# Interface Morphology of $Ge_n/Si$ Quantum Wells Studied with Raman Spectroscopy and High Resolution X-Ray Diffraction

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#### In commemoration of Roberto Luzzi's 60th birthday

Received April 15, 1997

We report Raman scattering and high-resolution X-ray diffraction measurements performed on a series of MBE-grown  $Si/Ge_n/Si$  quantum wells with *n* varying from 3 to 6. Our results are consistent with a gradual evolution of the Si/Ge interface which starts with Ge segregation and formation of terraces for low Ge coverage, to smooth 2D Ge layers, bounded by interfacial alloy layers, for coverages superior to 4MLs.

#### I. Introduction

Structures obtained by alternating a few monolayers (MLs) of Si and Ge have received a lot of attention, both for their intriguing electronic properties and for their potential device application[1]. The optical and electronic properties of these structures, and consequently the performance of the devices, depend strongly on the properties of the Si/Ge interface. Hence, it becomes important to develop experimental methods which diagnose interface roughness on the different scales in which it may appear in Si/Ge quantum wells (QWs) and superlattices (SLs).

It was recently shown that Raman scattering by optic phonons could be very effective in diagnosing interface roughness in Si/Ge nanostructures[2, 3, 4]. The shape and position of the Raman lines were used to detect roughness on two typical length scales. On the atomic scale, roughness manifests itself by the formation of  $\text{Ge}_x \text{Si}_{1-x}$  alloy layers, of  $\sim \pm 1ML$  depth, around the Si/Ge interface. The second type, terracing, has a much larger lateral scale and results in the existence of more than one characteristic well-width within a given Ge layer. This produces changes in lineshape and position of the Raman line originating in vibrations confined within the Ge layers as the wavelength of the exciting radiation is varied[2]. Theoretical models used to simulate the Raman spectrum of terraced samples allow quantitative estimation of the depth of these terraces[4].

Recently Sunamura et al performed a low temperature photoluminescence (PL) study on Ge QWs of nominal widths varying between 1 and 12 MLS, obtained by gas-source molecular-beam epitaxy on Si (001) substrates[5]. The observed PL-features are interpreted as recombinations taking place within the Ge-QWs. With this assumption, they conclude that growth initiates in a two dimensional (2D) way up to a given critical average thickness ( $\sim 3.7MLs$ ) and changes abruptly to 3*D*-island formation as the nominal thickness increases. Their interpretation does not explicitly include the formation of interfacial alloy layers (atomic-scale roughness), with the attending possibility of recombination at precisely those regions of the sample. The latter possibility would be in line with current theoretical ideas[6]. In view of this, confirmation of the conclusions of Sunamura et al. should be sought in other experimental sources.

In the present work we undertake a study of the interfaces of  $Si/Ge_n/Si$  QWs using Raman spectroscopy and high-resolution X-ray diffraction. Our conclusions are at variance with those of Sunamura et al. Their experimental data, however, can be interpreted within the framework of our vision of the interface, provided that one accepts that their PL signal is produced by recombination at the interfacial alloy layers rather that in the Ge QWs.

### II. Experimental Details

Our samples were grown by molecular beam epitaxy (MBE) at  $T = 500^{\circ}C$  on Si (001) substrates. They consist of a thick (200nm) Si buffer layer followed by 25 repetitions of Ge<sub>n</sub> layers (n = 3, 4, 5 and 6), separated from one another by 70MLs-thick Si spacer-layers. Depending on the type of experiment being performed, the samples can be viewed as isolated Ge<sub>n</sub> QWs or Ge<sub>n</sub>Si<sub>m</sub> periodic structures with  $m \gg n$ . The first description determines the optical response of the samples, while the second defines the shape of the rocking curves obtained in the high-resolution X-ray diffraction experiments.

High resolution diffraction profiles  $(\Omega - \operatorname{rocking})$ curves) were obtained for all samples using a Phillips Materials research diffractometer equipped with a twocrystal four-reflection Ge (200) monochromator, which provides a nearly parallel (5-15 seconds of arc divergence) and highly monochromatic  $(\Delta \lambda / \lambda \sim 3 \times 10^{-5})$ X-ray beam. The  $Cu-K_{\alpha}$  line from the point-focus side of a long fine-focus tube was used as an X-ray source. Dynamical theory simulations of diffraction profiles were performed, based on the nominal parameters of the samples, using a program which models the diffraction from perfect substrates and epitaxial layers with the Tagaki-Taupin formalism<sup>[7]</sup>. Two-dimensional reciprocal-space maps were obtained performing a sequence of  $\Omega - 2\Theta$  scans, with an offset of  $\Omega$ , using the same high-resolution diffractometer.

