An infrared absorption investigation of hydrogen, deuterium, and nitrogen in ZnSe grown by molecular beam epitaxy

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(Received 31 May 1996; accepted for publication 22 August 1996)

Surprising concentrations of hydrogen and deuterium, as high as 5×10^{20} cm^{-3}, were incorporated into nitrogen-doped ZnSe grown on GaAs by molecular beam epitaxy. Infrared absorption bands due to local vibration modes were observed at 3193 and 783 cm^{-1} for ZnSe:N,H samples, and at 2368 cm^{-1} for ZnSe:N,D samples using Fourier transform infrared spectroscopy. The isotopic shift in the absorption band agrees with predictions of a simple harmonic oscillator approximation for N–H bonding. The variation of the absorption band associated with substitutional nitrogen with nitrogen concentration indicates that not all nitrogen is substitutional, and also exhibited significant changes related to hydrogen incorporation. © *1996 American Institute of Physics.*
[S0021-8979(96)01423-5]

I. INTRODUCTION

It is well known that hydrogen passivates dopants in semiconductors by bonding to the dopant atoms to form complexes or compensating centers. Extensive studies have been made in Si and III–V materials such as GaAs and InP.[1] Hydrogen compensation is a significant problem with nitrogen doping of ZnSe grown by metalorganic chemical vapor deposition (MOCVD)[2] and gas-source molecular beam epitaxy (GSMBE).[3] Absorption bands due to local vibration modes (LVMs) observed in nitrogen-doped ZnSe grown by MOCVD[2,4] are attributed to N–H bonding. These results suggest that hydrogen forms a compensating complex with nitrogen in nitrogen-doped ZnSe, with the hydrogen bonding primarily to the nitrogen. We report the effects of intentional incorporation of hydrogen and deuterium in nitrogen-doped ZnSe grown by conventional molecular beam epitaxy (MBE), and for the first time, the LVM for N–D bonding in ZnSe. The agreement between the observed isotope shift in the LVM frequency and predictions with simple harmonic oscillator theory provides strong support for N–H bonding. We also report the first observation of the absorption band associated with substitutional nitrogen[5] in as-grown ZnSe:N.

II. EXPERIMENT

Nitrogen-doped ZnSe layers were grown on semi-insulating, (100)-oriented GaAs substrates using a custom MBE system at West Virginia University. High purity (7N) elemental zinc and selenium were used as source materials. Nitrogen doping was achieved using an rf plasma atomic nitrogen source from Oxford (Model No. CARS25) operating at plasma power of 200 W and a nominal system pressure 2×10^{-6} Torr. An EPI thermal cracker using either hydrogen or deuterium gas at 1×10^{-6} Torr system pressure was employed for hydrogen or deuterium doping. All doped samples were grown with a 0.25-μm-thick, undoped ZnSe buffer layer prior to the doped layer growth. Typical doped layer thickness was 1–2 μm with a growth rate of 0.2–0.4 μm/h. The II/VI beam equivalent pressure (BEP) ratio ranged from 2 to 0.5, while growth temperatures were 250 °C and 300 °C. Substrate preparation was the same as previously reported.[6]

Secondary ion mass spectrometry (SIMS) measurements were made at Charles Evans and Associates (Redwood, CA) to determine the doping concentration profiles of nitrogen, hydrogen, and deuterium in ZnSe samples using Cs(+) ions. Nitrogen concentrations were determined to an absolute accuracy of ±20% by direct comparison with a nitrogen-implanted ZnSe sample measured in the same SIMS sample set. Hydrogen and deuterium measurements were made using archived relative sensitivity factors and are quoted to within a factor of 2. The minimum detectable concentrations of the SIMS measurement were limited by residual background gases in the SIMS system itself. Measurements made on undoped ZnSe layers indicated minimum detectabilities of 1×10^{17}, 2×10^{18}, and 5×10^{16} cm^{-3} for nitrogen, hydrogen, and deuterium, respectively.

