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NOTICE

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ABSTRACT

GaSb-based semiconductors are of interest for mid-infrared optoelectronic and high-speed electronic devices. Accurate determination of electrical properties is essential for optimizing the performance of these devices. However, electrical characterization of these semiconductors is not straightforward since semi-insulating (SI) GaSb substrates for Hall measurements are not available. In this work, the capability of Raman spectroscopy for determination of the majority carrier concentration in n-GaInAsSb epilayers was investigated. Raman spectroscopy offers the advantage of being non-contact and spatially resolved. Furthermore, the type of substrate used for the epilayer does not affect the measurement. However, for antimonide-based materials, traditionally employed Raman laser sources and detectors are not optimized for the analysis wavelength range dictated by the narrow band gap of these materials. Therefore, a near-infrared Raman spectroscopic system, optimized for antimonide-based materials, was developed. $Ga_{0.85}In_{0.15}As_{0.13}Sb_{0.87}$ epilayers were grown by organometallic vapor phase epitaxy with doping levels in the range 2 to 80 x 10^{17} cm^{-3}, as measured by secondary ion mass spectrometry. For a particular nominal doping level, epilayers were grown both lattice matched to n-GaSb substrates and lattice-mismatched to SI GaAs substrates under nominally identical conditions. Single magnetic field Hall measurements were performed on the epilayers grown on SI GaAs substrates, while Raman spectroscopy was used to measure the carrier concentration of epilayers grown on GaSb and the corresponding SI GaAs substrates. Compared to Hall measurements, Raman spectra indicated that the GaInAsSb epilayers grown on GaSb substrates have higher free carrier concentrations than the corresponding epilayers grown on SI GaAs substrates under nominally identical conditions. This is contrary to the assumption that for nominally identical growth conditions, the resulting carrier concentration is independent of substrate, and possible mechanisms will be discussed.

INTRODUCTION

GaSb-based group III-V semiconductors are of interest for mid-infrared sources and detectors and low-power, high-speed electronic devices [1]. Of this class of materials, $Ga_{1-x}In_xAs_ySb_{1-y}$, with a composition-dependent direct energy gap in the wavelength range from 1.7 μm (0.726 eV) to 4.2 μm (0.296 eV), has attracted interest for optoelectronic devices operating in the mid-infrared, e.g., lasers, photodetectors, and thermophotovoltaic devices [2]. Accurate determination of electrical properties is essential for optimizing the performance of GaInAsSb devices. However, electrical characterization of GaInAsSb devices grown lattice-matched to GaSb is complicated by the scarcity of semi-insulating (SI) GaSb substrates for Hall effect measurements. In addition, there is a relatively small energy difference between the Γ and L conduction band minima in GaSb and many GaSb-based alloys with GaSb-rich compositions. As a result, multiple conduction band minima are occupied at room temperature at intermediate doping levels and even at low temperatures at high doping levels. Multiple carrier type analysis

of single field Hall effect measurements requires a knowledge of the ratio of the electron mobility of all carrier types, information which is not typically available. Hence, the presence of multiple carrier types makes unambiguous interpretation of single magnetic field Hall effect measurements difficult. So, alternative methods of determining electrical properties would be particularly useful for GaInAsSb-based device development.

Raman spectroscopy has long been used to determine carrier concentrations and, less often, mobilities in compound semiconductors [3]. Raman spectroscopy is attractive for such investigations because this technique is non-contact and spatially resolved. However, to the authors' knowledge, Raman spectroscopy has not yet been employed to determine carrier concentrations in n-type GaInAsSb. This could be due in part to the difficulty in employing the more traditional Raman spectroscopic systems, e.g., based on visible laser wavelengths, to probe bulk carrier properties of antimonide-based materials. The difficulty arises because the optical penetration depth is shallow in antimonide-based materials for visible wavelengths, e.g., a ca. 20 nm penetration depth in $Ga_{0.85}In_{0.15}As_{0.14}Sb_{0.86}$ for 514.5 nm radiation [4]. In addition, a surface space charge region (SSCR) that can be of comparable thickness to the penetration depth of visible radiation typically exists on the surface of antimonide-based materials. For example, an accumulation layer estimated to be 15 nm thick exists on surfaces of p-GaSb with a bulk hole concentration of ca. 4×10^{16} cm^{-3} [5] while a depletion layer estimated to be 15 nm to 20 nm thick exists on surfaces of n-GaSb with a bulk electron concentration of ca. 2×10^{18} cm^{-3} [6]. Hence, utilization of a less strongly absorbed excitation wavelength is necessary to better investigate bulk carrier properties in GaSb-based materials.