Raman experiments were performed at room temperature with a Jobin-Ivon micro-Raman spectrometer equipped with CCD detection. Several discrete lines from argon and krypton ion lasers were used as exciting radiation. The backscattering configuration z(x, y) zwas used, where z is the (001)growth direction and x and y are the other two cubic axes. This configuration minimizes the contributions of second-order Raman scattering from the Si-parts of our samples.

#### III. Results and discussion

The Raman spectra from the  $Si/Ge_n/Si$  QWs has a very strong peak at  $\omega \sim 520 cm^{-1}$  due to the Si-parts of the sample, another, weaker one, at  $\omega \sim 300 cm^{-1}$ originating in vibrations confined within the Ge-layers and a complex structure in the region between 400 - $450 cm^{-1}$ [4]. This ubiquitous multiple peak structure appears in strain-symmetrized SLs[8, 9, 10, 11, 12, 13] as well as in single and multiple Ge-QWs grown lattice matched on Si substrates [2, 3]. This feature can be unequivocally attributed to presence of  $\operatorname{Ge}_x \operatorname{Si}_{1-x}$  alloy layers at the Si/Ge interface, since it is identical in shape and position to the peaks appearing in the spectra of bulk  $\operatorname{Ge}_x \operatorname{Si}_{1-x}$  alloys [14, 15, 16]. This can be appreciated in Fig. 1, where the relevant portion of the Raman spectra of our QW-samples is reproduced, together with that of a thick  $Ge_{0.5}Si_{0.5}$  alloys-layer deposited by MBE on a Si (001) substrate (top curve). This spectrum is identical to that of the 6ML Ge QW displayed immediately below. The spectra in this figure are composed of a main peak at  $\omega \sim 410 cm^{-1}$  (A) followed by subsidiary peaks (B,C,...) at higher frequencies. The detailed lattice dynamical calculations of de Gironcoli and Baroni identifies the first peak as being produced by the vibrations of the Si-Ge bond and the others as arising from the vibrations of the Si-Si bond when surrounded by a different number of Ge neighbors[16]. For homogeneous bulk alloys the ratio  $I_B/I_A$  decreases monotonically as the Ge molar fraction increases, in the range  $0 \le x \le 0.5$ . This trend is shown in the inset of Fig.1 (open circles), obtained from the data of Renucci et al [14]. In the spectra of the  $Si/Ge_n/Si$  QWs this ratio depends on the nominal value of the Ge layer thickness, decreasing monotonically as n increases, as shown by full circles in the inset of Fig. 1. In fact, the behavior of this ratio as a function of nin the QWs mirrors that of its behavior in bulk alloys as a function of x. This comparison leads to the conclusion that alloying at the Si/Ge interface occurs for all

samples, but that the alloy composition varies in such a way that the effective Ge-molar fraction increases as n increases, stabilizing at  $x \sim 0.5$  for  $n \gtrsim 5$ . The fact that the Ge molar fraction is low for small values of npoints out to segregation of Ge at these low coverages,

which could lead to the formation of steps or terraces.



Figure 1: Raman spectra in the region of the Si-Ge vibrations, of a thick  $\text{Ge}_{0.5}\text{Si}_{0.5}$  layer (top curve) and of our  $\text{Ge}_n$ QWs. (Inset) Ratio of intensities of peaks B and A vs. alloy composition in bulk alloys and vs. n in the QWs.

The presence of terraces also affects the Raman spectrum of the material, but their effects are seen in the peak originating in the optical modes confined within the Ge layers  $(\omega \sim 300 cm^{-1})[2, 3, 4]$ . Terracing on a large enough lateral scale produces a Raman peak, in this frequency range, which changes in position and shape as the wavelength of the incident laser  $(\lambda_L)$  is changed. This resonant effect occurs because the observed line is a superposition of Raman lines produced by phonons confined in Ge quantum wells of different thicknesses. These QWs are produced by terraces within a given Ge layer. In order to produce the resonant effect, the lateral dimensions of these terraces must be at least of the same order as the radius of the exciton involved in the resonance i.e.:  $l \gtrsim 3 - 10 nm$ . Thus, the laser beam (  $D\gtrsim 1\mu m)$  samples a large number of these terraces i.e.: a large number of QWs of different

