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Reactor Pressure Dependence of Properties of Undoped ZnSe Grown by Low-Pressure OMVPE

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Undoped ZnSe epitaxial layers were successfully grown at a temperature ranging from 250 to 350°C onto (100) GaAs substrates by a low-pressure organometallic vapor-phase epitaxy using dimethylzinc (DMZ) and H_2Se as source materials. The epilayers exhibited photoluminescent spectra at room temperature consisting of strong near band-edge emission at 2.69 eV and weak deep-level emission at around 2.0 eV. The intensity ratio of the near band-edge to the deep-level emissions was observed to increase with decreasing the reactor pressure.

§ 1 Introduction

ZnSe with a direct band-gap energy of 2.7 eV at room temperature is a promising material for blue light emitting devices which can be widely used in various optoelectronic application. For such application, however, high-quality single crystals are essential in which electrical and optical properties can be well-controlled.

An organometallic vapor-phase epitaxy(OMVPE) for the growth of ZnSe has recently attracted much attention, because of its feasibility of epilayer growth and impurity doping at lower growth temperatures, T_G's [1-6] (T_G denotes the substrate temperature) than other conventional vapor-phase epitaxial methods [7]. Recently, highly conductive n-type ZnSe epilayers have been grown onto GaAs substrates without intentional doping at a T_G as low as 250°C by a low-pressure OMVPE [5]. However, optimization of the growth parameters such as growth rate, growth temperature, reactor pressure, and residual impurities in the source gases is still of great importance for the growing ZnSe epilayers with quality high enough for device application.

In this paper, we describe the OMVPE growth of undoped ZnSe epilayers onto (100) GaAs substrate as a function of reactor pressure P_G, and the influence of P_G on growth rate and electrical and luminescent properties is reported.

§2 Experimental

The low-pressure OMVPE growth system (Samco MCV-1030A) used in this work is illustrated in Fig.1. The ZnSe layers were grown using dimethylzinc ($(CH_3)_2Zn$, DMZ) and a 5%-H_2Se diluted in H_2 as source materials at a T_G = 250 ∿ 350°C onto Cr-doped semi-insulating (100) GaAs substrates. In the present experiment, the flow rates of the source gases into the reactor were kept constant, i.e., [VI]/[II]=2.9 with $[H_2Se]=9.3\times10^{-5}$ mol/min and $[DMZ]=3.2\times10^{-5}$ mol/min. The reactor pressure was controlled by a throttle valve placed between the reactor tube and a normal rotary pump (850 l/min), and the growth was carried out at a P_G in a pressure range from 10 to 0.1 Torr.

Prior to the growth, the GaAs substrates were etched for 2 min by a solution of H_2SO_4 : H_2O_2 : H_2O= 5:1:1 in volume, followed by a thorough rinse in pure methanol. After being loaded into the reactor, the substrate was heated in a pure hydrogen stream at 550°C for about 10 min for a heat cleaning, and then the substrate was held at a T_G between 250 and 350°C.

§3 Results and Discussions

3-1 Growth Rate and Morphology

The crystalline quality of the grown layers was characterised by measurements of X-ray diffraction and RHEED. At T_G's higher than 250°C, the layers were confirmed to be epitaxial.

The growth rate of the ZnSe layer was investigated as a function of P_G. As shown in Fig. 2, the rate is seen to increase with increasing P_G but to tend to be saturated at P_G's higher than about 1 Torr, almost regardless of T_G's ranging from 280 to 320°C. Since the flow rate of each source gas supplied into the reactor is maintained at a constant value, the rise of P_G results in decrease in velocity thus increase in concentration of the source gases. Therefore, the saturation effect of the growth rate at high P_G's could be interpreted in terms of some premature reactions due to the high concentration of the source gases; the occurrence of these reactions in vapor phase make less contribution to increase in the deposition rate of ZnSe onto the substrate.

Typical examples of the surface morphology of about 4 μm thick layers grown at T_G=350°C at two different P_G's of 0.1 and 6.2 Torr respectively, as shown in Fig. 3. Similar to a morphology observed by Stutius [8], hillocks along <0$\bar{1}\bar{1}$> direction appear and remarkable change in the morphology cannot be seen between the two epilayers. The mechanism of such a hillock formation remains unknown, and the elucidation of the reaction mechanism of the source materials used is essential to obtain a specular surface morphology needed for device applications.

