Properties of ZnSe nanocrystalline thin films prepared by thermal evaporation

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Abstract. ZnSe thin films with thickness of 30 nm and 50 nm were prepared on Corning 7059 glass substrates at room temperature by applying periodically interrupted physical vapour deposition of ZnSe and various deposition rates. All as-deposited films were annealed at 200°C and some of them were further annealed at 400°C. Results from spectroscopic ellipsometry have shown that the porosity of the films which is important for the ethanol sensitivity decreases with increasing deposition rate and annealing temperature. The porosity changes caused by annealing of the films at 400°C are accompanied with thickness decrease.

1. Introduction
ZnSe films have various applications such as optoelectronic devices, blue-green laser diodes, transistors, white-light LEDs, tunable IR laser diodes for remote sensing, continuous wave ZnSe-based laser diodes and UV detectors [1]. Like other metal chalcogenides [2-6] they might be appropriate for application in gas sensors but at present there are only few reports on the gas sensing properties of ZnSe. Most probably this is due to the decomposition and oxidation of ZnSe at temperatures higher than 200°C [7]. On the other hand at room temperature the sensitivity of ZnSe thin films gets significantly worse. They could be applicable for gas detection if a good sensitivity could be achieved.

Recently we have reported results on the room temperature sensitivity to ethanol vapors [8] of as-deposited ZnSe layers of various thicknesses as well as relaxed films kept for two months at 25°C in air. Investigating the effect of films microstructure and porosity on the sensitivity, we have observed good sensitivity that increased with decreasing thickness. Moreover, the sensitivity of as-deposited layers was higher than that of the relaxed ones, which has been explained with the higher porosity of as-deposited films. These results motivated us to look for deposition conditions which could result in further increase of the films sensitivity.

In this study, the influence of the deposition rate and the further decrease of film thickness on the surface morphology, structural and electrical properties as well as on the room temperature sensitivity to ethanol vapors of thin ZnSe films deposited by thermal evaporation in vacuum are investigated. The effect of annealing temperature is also studied.

2. Experimental details
Single layers of ZnSe having thicknesses of 50 and 30 nm were deposited on Corning 7059 glass substrates at room temperature with deposition rates \( V_d = 0.2, 0.5 \) and \( 1.5 \) nm s\(^{-1}\). The layers were produced by thermal evaporation of powdered ZnSe (Merck, Suprapure) at a residual pressure of \( 3\times10^{-4} \) Pa from a tantalum crucible located at the bottom of a cylindrical screen (not intentionally
heated). The top of the screen is close to the substrates; thus evaporation in a quasi-closed volume was carried out. The deposition rate and layer thickness were controlled by a preliminary calibrated quartz microbalance system. The layers have been produced by applying periodically interrupted (step-by-step) deposition during which the substrates were rotated at a rate of 8 rpm thus spending only 1/12 part of the turn time over the crucible. At each step a small portion of ZnSe vapors condenses on the substrates with a time interval between the steps and thus a large number of such sublayers form the films. All as-deposited films were annealed at 200°C and part of them was further annealed at 400°C for 1 h in Ar atmosphere.

X-ray diffraction (XRD) measurements were performed by PANalytical Empyrean diffractometer using the CuKα line to study the films crystal structure.

The ellipsometry measurements were performed using a Woollam M2000D spectroscopic ellipsometer with a wavelength range from 193 nm to 1000 nm. The software used for data acquisition and analysis was CompleteEASE 5.10 J. A. Woollam Co., Inc. The spectroscopic ellipsometry data Ψ and Δ were taken in the wavelength range from 193 to 1000 nm at angles of incidence of 50º, 55º and 60º. A model based on the Bruggeman effective medium approximation was applied on a modeled structure which consists of glass substrate and a porous ZnSe layer. The surface roughness was also taken into account. It has been modeled using the standard procedure of an effective medium composition with 50% voids and 50% layer material. The preparation conditions and parameters of the films determined by spectroscopic ellipsometry (SE) are presented in table 1.

