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Raman properties of GaSb nanoparticles embedded in SiO_2 films*

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The Raman shifts of nanocrystalline GaSb excited by an Ar^+ ion laser at wavelengths 514.5, 496.5, 488.0, 476.5, and 457.9nm are studied by an SPEX-1403 laser Raman spectrometer respectively, and they are explained by phonon confinement, tensile stress, resonant Raman scattering and quantum size effects. The Stokes and anti-Stokes Raman spectra of GaSb nanocrystals strongly support the Raman feature of GaSb nanocrystals. The calculated optical spectra compare well with experimental data on Raman scattering GaSb nanocrystals.

Keywords: GaSb nanocrystals, novel Raman properties, phonon confinement and tensile stress effects
PACC: 7865K, 7360F, 7830

1. Introduction

The behaviours of semiconductor nanostructures embedded in a dielectric matrix are significantly different from those of other low-dimensional semiconductor heterostructures.[1−10] Indeed, electronic states of these nanostructures have to be treated with the interactions between real surfaces or interfaces and the surrounding material. Phonon states are also modified in semiconductor nanostructures from those of the bulk. The purpose of this article is to discuss the Raman properties of GaSb nanocrystals embedded in SiO_2 host by radio frequency magnetron co-sputtering. We explain the shifts of the Raman peaks at 514.5, 496.5, 488.0, 476.5, and 457.9nm excitation lines of an Ar^+ ion laser. The Stokes and anti-Stokes Raman spectra of the GaSb nanoparticles embedded in a SiO_2 matrix are also measured for comparison and better understanding of the origin of phonon-confinement and tensile-stress effects.

2. Experimental method

GaSb nanocrystals growing in SiO_2 host by radio frequency magnetron co-sputtering are described elsewhere.[11,12] The target used was a SiO_2 glassy plate of 60mm in diameter, with several chips of polycrystalline GaSb attached. By varying the number of GaSb chips, the semiconductor concentration in the deposited film can be controlled to a desired value. In this work the effective sputtered area ratio between the semiconductor chips and SiO_2 plate was fixed at 20%. Some glass substrates (10mm×10mm ×1mm) were ultrasonically cleaned successively in acetone, alcohol, and de-ionized water in order to obtain a clean surface before being placed in a vacuum chamber. The target was separated from the substrate by 5cm. When the chamber was evacuated down to a pressure of 2.7×10^{-3} Pa, high purity (99.9999%) argon gas was introduced. During sputtering, the chamber pressure was maintained at 2Pa. The voltage applied to the radio frequency sputtering gun was 1000V. All runs started with presputtering the target for 15 minutes to ensure good quality of GaSb films. The films grew at various substrate temperatures for various durations.

Room temperature Raman spectra of GaSb nanocrystals were recorded with an SPEX-1403 laser Raman spectrometer. The exciting source was an Ar^+ ion laser at 514.5, 496.5, 488.0, 476.5, and 457.9nm lines operated in the backscattering mode and the resolution of the instrument was $1cm^{-1}$. The Stokes and anti-Stokes Raman spectra of GaSb nanocrystals

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were also recorded with an SPEX-1403 laser Raman spectrometer with excitation of an argon ion laser at 514.5nm at room temperature in the backscattering mode. The power output of the laser was kept within 200mW and a cylindrical lens was used to avoid overheating of the samples.

3. Results and discussion

The nanocrystalline GaSb–SiO_2 films were characterized with a rotating anode D / max-rA type x-ray diffractometer at an operating voltage of 40kV and a current of 100mA. The experimental results[11] indicate that the GaSb nanocrystals are of a typical zinc-blende structure. The average size of the nanocrystals is about 4.1nm estimated by the x-ray diffraction peak using the Scherrer method.

Figure 1 shows the Raman shifts of nanocrystalline GaSb excited by lasers at wavelengths 514.5, 496.5, 488.0, 476.5, and 457.9nm. From Fig.1, one can see red shifts of Raman peaks as the excited wavelength increases. The shifts of Raman peaks excited at the different wavelengths are shown in Table 1.

