau fringes. The film thickness ranged from 120 to 400 nm.

The optical absorbance of the samples was measured with unpolarized light at normal incidence in the wavelength range 350–900 nm using a double beam spectrophotometer (Varian DMS 100 S u.v. visible).

X-ray diffraction characterization of films was carried out using filtered CuK_α radiation (Phillips PM 8203) operated at 40 kV and 25 mA.

3. Results and discussion

The structures of as-deposited $Te_{46}As_{32}Ge_{10}Si_{12}$ and $Te_{41}As_{37}Ge_{10}Si_{12}$ were investigated using X-ray diffraction patterns. As demonstrated in Fig. 1 there is no evidence of molecular units corresponding to the crystallization, indicating the amorphous nature of the prepared films.

3.1. Optical properties

The variation of optical absorbance of as-deposited and annealed films of $Te_{46}As_{32}Ge_{10}Si_{12}$ and $Te_{41}As_{37}Ge_{10}Si_{12}$ having different thicknesses (120–400 nm) and different annealing temperatures
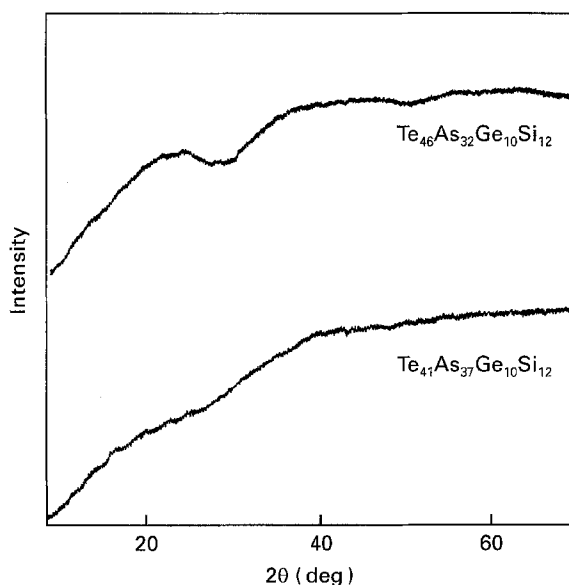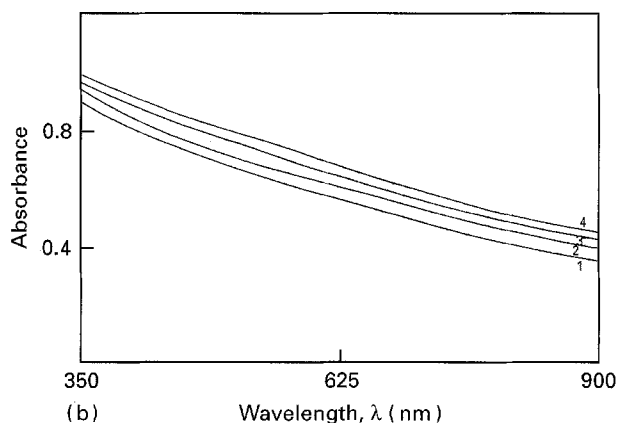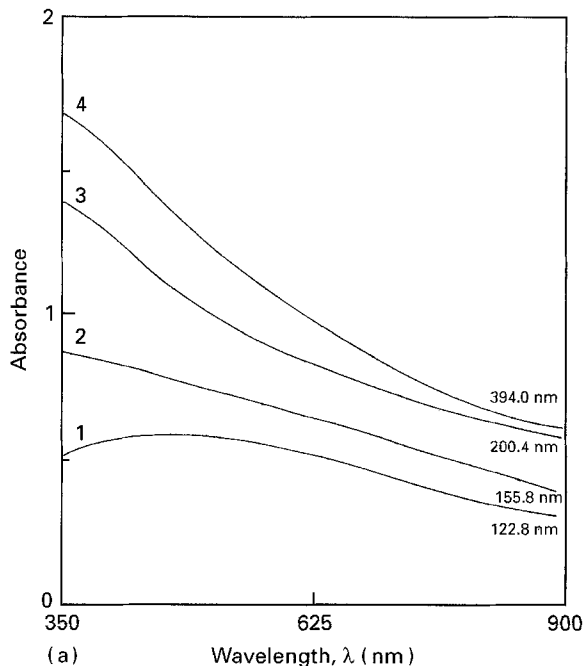
Figure 2 Optical absorption spectra as a function of wavelength: (a) for $Te_{46}As_{32}Ge_{10}Si_{12}$ thin films having different thicknesses, and (b) $Te_{41}As_{37}Ge_{10}Si_{12}$ thin films annealed at different temperatures (thickness 299.5 nm). (1) 298 K, (2) 323 K, (3) 373 K, (4) 423 K.

ranging from 298 to 423 K as a function of photon energy are shown in Fig. 2a, b. It can be seen that the position of the fundamental absorption edge shifts to the higher wavelength region with increasing thicknesses and annealing temperature; beside that there is no sharp absorption edge and this is a characteristic of the glassy state.

