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Raman scattering of polycrystalline GaSb thin films grown by the co-evaporation process*

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This paper reports that GaSb thin films have been co-deposited on soda-lime glass substrates. The GaSb thin film structural properties are characterized by Raman spectroscopy. The Sb–A_{1g}/GaSb–TO ratio decreases rapidly with the increase of substrate temperature, which suggests a small amount of crystalline Sb in the GaSb thin film and suggests that Sb atoms in the thin film decrease. In Raman spectra, the transverse optical (TO) mode intensity is stronger than that of the longitudinal optical (LO) mode, which indicates that all the samples are disordered. The LO/TO intensity ratio increases with increasing substrate temperature which suggests the improved polycrystalline quality of the GaSb thin film. A downshift of the TO and LO frequencies of the polycrystalline GaSb thin film to single crystalline bulk GaSb Raman spectra is also observed. The uniaxial stress in GaSb thin film is calculated and the value is around 1.0 GPa. The uniaxial stress decreases with increasing substrate temperature. These results suggest that a higher substrate temperature is beneficial in relaxing the stress in GaSb thin film.

Keywords: GaSb, co-evaporation, Raman, stress
PACC: 7280E, 6855, 3220F, 0630M

1. Introduction

GaSb is an important III–V semiconductor for detectors, semiconductor lasers, and thermophotovoltaic devices which operate in the mid-infrared range.[1] Organic metallic vapour phase epitaxy,[2] molecular beam epitaxy[3,4] and liquid phase epitaxy[5,6] have been utilized in the growth of GaSb material. All these methods are high processing cost technologies; one possibility of reducing the processing cost is the co-evaporation method.

Raman scattering is well known as a useful means of investigating the structures in semiconductors. Raman scattering can give effective information about various crystalline structures from single crystalline to amorphous samples. A number of Raman studies on single crystalline GaSb samples[7−9] and amorphous GaSb samples[10−12] have been reported. However, a Raman study on polycrystalline GaSb has not yet been reported.

In this work, we successfully obtain GaSb thin films grown by co-evaporation on soda-lime glass substrates. Using room-temperature Raman spectroscopy, we have carried out a systematic study of the effects of substrate temperature on the structure of polycrystalline GaSb films, Sb content and substrate stress.

2. Experimental details

Thin films of GaSb were deposited on thoroughly cleaned soda-lime glass substrates at different substrate temperatures. The base pressure of the evaporation system chamber was better than 1×10^{-4} Pa before deposition. In this system, vapours of the individual high purity Ga(99.9999%) and Sb(99.9999%) elementary source materials were ejected through a nozzle (a perforation on the top lid) of the crucible. The substrate rotated at 30 rpm during deposition and the deposition rate was maintained at 20 nm·min^{-1}.

Room-temperature Raman scattering was performed in the backscattering geometry by employing the 514.5 nm line of an argon-ion laser. The information depth of Raman spectroscopy is defined as $(2\alpha)^{-1}$, where α is the absorption coefficient. For GaSb probed with 514.5 nm radiation, the information depth is about 10 nm.[13]

In spite of this fact we could not identify charac-

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teristic surface effects in any of the Raman spectra of the measured GaSb films. A low laser power was used to prevent local heating of the sample. The incident laser was focused by a 50× objective lens to a spot of about 2 μm on the sample surface. The scattered signal was collected by the same objective lens. In order to reduce the background signal and to increase the accuracy of the measurements, the near-laser signal was chopped-off by a suitable notch-filter and the slit width was reduced to about 20 μm. The scattered light was dispersed by a Renishaw spectrometer and the spectra were recorded using a CCD detector.

3. Results and discussion

The x-ray diffraction (XRD) patterns of GaSb thin films were recorded in the range of $2\theta = 15^\circ - 85^\circ$ by using CuKα radiation (not presented). The XRD spectra revealed that the thin films are polycrystalline in structure. The thin films are dominated by three principal orientations: (111), (220) and (311). All the GaSb films have highly (111) preferred orientations. For III–V semiconductors like GaSb and other zinc-blende structures, the first-order Raman spectrum usually consists of two Raman modes corresponding to the longitudinal optical (LO) and transverse optical (TO) phonons associated with the Brillouin zone centre. The zone centre phonons corresponding to TO and LO modes obey the following selection rules for zinc-blende-type crystals. Only the TO mode is allowed for scattering by (110) orientation, whereas the LO mode is allowed for (100) orientation.[14] The (111) preferred orientation of GaSb thin films provides the possibility of observing by Raman selection rules both TO and LO phonons.

