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Structural characterization and photoluminescence of ZnSe nanolayers♣

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Single layers of ZnSe (30, 40, 50, 70, 100 nm and 1 μm thick) are deposited at room substrate temperature by thermal evaporation of ZnSe powder in vacuum. The film surface morphology and structure are investigated by Atomic Force Microscopy (AFM). The as-deposited films are smooth and homogeneous while the relaxed ones show pits on the surface and a root mean square roughness of 2 - 4 nm. It is assumed that as-deposited films are highly strained and the strain relaxation with time creates pits and increases the surface roughness. Optical transmission measurements on relaxed films (≤ 100 nm thick) show an energy dependence of the absorption coefficient typical of amorphous materials, but the AFM data indicate the presence of nanocrystals (apparent grain size 25 - 30 nm). Therefore, it is assumed that the layers contain two phases, amorphous and crystalline, and the portion of the crystalline phase decreases with decreasing thickness. Photoluminescence (PL) measurements carried out at various temperatures in the range 20 – 300 K reveal two bands in the spectra of all films, centred at ~ 500 and ~ 550 nm. The bands are related to radiative recombination in the crystal phase, via two kinds of deep acceptors which are not discrete but have certain energy distributions in the forbidden gap.

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1. Introduction

Wide band gap II-VI nanostructured semiconductors are promising materials for the fabrication of light emitting devices, and a number of research groups worldwide are focusing on the development of II-VI semiconductor based optoelectronic devices [1,2]. Also, thin nanostructured semiconductor films, in particular II-VI ones, are promising materials for gas sensor applications [3 and references therein], since in such layers the sensing surface is significantly larger than the geometric one.

In this study, thin single layers of ZnSe are deposited at room substrate temperature by thermal evaporation of ZnSe in vacuum. Atomic force microscopy is applied in the investigation of the film surface morphology and structure. Optical transmission measurements are performed in order to determine the optical band gap of the layers and to get information about the film crystallinity.

Photoluminescence (PL) measurements are carried out at various temperatures in the range 20 – 300 K, and conclusions are made about the processes affecting the radiative recombination in nanocrystalline ZnSe layers.

2. Experimental details

Single layers of ZnSe having thicknesses of 30, 40, 50, 70, 100 nm and 1 μm were deposited on crystalline p-Si substrates held at 25 C. The layers were produced by physical evaporation of powdered ZnSe (Merck, Suprapure) at a residual pressure of ~ $3x10^{-4}$ Pa from a tantalum crucible located at the bottom of a cylindrical screen (not intentionally heated). The top of the screen was close to the substrates; thus evaporation in a quasi-closed volume was carried out. A preliminary calibrated quartz microbalance system was used to control the nominal layer thickness and deposition rate (V_d = 1.5 nm/s). Step-by-step deposition was carried out, during which the substrates were rotated, spending only 1/12 part of the turn time over the ZnSe source. During the deposition, the substrates were rotated at a rate of 8 turns/min. Thus, more than 30 'sublayers', with a nominal thickness of ~ 1.0 nm in each step, formed the respective layer.

The ZnSe layer microstructure was explored using a Nanoscan Atomic Force Microscope using a tapping mode. An area of 6.64x6.64 μm^2 was scanned with various

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steps (512x512, 1024x1024 and 2048x2048). For the optical transmission measurements, a SPECORD UV VIS spectrophotometer was used. The PL measurements were performed in vacuum at various temperatures in the range 20 – 300 K, using the 325 nm UV line (3.81 eV) of a He-Cd laser, a Jobin-Yvon U1000 monochromator and a photomultiplier as the detector.

3. Results and discussion

Figs. 1(a) and (b) show two-dimensional (2D) AFM images of a 50 nm thick ZnSe film, measured 5 days and 65 days after the deposition. The sample was kept in air at room temperature. It is seen that the "fresh" film is homogeneous and rather smooth (the root mean square roughness, (rms) = 0.44 nm) (Fig. 1(a)). After 60 days, pores of various sizes were observed, and the film roughness increased by ~ 5 times (Fig. 1(b)). It is known [4] that ZnSe layers having thicknesses < 500 nm are highly strained. Therefore, the observed structural changes with time can be related to a certain relaxation of the strain which creates pits and increases the film roughness. A third set of measurements, performed 120 days after the second one, did not show any further structural changes. In order to have a stabilized structure of all layers studied, all PL and transmission measurements were carried out on samples kept in air at room temperature for more than 60 days.

