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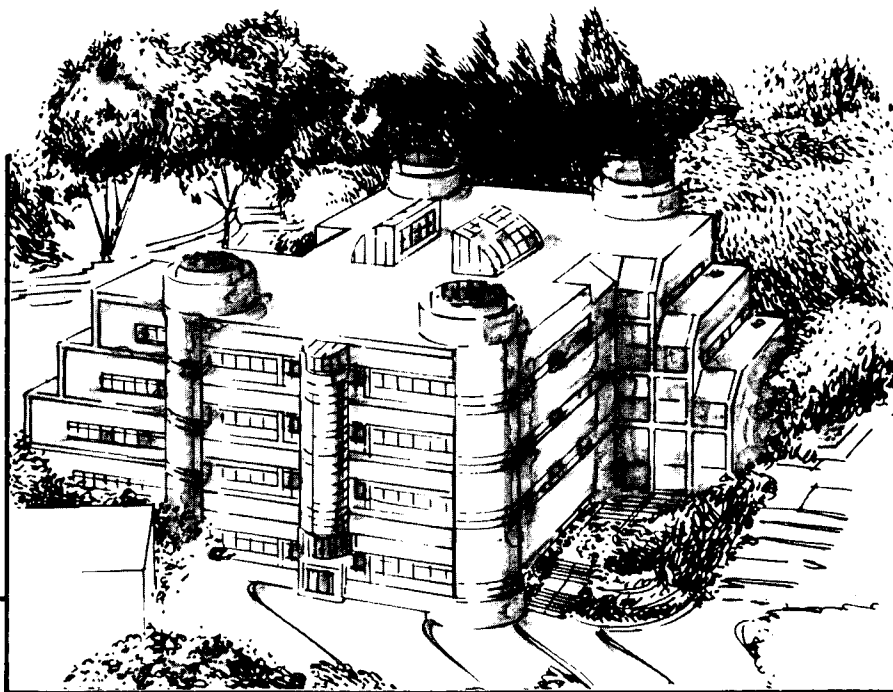
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OPTICAL SPECTROSCOPY OF A NITROGEN-HYDROGEN COMPLEX IN ZnSe

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ABSTRACT

We have observed two local vibrational modes related to H bonded to N acceptors in ZnSe samples grown by metal organic vapor phase epitaxy. The modes have been seen in both infrared and Raman spectroscopy. The new mode seen at 3194 cm^{-1} is assigned to an N-H stretching vibrational mode and the mode found at 783 cm^{-1} is tentatively assigned to an N-H wagging vibrational mode. Polarized Raman spectroscopy was used to determine that the symmetry of the defect complex is C_{3v} , which implies that the H atom is in either a bonding or anti-bonding position.

1 INTRODUCTION

The attempt to develop blue lasers has led to a vigorous effort to achieve high doping levels in thin films of ZnSe, which has a bandgap of 2.73 eV. While it is relatively simple to dope ZnSe n-type, it has proven to be extremely difficult to achieve high levels of p-type doping. The difficulty in doping ZnSe both heavily n-type and p-type is actually a problem encountered when working with all wide-band gap semiconductors: An additional example is ZnTe, which can only be doped p-type. The origin of this behavior is not agreed upon, but several explanations have been suggested.¹⁻³ In the case of ZnSe, the difficulties doping samples p-type have been partially overcome using N as the impurity. N sits on the Se site where it acts as an acceptor. Recently, net acceptor concentrations as high as 10^{18} cm^{-3} have been achieved using molecular beam epitaxy (MBE).⁴ It would be preferable, though, to grow such layers using metal organic vapor phase epitaxy (MOVPE), which is a much less expensive technique. Unfortunately, attempts to grow heavily doped p-type layers by MOVPE have proven unsuccessful. One possible explanation for this lack of success is that the N acceptors are passivated by H present during the growth process. The possible sources of H in the growth process include 1) the use of NH_3 as the source of N, 2) the use of H_2 as a carrier gas and 3) the decomposition products of the Zn and Se precursor molecules. In this paper we present spectroscopic evidence that H is bonding to the N impurities, implying that it is extremely likely that the proposed passivation is actually taking place.