Figure 1 shows Raman scattering spectra of GaSb grown on soda-lime glass at different substrate temperatures. The Raman spectra present mainly three vibrational bands centred at around 160.4, 223.3 and 232.0 cm^{-1}. In accordance with Refs.[15, 16], we conclude that the lines observed at around 160.4 cm^{-1} might be associated with the A_{1g} Sb–Sb bond vibrations mode. The other two lines at 223.3 and 232.0 cm^{-1} correspond to the LO and TO phonon modes, respectively, and are very close to the TO and LO phonons of single crystalline GaSb.[17] The value of the Sb–A_{1g}/GaSb–TO line intensity ratio observed in each spectrum is small which suggests a small amount of crystalline Sb in these samples. Substrate temperature dependence of the Sb–A_{1g}/GaSb–TO line Raman peak intensities for increasing substrate temperature from 480 °C to 560 °C is shown in Fig.2. The Sb–A_{1g}/GaSb–TO ratio decreases rapidly with the increase of substrate temperature. Several reasons can be suggested to explain this discrepancy. One of them is that, when the substrate temperature increases, the Sb atoms with higher energy easily form GaSb with the Ga atoms, so the Sb atoms in the thin film decrease. In all Raman spectra, the TO mode intensity is always stronger than that of the LO mode, which indicates that all the samples are disordered. The LO/TO intensity ratio is an index of the degree of GaSb crystal symmetry ordering.[15] The increase of the LO/TO intensity ratio with increasing substrate temperature is seen in Fig.2. The LO/TO intensity ratio increases with the increase of substrate temperature. These results suggest that the polycrystalline quality of GaSb thin film is improved with the increase of substrate temperature.

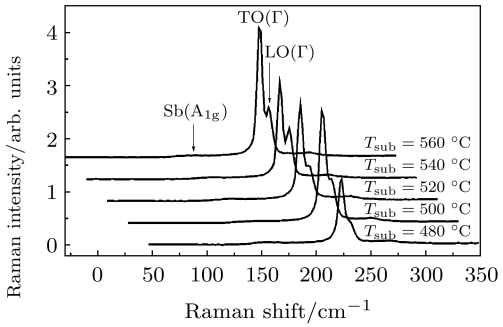


Fig.1. Raman spectra of polycrystalline GaSb samples grown at different substrate temperatures.

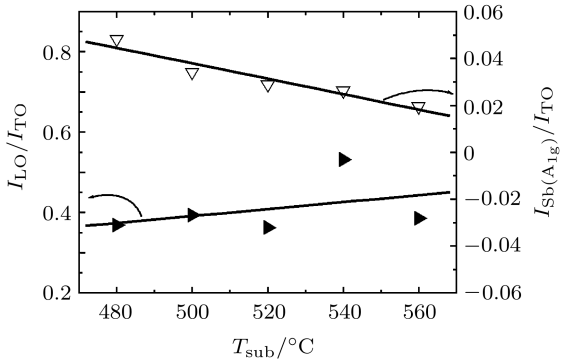


Fig.2. Sb–A_{1g}/GaSb–TO and GaSb–LO /GaSb–TO line Raman intensity ratios for GaSb with different substrate temperatures.

A downshift of the TO and LO frequencies of polycrystalline GaSb thin film to single crystalline bulk GaSb Raman spectra is also observed. These results are summarized in Fig.3, in which the frequencies are plotted as a function of the substrate temper-

ature. The origin of this difference can be attributed to strains due to the difference between the thermal expansion coefficients of GaSb thin film and the soda-lime glass substrate. We attempt to explain the shift of the TO and LO frequencies by calculating the uniaxial stress in GaSb thin film.