III. RESULTS AND DISCUSSION

The depth profile for nitrogen and hydrogen concentrations in a nitrogen-doped ZnSe sample grown under an atomic hydrogen flux is shown in Fig. 1(a). The SIMS spectra is divided into five separate regions (dashed lines). An undoped (u) ZnSe buffer layer was grown directly on the GaAs substrate (s). The doped portion of the layer was grown under a continuous atomic hydrogen (a-H) flux. The rf-plasma source was used to provide atomic nitrogen (a-N) during doped layer growth, resulting in a nitrogen concentration of about 3×10^{19} cm^{-3} in this layer. Surprisingly, the hydrogen level was 5×10^{20} cm^{-3} in the doped layer, which represents a concentration of almost 1 at. %. During growth of the doped layer, the plasma was turned off while maintaining the nitrogen flow, resulting in a region grown under a molecular, rather than atomic, nitrogen flux (m-N). As expected, there is a corresponding decrease in nitrogen concentration. The nitrogen levels then increased back to their previous values when the rf-plasma source was restarted. The

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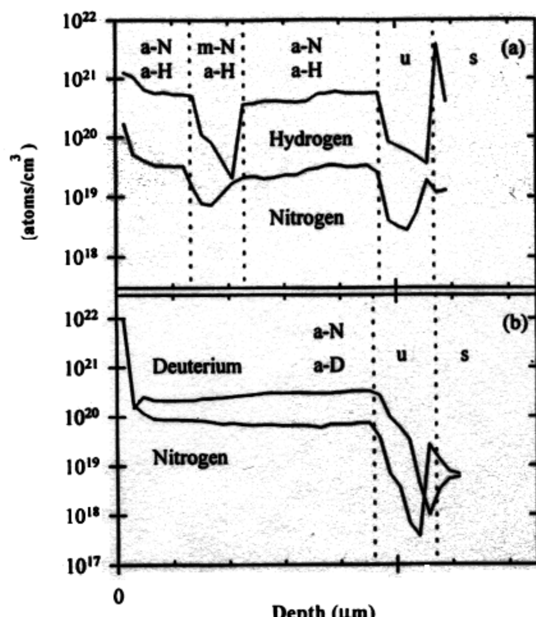

FIG. 1. SIMS profile of ZnSe:N layers grown by MBE (a) under an atomic hydrogen flux, and (b) under an atomic deuterium flux. Dashed lines separate regions with differing growth conditions represented by *s*: GaAs substrate; *u*: undoped ZnSe buffer layer; *a*-H (*a*-D): atomic hydrogen (deuterium) flux present; *a*-N: atomic nitrogen flux present; and *m*-N: molecular nitrogen flux present.

variation in hydrogen concentration throughout the sample's depth closely tracks that of nitrogen. The hydrogen incorporation was clearly influenced by nitrogen incorporation in the ZnSe similar to the phenomenon observed in nitrogen-doped ZnSe grown by GSMBE.[3] For several layers, deuterium was used during nitrogen-doped ZnSe growth to investigate both the nature of the N–H bond through isotopic substitution and low-level incorporation of hydrogen. Figure 1(b) shows the SIMS depth profile of a nitrogen-doped ZnSe sample grown under a deuterium flux, with the different regions labeled similar to Fig. 1(a). The nitrogen concentration was 8×10^{19} cm^{-3} and the deuterium concentration was 3×10^{20} cm^{-3}, again at a surprisingly high level in the doped layer.

The abrupt spikes at the surface and the substrate–epilayer interface in the SIMS data shown in Figs. 1(a) and 1(b) are artifacts of the measurement and contain no useful information. However, the less-than-abrupt profiles observed for nitrogen and hydrogen (deuterium) in the portion of the layer in Fig. 1(a) grown under molecular nitrogen, and in the undoped region of both layers shown in Figs. 1(a) and 1(b), are suggestive of significant diffusion from the heavily doped regions. It is not clear at this point if this is a true phenomenon since special care must be taken in sputtering rates and profiles during SIMS to get an accurate representation of concentration profiles. A more detailed study of nitrogen and hydrogen diffusion is planned for the future to address this question.