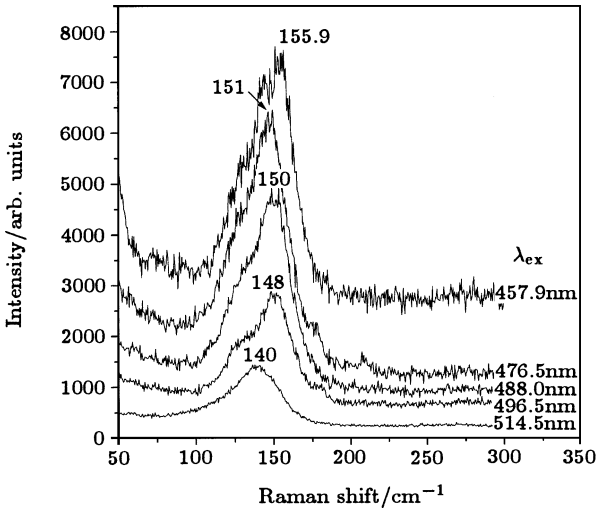


Fig.1. The Raman shifts of nanocrystalline GaSb excited by an Ar^+ ion laser at the different lines.

Table 1. The shifts of Raman peaks excited by the different wavelengths.

Wavelength of the excitation line/nm	Position of the Raman peak/cm^{-1}	Shift of the Raman peak/cm^{-1}	Variation of full width at half maximum (FWHM) of Raman peak/cm^{-1}
514.5	140.0		46.2
496.5	148.0	8	45.2
488.0	150.0	10	44.1
476.5	151.0	11	43.2
457.9	155.9	15.9	38.7

According to Fig.1 and Table 1, and compared to the Raman peaks of nanocrystalline GaSb excited at a line of 514.5nm, the Raman peaks of nanocrystalline GaSb excited at lines of 496.5, 488.0, 476.5 and 457.9nm have 8, 10, 11 and 15.9cm^{-1} red shifts, respectively, and the maximum of the full width at half maximum (FWHM) of Raman peak is widened by about 7.5cm^{-1}. More experimental data show that the data in Fig.1 and Table 1 are independent of the intensity of exciting line. One can find the Raman spectra of nanocrystalline GaSb and the ones of the bulk GaSb in Refs.[11,12] Compared to the Raman spectra of bulk GaSb,[11,13] where the TO and LO modes are at 225.6 and 236.1cm^{-1}, respectively, nanocrystalline GaSb has the large red shifts of Raman peaks, which originate from phonon confinement[11,13–15] and tensile stress effects.[13–16]

First, we discuss the Raman peak red shift by the phonon confinement effect using the theory of Richter *et al*[15] and Campbell *et al.*[14] Richter *et al*[15] considered only spherical microcrystals and compared their results obtained from silicon films prepared by the plasma transport method. Campbell *et al*[14] further considered the exact effects of different microcrystal sizes and shapes. They showed that there were significant differences among spherical, columnar, and thin slab microcrystals. They neglected scale factors and assumed the phonon mode at the reduced wavevector starting from a point q_0=0 which is appropriate for one phonon scattering. The first-order Raman spectrum, $I(\omega)$, is

$$I(\omega) \cong \int \mathrm{d}^3q|C(0,q)|^2/\{[\omega-\omega(q)]^2+(\Gamma_0/2)^2\}, \quad (1)$$

where $I(\omega)$ represents the confined Raman line shape, d^3q is the volume element in momentum space, $\omega(q)$ is the phonon dispersion relation, Γ_0 is the natural linewidth, and $C(0,q)$ is the Fourier coefficient of the phonon confinement function. From formula (1), the central frequency red shift of nanocrystalline GaSb–

SiO_2 composite films is estimated at about several cm^{-1}. Obviously, it is smaller than our experimental results. So, another source of red shift of the Raman peak should be considered. Second, in order to explain the results, we should further consider the tensile stress caused by the mismatching of the different thermal expansion coefficients. The hint figure of GaSb nanocrystals embedded in SiO_2 host is shown in Fig.2.

