

## Optical and Electronic Properties of ZnSe

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Optical and electronic properties of ZnSe films prepared by sputtering have been investigated on the basis of experiments on photocurrent  $I_p$ , dc-dark current  $I_d$  and X-ray diffraction. It is found that both  $I_p$  and  $I_d$  are dominated by the defect centers with acceptor nature located at 2.5eV and 2.2eV below the conduction band in band gap associated with oxygen interstitial and a complex involving oxygen interstitial in ZnSe.

### 1. INTRODUCTION

ZnSe is a semiconductor with a large direct band gap of 2.7eV at room temperature, and has potential as the material of opto-electronic devices. However, it is extremely difficult to obtain low resistive ZnSe with p-type conduction, and this difficulty has been believed to be caused by incorporation of residual impurities [1] and/or generation of self-compensation centers [2]. This is due to the fact that the general understanding of the optical and electronic properties associated with lattice defects in ZnSe is not complete.

The purpose of the present study is to examine how structural lattice defects affect the photo-electronic behavior in ZnSe films prepared by sputtering. In particular, our interest is focused on lattice defects created during the deposition of amorphous ZnSe (a-ZnSe) and by annealing treatments, and we discuss the opto-electronic properties associated with them on the basis of measurements of photocurrent  $I_p$ , dc-dark current  $I_d$ , and X-ray diffraction.

### 2. EXPERIMENTAL

Films of ZnSe were deposited onto the fused silica substrate ( $30 \times 20 \times 0.3 \text{ mm}^3$ ) using r.f. sputtering apparatus. The sputtering target was a high purity ZnSe disk of 2 inches in diameter. As shown in Table 1, the

sputtering gas was pure Ar (with flow rate of 16sccm) for the specimen NOs ZS11 and ZS12 and a mixture gas of Ar(15sccm) and  $\text{O}_2$ (1.0sccm) for ZSO11 and ZSO13 and of Ar(13sccm) and  $\text{O}_2$ (3.0sccm) for ZSO12 and ZSO14 at about  $2 \times 10^{-3}$  Torr. Here, the mixture gas was used in order to clarify the behavior of native defects in ZnSe with the annealing. Temperature of the substrates was room temperature and 200°C. The thickness of the deposited ZnSe films is about 5000Å with the deposition rate of about 1.2Å/s.

After the deposition at 200°C, the annealing treatments were successively performed at  $T_A = 200^\circ\text{C}$  for  $t_A = 4$  min for ZS11, ZSO11 and ZSO12 and for  $t_A = 120$  min for ZS12, ZSO13 and ZSO14, where  $T_A$  and  $t_A$  denote temperature and time of annealing, in vacuum ( $< 10^{-5}$  Torr) using a chamber of the sputtering apparatus.

Measurements of the photocurrent and dc-dark current were performed for as-deposited and annealed specimens with the coplanar structure with a length in 7mm and a gap in 0.8mm formed by vacuum-deposited Al electrodes. Ohmic characteristics were obtained in the dark and also under illumination at electric fields of less than 850V/cm. The photocurrent  $I_p$  was measured at 750V/cm using an electrometer at room temperature as a function of wavelength of excited light between 350 and 700nm with a resolution of 1nm. The dc-dark current  $I_d$ , namely thermally activated

current, passing through the specimen was measured at 30V/cm as a function of temperature ranging from 290 to 418K. All measurements of  $I_p$  and  $I_a$  were carried out in a cryostat evacuated to  $10^{-5}$ Torr.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig.1 are shown experimental results of X-ray diffraction pattern for the specimens of ZS11, ZSO11 and ZSO12 annealed at 200°C for 4min. In this figure, it is seen that the specimen prepared using pure Ar(ZS11) has polycrystalline (poly) structure, whereas those using a mixture of Ar and O<sub>2</sub> (ZSO11 and ZSO12) become amorphous one. These results were also unchanged for the specimens of ZSO13 and ZSO14 annealed at 200°C for 120min. From this structural difference, it is suggested that oxygen atoms existing in ZnSe disturb largely atomic configuration in ZnSe. Here, results of composition analysis obtained by ESCA are presented in Table 1.