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II) EXPERIMENTAL DETAILS

The ZnSe layers used for this study were grown by photo-assisted MOVPE on (100) semi-insulating GaAs substrates using a Hg lamp with an illumination intensity of 50 mW/cm^2 and Dimethyl-Zinc and Dimethyl-Selenium as the precursors. The growth temperature was $350 \text{ }^\circ\text{C}$ and the layers were $2.5\text{-}3 \text{ }\mu\text{m}$ thick. The layers containing nitrogen were delta doped with NH_3 using flow modulation epitaxy.⁵ (Our samples are not those referred to in reference 5). Photo-assisted MOVPE is used because the illumination generates free carriers near the growth surface which aid in the cracking of Dimethyl-Zinc and Dimethyl-Selenium^{6,7}. This allows the growth to take place at a lower temperature, thereby increasing the sticking coefficient of the N. Even though Secondary Ion Mass Spectroscopy (SIMS) measurements revealed N concentrations above $3 \times 10^{18} \text{ cm}^{-3}$, capacitance-voltage measurements showed the net active acceptor concentrations to be less than 10^{15} cm^{-3} .

Infrared absorption spectra were obtained using a Digilab 80-E Fourier transform spectrometer. Spectra were taken at 9 K with a resolution of 0.5 cm^{-1} and at 300 K with a resolution of 1 cm^{-1} . A Ge:Cu photoconductor was used as the detector. ZnSe epilayers grown without nitrogen doping were used as reference samples.

Room temperature Raman scattering measurements were performed in a pseudobackscattering geometry. The focused beam from an argon-ion laser (514.5 nm) was incident on the sample at 65° to the normal. The laser power was 120 mW and the spot diameter was $10 \text{ }\mu\text{m}$. The backscattered light was analyzed with a single grating monochromator and detected using a microchannel plate photomultiplier. A holographic notch filter was used to suppress elastically scattered light. Polarized spectra were corrected for differences in grating efficiency by calibration with a white light source. The spectral resolution was 2 cm^{-1} . The polarization geometry is defined with respect to the sample surface ([100]): the x, y, and z axes are parallel to the [100], [010], and [001], respectively, while the y' and z' axes are parallel to $[01\bar{1}]$ and $[011]$, respectively.

III) RESULTS AND DISCUSSION

We first discuss our infrared absorption results, shown in Figure 1. Peaks are seen at 3194 cm^{-1} and 783 cm^{-1} at 9K . Both of these peaks are assigned to vibrational modes of a N-H complex, as we now discuss. We assign the peak at 3194 cm^{-1} to the N-H stretching vibrational mode based on the following arguments. First, we reiterate that the reference samples for these studies were undoped ZnSe layers. We also took absorption spectra of the undoped layer using the substrate as a reference and did not see either peak. Second, we confirmed that our samples have a high concentration of N using Secondary Ion Mass Spectroscopy (SIMS), which revealed nitrogen and hydrogen concentrations above $3 \times 10^{18} \text{ cm}^{-3}$. Considering the typical strength of infrared absorption by local vibrational modes, it is unlikely that an LVM could be observed in a $2\text{-}3 \text{ }\mu\text{m}$ thick layer unless the associated impurities were present in concentrations of at least 10^{18} cm^{-3} . The SIMS results also demonstrated that the concentration of the N impurities was correlated with that of the H. Third, the frequency is reasonable for a N-H bond. The frequency of the N-H vibration in the ammonium molecule is 3444 cm^{-1} ,⁸ which is roughly 8% higher than the mode we observe. It is known empirically that many X-H (where X represents an impurity) LVM frequencies are several percent lower in the lattice than in a free molecule.⁹ This is quite reasonable since some of the electron density of the impurity-hydrogen bond is probably present in a weak bond between the impurity and the nearest neighbor host lattice atom. The N-H LVM frequency was observed to be 2886 cm^{-1} in GaP ¹⁰ and a line at 3079 cm^{-1} in GaAs has been tentatively

identified as being due to a N-H bond.¹⁰ Finally, only N-H, C-H, and O-H bonds have been found to have LVMS in this frequency range in semiconductors.⁸ Since the sample was not intentionally doped with O or C, it is improbable that they are present in concentrations approaching 10^{18} cm^{-3} .

Polarized Raman spectroscopy was used to probe the symmetry of the defect. As seen in Figure 2, the N-H stretch vibration is most intense in the $X(Z'Z')\bar{X}$ and $X(ZZ)\bar{X}$ geometries, is weaker in the $X(ZY)\bar{X}$ geometry, and is not observed in the $X(Z'Y')\bar{X}$ geometry.¹¹ Although the $X(ZY)\bar{X}$ peak is small, it is reproducible and is observed in both samples where the peak is seen in infrared absorption. Selection rules for Raman scattering at tetrahedral, trigonal, orthorhombic, and monoclinic centers may be obtained in a straightforward manner.¹² The results shown in Figure 2 are only consistent with a defect of C_{3v} symmetry, which is the symmetry commonly observed for other H-passivated donor and acceptor impurities which have been studied.¹³ All other modes of a trigonal center, and modes of lower point group symmetry, predict a finite scattering intensity in the $X(Z'Y')\bar{X}$ geometry.

