

Hydrogen passivation of Se and Te in AlSb

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Using infrared absorption spectroscopy we have observed local vibrational modes (LVM's) arising from *DX*-hydrogen complex in AlSb. Hydrogen was diffused into bulk AlSb:Se and AlSb:Te by annealing in sealed quartz ampoules with either hydrogen gas or methanol (CH_3OH). The persistent photoabsorption of the *DX*-like Se donor is significantly reduced after hydrogenation. In hydrogenated AlSb:Se, we attribute the LVM peaks at 1608.6 and 1615.7 cm^{-1} to hydrogen stretch modes. Deuterated AlSb:Se has only one stretch mode at 1173.4 cm^{-1} . The second, third, and fourth harmonics of the wag modes are observed and show splittings consistent with C_{3v} symmetry. In AlSb:Te, we find a hydrogen stretch mode at 1599.0 cm^{-1} and a deuterium mode at 1164.4 cm^{-1} . We propose a model in which the hydrogen attaches to an aluminum in a $[111]$ antibonding orientation. [S0163-1829(96)04824-2]

I. INTRODUCTION

Hydrogen passivation of defects and impurities in semiconductors has been studied extensively over the past decade.¹ Following the discoveries that hydrogen passivates donors² and acceptors³ in GaAs, hydrogen-related complexes were discovered in numerous compound semiconductors.⁴ An important tool for studying the structure of hydrogen-related complexes is local vibrational mode (LVM) spectroscopy, since hydrogen-related vibrational frequencies are typically much higher than the lattice phonon frequencies and the substitution of deuterium for hydrogen results in a significant isotope shift.⁵ In this study, we report LVM's corresponding to *DX*-hydrogen complexes in AlSb. In most semiconductors, the *DX* state is the ground state only when the semiconductor is an alloy or when hydrostatic pressure is applied. In AlSb, however, the ground states of Se (Refs. 6 and 7) and Te (Ref. 8) donors are *DX* states, making them convenient for spectroscopic studies.

Hydrogen can be introduced into a sample by boiling in water, electrolysis, implantation, exposure to a hydrogen plasma, or contamination during the growth process.¹ In this paper, we show that annealing bulk AlSb:Se or AlSb:Te in a hydrogen atmosphere at temperatures as low as 700°C followed by a rapid quench leads to the formation of *DX*-hydrogen complexes. We have also found that hydrogen passivation can occur by annealing in methanol (CH_3OH) vapor. Stavola and co-workers demonstrated that annealing in hydrogen passivates shallow acceptors⁹ and platinum¹⁰ in silicon. Annealing of heavily doped epitaxial GaAs:C layers in a hydrogen ambient was shown to passivate the carbon acceptor.¹¹

II. EXPERIMENTAL DETAILS

The AlSb crystals were grown by the Czochralski technique from selenium- or tellurium-doped melts. The growth

was performed in a Sb-enriched melt, with an atomic fraction $[\text{Sb}]/([\text{Sb}]+[\text{Al}])=0.515$. Some of the samples were sealed in evacuated quartz ampoules with a $\frac{1}{3}$ -atm H_2 or D_2 ambient and annealed for 1 h at temperatures ranging from 700 to 950°C . After completion of the diffusion, the samples were quenched to room temperature by dropping the ampoules into ethylene glycol. Some AlSb samples were sealed in quartz ampoules with $0.3\text{-ml CH}_3\text{OH}$ or methanol- d_4 (CD_3OD) and annealed for 1 h at 900°C , followed by a rapid quench. Since an unknown fraction of the methanol evaporated before the ampoules were completely sealed, it was not possible to determine the methanol vapor pressure. To remove the surface damage from annealing in hydrogen, approximately $50\text{ }\mu\text{m}$ of the surface were lapped with a

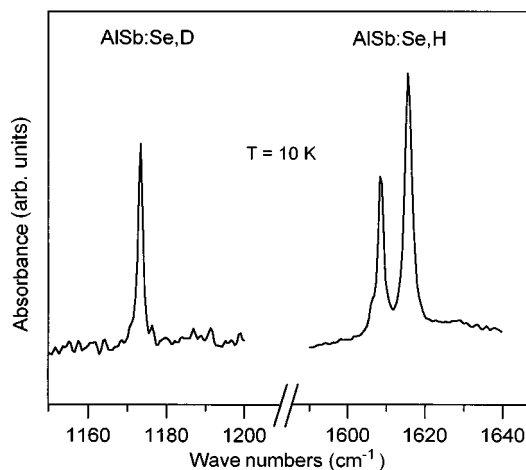


FIG. 1. Infrared absorption peaks of deuterated and hydrogenated AlSb:Se at a temperature of 10 K. The peaks are attributed to bond-stretching modes, with the deuterium and hydrogen attached to an aluminum atom.

