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High Electron-Mobility ZnSe Films Grown by Low-Pressure MOCVD

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Growth of high electron mobility ZnSe films has been examined by low-pressure MOCVD. It is shown that the films having electron mobilities as high as 8400 $cm^2/V.sec$ at about 40 K can be obtained. The shallow donor concentration in these nominally undoped films are about 10^{15} - 10^{16} cm^{-3}. It is shown that the growth rate of the films should be set carefully low to obtain high quality films, since the growth temperature for the films is extremely low.

1. Introduction

For II-VI compounds such as ZnSe, MOCVD is expected to be a method which will overcome the "self-compensation effect", since the epitaxy temperature is very low and device quality films can be obtained as well as in the case of MBE. Several workers[1-5] have recently demonstrated MOCVD of ZnSe films on GaAs substrates, and the films were characterized by photoluminescence, electrical properties, etc. However, although MOCVD ZnSe films exhibited a strong near-band-edge photoluminescence as well as in the case of MBE ZnSe films, the electron mobility in MOCVD films at low temperatures (77 K or below) was much lower than that of MBE films.[6]

The authors have already reported that how the growth conditions, such as the substrate temperature and the VI/II source gas molar ratio, affect the photoluminescence and electrical properties of ZnSe films grown on (100) GaAs.[7,8] Furthermore, it has been pointed out that the growth rate of the films should be very low to obtain high quality films,[9] because the growth temperature for MOCVD of ZnSe is extremely low compared to that for MOCVD of other semiconductors such as GaAs.

In this paper, high quality ZnSe films obtained under optimum growth conditions, which were determined on the basis of the data obtained in our previous work, have been characterized by the temperature dependence of electron mobility in the range from 15 to 300 K and DLTS analysis. It is shown for the first time that high quality films having electron mobilities as high as about 8400 $cm^2/V.sec$ at around 40 K can be grown by low-pressure MOCVD and the concentration of electron-trap deep centers in the films is less than the shallow donor concentration by a factor of about 100.

2. Experimental

ZnSe films were deposited by low-pressure MOCVD using DMZn and H_2Se diluted to 10 % in H_2 as reactants. Sample preparation and measurements of ZnSe layer characteristics were performed almost the same way as previously reported.[7-9] Typical flow rates were 4 x 10^{-6} mol/min for dimethylzinc (DMZn), and 2 x 10^{-4} mol/min for H_2Se. The substrate temperature during the deposition was varied in the range 325 - 350°C in the present work. The reactor pressure was maintained at between 0.33 and 1.0 Torr. For the substrate material, Cr-doped and/or undoped semiinsulating (100) GaAs was used.

Electrical properties were measured by the Van der Pauw method. For the DLTS measurements of ZnSe films, planer-type Au-ZnSe Schottky diodes were used.

3. Results and Discussion

Electrical and photoluminescence properties of nominally undoped ZnSe films are greatly influenced by the substrate temperature during the growth and the $(H_2Se)/(DMZn)$ source gas molar ratio, and their effects on the layer characteristics can be briefly summarized as follows:[7-9]

(1) The carrier concentration in the nominally undoped films is mainly determined by the substrate temperature. The carrier concentration decreases with the substrate temperature, and it can be controlled between 10^{15} and 10^{19} if the substrate temperature are below 350°C. When the substrate temperature exceeds 350°C, the films become highly resistive.

(2) The carrier concentration in the films also decreases with the (VI)/(II) source gas molar ratio and higher source gas molar ratio is preferable from the viewpoint of obtaining the films with low impurity concentrations.

Furthermore, as stated before, since the growth temperature for MOCVD of ZnSe is very low, the film growth rate must be very low to obtain good crystallinity films so that the film growth is controlled by the mass-transport rate. Since the purpose of the present investigation is to grow electrically high quality ZnSe films (i.e., low impurity concentraion and high electron mobility), the substrate temperature and the VI/II source gas molar ratio were set at 325

- 350°C and 50, respectively.

Generally, since the electron mobility in heteroepitaxial films increases with the thickness, first, the film thickness dependence of electrical properties of ZnSe films grown at 350°C has been examined. The reactor pressure was maintained at 1 Torr, and the growth rate of the films was about 0.85 μm under conditions stated above. The results are shown in Fig.1. The electron mobility at 77 K increases with the film thickness and it is about 3000 - 5000 and about 1100 $cm^2/V.sec$ for 3 and 1 μm thick films, respectively. It is shown that in order to reduce the effect of lattice mismatch between the layer and the substrate on the electron mobility, the film thickness should be greater than about 1 μm for the growth conditions stated above. Because the electron mobility in the 0.5 μm thick film is remarkably smaller than that of others. As for