In this work, the capability of Raman spectroscopy for determination of the majority carrier concentration in n-GaInAsSb epilayers was investigated. A near-infrared Raman spectroscopic system was developed and used to determine carrier properties in n-GaInAsSb epilayers grown under nominally identical conditions on GaSb and SI GaAs substrates. This allowed the direct comparison of carrier densities in epilayers grown on both substrates, a comparison that is impossible using single magnetic field Hall effect measurements.

EXPERIMENTAL DETAILS

$Ga_{0.85}In_{0.15}As_{0.13}Sb_{0.87}$ epitaxial layers were grown on both n-GaSb and semi-insulating (SI) GaAs substrates, (001) miscut 6° toward (1-11)B. Solution trimethylindium, triethylgallium, tertiarybutylarsine, and trimethylantimony were used as precursors. Diethyltellurium (DETe), 10 ppm diluted in H_2, was used as the n-type dopant and the DETe mole fraction ranged from 5×10^{-9} to 100×10^{-9}. The layers were grown in a previously described vertical rotating-disk OMVPE reactor [7] with H_2 carrier gas flow rate of 10 slpm; reactor pressure of 20 kPa (150 Torr); and susceptor rotation rate of 250 rpm. GaInAsSb epilayers were grown at 525 °C and a V/III ratio of 1.8. The alloy composition of GaInAsSb corresponds to a 300 K photoluminescence peak emission at 2.3 µm for epilayers that are nominally lattice-matched to GaSb. n-GaInAsSb was grown on an unintentionally doped (UID) GaSb buffer that was first deposited on the n-GaSb or SI GaAs substrate at 550 °C. Growth was interrupted after the buffer layer deposition to reduce the temperature to 525 °C, and subsequently n-GaInAsSb was grown. The buffer layer thickness was 0.1 µm for n-GaInAsSb on n-GaSb substrates, while it was 0.4 µm for layers grown on SI GaAs. The thicker buffer layer was used in order to reduce the contribution of electrically active defects that result from the lattice mismatch between the

GaInAsSb and GaAs [2]. UID GaInAsSb epilayers are lightly p-type. The n-doped epilayers are 2 μm to 3 μm in thickness.

Carrier concentration and mobility were determined for n-GaInAsSb grown on SI GaAs substrates. The determinations were based upon van der Pauw Hall effect measurements performed at 300 K using a 10 KG field. The atomic Te concentration was determined for epilayers grown on both SI GaAs and n-GaSb substrates, and was measured by secondary ion mass spectroscopy (SIMS) using a Cs^+ primary ion beam. Calibration of the absolute Te concentration is based on GaInAsSb standards that were ion implanted with Te.

Raman spectroscopic measurements were performed at (nominally) room temperature in a backscattering geometry described by $z(x, y)\bar{z}$, where x, y, z, and $\bar{z}$ denote [100], [010], [001], and [00$\bar{1}$], respectively. Raman scattering was excited using 752.5 nm radiation from a krypton ion laser. The penetration depth of 752.5 nm radiation in $Ga_{0.85}In_{0.15}As_{0.14}Sb_{0.86}$ has been reported to be 100 nm [4]. It is assumed that this is approximately the same penetration depth of 752.5 nm radiation in $Ga_{0.85}In_{0.15}As_{0.13}Sb_{0.87}$ (the composition investigated in this work). A holographic laser bandpass filter was used to remove laser plasma lines. All Raman spectra were obtained using appropriate instrumentation that included a 752.5 nm holographic notch filter (150 cm^{-1} nominal spectral edgewidth and 6.0 nominal optical density), a dichroic sheet polarizer, a bandpass filter (optimized to pass radiation in the ca. 750 nm to 1100 nm wavelength range and used to reduce potential interference from reentrant light), a 0.5 m focal length, f/6.5 aperture ratio imaging spectrograph equipped with a 1200 groove/mm grating blazed at 500 nm, and a 1024 x 128 pixel array (26 μm x 26 μm square pixels) back-illuminated, thermo-electrically cooled (to -89 °C), deep depletion charge coupled device camera system. The instrumental bandpass (FWHM) was ca. 3.3 cm^{-1}. Less than 75 mW of laser radiation was focused with a spherical lens on to the specimen to produce an approximately 230 μm diameter spot. All Raman intensities were corrected for the wavelength-dependent response of the optical system using a white-light source of known relative irradiance.