The usual method for determining the value of E_g involves plotting a graph of $(\alpha h\omega)^S$ versus photon energy, $h\omega$, according to Equation 2. If an appropriate value of $M^{-1}(s)$ is used to linearize the graph,

Figure 1 X-ray diffraction patterns of the glass samples $Te_{41}As_{37}Ge_{10}Si_{12}$ and $Te_{46}As_{32}Ge_{10}Si_{12}$ in thin film form.

the value of E_g will be given by intercept on the $h\omega$ axis.

Fig. 3a–e shows $(\alpha h\omega)$ versus $h\omega$ with $M = 1/2, 2/3, 1, 3/2, 2$ for $Te_{46}As_{32}Ge_{10}Si_{12}$ at different thicknesses as a representative example. By comparing the fits for these values of M, one concludes that $M = 1$ was the best. It may be noted that the evaluated value of the

band gap, E_g, depends on the choice of M; this choice indicating the existence of the allowed indirect transition. Fig. 3f illustrates $(\alpha h\omega)$ versus $h\omega$ for $Te_{41}As_{37}Ge_{10}Si_{12}$ of 299.5 nm thickness at different temperatures. From Fig. 3a, e, f one observes that the values of the optical band gaps, E_g, coincide with many workers [3,7,8]. Different authors [15–19]
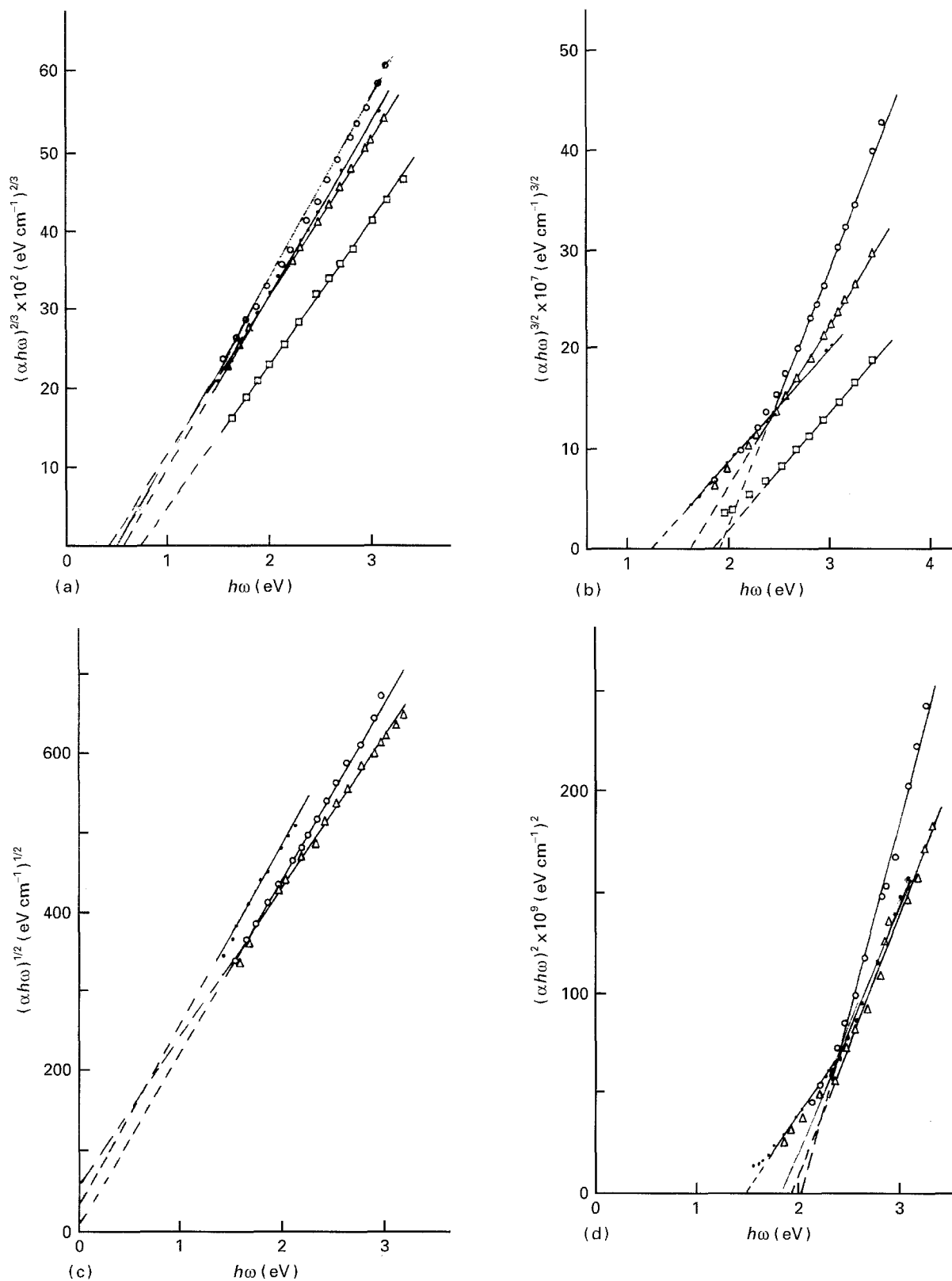

