

# Evolution of the intermixing process in Ge/Si(111) self-assembled islands

N. Motta <sup>a,\*</sup>, F. Rosei <sup>a</sup>, A. Sgarlata <sup>a</sup>, G. Capellini <sup>b</sup>, S. Mobilio <sup>b,1</sup>, F. Boscherini <sup>c</sup>

<sup>a</sup> INFN Dipartimento di Fisica, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy

<sup>b</sup> INFN Dipartimento di Fisica, Università di RomaTre, Via della vasca, Navale, 00100 Rome, Italy

<sup>c</sup> INFN Dipartimento di Fisica, Università di Bologna, viale C. Berti Pichat 6/2, 40127 Bologna, Italy

## Abstract

In this contribution we present a study of the Ge–Si intermixing process that arises during the growth of Ge/Si(111) self-assembled islands. The samples, grown by means of a molecular beam epitaxy (MBE)-like technique, have been characterized by in-situ scanning tunneling microscopy (STM) and atomic force microscopy (AFM) complemented by ex-situ X-ray absorption fine structure (XAFS). We have observed by STM a change in the island morphological evolution, from truncated tetrahedra to atoll-like islands, that can be related to the misfit the reduction effect induced by the intermixing process. We have evaluated the intermixing by measuring the average coordination numbers of Si and Ge around a Ge atom by XAFS. We show that the Si content in the nominally pure Ge wetting layer reaches 50% while in the three-dimensional (3-D) islands it is about 25%, and that the intermixing increases with increasing deposition temperature in the 450–530 °C range. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Scanning tunneling microscopy; Atomic force microscopy; X-ray absorption fine structure

## 1. Introduction

Recently, we have demonstrated that the SiGe intermixing plays an important role in the Stranski–Krastanow growth of Ge dots on Si for  $T$  between 450 and 600 °C [1,2]. Through X-ray absorption fine structure (XAFS) measurements and atomic force microscopy (AFM) imaging, we have provided data on the amount of Si in the Ge epilayer and in the islands, as a function of the deposited thickness. We have found that for Ge/Si(001) the average Ge atom is surrounded by  $1.2 \pm 0.3$  Si atoms. We have also analyzed the Ge/Si(111) wetting layer, up to 1.7 nm in deposited thickness, finding  $2.0 \pm 0.3$  Si atoms around each Ge.

In the present paper, we will analyze the XAFS measurements performed on a wider range of Ge film

thickness on Si(111), and we compare all these data to Scanning Tunneling Microscopy (STM) and AFM measurements; with this set of information we try to better understand the intermixing phenomenon.

## 2. Experimental

The Ge/Si(111) samples were grown by physical vapor deposition (PVD) in a Ultra High Vacuum (UHV) chamber equipped with an e-gun evaporator and a commercial Variable Temperature STM–AFM, with a base pressure  $p \sim 4 \times 10^{-11}$  mbar [3].

The Si(111) substrates (both n-type and p-type) were flashed at 1250 °C to prepare the  $7 \times 7$  reconstructed surface. Ge was evaporated at about  $0.1 \text{ nm min}^{-1}$  on the so prepared substrates kept at temperatures in the range 450–530 °C. A new Si sample was prepared for each Ge deposition in order to minimize the uncertainty of successive evaporations. We have grown two series of samples: the first one at  $450 \pm 10$  °C and the second one at  $530 \pm 10$  °C.

\* Corresponding author.

E-mail address: [motta@roma2.infn.it](mailto:motta@roma2.infn.it) (N. Motta).

<sup>1</sup> Present address: INFN, Laboratori Nazionali di Frascati, CP 13, 00044 Frascati, Rome, Italy.

### 3. STM results

The three-dimensional (3-D) island nucleation starts at a Ge coverage between 3 and 5 ML, with a clear dependence on the Ge flux and on the substrate temperature as already noted by Kamins et al. [4,5] for Ge growth on Si(001) substrates by Chemical Vapor Deposition (CVD). Initially the islands nucleate as truncated pyramids, as shown in Fig. 1a, with one corner pointing in the  $\langle 11\bar{2} \rangle$  direction; as already noted by Köhler et al. [6], this is due to anisotropy of the growth rate. Fig. 1(b), which displays the gradient of the topographic image, shows clearly that the island grows independently of the steps on the substrate, and that the top facet is a  $\langle 111 \rangle$  plane, as expected from energetic arguments [7]. This facet is always reconstructed  $7 \times 7$ , if the growth temperature exceeds 400 °C [8]. The next step in the island evolution, as the amount of Ge deposited is increased, is shown in Fig. 2(a). The island

displayed here is much taller than the previous one and new steep facets are present.