Table I contains a summary of hydrogen, deuterium and nitrogen concentrations for various growth conditions. Hydrogen incorporation in ZnSe is significant only when both atomic hydrogen and atomic nitrogen were present during the growth (ZnSe:N,H). The decrease in hydrogen concentration when molecular nitrogen replaces atomic nitrogen during growth shown in Fig. 1(a) clearly demonstrates this effect. In nitrogen-doped ZnSe exposed to molecular deuterium during growth ($ZnSe:N,D_2$), a deuterium level at 10^{18} cm^{-3} and nitrogen level at 8×10^{19} cm^{-3} were observed, indicating a low hydrogen incorporation efficiency for molecular vs atomic deuterium. This low "cracking" efficiency indicates that the background levels of molecular hydrogen typically found in an MBE system may not be an issue for compensation of nitrogen-doped ZnSe. In addition, we did not observe measurable deuterium incorporation for undoped layers grown under an atomic deuterium flux. Hydrogen incorporation in ZnSe also depends on the growth conditions. The highest nitrogen and hydrogen concentrations were obtained for Zn-rich conditions at the lower growth temperature. The highest hydrogen level was 5×10^{20} cm^{-3}, more than one order higher than the nitrogen level in the same layer. As expected, Zn-rich conditions are more favorable to nitrogen incorporation in ZnSe since nitrogen occupies a Se site for *p*-type doping in ZnSe.[7,8]

TABLE I. Hydrogen, deuterium, and nitrogen concentrations in ZnSe for various growth conditions. The nitrogen source rf power was 200 W and the hydrogen/deuterium pressures were maintained at 1×10^{-6} Torr whenever present.

Sample	T_{growth} (°C)	Zn/Se ratio	N flux ($\times10^{-6}$ Torr BEP)	[N] ($\times10^{19}$ cm^{-3})	[H] or [D] ($\times10^{19}$ cm^{-3})
	250	1.8	3.0	3.0	50
	250	2.0	4.7	8.0	30
	250	0.6	4.7	1.5	1.8
	300	0.5	1.5	0.4	1.0
	300	0.5	3.2	1.5	background
	300	0.5	0	background	background
	300	1.2	5.1	8.0	0.1

Fourier transform infrared (FTIR) spectroscopy was performed both at room temperature and 15 K on the ZnSe samples using a Nicolet model 550 FTIR spectrometer. Absorption bands were observed at 783 and 3193 cm^{-1} in nitrogen-doped ZnSe samples grown under an atomic hydrogen flux similar to that previously reported for MOCVD growth.[2,4] These peaks were absent from ZnSe samples grown only with either an atomic nitrogen or an atomic hydrogen flux, as well as from undoped ZnSe samples. The 3194 cm^{-1} band has been tentatively assigned to the stretching mode, and the 783 cm^{-1} band to the wagging mode of the N–H bond in ZnSe based on absorption bands observed in ammonia[1] and N–H bonding in GaAs and GaP.[9]

The effect of isotopic substitution on the observed vibrational frequency is very useful for identification of the species that comprise a defect complex.[1,10] For example, the large frequency shift that results upon the substitution of deuterium for hydrogen leads to an unambiguous assignment of hydrogen bonding. In the harmonic oscillator approximation, the vibrational frequency of an X–H oscillator is assumed to be inversely proportional to the square root of the reduced mass of the oscillator, $\omega(\mathrm{H})\propto[m_X m_H/(m_X+m_H)]^{-1/2}$, where m_H and m_X are the masses of hydrogen and the other

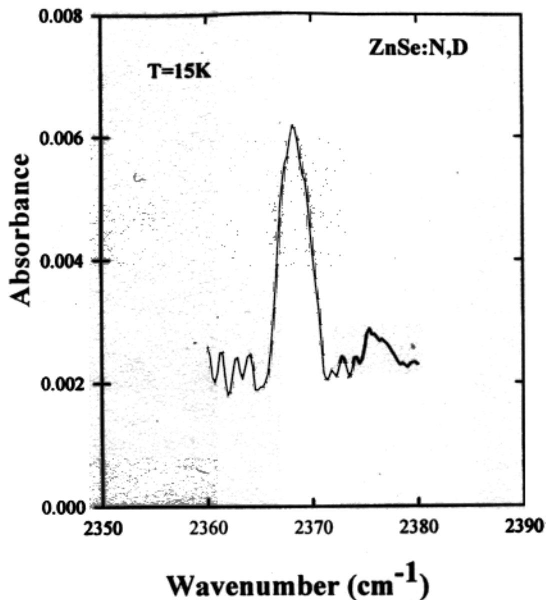

FIG. 2. FTIR spectrum at 15 K of a ZnSe:N layer grown under an atomic deuterium flux by MBE.

