The Journal of Korean Vacuum Science & Technology
Vol. 2, No. 2, October 1998, pp. 118~121

MOVPE of ZnSe with DIPSe and DMZn

Jeung-Soo Huh and Jeong-Ok Lim*

Department of Metallurgical Engineering
**Medical Research Institute, Kyungpook National University, Taegu, 702-701, Korea*
(Received August 26, 1998)

Abstract – Diisopropylselenide (DIPSe) is employed for the metalorganic vapor phase epitaxy (MOVPE) of ZnSe in order to eliminate premature gas phase reaction while maintaining negligible carbon incorporation and preserving relatively low growth temperature. In combination with dimethylzinc, single crystalline ZnSe layers were grown on GaAs at temperature around 450°C. Secondary ion mass spectrometry showed a negligible carbon incorporation in ZnSe films grown from DIPSe even at high [VI]/[II] ratios, in contrast of a carbon concentration of 10^{21} cm^{-3} in ZnSe films grown from diallyselenide (DASe). Crystalline and interface quality are demonstrated by secondary electron microscopy, secondary ion mass spectroscopy and double crystal X-ray diffraction.

1. Introduction

High quality epitaxial layers of ZnSe whose doping can be controlled have great potential for photonic and electronic applications such as blue light emitting diodes and optical recording systems. Lowering the growth temperature is also of particular importance in order to reduce the formation of native defects, improve dopant incorporation and control stoichiometry at hetero-junction. Growth temperature below 350°C can be only obtained with H_2Se as a selenium precursor in combination with zinc alkyls, from which the highest quality of ZnSe has been obtained [1]. However, the premature gas phase reaction between group II alkyl and group VI hydride adversely affects surface morphology and film thickness uniformify. Combined with its high volatility and flammability, H_2Se constitutes a health threat with a threshold limit value (TLV) of only 50 ppb [2]. Safety concerns and parasitic prereactions have already motivated the development of alternative Se sources which would be less likely to participate in parasitic reactions and be less hazardous [3]. The use of alkyl selenide has been shown to produce films with good surface morphology and photoluminescence spectra, but a high growth temperatures above 500°C is necessary for acceptable growth rate [4]. In ZnSe MOVPE growth chemistry and film properties can be controlled by changing the structures of the precursor species. From the general stability trend of metalorganics, thermal stability is decreased by increasing the number of hydrocarbon radicals directly bonded to the central carbon atom [5]. Hence, the reduction of growth temperature of ZnSe would be possible with diisopropylselenide.

Novel Se precursor, Diisopropyl selenide has been employed in conjunction with DMZn in order to eliminate parasitic prereaction while maintaining negligible carbon incorporation. This new Se source should show low reactivity at an ambient temperature, relatively high vapor pressure, acceptable toxicity and a suitable pyrolysis mechanism for negligible carbon incorporation.

2. Experimental

The ZnSe films were grown in a vertical down-flow OMVPE reactor equipped with a laser interferometer for in-situ growth rate measure-

ments. Electronic grade dimethylzinc(DMZn) as a Zn precursor was used in conjunction with novel organometallic Se source, diisopropylselenide (Air Products). Substrates were semi-insulating (100) GaAs, misoriented 2° toward <110> and were prepared according to standard procedure[6]. The deposition sequence was initiated with native oxide removal in 0.4 slm H_2 flow with Se overpressure in order to suppress As desorption. The films were grown at 300 Torr with a total flow rate of 1 slm of H_2 through the reactor. The growth temperature varied between 350~500°C. The DMZn delivery rate was maintained at 20 μmol/min while the delivery rate of DIPSe was varied between 10-120 μmol/min.

The surface morphology of ZnSe films was examined by scanning electron microscopy (SEM). The lattice parameter of ZnSe epilayer was measured by the double crystal diffractometer. A double crystal diffractometer (model 300, BEDE Scientific, Inc.) with $Cu_{K_{\alpha l}}$ radiation from a rotating anode X-ray generator (Model RU-200, Rigagu) is used. Symmetric ZnSe (004) rocking curves are taken and full widths at half maximum (FWHM) are compared for quantitative analysis of the quality of epitaxial layers.