The contact angles between the islands facets and the substrate have been measured, showing that the larger facets are  $\langle 100 \rangle$  planes, forming an angle of  $\approx 55^\circ$  with the  $\langle 111 \rangle$  plane of the substrate, while the new facets form an angle of  $\approx 43^\circ$  with the substrate, representing  $\langle 11\bar{7} \rangle$  planes. Although, this facet is not an equilibrium one for the Ge, it can be stabilized by the hetero-epitaxial strain, as demonstrated by Muller et al. [9]. We point out that some of the values obtained for the facet angles are unusually high with respect to Ge/Si (001) islands, but the appearance of these steep facets (with higher energy) can be compensated by enlargement of the (111) top facet, leading to a total reduction of the island surface energy. An erosion of the substrate is visible around the island in Fig. 2(a). The erosion is also visible in the center of the island in Fig. 2(b). We have observed similar trenches in many islands, with

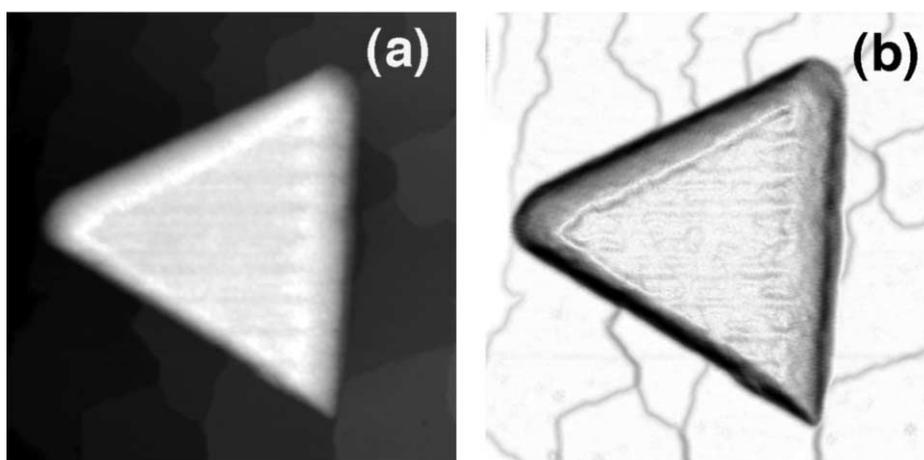


Fig. 1. STM topography of a Ge island deposited on Si(111);  $T = 530$  °C,  $\theta = 2.0$  nm; image dimensions are  $(236 \times 236 \times 8.5)$  nm<sup>3</sup>; (a) topographic image; (b) gradient mode image: the gray levels correspond to the angles on the original images (white, 0°; black, 40°).

