Applied Physics Letters

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Cite as: Appl. Phys. Lett. **76**, 682 (2000); https://doi.org/10.1063/1.125860
Submitted: 29 July 1999 . Accepted: 03 December 1999 . Published Online: 01 February 2000

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Ge–Si intermixing in Ge quantum dots on Si(001) and Si(111)

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(Received 29 July 1999; accepted for publication 3 December 1999)

Exploiting Ge K-edge x-ray absorption spectroscopy we provide direct evidence of Si–Ge intermixing in self-organized strained and unstrained Ge quantum dots on Si, and provide a quantitative measurement of the average composition. For Ge/Si(001) dots with equivalent thickness in the range 5.8–38 nm and morphology ranging from that typical of coherently strained to that associated with relaxed dots we find that the average Si composition is approximately 30%. For Ge/Si(111), we find that the wetting layer has a Si composition near 50%. We discuss these results in terms of the energetics of dot formation and argue that strain-enhanced diffusion of Si into Ge should be considered as an important factor in minimizing the strain energy of the system.
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There recently has been considerable interest in the improvement of the electron-hole recombination efficiency of indirect gap semiconductors by quantum confinement effects[1,2] as this could lead to the development of Si-based optoelectronics. Semiconductor quantum dots can be realized making use of the self-organization process arising in the Stranski–Krastanov (SK) growth mode for lattice mismatched heteroepitaxy. In this type of growth the strain energy due to the lattice mismatch is reduced by islanding; the decrease in energy due to islanding is partially compensated by an increase of surface energy due to the greater surface/bulk ratio of an ensemble of dots with respect to a two-dimensional (2D) layer. The particular strain distribution in the dots is responsible for the rather narrow size distribution which can be obtained in this type of growth.[3]

In the recent literature there have been indications that a significant degree of Si–Ge intermixing might exist for Ge dots deposited on Si substrates. For example, a recent atomic force microscopy (AFM) study[4] of annealed Ge dots has suggested that Si–Ge intermixing might exist, based on the measurement of their volume; a micro-Raman investigation[5] of large ($\sim 2\ \mu$m), relaxed, dots provided evidence for the presence of Si inside these dots. Intermixing in thinner epilayers has been detected by surface x-ray absorption fine structure[6] (XAFS). However, no direct proof of the existence of intermixing in small, strained dots has been provided; in fact, there is little information altogether on the local bonding in Ge quantum dots. The purpose of the present contribution is to demonstrate, with the use of Ge K-edge XAFS in the fluorescence mode, the presence of Si–Ge intermixing and to provide a quantitative measurement of the Si concentration.

Two series of samples have been investigated, both consisting of a SK growth of Ge quantum dots. Ge dots on Si(001) were deposited by low pressure chemical vapor deposition. High purity germane with no carrier gas at a pressure of 0.5 mTorr was used; the substrate temperature was 600 °C and the growth rate 4 nm/min. The samples were characterized by *in situ* photoelectron spectroscopy and reflection high energy electron diffraction (RHEED) and *ex situ* (AFM).[2,7] Six samples were studied, with an equivalent thickness (i.e., the thickness which would result if the Ge atoms formed a homogeneous 2D layer) ranging from 5.8 to 38 nm. The maximum height of the dots obtained in these conditions is ~ 60 nm while the distribution of base widths ranges between 50 and 500 nm. AFM allowed to identify dots with pointed and truncated pyramid morphology.[7] A clear correspondence between these morphological differences and the strain state exists, with pointed (truncated) pyramids being associated with coherently strained (relaxed) dots. Recent electron microscopy studies[8] have clearly shown the presence of misfit dislocations in truncated pyramids. By counting the number of each type of dot the relative volume of truncated pyramids was obtained and is plotted in Fig. 1; it ranges from 10% to 90% thus providing the full range. We point out that in coherently strained dots the distribution of strain is not homogeneous as in a 2D epilayer

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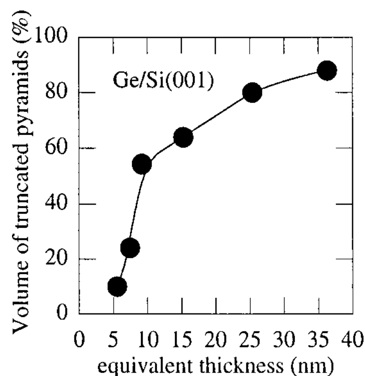

FIG. 1. The relative volume of truncated pyramids for Ge/Si(001) samples, as determined from AFM. The line is a guide to the eye.

below the critical thickness and that the ordinate of Fig. 1 cannot be simply be taken to be proportional to any element of the strain tensor.

