논문 96-5-2-08

OMVPE and Plasma-Assisted Doping of ZnSe with Dimethlzinc:triethylamine Adduct Source

Jeung-Soo Huh[#] and Jeong-Ok Lim[*]

Abstract

The growth and microwave plasma assisted nitrogen doping of ZnSe by low pressure organometallic vapor phase epitaxy(OMVPE) has been investigated in a vertical downflow reactor equipped with a laser interferometer for *in-situ* growth rate measurements. Particular emphasis is placed on understanding growth characteristics of H_2Se and the new adduct source dimethylzinc:triethyllamine(DMZn:NEt_3) as compared with those obtained with H_2Se and DMZn. At lower temperatures (<300℃) and pressures(<30Torr), growth rates are higher with the adduct source and the surface morphology is improved relative to films synthesized with DMZn. Hall measurements and photoluminescence spectra of the grown films demonstrate that DMZn and DMZn:NEt_3 produce material with comparable electronic and optical properties. Microwave plasma decomposition of ammonia is investigated as a possible approach to increasing nitrogen incorporation in ZnSe and photoluminescence spectra are compared to those realized with conventional ammonia doping.

1. Introduction

The successful p-type doping of ZnSe by nitrogen through the use of rf plasma sources in molecular beam epitaxy(MBE) systems and the related development of quantum well devices [1,2] have renewed interest in thin film deposition of wide band Ⅱ-Ⅵ compound semiconductors. The advances made in MBE have yet to be mirrored by organometallic vapor phase epitaxy (OMVPE) which would have advantages for manufacturing of large area devices. There have been several reports of apparent p-type doping of ZnSe by lithium and nitrogen[3-5], but although significant nitrogen incorporation levels have been measured ($\sim 10^{18}cm^{-3}$), the p-type conductivity has been very low, if at all detectable, ($\sim 10^{15}cm^{-3}$). Film with excellent electronic and optical properties have been synthesized at relatively low temperatures (<350℃) through the use of hydrogen selenide (H_2Se) and dimethylzinc(DMZn) [6]. The film morphology was, however, poor, presumably because of parasitic prereactions in the gas-phase between the selenium and zinc reagents. The use of Lewis bases, such as triethylamine(NEt_3), complexed with the zinc triethylamine source(i.e. DMZn:NEt_3) has been found to minimize prereactions with hydrogen selenide and improved growth morphology for OMVPE at atmospheric pressure[7]. Nevertheless, this approach allows one to exploit the low growth temperatures and good electrical properties associated with the use of hydrogen selenide while having reduced problems with prereactions. Here we report on further investigations of the

Department of Metallurgical Engineering, Kyungpook National University
* Sensor Technology Research Center, Kyungpook National University
<접수일자 : 1996년 1월 11일>

growth characteristics of the DMZn:NEt_3-H_2Se system with particular emphasis on identifying low pressure conditions where plasma stimulated doping may be feasible.

2. Experimental Procedures

Figure 1 shows a schematic diagram of the low pressure vertical, stagnation flow OMVPE reactor used for growth and a microwave plasma stimulated nitrogen doping of ZnSe. An Evanson 1/4 - λ microwave cavity (Optos Instrument), energized by a 100W, 2.45GHz power supply, was installed around the quartz tube immediately upstream of the substrate for generation of a NH_3 plasma.

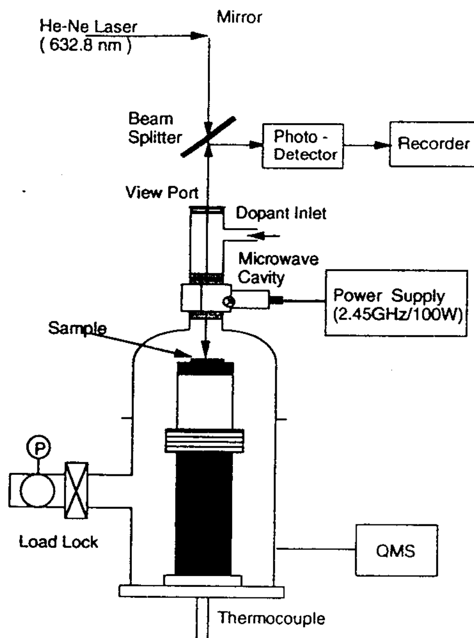

Fig. 1. Schematic diagram of low pressure OMVPE reactor equipped with microwave plasma cavity.

