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Composition of Ge(Si) islands in the growth of Ge on Si(111)

Fulvio Ratto and Federico Rosei[a)]
INRS-EMT, Université du Quebec, 1650 Boul. Lionel Boulet, J3X 1S2 Varennes, Quebec, Canada

Andrea Locatelli, Salia Cherifi, Stefano Fontana, and Stefan Heun
Sincrotrone Trieste S.C.p.A., S.S. 14 Km 163.5, 34012 Trieste, Italy

Pierre-David Szkutnik, Anna Sgarlata, and Maurizio De Crescenzi
Dipartimento di Fisica and Unità INFM, Università di Roma II, Via della Ricerca Scientifica n.1, 00133 Roma, Italy

Nunzio Motta
Dipartimento di Fisica and Unità INFM, Università di Roma TRE, Via della Vasca Navale 84, 00100 Roma, Italy

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X-ray photoemission electron microscopy (XPEEM) is used to investigate the chemical composition of Ge/Si individual islands obtained by depositing Ge on Si(111) substrates in the temperature range 460–560 °C. We are able to correlate specific island shapes with a definite chemical contrast in XPEEM images, at each given temperature. In particular, strained triangular islands exhibit a Si surface content of 5%–20%, whereas it grows up to 30%–40% for "*atoll-like*" structures. The island's stage of evolution is shown to be correlated with its surface composition. Finally, by plotting intensity contour maps, we find that island centers are rich in Si. *© 2004 American Institute of Physics.* [DOI: 10.1063/1.1758304]

Current attempts to advance the existing Si technology and to integrate micro- and optoelectronic devices on the same Si wafer have spurred significant efforts, directed toward the possibility of growing Ge nanostructures on silicon, with particular interest in quantum dots (QDs).[1–4] The aim is to exploit the electronic properties of these novel systems to engineer completely new components that are compatible with today's Si-based devices. In this context, the growth of QDs by self-assembly is an emerging technology.

There are at least three critical issues to be addressed in the growth of self-assembled semiconductor QDs, namely: (i) the controlled positioning of QDs on a suitable substrate;[5,6] (ii) the ability to grow *stable* dots with the uniform size and shape;[7] (iii) the control of the composition of individual QDs, which ultimately determines their physical properties.[8–11]

Intermixing has been previously investigated in different systems, either statistically from sets of islands,[12] or by analyzing the cross section of single QDs.[13] In this letter, we report spectro-microscopy measurements of Ge/Si alloying from the surface of *individual* Ge islands grown on Si(111), which allows the representation of their stoichiometry by means of two-dimensional contour maps. The islands nucleate as a result of a *modified* Stranski–Krastanov growth process,[14] when Ge coverage exceeds ~3 monolayers (ML).

After degassing at 600 °C for several hours, Si(111) was flashed at ~1200 °C in ultrahigh vacuum conditions. Three samples were grown at substrate temperatures of 460, 530, and 560 °C, depositing ~10 ML of germanium by molecular beam epitaxy. The morphology and chemical contrast of the grown structures was studied at room temperature by x-ray photoemission electron microscopy (XPEEM) at the Nanospectroscopy beamline (Elettra, Trieste),[15] allowing one to acquire photoelectron spectra with high lateral resolution.[13,16] Imaging was carried out at energies close to the Si $2p$ and Ge $3d$ core levels, thereby highlighting Si- or Ge-rich areas of the surface.[17]

Figure 1 displays a comparison between XPEEM images obtained by integrating the Si $2p$ and Ge $3d$ spectra from the same surface region. In the Si $2p$ image the wetting layer (WL) appears brighter than the three-dimensional (3D) islands, indicating that the latter contain less silicon.[18] The opposite contrast is revealed in the Ge $3d$ photoelectrons image.[19] Islands with different heights coexist on the surface at a given temperature.[14] At the same time, islands with different aspect ratios exhibit a different chemical contrast, correlating geometrical features to the relative Si/Ge concentration.[20] We therefore conclude that these parameters are equivalent to describe the stage of evolution of an individual island. In particular, structures richer in Si appear to be flatter. This supports the suggested picture of a morphological transition leading to the formation of *atoll-like* islands,[14] if ripening occurs through the progress of the intermixing process. Together with the formation of a trench around the islands,[18] this results in a partial release of the accumulated strain energy due to the lattice mismatch.[21]