TABLE I. Peak positions, widths, areas, and isotopic frequency ratios of hydrogen and deuterium related LVM's in AlSb:Se and AlSb:Te at liquid-helium temperature. The areas of the stretch modes are normalized to unity. FWHM denotes full width at half maximum.

H mode	ν (cm^{-1})	FWHM (cm^{-1})	Area	D mode	ν (cm^{-1})	FWHM (cm^{-1})	Area	$r = \nu_H/\nu_D$
Se-H								
Stretch 1	1608.6	1.5	1	Stretch	1173.4	1.4	1	1.3709
2	1615.7	2.2	2.4					1.3769
Wag								
Second harmonics	665.7	1.2	8.0	Second harmonics	478.3	1.5	3.7	1.3921
Third harmonics	692.2	0.5	0.91	Third harmonics	497.4	0.5	0.44	1.3916
Fourth harmonics	992.6	4.7	0.83	Fourth harmonics	717.5	0.4	0.2	1.3834
	1031.8	0.9	0.048		742.2	1.0	0.033	1.3902
	1315.8	1.5	0.25		948.4	1.2	0.046	1.3874
	1333.0	1.5	0.16		957.4	1.3	0.014	1.3923
Te-H								
Stretch	1599.0	1.3		Stretch	1164.4	1.0		1.3732
Wag (second harmonic)	665.0	1.0		Wag (second harmonic)	478.2	1.3		1.3906

slurry of 3 μm SiC grit and water, followed by a polish with a slurry of 0.3 μm Al_2O_3 powder and methanol. After polishing, the samples were approximately 2 mm thick.

Infrared absorption spectra above 500 cm^{-1} were obtained with a Bomem DA8 spectrometer with a KBr beam splitter and an external mercury cadmium telluride detector. For spectra below 500 cm^{-1} we used a 3- μm Mylar beam splitter and a deuterated tryglycine sulfate detector. The samples were placed in a Janis continuous-flow liquid helium-cryostat with ZnSe windows for spectra above 500 cm^{-1} and polypropylene windows for spectra below 500 cm^{-1} . We used instrumental resolutions ranging from 0.1 to 1 cm^{-1} such that all the LVM peaks were fully resolved.

III. RESULTS AND DISCUSSION

A. LVM's in AlSb:Se,H

AlSb:Se samples that were annealed in H_2 or CH_3OH at 900 $^\circ\text{C}$ for 1 h have infrared absorption peaks at 1608.6 and 1615.7 cm^{-1} at a temperature of 10 K (Fig. 1). Some of the as-grown samples also show these peaks with much smaller absorption strengths, indicating the presence of hydrogen in the growth process. Longer H_2 -annealing times do not increase the size of the peaks, so a 1-h H_2 anneal is probably sufficient to diffuse the hydrogen through the entire bulk. We attribute the peaks at 1608.6 and 1615.7 cm^{-1} to hydrogen stretch modes. Since the bond-stretching mode of the free diatomic molecule AlH is 1624 cm^{-1} ,¹² while the hydrogen stretch modes of H_2Se and SbH_3 are 2345 and 1891 cm^{-1} , respectively,¹³ we propose that the hydrogen binds to an aluminum atom.

AlSb:Se samples that were annealed in D_2 or CD_3OD at 900 $^\circ\text{C}$ for 1 h have only one stretch mode at 1173.4 cm^{-1} at a temperature of 10 K. AlSb:Se samples that were annealed in a mixture of H_2 and D_2 have the hydrogen- and deuterium-related peaks but no new peaks that would have indicated a multihydrogen complex. The isotopic frequency

ratios, $r = \nu_H/\nu_D$, are close to $\sqrt{2}$, indicating that the vibrational modes are dominated by the motion of the hydrogen and not the aluminum. For the stretch modes, since there are two hydrogen peaks, there are two r values, $r = 1.3709$ and