Dimethylzinc:triethylamine (DMZn:NEt_3, Epichem), Dimethylzinc(DMZn, Air products), and hydrogen selenide (H_2Se, Solkatronic Chemicals) were used as reactants and ammonia(NH_3, Matheson) was selected as a dopant source. Substrates were semi-insulating(100) GaAs, misoriented 2° towards <110> and were prepared according to standard procedures[8]. Samples were grown at temperatures between 225℃-400℃. All films investigated in the present study were 5±0.5μm thick and single crystalline, as confirmed by X-ray diffraction and photoluminescence(PL). The surface morphology was examined by scanning electron microscopy (SEM). Electrical properties were evaluated by measurements of sample resistivity and Hall-effect mobilities. PL spectra were obtained at 4K by using He-Cd laser (λ =325nm) at low density (<10mW/cm^2) and analyzed using a 0.85m SPEX 1404 double grating monochromator and GaAs photon multiplier tube. Spectral resolution in the range of interest was better than 0.5cm^{-1}.

3. Results and Discussion

A. Film Properties

Surface morphologies of ZnSe films prepared with DMZn and the adduct, DMZn:NEt_3 are determined from SEM measurement. Since epilayer crystallinity and morphology greatly depend on the growth temperature, SEM photographs of films grown between 275℃-375℃ are shown in figure 2. In agreement with previous reports[8], ZnSe layers grown by using H_2Se and DMZn exhibit a ridge-shape hillock structure, parallel to the (011) cleavage plane. Films synthesized with DMZn:NEt_3 display a similar surface morphology at high temperatures (325℃) where as at reduced temperature(275℃) the surface is smoother than that obtained with DMZn. At 375℃ the hillock has lost their sharp, well defined edges. Higher growth temperatures resulted in further coarsening of the surface.

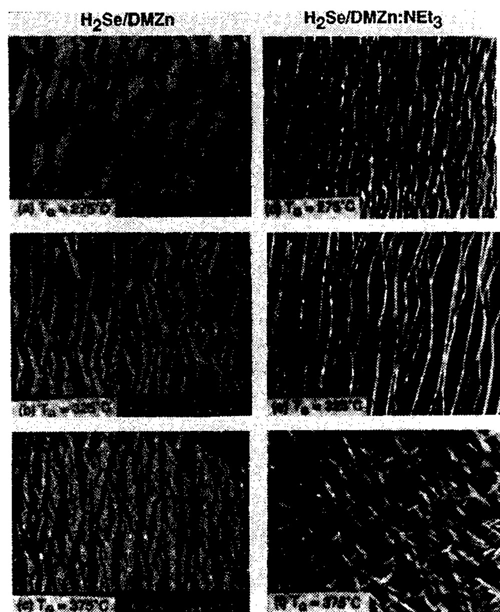

Fig. 2. SEM micrographs of ZnSe grown H_2Se and either DMZn (left hand side) or DMZn:NEt_3 (right hand side). Conditions: VI/II=10, P=30 Torr, and growth temperatures (a), (c) T_G=275℃ and (b), (d) T_G=325℃ and (c), (f) T_G=375℃.

Figure 3 compares measured growth rates for the different source combinations : DMZn and DMZn:NEt_3 as a function of growth temperature. The growth rate appears to be limited by some process at lower temperature and decrease exponentially at higher temperatures. The unusual decline in ZnSe growth rate observed for DMZn/H_2Se with increases in temperature is due to a competitive parasitic reaction having a lower activation energy than normal growth process and parasitic reaction is becoming dominant at high temperature. Use of Lewis base adduct increases the deposition rate at low temperatures, but has no effect at high temperatures. This behavior is consistent with the relatively low energies involved in adduct formation and stabilization (~10kcal/mol) compared to those required to break chemical bond (~40kcal/mol). Thus, at high temperatures the adduct is dissociated, and stabilization of any intermediate formed is no longer formed. It is apparent that there are no kinetic or mass transfer limited regimes, which would be another indication of parasitic prereactions occurring between H_2Se and the Zn sources.

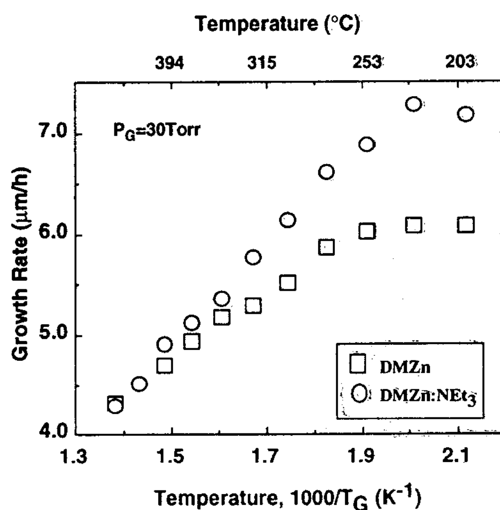

Fig. 3. Growth rates of ZnSe as a function of reciprocal growth temperature(K). Layers deposited at 30 Torr with H_2Se and either DMZn or the adduct DMZn:NEt_3 (VI/II=10 and H_2Se flow rate 150μ mol/min).