Measurement of the carbon impurity levels in ZnSe was performed by secondary ion mass spectrometry (SIMS) with a detection limit for ^{12}C around 5×10^{17} cm^{-3}. Undoped ZnSe films grown from H_2Se/DMZn and showing no detectable carbon impurities were implanted with ^{12}C to provide an internal standard for SIMS measurement of the carbon concentration in ZnSe films. The implant had a peak ^{12}C concentration of 1×10^{19} cm^{-3}. The SIMS measurements were carried out with a Cameca IMS-4f spectrometer using C_s^+ primary ion beam with an incident energy of 10keV and ion current of 33nA, rastered over an area 100×100 μm^2. Negative secondary ions were monitored. Depth scales for the SIMS profiles were determined from measurements of the crater depths with a calibrated profilometer.

3. Results and Discussions

Growth rate were measured as a function of reciprocal growth temperature for ZnSe films grown from DIPSe in Figure 1. The growth rate is controlled by chemical kinetics below 450°C with apparent activation energy of 20Kcal/mol and become constant at higher temperatures which is indicative of mass controlled region. Figure 2 gives detailed growth rate dependence on the molar flow rate of DIPSe source at 450°C. The delivery rate of DMZn is constant with 20

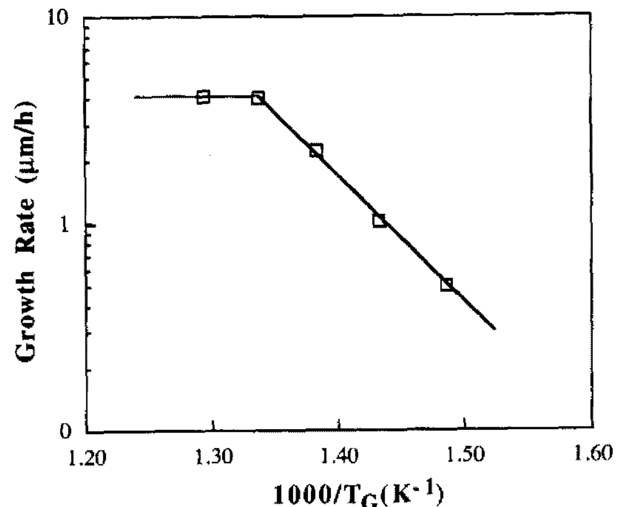

Fig. 1. The effect of temperature on the growth rate of ZnSe from DIPSe/DMZn (DMZn=20 μmol/min, VI/II = 2).

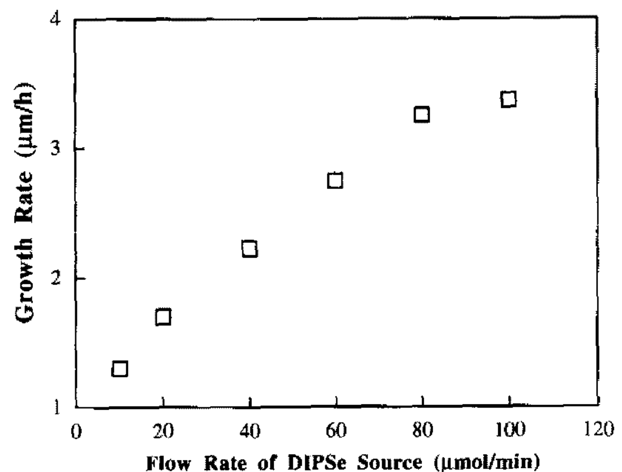

Fig. 2. The growth rate of ZnSe as a function of DIPSe source flow rate at 450°C (DMZn = 20 μmol/min).

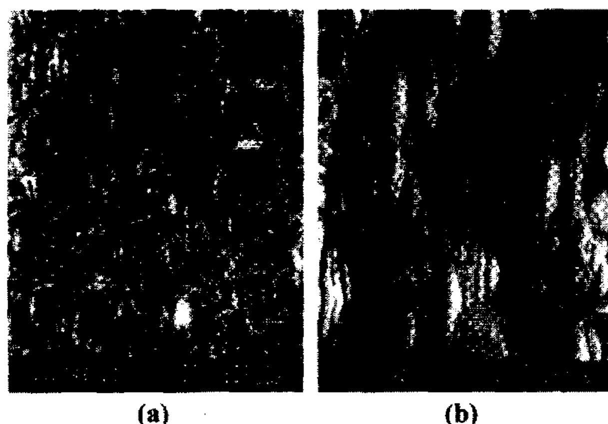

Fig. 3. Surface morphology of ZnSe from DIPSe/DMZn at two different growth temperature (a) 400°C and (b) 450°C.

