Journal of Luminescence 48 & 49 (1991) 685-688
North-Holland

Photovoltaic characteristics of a ZnS_xSe_{1-x}/GaAs heterojunction with gradually changed x

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Heteroepitaxial layers of ZnS_xSe_{1-x} with gradually changed x are grown on GaAs substrates by means of VPE. ZnS and ZnSe powders are vaporized and the vapor is carried by a flow of H_2 gas. Their photovoltaic characteristics are studied. An open circuit voltage of 0.76 V and a short circuit current of 32.9 mA cm^{-2} are obtained. The highest efficiency for the solar cells of ZnS_xSe_{1-x}/GaAs without antireflection coatings is 11%, 2% higher than that of ZnSe/GaAs cells fabricated in our laboratory. This value is found to be strongly dependent on the annealing temperature of ZnS_xSe_{1-x} thin film.

1. Introduction

Recently, increasing attention has been paid to the development of photoelectric conversion devices utilizing semiconductor heterojunctions. n-ZnSe/p-GaAs solar cells have been regarded as one of the promising candidates for achieving high efficiency as well as a flat photoresponse spectrum in the visible region. Sahai et al. [1] predicted that a n-ZnSe/p-GaAs heterojunction has the potential of surmounting GaAs and Si solar cells in efficiency. Gaugash et al. [2] described photovoltaic cells of ZnSe/GaAs on ZnSe substrates. The efficiency is about 8-9% under simulated solar conditions. In the ZnSe/GaAs cells, ZnSe was deposited by CVD onto GaAs substrates. The efficiency is reported to be 7% by Besomi [3].

Although the band gap of ZnSe($E_g - 2.7$ eV) is wide enough to transmit the whole visible effectively into narrow-gap GaAs($E_g = 1.43$ eV), there is still a "dead layer" in these cells. It is very significant to develop a cell with wider E_g for space technology in order to use the ultraviolet region of sun light. For this reason, we prepared ZnS_xSe_{1-x}/GaAs heterojunction devices in which the x value is gradually varied from 0 to 1 on the basis of ZnSe/GaAs cell.

2. Experimental details

ZnSe source was synthetized from single substance Zn (99.99999%) and Se (99.9999%) under a H_2-O_2 flame. It was then purified twice. p-GaAs single crystals (Zn-doped, p: 10^{18} cm^{-3}) were used as substrates. Its orientation is (1 0 0) or 2° decline from (1 1 0). Before epitaxy, polished GaAs substrates were rinsed with $ClCHCCl_2$, CH_3COCH_3, C_2H_5OH and de-ionized water, etched with a solution of 3:1:1 $H_2SO_4:H_2O:H_2O_2$ at 50°C for 1 min and treated in boiling HCl for 3 min. Then the substrates were thoroughly rinsed with de-ionized water and put into the reaction chamber. The substrates, and the ZnSe and ZnS sources were heated 100°C for 12 h, at 300°C for 1 h and at 620°C for 5 min in order to remove the water and organic matters. Figure 1 shows the relation between x and T_{ZnS} (temperature of ZnS source). Table 1 gives the typical growth conditions for ZnS_xSe_{1-x} thin film on the substrates of GaAs.

As the resistivity of as-grown ZnS_xSe_{1-x} layers is as high as 10^5 Ωcm, the sufficient output current from the junction cannot be obtained. We reduced the sample resistivity by means of Zn saturated vapour at 600°C for 15 h as stated in ref. [4]. This method is found to be more effective for the

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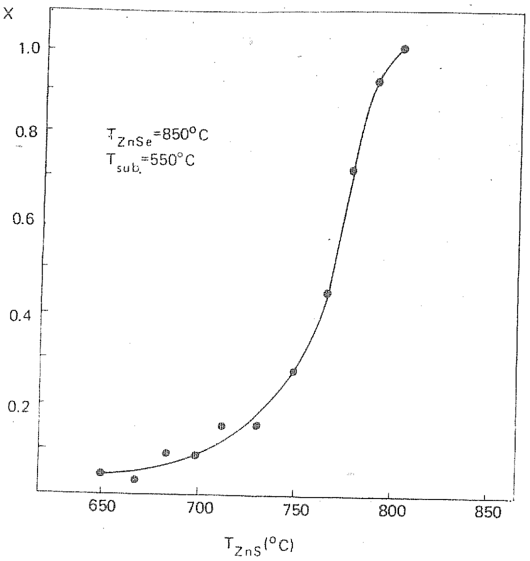

Fig. 1. Relation between x value and T_{ZnS}.