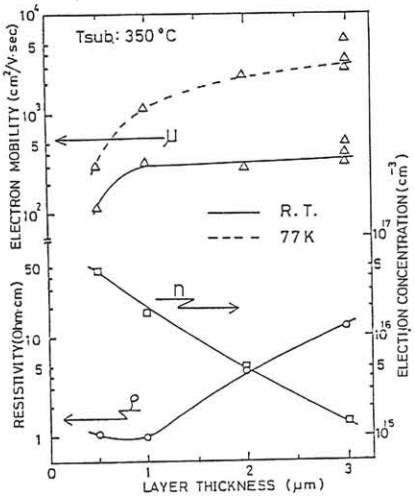

Fig.1 Film thickness dependence of nominally undoped ZnSe films grown at 350°C and 1 Torr

the carrier concentration, it monotonically decreases with the film thickness. It is shown that ZnSe films with carrier concentrations as low as 10^{15} - 10^{16} cm^{-3} can be easily grown when the film thickness is 1-3 μm. The reason why the carrier concentration decreases with the thickness is not clear as yet, but the result of thickness dependence of the carrier concentration may imply that the origin of the dominant donor species in these unintentionally doped ZnSe films is attributed to the diffused species from the substrate surface.

Figure 2 shows the temperature dependence of electron mobility in a nominally undoped ZnSe films grown on (100) GaAs at 350°C. The film was grown at 350°C and its thickness is 3 μm. The electron mobility becomes a maximum at around 40 K and it is as high as 8400 $cm^2/V.sec$. To author's knowledge, this is the highest value ever observed in epitaxial ZnSe films. Since the maximum value of the electron mobility is quite large and it is observed at very low temperature, the concentration of electron-scattering centers in the film is considered to be low. The carrier concentration in the film is as low as 5 x 10^{15} cm^{-3} at room temperature. The reason why such

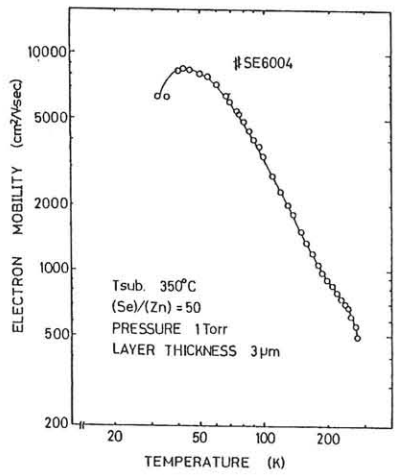

Fig.2 Temperature dependence of electron mobility in a 3 μm thick ZnSe film.

high electron mobility and low carrier concentration films can be obtained is attributed partly to the effect of the low film growth rate and partly to the optimization of other growth conditions such as the substrate temperature and VI/II source gas molar ratio.

The activation energy for donor species taken simply from the temperature dependence of the carrier concentration in a nominally undoped films grown at about 350°C is almost the same as that previously reported for a shallow hydrogenic donor.[10] This indicates that the degree of the carrier compensation is low. According to the least-squares curve fitting of the observed data to the equation for a partially compensated semiconductor, the compensation ratio in the films is about 0.1.[11]

As mentioned before, the ZnSe layer characteristics are remarkably influenced by the growth rate and it should be very low to obtain high quality ZnSe films. Then, in order to obtain much higher quality ZnSe films, electrical properties of the films grown under reduced growth rate have been examined. In practice, the films were grown at lower reactor pressure, because the growth rate decreases with the decrease in the pressure

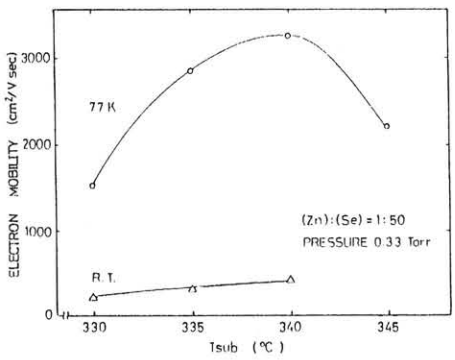

Fig.3 Growth temperature dependence of electron mobility at 77 K and 300 K in the films grown at reduced growth rate (about 0.2 - 0.3 μm/hr).

due to the effect of pressure dependence of the sticking coefficient of DMZn.[12] Figure 3 shows the growth temperature dependence of the electron mobilities at 77 and 300 K in the films grown at about 0.33 Torr. The growth rate of these films were about 0.25 - 0.3 μm/hr, and the film thickness is about 0.76 - 0.88 μm. It is shown that, although the film thickness is less than 1 μm, the electron mobility at 77 K in the film grown at 340°C is as high as 3280 $cm^2/V.sec$. As shown in Fig.1, the electron mobility at 77 K in the film grown under the growth rate of about 0.8 μm/hr is about 1100 $cm^2/V.sec$, which is much smaller than that of the film grown at reduced growth rate. Thus, it was reconfirmed that the growth rate of the film must be very low to obtain high quality films since the growth temperature is extremely low. Furthermore, the resistivity of the films grown at 350°C was so high that it was difficult to measure their electrical properties, though the resistivity of the film grown at the same temperature at 1 Torr remained to be low. It was found that the substrate temperature, at which the resistivity of the films becomes very high, tends to be low as the reactor pressure decreases.