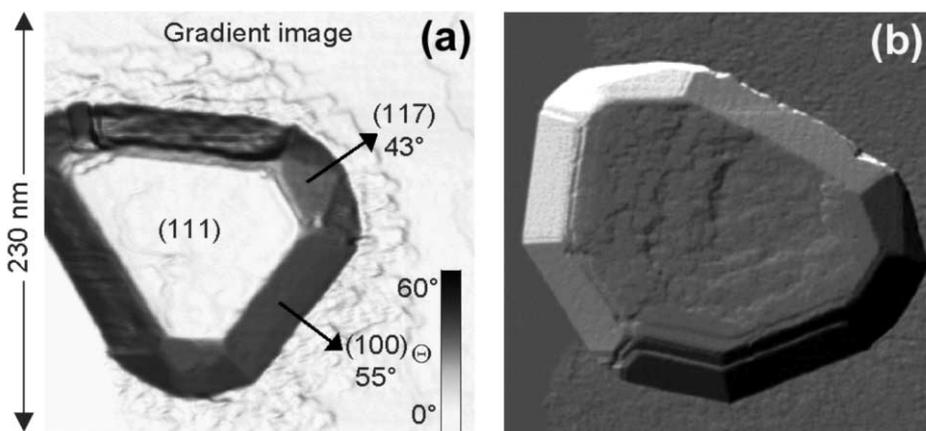


Fig. 2. (a) STM topography, imaged in gradient mode, of a Ge island deposited on Si(111) for  $T = 450$  °C and  $\theta = 2.5$  nm. Image dimensions are  $(230 \times 230 \times 40)$  nm<sup>3</sup>. The gray levels correspond to the angles on the original images (white, 0°; black, 60°). (b) STM topography, imaged in differential mode, of a Ge island grown on Si(111) for  $T = 450$  °C and  $\theta = 4.5$  nm. Image dimensions are  $(230 \times 230 \times 42)$  nm<sup>3</sup>.

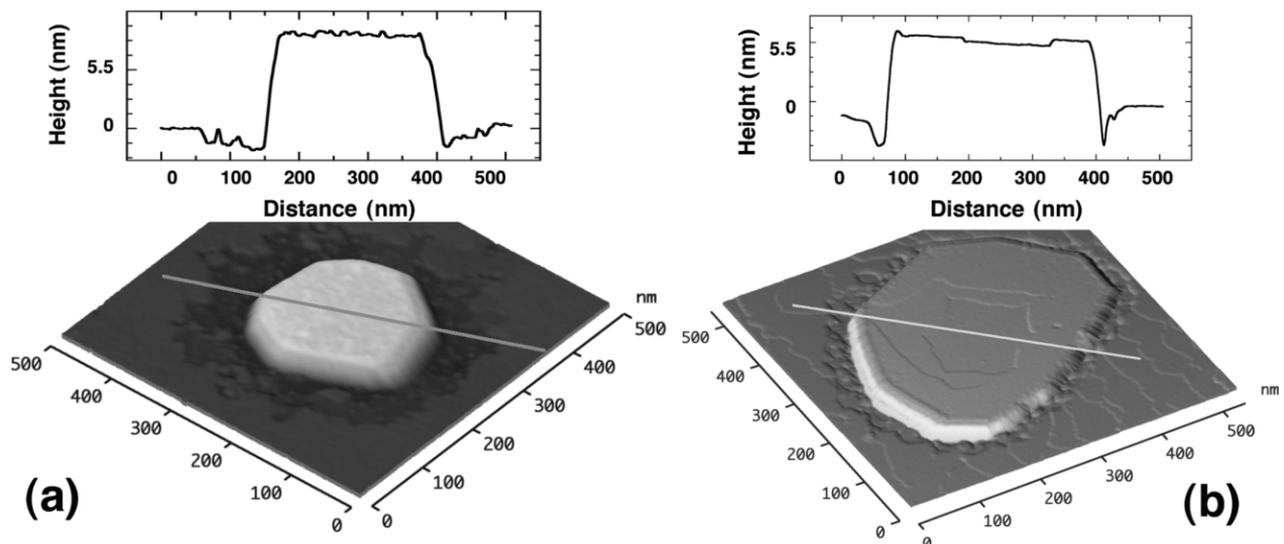


Fig. 3. Ge/Si(111): (a)  $500 \times 500 \text{ nm}^2$  STM image of an island at the first stage of ripening. Island height, 10 nm. (b)  $527 \times 527 \text{ nm}^2$  AFM image of an island transformed in atoll at the final stage; island height, 8 nm. The cross section along the gray lines are shown in the insets. The two islands belongs to different samples (3.5 and 2.5 nm of Ge/Si(111) grown at  $T = 530 \text{ }^\circ\text{C}$ , respectively).

increasing depth, as the islands become more round and flat.