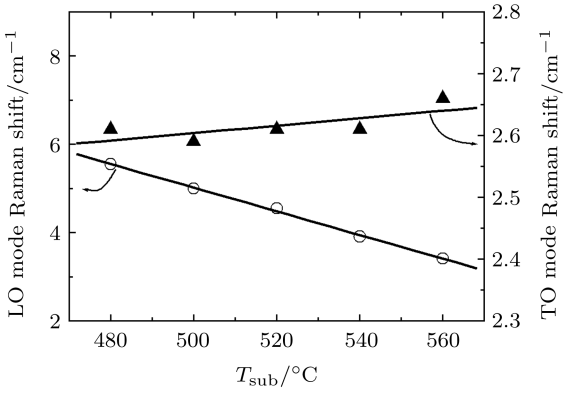


Fig.3. Frequency shift of TO and LO modes versus substrate temperature.

In accordance with Ref.[18], in the presence of strain, for the $\boldsymbol{k}=0$ triply degenerate optical modes in diamond-type crystals to terms linear in the strain, we obtain the following dynamical equation:

$$\begin{aligned}\bar{m}\ddot{u}_i &= -\sum_k K_{ik}u_k \\ &= -\left(K_{ii}^{(0)}u_i+\sum_{klm}\frac{\partial K_{ik}}{\partial\varepsilon_{lm}}\varepsilon_{lm}u_k\right), \end{aligned} \tag{1}$$

where u_i is the ith component of the relative displacement of the two atoms in the unit cell; $\bar{m}$ is the reduced mass of the two atoms; $K_{ii}^{(0)}=\bar{m}\omega_0^2$ is the effective spring constant of the $F_{2\rm g}$ modes in the absence of strain.

From Eq.(1) and the above considerations we can obtain the following secular equation whose solutions yield the frequencies of the optical phonons in the presence of strain:

$$\begin{vmatrix} p\varepsilon_{xx}+q\left(\varepsilon_{yy}+\varepsilon_{zz}\right)-\lambda & 2\gamma\varepsilon_{xy} & 2\gamma\varepsilon_{xz} \\ 2\gamma\varepsilon_{xy} & p\varepsilon_{yy}+q\left(\varepsilon_{zz}+\varepsilon_{xx}\right)-\lambda & 2\gamma\varepsilon_{yz} \\ 2\gamma\varepsilon_{xz} & 2\gamma\varepsilon_{yz} & p\varepsilon_{zz}+q\left(\varepsilon_{xx}+\varepsilon_{yy}\right)-\lambda \end{vmatrix} \equiv 0, \tag{2}$$

where $\lambda=\Omega^2-\omega_0^2$ and $\Omega\approx\omega_0+\dfrac{\lambda}{2\omega_0}$ is the strain-dependent frequency of the optical phonons. The secular equation refers to the crystallographic axes, $\hat{x}=[100]$, $\hat{y}=[010]$, $\hat{z}=[001]$. Diagonalization of Eq.(2) yields a set of three eigenvectors of the optical phonons which is split into a singlet ($\Omega_{\rm s}$) with eigenvector parallel to the stress and a doublet ($\Omega_{\rm d}$) with eigenvectors perpendicular to the stress. For these two stress directions we find

$$\Omega_{\rm s}=\omega_0+\Delta\Omega_{\rm H}+\frac{2}{3}\Delta\Omega, \tag{3}$$

$$\Omega_{\rm d}=\omega_0+\Delta\Omega_{\rm H}-\frac{1}{3}\Delta\Omega, \tag{4}$$

where ω_0 is the frequency of the $\boldsymbol{k}=0$ optical phonons in the absence of stress.

For the applied stress $X\,\|[111]$,

$$\Delta\Omega_{\rm H}=\left(\frac{X}{6\omega_0}\right)(p+2q)\left(S_{11}+2S_{12}\right), \tag{5}$$

$$\Delta\Omega=\Omega_{\rm s}-\Omega_{\rm d}=\left(\frac{X}{2\omega_0}\right)\gamma S_{44}. \tag{6}$$

In the above equations S_{ij} are elastic compliance constants referring to the cubic axes. Since the strain-induced changes in the Raman tensor are relatively small, as a good approximation the scattering is determined by the first-order Raman scattering tensor of a crystal.

