Photoinduced interdiffusion in nanolayered Se/As$_2$S$_3$ films: Optical and x-ray photoelectron spectroscopic studies

K. V. Adarsh and K. S. Sangunni
Department of Physics, Indian Institute of Science, Bangalore, 560012, India

T. Shripathi
UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Dindore 452 017, India

S. Kokenyesi
Department of Experimental Physics, University of Debrecen, Bem ter 18/a, Debrecen 4026, Hungary

M. Shipljak
Uzhgorod National University, Pidhirna 46, Uzhgorod 88000, Ukraine

(Received 13 November 2005; accepted 6 March 2006; published online 11 May 2006)

Photoinduced interdiffusion was observed above band gap light in nanolayered Se/As$_2$S$_3$ films. It is discussed in terms of the optical parameters such as band gap, Urbach edge ($E_u$) [F. Urbach, Phys. Rev. 92, 1324 (1953)], and $B^{1/2}$ (Tauc’s parameter) [J. Tauc et al., Phys. Status Solidi 15, 627 (1966)]. Experimental data of $B^{1/2}$ and $E_u$ for as-prepared samples do not show clear correlation implied by the Mott-Davis model [N. F. Mott and E. A. Davis, Electronic Process in Non-crystalline Materials (Clarendon, Oxford 1979), p. 287]. It is also shown that the optical parameters can be changed with a change in the Se sublayer thickness. Variations of these optical parameters as a function of modulation period and photoinduced interdiffusion were discussed in terms of the quantum confinement effect and changes in the valence and conduction bands. We proposed a model to explain the mechanism of Se diffusion in As$_2$S$_3$, which suggests that diffusion takes place through the wrong bonds. X-ray photoelectron spectroscopy (XPS) is used to investigate the chemical alternations in the bonding. The proposed model was supported by the XPS data. © 2006 American Institute of Physics. [DOI: 10.1063/1.2193061]

INTRODUCTION

Availability of amorphous semiconductors in the form of high quality multilayers provides potential applications in the field of micro- and optoelectronics.1,2 Among amorphous multilayers (AMLs) chalcogenide multilayers are attractive because of the prominent photoinduced effects. Studies in chalcogenide AML have been directed towards two phenomena. One is photoinduced diffusion in short period multilayer systems, which finds potential applications in holographic recording and fabrication of phase gratings.2,3 The other is photodarkening or bleaching,4–8 which is also known in thick films.6,9 Studies on nanostructured chalcogenides are still at the infant stage. Although the misfit problems in AML are because of the prominent photoinduced effects. Studies in chalcogenide AML have been directed towards two phenomena. One is photoinduced diffusion in short period multilayer systems, which finds potential applications in holographic recording and fabrication of phase gratings.2,3 The other is photodarkening or bleaching,4–8 which is also known in thick films.6,9 Studies on nanostructured chalcogenides are still at the infant stage. Although the misfit problems in AML are

...
diation, respectively. The diffusional intermixing will affect several parameters of the multilayer, i.e., layer thickness, refractive index, optical band gap, and photoluminescence.\textsuperscript{12-14,16} Reported results showed that there is a change in optical absorption edge, layer thickness, photoluminescence (PL) intensity, PL width, conductivity, and photocconductivity.\textsuperscript{12,14} These results indicate that light- and thermo-stimulated interdiffusion effects are rather similar. The changes in these properties are explained based on the formation of ternary solid solution due to interdiffusion.