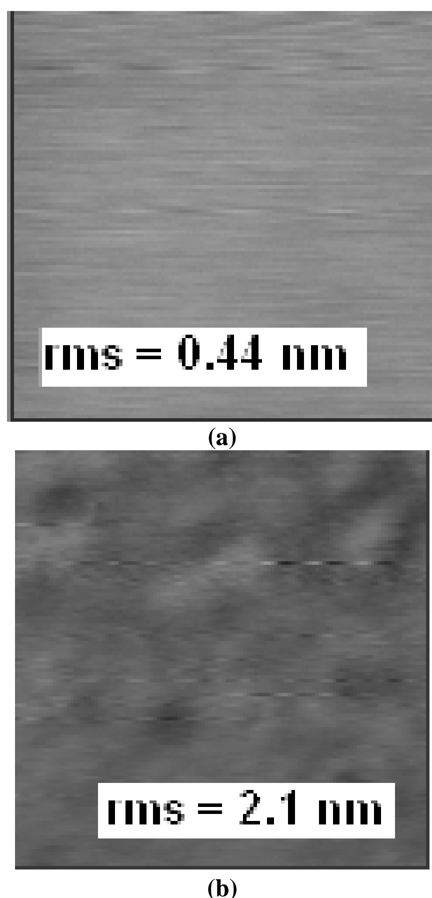

Fig. 1. Two-dimensional AFM images (3x3 μm^2) of a ZnSe layer 50 nm thick, which was kept in air at room temperature for 5 days (a) and 65 days (b).

To clarify whether the reduction in the thickness results in some changes in the layer structure, AFM investigations were performed on a series of layers with various thicknesses (30, 40, 50, 70 and 100 nm). Fig. 2 depicts a 3D image of the surface of a ZnSe layer having a thickness of 30 nm, in which the pits suggested on the basis of the 2D images are clearly seen. The results obtained for the other samples were very similar. The rms roughness of the layers varied between 2 and 4 nm and did not show a thickness dependence. The roughness of the relaxed films was comparable to or smaller than that reported by other authors for films of similar thicknesses, deposited by atomic layer [5] and chemical bath [6] processes.

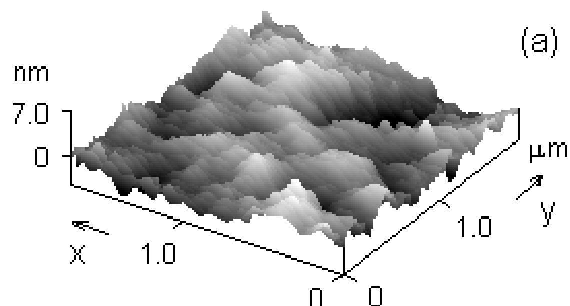

Fig. 2. Three-dimensional AFM image of the surface of a ZnSe layer having a thickness of 30 nm

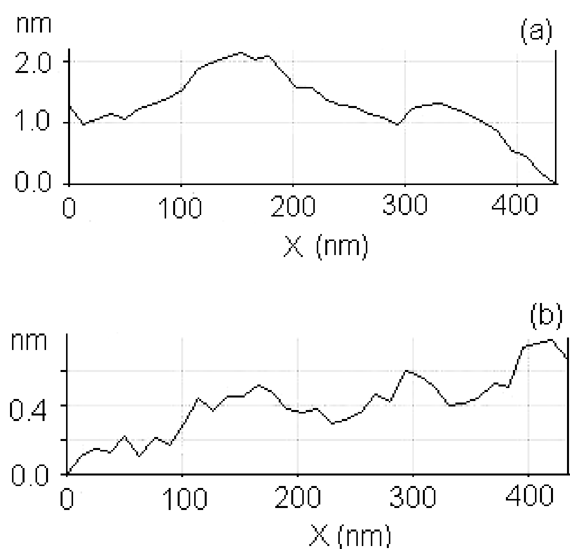

Fig. 3. Surface profile of two layers along a random line parallel to the x - axis of scanning: 30 nm (a) and 70 nm (b) thick. The scans were performed with 2048x2048 steps.