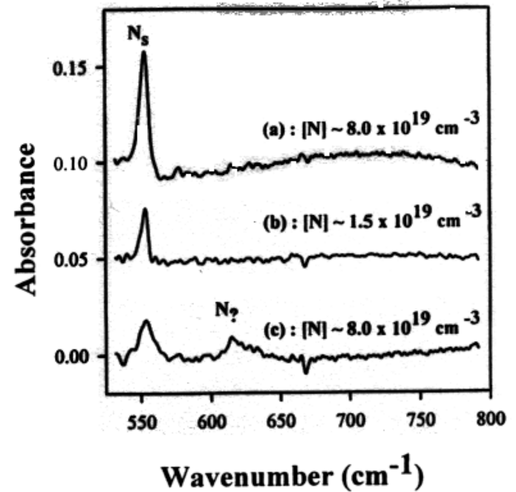

FIG. 3. Room temperature FTIR spectrum of (a) ZnSe:N, (b) ZnSe:N, and (c) ZnSe:N,D. Spectra are arbitrarily shifted along the absorbance axis for display.

atom, respectively. Hence, for an ideal harmonic oscillator,

$$r=\omega(\mathrm{H})/\omega(\mathrm{D})=[2(m_X+1)/(m_X+2)]^{1/2},$$

for X, H, and D atoms of masses m_X, 1, and 2, respectively. For a particular atom attached to hydrogen, the frequency shift can be predicted by this ratio. The calculated frequency ratio is 1.369 for a N–H bond, which can be compared to the experimental value of 1.342 for the N–H bond stretching mode in ammonia. In nitrogen-doped ZnSe samples grown under deuterium flux by MBE, a new absorption band was observed at 2368 cm^{-1} as shown in Fig. 2, which corresponds to the sample with the concentration depth profile in Fig. 1(b). Taking this 2368 cm^{-1} band and the 3194 cm^{-1} band in the ZnSe:N,H sample as the set of vibrational frequencies corresponding to N–D and N–H bonds respectively, the ratio was calculated to be 1.348. The excellent agreement between this value, that of ammonia, and the predicted ratio leads us to conclude that the 2368 cm^{-1} absorption band belongs to the N–D stretching mode in ZnSe, and unambiguously identifies that N–H bonding is occurring in the ZnSe:N,H samples.

Another interesting aspect of this study is the large concentration of hydrogen observed for samples grown under Zn-rich conditions. Theoretical studies such as the recent one by Neugebauer and Van de Walle[11] concerning GaN indicate that hydrogen is more stable (and thus more highly incorporated) in p-type than in undoped or n-type material. The former case is in agreement with the present study, while hydrogen was not observed to be highly incorporated in heavily n-type material in previous MOCVD[2] and GSMBE[3] studies. Neugebauer's calculation implies a one-to-one incorporation of hydrogen-to-acceptor, which is what we essentially observed for Se-rich ZnSe:N,H growth and for hydrogen incorporation in nitrogen-doped CdTe in a previous study.[12] It is not clear how the "excess" hydrogen is being incorporated in the samples grown for this study based on the measurements made to date. One possibility is that hydrogen is incorporated on vacancy-sites (either Zn or Se) similar to observations for Si and Ge.[13] Absorption bands due to Zn–H, Zn–D, Se–H, and Se–D have been reported to occur at 1315, 950, 2150, and 1560 cm^{-1}, respectively.[14] We did not observe such features in our FTIR spectra. However, this does not preclude such a mechanism for hydrogen incorporation. By relating the measured absorbance to the total number of potential absorbers (H or D bonds) in these prior studies, we would expect signals comparable to the noise in our FTIR system, even without any interference from other interactions such as N–H bonding. Further work is required to completely understand this phenomenon.