The remarkable difference in the photodiffusion in Ag/As–S (Ref. 17) multilayers (MLs) and Se/As\textsubscript{2}S\textsubscript{3} MLs (Ref. 18) are that Ag can easily diffuse into a depth of 1 \( \mu \text{m} \), but for Se this depth has been estimated to be less than 100 Å. But the process by which Se diffuses into As\textsubscript{2}S\textsubscript{3} is still unclear. The difference in diffusion length may be due to ionized silver atoms migrating electrically. Since Se has chainlike molecular structures, photoinduced breakage of the molecules into isolated single atoms may occur with difficulty. So, Tanaka \textit{et al.} suggested that neutral Se fragments, which could be produced by illumination, thermally diffuse into the neighboring amorphous regions.\textsuperscript{19} In this article, interdiffusion in Se/As\textsubscript{2}S\textsubscript{3} multilayered samples are studied by optical absorption and x-ray photoelectron spectroscopy (XPS). Raman scattering and infrared spectroscopy techniques were used to study the interdiffusion, but the results were not satisfactory with regard to the intermixing.\textsuperscript{12} The characteristic spectra of components in the multilayer and those of the mixed layer were rather similar. In order to understand the diffusion mechanism of Se into As\textsubscript{2}S\textsubscript{3} we mainly used the Tauc parameter (\( B^{1/2} \)) and Urbach energy. The main reason for using the above parameters is that they give information about the distribution of electronic states in the absorption region. XPS is used to analyze the new bonds formed between the components due to interdiffusion. XPS is a useful surface analytical technique to study the chemical state and local environment of an atom.\textsuperscript{9,20} The chemical bonding is often realized through correlation with chemical shifts in XPS binding energies of the corresponding elements. The effective optical band gap of the samples was determined using the equation

\[ a h \nu = B (\nu - E_g)^2, \]

where \( a \), \( h \), \( \nu \), \( E_g \), and \( B \) are the absorption coefficient, Plank's constant, frequency, optical band gap, and a constant (Tauc parameter), respectively.\textsuperscript{21} The constant \( B \) includes information on the convolution of the valence band and conduction band states and on the matrix element of optical transitions, which reflects not only the relaxed \( k \) selection rule but also the disorder induced spatial correlation of optical transitions between the valence band and conduction band.\textsuperscript{21} Moreover, \( B \) is highly dependent on the character of the bonding. At the energy levels where the Tauc model is used (for photon energies corresponding to \( a > 10^4 \)), the joint density of states does not include tail states. The information at the band tails were obtained from the Urbach edge. The origin of the Urbach edge is still unclear, but two general mechanisms may be responsible: either the exponential dependence of \( a \) (absorption coefficient) arises from an exponential energy dependence of the valence and conduction band densities at the band edges (neglecting matrix element effects) or a universal absorption mechanism exists, which gives rise to the exponential behavior of \( a \), e.g., the field-broadened exciton model of Dow and Redfield.\textsuperscript{22} Abel and Yoyozawa,\textsuperscript{23} and Soukoulis \textit{et al.}\textsuperscript{24} Theoretically it has been shown that exponential band tails can result from potential fluctuations associated with structural disorder.\textsuperscript{24} Although there is experimental evidence in the case of a-Si:H that the magnitude of the \( E_g \) (Urbach energy) is determined by the degree of disorder, that of chalcogenide is not very clear.

**EXPERIMENTAL PROCEDURES**

Se/As\textsubscript{2}S\textsubscript{3}-type ML1 (sublayer thickness of a-Se and As\textsubscript{2}S\textsubscript{3} are 3–4 and 11–12 nm) and ML2 (a-Se: 1–2 nm, As\textsubscript{2}S\textsubscript{3}: 11–12 nm) were prepared by a cyclic thermal evaporation technique from bulk (powdered) a-Se and As\textsubscript{2}S\textsubscript{3}. Deposition rates were 2–10 nm/s in a vacuum of \( 5 \times 10^{-4} \) Pa. Periodicity was monitored by the low angle x-ray diffraction method.\textsuperscript{5} To study photostimulated effects we irradiated the as-prepared samples with a diode pumped solid state laser of wavelength 532 nm and a power density of 1 \( \text{W/cm}^2 \) up to 40 min at room temperature. The UV-visible-IR transmission spectrum was measured in the wavelength range from 400 to 1200 nm. Surface chemistry of the samples was studied by using electron spectroscopy for chemical analysis (ESCA) at a vacuum of \( \sim 10^{-9} \) Torr. A monochromatic Al K\( \alpha \) x-ray source (\( h\nu = 1487 \) eV) was used for the analysis. For insulators such as glasses, the charging effect can change the binding energy (BE) of the electrons from sample to sample. So the measurement of the absolute BE of electrons from a specified energy level is not reliable. The C 1s line from either adventitious carbon or intentionally added graphite powder on the surface has been widely used for charge referencing.\textsuperscript{25,26} For this study, the adventitious carbon was used as a reference and the BE of the reference C 1s line was set as 284.6 eV. For each sample, a calibration factor was calculated from the difference between the measured C 1s BE and the reference value 284.6 eV.\textsuperscript{27} The original BE data were corrected according to the calibration factor.