3-2 Electrical Properties

The electrical properties of the grown layers on semi-insulating (100) GaAs substrate (>10^7 Ω•cm) were measured by the van der Pauw method. The layers grown at T_G's adopted here showed a low resistive n-type conductivity without any intentional doping and no remarkable P_G dependence of the electrical properties. At T_G=300°C, for example, electron concentration in the epilayers grown at P_G's between 0.1 and 6.5 Torr were of the order of 10^{16} cm^{-3}. It is still not known whether the origin of donor species is due to intrinsic defects such as selenium vacancy or to some extrinsic impurities. However, it should be noted that the OMVPE technique can produce such high conductive ZnSe layers in which the concentration of acceptor-like impurities or defects which compensate the donor is thought to be greately reduced.

3-3 Photoluminescence

Photoluminescence(PL) spectra were measured by 365nm excitation from a 500-W Hg lamp using a conventional lock-in technique. Figure 4 shows PL spectra at 300K (room temperature, RT), 77K, and 4.2K, respectively, of a 8 m thick epilayer grown at T_G=300°C and P_G=0.1 Torr which is the lowest pressure attainable in the present system. At RT and 77K, the spectra consisted of strong near band-edge emissions peaking at 2.689 eV and 2.786 eV respectively and very weak self-activated (SA) emissions at a longer wavelength region. Taking into account the emission peak energy and the temperature dependence of free exciton energy in ZnSe [9], the near band-edge emission at each temperature may be arised from radiative recombination of shallow donor electrons and free holes (FB) in the valence band. At 4.2K, the I_2 line, exciton emission bound to neutral donor, located at 2.797 eV [3] predominated over an entire spectrum and no D-A pair emission was observed. These results mean again that the concentration of acceptor-like impurities or defects is extremely reduced in the epilayers grown under those growth conditions.

When the reactor pressure was decreased, the intensity ratio of the near band-edge emission to the SA emission in the PL spectrum at RT was observed to have remarkable P_G dependence as shown in Fig. 5 where the ratio is seen to increase with decreasing P_G in the epilayers at T_G=300 and 350°C. Although the definite reasons for the P_G dependence have not been well-understood at the present stage of this work, if we assume that the higher growth rate at a growth temperature as low as 300 to 350°C would cause the less crystalline quality, the relative increase in the SA emission intensity at higher P_G's, i.e., at higher growth rates could be explained in terms of the dependence on the growth rate of the microscopic crystalline quality which can be revealed neither by the Hall measurements nor by the X-ray measurements used here. The facts that the saturation effect in the growth rate was seen at higher P_G's, as described in the previous section, and that the ZnSe layers grown at a very low temperature of 200°C was substantially polycrystal and exhibited the intense SA emission would support in part the above consideration.

§4 Summary

By the low-pressure OMVPE technique, we have succeeded in growing highly conductive ZnSe epilayers (ρ= 0.1∿10 Ω•cm) onto (100) GaAs substrate with strong near band-edge blue emission at a growth temperature as low as 250 ∿ 350°C and at a reactor pressure as low as 0.1 Torr which is the lowest pressure attainable in the present growth system.

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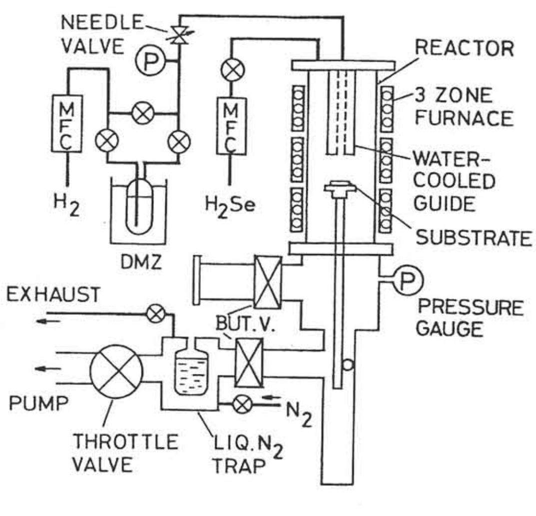

Fig. 1 Schematic illustration of an OMVPE equipment used in the present experiment.

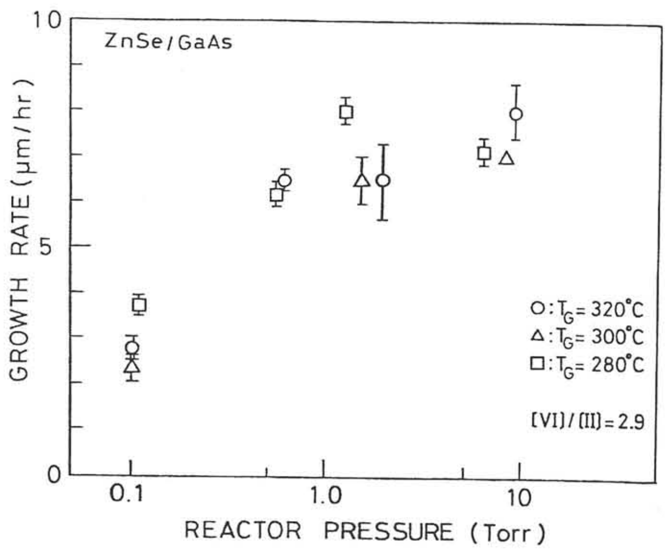

Fig. 2 Reactor-pressure dependence of the growth rates of the epilayers grown at T_G=280-320°C.