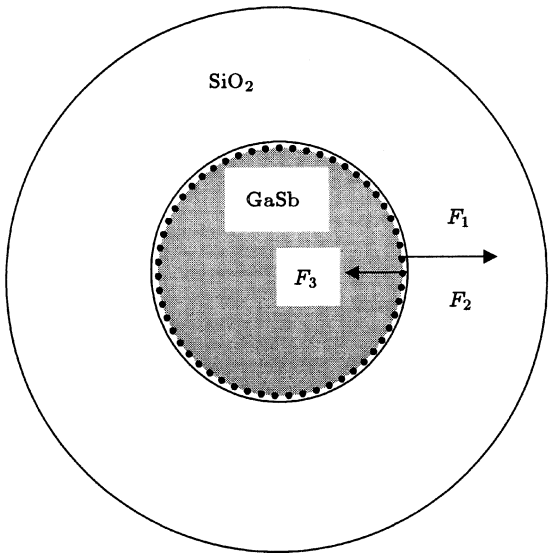


Fig.2. The hint figure of GaSb nanocrystals embedded in SiO_2 host.

One can obviously see that there are a large number of atoms on the surfaces of GaSb nanocrystals due to quantum size effect. Also, it is well known that there are three forces (F_1, F_2 and F_3 shown in Fig.2) exerted on the nanocrystalline GaSb. F_1, which called interface covalent force, originates from Sb=O owing to the binding energy of Sb3d close to that of O1s. The XPS and XRD data[11,13] strongly support that the tensile stress exists in the GaSb nanocrystals. F_2 is called thermal expansion force which is caused by the mismatching of the different thermal expansion coefficients, and F_3 is considered as the compressed force of SiO_2 matrix. The resultant force F exerted on the GaSb nanocrystals is equal to $F_1+F_2-F_3$. The average stress is about $1.6\times10^{10}N/m^2$ estimated according to the XRD of the composite film.[11,17] Richter *et al*[15] pointed out that tensile and compressive stresses could bring a red shift and a blue shift to the Raman line respectively. Raisin *et al*[16] studied GaSb/GaAs heteroepitaxy by Raman spectroscopy. The value of the residual strain ε can be deduced from the LO single relative frequency shift by[16]

$$\Delta\omega/\omega = [(S_{11}+2S_{12})(K_{11}+2K_{12}) - (S_{11}-S_{12})(K_{11}-K_{12})]\varepsilon/6(S_{11}+S_{12}), \quad (2)$$

where the S_{ij} is the elasticity constants and K_{ij} are the reduced phonon deformation potentials.

Therefore, as an example, we have estimated the Raman shift of the LO mode. From formula (1) the Raman shift are estimated to be about $6.21cm^{-1}$. Also, from formula (2) the Raman shifts are estimated to be about $86.11cm^{-1}$. These are basically consistent with the experimental results. Consequently, compared to the Raman red shift of the bulk GaSb, the large Raman red shift of the GaSb-SiO_2 composite film could be explained by tensile stress and phonon confinement effects.