Electrical properties of selected ZnSe films grown from H_2Se/DMZn:NEt_3 were measured. All sample measured were n-type with 300K net carrier concentrations ranging from 1.7×10^{14} to $2.3 \times 10^{16} cm^{-3}$. The 77K mobility value of 4309cm^2/Vsec is relatively high for ZnSe films from H_2Se/DMZn:NEt_3 since the purity DMZn:NEt_3 source is not pure enough to compare with commercially pure DMZn presently.

A typical low temperature(4K) photoluminescence (PL) spectrum of normally undoped ZnSe samples, grown at the optimal condition of GaAs substrates, is shown in figure 4. An expansion of

near-band-edge emission is given in the inset of the figure. This sample was grown at 325℃, 30Torr and Ⅵ/Ⅱ ratio of 8. The spectrum is dominated by a strong near-band-edge(NBE) emission, while the broad emission at smaller energies(deep levels) is weak. The 4K spectrum is dominated by a intense and narrow peak at 2.7954eV(I_x^{lh}). This is due to a radiative recombination of an exciton bound to a neutral donor, identified as chlorine which can explain the n-type conductivity of these films. A second dominant peak is clearly defined at 2.7970(I_x^{hh}) and has been attributed to recombination of exitons bound to the same shallow extrinsic neutral donor. There are also two peaks due to free exciton recombination : the very intense E_x^{lh} at 2.8002eV and, on the high side, the E_x^{hh} at 2.8026eV. The samples are ~3㎛ thick.

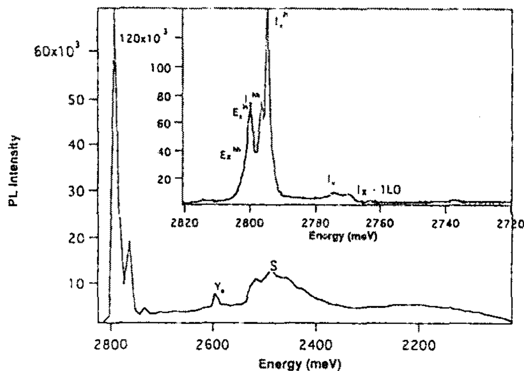

Fig. 4. The photoluminescence spectrum of ZnSe from H_2Se and DMZn:NEt_3. The inset of the figure is an enlargement of the near-band-edge luminescenec spectrum.

Figure 5 shows the near - band - edge photoluminescence spectra for ZnSe grown with the adduct at different temperatures. The spectra are similar to those previously reported for DMZn [9], and display no sign of nitrogen incorporation from the amine portion of adduct. The intensity of the donor-bound exciton peak, I_x^{lh}(2.7954eV), decreases relative to that of the free exciton peak, E_x^{lh}(2.8002eV), with increasing growth temperature.

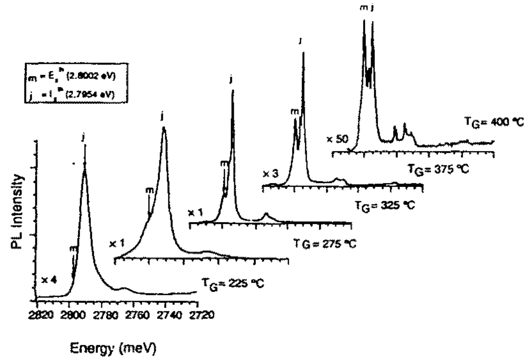

Fig. 5. Variation in near-band-edge photoluminescence spectra of ZnSe films with different growth temperature. E_x^{lh} : m ; I_X^{lh} : j. Films deposited with DMZn:NEt_3 and H_2Se at 30 Torr and Ⅵ/Ⅱ=10.

B. Nitrogen Doping

The above growth and characterization results demonstrate that it is feasible to deposit high quality ZnSe at low pressures through the use of the new adduct source. This mode of operation then provides the opportunity for exploring microwave plasma stimulated doping in addition to admitting the usual advantages of low pressure operation, such as improved uniformity and reduced natural convection effects. Here we present preliminary results of plasma doping in OMVPE of ZnSe. A remote microwave plasma source (cf. Figure 1) was used to precrack NH_3 upstream of the substrate and to avoid plasma cracking of the Se and Zn reagents. Initial investigations showed that feeding the reagents through the plasma zone resulted in excessive precracking and poor quality ZnSe films. With the remote plasma source the ZnSe growth characteristics were similar to those described above.

Figure 6 compares PL spectra for undoped ZnSe (a), NH3 doped ZnSe (b), and microwave plasma doped ZnSe (c). The PL spectrum for

undoped ZnSe (a) has a dominant donor bound exciton peak, I_x^{lh}, with negligible donor-acceptor pairs with zero phonon peak appearing at 2.695eV. The acceptor bound excitonic transition at 2.7906eV further indicates that nitrogen has been incorporated in the ZnSe. The PL data (c) resulting from remote plasma precracking of NH_3 show similar structure as that in (b) with an increased acceptor bound peak suggesting additional nitrogen incorporation.