In Fig. 3(a and b) two islands at subsequent ripening stages are shown. The erosion, which in some case can be up to 4 nm deep (12 ML) is shown in cross section in the two insets, and in the final stage (Fig. 3(b)) occurs both around the island and in the center of it, transforming the island into an ‘atoll’ [10]. It is worth noting that a similar erosion was previously reported (for the first time) by Kamins et al. [4] on Ge/Si (100); however, they could not identify its origin because the oxidation of their samples (measured by AFM in air) prevented a clear imaging of the trench. The depth of this depression was about 1 nm. The formation of trenches around the islands has also been recently reported by X.Z. Liao et al. [11], and by Chaparro et al. [12] for Ge grown on Si(001). Liao et al. [11] use MBE for deposition at  $700 \text{ }^\circ\text{C}$ , finding depressions up to 7 nm deep (about 21 ML). Chaparro et al. [12], which use growth conditions closer to ours ( $450\text{--}650 \text{ }^\circ\text{C}$ ), reported trench depths varying from less than 1 nm for small island base widths ( $\approx 100 \text{ nm}$ ) to about 5–6 nm for large base widths ( $\approx 300 \text{ nm}$ ). These authors interpret the trench formation as an effective strain-relief mechanism at the relatively high temperatures they use for growth.

Consistently with these results, we support the idea that this erosion could be assigned to the strong Ge–Si intermixing which draws material from the substrate to create the alloy in the island. Now we can say that in semiconductor heteroepitaxy there are basically four possible mechanisms for strain relief: (a) island nucleation and evolution (shape transition and faceting); (b) formation of dislocations; (c) intermixing and alloying;

(d) formation of trenches around the islands. In most cases, a combination of these four mechanisms takes place, and it must be emphasized that for the development of applications the formation of misfit dislocations and the occurrence of intermixing can be highly undesired. With simple geometrical analysis, Liao et al. [11] assumed that the Si missing from the trenches has gone into alloying within the islands. Seifert et al. [10] have justified the formation of trenches by using a simple model for the local strain energy density. On the WL a compressive area forms around an island, in which the strain energy difference (measured with respect to that of the WL far from the island) is large and positive, while inside the island it is negative [13]. This strain energy gradient is the driving force for the atom current from the WL towards the island [14].

The overall process can be qualitatively described as follows, the islands grow vertically up to a critical height, which has been estimated to be about 48 nm by Capellini et al. [15] after which the strain energy stored inside the islands can be partially relieved by introducing dislocations, or by a morphological transition of the island which progressively becomes more rounded in shape. The island now experiences a lateral growth, with material flow from the top to the edges; at the same time, the strain propagation along the substrate moves atoms from the WL to the island, eroding the WL itself and the substrate underneath. The driving force coming from the strain can explain also the erosion of the central part in the fully ripened island. We think that, according to recent calculations [16,17], the Ge atoms move towards the edge of the island’s top facet, where the strain energy can be more efficiently relaxed [14]. The Si atoms, that come from the sub-

strate in order to relax the strain inside the island, have not enough mobility [18] to totally replace the Ge atoms lacking, giving origin to the characteristic ‘atoll’ shape. Remarkably, we would like to point out that this phenomenon is only observed for Ge grown on Si(111), and has no counterpart on the Si(001) surface.

#### 4. XAFS data and results

XAFS spectra at the Ge K-edge were recorded at the ‘GILDA’ beamline at ESRF, Grenoble. A sagittally focussing Si(311) monochromator was used [19], and harmonics were rejected using a pair of grazing incidence mirrors. The Ge absorption coefficient was monitored in the fluorescence mode by using a thirteen-element hyperpure Ge detector with fast digital electronics. In order to reduce spectral distortions due

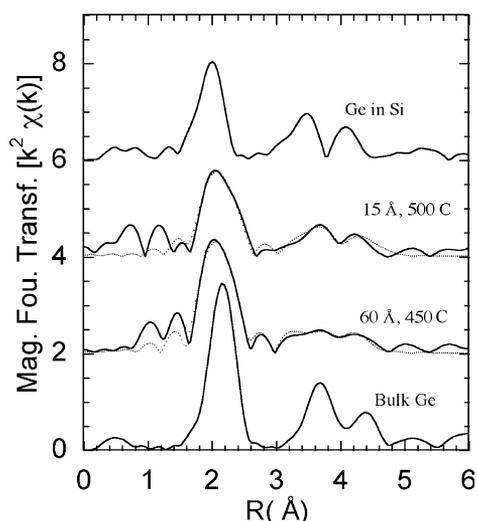


Fig. 4. Fourier transform of XAFS spectra around a Ge absorber (continuous line) along with the fitting of the first three coordination shells (dotted line). The top one refers to a Ge impurity in a Si matrix, and the bottom one to a bulk Ge sample.

