Carbon incorporation in ZnSe grown by metalorganic chemical vapor deposition

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

J. E. Potts and Steven J. Pachuta
3M Company, 201-1N-35 3M Center, St. Paul, Minnesota 55144

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Carbon incorporation in ZnSe films grown by metalorganic chemical vapor deposition is reported. Secondary-ion mass spectrometry measurements in ZnSe films grown from methylallylselenide and dimethylzinc show an enhanced carbon accumulation at the interface between ZnSe and GaAs. The carbon incorporation in the bulk ZnSe increases with the VI/II ratio and for a value of VI/II = 3–4, the amount of incorporated carbon abruptly jumps to concentrations of 10^{21} cm^{-3}, whereupon the films become polycrystalline. A new shallow peak I^C at 2.7920 eV dominates the near-band-edge low-temperature photoluminescence spectra of all carbon-contaminated ZnSe films. The intensity and linewidth of I^C increase with the VI/II ratio in a similar manner to the carbon concentration. This peak is proposed to be due to the radiative decay of excitons bound to a complex defect, which is associated with the presence of carbon in the films.

Carbon is a possible impurity in the metalorganic chemical vapor deposition (MOCVD) of compound semiconductors since it is inherent to the growth precursor. ^{13}C isotopic labeling studies[1] in the growth of III-V compounds as well as controlled addition of hydrocarbons[2,3] have confirmed that carbon originates from the organometallic sources used in the MOCVD process. Carbon behaves as a shallow acceptor in GaAs and AlGaAs, and its incorporation has attracted considerable attention[1–3] both as an undesirable contaminate, resulting as a by-product of the growth reactions, and as a key to understanding the growth chemistry. As opposed to these extensive studies of carbon incorporation in GaAs, the problem has not been pursued for epitaxial ZnSe grown by MOCVD and the optoelectronic behavior of carbon impurities in ZnSe has not been characterized. Specifically, no peak in the photoluminescence (PL) spectrum of ZnSe is known to be related to or tentatively attributed to carbon. We report here the first experimental evidence for carbon incorporation in ZnSe grown by MOCVD, and correlate the presence of carbon impurities with a PL peak, appearing only in carbon-contaminated films.

Methylallylselenide (MASe), a novel organometallic Se source, was used to grow ZnSe films in a loadlock-equipped, vertical stagnation point flow MOCVD reactor. A mass spectrometer system with a sampling port immediately downstream of the susceptor was used to monitor stable reaction by-products. Further details of the reactor design, control, and gas handling system will be published elsewhere.[4] Electronic grade dimethylzinc (DMZn) was used as the Zn source. The ZnSe films were grown epitaxially on semi-insulating (100)GaAs substrates, misoriented 2° towards ⟨110⟩. The substrates were degreased and etched according to standard procedures[5] before being placed on a Mo susceptor inside the load lock. The reactor was pumped down to a base pressure of 1×10^{-8} Torr and then purged overnight with H_2 at low pressure prior to growth. After transferring the substrate into the main reactor chamber, the deposition sequence was initiated with native oxide desorption in 1 slm H_2 flow at 650 °C and a total reactor pressure of 300 Torr for 10 min. After a short adjustment to the growth temperature (T_G), growth was initiated by simultaneously flowing the MASe and DMZn (diluted in H_2) into the reactor. The ZnSe films were grown at 300 Torr and 520 °C with constant DMZn flow rate at 20 μmol/min, while the molar flow rate of MASe was varied from 10 to 120 μmol/min. The variation in the VI/II ratio resulted in different carbon incorporation in the films.

Measurement of the carbon impurity levels in ZnSe was performed by secondary-ion mass spectrometry (SIMS) with a detection limit for ^{12}C around 1×10^{18} cm^{-3}. A nominally undoped ZnSe film grown by molecular beam epitaxy (MBE) and showing no detectable carbon impurities was implanted with ^{12}C to provide an internal standard for SIMS measurements of the carbon concentration in the MOCVD-grown ZnSe films. The implant had a peak ^{12}C concentration of 1×10^{20} cm^{-3}. The SIMS measurements[6] were carried out with a Cameca IMS-4f spectrometer using a Cs^+ primary ion beam with an incident energy of 14.5 keV and an ion current of 150 nA, rastered over an area of 250×250 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.