Surface profiles of two samples of different thickness, taken along random lines parallel to the X-axis are shown in Figs. 3(a) and (b). Large and small scale variations in the height of the surface points are observed. The latter are better seen in the thicker layer, while the former can be assigned to the existence of pits and high regions on the film surface. As for the latter, one can assume that they are related to grains with a maximum size of 25-30 nm in all samples.

It has been reported [4-6] that, independently of the deposition method used, the structure of ZnSe layers with $d \leq 100$nm is a mixture of nanocrystals (with average sizes of 5 - 10 nm) embedded in an amorphous matrix. Some authors have even claimed [5] that films deposited on glass or amorphous quartz substrates are completely amorphous. This justifies the assumption of the co-existence of crystalline and amorphous phases in our ZnSe layers, having thicknesses between 30 and 100 nm. It should be noticed that the average crystallite size in the films studied is quite large, and one cannot expect well expressed quantum size effects. The short scale variations are more frequently seen in the thicker layers, and therefore one can assume that the portion of the amorphous phase increases with decreasing layer thickness. The results obtained from the optical transmission measurements performed on films with $d \leq 100$ nm support this assumption. It has been ascertained that in such films the $\alpha(E)$ (α - absorption coefficient, E – energy) dependence (not shown in this short paper) is linear in coordinates corresponding to indirect electronic transitions typical of amorphous materials. The optical band gap E_g^o of amorphous ZnSe (< 2.5 eV) is smaller than that determined at room temperature for 1 μm ZnSe films (2.67 eV [7]). This observation confirms the existence of a large quantity of the amorphous phase, which dominates the absorption in layers having thicknesses $d \leq 100$ nm. On the other hand, it has been ascertained [8] that the film absorption of ZnSe layers having thicknesses of 1 μm is dominated by the crystal phase. Hence, if an amorphous phase exists in those films, its amount should be rather small.

Fig. 4 shows PL spectra of a ZnSe layer having thickness of 30 nm, measured at seven different temperatures in the range 20 - 300 K. Similar sets of PL spectra were measured on all other samples including the 1 μm one. As seen, a gradual intensity decrease is observed with decreasing temperature. The only exception is the spectrum measured at 20 K. For the 1 μm sample, the intensity decrease starts from 20 K. However, some other samples showed different temperature dependences. This preliminary observation could be due to photoinduced structural changes in the amorphous phase, but this point requires a more careful investigation.

The shapes of all spectra are asymmetric, and therefore fitting has been performed of each experimental spectrum with two Gaussian bands whose position depends on the temperature. Before the fitting procedure, all spectra were corrected for the spectral sensitivity of the measuring system.

Fig. 5 depicts the result obtained in this way, for the PL spectrum. It is seen that the band at the lower energy is of higher intensity; such a relation between the band intensities has been observed for most spectra. The temperature dependences of the maximum positions of both bands are shown in Fig. 6. Practically the same temperature dependences have been obtained for all other samples. Both bands display a similar red shift of about 0.2 - 0.25 eV with increasing temperature. This is a higher value than the expected E_g^o decrease with temperature, of ~ 0.1 eV in crystalline ZnSe [8,9].

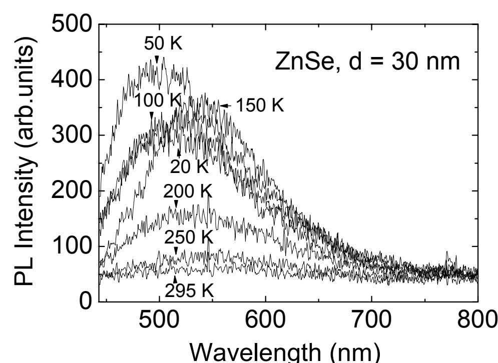

Fig. 4. Photoluminescence spectra of a ZnSe layer having a thickness of 30 nm. The spectra were measured in the temperature range 20 – 300 K in vacuum.