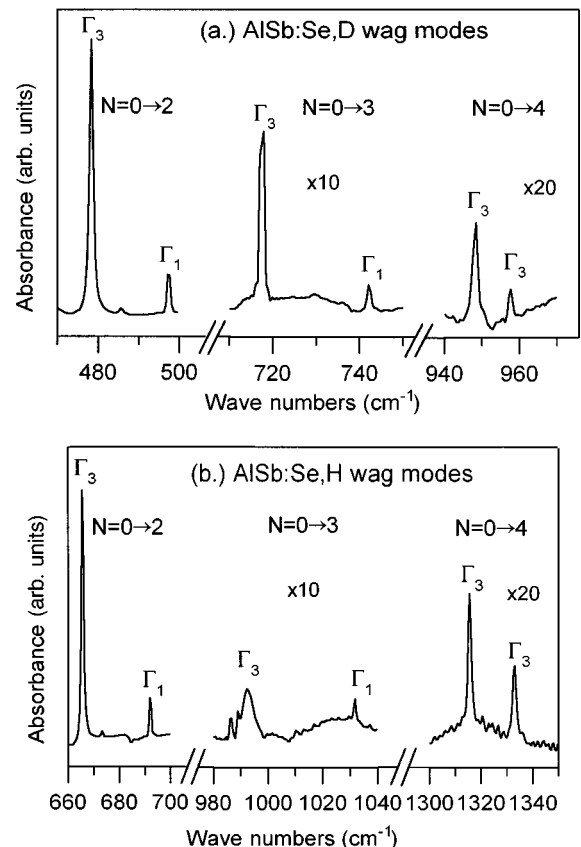


FIG. 2. Infrared absorption peaks of deuterated and hydrogenated AlSb:Se. The peaks are attributed to the second, third, and fourth harmonics of the hydrogen and deuterium wag modes.

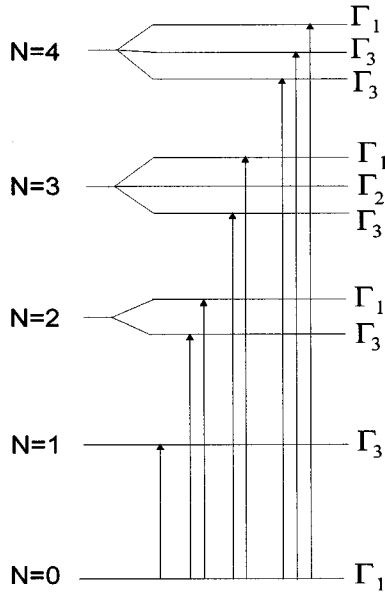


FIG. 3. The splitting of the hydrogen and deuterium wag modes in C_{3v} symmetry. The dipole allowed transitions are the $\Gamma_1 \rightarrow \Gamma_1$ and $\Gamma_1 \rightarrow \Gamma_3$ transitions.

1.3769. The peak positions, widths, areas, and r values of the LVM's are given in Table I. The fundamental transitions of the Se-D and Se-H wag modes are not observed, since the spectral regions where we expect to find them have significant phonon absorption features. The second, third, and fourth harmonics of the Se-D and Se-H wag modes have been observed (Fig. 2). The splittings of the peaks are a result of the threefold symmetry of the complex, as explained below. The energy-level spacings are approximately 240 and 330 cm^{-1} for the Se-D and Se-H wag modes, respectively. It should be noted that the fine structure and broadening of the Se-H third harmonic are not currently understood. In addition, there are small peaks at 486 and 673 cm^{-1} that may correspond to unidentified deuterium- and hydrogen-related complexes.

The splittings of the wag harmonics are consistent with a complex that possesses C_{3v} symmetry. In the plane perpendicular to the [111] axis, the C_{3v} potential is given by^{14,15}

$$V(x, y) = k/2(x^2 + y^2) + B(xy^2 - x^3/3) + C(x^2 + y^2)^2 + \dots, \quad (1)$$

where x and y are parallel to the $[1\bar{1}0]$ and $[11\bar{2}]$ crystallographic axes, respectively. For simplicity, we have omitted the wag-stretch coupling terms. The anharmonic terms in Eq. (1) lift the threefold degeneracy of the wave functions for $N = n_x + n_y > 1$. The predicted splittings are shown in Fig. 3. The dipole-allowed transitions are the $\Gamma_1 \rightarrow \Gamma_1$ and $\Gamma_1 \rightarrow \Gamma_3$ transitions. The higher harmonics give rise to weaker peaks, since they require higher-ordered anharmonic terms in Eq. (1).

