High quality epitaxial ZnSe and the relationship between electron mobility and photoluminescence characteristics

Konstantinos P. Giapis, Da-Cheng Lu, and Klavs F. Jensen
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

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High quality epitaxial layers of nominally undoped ZnSe have been grown by metalorganic chemical vapor deposition at low temperature (325 °C) and pressure (30 Torr), using dimethylzinc and hydrogen selenide. All layers were unintentionally doped *n* type with net carrier concentrations of 6.4×10^{14}–1.5×10^{16} cm^{-3} and exhibited very high mobility at room temperature (up to 500 cm^2/V s) as well as at 77 K, where the measured value of 9250 cm^2/V s is the highest so far reported for vapor phase growth. Additional evidence for the high quality of the material is provided by photoluminescence. Experimental results indicate a correlation between the photoluminescence characteristics and the electrical properties that may be useful in assessing the quality of ZnSe films.

High quality epitaxial layers of ZnSe that can be doped controllably have a well-recognized potential use in blue light-emitting diodes and lasers. Significant progress towards this goal has recently been made by metalorganic chemical vapor deposition (MOCVD), including improvements in surface morphology, near-band-edge (NBE) photoluminescence, and electrical properties,[1–3] as well as reports of measurable *p*-type conductivity in ZnSe.[4] Here, we report further improvements in material quality of nominally undoped ZnSe prepared by MOCVD, as evidenced by its photoluminescence (PL) characteristics and its electrical properties. Experimental data indicate an empirical correlation between electron mobility and PL characteristics, which is proposed as a means for assessing high quality ZnSe films, independent of the growth technique.

ZnSe was grown in a loadlock equipped MOCVD reactor, designed for the growth of ZnSe. The reactants used were "electronic" grade dimethylzinc (DMZ) and hydrogen selenide (H_2Se), *in situ* produced from Pd-purified hydrogen and 99.9999% pure selenium. The H_2Se was formed in a small reactor unit, separated from selenium and partially condensed, so that a controlled amount of H_2Se in H_2 could be introduced into the reaction chamber. Typically, flow rates of DMZ and H_2Se were kept at 20 and 35 μmol/min, respectively. The substrates were semi-insulating GaAs (100), oriented 2° towards ⟨110⟩ and were prepared according to standard procedures.[5] The GaAs wafer was placed on a Mo susceptor inside the loadlock and pumped down to a pressure of 1×10^{-7} Torr, then transferred into the main reactor chamber where it was heat treated at 650 °C for 10 min in 1 slm H_2 flow, while the reactor was kept at 300 Torr. The samples discussed here were grown at 325 °C, while the reactor pressure was varied between 30–100 Torr and the nozzle to susceptor distance between 20–50 mm. This led to a variation in the growth rate between 24 and 32 μm/h and had a profound effect on the incorporation of impurities in the films.

All layers investigated in the present study were single crystalline, of thickness between 8–32 μm and showed features common to ZnSe of comparable thickness grown from identical sources, i.e., hillocks in the ⟨110⟩ direction.[5,6] Electrical properties were evaluated by measurements of resistivity and Hall effect. Ohmic contacts were made by pressing small pieces of In on the freshly grown ZnSe surface, followed by annealing in purified H_2 for 5 min at 300 °C. Formation of ohmic contacts was verified using a curve tracer. Photoluminescence spectra recorded before and after annealing were identical in sharpness and intensity of peaks, indicating that annealing at the above conditions had no significant effect on the properties of the films.

Results of film characteristics at 300 and at 77 K are listed in Table I. All samples investigated were *n* type with 300 K net carrier concentrations ranging from 6.4×10^{14} to 1.5×10^{16} cm^{-3}. The 77 K value of mobility for run No. 62 of

TABLE I. Experimental and calculated electrical properties of undoped ZnSe. n and μ are the net carrier concentration and mobility at the corresponding temperature. N_A and N_D are the total acceptor and donor concentrations, θ is the compensation ratio. $\Delta E(I_x)$ is the linewidth of the I_x peak in the PL spectra and $R(I_x/\mathrm{DL})$ is the maximum NBE peak to the DL intensity ratio, commonly cited in the literature.