SIMS depth profiles of the ^{12}C peak are shown in Fig. 1 for ZnSe films grown by MOCVD from different source combinations as well as by MBE. The apparent higher carbon levels in the bulk GaAs than in the bulk ZnSe for curves (a)–(c) are believed to be due to differences in SIMS sensitivity (detection limit of ^{12}C) in the two lattice matrices.[7] Growth from MASe/DMZn at VI/II = 1 results in a film, which shows a dramatic increase of several orders of magnitude of the ^{12}C concentration in a region near the ZnSe/GaAs interface, as illustrated by curve (a) in Fig. 1. This is

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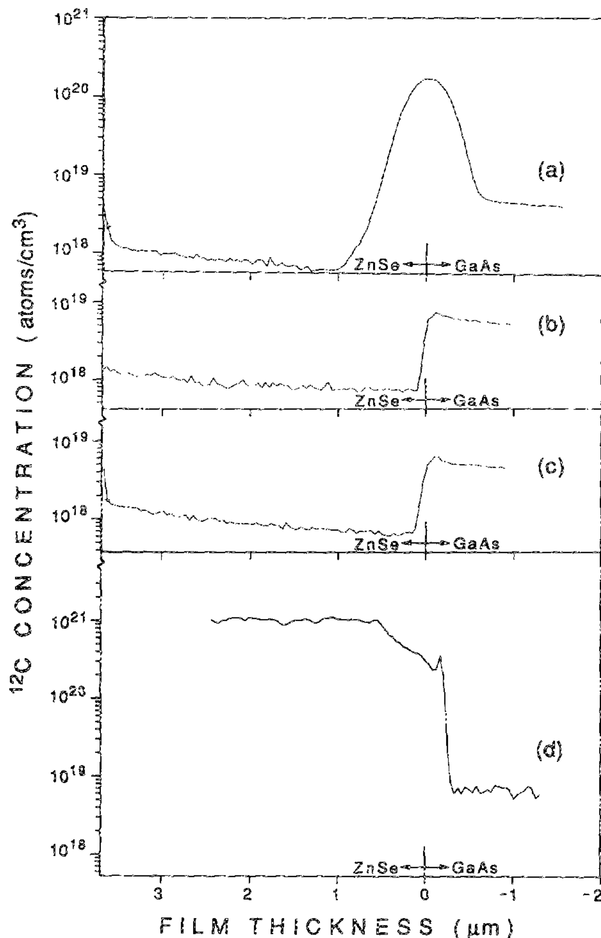

FIG. 1. Carbon depth profiles for different ZnSe films detected as $^{12}C^-$ ion by SIMS. The position of the ZnSe/GaAs interface is estimated by monitoring the molecular ion $^{138}ZnSe^-$. (a) MOCVD-grown film from MASe/DMZn at VI/II = 1. (b) MOCVD-grown film from H_2Se/DMZn at VI/II = 10, immediately after film (a) in the same reactor. (c) MBE-grown film. (d) MOCVD-grown film from MASe/DMZn at VI/II = 4.

not due to surface preparation effects; growth of ZnSe from H_2Se/DMZn at VI/II = 10 in the same MOCVD system, immediately after the MASe experiment and with the same preparation sequence, produces material for which the "bump" in the carbon concentration at the ZnSe/GaAs interface is absent as shown in curve (b), Fig. 1. The depth profile (c) is for a ZnSe sample grown by MBE[8] on the GaAs substrate, cleaned in a manner similar to the other ones and preheated in vacuum for oxide desorption. Again the carbon concentration is below the detection limit and no significant increase in carbon is observed near the interface. Therefore, it appears that the large ^{12}C signal near the ZnSe/GaAs interface is due to the incorporation of ^{12}C impurities originating from the organometallic Se precursor, MASe.