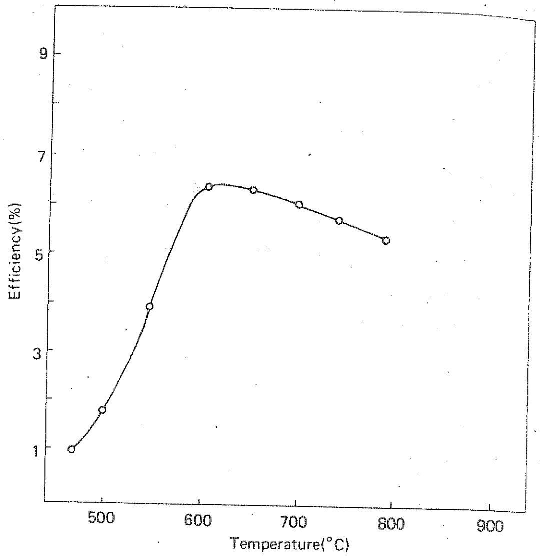

Fig. 2. Efficiency of ZnS_xSe_{1-x} solar cells as a function of annealing temperature.

ZnS_xSe_{1-x} thin layers. As GaAs substrates are doped with Zn(10^{18} cm^{-3}), Zn-treatment for ZnS_xSe_{1-x} does not destroy the electrical properties of the junction [5]. A series of experiments for reducing resistivity have been done at different temperature and the dependence of efficiency on annealing temperature has been obtained (fig. 2).

On both sides of the samples In electrodes were formed by means of the annealing at 300°C in a N_2 atmosphere for 3 min. In order to compare these cells with those of ZnSe/ GaAs, thin layers of ZnSe were grown onto GaAs substrates in the same way as in $ZnS_xSe_{1-x}/GaAs$.

3. Results and discussion

Figure 3 is the X-ray diffraction pattern of (4 0 0) for $ZnS_xSe_{1-x}/GaAs$. The diffractive angles for ZnSe, GaAs and ZnS are 66.12°, 66.25° and 69.70°, respectively. Figure 3 shows a continuous band from 66.081° to 69.699° as well as three sharp diffractive peaks ascribed to ZnSe, GaAs and Zns. This means that x in thin films of ZnS_xSe_{1-x} is gradually changed from 0 to 1. The other experiments, such as the photoluminescence spectra, also lead to this conclusion.

Table 1
Growth conditions for $ZnS_xSe_{1-x}/GaAs$ (x: 0-1).

T_{ZnSe}	T_{ZnS}		$T_{sub.}$	$J^{H_2}_{ZnSe} = J^{H_2}_{ZnS}$
	Temperature range	Heating rate		
850°C	25°C–500°C 500°C–650°C 650°C–800°C	1.5°C/min 0.5°C/min 0.25°C/min	550°C	50 cm^3/min

T_{ZnSe}: temperature of ZnSe source.
T_{ZnS}: temperature of ZnS source.
$T_{sub.}$: temperature of GaAs substrates.
$J^{H_2}_{ZnSe}(J^{H_2}_{ZnS})$: H_2 rate of flow for ZnSe(ZnS) source.

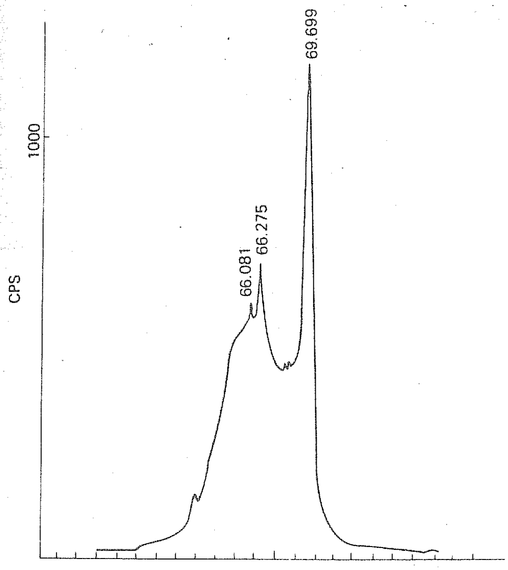

Fig. 3. X-ray diffraction pattern (4 0 0) ZnS_xSe_{1-x}/GaAs.