DISCUSSION

Figure 1 shows the Raman spectra of UID and doped GaInAsSb epilayers grown on GaAs substrates with the carrier densities determined from Hall effect measurements indicated. Similar spectra were obtained for the GaInAsSb epilayers grown on GaSb. The UID GaInAsSb spectrum exhibits two intense peaks at ca. 230 cm^{-1} and ca. 246 cm^{-1}. The ca. 230 cm^{-1} peak is attributed to a combination of the GaSb-like and InAs-like longitudinal optic (LO) phonon modes while the ca. 246 cm^{-1} peak is attributed to the GaAs-like LO phonon mode [8]. The weaker features at ca. 200 cm^{-1} and lower wavenumbers are the rotational Raman scattering from oxygen and nitrogen in air. It is apparent from Figure 1 that the presence of free carriers modifies the appearance (relative intensity and FWHM) of the LO phonon modes. These modifications are due to a number of factors. In the case of compound semiconductors with SSCR's thinner than the optical penetration depth, one expects a superposition of scattering from the SSCR and the bulk. The scattering from a depletion layer SSCR approximates the scattering observed from an epilayer in which no free carriers are present, i.e., similar to the UID spectrum. In the bulk, the free electrons can interact with the polar LO phonon modes resulting in coupled phonon-plamson modes of mixed phonon and plasmon character [3]. Raman scattering from the bulk will involve these coupled phonon-plasmon modes and is the signal of interest in this work. Although, to the authors' knowledge, no observation of the coupled modes in quaternary
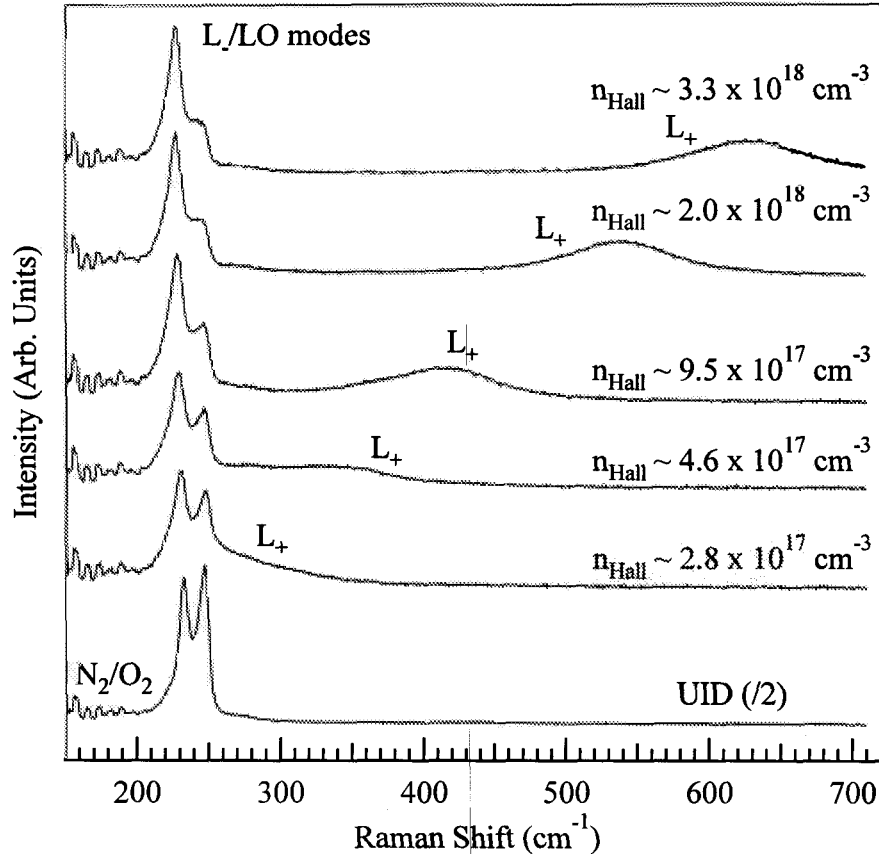
L_/LO modes