The ^{12}C concentration in the bulk of ZnSe sample grown from MASe/DMZn at VI/II = 1 [Fig. 1(a)] is at the detection limit of our SIMS apparatus. When the flow rate of MASe is increased relative to the DMZn, the ^{12}C concentration in the bulk of the films becomes detectable and at a molar ratio VI/II = 4 the carbon level is almost four orders of magnitude above the detection limit, as illustrated by the depth profile (d) in Fig. 1. The strong variation of the ^{12}C

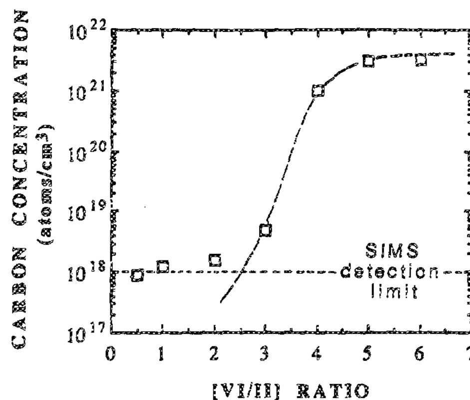

FIG. 2. Carbon concentration in the bulk of ZnSe films grown from MASe/DMZn plotted vs the [VI/II] inlet molar ratio.

concentration in the bulk of the ZnSe films (as measured by SIMS) with the VI/II ratio is apparent in Fig. 2. The increase in the amount of incorporated carbon is accompanied by a marked degradation in crystalline quality as evidenced by scanning electron microscopy (SEM) and electron channeling patterns. At the point of the steep change in ^{12}C concentration (VI/II$\approx$3.5), the ZnSe films become polycrystalline. Such a dramatic change of structures is not observed for similar VI/II values, when H_2Se or diethylselenide are used as the Se precursors.[4] The accumulation of carbon at the ZnSe/GaAs interface is also likely to be responsible for the peculiar morphology of ZnSe films grown from MASe/DMZn reported earlier.[9]

The low-temperature (9 K) photoluminescence (PL) spectrum of a ZnSe sample grown at VI/II = 1 is shown in Fig. 3(a). Peak notation and assignment has been reported previously.[10] In contrast to the PL spectrum of a typical

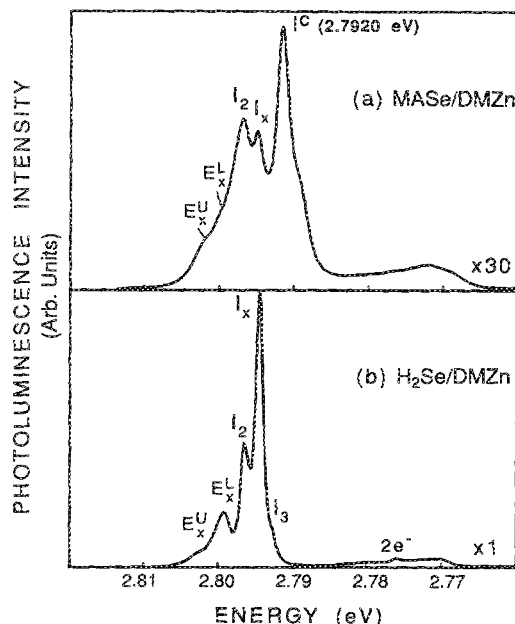

FIG. 3. Expanded near-band-edge PL spectra of ZnSe films taken at 9 K. (a) Film grown from MASe/DMZn at VI/II = 1. (b) Film grown from H_2Se/DMZn at VI/II = 10, immediately after film (a) in the same MOCVD reactor.

