Karmiat El-Sayed

X-RAY DIFFRACTION STUDIES OF OXYGEN IMPLANTATION IN ZnSe SEMICONDUCTOR MATERIAL

THESIS

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By

AHMED ALY MOHAMED ALY

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SUMMARY

The apparent size, strain, and dislocation density were determined for the principle plane (111) and (220) for the powder form and only (111) plane for the thin films form. The analysis showed that for both planes (111) and (220) the crystal size increases while the strain and dislocation density decreases with increasing temperature but this increase and decrease were found to be of different rate for each plane, this was explained by considering that two processes are taking place at each temperature, these two processes are the annealing and the oxygen diffusion.

It was found that the action of the annealing effect is opposite to the action of oxygen diffusion which takes place in the octahedral positions of the ZnSe lattice. In the early stage of heating (where oxygen diffusion is not effective) the annealing effect was predominant and accordingly the crystallite size increases while the strain decrease, this means that the oxygen diffusion which causes strain are less effective in the early stage of heating than the annealing effect.

But after that, the behavior of the crystallite size and the strain values behaved differently: (1) For the (111) plane, the crystallite size increases steadily up to 400 °C while the strain is found to be greater than that along [220] direction and it decreases with temperature steadily up to 350 °C then it decreases sharply. (2) For the (220) plane, the size remains nearly constant from room temperature up to 350°C and then increases sharply at 400°C ,and the strain decreases with the same rate (111) up to 350 °C and it remains constant after that

For the ZnO phase, the crystallite size increases with temperature along both directions [10.1] and [00.2] but with different rates, also the strain decreases linearly with temperature. This agrees very well with the behavior of the annealing effect.

In order to see the effect of heating on the transformed ZnO and see if the phase obtained from ZnSe transformation is free from any defect, structure refinement was applied to the transform ZnO using Rietveld method and also the microstructural parameters were determined at different temperatures. The results showed that the structure of ZnO is hexagonal with Zn at 0 0 0 and O at 0 0 0.389 with a good reliable factor of (R = 0.03) and the microstructural parameters is consistent with the values obtained from the decomposition analysis. Rietveld method was also applied to determine ZnSe structure analysis and microstructural parameters, the results obtained were not of good reliablity factors for samples annealed above room temperatures, also the results of the microstructural parameters were not consistent with those obtained by the decomposition method which means that Rietveld method is not applicable to samples when impurities or oxygen diffusion into interstitial positions.

CHAPTER I

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INTRODUCTION

Heat treatment of thin films usually has a considerable influence on the properties of such films. Annealing thin films will affect the physical properties of the film material, one or more changes in the film may reduce the concentration of defects which appear in the interior of the film due to nonuniformity of the condensation conditions, or it may, reevaporates some of the film material or some of its components. Sometimes an interaction of the film material with molecules in the ambient atmosphere may occur. This markedly changes the electrophysical properties of the films and thereby their applications.

I-1. Early Work on ZnSe Material

The crystal structure of ZnSe is zinc-blende structure with two atoms per unit cell; the full space group is $F\bar{4}3M$ *Continenza, et al 1988) [1]*, which includes 24 symmetry operations and excludes inversion symmetry. Technological and theoretical interest in ZnSe has been growing recently due to its appealing electrical and optical properties. Considerable efforts is beeing devoted to realize a P- type material by using different techniques as, for example, by doping or growing with impurities such as Li or Cl.

Further, ZnSe has proved to be a particularly interesting dilute magnetic semiconductor when doped with Mn. Finally, the very recent molecular-beam epitaxy [MBE] growth of BCC Fe and Ni single crystal on ZnSe is opening up the possibility of using such materials as micro-electronic magnetic switches *conteninza, et al (1988) [1]*.

Heating polished disks of Zinc selenide in the atmosphere of the furnace led to their oxidation, which is accompanied by losses in weight Fig.*(1)*. The weight losses during the initial stage of heating increased slightly with insiginificant fluctuations and subsequently began to be placed by a sharp increase in loss. It is therefore necessary to know the temperature range at which ZnSe powders and crystal do not undergo marked oxidation and also to get a clear picture of their kinetics and mechanism at higher temperatures. The oxidation of Zinc slenide crystal is a complex heterogeneous process. It involves a series of chemical reactions which take place during the decomposition of the initial material and formation of the final products associated with the condition of the external and internal mass exchange. The chemical phase compostions of the solid oxidation products and the gas phase condensation were established by chemical, spectrophotometer, and analysis. The transmission spectra of the samples over the range $2.5 < \lambda < 25$ μm were recorded on a specord 751 spectrometer *kulakov, et al. (1981) [2]*.

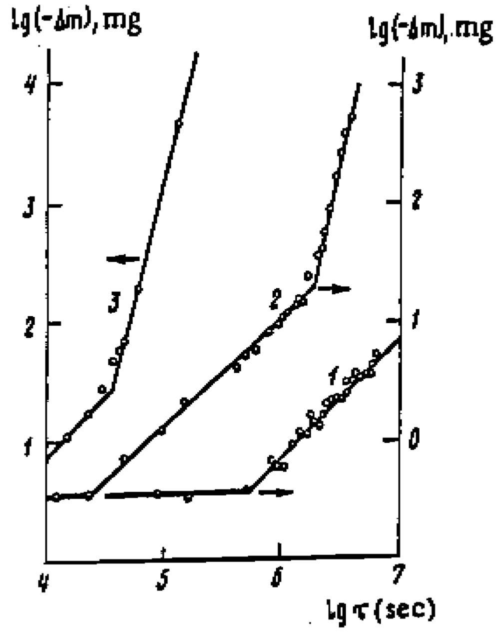

Fig.(1) Losses in weight of ZnSe samples as a function of heating time.

