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Surface phonon observed in GaAs wire crystals grown on porous Si

S W da Silva†, J C Galzerani‡, D I Lubyshev§ and P Basmaji§

† Instituto de Física, Universidade de Brasília, 70910-900 Brasília, Distrito Federal, Brazil
‡ Departamento de Física, Universidade Federal de São Carlos, 13565-905 São Carlos, São Paulo, Brazil
§ Instituto de Física de São Carlos, Universidade de São Paulo, 13560-970 São Carlos, São Paulo, Brazil

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Abstract. GaAs epitaxially grown on porous Si (PS) showed the presence of wires with typical diameters of 60 nm, and lengths in the range 6–10 μm. The Raman spectra of these samples were studied, and we focused attention on two additional modes appearing as 'shoulders' to the LO and TO GaAs lines. The former could be assigned to a surface phonon, and the latter to the presence of As clusters.

The epitaxy of GaAs on Si substrates has attracted great interest due to its potential for applications in optoelectronics. However, the 4% mismatch between the GaAs and Si lattice constants generates a high density of misfit dislocations, and the problem is compounded by the remarkable difference in the thermal expansion coefficients of these materials, resulting in a considerable tensile stress in the GaAs layers.

Porous Si (PS) has a large number of pores and a coherent set of small crystalline columns with dimensions varying from 30 to 100 Å [1]. A PS layer is thus considered to be a flexible material, and a promising substrate for the growth of good quality crystalline GaAs [2]. In this work, we studied the growth mechanism of GaAs on PS using Raman scattering with several excitation lines. It is known from previous scanning electron microscopy measurements in the same samples [3] that for a substrate temperature of 400 °C, long wire-like crystals of GaAs appear. In a previous paper, micro-Raman spectroscopy was applied to the same samples [4] in order to study the structure and composition of the GaAs film. Two different excitation energies allowed the inspection of the near surface and the bulk of the film; these analyses indicated that a predominantly amorphous GaAs region is buried at the PS–GaAs interface, followed by microcrystalline GaAs cylindrical structures.

We studied the (macro) Raman spectra of these samples, focusing our attention on the two modes appearing as 'shoulders' to the LO and TO GaAs phonons. More specifically, we found evidence that the former could be associated with a surface phonon.

The Si substrates used were $\langle 111 \rangle$ oriented, boron-doped p-type silicon with 10 Ω cm resistivity. After proper electrochemical preparation [3], all samples exhibited visible photoluminescence at 300 K. GaAs was epitaxially deposited on these PS substrates in a MECA 2000 MBE installation, according to the method described elsewhere [3]. The substrate temperature was varied between 200 and 500 °C.

The epitaxially grown layers have shown island structures, with sizes varying between 20 and 40 μm [3]. However, for GaAs grown on PS at 400 °C, scanning electron microscopy

(SEM) has shown the appearance of GaAs wires, with higher densities in the crack borders which cross the surface of the GaAs/PS islands. The typical wire diameter was found to be 60 nm, and their lengths are in the range 6–10 μm.

These samples were analysed by Raman spectroscopy at room temperature and at 80 K, using the 5145 Å, 4965 Å, 4880 Å and 4597 Å lines of an Ar^+ laser. For these experiments, the scattered light was dispersed through a JY-U1000 double spectrometer and analysed by a photomultiplier tube with a photon counting system.

