

Vibrational spectroscopy of arsenic-hydrogen complexes in ZnSe

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Using infrared absorption spectroscopy, we have observed hydrogen local vibrational modes (LVMs) in arsenic-doped ZnSe grown by metalorganic chemical vapor deposition (MOCVD). When hydrogen is used as a carrier gas, we find an absorption peak at 2165.6 cm^{-1} , which we attribute to a bond-stretching mode of a hydrogen attached to an arsenic acceptor in a bond-centered orientation. With deuterium substituting the hydrogen carrier gas, we find an additional peak at 1557.1 cm^{-1} with $1/3$ the intensity of the hydrogen peak. The isotopic frequency ratio is $r = v_{\text{H}}/v_{\text{D}} = 1.3908$, similar to values found in many hydrogen/deuterium-related complexes. The larger area of the hydrogen peak indicates that most of the hydrogen comes from decomposition reactions involving the metalorganic molecules. The temperature dependent shift of the ZnSe:As,H mode is proportional to the lattice thermal energy $U(T)$, a consequence of the anharmonic coupling between the LVMs and the lattice phonons. [S0003-6951(96)03324-4]

The interest in developing blue light-emitting diodes and diode lasers has focused a great deal of research on the growth and doping of wide-band-gap semiconductors. Continuous wave ZnSe-based laser diodes have been fabricated from epilayers grown by molecular beam epitaxy (MBE), with high p -type doping achieved via a radio frequency plasma nitrogen source.^{1,2} Epilayers grown by metalorganic chemical vapor deposition (MOCVD), however, have proved resistant to p -type doping.^{3,4} Hydrogen plays a role in neutralizing the nitrogen acceptors, as shown by the observation of the local vibrational mode (LVM) of the N–H complex in MOCVD-grown ZnSe layers.^{5,6} Although arsenic-doped bulk ZnSe has only deep-level photoluminescence peaks,⁷ there is evidence that arsenic has a shallow acceptor level in ZnSe epilayers grown by MBE.⁸ The incorporation of hydrogen in arsenic and nitrogen doped MOCVD-grown ZnSe has been studied by secondary ion mass spectrometry (SIMS).⁹ In this letter, we report the observation of LVMs corresponding to an As–H complex in ZnSe.

The epitaxial ZnSe films were deposited on (100) GaAs substrates by MOCVD. The precursors to ZnSe were diisopropylselenide (DIPSe) and diethylzinc (DEZn) and the source of arsenic was tertiarybutylarsine (TBA). Pd-purified hydrogen, deuterium, or high-purity nitrogen was used as the carrier gas. The growth temperature was $464\text{ }^{\circ}\text{C}$, the molar flow ratio DIPSe/DEZn was 4, and the layers were $\sim 3\text{ }\mu\text{m}$ thick. Additional details of the MOCVD system are given in Ref. 9.

Infrared absorption spectra were obtained with a Bomem DA8 spectrometer with a KBr beamsplitter and an external mercury cadmium telluride (MCT) detector. The samples were placed in a Janis continuous-flow liquid helium cryostat with ZnSe windows. To detect the weaker absorption peak of the deuterated sample, a Ge:Cu photoconductor was

mounted directly behind the sample. The instrumental resolution of the spectrometer was 1 cm^{-1} .

The sample that was grown with hydrogen as a carrier gas has an infrared absorption peak at 2165.6 cm^{-1} at a sample temperature of 7 K. When nitrogen is used as a carrier gas, we find the same peak, but its area is reduced by a factor of 14, in good agreement with SIMS measurements⁹ which show that the sample grown with hydrogen has $[\text{H}] = 1.5 \times 10^{19}\text{ cm}^{-3}$ while the sample grown with nitrogen has $[\text{H}] = 1 \times 10^{18}\text{ cm}^{-3}$. In this case, the hydrogen most likely comes from the metalorganic molecules. The sample that was grown with deuterium as a carrier gas has an absorption peak at 1557.1 cm^{-1} , along with the hydrogen-related peak at 2165.6 cm^{-1} (Fig. 1). The isotopic frequency ratio is $r = v_{\text{H}}/v_{\text{D}} = 1.3908$. The peak positions, widths, areas, and r values of the LVMs are given in Table I. The area of the hydrogen-related peak is ~ 3 times that of the deuterium-related peak. Previous SIMS measurements show $[\text{H}] = 6 \times 10^{18}\text{ cm}^{-3}$ and $[\text{D}] = 1 \times 10^{18}\text{ cm}^{-3}$. These results indicate that most of the hydrogen incorporation comes from byproducts of reactions involving the hydrogen carrier gas and the metalorganic molecules. A sample which was grown at a lower temperature ($360\text{ }^{\circ}\text{C}$) contains high concentrations of hydrogen and arsenic ($[\text{H}] = 3 \times 10^{20}\text{ cm}^{-3}$ and $[\text{As}] = 1.8 \times 10^{21}\text{ cm}^{-3}$) but does not show the hydrogen-related peak. At the lower growth temperature, hydrogen may be incorporated in forms which are infrared inactive, such as interstitial H_2 molecules.

