THE EFFECT OF THE ADDITION OF Ag AND AgI ON THE DENSITY OF DEFECT STATES IN a-Se

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The optical and the electrical properties of amorphous selenium, a-Se, and amorphous selenium containing silver, $a\text{-}Se_{100-x}Ag_x$, with $x<5$, or silver iodine, $Se_{100-x}(AgI)_x$ and $Se_{100-2x}Ag_xI_x$, with $x \leq 15$, were studied in order to determine the influence of each additive on the density of defect states in a-Se. Our results show that the addition of Ag or of AgI does not induce any impurity bands in the gap of a-Se. In some of the $a\text{-}Se_{1-x}Ag_x$ compositions an additional sharp peak appears at 1.9 eV. This peak has been related to accidental oxygen contamination of the particular samples and not to Ag related states. The optical gap decreases by 0.1eV with the addition of 5 at. % Ag or with 15 at. % AgI into the a-Se matrix. The spectral dependence of the photoconductivity shows a peak at 2.4 eV, which is attributed to band-to-band optical transitions. The spectral dependence of the absorption coefficient is compared to the dc photoconductivity per incident photon flux.

1. Introduction

The addition of different elements into the chalcogenide glasses in order to modify their opto-electronic properties was popular even from the late 60s. Different ways of preparation are reported in which silver is added either during the preparation of the amorphous alloys [1-3] or with the photo-dissolution technique [4-6]. Silver-chalcogenide glasses have attracted much interest in glass science and technology either for their potential applications in holographic recording and photolithography, or as fast-ion-conducting glasses, in solid-state batteries. In glasses with high concentrations of Ag ($>15\%$), the electrical conductivity is governed by the Ag^+ ionic conduction [5], while for small percentages of Ag ($x<5$) hole conductivity is dominated.

In the present work the absorption coefficient and the photoconductivity of compositions with low concentration of Ag ($<5\%$) are measured. It was found that higher percentages of Ag kill the photoconductivity of a-Se. Compositions with several concentrations of silver and iodine were also investigated.

2. Experimental

The samples were prepared in Sofia, either in the bulk form (i.e. melt quenched from the liquid state) or/and as thin films prepared by flash evaporation of the corresponding bulk material. Several preparations of samples with the same composition were carried out. The samples were placed in a cryostat under vacuum and in the dark for a few days before measuring. All measurements were made at room temperature. At higher temperatures crystallization or phase separation take place. Electrical contacts, with the gap geometry, were painted or evaporated. Ohmic behaviour, in the dark and under illumination, was observed up to 60 V in a-Se samples and up to 20 V, for the alloys. The I-V characteristics of the thin films particularly with high concentrations of Ag were mostly non-

linear, as the Ag is expected to reduce the energy barrier between the semiconductor and the contact. In some cases it was found, that the contacts were shorted after the application of a high electric field and in some cases, under illumination, a photocurrent could be measured even when the applied voltage on the sample was zero [5]. These contact-related problems made us to concentrate on materials with x≤5.

A 75 W halogen lamp and a Jobin-Yvon 0.25m monochromator were used to illuminate the samples with monochromatic light in the range of 460 nm to 1400 nm. In order to calculate the absorption coefficient, the intensity of the incident, I_0, and the transmitted light, I, through the sample was measured with a silicon or a germanium detector at the shorter and at the longer wavelengths, respectively. The measurements were repeated to more than one sample from the same or from different preparations.

