Room temperature sensitivity of ZnSe nanolayers to ethanol vapours

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Abstract: Layers of ZnSe (50, 110 and 160 nm thick) are deposited at room substrate temperature by thermal evaporation of ZnSe powder in vacuum. As-deposited and relaxed layers are investigated by spectroscopic ellipsometry to get information about their optical properties, porosity and surface roughness. The obtained data indicate that all layers are nanocrystalline and the lattice relaxation causes a porosity decrease and surface roughness increase. Ethanol sensing experiments are carried out at room temperature in air and results show an increase of the layers sensitivity with decreasing thickness while the relaxation causes sensitivity decrease. The sensitivity behavior is discussed considering the changes in the films porosity and the ethanol related decrease of the potential barriers at the nanocrystallite interfaces.

1. Introduction

The gas detection is related mainly with surface processes and therefore thin films are very suitable for gas sensors. Semiconductor thin films are widely used for resistive gas sensing, especially metal oxides, which have high sensitivity, stability and relative short response times at high working temperatures (200 – 300 °C). However at room temperature their sensing properties worsen significantly and during the last few decades much attention has been given up to the problem of room temperature sensing [1]. Nanostructured semiconductor films, in particular metal chalcogenides [2], are considered as promising materials for sensitive element in gas sensors due to their high surface-to-volume ratio and high porosity. Good gas sensitivity at room temperature has been reported for nanocrystalline thin films from CdS and CdSe [3], as well as in ZnO nanostructured thin films [4, 5].

ZnSe has been widely used in fabrication of various optoelectronic devices [6] such as blue-green laser diodes, tunable mid-IR laser diodes for remote sensing, white-light LEDs, continuous wave ZnSe-based laser diodes and UV photodetectors. However, there are almost no reports on ZnSe as a gas sensor probably because of its decomposition and oxidation at temperatures higher than 200 °C. It can be appropriate for detection of gases at room temperature or temperatures below 200 °C if a good sensitivity is achieved.

In this study ZnSe thin layers have been prepared by thermal evaporation of ZnSe powder in high vacuum. The effect of the microstructure and porosity of the layers on the room temperature sensitivity to ethanol vapors have been investigated.

2. Experimental

Layers of ZnSe having thicknesses of 50, 110 and 160 nm were deposited on Corning 7059 glass substrates kept at 25 °C. The layers were produced by physical evaporation of powdered ZnSe (Merck, Suprapure) at a residual pressure of 3×10⁻⁴ 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 (V_d = 0.5 nm s⁻¹) and layer thickness were controlled by a preliminary calibrated quartz microbalance system. The films were
grown in a step-by-step manner i.e. during the film deposition the substrates were rotated at a rate of 8 turns min\(^{-1}\) spending only 1/12 part of the turn time over the ZnSe crucible. At each step a small portion of ZnSe vapors condense on the substrates with a time interval between the steps and the films were formed from a large number of such portions. It has been shown that this deposition approach results in nanocrystal size reduction in CdSe layers and this increases gas sensitivity of those films [3].

Ellipsometric measurements were carried out by an automatic M2000D spectroscopic ellipsometer (J.A. Woollam, Germany). Angles of incidence from 50° to 65° by 5° were used in the wavelength range of 400–1000 nm and the obtained data were further fitted using Woollam’s CompleteEASE program. 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 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 using planar Ohmic-like indium contacts on the top surface of the films. The measurements were carried out under a closed glass test chamber, under atmospheric conditions, having a volume of 1500 cm\(^3\) in which vapors were produced 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 \(I_{\text{max}}\) 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.