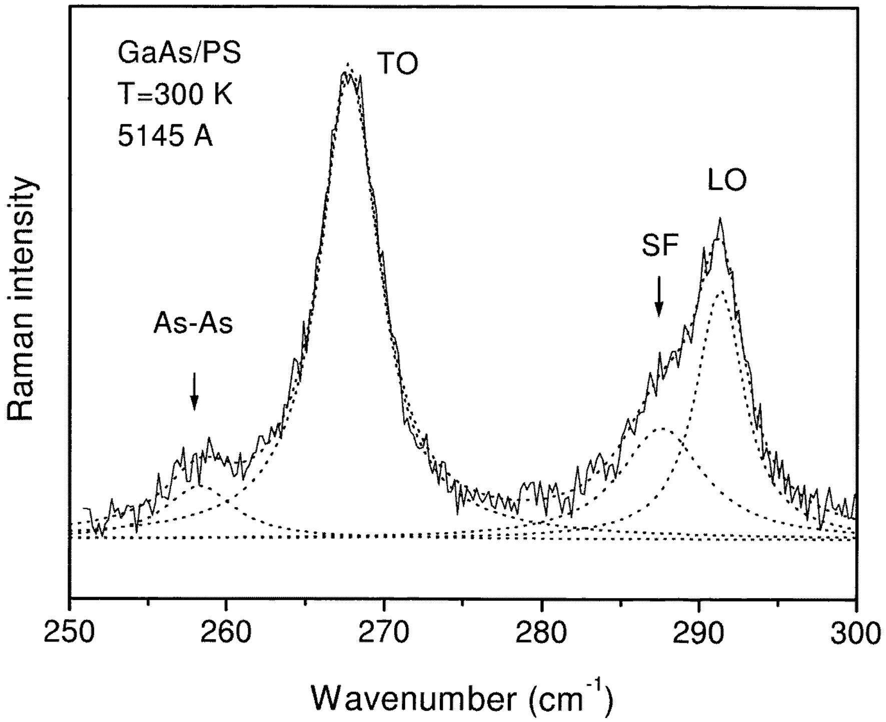

Figure 1. Raman spectrum of GaAs/PS. The dotted lines correspond to the fitting of the spectrum calculated as a sum of Lorentzian peaks.

Figure 1 shows a typical first-order Raman spectrum, recorded at room temperature under non-resonant conditions, for those samples of GaAs grown on PS that exhibited wire formation. The spectrum is dominated by two prominent features located around 268 and 291.3 cm^{-1}. These modes show no appreciable shifts in comparison with the GaAs bulk frequencies (269 and 292 cm^{-1} for the TO and the LO, respectively [5, 6]), so the post-growth tensile stress can be considered negligible for this sample. Peaks observed at 260 cm^{-1} (figure 1) and 200 cm^{-1} (not shown here) can be assigned to As–As vibration [7, 8]. This was confirmed by experiment when the samples were subjected to thermal annealing; the Raman intensities of these modes increased with annealing temperature due to cluster enlargement. Thus our results provide evidence of As cluster formation in the sample studied.

The constant observation in our GaAs/PS spectra of peaks due to As clusters support one of the growth mechanisms proposed in [3] for these samples. According to that work, the growth mechanism of GaAs wire crystals on PS can be explained by the transport of Ga and As atoms to the wire tops due to the existence of a thick semi-adsorptional layer of Ga and As adatoms on the surface of the GaAs at substrate temperatures lower than 400 °C. At 400 °C, the surface of the GaAs layer has an over-monolayer ordered coverage of As adatoms with the As stable (2×2) structure and an additional number of adsorbed As atoms in a disordered phase. Therefore at low temperatures, as suggested in [3], the surface kinetics of atom incorporation decrease, resulting in the appearance of semi-adsorptional layers with Ga and As clusters. This layer on the solid surface is similar to the saturated metal–liquid phase, and crystal growth in this case is governed by the vapour–semi-adsorptional-layer–solid growth mechanism.

Moreover, in addition to the longitudinal optical (LO) and transverse optical (TO) modes we observed an additional band that develops as a shoulder in the low-frequency side of the LO mode. The fitting of this spectrum to a sum of Lorentzian peaks reveals a mode around 287.6 cm^{-1}. At 80 K the spectrum suffers the expected temperature shifts but the same features are still present.