The two most probable models for the passivated complex are illustrated in Figure 3. The correct model must have C_{3v} symmetry and have the H atom bonded to the N acceptor. Drawing an analogy with C passivation in GaAs,^{14,15} the H atom could be bonded to the N atom in a bonding direction, with

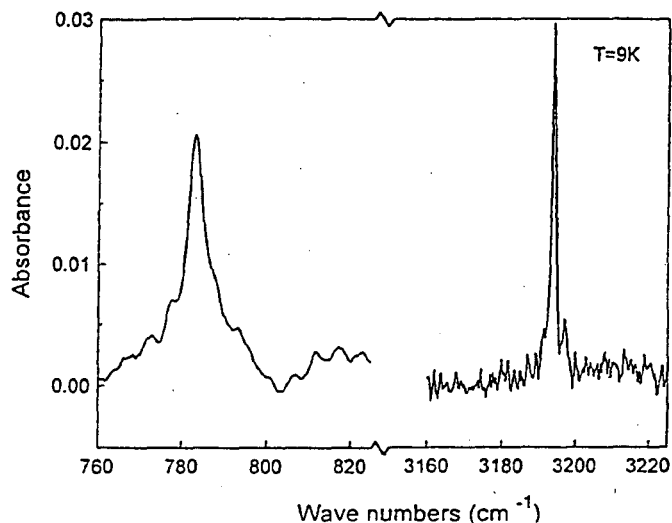


Fig. 1. Infrared absorption spectra of ZnSe:N showing the two N-H local vibrational mode peaks. $T = 9\text{K}$.

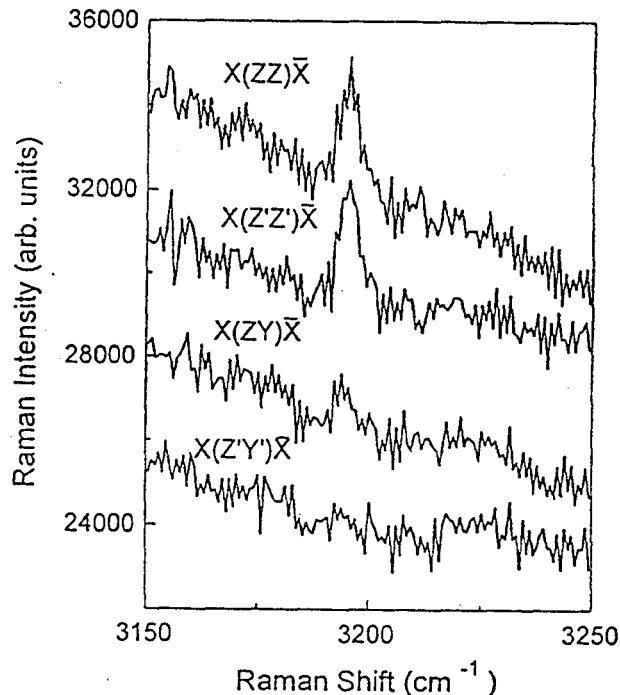


Fig. 2. Polarized Raman measurements of the 3194 cm^{-1} local vibrational mode. $T = 300\text{K}$. The polarization geometry is defined with respect to the sample surface ($[100]$). Spectra are offset vertically for clarity.

the bond to the nearest neighbor Zn atom being very weak. The other possibility is that the H atom is bonded to the N atom in an anti-bonding direction, but this geometry has not previously been observed for acceptor passivation.

We tentatively assign the peak at 783 cm^{-1} to the wag mode of the N-H complex. The relative strengths of the 783 cm^{-1} and 3194 cm^{-1} peak are the same in both samples we observed, suggesting they are related to the same defect. As seen in Figure 4, in polarized Raman scattering the 783 cm^{-1} peak is observed for the four scattering geometries described above, which is consistent with the E symmetry expected for a wag mode. The frequency of this peak is too high to be identified with a stretching or wagging vibration of the Zn-N or Se-N bonds.