Figure 2 shows experimental curves of photocurrent  $I_p$  against wavelength of excited light for the specimens of ZS12, ZSO13 and ZSO14 annealed at  $T_A=200^\circ\text{C}$  for  $t_A=120\text{min}$ . In Fig.2, a hump of photocurrent  $I_p$  is observed at 430nm and 500nm for all specimens. The hump at 430nm, which is nearly equal to a photon energy of 2.8eV, corresponds to band-to-band excitation in ZnSe. The hump of  $I_p$  at 500nm(2.5eV) is thought to be caused by flow of electrons excited by photon absorption from a defect center (I) to the conduction band  $E_c$  in ZnSe as shown in Fig.3. Furthermore, a hump of  $I_p$  at about 550nm(2.2eV) is observed for the specimens ZSO13 and ZSO14 annealed at 200°C for 120min, and is also considered to be due to the flow of electrons emitted from an another defect center(II) to the conduction band  $E_c$  in a-ZnSe. Origin of these defect centers will be discussed later.

Figure 4 shows Arrhenius plots of experimental dc-dark conductivity  $\sigma_a$  obtained from the measured  $I_a$  for the same specimens as those used for photocurrent measurements presented in Fig.2. Thermal activation energy

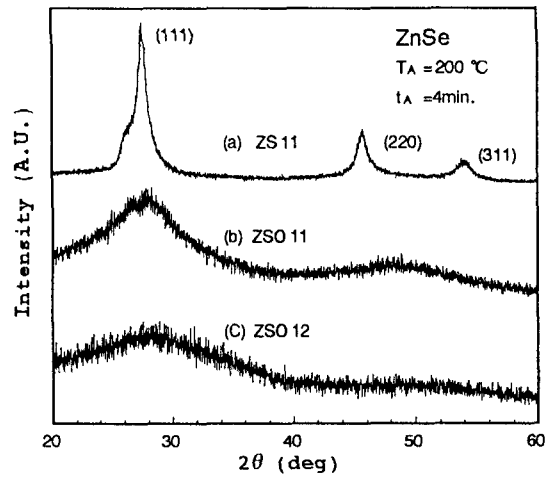


Figure 1. X-ray diffraction patterns for sputtered ZnSe films. Deposition was performed using pure Ar(16.0sccm) for the specimen ZS11, and using a mixture of Ar(15.0sccm) and O<sub>2</sub>(1.0sccm) for ZSO11 and of Ar(13.0sccm) and O<sub>2</sub>(3.0sccm) for ZSO12. These specimens were annealed at 200°C for 4min.

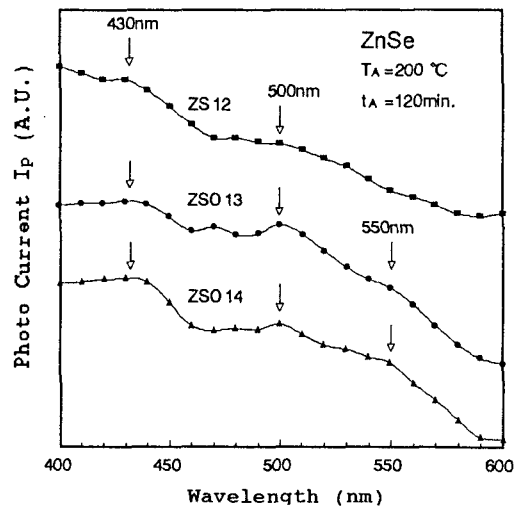


Figure 2. Photocurrent  $I_p$  measured at room temperature plotted against wavelength of excited light for sputtered ZnSe films. Specimen ZS12 was prepared using pure Ar(16.0sccm), ZSO13 using a mixture of Ar(15.0sccm) and O<sub>2</sub>(1.0sccm) and ZSO14 using a mixture of Ar(13.0sccm) and O<sub>2</sub>(3.0sccm). These specimens were annealed at 200°C for 120min.