$n_{Hall} \sim 3.3 \times 10^{18}$ cm^{-3}

L_+

$n_{Hall} \sim 2.0 \times 10^{18}$ cm^{-3}

L_+

L_+

$n_{Hall} \sim 9.5 \times 10^{17}$ cm^{-3}

L_+

$n_{Hall} \sim 4.6 \times 10^{17}$ cm^{-3}

L_+

$n_{Hall} \sim 2.8 \times 10^{17}$ cm^{-3}

N_2/O_2

UID (/2)

Intensity (Arb. Units)

200   300   400   500   600   700

Raman Shift (cm^{-1})

Figure 1. Raman spectra of UID and doped GaInAsSb epilayers grown on GaAs substrates. The carrier density determined from the Hall effect measurement is indicated. The spectra are offset on the vertical scale for clarity.

compounds have been reported, one might reasonably expect to identify up to four coupled modes, depending on the lattice dynamics of the particular alloy. In addition, the coupled modes are often observed near the LO phonon mode wavenumbers in low-effective mass and low-phonon energy materials [9], i.e., the case for GaInAsSb. Hence, the relatively small wavenumber difference between the various LO phonon modes and the likelihood of the coupled modes being observed at wavenumbers near those of the LO phonon modes make it impossible to resolve all phonon and coupled modes. Thus, it is difficult to definitively identify the origin of all of the trends observed in the spectra in Figure 1. An important exception is the behavior of the mode denoted L_+ in Figure 1 which is the highest-frequency coupled mode. The L_+ mode is relatively well resolved, especially at higher doping levels, and the L_+ wavenumber increases with increasing electron density. Hence, the L_+ wavenumber can be used as a qualitative measurement of electron density.

Figure 2 shows the L_+ wavenumber obtained from spectra of n-GaInAsSb grown on GaSb and SI GaAs substrates plotted as a function of DETe mole fraction in the reactor. Error bars are plotted but not visible on this scale. The error in the L_+ wavenumber is taken to be ±5% of the peak FWHM. As shown in Figure 1, the L_+ mode wavenumber increases with increasing DETe mass flow, indicating a higher carrier density at higher DETe mass flow (dopant density). In addition, the L_+ mode wavenumber is observed at a consistently higher wavenumber for
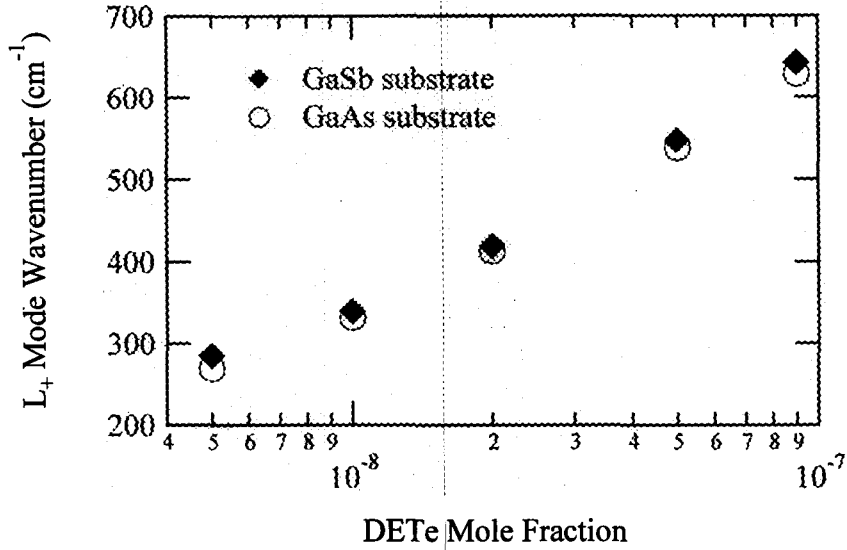
700