We finally discuss one additional possibility for the identification of the two LVM peaks we observe. Our samples were initially characterized by photoluminescence spectroscopy carried out at 7K. The spectra were dominated by donor-acceptor pair transitions and did not show any excitonic transitions. The donor-acceptor pair transitions were seen to occur at longer wavelengths than in samples grown under similar conditions with N concentrations of approximately $1 \times 10^{18}\text{ cm}^{-3}$. It has been suggested that this difference in emission wavelength could be due to the presence of nitrogen related compensating defect complexes, such as a $V_{\text{Se}}\text{-Zn-N}_{\text{Se}}$ complex.¹⁶ Since these complexes have not been

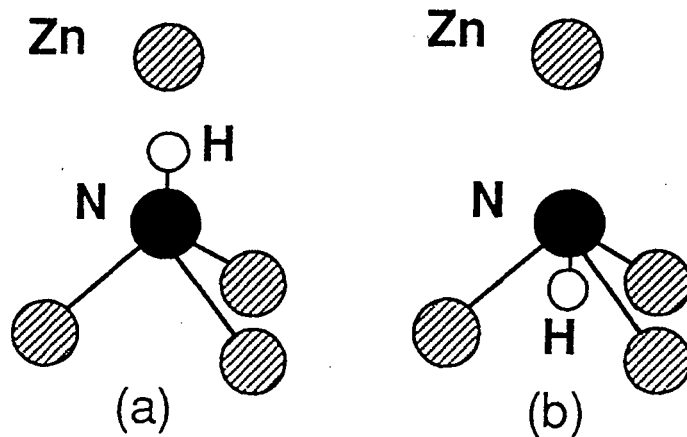


Fig. 3. Possible models for H-passivation of the N acceptor with a) the H atom in a bonding site and b) the H atom in an anti-bonding site.

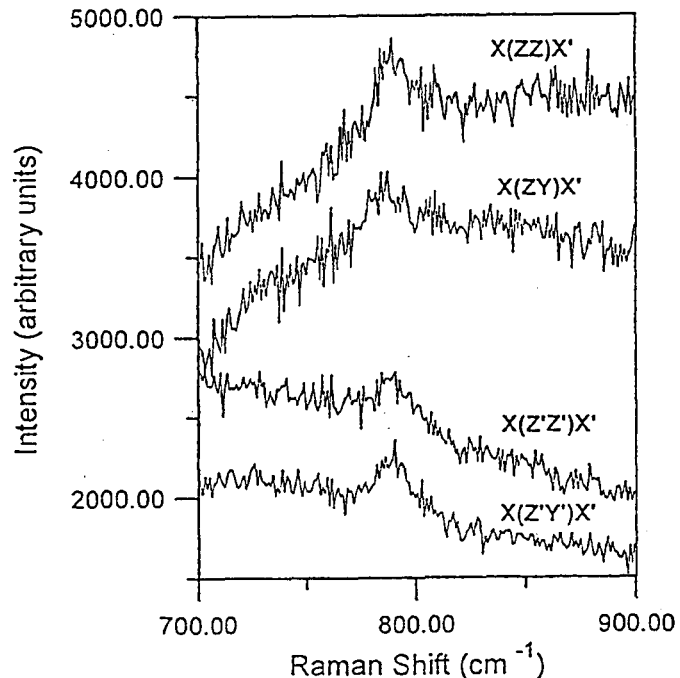


Fig. 4. Polarized Raman measurements of the 783 cm^{-1} local vibrational mode. $T = 300\text{K}$. The polarization geometry is defined with respect to the sample surface ($[100]$). Spectra are offset vertically for clarity.

positively identified, we cannot completely exclude the possibility that we are observing LVMs of H bonded to a N atom which is part of such a defect. However, given the high symmetry of the defect we observe and the narrowness of the LVM peaks (which become even narrower upon annealing of the samples), the most reasonable explanation for our data is that we are observing LVMs of H bonded to an uncomplexed substitutional N impurity.

In order to determine whether or not the N-H bond could be broken by annealing, the samples were capped with SiO₂ and heated to 650 and 750 °C. Figure 5 shows infrared absorption spectra of the wag mode for unannealed and annealed samples. While the

LVM peak does narrow, the area of the peak does not change, implying that there is no change in the concentration of the N-H centers. The narrowing of the peaks is likely to be due to a relaxation of strain present in the epilayer. A similar result is seen for the high frequency stretch mode.

The positions and FWHM of the observed peaks at 9K and 300K are listed in Table 1. We note the unusual feature that the frequency of the 783 cm⁻¹ peak increases with increasing temperature. This behavior is not presently understood.