We have assigned the stronger peaks in each pair to transitions from the ground (Γ_1) state to doubly degenerate Γ_3 states, while the weaker peaks correspond to transitions to a Γ_1 state. The $\Gamma_1 \rightarrow \Gamma_1$ transition corresponds to an induced electric dipole in the z direction, which is relatively small for a wag mode. The observed Γ_1 peaks are approximately 1/10

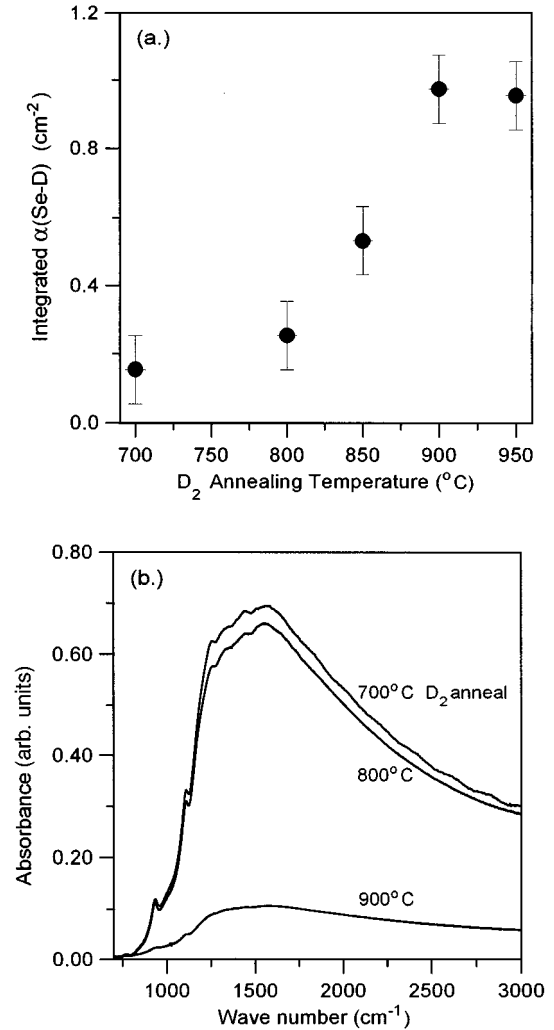


FIG. 4. (a) Integrated absorption of the Se-D peak in AlSb:Se as a function of D_2 annealing temperature. Samples were annealed in $\frac{1}{3}$ -atm D_2 for 1 h. (b) Persistent photoabsorption in AlSb:Se for annealing temperatures of 700, 800, and 900 $^{\circ}\text{C}$. The correlation between the increasing Se-D peak area and decreasing photoabsorption indicates that a significant fraction of Se DX centers are passivated.

the area of the Γ_3 peaks. The small size of the Γ_1 peaks may explain why we do not observe the Γ_1 mode of the fourth harmonic.

B. Electronic spectrum of passivated AlSb:Se

In addition to LVM's, we observed the effect of hydrogenation on the Se electronic spectrum. At temperatures below 90 K, AlSb:Se exhibits a large photoinduced persistent optical absorption.⁶ When AlSb:Se samples are exposed to light of energy 1 eV or more, the Se donors are transformed from a deep DX -like state to a metastable hydrogenic state. The hydrogenic absorption spectrum extends from 0.1 to 1.5 eV and is due to the excitation of the electron from the hydrogenic ground state to the X_1 and X_3 conduction bands. The hydrogenic spectrum was first measured by Ahlburn and Ramdas,¹⁶ long before the existence of DX centers was established.

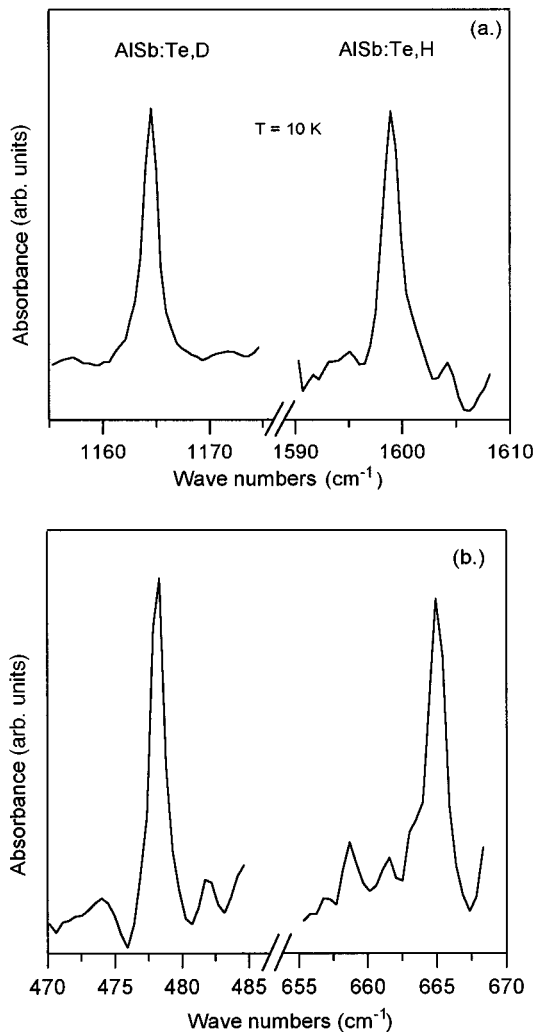


FIG. 5. Infrared absorption peaks of deuterated and hydrogenated AISb:Te. (a) Bond-stretching modes. (b) Second-harmonic wag modes. The LVM frequencies are similar to the Se-D and Se-H modes, providing evidence for the antibonding model.

