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ArF Excimer Laser Induced Epitaxial Growth of ZnSe on GaAs Using Organic Compounds

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ArF excimer laser irradiation effects were examined in the epitaxial growth of ZnSe using metal organic compounds as source materials. An enhancement of the growth rate and a lowering of the epitaxial growth temperature have been confirmed as compared with conventional MOCVD. The dominant kinetics of the laser irradiation growth seems to be likely an excitation of DMSe or some gas/surface reaction. The relative PL intensity of the deep emission band to the exciton emission band was very weak.

1 Introduction

Wide band gap II-VI compound semiconductors, ZnSe and ZnS, have a potential application in blue light emitting devices. Metal organic chemical vapor deposition (MOCVD), a successful epitaxial growth technique for III-V materials, is also valid for the epitaxial growth of these II-VI compound semiconductors.(1) However, it is more difficult to reduce intrinsic defect formation in II-VI semiconductor crystal growth than in a III-V semiconductor. The ZnSe epitaxial layer quality for p-n junction devices have not been reported as yet. The photo-induced epitaxial growth technique has possibilities of improving crystal quality, because of its low temperature growth due to the excitation of surface reactions including surface migration and photolysis of source materials.(2)-(6)

In this paper, the authors have demonstrated for the first time the ArF excimer laser induced epitaxial growth of ZnSe on GaAs using metal organic compounds as source materials and have discussed the laser irradiation effects on the growth rate, epitaxial growth temperature and quality of the epitaxial films.

2 Experimental

2-1 Laser induced MOCVD growth

Figure 1 shows a schematic diagram of the experimantal apparatus. The growth chamber is made of stainless steel, which can be exhausted to a pressure of 10^{-7} torr by cryo-pump prior to introducing source gases. The growth chamber is equipped with a loading chamber, so the substrate can be introduced to the growth chamber without exposure to atmosphere. Cr-doped semi-insulating (100)GaAs wafers were used as substrates. The substrate was placed on a carbon susceptor which was heated by a halogen lamp. The growth temperature was monitored by a pyrometer. Dimethylzinc (DMZn) and dimethylselenide (DMSe) were used as source materials, which could absorb the ArF excimer laser energy (λ=193nm).(7)(8) During growth,the substrate was irradiated by an ArF excimer laser beam through a synthetic quartz window. Hydrogen gas purge was used to prevent deposition of ZnSe on the

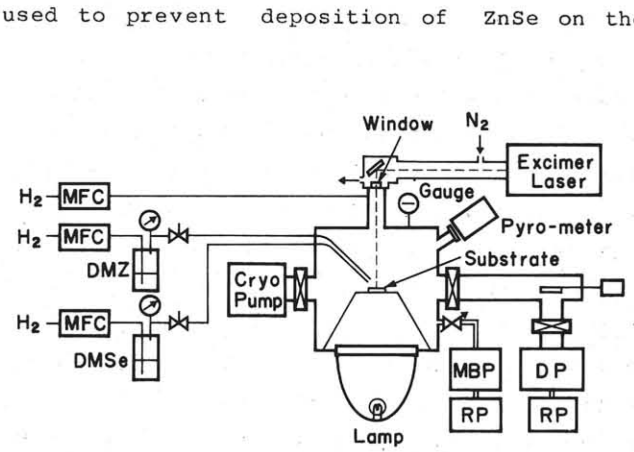

Fig.1 Schematic diagram of the experimental apparatus

window. The growth of ZnSe was carried out under low pressure. Typical growth parameters are listed in Table 1.

Table 1 Typical growth parameters

DMZn Flow Rate (Q_{II})	7.7×10^{-5} mol/min H_2 39sccm
DMSe Flow Rate (Q_{VI})	1.07×10^{-4} mol/min H_2 100sccm
H_2 (Window Purge)	200 sccm
Growth Pressure (P_G)	50 Torr
Growth Temperature (T_S)	200°C ~ 400°C
Introduced Laser Power (I_0)	2.4 W/cm^2 (80pps)

2-2 Evaluations

Thicknesses of the grown layers were observed by using a scanning electron microscope. The crystallinity of the grown layers was evaluated from X-ray diffraction and double crystal X-ray diffraction measurements by the Cu Kα1 line. The quality of the grown layers was evaluated by the photoluminescence spectrum at 4.2K using a He-Cd laser (λ=325nm) as the excitation source.