Polar zinc-blende-type semiconductors have $T_{\rm d}$ point symmetry. The Raman-active $F_{2\rm g}$ modes are still threefold degenerate at $\boldsymbol{k}=0$. For [111] stress and with a scattering vector $\Delta\boldsymbol{k}$ perpendicular to the stress, the Coulomb interaction and the stress in the Hamiltonian are simultaneously diagonalized in a set of axes which contains the stress axis and $\Delta\boldsymbol{k}$. If the LO–TO splitting is small, one can assume that it is independent of stress. The behaviour of these phonons under stress can be simply obtained by adding the LO–TO splitting to Eqs.(3) and (4) in the appropriate way: one of the doublet components becomes the LO phonon while the singlet and the other doublet component become the TO phonons. We thus obtain

$$\text{LO phonon}: \Omega_{\rm d}=\omega_{\rm LO}+\Delta\Omega_{\rm H}-\frac{1}{3}\Delta\Omega, \tag{7a}$$

$$\text{TO phonon}: \begin{cases} \Omega_{\rm d}=\omega_{\rm TO}+\Delta\Omega_{\rm H}-\dfrac{1}{3}\Delta\Omega, \\ \Omega_{\rm s}=\omega_{\rm TO}+\Delta\Omega_{\rm H}+\dfrac{2}{3}\Delta\Omega, \end{cases} \tag{7b}$$

where $\Delta\Omega_{\rm H}$ and $\Delta\Omega$ are given by Eqs.(5) and (6), with ω_0 replaced by either $\omega_{\rm LO}$ and $\omega_{\rm TO}$. If the stress dependence of LO–TO splitting becomes significant, in Eqs.(5) and (6) we can use two sets of values for p, q, and γ, one for the LO phonon and the other for the TO phonons. For stress parallel to the [111] face the LO phonon has symmetry $F_{2\rm g}\,(x'')$ while the TO phonons have symmetry $F_{2\rm g}\,(y'')$ and $F_{2\rm g}\,(z'')$.

Using the values of the parameters in Table 1, we can use the singlet component of the TO mode in Eq.(7b) to calculate the uniaxial stress in GaSb thin film. The values of uniaxial stress are around 1.0 GPa. The results are summarized in Fig.4, in which the uniaxial stress is plotted as a function of temperature. The uniaxial stress decreases with the increase of substrate temperature. These results suggest that a higher substrate temperature is beneficial in relaxing the stress in GaSb thin film.

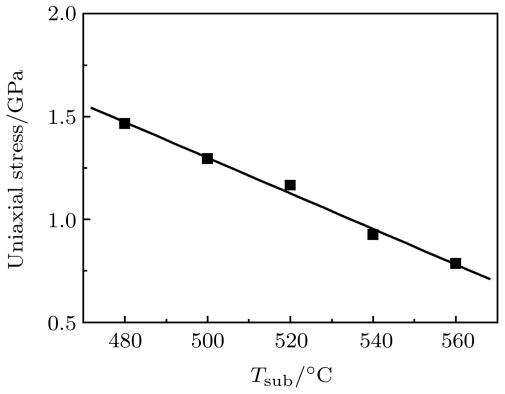


Fig.4. Temperature dependence of the stresses on GaSb thin films.

Table 1. The values of GaSb parameters for calculation.

$S_{11}+2S_{12}$ /10^{-6}Pa	$S_{11}-S_{12}$ /10^{-6}Pa	S_{44} /10^{-6}Pa	ω_0 /10^{28}sec^{-2}
0.591	2.08	2.31	0.184

4. Conclusions

GaSb thin films were co-deposited on soda-lime glass substrates. The Sb–A_{1g}/GaSb–TO ratio decreased rapidly with the increase of substrate temperature, which suggests that Sb atoms in the thin film constitute a small proportion and decrease with the increase of substrate temperature. In Raman spectra, the TO mode intensity is stronger than that of the LO mode. The LO/TO intensity ratio increases with the increase of substrate temperature. A downshift of the TO and LO frequencies of polycrystalline GaSb thin film to single crystalline bulk GaSb Raman spectra is also observed. We calculate the uniaxial stress in GaSb thin film; the values of uniaxial stress are around 1.0 GPa. The uniaxial stress decreases with increasing substrate temperature. The results presented in this work indicate that control of the substrate temperature is crucial to improve the polycrystalline quality of polycrystalline GaSb thin film.

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