3. Results

The energy variation of the absorption coefficient gives an indication of the distribution of the density of states at the band edge [8]. The absorption coefficient was calculated from the relation: $\alpha=1/d \, [\ln (1-R)^2 / T]$, when the thickness, d, the reflectivity, R and the transmission, T, are known. In order to have the complete spectral variation of the absorption coefficient, bulk and thin films, of similar compositions, were measured. The absorption of the bulk material gives information about the defect density in the centre of the energy gap, while that of the thin films, for the shape of the Urbach tail. For simplicity in the following we will take as optical gap, E_{o4}, the energy at $\alpha=2\times10^4$ cm^{-1}.
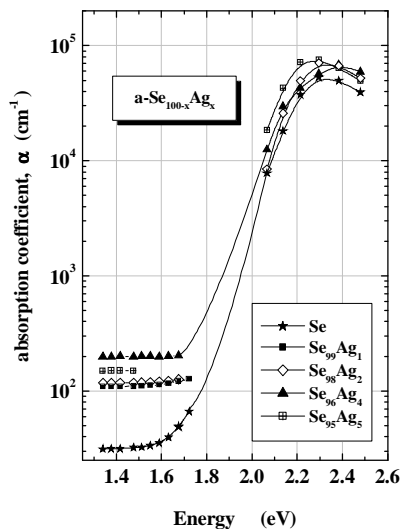

Fig. 1. The energy variation of the absorption coefficient of a-Se$_{100-x}$Ag$_x$. The line is a guide to the eye.

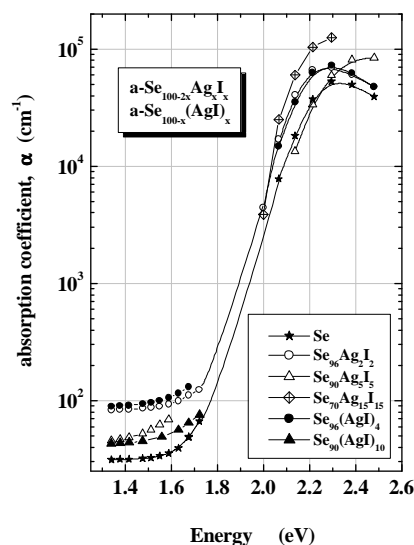Fig. 2. The absorption coefficient of a-Se$_{100-2x}$Ag$_x$I$_x$ and a-Se$_{100-x}$(AgI)$_x$. The line is a guide to the eye.

In Fig. 1 the absorption coefficient of bulk samples and thin films of a-Se$_{100-x}$Ag$_x$ with x=0, 1, 2, 4 and 5 are plotted. The large thickness (d~1 mm) of the bulk samples allows the very low absorption region, E<1.8 eV, to be measured. In this region the absorption coefficient is independent of the photon energy. In contrast, the thickness of the thin films (d~600-700 nm) permits to measure the absorption at the high-energy region and the determination of the energy gap. The set in of the interference fringes and the lack of films with different thicknesses, do not allowed us to extent our measurements to lower energies. The line that connects the experimental data of the bulk and the film of the same composition is a guide to the eye. From Fig. 1, we can see that the addition of Ag has a

small effect on the optical gap that decreases gradually by ~0.1 eV up to the 5% Ag. The addition of <2 at % Ag increases the mid-gap absorption by a factor of 4, a further increase by a factor of 2 is observed when x=5. Usually the mid-gap absorption is attributed to the density of defect sites of the material [8]. We believe that the observed increase of the mid-gap absorption in the present results could not be attributed solely to the increase of the disorder induced by the additives but it could also be related to some additional experimental factors that will be analysed below and could be wrongly interpreted as an increase in the midgap absorption. The brittleness of the alloys increased with the addition of Ag, and, as a result, the samples break easily during polishing and very small bulk samples must to be used. In some cases, when a sample was polished further, the midgap absorption found to be higher, indicating that the number of cracks and voids inside the sample increase and a small percent of the light will be scattered. As the scattered light is not transmitted through the sample is considered as absorbed, resulting in a (false) increase of the mid-gap absorption.