μmol/min. The growth rate is increasing linearly with DIPSe flow rate at the kinetic limited region of T_G=450°C.

The morphology of ZnSe epilayers grown from DIPSe reveals a highly faceted morphology, which shows different refractivity from the specific plane. In Figure 3, the surface morphology of ZnSe grown from two different temperature was shown. At higher temperature (450°C), the size of hexagonal shaped structure was bigger than one from low temperature (400°C).

SIMS profiles of DIPSe/DMZn grown ZnSe films are shown in Figure 4 with the ion, $^{12}C^-$ for carbon detection and the mass 138, representing $ZnSe^-$ in the epilayer and Ga_2- in the substrate. The $^{12}C^-$ signal shows a sharp increase of carbon concentration in a region near the ZnSe/GaAs interface. Saito *et al.*[7] attributed the carbon peak at the interface to possible carbon residues present on the substrate surface, even though the substrate were carefully etched with H_2SO_4 mixture solution and rinsed with deionized water. This carbon interface peak is detectable in the ZnSe films which have grown from a wide range of Se precursors including H_2Se.

Figure 5 compares SIMS depth profiles for ^{12}C for ZnSe films grown with different selenide sources. The ^{12}C concentration in the bulk of the ZnSe films grown from DASe always stays above 10^{20}atoms/cm^3. In contrast, the bulk ZnSe films from DIPSe show no significant carbon incorporation (below detection limit, 5×10^{17} atoms/cm^3) even at high VI/II ratio of 4. This dramatic difference in carbon concentration in ZnSe films from DASe vs. DIPSe suggests that different decomposition mechanisms are responsible for carbon incorporation [8].

The full width at half maximum of 2 μm thick

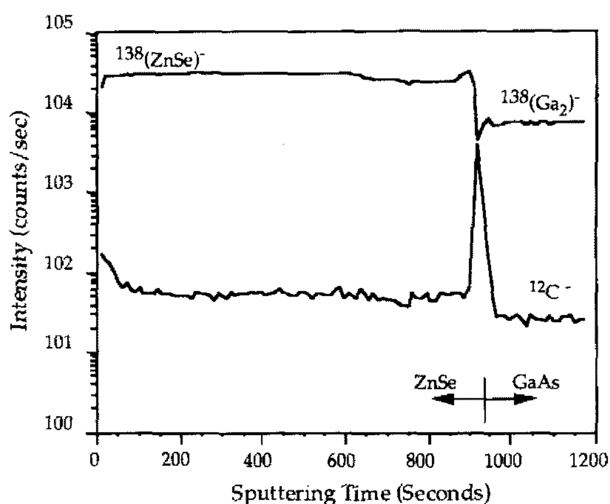

Fig. 4. SIMS depth profiles for carbon (^{12}C) in ZnSe grown on GaAs. Mass 138 represents $ZnSe^-$ in the epilayer and Ga_2^- in the substrate.

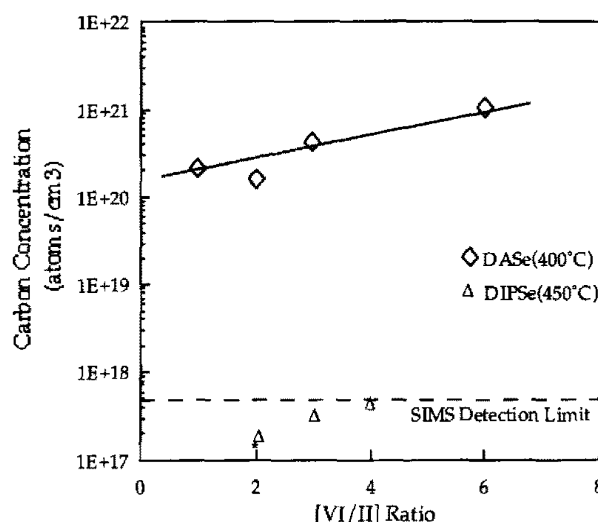

Fig. 5. Dependence of ^{12}C concentration as determined by SIMS on the VI/II ratio for ZnSe films grown from DASe (◇) at 400°C and DIPSe (△) at 450°C.