The morphology of the deposited films was investigated by atomic force microscopy (AFM). The AFM measurements were performed on scanning probe microscope Multimode V (Bruker, ex. Veeco, Santa Barbara, CA). The images were taken in tapping mode, and each sample has been investigated on different points of the surface. Measurements at scales 1 and 5 μm were carried out. The root mean square roughness (RMS) of the samples surface was determined on 5×5 μm² surface area. Before the analysis the images were just flattened. They were further processed using SPIP™ 6.1.0 program.

Electrical measurements were performed by means of a Keithley 6487 picoammeter under applied voltage of 100 V in the temperature range 293-420 K. Temperature dependences of the dark current were obtained at a heating rate of 0.1 K s⁻¹. Planar indium contacts on the top surface of the layers were used. The contacts were 5 mm long and 1.5 mm spaced. Current–voltage characteristics measured in the voltage range 10⁻¹⁰² V showed Ohmic-like behaviour.

The layer’s response to ethanol vapors at room temperature was studied by measuring the changes of the dc dark current through the layers at room temperature. The measurements were carried out using homemade equipment under a closed glass test chamber having a volume of 1500 cm³ in which ethanol vapors were produced in atmospheric air by evaporating 100-500 µL of liquid ethanol (99.7%). The amount of the liquid ethanol is used below as measure of the ethanol vapor concentration. During the measurement, the vapors were homogeneously distributed inside the chamber by a propeller. A current increase was observed upon film exposure to ethanol vapors as the maximum current value $I_{max}$ was achieved 3 min after starting ethanol evaporation. For all samples concentration dependences were measured starting with the minimum concentration and then the ethanol concentration was gradually increased. The ethanol vapors were removed by opening the glass chamber and exposing the sample to atmospheric air [8].

3. Results and discussion

X-ray diffraction pattern of a 50 nm thick film is shown in figure 1. It reveals that films are microcrystalline rather than amorphous. ZnSe has either cubic, zinc blend type structure or hexagonal, wurtzite type structure. In the XRD spectrum a high intensity peak at $2\theta = 27.2^\circ$ as well as a peak at $2\theta = 45.6^\circ$ with smaller intensity are seen. The observed diffraction peaks are characteristic of zinc blend structure with (111) and (220) orientation (JCPDS 37-146). The higher intensity of the first peak indicates that (111) is the preferred orientation.
Three-dimensional (3D) AFM image of a 30 nm thick film is shown in figure 2. It reveals a relatively smooth surface and microcrystalline structure. The images of the other films are similar. The grain size determined from the AFM images displays a tendency to increase with increasing both deposition rate and film thickness. For example, values of 16-25 nm are determined for the grain sizes in the 30 nm films deposited with $V_d = 0.2$ nm s$^{-1}$. For films with thickness 50 nm deposited with the same rate the grain sizes are in the range 20-50 nm. The highest root mean square roughness was obtained for the films deposited with $V_d = 1.5$ nm s$^{-1}$.

![Figure 2. 3D AFM image of a 30 nm thick ZnSe film deposited at a rate of 0.2 nm s$^{-1}$.](image)

Table 1. Preparation conditions and parameters of the films determined by spectroscopic ellipsometry