3. Results and discussion

The porosity and surface roughness of sensing films are important characteristics which strongly influence their chemical sensitivity. In order to get information about ZnSe layers’ porosity and roughness they were characterized by spectroscopic ellipsometry (SE). ZnSe is a direct band gap semiconductor and from the optical absorption data obtained by SE one can get information about the films crystallinity – are they predominantly crystalline or amorphous. Figure 1(a) shows the absorption spectrum of a 50 nm thick film presented in coordinates corresponding to direct allowed electron transitions between the conduction and valence bands \((\alpha E \sim (E-E_g)^{1/2})\), \(E_g\) - optical band gap, \(E\) – light energy). Such transitions are typical for crystalline materials with a direct band gap. Figure 1(b) presents the same spectrum in coordinates corresponding to indirect allowed transitions \((\alpha E \sim (E-E_g)^2)\), typical for amorphous materials. It is seen from the figure that the \(\alpha(E)\) dependence shows good linearity in the coordinates corresponding to direct electronic transitions typical for crystalline ZnSe. The results for the other two layer thicknesses are very similar and one can conclude that the films with all thicknesses are predominantly crystalline. The optical band gap determined from the intersection of the straight line with the \(x\)-axis is 2.64 eV for all thicknesses. It is in good agreement with the value we obtained for 1 µm thick microcrystalline ZnSe films (2.67 eV) [7]. Normally the thickness reduction results in a decrease of the crystallite size and if it is less than ~10 nm a band gap increase can be observed due to carriers’ confinement. No such effect is observed even for the 50 nm film which implies that the average crystallite size in the films with all thicknesses is larger than 10 nm which is in agreement with the atomic force microscopy (AFM) results showing that the grain size in ZnSe films having thickness in the range 30–100 nm is 25–30 nm [8, 9].
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Figure 1. Absorption spectrum of 50 nm thick films of ZnSe presented in coordinates corresponding to allowed direct (a) and indirect (b) electronic transitions between valence and conduction bands.

It has been reported [10–13] that, independently of the deposition method, the structure of ZnSe layers with \( d \leq 100 \) nm is a mixture of nanocrystals embedded in an amorphous matrix. Our previous investigations on ZnSe layers (prepared at same other conditions and deposition rate of 1.5 nm sec\(^{-1}\)) with thicknesses between 30 nm and 100 nm, have shown that the layers with all thicknesses contain two phases, amorphous and crystalline, and the portion of the crystalline phase decreases with decreasing thickness [9]. The predominantly crystalline structure of the 50 nm films here studied can be due to considerably lower deposition rate (0.5 nm sec\(^{-1}\)) than that applied for the deposition of the previously studied films. It seems that the smaller the material portions at each step of the step-by-step deposition process, the higher the film crystallinity. This result is interesting and could be used for preparation of ZnSe films with different ratio of crystalline-to-amorphous phases. Thus one could affect the films’ conductivity, gas sensitivity etc.

ZnSe layers having thicknesses less than 500 nm are highly strained and strain relaxation with time has been observed [11]. Our previous AFM investigations have shown that lattice relaxation takes place in the ZnSe layers during 2-month storage at 25 °C in air and this strongly affects the films surface [9]. In this study information for the surface roughness has been obtained from the results of SE measurements performed on as-deposited and relaxed films with thickness of 50 nm. The surface roughness of as-deposited layer is very small (\( \leq 0.5 \) nm) while the roughness of relaxed films (kept for four months at 25 °C in air) is around 2.6 nm. This observation is in very good agreement with the previous AFM results for 50 nm thick ZnSe film which showed that the surface of as-deposited films is homogeneous and rather smooth (root mean square roughness \( R_q = 0.44 \) nm). After relaxation for 2 months the AFM \( R_q \) increased by \( \approx 5 \) times and pits of various sizes were observed. A third set of measurements, performed four months after the second ones, did not show any further structural changes. Values of around 7.6 nm and 6.2 nm have been obtained from the SE data for the roughness of relaxed films with thickness of 160 nm and 110 nm, respectively. The roughness values obtained for the relaxed films are in good agreement with those reported by other authors for ZnSe films prepared by thermal evaporation in vacuum [9, 14–16].

The volume fraction of pores in all relaxed ZnSe films, determined by applying the Brugemann’s effective medium approach, is in the range of 0.15–0.19 which is in good agreement with the value of about 0.17 obtained previously for relaxed ZnSe films [8]. However the volume fraction of pores in as-deposited 50 nm films is much higher, around 0.3. Taking into account the surface roughness (AFM and SE) results for 50 nm thick films one can assume that the pores in as-deposited films are disposed in the layers’ volume, while the lattice relaxation results in appearance of pits on the layers surface but reduction of the pore fraction in the volume.