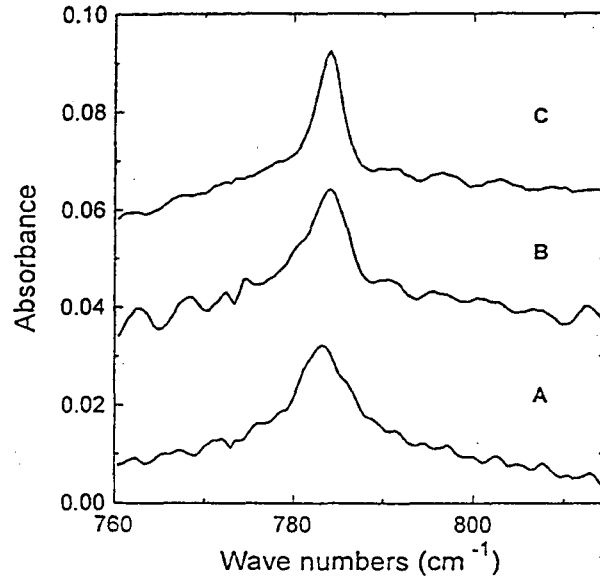


Fig. 5. Infrared absorption spectra of the N-H stretch mode in a) an unannealed sample b) a sample annealed at 650 °C c) a sample annealed at 750 °C.

Table I. Temperature dependence of frequency and FWHM of N-H LVM peaks

Temperature (K)	N-H Wag Mode (?)		N-H Stretch Mode	
	Peak Position (cm ⁻¹)	FWHM (cm ⁻¹)	Peak Position (cm ⁻¹)	FWHM (cm ⁻¹)
9	783.0	3.8	3193.6	1.5
300	789.3	9.0	3192.7	3.0

IV) CONCLUSION

In conclusion, using infrared absorption and polarized Raman scattering, we have discovered two new local vibrational modes in ZnSe:N,H. The higher frequency peak at 3194 cm⁻¹ is assigned to the stretch mode of a N-H bond, while the lower frequency peak at 783 cm⁻¹ is tentatively assigned to the N-H wag mode. The Raman polarization scattering results are only consistent with a C_{3v} symmetry for the defect, which implies that the H atom is either in a bonding

or an anti-bonding position. This study confirms that H forms a complex with N acceptors in ZnSe, implying that the presence of H during the growth process of MOVPE ZnSe plays a role in the problems encountered in achieving high p-type doping levels in this material.

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REFERENCES

- ¹ G. Mandel, Phys. Rev., 134, A1073 (1964).
- ² D. B. Laks, C. G. Van de Walle, G. F. Neumark, and S. T. Pantelides, Phys. Rev. Lett., 66, 648 (1991).
- ³ W. Walukiewicz, to be published in Proceedings of the 1993 Spring Meeting of the Materials Research Society.
- ⁴ J. Qiu, J. M. Depuydt, H. Cheng, and M. A. Haase, Appl. Phys. Lett., 59, 2992 (1991).
- ⁵ N. R. Taskar, B. A. Khan, D. R. Dorman, and K. Shahzad, Appl. Phys. Lett., 62, 270 (1993).
- ⁶ Sz. Fujita and Sg. Fujita, J. Crystal Growth 117, 67 (1992).
- ⁷ A. Yoshikawa and T. Okamoto, J. Crystal Growth 117, 107 (1992).
- ⁸ J. Chevalier, B. Clerjaud, and B. Pajot, in Semiconductors and Semimetals, eds. J. I. Pankove and N. M. Johnson, (Academic Press, Inc., Boston, 1991), Vol.34, p. 447.
- ⁹ B. Clerjaud, D. Cote, F. Gendron, W.-S. Hahn, M. Krause, C. Porte, and W. Ulrici, in Proceedings of the 16th International Conference on Defects in Semiconductors, edited by G. Davies, G. G. De Leo, and M. Stavola, (Trans Tech Publications, Switzerland, 1992), p.563.
- ¹⁰ B. Pajot, C. Song, and C. Porte, Proceedings of the 16th International Conference on Defects in Semiconductors, edited by G. Davies, G. G. De Leo, and M. Stavola, (Trans Tech Publications, Switzerland, 1992), p.581.
- ¹¹ In the notation [a(b,c)d], a (d) refers to the propagation vector of the incident (scattered) light, while b (c) refers to the polarization vector of the incident (scattered) light.
- ¹² M. Cardona, in Light Scattering in Solids II, edited by M. Cardona and G. Güntherodt, (Springer-Verlag, Berlin, 1982), p.19.
- ¹³ Semiconductors and Semimetals, eds. J. I. Pankove and N. M. Johnson, (Academic Press, Inc., Boston, 1991) Vol.34.
- ¹⁴ B. Clerjaud, F. Gendron, M. Krause, and W. Ulrici, Phys. Rev. Lett., 65, 1800 (1991).
- ¹⁵ R. Jones and S. Öberg, Phys. Rev. B, 44, 3673 (1991).
- ¹⁶ I. S. Haukssan, J. Simpson, S. Y. Wang, K. A. Prior, and B. C. Cavenett, Appl. Phys. Lett. 61, 2208 (1992).

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