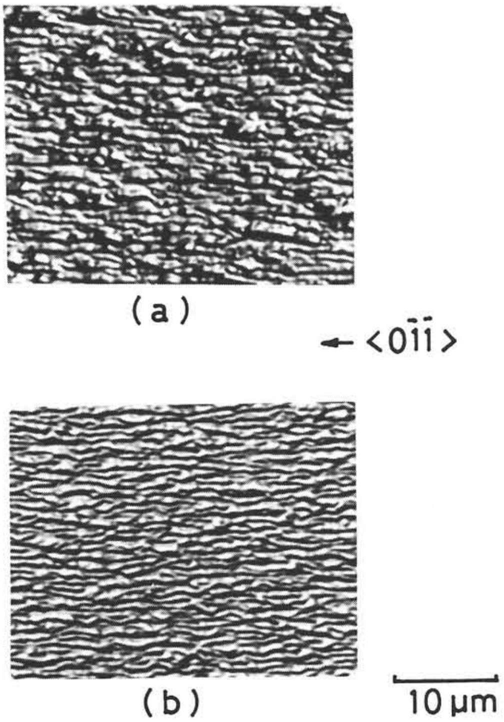

Fig. 3 Nomarski microphotographs of the epilayer surfaces at T_G=350°C; (a) at P_G=0.1 Torr, (b) at P_G=6.2 Torr. Thickness of the grown layers is about 4μm.

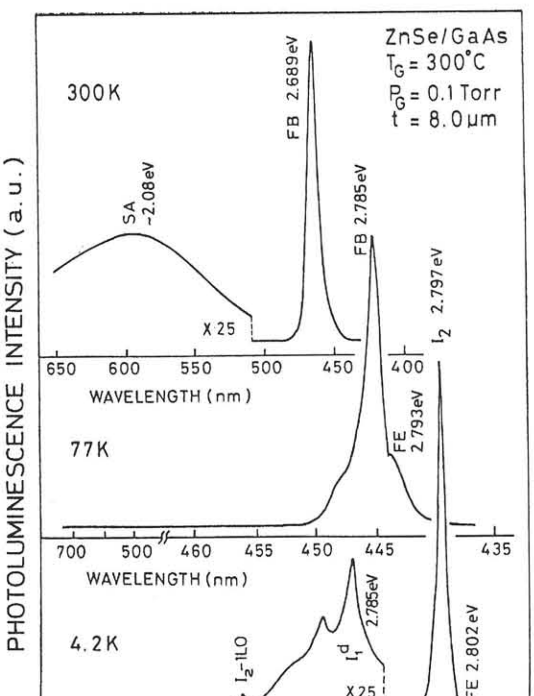

Fig. 4 Photoluminescence spectra at 300, 77, and 4.2K of an epilayer with thickness of 8.0 μm at T_G=300°C

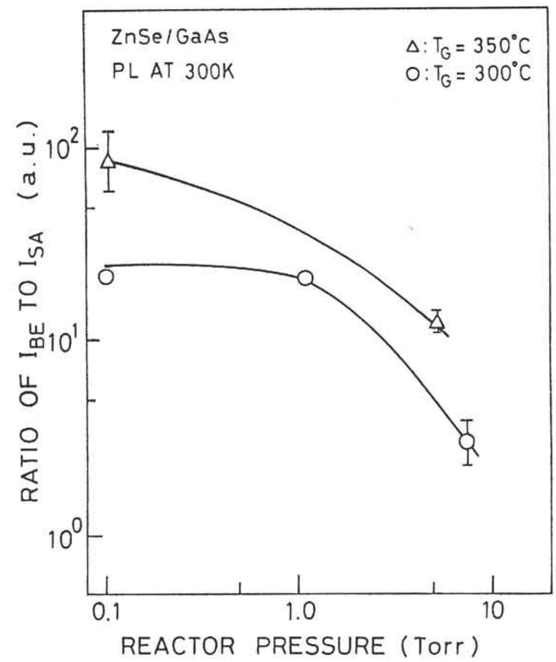

Fig. 5 Reactor-pressure dependence of the ratio of the near band-edge emission intensity (I_{BE}) to the SA emission intensity (I_{SA}).