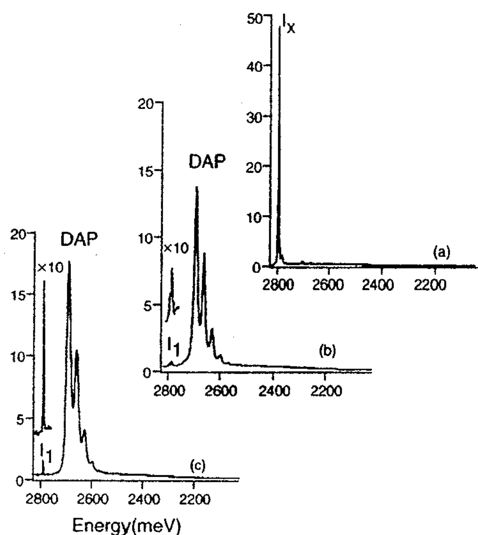

Fig. 6. Photoluminescence spectra of (a) undoped ZnSe, (b) NH_3 doped ZnSe, and (c) microwave plasma stimulated NH_3 doped ZnSe. (Conditions : growth temperature=275℃, pressure=3Torr, DMZn:NEt_3 flow rate=15μmol/min, Ⅵ/Ⅱ=10, NH_3/H_2Se=2.)

However, the films did not display measurable p-type conductivity as also reported in other nitrogen doping investigation of ZnSe[4]. The lack of measurable p-type conductivity of ZnSe when doping with NH_3 raises question of the role of hydrogen in the ZnSe films since hydrogen is known to influence electronic properties of many compound semiconductors[10].

4. Conclusions

Growth data demonstrate that use of the adduct reagent is particularly effective at lower temperatures (<300℃) and pressures (<30Torr). At those conditions growth rates are higher when using DMZn:NEt_3 and the surface morphology is improved relative to films synthesized with DMZn. Hall measurements and photoluminescence spectra of the grown films further show that DMZn:NEt_3 produce material with comparable electronic and optical properties to films grown with DMZn. Additional improvements in electronic properties of ZnSe may be expected, since the adduct is more easily purified than DMZn [11]. The low pressure growth open the possibility for microwave stimulated doping in OMVPE. First experiments with NH_3 shows promising results for this approach, but the deposition pressure will have to be reduced further to increase the concentration of radicals at the growth surface. This should also allow the replacement of NH_3 by N_2 as doping source.

5. Acknowledgment

The authors are grateful to Dr. K. F. Jensen(MIT) for OMVPE equipment and Kyungpook National University for financial support.

6. Reference

[1] R. M. Park, M, B. Troffer, C. M. Rouleau, J. M. Depuydt and M. A. Haase, *Appl. Phys. Lett., 57, 2127 (1990).*

[2] W. Xie, d. c. Grillo, R. L. Gunshor, M. Kobayashi, G. C. Hua, N. Otsuka, H. Jeon, J. Ding ans D. V. Nurmikko, *Appl. Phys. Lett., 60, 463 (1992)*

[3] H. Mitsuhashi, A. Yahata, T. Uemoto, A. Kamata, M. Okajima, K. Hirahara and T.

Beppu, *J. Crystal Growth, 101, 818, (1990).*

[4] A.Ohki, N. Shibata, K. Ando, and A. Katsui, *J. Crystal Growth, 99, 413, (1990).*

[5] T.Yasuda, I. Mitsuishi and H. Kukimoto, *Appl. Phys. Lett., 52, 57 (1988)*

[6] K. P. Giapis, D-C Lu and K. F. Jenson, *Appl. Phys. Lett., 54, 353 (1989)*

[7] P. J. Wright, P. J. Panbrook, B. Cockayne, A. C. Jones, E. D. Orell, K. P. O'Donnell and B. Henderson, *J. Crystal Growth, 94, 441, (1989)*

[8] W. S. tutius, *Appl. Phys. Lett., 38, 352 (1981)*

[9] K. P. Giapis, D-C Lu and K. F. Jenson, and J. E. Potts, *J. Crystal Growth, 104, 291, (1990)*

[10] B. Pajot, B. Clerjaud, and J. Chevallier, *Physica B 170, 371 (1991)*

[11] A. C. Jones, *Chemtronics 4, 15 (1989).*

著 者 紹 介

허 증 수

『센서학회지 제4권 제4호』 논문 95-4-4-12 참조.

현재 경북대학교 금속공학과 전임강사.

임 정 옥

『센서학회지 제4권 제4호』 논문 95-4-4-12 참조.

현재 STRC 전임연구원