The optical absorption of bulk and thin films of a-$Se_{100-2x}Ag_xI_x$, with x = 0, 2, 4, 5, 10, 15 and a-$Se_{100-x}(AgI)_x$, with x=4, 5 were measured. For clarity, in Fig. 2 only some of the above compositions are shown. The addition of 2% of silver and 2% iodine (as separate elements) or of 4 % of AgI (added as a compound) to the selenium during the material preparation, causes the mid-gap absorption to increase by a factor of 3, while with the further increase of Ag and I, the mid-gap absorption decreases. The optical gap follows a similar variation, showing a minimum at the composition x=2 and then decreases gradually up to x=5. The variation of the optical gap, E_{o4}, as a function of the Ag or the AgI content is shown in Fig. 3. The results for high concentration of AgI (x≥5), are in fair agreement with previous reported data [7]. The very shallow minimum that observed at 2% of AgI is believed to be real as the measurements were repeated to more than one sample. The original decrease of the optical gap, associated with an increase in the activation energy, has been reported in other cases [9].
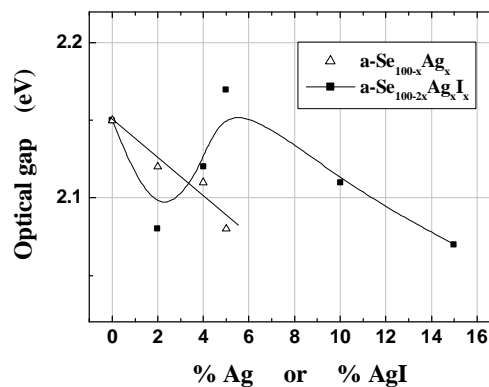

Fig. 3. The compositional variation of the optical gap, E_{o4}, of a-$Se_{100-x}Ag_x$ and $Se_{100-2x}Ag_xI_x$.
The lines are guide to the eye.

The dc dark conductivity was measured below room temperature. Its magnitude increased by one order of magnitude with the addition of up to 4 at. % Ag. For the a-Se films, the dc photoconductivity is about one order of magnitude higher than the dark conductivity and decreases by less than a factor of two with the addition of 5 at. % Ag. Compositions with higher concentrations of Ag or AgI show no photoconductivity. The spectral dependence of the dc photoconductivity of all the compositions that were studied, shows the main characteristic peak of the chalcogenide glasses [1, 2], which has been attributed to band-to-band optical transitions.

In Fig. 4 are plotted the spectral dependence of the normalized photoconductivity per incident photon, or the photosensitivity, of bulk samples with compositions a-$Se_{100-x}Ag_x$ with x=0, 1, 4 and 5 and of a-$Se_{96}(AgI)_4$. In the same graph it is, also, plotted the quantum efficiency of photogeneration of holes, η, of a-Se, from ref. [10]. It is obvious that the photosensitivity follows the spectral variation of the quantum efficiency and not that of the absorption coefficient. The bulk a-Se shows a levelling off at E<1.9 eV, while the samples with 1 and 5 at % Ag show a strong peak at 1.9 eV, which is not

present in the composition with 4 at % Ag. This feature is probably related with accidental oxygen contamination [11] of those samples during preparation.

In Fig. 5 are plotted the spectrum dependence of the normalised photoconductivity per incident photon, of thin films with compositions a-Se$_{100-x}$Ag$_x$ with x = 0, 2, 4 and 5. The optical absorption of a-Se is also plotted for comparison. The small features that were observed at very low photon energies (at E<1.9 eV) are due to interference fringes. The bulk material used for the flash evaporation of the film with x = 5 is the same as that of Fig. 4. Thus the kink at 2.0 eV observed in the film is probably related to the peak at 1.9 eV evidenced in the bulk material (Fig. 4). In contrast, the bulk material used for the flash evaporation of the films with x = 0 is different from that of Fig. 4. The lack of the 2.0 eV feature on this film supports the argument that they are not intrinsic to the material but is related to accidental contamination.
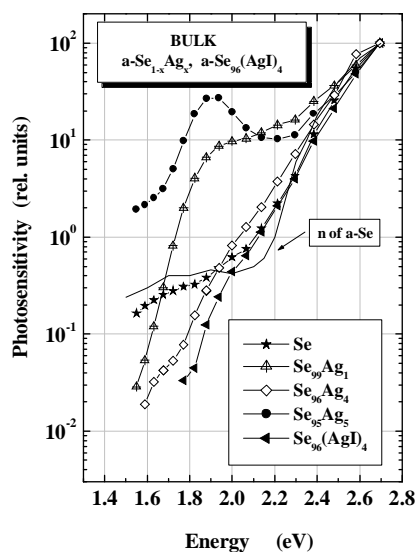