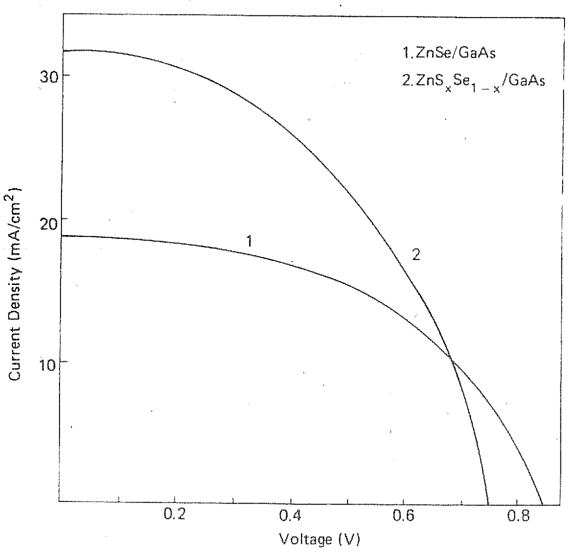

Fig. 4. J–V characteristics and simulated solar radiation of 100 mW/cm^2 for ZnSe/GaAs and ZnS_xSe_{1-x}/GaAs.

Figure 4 shows the J–V load characteristics excitation by simulated solar radiation of 100 mW cm^{-2} for n-ZnSe/p-GaAs and n-ZnS_xSe_{1-x}/GaAs (x: 0–1). The open circuit voltage is 0.86 V for ZnSe/GaAs, 0.76 V for ZnS_xSe_{1-x}/GaAs and the short circuit current is 18.5 mA cm^{-2} for ZnSe/GaAs, 32.9 mA cm^{-2} for ZnS_xSe_{1-x}/GaAs. The corresponding conversion efficiency is 9% for ZnSe/GaAs, and 11% for ZnS_xSe_{1-x}/GaAs.

The efficiency of a ZnS_xSe_{1-x}/GaAs solar cell is 2% higher than that of ZnSe/GaAs. The reason is that the ZnS_xSe_{1-x}/GaAs solar cell has a better spectral response in the range from 1.43 to 3.6 eV and this solar cell shows almost no "dead layer". However, using ZnSe/GaAs or ZnS_xSe_{1-x}/GaAs solar cells, the short circuit current is very low although the open circuit voltage is high. It is thought that a lot of defects exist in the interface. These defects capture carriers and the short circuit current is diminished.

The relation between the temperature at which we reduced the sample resistivity and solar cells efficiency has been studied (fig. 2). At temperatures lower than 600°C, the efficiency increases with increasing temperature. This is because the V_{Zn}(Zn vacancy) concentration in epitaxial layers is reduced and the intrinsic concentration of donors is increased. At temperatures higher than 600°C, the efficiency decreases because the donor concentration is so high that there is a shrink of the forbidden band which leads to the diminishing of the short circuit current.

4. Summary

ZnS_xSe_{1-x} thin films with gradually changed x have been grown successfully on GaAs substrates by VPE technique. A solar cell with 11% efficiency is obtained. At the same time, ZnSe/GaAs solar cells with 9% efficiency are achieved. This value of efficiency is the highest for ZnSe/GaAs. Efforts are under way for improving short circuit current.

Acknowledgement

The authors would like to thank Professor Yibing Li and Professor Xiwu Fan for helpful assistance.

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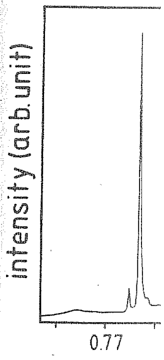

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