Figure 3 $(\alpha h\omega)^S$ as a function of photon energy for: (a)–(e) $Te_{46}As_{32}Ge_{10}Si_{12}$ having different thicknesses, d, and (f) for annealed films of $Te_{41}As_{37}Ge_{10}Si_{12}$. $d = (\bullet)$ 122.8 nm, $(\triangle)$ 155.8 nm, $(\bigcirc)$ 200.4 nm, $(\square)$ 394.0 nm.

Figure 3 Continued.

materials [20]. It is known that unsaturated bonds are produced as a result of an insufficient number of atoms deposited in the amorphous films [21].

The unsaturated bonds are responsible for the formation of some defects in the films, which produce localized states in amorphous solids [22]; the extent of these localized states may be quantified by analysis of the absorption edge.

As the molar percentage of As increased, the optical energy gap increased from 1.34 eV for As_{32} to 1.48 eV for As_{37}. Increasing the molar percentage of As caused an increase in the disorder of the system. This caused the defect or localized states to extend further into the band. This result is attributed to the nature of the chemical bonding in these systems.

Fig. 4a, b demonstrates that the exponential behaviour of the absorption edge, via Equation 1, is satisfied. The values of E_e obtained for different film thicknesses and different annealing temperatures for the compositions under investigation are shown in Tables II and III. It may be noted that the values of E_e are very much larger than 0.05 eV and vary with composition. The band width of the localized states increased from 0.909 eV for $Te_{41}As_{37}Ge_{10}Si_{12}$ to 1.40 eV for $Te_{46}As_{32}Ge_{10}Si_{12}$.

Tauc's model based on electronic transitions between localized states in the band edge tails may well be valid in these materials; an unambiguous interpretation of the nature of the absorption edge requires that the effect of temperature must be considered.

TABLE II The optical properties of $Te_{46-x}As_{32+x}Ge_{10}Si_{12}$ films having different thicknesses

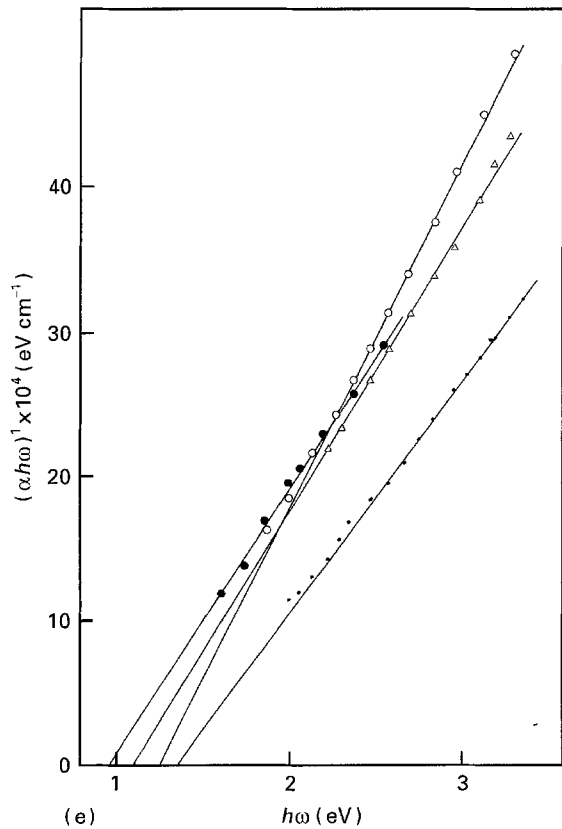| Composition	Thickness (nm)	E_g (eV)	B $(10^5\,cm^{-1}\,eV^{-1})$	E_e (eV)
$Te_{46}As_{32}Ge_{10}Si_{12}$	394.0	1.340	2.08	1.400
	200.4	1.240	1.32	1.800
	155.8	1.100	2.00	1.140
	122.8	0.970	1.92	1.370
$Te_{41}As_{37}Ge_{10}Si_{12}$	299.5	1.480	1.82	0.909
	203.4	1.392		1.149

have suggested different values of M for different glasses. Davis and Mott [13] obtained $M = 2$ for most amorphous semiconductors. However, for more complicated materials, Fagen and Fritzche [19] obtained $M = 3$, and $M = 1$ was obtained by others [18].