Run No.	Thickness (μm)	n_{300} (10^{15} cm^{-3})	n_{77} (10^{15} cm^{-3})	μ_{300} (cm^2/V s)	μ_{77} (cm^2/V s)	N_A (10^{15} cm^{-3})	N_D (10^{15} cm^{-3})	θ	$\Delta E(I_x)$ (meV)	$R(I_x/\mathrm{DL})$
48	32.0	15.0	7.0	500	3250	13.0	20.0	0.65	1.8	5000
50	31.2	4.8	2.5	460	5600	6.4	8.9	0.72	1.2	500
51	31.8	10.0	4.1	480	4600	8.3	12.0	0.67	1.6	1900
54	12.4	2.6	1.3	450	5650	6.1	7.4	0.82	1.5	1000
55	15.0	2.1	1.2	475	7700	4.3	5.5	0.78	1.0	500
62	8.3	0.9	0.6	475	9250	3.3	4.0	0.84	1.1	200
68	11.0	2.6	1.4	460	6250	5.5	6.9	0.79	1.1	270

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9250 cm^2/V s is to our knowledge the highest so far reported for ZnSe grown by a vapor phase deposition technique, including molecular beam epitaxy (MBE). Similar values have been reported for bulk-grown material.[7] In Figs. 1(a) and 1(b) we show the total electron mobility versus carrier concentration at 300 and 77 K, respectively. Data from other MOCVD[1-3] and MBE[8] studies of nominally undoped ZnSe are included for comparison. The solid curves have been reproduced from the theoretical work on electron transport in ZnSe by Ruda.[9] The 300 K mobility data, close to a constant (average) value of 480 cm^2/V s, fall outside the theoretical predictions of electron transport in ZnSe at room temperature. However, the model appears to work well at 77 K, where ionized impurity scattering becomes the dominant mechanism limiting electron mobility. For this scattering process, the mobility is given by the Brooks–Herring formula,[10] which is used to estimate N_A, N_D, and the compensation ratio θ from experimental values of the 77 K mobility and net carrier concentration. The results are summarized in Table I. For our films, θ falls between 0.65 and 0.85 in good agreement with the more extensive calculations by Ruda,[9] as can be seen by the fitting of our points from the curve with $\theta = 0.7$. The close agreement between our measured 77 K mobilities and theoretically predicted inherent limit mobilities is a further indication of the very high purity and quality of our material.

There is a possibility of measuring anomalously high apparent mobilities, resulting from inadvertently introducing conducting inhomogeneities in our ZnSe films.[11] However, this is unlikely because: (1) No mobilities exceeding the theoretical lattice scattering limited values have been measured. (2) ZnSe films with 77 K mobility in the high 8000 cm^2/V s region have been grown *reproducibly*. (3) If the samples had conducting inhomogeneities, they would appear to be quite uncompensated,[11] but run No. 62 (with the highest mobility at 77 K) is the most compensated among the runs. (4) The variation of the apparent Hall constant with the magnetic field has been considered for several samples. Upon increasing the magnetic field the Hall constant decreased as expected from theory.[12]

Photoluminescence (PL) spectra at room temperature and 9 K were obtained by using the UV output of an Ar^+ ion laser at low power densities (< 30 mW/cm^2) in an unfocused beam of diameter 2 mm, and analyzed using a 0.85-m SPEX 1403 double monochromator and photon counting electronics. Spectral resolution in the range of interest was better than 0.5 cm^{-1}. The PL spectra at room temperature and 9 K of our highest mobility sample are shown in Figs. 2(a) and 2(b). This sample was grown at 325 °C, 30 Torr, and [VI/II] ratio of 1.75. Both spectra are composed of a strong near-band-edge (NBE) emission, while the broad emission at smaller energies (deep levels) is very weak. The 9 K spectrum [Fig. 2(b)] is dominated by an intense and narrow peak at 2.7954 eV, identified as the commonly observed I_x.[13] This may be assigned to I_3·Ci, described by Dean *et al.*,[14] which would explain the *n*-type conductivity. In the expansion of the NBE emission spectra [Fig. 2(b), inset], a second dominant peak is clearly defined at 2.7970