In order to investigate deep levels in MOCVD ZnSe films, DLTS analysis of ZnSe films grown at 350°C and 1 Torr were performed. Figure 4 shows a DLTS spectrum for an Au-ZnSe Schottky diode. Two dominant peaks were observed in MOCVD ZnSe films as shown in the figure. The activation energy, capture cross section and the concentration of the deep center for two peaks are summarized in Table I. The activation energy for the peak observed at about 185 K (ME2) is 0.32 + 0.01 eV and its concentration is about 6×10^{12} - 1.5×10^{13} cm^{-3}. As for the peak observed at about 345 K (ME4), the activation was roughly estimated to be about 0.56 -0.66 eV, but since the observed DLTS signals for ME4 is very broad and noisy the calculated result is not so accurate. The carrier concentration in the film is about 1.5×10^{15} cm^{-3} at room temperature, and then the concentration of electron-trap deep centers in MOCVD films was found to be less than the shallow donor concentration by a factor of about 100.

Thus, it has been shown from the several experiments that both the carrier compensation ratio and the concentration of electron trap deep centers in nominally undoped ZnSe films grown under nearly optimum growth condition are rather low. From the fact stated above, the cause for the growth temperature dependence of the carrier concentration in the films can be

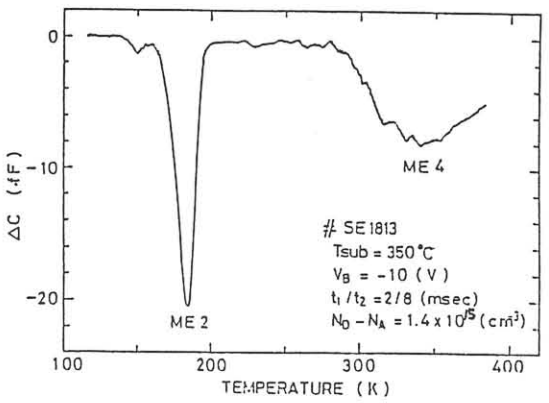

Fig.4 DLTS signal for a typical high quality ZnSe film.

explained. First, two reasons for the decrease in carrier concentration with the temperature were considered as follows:

(1) The concentration of the dominant donor species itself decreases with the temperature, while the concentration of the carrier compensation center being kept constant.

(2) Inverse case for (1), i.e., the concentration of the compensation center increases with the temperature, while the concentration of the dominant donor species being kept constant.

However, if the decrease in the carrier concentration with the temperature is attributed to the reason stated in the item (2), the carrier compensation ratio in the films grown at above 350°C becomes highly resistive. Then the reason stated in the item (1) is plausible for the cause of the decrease in the carrier concentration with the temperature. As for the dominant donor species in the unintentionally doped ZnSe, it will be discussed elsewhere.

4. Conclusion

Growth of high electron mobility ZnSe films has been examined by the low-pressure MOCVD. It has been shown that the films having electron mobilities as high as 8400 $cm^2/V.sec$ at about 40 K can be obtained under nearly optimum growth conditions. The shallow donor concentrations in these nominally undoped films are about 10^{15} - 10^{16} cm^{-3}. It was found that the electron trap deep center concentration in the film is less than the shallow donor concentration by a factor of about 100. Furthermore, it has been pointed out that in order to obtain high quality ZnSe

Table I Summary of DLTS analysis for MOCVD ZnSe films.

	Au No.	activation energy (eV)	capture cross section (cm^2)	trap concentration (cm^{-3})	peak Temp. range (K)
ME 2	1	0.319	8.93×10^{-15}	$(6.6-16) \times 10^{12}$	171-187
	3	0.334	2.53×10^{-14}		171-187
	4	0.325	1.70×10^{-14}	$(3.4-5.5) \times 10^{12}$	170-186
ME 4	1	0.557	7.69×10^{-16}	$(9.7-16) \times 10^{12}$	319-351
	3	0.661	6.14×10^{-14}		311-337
	4	0.657	4.62×10^{-14}	$(5.0-7.3) \times 10^{12}$	313-339

films the growth rate of the films must be set carefully low, since the growth temperature for the films is extremely low. It was found that the films having electron mobility as high as 3280 $cm^2/V.sec$ can be grown at reduced growth rate even though the film thickness is as low as 0.88 μm.

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