The contour plots reported in Fig. 2 clearly show the silicon surface concentration profile of the islands. A Si-rich central zone is generally observed, even in strained triangular islands which precede atoll formation. One interesting debate focuses on the topological characteristics of Si/Ge alloying in individual islands, which could cast light on the dynamics of the intermixing process. Different models have been proposed, pointing either to bulk driven alloying,[22] which tends to relax the strain due to the Si/Ge lattice mismatch, or to a surface mediated diffusion process,[23] which occurs randomly as a consequence of the high mobility of surface adatoms. If

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[a)] Author to whom correspondence should be addressed; electronic mail: rosei@inrs-emt.uquebec.ca

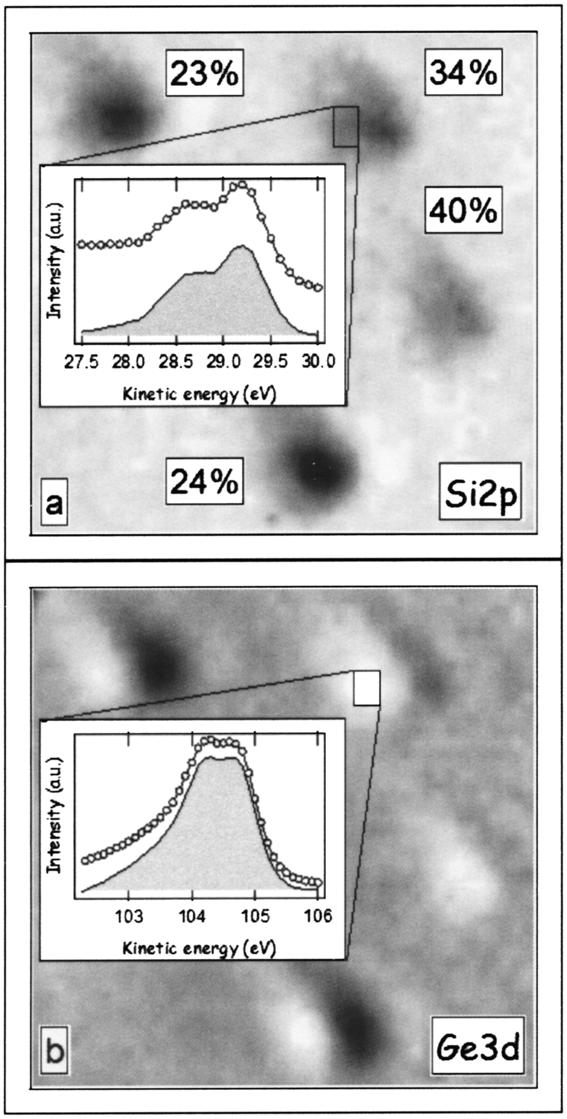

FIG. 1. 4×4 μm^2 integrated XPEEM images taken in correspondence of (a) the Si $2p$ core level peak and (b) the Ge $3d$ core level. Examples of spectra are shown in the insets. Circles: raw data; shaded curves: background subtracted data, averaged over the labeled regions. The micrographs are obtained by integrating the spectra with ~20 nm lateral resolution. The x-ray energy was 130.5 eV. The growth temperature was 560 °C. The measured Si concentrations for the 3D islands are labeled in panel (a).

the first phenomenon is predominant, then a Si-rich island core should result, as a consequence of atomic exchange processes at its base during growth. Conversely, if surface diffusion processes are dominant then alloying should prevail at island edges. Experimental studies on different systems at different growth conditions have alternatively shown a Si-richer center[12] or perimeter.[24] In the present case, which confirms bulk driven alloying, we can interpret the Si-rich central zones as a step in the pathway toward island evolution, until atolls appear.[25]

When photoelectron yields from very close regions of the same image are directly compared, and the spectra from all atomic species present on the sample are available, the chemical composition of the surface can be evaluated.[26] If we name the ratios between the Si $2p$ and the Ge $3d$ yields from the islands and from the WL in proximity of the islands as R_{Si} and R_{Ge}, respectively, and relate them through the island surface concentration, the Si concentration x_{Si} may be expressed as a function of R_{Si} and R_{Ge} through the simple relation:[27,28]