widths. Each one of these QWs contributes to the Raman spectrum with a line centered around a different frequency, in such a way that wider wells contribute to the higher-frequency part of the composite line and vice versa[4]. For low values of  $\omega_L$  resonant conditions are met for the wider wells, increasing the intensity of the high frequency side of the composite Raman line, which causes an apparent shift of its maximum towards higher frequency. As the laser photon-energy increases narrower wells meet the resonance condition, causing the low frequency part of the composite line to increase its intensity, which produces an asymmetric broadening and shift of its maximum towards lower frequencies. Fitting the Raman line with the contributions from QWs of different well-widths, the average thickness of the Ge-layers in each terrace can be estimated [4]. In this manner it was estimated that terracing is acute in  $Ge_5Si_m$  multiple QWs when  $m \sim 5$ , but this tendency decreases rapidly as the thickness of the separator Si layers increases [2, 3, 4]. In our case the Si spacer-layers are always thick  $(m \sim 70)$ , but the thickness of the Ge layers varies from one sample to another. In these samples we observe that the shape and position of this Raman line changes, with changing  $\lambda_L$ , for the samples with n = 3 and 4 but remains essentially unaltered for n = 5 and 6. Representative examples of this trend are shown in Fig. 2, where this spectral feature is displayed for two different values of  $\lambda_L$  and two  $\text{Ge}_n$  samples: n = 3 (bottom) and n = 6 (top). The spectrum of the sample with the thicker Ge-layer is identical for the two values of  $\lambda_L$ , while that of the sample with the thinner Ge-layers suffers visible alterations. The latter can be fitted with the contributions of two different well-widths, in the manner explained in ref.[4]. The results of these fits are displayed in Fig. 2, where the solid line is the fit with the composite (single) line for the sample with n = 3 (n = 6) and the dashed curves represent each one of the composing lines. The positions and widths (full-width at half-maximum) of each line used in the fits, for all our samples, are listed in table I, as well as the average width of the QW that produces this lines[4]. The latter show that while the samples with n = 3 and 4 contain more than one characteristic well-width, only one exists in the other two samples. In all cases the well width that contributes more strongly to the Raman peak is very nearly equal to the nominal value. The emerging picture, for the thinner terraced samples, is one of regions of relatively large lateral dimensions, with different well-widths in each layer, distributed randomly in the plane of the Si/Ge interface. Roughness on a lateral scale smaller than the exciton radius would not produce this resonant effect. Rather, it would contribute to increase the lifetime broadening of both the electronic and vibrational states. The existence of this roughness on a smaller scale is evident from the widths of the Raman lines  $(\Gamma \sim 17 cm^{-1})$  of the QW-samples, when compared to that of the corresponding line in bulk Ge taken under the same experimental conditions  $(\Gamma \sim 5 cm^{-1})$ .



Figure 2: Raman spectrum of the optical vibrations confined within the Ge layers, for two samples, taken with different laser wavelenghts ( $\lambda_L$ ). Experimental data (open-circles) are fitted with Lorentzian lineshapes (solid curves). For n = 3 sample the two Lorentzians composing the fit are shown as dashed curves.

The picture outlined above is confirmed by the measurements of high-resolution X-ray diffraction. In Fig. 3(a) we display the rocking curve for the sample with

n = 6 while in Fig. 3(b) we show the two-dimensional reciprocal-space map of the same sample. The experimental spectrum of Fig. 3(a) (top curve) is compared with a simulation, as previously explained (bottom curve). The good quality and parallelism of the layers is evidenced by the agreement between both curves, as well as by the appearance of satellite lines,  $S(\pm 1)$ , in the experimental spectrum. These features are also visible in the reciprocal-space map of Fig. 3(b). Similar results, with the attending conclusions, are obtained for the sample with n = 5 (not shown). In contrast, the results for the samples with n = 3 and 4 show bad parallelism and evidence of more than one characteristic period. Results for the former sample are shown in Fig. 4. Here the satellites of the simulation do not appear in the experimental spectrum. Worse even, additional lines appear, probably indicating the presence of more than one characteristic periodicity (n + m). This feature is also evident in the reciprocal-space map of Fig. 4(b)  $[S_1(0) \text{ and } S_2(0) \text{ respectively }]$ . The data from the Raman and X-ray diffraction measurements are consistent with the following picture of the Si/Ge interfaces in our samples:

- Alloying at the interface is always present. For thinner Ge coverage (n = 3 and 4) this alloy has a small Ge-molar fraction which grows as n becomes larger. This happens because Ge atoms segregate forming terraces of relatively large (at least 3 - 10nm) lateral dimensions.
- For n ≥ 5, the interfacial alloy composition stabilizes at x ∽ 0.5.
- A transition from terracing to layers of constant average thickness takes place between 4 and 5*MLs*.