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ZnSe sample grown from H_2Se/DMZn and shown in Fig. 3(b), the near-band-edge (NBE) emission is dominated by a new shallow I^C peak at 22 525 cm^{-1} (2.7920 eV).[11] In Fig. 4, the intensity of this peak, normalized to that of the free-exciton peak E_x^L, as well as its linewidth is plotted versus the VI/II ratio. They both increase with the VI/II ratio, showing similar behavior to the carbon concentration as measured by SIMS, while the other peaks in the NBE emission spectra remain unchanged. The I^C peak is also observed in ZnSe grown from diethylselenide/DMZn[4] but it is absent in MBE-grown material.[8] Assuming this peak is due to the radiative decay of a bound exciton, the exciton localization energy is 10.7 meV. Haynes' rule[12] would then give activation energies of 54 and 107 meV for simple substitutional donors or acceptors, respectively, whereas effective mass analysis[13] yields activation energies of approximately 29 ± 2 and 108 meV. Selectively excited photoluminescence experiments failed to produce conclusive evidence for two-electron or two-hole transitions, probably due to the broadness of the I^C peak.[14] Despite the coincidence of the predicted acceptor activation energy with the effective mass value, it is unlikely that the binding occurs at a simple substitutional site, but rather at a complex which is associated with the carbon impurity.[15] Identification of the nature of this complex awaits further study.

An unidentified PL peak, often marked as I_3, has been observed in other MOCVD studies,[16] especially when dimethylselenide was used as the Se precursor. Although the exact energy of this peak is not reported, estimation from the published NBE spectra in the aforementioned studies yields positions very close to our I^C. In addition, the possible connection between this peak and carbon impurities originating from the CH_3-Se• or its pyrolysis products has not been recognized. In a recent study of ZnSe grown by metalorganic molecular beam epitaxy (MOMBE) from H_2Se/DMZn, Oniyama *et al.*[17] found a dominant I_1^S peak at exactly the same position as our I^C (2.7920 eV). This peak was observed only when both sources were cracked before deposition, indicating that *both* methyl radicals and Se atoms were necessary for its appearance in the PL spectra of ZnSe films.

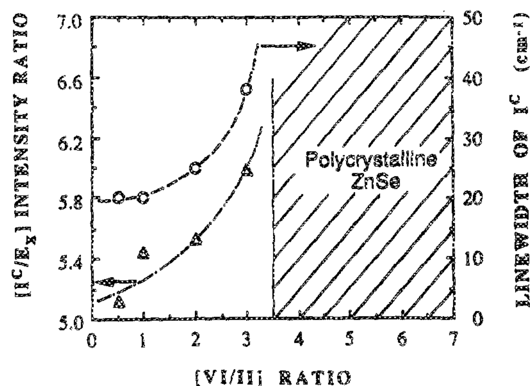

FIG. 4. Normalized PL intensity ratio $[I^C/E_x]$ and the linewidth of I^C plotted vs the [VI/II] ratio for ZnSe films grown from MASe/DMZn. For $[VI/II] \geqslant 3.5$ the films are polycrystalline, resulting in weak, broad, unresolved PL spectra.

The identification of carbon incorporation in ZnSe grown by MOCVD establishes an additional measure for evaluating organometallic Se sources as possible replacements of H_2Se. Since CH_3-Se• appears to be a significant factor in carbon incorporation, compounds which contain this moiety (such as methylselenol,[18] dimethylselenide,[16] methylallylselenide[9]) are expected to produce films with significant levels of carbon. In addition, processing conditions in MOCVD or MOMBE that would lead to Ch_3-Se• formation are likely to be detrimental to film quality. Confirmation of the I^C PL peak as being carbon related by other spectroscopic techniques would yield a useful tool for monitoring carbon incorporaton in ZnSe, analogous to the PL procedures used in GaAs studies.[2,3]

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[11]We have extensively studied doping of ZnSe by MOCVD and MBE using Li, Na, and N as impurities. The resulting doped films had PL spectra with acceptor-bound exciton positions well removed from the position reported here.

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[15]In all of the known cases of group IV incorporation in II–VI compounds, the group IV atom resides on the group II site as is demonstrated by electron paramagnetic resonance experiments [See, for example, K. Suto and M. Aoki, J. Phys. Soc. Jpn. **26**, 287 (1969); **24**, 955 (1968)]. Chemically, this seems reasonable for the case of ZnSe because carbon forms a strong compound with Se and not with Zn. Therefore, carbon should be (formally) a double donor.

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