3 Results and discussions

3-1 Laser irradiation effect on the growth rate

Figure 2 shows a growth temperature dependence of the growth rates with and without the laser irradiation. Under no laser irradiation (thermal MOCVD process), the growth rate depends strongly on the growth temperature. If the growth rate conforms to the Arrhenius' equation, the activation energy is about 24 kcal/mol.

Under laser irradiation, the growth rate increased dramatically as compared with that of the thermal MOCVD process, and had a constant value in the growth temperature range from 250°C to 400°C. This indicates that the laser irradiation growth is limited by photochemical reactions which are quite different from conventional MOCVD. In the temperature range over 400°C, the growth rate increased as the temperature was raised. It seems to be likely that a pyrolysis process in addition to a photochemical process contirbutes to the growth in the temperature range over 400°C. No film growth occurred below 200°C, but ZnSe flakes was deposited on the substrate.

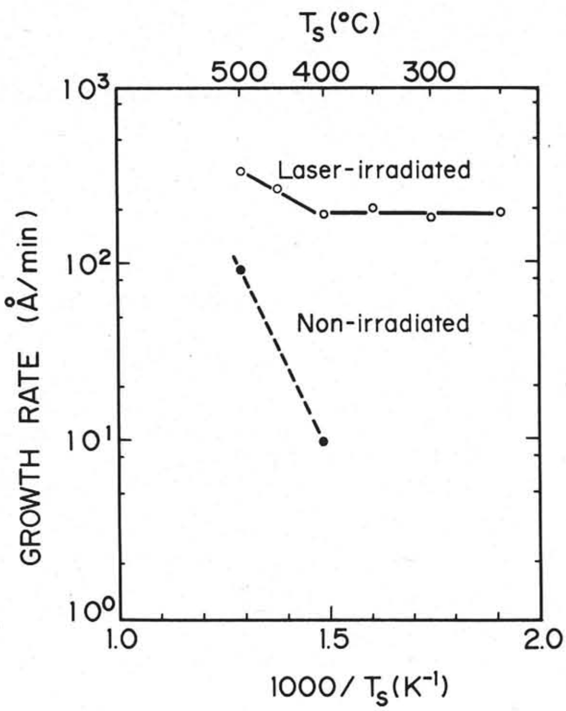

Fig.2 Temperature dependence of growth rate with and without laser irradiation. Other growth parameters are listed in Table 1

The crystallinity of the ZnSe films was characterized by the X-ray diffraction pattern. Single crystals were obtained in the growth temperature range over 350°C. The temperature of 350°C is rather low as compared with that of conventional MOCVD using metal organic compounds. Figure 3 shows the double crystal X-ray

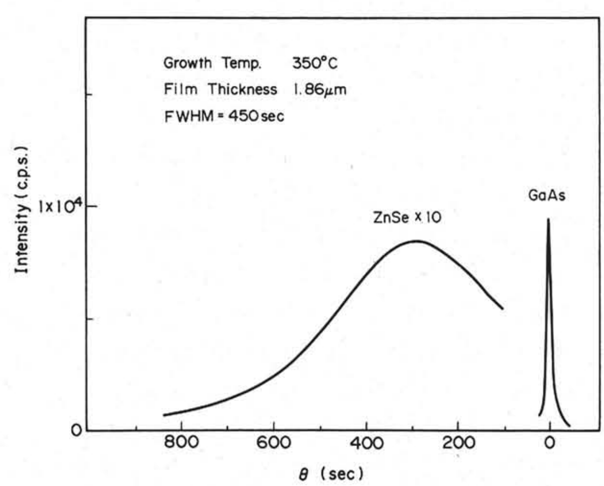

Fig.3 Double crystal x-ray diffraction pattern of ZnSe film grown at 350°C by laser irradiation.

diffraction pattern of a ZnSe film grown at 350 °C. Film thickness was 1.86μm. FWHM (full width at half maximum) was about 450 sec. A ZnSe single crystal which compares favorably with that of conventional MOCVD can be obtained at 350 °C by laser irradiation.