| Sample No | Intentional thickness, deposition rate, annealing temperature | SE Thickness nm | EMA (Void) % | $n$ at 632.8 nm |
|-----------|---------------------------------------------------------------|----------------|--------------|----------------|
| 1         | 50 nm, 0.2 nm s$^{-1}$, 200°C                                  | 82             | 22.4         | 2.23554        |
| 2         | 50 nm, 0.2 nm s$^{-1}$, 400°C                                  | 63             | 23.5         | 2.21600        |
| 3         | 50 nm, 0.5 nm s$^{-1}$, 200°C                                  | 57             | 17.0         | 2.32559        |
| 4         | 50 nm, 0.5 nm s$^{-1}$, 400°C                                  | 47             | 15.4         | 2.35169        |
| 5         | 30 nm, 0.2 nm s$^{-1}$, 200°C                                  | 45             | 35.5         | 2.00680        |
| 6         | 30 nm, 0.2 nm s$^{-1}$, 400°C                                  | 30             | 25.1         | 2.18841        |
| 7         | 30 nm, 0.5 nm s$^{-1}$, 200°C                                  | 38             | 19.9         | 2.27735        |
| 8         | 30 nm, 0.5 nm s$^{-1}$, 400°C                                  | 30             | 12.7         | 2.39655        |
| 9         | 30 nm, 1.5 nm s$^{-1}$, 200°C                                  | 30             | 8.8          | 2.45937        |
| 10        | 30 nm, 1.5 nm s$^{-1}$, 400°C                                  | 30             | 6.9          | 2.49025        |

The absorption coefficient data were obtained from the spectroscopic ellipsometry data. Figure 3 presents the Tauc plot of the absorption coefficient according to the relation...
(αE) ~ (E - E_g) \frac{1}{2} \quad (1)

where \( \alpha \) - absorption coefficient, \( E \) - photon energy, \( E_g \) - optical band gap. Relation (1) corresponds to direct allowed electron transitions between the conduction and valence bands characteristic for crystalline materials having direct band gap. Linear dependence of \( (\alpha E)^2 \) versus \( E \) was observed for all samples; it confirms the conclusion made by XRD and AFM that the films are microcrystalline. The band gap energies of the films \( E_g \) determined from the point of intersection of the straight line with the \( x \)-axis are in the range 2.63-2.7 eV. These values are in good agreement with those determined in our previous studies [8, 9] and show that the variation of the deposition rate does not significantly affect the lattice disorder and thus the optical band gap of the films. However, the deposition rate affects the films porosity.

**Figure 3.** Tauc plot of the absorption coefficient of a 30 nm thick ZnSe film deposited at a rate of 0.2 nm s\(^{-1}\).

It is seen from table 1 that the volume fraction of pores in the ZnSe films, determined by applying the Bruggeman effective medium approximation decreases with increasing the deposition rate and the annealing temperature. According to our previous results [8], because of the lattice relaxation, pits appear on the layers surface but the pore fraction in the volume reduces. Therefore, we suppose that the annealing at 400°C causes structural relaxation, densification of the films and thus a decrease of the pores fraction. The highest porosity observed in the 30 nm film deposited with \( V_d = 0.2 \) nm s\(^{-1}\) could be related to both the very small portions of material which form the sublayers in the films during the deposition and to the small thickness.

**Temperature dependence of dark conductivity (\( \sigma_d \)) in the temperature range 293-420 K is shown in figure 4. The Arrhenius plot of \( \sigma_d \) versus 1000/T is linear and the dark current activation energies were calculated from the slope according to the equation

\[
\sigma_d = \sigma_0 \exp\left(-\frac{E_{ad}}{kT}\right),
\]

where \( E_{ad} \) is the activation energy, \( k \) - Boltzman’s constant. Dark current activation energies for all films are \( E_{ad} \sim 0.8 \) eV and do not change significantly when varying the deposition rate and annealing temperature. In the investigated temperature range, the electronic transport properties of thin semiconductor films are strongly influenced by their structural characteristics. As it is seen from the structural and optical studies, the films are microcrystalline with grain sizes determined from the AFM images in the range 16-50 nm. Defects at crystallite boundaries of microcrystalline films result in trapping states with large concentration. The trapped carriers form potential barriers and \( E_{ad} \) depends on the height of these barriers. Due to the existence of traps, the grains become partially depleted. However, it was calculated [10] for microcrystalline thin films with grain size less than 100 nm that even a band...
bending of $\sim 0.1$ eV causes almost full depletion of grains and strong reduction of potential barriers. For this reason in such materials $E_{ad}$ gives information about the energy distance between the Fermi level and the bottom of the conduction band. The obtained $E_{ad}$ values are relatively high and don’t depend on preparation conditions which implies that strong depletion occurs in all films.