The Raman phenomena mentioned above have also been found in porous Si,[18,19] silicon nanowires,[20,21] silicon nanocrystals,[22] and carbon nanotubes.[23,24] Zhang *et al*[18] studied the intrinsic Raman spectrum of porous silicon formed on nondegenerate p-type silicon by using a laser at different incident wavelengths and found that intrinsic Raman frequencies had small up-shift variations, whereas the Raman linewidths became narrow, with increasing the wavelength of the laser. These phenomena were interpreted by using the phonon confinement effect and resonant Raman scattering. Rao *et al*[23] studied diameter selected Raman scattering from vibrational modes in carbon nanotubes, and found resonant Raman scattering process excited by a laser at wavelengths ranging from 514.5nm to 1320nm. This resonance results from one-dimensional quantum confinement of the electrons in the nanotubes. Milnera *et al*[24] studied the resonance excitation and intertube interaction from quasicontinuously distributed helicities in single wall carbon nanotubes. They used a large number of lasers at wavelengths ranging from the deep blue (459nm) to the infrared (1068.6nm). They found that the resonant excitation exhibited an oscillatory behavior and had up-shifted by 8.5% on the average. Obviously, the experimental results of nanocrystalline GaSb described in Fig.1 are contrary to those of porous silicon, silicon nanowires and nanotubes. Firstly, the Raman scattering has blue shifts (up-shifts) with increasing the exciting wavelength of laser for silicon nanocrystals and nanotubes, whereas the Raman scattering has red shifts (down-shifts) for

nanocrystalline GaSb with increasing the excitation wavelength of laser. Secondly, the Raman peaks of silicon nanocrystal and nanotubes are due mainly to the scatters from Si—Si and C—C bonds respectively, whereas the Raman peaks of GaSb nanocrystals are mainly attributed to the scatters from Ga—Ga, Ga—Sb and Sb—Sb bonds. Moreover, GaSb nanocrystals are affected by tensile stress because of being embedded in a SiO_2 matrix. So we have to find another view to interpret our experimental results. We think that there is a distribution of GaSb nanoparticles in the films, such as a Lorentzian or Gaussian size distribution function. Owing to the quantum size effect, the GaSb nanocrystals will be vibrating when excited by a laser. So, we can consider the GaSb nanoparticles correspondingly as optical vibrons[25] with different momenta. Trallero-Giner *et al*[25] studied the optical vibrons in CdSe quantum dots. They presented a detailed analysis of Raman line shape in terms of size distribution, phonon linewidths, and photon energy of the exciting laser. They found that the relative contribution of the excitonic and vibronic states to the Raman line shape depended on the incoming laser frequency, the excitonic oscillator strength, and the exciton–vibron interaction. Raman scattering can be used to describe an interaction process of photon–electron–phonon. Saio *et al*[26] studied the phonon dispersion relation by double-resonant Raman scattering. They thought that in the Stokes (phonon emission) process, an electron with momentum k [or electron energy $E^i(k)$] was excited by the incident laser photon in an electron-hole creation process, and scattered by emitting a phonon with momentum q to the state with momentum $k+q$ [or energy $E(k+q)$], then scattered again, finally came back to $k[E^f(k)]$ to recombine with a hole. In the one-phonon emission Stokes process, one of the two scattering processes ($k \rightarrow k+q, k+q \rightarrow k$) is inelastic with a phonon emission process, and the other is an elastic scattering process. So we think that these nano-vibrons, which have the same momenta as those of the photons, will be able to gain a prior energy for vibrating. Therefore, when excited by short wavelength light, the nano-vibrons will be vibrating and scattering at a very high frequency because the photon has more high momentum. Thereby the blue Raman shifts (up-shifts) can be measured. When excited by the long wavelength light, the nano-vibrons will be vibrating and scattering at a very low frequency because the photon has less momentum. Therefore, the red Raman shifts (down-shifts) will be observed. In addition, there are many factors involved such as the inner stress in the film, and the shapes of the GaSb nanocrystals, which will bring about very small Raman shifts.

The Stokes and anti-Stokes Raman spectra of GaSb nanocrystals are shown in Fig.3, which are excited by a 514.5nm line of Ar^+ laser. One can see that the intensities of Stokes and anti-Stokes Raman peaks of nanocrystalline GaSb are enhanced, compared with those of bulk GaSb, which originate from the resonant Raman scattering occurring during the scattering of some photons.