Fig. 4. The spectral variation of the photosensitivity of bulk a-Se$_{100-x}$Ag$_x$, with x=0, 1, 4, 5 and a-Se$_{96}$(AgI)$_4$. The quantum efficiency, η, of a-Se [10] is also plotted.
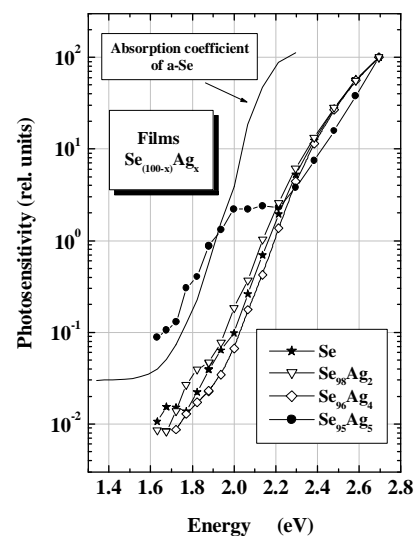
Fig. 5. The spectral variation of the photosensitivity of flash evaporated films of a-Se$_{100-x}$Ag$_x$, with x=0, 2, 4 and 5. The absorption coefficient of a-Se is also plotted.

4. Discussion

The general feature of our results is that the addition of Ag or AgI to a-Se results in the decrease of the optical gap and the increase of the midgap states. No defect states, due to the additives was found to be induced into the energy gap. Our results could be explained as follow: It has been proposed [3] that Ag is introduced as three or four fold-coordinated element and cross-links the Se chains, while the iodine (I) acts as a chain terminator. It has also been argued [6] that the energy of the Ag 4d bands lies near the top of the valance band formed by the lone pairs of the Se atoms. The two bands interact forming d-p bonding states in the upper valence region. This energy band picture could cause the observed decrease of the optical gap of a-Se with the addition of Ag or AgI.

Comparing Figs 1 & 2, it could argue that alloys with similar concentrations of Ag cause a smaller increase of the mid-gap absorption in case when iodine is present. In general, the addition of a third element in a sample matrix increases the structural disorder but in this case, it could be suggested that the addition of iodine reduces the number of deep defects created by the addition of Ag. In practice we noticed that the compositions with AgI were less brittle than the ones containing only Ag, indicating that the compactness of the last compositions increases.

The spectral dependence of the photoconductivity of bulk a-Se (Fig. 4) and of a-Se with 1 and 5% Ag demonstrates the existence of a large distribution of deep states in the gap (E<2.0 eV). This

feature do not exist for a-Se with 2% Ag, and this fact raises the question regarding the intrinsic character of this feature. Indeed, a similar feature appears in the a-Se with 5% Ag film (Fig. 5) prepared from the evaporation of the same bulk material as that related to Fig. 4, but it does not exist in the evaporated a-Se film that were prepared by the evaporation of a different bulk material. These states were attributed to accidental oxygen contamination during preparation of some samples. It is known [8] that pure a-Se is very sensitive to contamination. It has been shown that only few hundred of ppm of oxygen or chlorine increase the dc conductivity of a-Se by several orders of magnitude and induce a sharp peak of defect states deep in the energy gap [11]. These data show that the effect of Ag or AgI is limited only to the small decrease of the energy gap of a-Se, in agreement with the energy diagram shown in [6]. Induced states close to the middle of the energy gap are most probably related to accidental contamination.

5. Conclusions

Our results, on bulk glassy compositions and flash evaporated thin films of selenium and selenium containing Ag or AgI, indicate that the addition of less than 5 at. % Ag or AgI into the a-Se matrix, increases the mid-gap absorption and decrease the optical gap. No impurities bands due to Ag or AgI were detected. The sharp peaks observed at low energies in some photoconductivity spectra, have been attributed to accidental contamination of the particular compositions.

Acknowledgements

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