$\Delta E$  of  $\sigma_a$  is estimated from a slope of a straight line of  $\sigma_a$  vs.  $1/T$  shown in Fig.4: We obtained  $\Delta E=0.36\text{eV}$  for ZS12,  $\Delta E=0.69\text{eV}$  for ZSO13 and  $\Delta E=0.61\text{eV}$  for ZSO14. It will be pointed out later that these values of  $\Delta E$  correspond to a thermal ionization energy of acceptor center located above the valence band edge  $E_v$  in ZnSe. It is seen that the value of  $\Delta E \approx 0.6\text{eV}$  for the specimens with a large amount of oxygen, namely ZSO13 with 13.5at% O and ZSO14 with 30at% O, is larger than  $\Delta E=0.36\text{eV}$  for ZS12 with 0.8at% O. It should be noted here that the specimen ZS12 was prepared using only pure Ar, but it contains a small amount of oxygen (2.8at%) introduced probably due to contamination for a longer annealing time ( $t_A=120\text{min}$ ).

In the following, we discuss the behavior of defect centers characterizing the experimental photocurrent  $I_p$  and dc-dark current  $I_a$  shown in Figs.2 and 4. If the defect center (I) with 2.5eV and (II) with 2.2eV obtained from the measured  $I_p$  can act as acceptor centers in a-ZnSe,  $I_a$  by holes activated thermally from these centers to the valence band edge  $E_v$  should be observable. Surely, as shown in Fig.4,  $I_a$  supporting this idea was observed above room temperature, giving the activation energy of  $I_a$  with  $\Delta E=0.36\text{eV}$  (the specimen No ZS12) and with  $\Delta E=0.61\text{eV}$  (ZSO14) and  $0.69\text{eV}$  (ZSO13) above the valence band edge  $E_v$ . However,  $I_a$  with  $\Delta E=0.36\text{eV}$  for ZSO13 and ZSO14 was unmeasured, and it shows that the center (I) acts only as an electron emitting one to the conduction band  $E_c$  caused by absorption of photon with  $\sim 2.5\text{eV}$ . It is interesting to note that  $\Delta E=0.36\text{eV}$  (ZS12) of  $I_a$  nearly coincides with that estimated by subtracting 2.5eV (the excited photon energy showing a hump of  $I_p$  at 500nm in Fig.2) from 2.8eV of the experimental band gap  $E_g$  in a-ZnSe. Also, the same discussion can be made for the specimens ZSO14 and ZSO13: Values of  $\Delta E = 0.61\text{eV}$  and  $0.69\text{eV}$  for  $I_a$  are nearly equal to that of a difference between 2.8eV and 2.2eV as shown in Fig.3. Thus, it is reasonable to consider that the defect center (I) for ZS12 and (II) for ZSO13 and ZSO14 behave as the acceptor ones in a-ZnSe.

Possibilities that the defects in ZnSe show

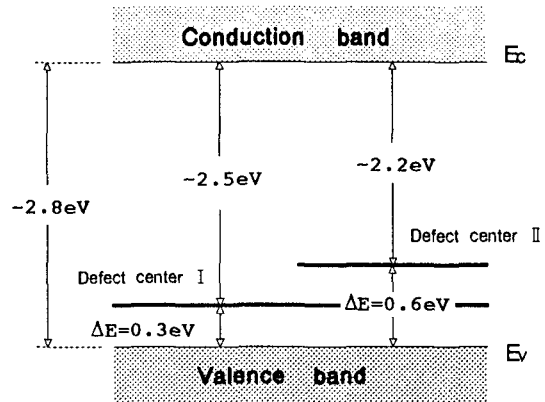


Figure 3. Energy band diagram characterizing the photocurrent and dc-dark current measured for ZnSe films prepared using pure Ar and a mixture of Ar and  $O_2$ .