The mode at 287.6 cm^{-1} (at room temperature) has the same characteristics as the modes observed by Watt *et al* [9] in the Raman spectra of lithographically defined GaAs cylinder arrays, and the additional feature was assigned to a surface phonon observable due to the low dimensionality of the GaAs wires. However, in our case we did not observe a dependence of the Raman intensity of these modes on the angle of the incident light, as occurred in [9]. The cylinders of GaAs formed during the growth did not show a preferential order, being randomly distributed; this explains the breakdown of the Raman selection rules observed in the cross and parallel polarized spectra, and the independence of the Raman intensities of the observed modes with the variation in the incident light direction.

According to [9], the origin of these modes is explained by the low dimensionality of the GaAs wires. A simple model to describe the surface phonons arising from cylindrical samples, which is valid when the sample size is small in comparison with the infrared radiation wavelengths, is given by Ruppin and Englman [10]. These modes lie between the bulk LO and TO modes and depend on the cylinder radius and the dielectric constant of the surrounding medium. The expression relating the surface phonon frequencies to the cylinder size and the dielectric constant is

$$\left(\frac{\omega_{nk}}{\omega_{TO}}\right)^2 = \frac{\varepsilon_o - \varepsilon_m \rho_{nk}}{\varepsilon_\infty - \varepsilon_m \rho_{nk}} \tag{1}$$

where $\rho_{nk} = [K_n'(\boldsymbol{k}R)I_n(\boldsymbol{k}R)]/[K_n(\boldsymbol{k}R)I_n'(\boldsymbol{k}R)]$ with ω_{nk}, surface phonon frequency of order n for wavevector $\boldsymbol{k}$; ω_{TO}, bulk TO phonon frequency; ε_o, ε_∞, static and dynamic dielectric constants, respectively; ε_m, dielectric constant of the surrounding medium; I_n, K_n, modified Bessel functions of order n; I_n', K_n', first derivatives of the modified Bessel functions of order n.

In our case we have an array of disordered wires and their diameters can be averaged to 60 nm. If we introduce this value in the above equation with $\varepsilon_o = 12.9$, $\varepsilon_\infty = 10.9$ and $\varepsilon_m = 1$, we obtain for the lowest order ($n = 0$) surface phonon a frequency 286 cm^{-1}, in close agreement with the value observed in our room temperature measurements (287.6 cm^{-1}). In order to check the validity of the model, we have changed the wavelength of the incident light, performing measurements with the 5145 Å, 4965 Å, 4880 Å and 4597 Å lines. In table 1, we show these results, in comparison with the above model, for $T = 80$ K. In this table $\boldsymbol{k}R$ is the product of the wavevector of the light inside the material times the cylinder radius. Yet, according to the Ruppin and Englman model [10], the frequency of the surface phonon should strongly depend on the dielectric constant of the surrounding media (ε_m). In order to check this behaviour, we covered the sample with a

Table 1. The calculated and measured surface phonon frequencies for different values of kR, the product of the wavevector of light inside the material and the cylinder radius ($R = 30$ nm).

	Phonon frequency (cm^{-1})	
kR	Experiment	Theory
1.55	288.8	289.6
1.65	288.9	289.9
1.70	289.0	290.0
1.78	290.0	290.1
1.94	290.5	290.3

nujol layer, which has a dielectric constant of 2. The Raman spectrum of the same sample measured with a nujol layer shows a decrease of the surface phonon frequency from 287.7 to 283 cm^{-1} (at room temperature), in good agreement with theory (282.3 cm^{-1}).

In conclusion, GaAs layers grown by molecular beam epitaxy on PS showed the presence of narrow GaAs wires. The Raman spectra are dominated by the LO and TO GaAs modes, and their positions and linewidths are comparable to those observed in bulk GaAs. However, the same spectra show evidence of an additional band located between LO and TO modes. This mode could be assigned to a surface phonon, here present due to the low dimensionality of the GaAs wires. A strong presence of As clusters has also been observed in these samples.

Acknowledgments

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