The hydrogen bond-stretching modes of the free molecules H_2Se , AsH_3 , and ZnH are 2345 ,¹⁰ 2116 ,¹⁰ and 1553 cm^{-1} ,¹¹ respectively. Since the frequency of the ZnSe:As,H mode is 2165.6 cm^{-1} , we propose that the hydrogen binds directly to the arsenic acceptor. In several respects, the As–H complex in ZnSe is similar to the Zn–H complex in GaAs.¹² In GaAs, zinc is an acceptor which occupies a substitutional gallium site. Hydrogen passivates zinc by attaching to a host arsenic atom, in a bond-centered orientation, adjacent to the

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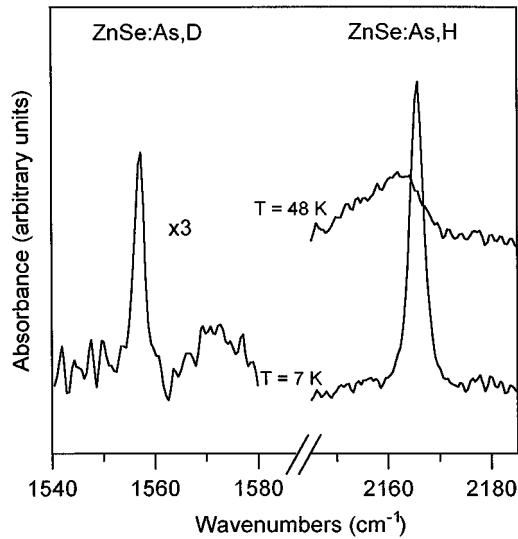


FIG. 1. Infrared absorption peaks corresponding to As–H and As–D complexes in MOCVD-grown ZnSe. The shift and linewidth broadening of the As–H LVM at higher temperatures is due to interactions with the lattice phonons.

zinc acceptor. In ZnSe:As it is likely that the hydrogen attaches to the arsenic acceptor, in a bond-centered orientation, adjacent to the host zinc atom (Fig. 2). The stretch mode of the GaAs:Zn,H complex is 2146.0 cm^{-1} at a temperature of 6 K and the isotopic frequency ratio is $r=1.3860$ (Table I). The fact that the isotopic ratios and LVM frequencies of the two complexes are very similar lends further support to the bond-centered model.

The temperature dependent behavior of the ZnSe:As,H LVM is shown in Fig. 1. The linewidth broadening and shift to lower energy with increasing temperature have been observed in numerous semiconductor systems and are believed to be caused by anharmonic coupling between the localized mode and the extended lattice phonons. As explained in Refs. 13 and 14, to first order the LVM shift is proportional to the lattice thermal energy $U(T)$

$$\delta(\hbar\omega) = \frac{\beta}{N_A} U(T), \quad (1)$$

where $U(T)$ is given in units of energy per mole, N_A is Avagadro's number, and β is a dimensionless constant. We obtained the values of $U(T)$ by numerically integrating the reported experimental values of the specific heat $C_v(T)$,¹⁵ neglecting the zero temperature energy. The data can be approximated by a linear least-squares fit to Eq. (1), with $\beta = -0.17$. The temperature dependent shift and the fit are shown in Fig. 3. At 77 K, the shift of the ZnSe:As,H mode is

TABLE I. Peaks, widths, and isotopic frequency ratios of As–H and As–D LVMs in GaAs:Zn and ZnSe:As.

Compound	As–H stretch mode		As–D stretch mode		$r = \nu_H/\nu_D$
	Peak (cm ⁻¹)	FWHM (cm ⁻¹)	Peak (cm ⁻¹)	FWHM (cm ⁻¹)	
GaAs:Zn ^a	2146.9	1.8	1549.1	0.9	1.3860
ZnSe:As	2165.6	2.8	1557.1	1.9	1.3908

^aSee Ref. 12.

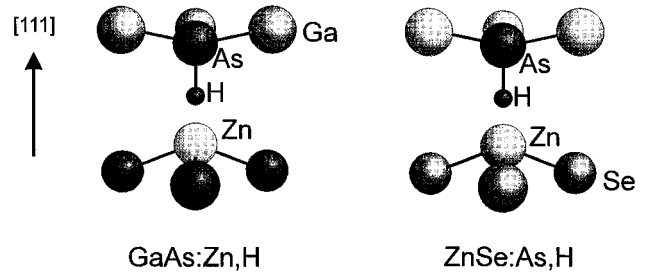


FIG. 2. Tentative model of ZnSe:As,H complex, as compared with the GaAs:Zn,H complex. In both complexes, the hydrogen sits in a bond-centered orientation between an arsenic and a zinc.

approximately twice that of the GaAs:Zn,H mode.