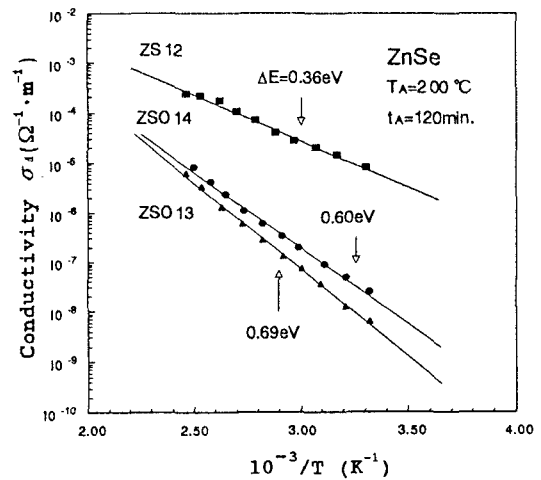


Figure 4. Arrhenius plots of conductivity  $\sigma_a$  obtained from measured dc-dark current for sputtered ZnSe films. Specimens of ZS12 (prepared using 16.0sccm Ar), ZSO13 (a mixture of 15.0sccm Ar and 1.0sccm  $O_2$ ) and ZSO14 (13.0sccm Ar and 3.0sccm  $O_2$ ) were annealed at  $200^\circ\text{C}$  for 120min.

the acceptor nature have been discussed by other workers: Igaki and Satoh reported [3] that the p-type conduction may be caused by Zn vacancies or complexes containing Zn vacancies as native acceptors in Se rich ZnSe crystals. On the other hand, Helms pointed out [4] that the p-type nature will arise from the defects associated with interstitial oxygen

Specimen NO	Ar (sccm)	O <sub>2</sub> (sccm)	T <sub>A</sub> (°C)	t <sub>A</sub> (min)	Zn(at%)	Se(at%)	O(at%)
ZS 11	16.0	0	200	4	50.7	49.3	0
ZSO 11	15.0	1.0	200	4	50.5	37.5	12.0
ZSO 12	13.0	3.0	200	4	50.0	19.4	30.6
ZS 12	16.0	0	200	120	49.2	48.0	2.8
ZSO 13	15.0	1.0	200	120	51.0	35.5	13.5
ZSO 14	13.0	3.0	200	120	50.2	19.8	30.0

Table 1. Conditions of sputtering and annealing treatments for ZnSe films including results of composition analysis for them.

or a complex involving interstitial oxygen using Zn/Se/O phase diagram for ZnSe containing oxygen. In the case of the present work, a possibility relating to Zn vacancies is excluded because the ratio Se/Zn is less than unity for all specimens as presented in Table 1. In this respect, it should be noted here that the poly specimen of ZS12 is nearly at stoichiometry, but it contains 2.8at.%O. The amorphous specimens of ZSO13 and ZSO14 contain a large amount of oxygen such as 13.5 and 30at.%O and deviate considerably from stoichiometric composition, especially a lack of Se. Thus, it is expected that the center (I) with acceptor nature observed at 0.36eV above  $E_v$  for ZS12 is mainly associated with the small amount of interstitial oxygen in poly-ZnSe. For ZSO13 and ZSO14, as mentioned above, the center (I) located at  $\sim 2.5$ eV below  $E_c$  behaves only as an electron emitting center to the conduction band caused by photon absorption as shown in Fig.3. The reason for this is not clear at present.

On the other hand, the defect center (II) showing the acceptor nature observed by the measurements of  $I_p$  and  $I_d$  for ZSO13 and ZSO14 can be explained as follows: In view of the fact that the specimens ZSO13 and ZSO14 contain a large amount of oxygen and Se defects as shown in Table 1, it is expected that a number of interstitial oxygen and a complex involving interstitial oxygen related to Se defect should exist in these specimens. Hence, we conclude that the defect center (II) is associated with interstitial oxygen and a complex involving interstitial

oxygen related to Se defects as pointed out by Helms[4], so that the photocurrent and dc-dark current are dominated by this center with acceptor nature in a-ZnSe.

Finally, we comment on the acceptor nature with respect to the defect center(II)[4]. In compound such as selenites, the selenium is considered to have the valences of 6 or 4, so that some electron transfer from the selenium atom to the oxygen would be expected, in addition to that from the zinc atom. In this respect, we would expect the oxygen interstitials present in ZnSe to behave in a similar fashion. Hence, the excess positive charge would be distributed around the neighboring Zn and Se atoms leading to an defect level with effective acceptor character.

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