The ratio $S = (I_{\text{max}} - I_0) / I_0$ is used as a measure of the films sensitivity to ethanol vapors, in which $I_0$ denotes the current in the reference gas (air) and $I_{\text{max}}$ is the maximum current achieved upon exposure to ethanol vapors. As it was shown above, the films are nanocrystalline and have significant porosity. Their electrical conductivity is strongly influenced by the defects at the grain boundaries, in particular absorbed oxygen atoms, and the total pores surface. In n-type semiconductors, it is considered that electrons are most frequently trapped in states that originate from adsorbed oxygen atoms and/or molecules. When exposed to a chemically reducing gas, like ethanol, interaction between gas molecules and the oxygen occurs, which results in removal of oxygen from the grain interfaces and increase of the dark current [11, 12].

\[ S = \frac{(I_{\text{max}} - I_0)}{I_0} \]

\[ \text{Sample 1} \]
\[ \text{Sample 3} \]
\[ \text{Sample 5} \]

**Figure 5.** Room temperature sensitivity to ethanol of 30 nm (samples 5, 6) and 50 nm (samples 1, 2, 3) thick ZnSe films, $V_d = 0.2$ nm s$^{-1}$ (samples 1, 2, 5, 6) and $V_d = 0.5$ nm s$^{-1}$ (sample 3), annealed at 200°C (a) and annealed at 400°C (b).

Chemical sensitivity to ethanol vapors in air of 30 nm and 50 nm thick films deposited at rates of 0.2 and 0.5 nm s$^{-1}$ annealed at 200°C (a) and 400°C (b) is shown in figure 5. It is seen that the sensitivity of the 30 nm thick films is rather low at lower concentrations (100-300 µl) and does not increase significantly after annealing at 400°C. The sensitivity of the 30 nm films deposited at 0.5 and 1.5 nm/s shows similar behavior. Independently of the deposition rate the 50 nm samples annealed at 200°C show a linear sensitivity increase with increasing ethanol concentration which is important for application purposes. Moreover at low concentrations $S$ is significantly higher than that of the 30 nm samples and it increases with decreasing deposition rate (figure 5(a)). It is seen from figure 5(b) that the annealing at 400°C deteriorates the sensitivity concentration dependence of the 50 nm films. Based on these results and those reported in reference [8] one can conclude that the films with thickness of 50 nm, deposited at $V_d = 0.2$ nm s$^{-1}$ and annealed at 200°C show sensing properties which make them suitable for ethanol detection at room temperature. In [8] we have observed well pronounced dependence of ZnSe thin films sensitivity to ethanol vapors on films porosity. The results of this study support this conclusion. The films porosity increases with decreasing deposition rate (table 1) as the porosity of the 50 nm films ($V_d = 0.2$ nm s$^{-1}$, sample 1) is higher than that of sample 3 ($V_d = 0.5$ nm s$^{-1}$). In result an $S$ increase is observed.

### 4. Conclusions

ZnSe thin films with thickness 30 and 50 nm have been prepared by means of periodically interrupted physical vapor deposition and further annealed at 200°C and 400°C. The XRD results have revealed
that the films are microcrystalline and have cubic structure with (111) preferred orientation. According to the AFM data, the grain size shows a tendency to increase with increasing both deposition rate and film thickness. Absorption spectra have revealed direct allowed transitions and band gap energies in the range 2.63-2.7 eV which confirms that the films are crystalline. The obtained dark current activation energies have not changed significantly with preparation conditions. Their high values have been related to strong crystallite depletion in all films. It has been found that films porosity decreases with increasing both the deposition rate and the annealing temperature. The experiments on chemical sensitivity to ethanol vapors have shown that films porosity plays an important role for the films sensitivity. Best sensing properties have been obtained for the films with thickness of 50 nm, deposited at the lowest rate of 0.2 nm s\(^{-1}\) and annealed at 200°C.

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