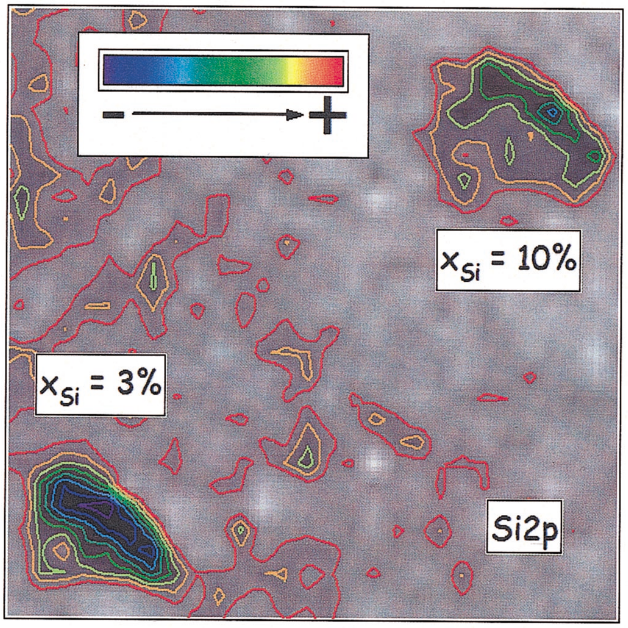

FIG. 2. (Color) 2×2 μm^2 integrated XPEEM image taken at the Si $2p$ core level, together with the contour plots from a more (top) and a less (bottom) ripened island. Photoelectron yields are increasing from blue (lowest) to red (highest). The darkest regions in the panels are produced by the shadows of the 3D islands, due to the 16° grazing incidence angle of the x-ray beam. The growth temperature was 530 °C. The estimated surface Si concentrations for the selected islands are indicated. The wetting layer appears to be inhomogeneous.

$$x_{Si}=\frac{R_{Ge}-1}{R_{Ge}/R_{Si}-1}. \tag{1}$$

Equation (1) allows one to estimate the islands' Si surface concentrations x_{Si} from a set of individual islands grown at a given substrate temperature and to relate them to their geometrical features.[29] Figure 3 displays a graph of Si concentration plotted as a function of island base area. The plot clearly shows that islands with different morphological and chemical characteristics coexist at the three different growth temperatures. The following description is thus suggested:

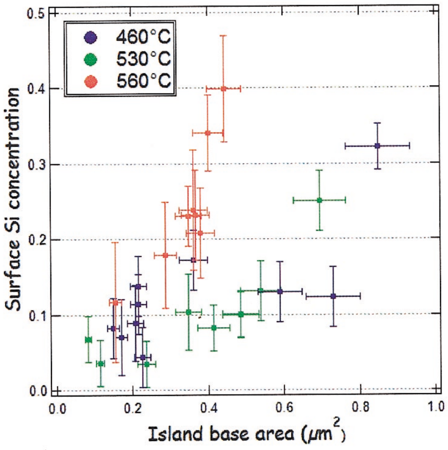

FIG. 3. (Color) Base area dependence of the Si surface content in the observed islands. At each deposition temperature, the stoichiometry is determined by the island's lateral dimensions.

the ripening stage of an individual island can be equivalently associated with its geometrical features or to the island's Si surface concentration, at a given growth temperature. The latter defines the details of the stoichiometry–morphology relation in the single 3D islands and determines the population of the coexisting species. Most islands have a Si concentration ranging from 5% to 20% and a reduced area or high aspect ratio, whereas ripened islands are typically characterized by a value of x_{Si} greater than 25%. The measured Si concentrations are consistently lower than the 50% value previously reported for the WL.[30] Increasing the temperature alters the relative population of the two species, privileging ripened islands,[14] also shifting the surface Si concentration of strained islands to higher values. We remark that the data sets obtained at 460 and 530 °C do not exhibit major changes, while evident alterations of x_{Si} values are found at 560 °C. This is clearly related to the kinetic activation of the diffusion processes between the substrate, the WL, and the 3D islands. However, this does not allow us to establish whether they occur predominantly at the surface or at the underlying layers (e.g., through vacancy migration). Moreover, the outlining of two distinct island species at these temperatures points to the existence of two metastable configurations, which rules out an island evolution caused by Ostwald ripening alone.[31] Nevertheless, it was previously shown that room temperature imaging does not allow one to relate the observed statistics to island thermodynamics at a given deposition temperature.[32]

In conclusion, we have shown that specific geometrical features are unambiguously related to a definite chemical contrast in XPEEM images in the temperature range 460–560 °C, and thus to a specific Si/Ge composition at the island's surface. XPEEM yields quantitative information and leads to surface concentration–morphology graphs for sets of individual islands. This technique can also be used to plot contour maps which indicate concentration gradients at the surface of single Ge(Si) islands. The resulting values point to the presence of two island configurations: strained triangular islands characterized by a Si surface concentration of 5%–20%, and ripened atolls that contain up to 30%–40% Si. Higher growth temperatures induce faster ripening of the 3D islands and a shift of the surface Si content in the strained islands toward higher values, indicating a thermally activated interdiffusion process that partially relaxes the strain energy in the islands. This set of observations may be used to control the composition/morphology of self-assembled semiconductor QDs.

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