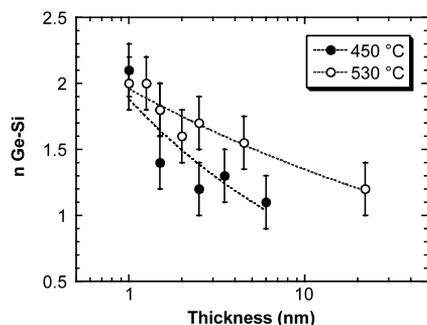


Fig. 5. Average number of Si atoms found around a Ge absorber by fitting the EXAFS data of the Ge/Si(111) samples grown at 450 and 530 °C substrate temperature.

to the excitation of Bragg peaks in the substrate and to reduce the thermal damping of the signal, samples were mounted on a vibrating and liquid-nitrogen cooled holder. A powder sample of bulk Ge and a sample consisting of 1 at.% of Ge in a Si epilayer were measured as references, respectively, in the transmission and fluorescence mode.

XAFS data were analyzed with the UWXAFS package [20] and with the FEFF 8.0 ab-initio simulation program [21]. Raw XAFS data were background-subtracted using the AUTOBK routine. As previously reported for the Si(001) surface [1] it was directly evident, in the raw data, that in all samples Ge was coordinated both with Si and with Ge atoms. With an improvement in the data analysis procedure previously adopted we analyzed the present spectra up to the third coordination shell.

Theoretical signals for a Ge atom embedded in either a Ge or a Si matrix were simulated for the first three coordination shells. The quality of the simulation was checked against the experimental spectra relative to bulk Ge and 1 at.% of Ge in Si, and proved to be excellent. Spectra of the samples were then fitted using a linear combination of signals relative to Ge in a Ge or Si matrix using a  $k^2$  weight; the fitting was performed in the  $R$ -range 1.6–4.5 Å on the signal filtered in the  $k$ -range 2.75–12 Å<sup>-1</sup>. The total coordination numbers for the first, second and third shells were fixed to 4, 12 and 12, respectively, and the common fitting parameter for all shells was the relative Ge–Si coordination number  $N$ . In Fig. 4 we show representative spectra (continuous lines) and fits (dots), illustrating the excellent quality of the fits.

In Fig. 5, the number of Si atoms around a Ge atom, as obtained from the EXAFS fitting are shown as a function of the deposited Ge thickness for Ge/Si(111) samples. The data refers to two substrate temperatures,  $450 \pm 10$  and  $530 \pm 10$  °C. A clear trend can be noticed: with increasing thickness the number of Si atoms surrounding Ge decreases from 2 to 1. Therefore, the observed average intermixing is higher in sample in which only a wetting layer is present (50% Si average content) with respect to those, deposited at the same temperature, with a high island density (25% Si average content). This result is in agreement with the prediction of island enrichment in Ge reported by Tersoff [16]. Moreover, the samples grown at higher  $T$  display, as expected, higher values of  $N$  indicating a larger intermixing. Interesting experiments on this point have been performed by Capellini et al. [22], who analyzed by X-ray photoelectron spectroscopy (XPS) the Si content in Ge/Si(001) islands grown at different temperatures by CVD, finding an increase with  $T$  of the intermixing in the islands. We suppose that the Si content in the islands is limited both by the diffusion factor (the

height of the islands can reach 50 nm), and by the fact that the lattice in the islands is more relaxed than in the wetting layer, reducing the driving force for the intermixing.

## 5. Conclusions

We have analyzed the effects of intermixing in Ge/Si(111) islands, by comparing tunneling microscopy and X-ray absorption measurements of samples grown by Physical Vapor Deposition in UHV.

By using STM in-situ we have observed the nucleation of 3-D islands, which exhibit different shapes, starting from strained coherent nanocrystals (truncated tetrahedra), with intermediate rounded shapes, and ending in relaxed, dislocated islands, with an atoll like shape.