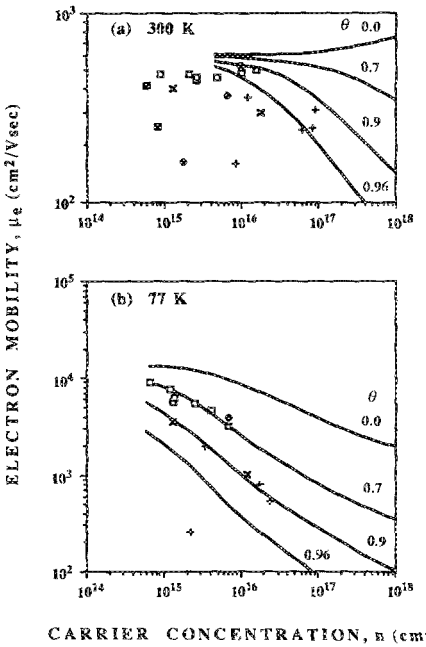

FIG. 1. Comparison of the Hall electron mobility vs carrier concentration at (a) 300 K and (b) 77 K for ZnSe. The symbols correspond to experimental data points for nominally undoped films as follows: (□) this study, (+) Ref. 1, (×) Ref. 2, (▩) Ref. 3. (◈) Ref. 8. The solid curves represent the calculated values of mobility vs carrier concentration for different compensation ratios, reproduced from the work of Ruda (Ref. 9).

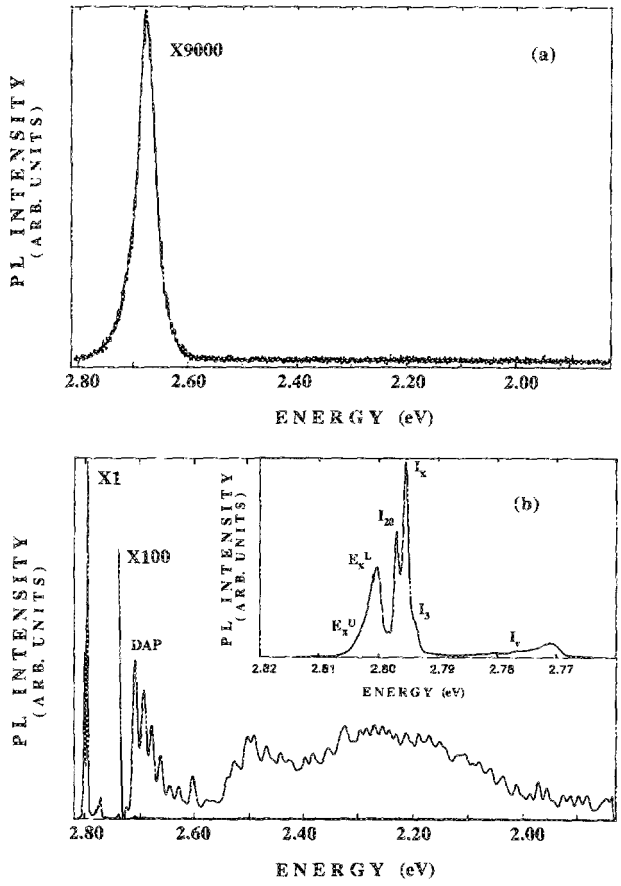

FIG. 2. (a) Room-temperature photoluminescence spectrum for the ZnSe sample with the highest mobility at 77 K. (b) The corresponding 9 K PL spectrum. The inset of this figure is an enlargement of the NBE luminescence. The dominant feature in this spectrum is I_x, but the E_x^L is distinct and of comparable intensity with I_x.