The sensitivity of ZnSe films to ethanol vapors was measured on both as deposited and relaxed films at identical conditions. The ratio \( S = (I_{\text{max}} - I_0) / I_0 \) is used as measure of the films ethanol
sensitivity $S$, 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. Figure 2 shows concentration dependences of the sensitivity of as-deposited and relaxed films with three different thicknesses. Distinct thickness dependence is seen from the figure. The chemical sensitivity of the films increases with decreasing thickness. The as-deposited films with thickness of 50 nm and 110 nm show a linear increase with the increase of the concentration of ethanol vapors while after the lattice relaxation only the 50 nm thick film shows such linearity. The linear response is an important parameter for practical application of sensing materials. A comparison of the $S$-values in figure 2(a) and (b) shows that the sensitivity of each as-deposited film is higher than that measured after lattice strain relaxation. Taking into account that the relaxation causes porosity decrease and roughness increase one can conclude that porosity has stronger effect on the layer sensitivity than surface roughness.

![Figure 2](image_url)

**Figure 2.** Room temperature sensitivity to ethanol of as-deposited (a) and relaxed (b) ZnSe layers with different thicknesses denoted in the figure.

Dark current in air and the films’ response $I_{\text{max}}$ of the 50 nm thick as-deposited and relaxed ZnSe layer to ethanol vapors are shown in figure 3 for illustration. The results for the layers with other two thicknesses are very similar. It is seen from the figure that both $I_0$ and $I_{\text{max}}$ obtained for the relaxed layer are lower than the corresponding values in as-deposited one.

![Figure 3](image_url)

**Figure 3.** Dark current in air ($I_0$) and the maximum value of the current measured upon exposure to ethanol vapors of various concentration obtained for a 50 nm thick ZnSe layer at room temperature. 1 - as-deposited layer, 2 - relaxed layer.
According to a common model based on the fact that polycrystalline films consist of a large number of grains, contacting at their boundaries [17, 18], the electrical behaviour of such films is governed by the formation of double Schottky potential barriers at the interface of adjacent grains. These barriers are caused by charge trapping at the interface. In n-type semiconductors it is considered that electrons are most frequently trapped in states which originate from adsorbed oxygen atoms and/or molecules. The height of the barriers determines the conductance of the film; the higher the barrier, the lower the current. 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, the barrier height decreases and the dark current increases.

Adopting this model one can explain the observed thickness dependence of the layers sensitivity and the relaxation effect in the following way. Among the parameters affecting the sensitivity of the layers is the penetration of the analyte molecules/atoms into the layers depth; the higher the depth, the higher the sensitivity. The penetration is influenced by the mobility of the gas molecules i.e. of the measurement temperature, as well as by the existence of pores and interfaces which facilitate the movement of molecules. Our sensing experiments were carried out at room temperature and one can expect a low mobility of the ethanol molecules and a limited penetration depth. AFM results have shown that the grain size in all ZnSe films with thickness in the range 30–100 nm is 25–30 nm, the SE results for the relaxed layers show similar porosity of the layers. Hence one can assume that the ethanol penetration depth i.e. the layer part in which the barrier height is reduced and the electrical conductivity is increased is approximately equal in all layers. This means that the relative part with an increased conductivity is smaller in the thicker layers, which explains the sensitivity increase with decreasing layer thickness. The higher sensitivity of the as-deposited layers can be rated to the higher porosity while the lower conductivity of the relaxed films is probably due to continued oxygen adsorption and electron trapping by the adsorbed molecules.

4. Conclusions
First results on the effect of microstructure and porosity of as-deposited layers from ZnSe with thickness 50, 110 and 160 nm on their room temperature sensitivity to ethanol vapors have been presented. The effect of the crystal lattice strain relaxation was also explored. It has been found that all as-deposited and relaxed films are nanocrystalline. The porosity of the layers in as-deposited state is high (~30%) and significantly decreases upon relaxation (down to 15-19%), while the surface roughness of the relaxed films is higher than that of the as-deposited ones. The ethanol sensing experiments have shown that the layers sensitivity increases with decreasing thickness which has been related to low mobility and relative small penetration depth of the ethanol molecules at room temperature. The relaxation causes a sensitivity decrease and this result has indicated that the layer porosity has stronger effect on the layer sensitivity than the surface roughness. The 50 nm thick films have demonstrated good sensitivity and linear response in both as-deposited and relaxed states which makes them perspective for practical detection of high concentrations of ethanol vapors at room temperature.

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