We also observed the absorption band at 553 cm^{-1} which was previously attributed to substitutional nitrogen in ZnSe in a nitrogen ion-implantation study.[5] To our knowledge, this is the first time such absorption has been reported in as-grown epitaxial material. Three such spectra are shown in Fig. 3. While similar to the previously reported spectra, several significant differences exist. First, the full width at half maximum (FWHM) is smaller by a factor of 2 for comparable nitrogen concentrations, indicating that some residual damage may have remained in the ion-implanted samples. For example, Stein[5] quotes an FWHM of 15 cm^{-1} for a nitrogen concentration of $\sim 5\times 10^{19}$ cm^{-3}, while we observe an FWHM of 7 cm^{-1} for a concentration of 8×10^{19} cm^{-3} [Fig. 3(a)]. Additionally, Stein[5] observed additional N-related features at about 620 cm^{-1} which were absent from all ZnSe:N samples examined in the present study. However, a weak absorption band appears at about 620 cm^{-1} in ZnSe:N,H and ZnSe:N,D samples along with a concomitant decrease in the intensity of the 553 cm^{-1} band, as shown in Fig. 3(c). The decrease is consistent with N–H bond formation which would alter either the charge state or the local force constants for vibration at the nitrogen site. The absorption at 620 cm^{-1} may be associated with structural rearrangement around the nitrogen site, which could occur due to either the implantation process in the previous study[5] or lat-

tice relaxation related to N–H bond formation.

Comparison of Figs. 3(a) and 3(b) indicate that the absorption band at 553 cm^{-1} increases with increasing nitrogen concentration. However, the relative increase in area under the absorption curve does not increase proportionately to the increase in nitrogen concentration. Based on the integrated area under the peak shown as Fig. 3(b), we would have expected the absorption peak shown in Fig. 3(a) to be approximately twice as large. Though preliminary, this result is direct evidence that a significant proportion of the incorporated nitrogen does not occupy a simple substitutional site. Thus, there are at least two inequivalent sites for nitrogen incorporation. Since these concentrations are above the theoretical solubility limit for substitutional N in ZnSe,[15] this may provide indirect evidence of N–N pairing. It is well known that a self-compensation mechanism exists for nitrogen doping of ZnSe based on transport measurements,[16–18] and that significant non-radiative centers are created above a certain nitrogen concentration level.[19,20] At present, however, the actual mechanisms for compensation are still speculative.[21] Further study of the relationship between FTIR absorption signatures and N concentration is planned, since understanding of this phenomenon may help us to identify the mechanisms responsible for limiting the maximum level of p-type doping in ZnSe.

IV. SUMMARY

In conclusion, hydrogen and deuterium were incorporated into nitrogen-doped ZnSe grown by MBE. Surprisingly high levels of hydrogen and deuterium were observed, with hydrogen concentrations as high as 5×10^{20} cm^{-3} in a ZnSe:N layer with a nitrogen concentration at 3×10^{19} cm^{-3}. It was found that hydrogen incorporation closely tracks the nitrogen incorporation in ZnSe. The hydrogen incorporation was significant only when both atomic hydrogen and atomic nitrogen were present during growth. Samples with the highest hydrogen and nitrogen concentrations were grown under a Zn-rich condition. Local vibration modes were observed at 3193 and 783 cm^{-1} for ZnSe:N,H samples and at 2368 cm^{-1} for ZnSe:N,D samples by Fourier transform infrared spectroscopy. The isotopic LVM peak shift agrees very well with the prediction from a one-dimensional harmonic oscillator approximation which strongly supports the formation of N–H bonds in ZnSe. Observations of the variation of the 553 cm^{-1} absorption band associated with substitutional nitrogen are consistent with N–H bonding and provide evidence of nonsubstitutional nitrogen incorporation possibly related to N–N pairing in heavily doped samples.

This work was supported by the West Virginia/National Science Foundation EPSCoR program and two NSF instrumentation Grants, Nos. DMR92-08130 and DMR92-14350. We would like to extend a special appreciation to L. E. Halliburton for sharing the FTIR facilities.

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