**RESULTS AND DISCUSSIONS**

Photoinduced interdiffusion was observed with above band gap light (2.37 eV). The optical absorption edge was measured and the results were interpreted based on the model of effective optical media.\textsuperscript{12,13} According to this model, narrow band gap “well” layers determine the absorption and the contribution from the wide band gap “barrier” layers is small. The effective optical band gap of our samples was determined using the equation

\[ (a h \nu)^{1/2} = B^{1/2} (h \nu - E_g). \]

Equation (5) is valid for a number of amorphous materials in the spectral region of large \( \alpha \) (10\textsuperscript{4} < \( \alpha < 10^5 \)), i.e., Tauc region.\textsuperscript{12,28} Se well layers determine the optical band gap in our AMLs and the band gap values are given in Table I. The optical band gap of ML1 is less than the optical band gap of...
TABLE I. Slope of the Urbach edge and optical band gap of the samples. Here the slope of the Urbach edge is at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Urbach energy (meV) ($E_u$)</th>
<th>Optical band gap (eV)</th>
<th>$B^{1/2}$ (cm$^{-1/2}$ eV$^{-1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML1</td>
<td>165±1</td>
<td>1.90±0.002</td>
<td>294±1</td>
</tr>
<tr>
<td>IML1</td>
<td>160±1</td>
<td>2.06±0.002</td>
<td>329±2</td>
</tr>
<tr>
<td>ML2</td>
<td>205±3</td>
<td>2.19±0.002</td>
<td>343±2</td>
</tr>
<tr>
<td>IML2</td>
<td>149±2</td>
<td>2.24±0.002</td>
<td>478±2</td>
</tr>
</tbody>
</table>

ML2. This blueshift in optical band gap is due to the quantum confinement effect, which was known in amorphous superlattices. The optical band gap of irradiated samples clearly shows a blueshift compared to the corresponding as-prepared samples. The blueshift can be explained by the creation of new bonds between the components due to interdiffusion and formation of continuous rows of ternary solid solutions.

The parameter $B^{1/2}$ of the Tauc region [Eq. (5)] depends on the product of the oscillator strength of the optical transition, the deformation potential, and the mean deviation of the atomic coordinates. The values of $B^{1/2}$ of the irradiated and as-prepared films are listed in Table I. The $B^{1/2}$ value of ML2 is greater than that of ML1. This increase in the $B^{1/2}$ value may be due to the changes in the electronic states because of the well-known quantum confinement effects. A decrease in Se sublayer thickness will result in an increase in structural disorder connected with possible bond angle distribution change. Based on the experiments in a-Ge–H, a-Si–H, a-SiN, and a-GeN based alloys, Zanatta and Chambouleyron proved that $B^{1/2}$ is sensitive to topological disorder only when electronic structural changes occur. So we assume that the change in structural disorder will not affect the $B^{1/2}$ values. $B^{1/2}$ values of the irradiated samples are much greater than that of the as-prepared samples. During photodiffusion the density of Se–Se bonds decreases and changes in conduction and valence band states may occur. As a consequence, the absorption edge becomes steeper and $B^{1/2}$ presents a high value, similar to the results observed by J. Robertson in a-Si and a-Ge alloys, a decreasing $B^{1/2}$ has been observed with decrease in the Si–Si and Ge–Ge bond density. Before irradiation, the Se layers determine the $B^{1/2}$ values. But after irradiation, it is determined by the solid solution of As$_2$S$_3$–Se having Se–S or Se–As bonds.

In the exponential part of the absorption edge (where $a<10^3$), the absorption coefficient is governed by the so-called Urbach rule:

$$\alpha(h\nu) = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right),$$

where the Urbach energy $E_u$ characterizes the slope of this region. Plotting the dependence of log($\alpha$) on photon energy will give a straight line. The calculated value of $E_u$, the inverse of the slope of the straight line, gives the width of the tails of the localized states into the gap at band edges. It is known that the Urbach edge is a useful parameter to evaluate the degree of disorder. Although there is experimental evidence in the case of a-Si:H that the magnitude of $E_u$ is determined by the degree of disorder, that of the chalcogenides is not very clear. Tanaka et al. have reported that the slope of the Urbach absorption edge does not change as a function of the quench temperature, even though the extended x-ray absorption fine structure (EXAFS) measurements have indicated structural disorder. These contradictory results are explained in terms of the lone pair nature of the top of the valence band, i.e., tailing of the valence band is mainly responsible for the Urbach edge. Intramolecular fluctuations (bond length and bond angle) have little effect. The values of $E_u$ of the irradiated and as-prepared films are listed in Table I. The Urbach energy $E_u$ of ML2 is much greater than that of ML1. The increase in $E_u$ may be due to the quantum confinement effects that induce an increase in band gap, which may lead to an increase in the degree of tailing. A decrease in Se sublayer thickness results in a small increase in structural disorder connected with a possible bond angle distribution change, similar to that of a-Si: H/ a-SiN$_x$ superlattices. But this has very little effect on the change in the Urbach edge. A decrease in Urbach energy $E_u$ is observed after photodiffusion. During photodiffusion the density of Se–Se bonds decreases and changes in conduction and valence band states may occur.

We tried to associate the $B^{1/2}$ with the Urbach energy based on the model proposed by Mott and Davis in which

$$B \propto \frac{[N(E_0)]^2}{(n_0\Delta E_0)},$$

where $N(E_0)$, $n_0$, and $\Delta E_0$ are the density of states at the conduction band edge, the index of refraction, and the width of the conduction band tail, respectively. Experimental data of $B^{1/2}$ and $E_u$ for as-prepared samples do not show the clear correlation implied by the above equation, i.e., both $B^{1/2}$ and $E_u$ increase with a decrease in Se thickness. In the case of ML1 and IML1, the $E_u$ does not change much, but the $B^{1/2}$ changes appreciably (Fig. 1). But for ML2 and IML2, both the values change appreciably. The increase in $B^{1/2}$ of the
irradiated samples over the respective as-prepared samples can be explained based on the change in refractive index, changes in the density of states at the conduction band edge, and \( \Delta E_c \). Palyok et al.\(^2\) and Kikineshi et al.\(^15\) found that the refractive index decreases with photodiffusion in Se/As\(_2\)S\(_3\) multilayers. But there are no experimental evidences available for the variation of the other two parameters. The maximum decrease in refractive index is only 4%. In the case of ML1 and IML1 there is only a small change in the Urbach energy (we assume that \( n_0 \) and \( \Delta E_c \) are more or less constant for ML1 and IML1), but the \( B^{1/2} \) changes considerably. From this we infer that the \( N(E_c) \) increases with photodiffusion. Before irradiation, in Se/As\(_2\)S\(_3\) multilayers the valence band and conduction bands are formed by the lone pair electrons of Se and the empty antibonding orbital, but after irradiation it is determined by the solid solution of Se–As\(_2\)S\(_3\). During photodiffusion the density of Se–Se bonds decreases and changes in conduction and valence band states may occur. The higher values of \( B^{1/2} \) and lower values of \( E_c \) of the irradiated samples over the corresponding as-prepared samples clearly indicate that the irradiated samples are more ordered (chemically) than the as-prepared samples, i.e., the removal of homopolar bonds and formation of heteropolar bonds after photodiffusion (Fig. 2).

A typical XPS spectrum of Se/As\(_2\)S\(_3\) multilayer is shown in Fig. 3. Se, As, and S have many photoelectron and Auger peaks (Fig. 4). The detailed information about the BE of all those peaks can be found in Ref. 39. The BE of As 3d and Se 3d of all the samples are listed in Table II. The BE of the Se 3d peak of ML1 and ML2 are at the same energy, i.e., 55.1 eV. Since the BE of elemental Se is 55 eV,\(^{35}\) we assume that this peak is due to the Se–Se bond. In addition to the peak at 55.1 eV, it has a satellite peak at 56.3 eV. This represents the S–Se bond. Because S has a higher electronegativity than Se,\(^{40}\) the BE of Se shifts to higher energy. It is evident that there are Se–Se and S–Se bonds in the as-prepared samples. The BE spectra of As 3d contain two peaks in ML1 and three peaks in ML2 (Fig. 5). The peaks at 42.9 and 45 eV of ML1 and ML2 are due to the As–S bond and Se–Se bond. The peak at 41.8 eV present in ML2, which is absent in ML1, is due to the As–As bond, because the BE of the 3d peak of elemental As is at 41.9 eV. Even though As–As homopolar bonds exist in ML1 and ML2, the possible