The reaction products of the oxidation was identified from the transmission spectra of the samples which had undergo oxidation. This is shown in Fig.*(2)*. Accordingly the measurements, which agree with results in the transmission spectra shown in Fig.*(3)* are those of oxygen-containing compounds of Selenium and Zinc. By comparing the spectra of Figs.*(2)* and *(3)* it can be concluded that a hydrate of Zinc selenite is mainly present on the surface of the sample on the part of the curve for 573 K where the weight losses vary linearly with time (Fig.*(3)*, curve *(2)*).

From the transmission spectra the mechanism of oxidation for ZnSe by atmospheric oxygen *Steponova, et al (1975) [3]*, in the range 623-723 °K, is according to oxidized following the reaction,

$$ZnSe + 1/2\ O_2 \rightleftharpoons ZnO + Se \qquad (1)$$

$$Se + O_2 \rightleftharpoons SeO_2 \qquad (2)$$

or

$$ZnSe + 3/2\ O_2 \rightleftharpoons ZnO + SeO_2 \qquad (3)$$

Beginning at 723 K, $ZnSeO_3$ is formed

$$ZnSe + 3/2\ O_2 \rightleftharpoons ZnSeO_3 \qquad (4)$$

or

$$ZnO + SeO_2 \rightleftharpoons ZnSeO_3 \qquad (5)$$

reaction (4) is thermodynamically more probable. Thus the

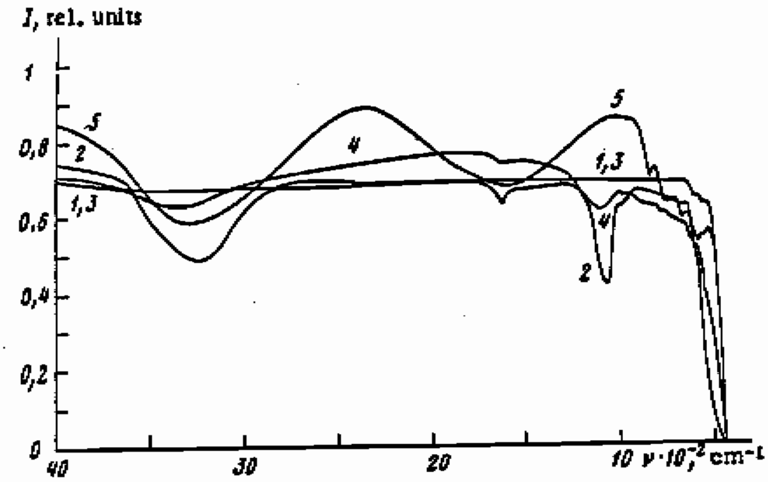

Fig. (2) Transmission spectra of ZnSe samples after heating. 1) Initial sample; 2) $6.5\cdot10^{6}$ sec at 573°K; 3) sample 2 after rinsing, 4) $2.8\cdot10^{6}$ sec at 673°K; 5) $2.2\cdot10^{4}$ at 773°K.

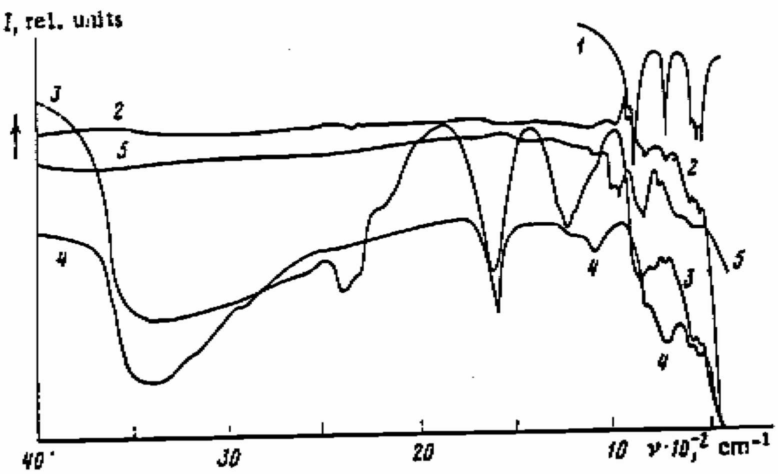

Fig. (3) Transmission spectra of oxygen-containing compounds of zinc and selenium. 1) Vacuum layer of SeO_2 [7]; 2) crystalline film of SeO_2 on ZnSe; 3) film of H_2SeO_3 hydrate with a thickness of ∿100 μm on ZnSe; 4) film of $ZnSeO_3$ hydrate with a thickness of ∿50 μm on ZnSe; 5) polished ZnO disk with a thickness of ∿30 μm.

overall oxidation reaction of ZnSe may be given by ,

$$3ZnSe + 7/2\ O_2 \rightleftharpoons 2ZnO + ZnSeO_3 + SeO_2 + Se \qquad (6)$$

The amount of oxidation products of ZnSe { ZnO & $ZnSeO_3$ & SeO_2 and Se } formed depends on the rate of heating of the specimens and the annealing time at the specific oxidation temperature, and as the temperature is increased, ZnO began to predominate among the oxidation product

I-2. Aims of The Present Work

* The present work was undertaken mainly in order to fully study the effect of annealing on the oxidation phases of ZnSe, bulk and thin films, at different temperatures.

* The other aim of the work is to follow the process of Oxygen diffusion into the interstitial holes during the annealing of ZnSe (bulk and thin film) at different temperatures by applying X-ray diffraction line profile analysis.

* To study the effect of annealing on the microstructural changes in ZnSe, like for example microstrain, crystallite size and dislocation density at different temperatures of annealing

* To find the relation between oxygen diffusion and microstructural change.

* To try several methods for size-strain analysis and accordingly choose the most adequate and effective one to be applied to similar materials as that for the present work.