We have observed and identified, for the first time in the case of Ge on Si(111), the formation of a trench around the ripened islands, due to the selective depletion of the WL, which derives from the high stress at the island border [10,17]. Furthermore, we have suggested that an intra-island relaxation leads to: (i) a progressive rounding of the island shape; (ii) a strong decrease of the height/base aspect ratio (due to a decrease of the height coupled to an increase of the width); (iii) a selective depletion of the central part which transforms the island into an atoll.

From the XAFS analysis it has been possible to evaluate the intermixing of Si in Ge in a series of samples with deposited thicknesses ranging from 0.5 to 22 nm, and substrate temperatures between 450 and 530 °C. By increasing the deposited material, we have found that the number of Si atoms surrounding Ge decrease from 2 to 1, i.e. a Si average content in the alloyed epilayer decreasing from 50 to 25%. The temperature dependence of the data indicates, as expected, a larger intermixing for the sample grown at higher temperatures.

## Acknowledgements

This work was partially supported by INFM. We are grateful to the GILDA staff for the excellent support.

## References

- [1] F. Boscherini, G. Capellini, L. Di Gaspare, F. Rosei, N. Motta, S. Mobilio, *Appl. Phys. Lett.* 76 (2000) 682.
- [2] F. Boscherini, G. Capellini, L. Di Gaspare, M. de Seta, F. Rosei, A. Sgarlata, N. Motta, S. Mobilio, *Thin Solid Films* 380 (2000) 173.
- [3] N. Motta, Proceedings of the NN2000 school, S. Margherita di Pula, Italy, in: S. Bellucci, M. De Crescenzi (Eds.), *SIF Conference Proceedings Series*, Bologna, 2001.
- [4] T.I. Kamins, E.C. Carr, R.S. Williams, S.J. Rosner, *J. Appl. Phys.* 81 (1997) 211.
- [5] T.I. Kamins, G. Medeiros-Ribeiro, D.A.A. Ohlberg, R.S. Williams, *J. Appl. Phys.* 85 (1999) 1159.
- [6] U. Köhler, O. Jusko, G. Pietsch, B. Muller, M. Henzler, *Surf. Sci.* 248 (1991) 321.
- [7] D.J. Eaglesham, M. Cerullo, *Phys. Rev. Lett.* 70 (1993) 1643.
- [8] N. Motta, A. Sgarlata, R. Calarco, Q. Nguyen, F. Patella, J. Castro-Cal, A. Balzarotti, M. De Crescenzi, *Surf. Sci.* 406 (1998) 254.
- [9] P. Muller, R. Kern, *Surf. Sci.* 457 (2000) 229.
- [10] W. Seifert, N. Carlsson, J. Johansson, M. Pistol, L. Samuelson, *J. Cryst. Growth* 170 (1997) 39.
- [11] X.Z. Liao, J. Zou, D.J.H. Cockayne, Z.M. Jiang, X. Wang, R. Leon, *Appl. Phys. Lett.* 77 (2000) 1304.
- [12] S.A. Chaparro, Y. Zhang, J. Drucker, *Appl. Phys. Lett.* 76 (2000) 3534.
- [13] H.T. Johnson, L.B. Freund, *J. Appl. Phys.* 81 (1997) 6083.
- [14] A.-L. Barabási, *Appl. Phys. Lett.* 70 (1997) 2565.
- [15] G. Capellini, N. Motta, A. Sgarlata, R. Calarco, *Solid State Comm.* 112 (1999) 145.
- [16] J. Tersoff, *Phys. Rev. Lett.* 81 (1998) 3183.
- [17] B.J. Spencer, J. Tersoff, *Phys. Rev. B* 63 (2001) 205424–205431.
- [18] J. Tersoff, *Phys. Rev. Lett.* 85 (2000) 2843.
- [19] S. Pascarelli, F. Boscherini, F. D'Acapito, J. Hrdy, C. Meneghini, S. Mobilio, *J. Synchrotron Radiation* 3 (1996) 147.
- [20] For description see <http://depts.washington.edu/uwxafs>.
- [21] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, *Phys. Rev. B* 58 (1998) 7565.
- [22] G. Capellini, M. De Seta, F. Evangelisti, *Appl. Phys. Lett.* 78 (2001) 303.