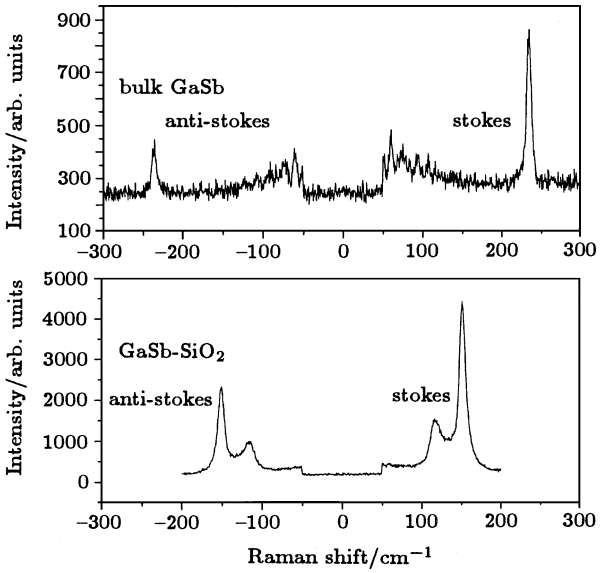


Fig.3. The Stokes and anti-Stokes Raman spectra of GaSb nanocrystals.

The relative intensities I_S/I_{AS} for a given laser line should be approximately equal to exp $(\hbar\omega_0/kT)$, where $\hbar\omega_0$ is the phonon energy.[27] At room temperature, $kT' \approx$24meV and the optical-phonon energies lie in a range of 25–65meV so that the Stokes line can be much stronger than the anti-Stokes one. This demonstrates that the Raman scattering phenomena of nanocrystalline GaSb described in Fig.1 are truly Raman active modes. The large red shifts of Raman peaks and an enhanced Raman intensity originate from the phonon confinement,[14,15] tensile stress effects[16] and resonant Raman scattering.[27] But for other anomalous Raman scattering phenomena of nanocrystalline GaSb, which cannot be explained by the Raman selection rules, the absolute values of the Stokes Raman shifts are a little larger (about 1.8cm^{-1}) than those of the anti-Stokes. This can be attributed to the reduced symmetry for nanocrystals and quantum wires,[28] but not to measurement error.

So we think that there are the size distributions of GaSb nanocrystals in the GaSb–SiO_2 composite films, thus the different Raman shifts are caused by the different sizes of nanoparticles of GaSb. From the theory of quantum statistics, one knows that the atomic number of the ground state is much larger than that of the excited state. Therefore, the consequence of iterative Raman scattering of different nanoparticles is that the Stokes Raman shifts are a little larger than those of the anti-Stokes. According to the features of the Stokes and anti-Stokes, one can estimate the sample temperature from the intensity ratio between Stokes and anti-Stokes Raman modes according to the relation[29]

$$I_S/I_{AS} = [(\omega_L - \omega)/(\omega_L + \omega)]^4 \exp(2\hbar\omega/k_B T), \quad (3)$$

where ω_L and ω are the frequencies of incident laser light and the phonon of the Raman mode considered, respectively, k_B is Boltzmann's constant, and T is the sample temperature. In our experiment, the sample is kept at room temperature ($\sim$300K) because no frequency shift induced by the change of the sample temperature is observed when the exciting power density is much lower than the current laser power density.

4. Conclusion

In summary, films of nanocrystalline GaSb embedded in SiO_2 host have been successfully grown on glass substrates by radio frequency magnetron co-sputtering. The Raman shifts of nanocrystalline GaSb excited by an Ar^+ ion laser at 514.5, 496.5, 488.0, 476.5, and 457.9nm lines are studied by an SPEX-1403 laser Raman spectrometer respectively, and they are explained by phonon confinement, tensile stress, resonance Raman scattering and quantum size effects. It is shown that there is a small change of Raman shifts at different excitation lines. In addition, the Stokes and anti-Stokes Raman spectra of GaSb nanocrystals excited by an argon laser at 514.5nm line were measured using an SPEX-1403 laser Raman spectrometer. These results strongly support the Raman feature of GaSb nanocrystals. The estimated Raman shifts of GaSb nanocrystals can be well compared with experimental data according to phonon confinement and tensile stress effects.

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