The band gaps obtained from $(\alpha h\omega)$ versus $h\omega$ plots of as-deposited and annealed $Te_{46-x}As_{32+x}Ge_{10}Si_{12}$ ($x = 0$ and 5) thin films as in Fig. 3a–f, and the evaluated E_g and B are listed in Tables II and III.

It is seen from these tables that the optical gap decreases with increasing annealing temperature and also increases with increasing thickness of $Te_{46}As_{32}Ge_{10}Si_{12}$ films. This variation may be explained by the presence of defects in amorphous

TABLE III Values of E_g and E_e as a function of temperature of heat treatment of $Te_{46-x}As_{32+x}Ge_{10}Si_{12}$ thin films

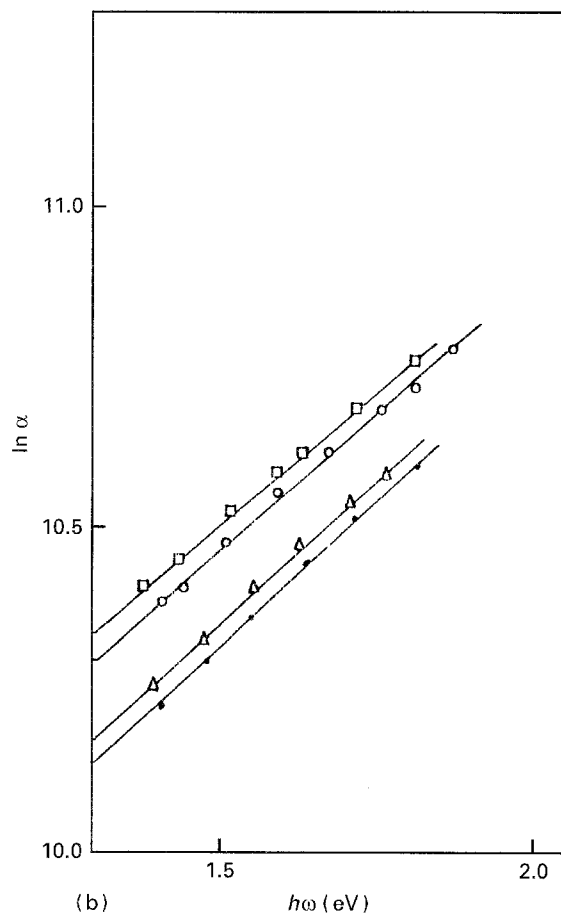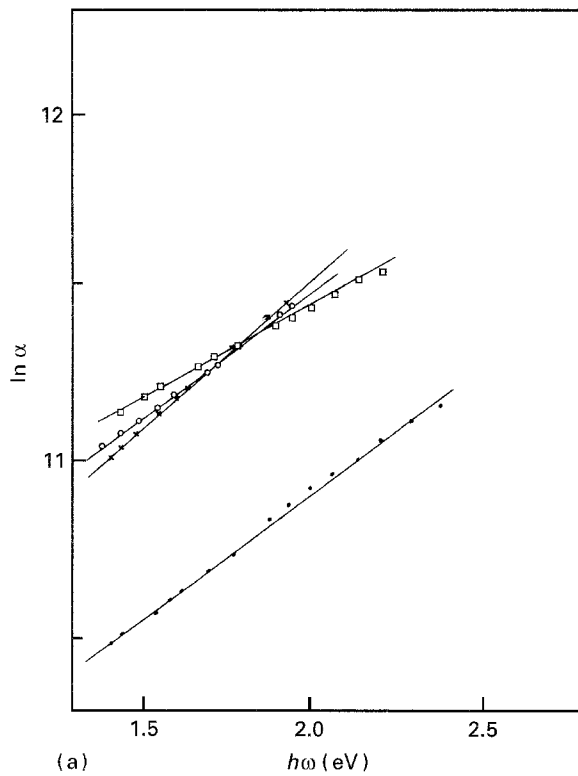| Composition	Temperature (K)	E_g (eV)	E_e (eV)
$Te_{41}As_{37}Ge_{10}Si_{12}$	291	1.48	0.909
(thickness 299.5 nm)	323	1.22	0.865
	373	1.06	0.935
	423	0.99	1.111
$Te_{46}As_{32}Ge_{10}Si_{12}$	293	1.34	1.400
(thickness 394.0 nm)	323	1.27	1.330
	373	1.20	1.300
	423	1.11	1.133

Figure 4 a, b Data of Fig. 2a, b replotted in accordance with the Urbach law. $d = $ (○) 122.8 nm, (×) 155.8 nm, (□) 200.4 nm, (●) 394.0 nm.

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