This conclusions are at variance with those of Sunamura et al.[5], drawn from low temperature PL spectra from samples similar to ours. Their samples were grown on Si (001) substrates, at  $700^{\circ}C$ , by gas-source molecular beam epitaxy and consisted in Ge<sub>n</sub> QWs embedded between thick Si layers  $(n \sim 1-12MLs)$ . They studied the PL spectra of these samples at 22K. For small values of n they observe sharp phonon-resolved luminescence, which they attribute to recombination in the Ge QWs. The peak of the no-phonon line shifts towards lower photon-energy as n increases. This is attributed to the diminishing of the confinement shift with increasing n. At  $n \sim 4$  an abrupt change occurs. A broad PL feature 636

appears at a photon-energy slightly lower than that of the sharp PL-lines. This feature gains in intensity with increasing n, while the sharp PL gradually fades away. Beyond this point peak positions in both the broad and sharp PL lines remain insensitive to further changes in n. They interpret this as a transition between 2D and 3D growth occurring at  $n \sim 4$ . The sharp PL lines would originate in 2D regions while the broad PL is attributed to recombination in 3D islands created by Ge segregation for larger values of n. The number of these islands would increase as n increases at the expense of the 2D regions, while the average size of both regions would remain constant. This explains both the increasing (decreasing) intensity of the broad (sharp) PL line and the fact that PL lines do not suffer any further shifts in their peak position as n increases beyond 4MLs. The alloy interfacial layers play no role in their analysis. However, it is possible that their PL lines originate precisely in those layers, rather than in the Ge QWs. This is in line with the theoretical results of Turton and Jaros, which predict that alloy scattering is the predominant mechanism for recombination in these materials[6]. In fact, the spectra of Sunamura et al. are identical to those obtained from  $Si/Ge_xSi_{1-x}$  QWs and SLs[17, 18]. In these samples sharp or broad PLlines are observed depending on the density of defects present in the alloy layer and it is possible to switch back and forth from one type of PL to the other by a sequence of ion-implantation (which creates defects) and annealing (which eliminates them)[18]. In all cases the broad PL feature peaks at a photon energy slightly lower than that of the sharp PL lines and both peaks track the band gap of the alloy layer as alloy composition changes. If we assume that the PL-lines in the spectra of Sunamura et al arise from recombination at the interfacial alloy layer, their results are entirely consistent with our conclusions. For low QW-thicknesses the interfacial alloy layers have a low average Ge molar fraction. Because of this, they are not very strained and do not have a large density of defects. Hence, they produce sharp PL lines. As n increases the molar fraction does so too and the PL peak shifts to lower photonenergies. Finally the molar fraction stabilizes at  $x \sim 0.5$ and peak positions remain constant from there on. The broad PL appears at larger n because the number of defects increases with increasing strain-energy. At very large n the number of defects becomes very large and only the broad PL line is observed. Thus, the Raman and PL results are brought into harmony, at the expense of relinquishing the 2D to 3D growth transition advocated by Sunamura et al[5].



Figure 3: (a) (004)-double-crystal diffraction rocking curves for the n = 6 sample (top curve) and the simulation based on dynamical theory for nominal sample composition ; (b) two dimwnsional reciprocal-space map obtained from a sequence of  $\Omega$ -2 $\Theta$  scans.



Figure 4. Same as Fig. 3 for sample with nominal composition n = 3MLm.

#### **IV.** Concluding Remarks

In conclusion, we have used Raman scattering and high-resolution X-ray diffraction to study the evolution of the Si/Ge interface of Si/Ge<sub>n</sub>/Si quantum wells, grown by MBE, as the nominal width of these wells increase from n = 3 to n = 6. A gradual transition, from Ge segregation with the formation of terraces at low values of n (3D) to 2D Ge layers of uniform width bounded by Ge<sub>0.5</sub>Si<sub>0.5</sub> interfacial alloylayers for widths larger than 4MLs, is inferred from our data. This picture is in agreement with previously reported data on similar samples grown by gas-source MBE, if one assumes that the PL lines are produced by recombination at these interfacial alloy layers. While the change from 2D to 3D growth is undoubtedly influenced by the method and conditions of growth, it is interesting that similar results are found in samples of entirely different origins.

## Acknowledgments

We would like to thank Mr. Fabiano Yokaichiya for his help with some of the X-ray diffraction measurements. This work was supported by research grants from FAPESP and FINEP and research fellowships from CNPq.

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