3-2 Growth kinetics

In order to study the growth kinetics in laser irradiation growth, dependences of the growth rate on induced laser power (I_0), and flow rates of DMZn (Q_{II}) and DMSe (Q_{VI}) were examined. These data are shown in Fig.4. Other growth parameters are listed in Table 1 and the growth temperature was 400 °C. The growth rate increases linearly as I_0 is raised. On the other hand, the growth rate had a maximum value at a certain flow rate of DMZn and DMSe. Here, we assumed that predominant effect of the laser irradiation was the excitation of source gas species in the gas phase. It seems that the concentration of reactive species near the surface is reflected in the growth rate. The concentrations of photoexcited DMZn and DMSe are in proportion to $P_{II}I_s$ and $P_{VI}I_s$, respectively, where P_{II}, P_{VI} and I_0 represent DMZn partial pressure, DMSe partial pressure and the laser intensity near the surface, respectively. I_s can be expressed approximately as $I_0\exp(-\alpha L)$,where α and L represent the gas phase absorption coefficient and optical path length between the window and substrate surface,respectively. Then the growth rate (R) can be expressed as Eq.(1) when both gas species are excited by the laser irradiation and can be expressed as Eq.(2) when a single source gas species is excited by the laser irradiation.

$$R \propto P_{II}\ P_{VI}\ I_0^2 \exp(-2\alpha L) \quad ...(1)$$

$$R \propto P_{II}\ P_{VI}\ I_0 \exp(-\alpha L) \quad ...(2)$$

As shown in Fig.5, all data points shown in Fig.4 composed a linear correlation, when the growth rates were plotted against Eq.(2). This indicates that a single source gas species is excited preferentially by the laser irradiation. DMSe will be excited predominantly by the laser irradiation, because DMSe is highly stable as compared with DMZn.[9] From the nature of Eq.(2), there is another possibility of an excitation of some gas/surface reaction such as a reaction of DMZn and DMSe on the surface or a decomposition of adsorbed species on the surface.

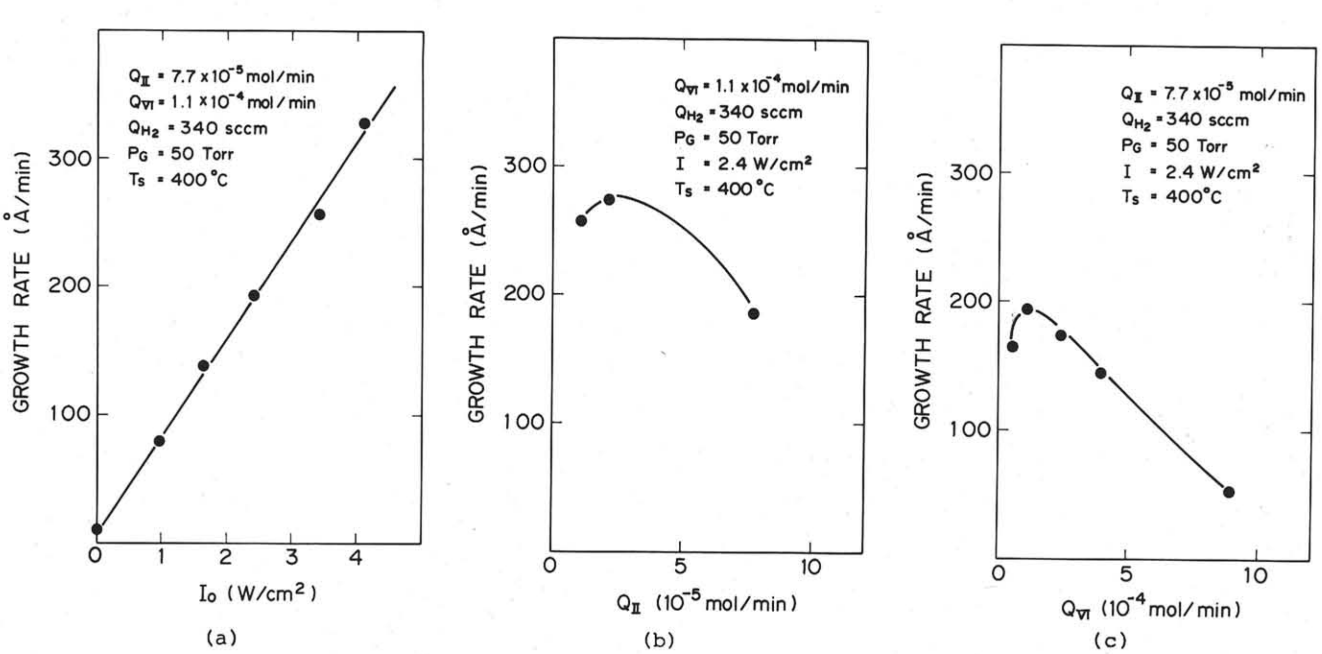

Fig.4 Dependences of the growth rate on (a) introduced laser power, (b) flow rates of DMZn and (c) DMSe. Other growth parameters are listed in Table 1.