![FIG. 2. Tauc plots of optical absorption coefficient \( (\alpha h\nu)^{1/2} \) vs \( h\nu \) for IML2. The experimental spectra are represented by symbols “o,” the solid line represents the theoretical fit.](image)

![FIG. 4. Different photoelectron and Auger peaks (As, S, and Se) between 150–280 eV. The detailed information about these peaks can be obtained from Ref. 33.](image)

![FIG. 3. Typical XPS spectra of ML1.](image)

![TABLE II. XPS core level BE values of As 3d and Se 3d for all the samples.](table)

<table>
<thead>
<tr>
<th>Sample</th>
<th>As (3d) (eV)</th>
<th>Se (3d) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML1</td>
<td>42.9, 45</td>
<td>55.1, 56.3</td>
</tr>
<tr>
<td>IML1</td>
<td>42.1, 42.9, 45</td>
<td>54.3, 55.1, 56.5</td>
</tr>
<tr>
<td>ML2</td>
<td>41.8, 42.9, 45</td>
<td>55.1, 56.3</td>
</tr>
<tr>
<td>IML2</td>
<td>42.9, 45</td>
<td>55.2, 56.5</td>
</tr>
</tbody>
</table>
reason for the absence of this peak in ML1 may be due to the thick Se layer (3–4 nm), which is on top of the As$_2$S$_3$ layer. The XPS signal will come mainly from the top 4–5 nm, i.e., from Se layer and the self-diffused boundary layers. We expect that As–As homopolar bonds exist only in the As$_2$S$_3$ layer and not in the diffused region. Nordman et al.\textsuperscript{41} suggested that irreversible photostuctural changes take place only at the strained sites (regions with homopolar bonds). So we assume that diffusion may take place through the strained sites. Therefore there is a very small probability of having the As–As bonds in the diffused region. Since in ML2 the top Se sublayer thickness is very small (1–2 nm), we will get the XPS signal from both the Se and As$_2$S$_3$ layers.

The BE spectra of As 3$d$ of IML1 and IML2 contain three and two peaks, respectively. The peaks at 42.9 and 45 eV of IML1 and IML2 are due to the As–S and Se–Se bonds, respectively. The peak at 42.1 eV that is present only in IML1 may be due to the As–Se bond. Since Se’s electronegativity is greater than As but less than Se,\textsuperscript{40} the BE of the As–Se bond will lie between the As–As and As–S bonds. So it is evident that during photodiffusion As–Se bonds are formed. The BE spectrum of Se 3$d$ contains three peaks in IML1 and two peaks in IML2 (Fig. 6). Peaks at 55.1 and 56.5 eV are due to Se–Se and S–Se bonds. The peak at 54.3 eV, which is present only in IML1, may be due to the As–Se bond. The As 3$d$ spectra of IML1 shows the As–Se bond formation. The possible reason for the absence of this bond in IML2 may be due to the lower concentration of Se.

If we compare the Se 3$d$ BE of the as-prepared and irradiated samples, we can infer the following. It is clear that during photodiffusion Se is forming bonds with both As and S. As–As bonds are present in the as-prepared samples. These bonds are converted into As–S or As–Se bonds with light irradiation. Earlier studies on unannealed films have shown that the evaporated As$_2$S$_3$ sublayer contains a large number of species such As, As$_4$, S$_2$, AsS$_3$, As$_4$S$_3$, As$_4$S$_4$, As$_2$, etc.\textsuperscript{42} This means that even in a stoichiometric film such as As$_2$S$_3$, where the stoichiometry would only allow As–S bonds, a large number of so-called wrong bonds (As–As, S–S) are present. Spectroscopic studies on unannealed films have shown that irreversible band gap light-induced photostuctural changes are mainly due to the photoinduced As–As bond breaking (As–As being the weakest bond) followed by the phonon-assisted creation of As–S bonds.\textsuperscript{41}

\[
2\text{As}_3^0 + \text{S}_2^0 + h\nu \leftrightarrow \text{As}_2^+ + \text{As}_2^- + \text{S}_2^0 + \text{phonon}
\]
\[
\leftrightarrow \text{As}_3^0 + \text{S}_3^+ + \text{As}_2^-.
\]