600 ● GaSb substrate
○ GaAs substrate

500

400

300

200

L$_+$ Mode Wavenumber (cm^{-1})

4 5 6 7 8 9   2   3   4 5 6 7 8 9
10^{-8} 10^{-7}

DETe Mole Fraction

Figure 2. The L$_+$ wavenumber obtained from spectra of n-GaInAsSb grown on GaSb substrates (●) and SI GaAs substrates (○) plotted as a function of DETe mole fraction in the reactor.

epilayers grown on GaSb vs. GaAs substrates, indicating a higher electron density in epilayers grown on GaSb vs. GaAs substrates.

As shown in Figure 2, a higher electron density was observed in epilayers grown on GaSb vs. GaAs substrates. A number of factors could contribute to this difference. One possibility is that dopant incorporation is different on the different substrates. However, SIMS results show no significant difference in dopant density on the different substrates. Assuming that dopant activation is the same on both substrates, it seems likely that the difference in carrier concentrations is related to the lattice mismatch between GaInAsSb and GaAs, a mismatch that does not exist between GaInAsSb and GaSb. Hence, the difference in carrier concentrations is attributed to electrically active defects originating in the epilayer-buffer layer-GaAs substrate interface region. The observation of a difference in epilayer carrier densities on different substrates is contrary to the assumption often made that for nominally identical growth conditions the resulting GaInAsSb carrier concentration is independent of substrate.

Qualitative comparison of carrier concentrations from the GaInAsSb Raman spectra is relatively straight-forward, however, quantitative comparison is more difficult. Only a brief description of the quantitative analysis will be given since a detailed description is not possible in the format of this report. The quantitative analysis involves simulating a Raman spectrum using the expression shown in equation 1 for the Raman scattering intensity, I, of the coupled phonon-plasmon mode system as a function of the scattering wavevector, q, and wavenumber, ω.

$$I \propto \text{Im}\left\{ \frac{-1}{\varepsilon(q,\omega)} \right\} \tag{1}$$

Where $\varepsilon(q, \omega)$ is the dielectric function. To describe the lattice contribution to the dielectric function, the GaInAsSb lattice was approximated by the weighted contributions from the four binary constituents (GaAs, InAs, GaSb, and InSb) using the expression for a 4-mode system described in ref. [10]. To describe the free electron contribution to the dielectric function, the

modified hydrodynamical model described in ref. [11], modified to include two carrier types, was used. Materials properties were obtained from the literature, althougth many GaInAsSb materials properties are not well established. The results from the simulation using equation 1 were then compared to the experimental spectrum and a global search minimization was performed to minimize the sum of the residuals squared. For these simulations, the only two fit parameters were the Fermi energy and the plasmon damping constant, both contained in the expression for the free electron contribution to the dielectric function. For a resulting Fermi energy, the total carrier density in the epilayer was then calculated. The electron densities determined from the spectral fits were inconsistent with the SIMS measurements. This indicates that a more sophisticated expression for the free electron contribution to the dielectric function is needed for the quantitative determination of electron density, probably one that includes Landau damping or a better description of conduction band non-parabolicity.

CONCLUSIONS

Raman spectroscopy is sensitive to electron density in n-type GaInAsSb. Raman spectroscopic measurements indicate that electron density is higher in GaInAsSb epilayers grown on GaSb substrates vs. SI GaAs substrates. The difference in carrier densities is attributed to electrically active defects originating in the epilayer-buffer layer-GaAs substrate interface region. The observation of a difference in epilayer carrier densities on different substrates is contrary to the assumption often made that for nominally identical growth conditions the resulting GaInAsSb carrier concentration is independent of substrate. The electron densities determined from the spectral fits were inconsistent with the SIMS measurements, indicating that a more sophisticated spectral model is needed for the quantitative determination of electron density from Raman spectra.

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