eV; this is referred to as I_{20} and has been attributed to recombination of excitons bound to shallow extrinsic neutral donors.[15] There are also two peaks due to free-exciton recombination: the very intense lower branch polariton, denoted E_x^L at 2.8002 eV and, on its high-energy side, the upper branch polariton, E_x^U at 2.8026 eV. The peak on the lower energy side of the I_x at 2.7938 eV is the I_3 line, presumably due to excitons bound to an ionized donor.[13] One also distinguishes a low I_v peak at 2.7768 eV and the phonon replica of the free exciton at 2.7711 eV. Very weak donor-acceptor pair emission is also observed, which means that the concentration of acceptor-like impurities or defects is considerably reduced in the films discussed here.[6] As compared to other PL results in the literature,[3,13,15,16] our PL spectra are distinguished for their sharp, narrow, and distinct peaks in the NBE region and the weakness of the I_1^d line, usually appearing at 2.782 eV and being attributed to Zn vacancies.[3,15] In fact, since there is no discernible I_1^d line in the PL spectra of all the samples discussed in this letter, we believe that our material is very close to being stoichiometric. Another manifestation of the purity of our films comes from the two to three orders of magnitude smaller deep level (DL) emission ($h\nu < 2.5$ eV), as compared to the NBE dominant peak. The DL emission appears as a weak, broad *Cu-green* emission at approximately 2.3 eV.

Features of low-temperature PL spectra, including the width of the I_x peak (ΔE), the ratio of the dominant NBE to DL intensities (R value), and the intensity of the dominant NBE emission, are frequently used in the literature[16] to judge the relative quality of the ZnSe films. Linewidths, measured at half maximum, serve as a criterion of film quality, since the PL lines broaden as the density of impurities and the sample inhomogeneity increase.[16,17] The I_x of Fig. 2(b) has a linewidth of $\Delta E = 1.1$ eV, among the narrowest of our samples with measurable mobility. The R value of the same sample was approximately 200, but we have grown material with an R value as high as 5000. However, our results (see Table I) indicate a reverse relationship between the R value and the quality of the material as determined by the electrical properties, in contradiction with previous reports.[3,16] This can be explained as follows: a very intense NBE peak, usually appearing with a large linewidth (broadening), is related to a higher concentration of radiative electron recombination centers in the films.[17] In the particular case of the dominant donor bound excitonic emission I_x, this implies a higher concentration of donors, which will result in an increased electron screening and scattering and therefore lower mobility values, especially at low temperatures where the ionized impurity scattering is dominant. This trend is clear in Fig. 3, where the 77 K mobility is shown to decrease with the linewidth of the I_x peak as well as with the intensity ratio $[I_x/E_x^L]$. This coupling of the electrical properties with the PL characteristics may provide a better means of assessing the quality of undoped ZnSe, rather than just interpreting the ambiguous R value, which may also vary with both the excitation power and wavelength.[16] Therefore, in cases of highly resistive undoped ZnSe films, one could use PL spectra with a *dominant* NBE emission (i.e., R value $\geqslant 75$) to judge the quality by examining the linewidth of the dominant peak as well as its intensity ratio over the intensity of the free exciton.

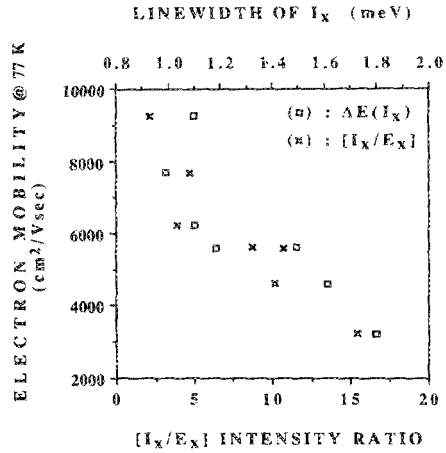

FIG. 3. Electron mobility at 77 K plotted vs the PL intensity of the I_x peak normalized over the intensity of the E_x peak ($\times$), as well as vs the linewidth of the I_x peak ($\square$).

In summary, we have shown that by using low-temperature MOCVD with additional purification of the starting materials, it is possible to grow epitaxial ZnSe with higher mobility than previously reported. We also have provided experimental results showing a direct relationship between the electrical properties and the PL characteristics of high quality ZnSe, which may be useful as a means for assessing the quality of ZnSe films. This study indicates that n-type (and possibly p-type) conductivity in ZnSe is limited by extrinsic impurities rather than vacancies or self-interstitials, which renews the hope of obtaining efficient p-n junction light-emitting devices from ZnSe.

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