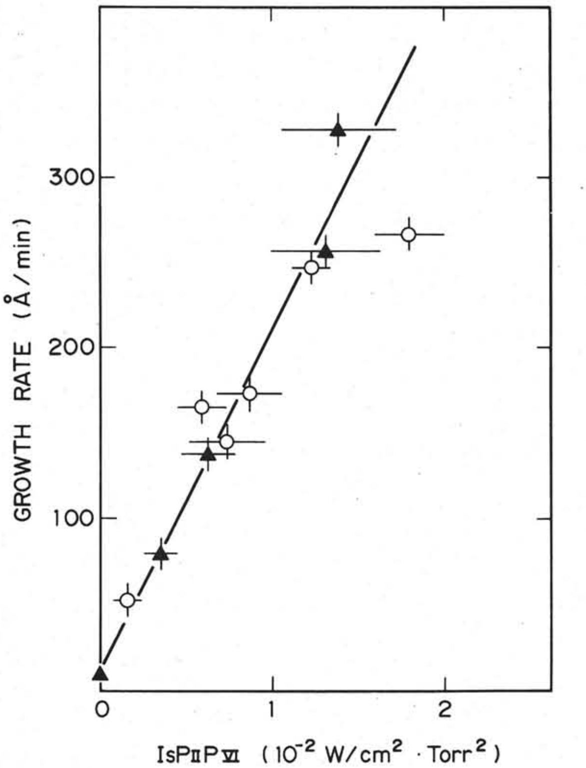

Fig.5 Growth rate against $P_{II}P_{VI}I_0\exp(-\alpha L)$ (▲), dependence of growth rate on introduced laser power.
(O), dependence of growth rate on flow rates of DMZn and DMSe.

3-3 Photoluminescence spectrum

Figure 6 shows a PL spectrum at 4.2K for a ZnSe film grown at 400 °C by laser irradiation. Film thickness was 1.98 μm. The spectrum consisted

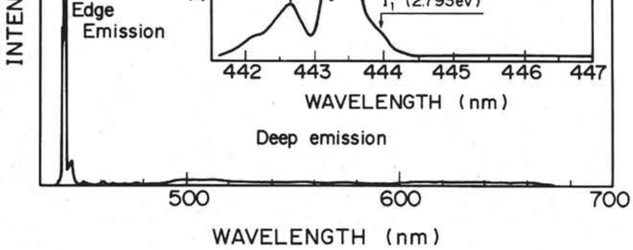

Fig.6 Photoluminescence spectrum at 4.2K of ZnSe film grown at 400°C by laser irradiation.

mainly of an edge emission band. The edge emission band consisted of a free exciton emission line E_x(2.801ev) and bound exciton emission lines I_2(2.798ev), I_x(2.796ev),[10] and I_1^S(2.793ev). The relative PL intensity of the deep emission band to the edge emission band was rather weak as compared with that of conventional MOCVD using metal organic compounds as source materials. It seems to be likely that complex defects due to intrinsic defects are small in the ZnSe films grown by the ArF laser irradiation.

4 Summary

The effects of ArF excimer laser irradiation on the growth of ZnSe using metal organic compounds have been confirmed. A large enhancement of the growth rate can be obtained in the growth temperature range from 250 °C to 400 °C. The predominant mechanism of the enhancement are speculated as the excitation of DMSe or some gas/surface reaction. It has been revealed that laser irradiation could realize epitaxial growth at low temperature. The relative PL intensity of the deep emission band to the exciton emission band was rather weak as compared with that of conventional MOCVD. The ArF excimer laser induced epitaxial growth is to be a promising technology in II-VI semiconductor epitaxial growth.

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