The broadening of LVMs is primarily determined by elastic phonon scattering which reduces the lifetime.¹³ In the Debye approximation this process leads to a temperature dependent linewidth

$$\delta\Gamma = \Gamma(T) - \Gamma(0) = A \left(\frac{T}{\theta_C} \right)^7 \int_0^{\theta_C/T} \frac{z^6 e^z}{(e^z - 1)^2} dz \quad (2)$$

where $k\theta_C/\hbar$ is the effective cutoff frequency and A is an empirical constant. For high temperatures, Eq. (2) reduces to

$$\delta\Gamma = \alpha T^2. \quad (3)$$

Elliot *et al.* point out that Eq. (3) is a good approximation even when T is a fraction of θ_C . Using Eq. (3), we obtain a fit to the data with $\alpha = 4 \times 10^{-3} \text{ cm}^{-1}/\text{K}^2$. The temperature dependent linewidth and the fit are plotted in Fig. 4.

The ZnSe:As,H mode has a slightly higher frequency, higher r factor, and stronger temperature dependence than the GaAs:Zn,H mode. These observations suggest that the coupling between the zinc and the hydrogen is slightly weaker in GaAs than in ZnSe. The effect of the zinc can be modeled as a repulsive potential which confines the hydrogen atom. The potential increases the frequency and the r factor, the latter because hydrogen has a larger amplitude than deuterium and overlaps the potential more. The temperature dependent shift of the frequency and linewidth are

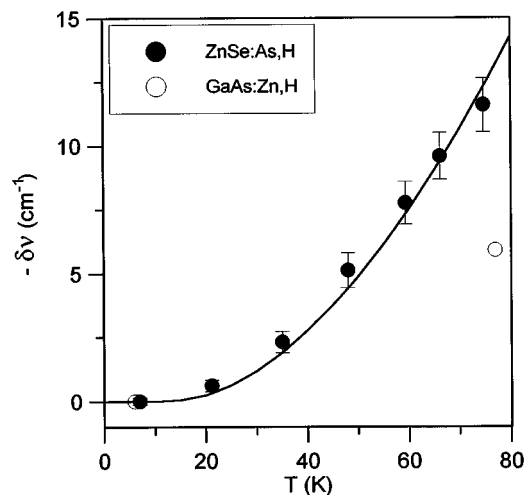


FIG. 3. Shift of the As–H LVM frequency with temperature for ZnSe (this work) and GaAs (Ref. 12). The solid line is a fit according to Eq. (1), with $\beta = -0.17$.

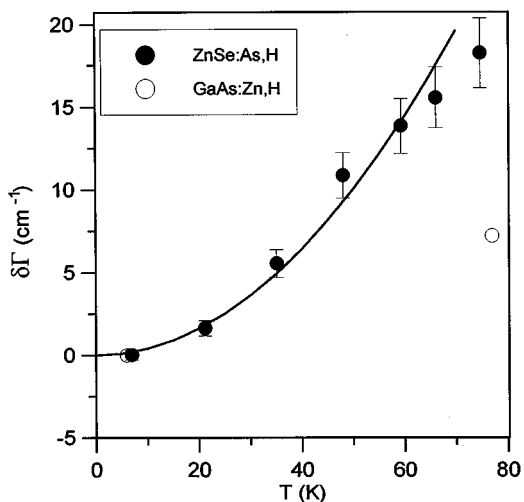


FIG. 4. Shift of the As-H LVM linewidth with temperature for ZnSe (this work) and GaAs (Ref. 12). The solid line is a fit according to Eq. (3), with $\alpha = 4 \times 10^{-3} \text{ cm}^{-1}/\text{K}^2$.

caused primarily by coupling between the hydrogen and the thermal motion of the zinc atom. Greater coupling leads to a LVM with a more pronounced temperature dependence. Although the cause of this greater coupling is not presently understood, it may be related to the fact that ZnSe is more ionic than GaAs.

In conclusion, we have discovered LVM peaks which we attribute to bond-stretching modes of As-H and As-D complexes in MOCVD-grown ZnSe. By analogy with the Zn-H complex in GaAs, we propose that the hydrogen binds directly to the arsenic acceptor in a bond-centered orientation, adjacent to a host zinc atom. Samples which were grown with deuterium as a carrier gas have a strong As-H peak and a weak As-D peak, indicating that the hydrogen originates primarily from byproducts of reactions involving

the metalorganic molecules and the carrier gas. Furthermore, it is clear that in *p*-type doping of MOCVD-grown ZnSe, hydrogen passivation plays a significant role.

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