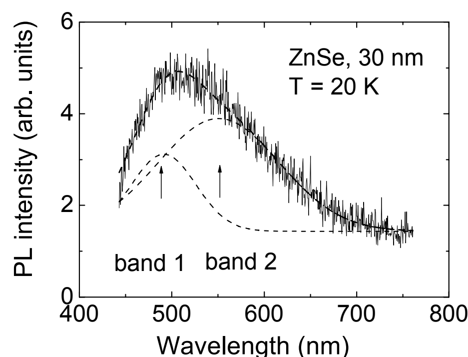

Fig. 5. Fitting of the PL spectrum measured at 20 K on a 30 nm ZnSe film.

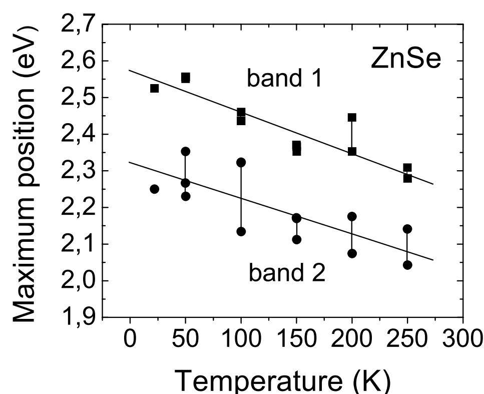

Fig. 6. Temperature dependences of the maximum positions of the two bands resolved in the PL spectra of all films studied. The lines between two points at same temperature indicate the variations in the maximum energy observed for all (up to 5) fittings of the corresponding spectra made.

Two or three bands have been observed in the PL spectra of polycrystalline ZnSe layers, peaked at around 2.6, 2.25 and 2.0 eV at room temperature [4,5,9]. All these bands display a temperature shift of < 0.1 eV. The first one is related [5,9] to free or bound excitons (so called edge emission); the other two are normally assigned to recombination of charge carriers in donor-acceptor pairs of shallow donors and deep acceptors, or electrons in the conduction band with holes captured in deep acceptors. Zn vacancies located at ~ 0.65 eV above the valence band are suggested as the deep acceptors responsible for the 2.0 eV band. The band at ~ 2.0 eV has not been resolved in our spectra, and this can be considered as an indication that the density of Zn vacancies in our films is low.

The observation of the mentioned bands enables us to conclude that in all the samples, the light emission comes from the crystalline phase. Because of the significant red shift of the observed band 1 with respect to the optical band gap, it cannot be related to edge emission. Hence, it can be suggested that both bands resolved in this study are related to recombination via deep acceptor states. In order to explain the observed rather strong temperature shift of the bands, one could assume that both kinds of acceptors, due to the existence of some disorder in the crystal phase, are not discrete but have quite a wide energy distribution in the forbidden gap. The temperature increase causes a release of charge carriers from the levels that are closer to the valence band. This can result in a decrease of the emission energy which is added to the temperature decrease of the optical band gap. The present study does not give information about the spatial location (at the interface or in the crystallite volume) and microscopic nature of the assumed two kinds of acceptor.

4. Conclusions

Atomic force microscopy, optical transmission and photoluminescence measurements have been carried out on single layers of ZnSe (30 nm - 1 μm thick) deposited at room substrate temperature by thermal evaporation of ZnSe in a vacuum. It has been shown that as-deposited films are highly strained and the strain relaxation with time creates pits and increases the film roughness. It has also been concluded that layers with $d \leq 100$ nm are mixtures of amorphous and crystalline phases and the portion of the crystalline phase decreases with decreasing thickness. Two bands centred at ~ 500 and ~ 550 nm have been observed in the PL spectra of all layers, related to radiative recombination in the crystal phase via two kinds of deep acceptors, which are not discrete but have certain energy distributions in the forbidden gap.

Acknowledgements

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