Here the superscript indices designate the electric charge of atoms, and the subscript indices their coordination number. After that phonon-assisted As–S bond formation takes place by using the lone pair \(\pi\) electrons\textsuperscript{43,44} of S$_2^0$. We expect all these defects in our As$_2$S$_3$ sublayer. XPS data of our samples show that during light irradiation these defects are removed, i.e., As atoms will form As–S or As–Se and S forms S–Se or S–As bonds (heteropolar bonds replace homopolar bonds). In our AMLs the above reaction takes place at the As$_2$S$_3$ rich region. But at the interfaces, in addition to the above reaction, the wrong sulphur bonds easily react with Se forming S–Se bonds. If the Se concentration in the multilayer is very high, Se can react to As–As wrong bonds and the reaction is as follows:

\[
2\text{As}_3^0 + \text{Se}_2^0 + h\nu \leftrightarrow \text{As}_2^+ + \text{As}_2^- + \text{Se}_2^0 + \text{phonon}
\]
\[
\leftrightarrow \text{As}_3^0 + \text{Se}_3^+ + \text{As}_2^-.
\]

The As–Se bond was observed in IML1, where the Se concentration is very high. If we compare the XPS data with the optical parameters of the as-prepared and irradiated samples, we will get a detailed picture about the chemical ordering (heteropolar bonds replace homopolar bonds). An increase in \(B_{1/2}\) and a decrease in the Urbach energy were observed with photodiffusion. After photodiffusion the samples become chemically ordered.

FIG. 5. As 3$d$ peak of IML2.

FIG. 6. Se 3$d$ peak of IML2.
Based on the above experimental data, we propose a simple model to explain the mechanism of Se diffusion in As$_2$S$_3$. The as-prepared As$_2$S$_3$ sublayer contains a large number of S–S and As–As wrong bonds. We assume that diffusion takes place through the reaction of Se$_0$ with the wrong S–S ($S_2^0$) bonds and As–As bonds. The Se$_2^0$/S$_2^0$ defects are known as annihilating defects (ADs). It should be noted that diffusion takes place mainly in strained sites (where wrong bonds are close to Se$_2^0$ sites). During light irradiation, a decrease in photoinduced viscosity leads to a mechanical stress gradient and thus enables the directed motion of ADs. These cycles continue until the local stresses are released and this dynamic state is comparable to that near the glass transition temperature. It is clear that the illuminated material will flow under uniaxial stress since the local bond changes and atomic motions tend to decrease the local strain energy. These cycles continue until local stresses are released and the concentration of As–S, As–Se, and S–Se bonds is large enough to increase the viscosity and prevent the AD diffusion. This atomic diffusion occurs through the lone pair electrons of Se and S [refer to Eqs. (8) and (9)]. The cumulative effect of local configuration changes produces changes in optical and electrical properties of the glass. If we compare the As and Se 3d peaks of IML1 and IML2, we can clearly see that Se is forming bonds with both As and S after irradiation, which supports the above discussion.

IV. CONCLUSIONS

We found that the Urbach edge ($E_U$) and $B^{1/2}$ (Tauc’s parameter) change with changes in Se sublayer thickness and also with photodiffusion. Experimental data of $B^{1/2}$ and $E_U$ for as-prepared samples do not show the clear correlation implied by the Mott-Davis model. The increase found in the $B^{1/2}$ after photodiffusion is coherent with the corresponding decrease of the Urbach energy. This fact is discussed in terms of the structural changes induced by the photoinduced interdiffusion, i.e., creation of new bonds between components, which modifies the conduction and valence bands. XPS analysis shows that, during photodiffusion, homopolar bonds are replaced by heteropolar bonds, i.e., the irradiated samples are chemically ordered than the corresponding as-prepared samples. We proposed a model to describe the photodiffusion, which suggests that diffusion takes place through the wrong bonds.

ACKNOWLEDGMENTS

One of the authors (K.V.A.) thanks CSIR for financial support. The authors thank the bilateral Indo-Hungarian R&D and Hungarian OTKA (N T046758) grants. The authors also thank the Inter-University Consortium for DAE facilities for XPS measurements.

32. F. Urbach, Phys. Rev. 92, 1324 (1953).