We measured the persistent optical absorption of AISb:Se samples that were annealed in a D_2 atmosphere at several temperatures ranging from 700 to 950 °C. The absorption spectra at 10 K after 2-min exposures to a white filament light bulb were measured and referenced to the spectra prior to exposure. Although only a fraction of the Se_{DX} centers are transferred into their hydrogenic states, the strength of the photoinduced absorption gives a relative measure of the Se_{DX} concentration. As shown in Fig. 4, the persistent absorption decreases with increasing annealing temperature, while the height of the Se-D stretch mode increases. The correlation between the LVM increase and the persistent absorption decrease indicates that the deuterium passivates a significant fraction of the Se DX centers.

C. LVM's in AISb:Te,H

AISb:Te samples that were annealed in H_2 or D_2 atmospheres at 900 °C for 1 h have stretch modes at 1599.0 and 1164.4 cm^{-1} , and second-harmonic wag modes at 665.0 and 478.2 cm^{-1} , respectively (Fig. 5). Like Se, Te also exhibits a DX -like bistability in AISb.⁸ In the samples that we stud-

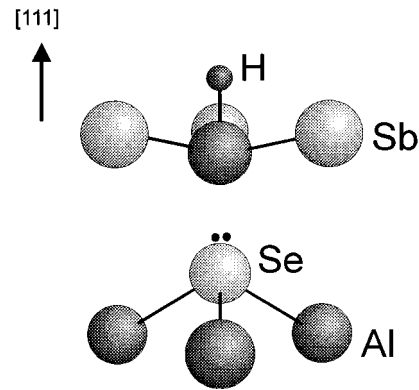


FIG. 6. Model for the structure of the DX -hydrogen complexes in AISb. The hydrogen attaches to an aluminum atom in a $[111]$ antibonding orientation.

ied, the Te-H peaks were 4 to 8 times weaker than the Se-H peaks, perhaps because hydrogen does not passivate Te as efficiently as Se. Because of significant continuum absorption from the Te donors, the second-harmonic wag modes were only visible in very thin (100 μm) samples. In these samples, the stretch modes were not visible, indicating that, as in the case of Se, the Te-H/D stretch modes are much weaker than the wag modes. The fact that the hydrogen stretch and wag modes of AISb:Se and AISb:Te have similar vibrational frequencies and r values provides evidence that the hydrogen attaches to an aluminum atom in an antibonding, rather than a bonding, orientation (Fig. 6). This finding is consistent with the study of Rahbi *et al.*¹⁷ and Vetterh ffer *et al.*,¹⁸ who measured the hydrogen modes in GaAs:Se and GaAs:Te to be 1507.5 and 1499.9 cm^{-1} , respectively. Those LVM's were attributed to hydrogen stretch modes, with the hydrogen attached to a gallium atom in an antibonding orientation. Since the hydrogen is weakly coupled to the donor, the LVM frequency does not depend strongly on the donor species.

Theoretical studies¹⁹ of the DX -hydrogen complex of GaAs:S under hydrostatic pressure suggest that two neutral hydrogen atoms can passivate a positively ionized donor and a negatively ionized DX center, resulting in two neutral complexes. The structures of the DX -hydrogen and donor-hydrogen complexes are identical, with the hydrogen in an antibonding $[111]$ orientation. Our results for DX -hydrogen complexes in AISb lend further support to the antibonding model.

IV. CONCLUSIONS

In conclusion, we have discovered that annealing AISb:Se and AISb:Te in hydrogen gas or methanol vapor results in the passivation of the Se and Te donors. The hydrogen stretch- and wag-mode harmonics are consistent with complexes that possess C_{3v} symmetry, with the hydrogen attached to an aluminum atom in a $[111]$ antibonding orientation. The antibonding model is similar to that of group-VI donor-hydrogen complexes in GaAs. We cannot presently explain why the Se-H complex has two stretch peaks while the Se-D complex has only one peak. Future studies should resolve that interesting anomaly.

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