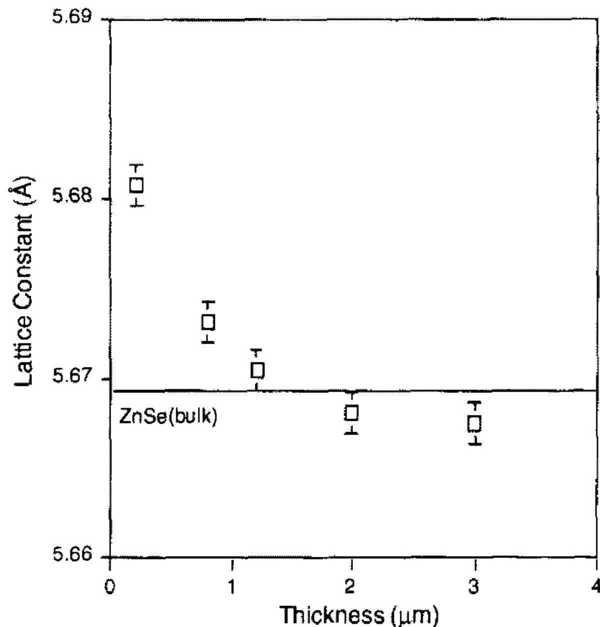

Fig. 6. Lattice parameter normal to the ZnSe surface measured by DCD as a function of the film thickness.

ZnSe epilayer on GaAs were 400-450 arcsec, which crystal quality appears relatively good. The lattice parameters of the ZnSe epilayer on the GaAs substrate were measured by double crystal X-ray diffractometry (DCD). Figure 6 shows the lattice spacing of ZnSe epilayers perpendicular to the heterointerface. Above an experimental critical thickness of 1500Å the lattice spacing start to decrease, indicating the rapid relieving of the mismatch lattice strain due to the formation of dislocations. The vertical lattice constant of the ZnSe layer with 0.2 μm thickness is 5.6808±0.0005Å, which is larger than the lattice parameter of bulk ZnSe (a_0= 5.6694Å). The lattice spacing becomes almost the same as that of bulk ZnSe when the film thickness reaches 1 μm, and becomes smaller than bulk ZnSe for films thicker than 1 μm, implying that the ZnSe layer suffers two-dimensional tensile stress. This tensile stress is mostly likely induced by the difference in thermal expansion coefficients between the ZnSe epilayer (6.8×10^{-8} K^{-1} at RT) and the GaAs substrate(5.7×10^{-6} K^{-1}). All ZnSe layers grown from DIPSe at 450°C appear to be highly resistive through the Hall effect measurements.

4. Conclusion

Diisopropyl selenide (DIPSe) has been used for high quality ZnSe growth in MOVPE. In order to reduce growth temperature, methyl or ethyl radical has been replaced with isopropyl radical since the metal-radical bond strength is considerably reduced. Good morphology, crystal quality of single crystalline ZnSe layers are demonstrated by SEM, DCD and SIMS.

Acknowledgment

This work is supported by the academic research fund of Ministry of Education, Republic of Korea, through Inter-University Semiconductor Research Center (ISRC 97-E-3030) in Seoul national University.

Reference

1. K. P. Giapis, D. C. Lu and K. F. Jensen, Appl. Phys. Lett. **54**, 353 (1989).
2. N. I. Sax, Daneerous Properties of Industrial Materials. 5th ed., New York, Van Norstrand Rheinhold (1979).
3. H. Mitsuhashi, I. Mitsuishi and H. Kukimoto, J. Cryst. Growth **77**, 219 (1986).
4. H. Mitsuihashi, I. Mitsuishi M. Mizuta and H. Kukimoto, Jpn. J. Appl. Phys. **24**, 578 (1985).
5. G. B. Stringfellow, Oreanometallic vapor Phase Epitaxv: Theory and Practice. Academic Press, pp. 15-50 (1990).
6. W. Stutius, Appl. Phys. Lett. **38**, 352 (1981).
7. J. Saito, T. Ishikawa, T. Nakamura, K. Nanbu, K. Kondo and A. Shibatomi, Jpn. J. Appl. Phys. **25**, 1216 (1986).
8. M. Danek, J. S. Huh, L. Foley and K. F. Klavs, J. Cryst.Growth **145**, 530 (1994).