Ge dots on Si(111) were deposited by molecular beam epitaxy. The n-type Si substrates used for the growth were flashed at 1250 °C to prepare the 7×7 reconstructed surface. Ge was evaporated at 0.5 Å/min from a Knudsen cell on the substrate kept at 500 °C. The samples were characterized by RHEED and scanning tunneling microscopy. Two samples were deposited, with equivalent thicknesses of 1.0 and 1.7 nm. The surface reconstruction was 5×5 in the case of the 1.0 nm sample, and a mixture of 5×5 and 7×7 in the case of 1.7 nm sample. The 1.0 nm sample is thus essentially constituted by the wetting layer only, while the 1.7 nm sample contains Ge islands exhibiting a 7×7 reconstruction.[9]

XAFS experiments at the Ge K edge were performed at the ''GILDA'' CRG beamline of the European Synchrotron Radiation Facility. A Si(113) dynamically sagitally focusing monochromator was used[10] and harmonics were eliminated with a pair of Pd-coated grazing incidence mirrors. The Ge K_α fluorescence intensity was monitored using a seven element hyper-pure Ge detector; digital amplifiers with a 1 μs peaking time were used. Care was taken to have equal total count rates for all samples ($\sim$20 000 c/s) in order to avoid systematic errors due to amplifier deadtime. In order to preferentially probe the structure either perpendicular or parallel to the growth plane spectra were acquired in two geometries:

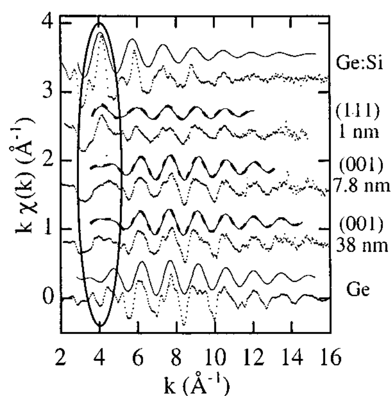

FIG. 2. Selected XAFS spectra. Dots: raw data; continuous line: first shell filtered; dotted line: fit. Substrate orientation and equivalent thickness are indicated. The ellipse highlights the spectral signature of Ge–Si bonds.

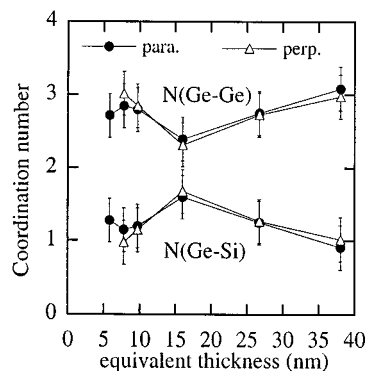

FIG. 3. Coordination numbers for Ge/Si(001).

with the angle between the electric vector of the photon beam and the normal to the surface either 15° or 75°, respectively.

XAFS data were analyzed using standard procedures.[11] Selected background-subtracted raw data are shown in Fig. 2; also shown are the spectra of two model samples: bulk Ge and a Ge impurity in a crystalline Si matrix. In the low k region there are significant differences between the spectra of the samples and that of Ge. In particular at $k=4$ Å^{-1} Ge has a negative oscillation, while all the samples exhibit a positive oscillation, in good coincidence with the spectrum for a Ge impurity in Si. This feature is highlighted with the ellipse. This observation clearly suggests that a significant number of Si atoms bound to the average Ge atom exist.

This qualitative observation was confirmed by quantitative analysis. The filtered first shell signal was obtained by performing a Fourier transform in the range 2.8–15.3 Å^{-1} and subsequently an inverse transform in the range 1.5–2.9 Å. The resulting first shell signal in k space was fitted with a linear combination of signals relative to Ge–Ge and Ge–Si bonds using the quoted experimental standards. The total coordination number (CN) was fixed to 4, with the ratio of Ge–Ge to Ge–Si CN a free parameter; the other free parameters were the Ge–Ge and Ge–Si bond lengths, a common energy shift and mean-square-relative displacements (MSRD) for the two bonds. Excellent fits were always obtained, as shown in Fig. 2.

In Fig. 3 we show the values of the Ge–Ge and Ge–Si CN's for Ge/Si(001) as a function of the equivalent coverage. Likewise, in Fig. 4 we show the values of the bond lengths. We note that there are no trends of both local structural parameters with equivalent thickness; we do not believe

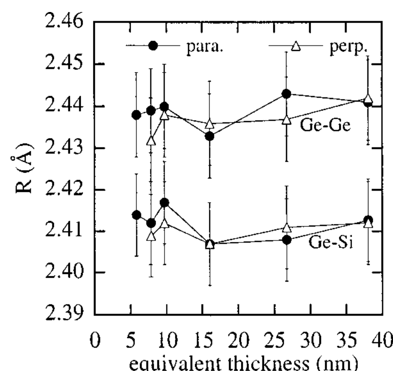

FIG. 4. Bond lengths for Ge/Si(001).

the slight deviation of the CN's at 15 nm equivalent thickness to be significant. For both samples deposited on Si(111) a Ge–Si CN of 2 ± 0.3 was found, and values for the bond lengths similar to those reported in Fig. 4. No difference between the values of bond lengths or CN's measured in the parallel and perpendicular geometry was detected.

The reported CN's measure the average coordination of Ge atoms in the dots. There is ample evidence that Ge–Si alloys are random alloys,[12] i.e., there is no preference for or against heteroatomic bonding; this is also compatible with the very similar electronegativities and the limited difference in covalent radius of the constituent atoms. We are therefore justified in using the CN's as a measurement of composition. Thus for Ge/Si(001) the average composition is close to $Ge_{0.7}Si_{0.3}$ while for the Ge/Si(111) samples it is close to $Ge_{0.5}Si_{0.5}$. The compositions are average values and neglect any gradients to which the XAFS technique is insensitive. The differences between the samples deposited on (001) and (111) might be related both to the different thicknesses and/or to the different diffusion coefficients perpendicular to the growth plane.

The Ge–Ge and Ge–Si bond lengths measured compare well with those reported in a recent comprehensive study of crystalline Ge–Si alloys[13] for a composition close to $Ge_{0.7}Si_{0.3}$. While this is satisfying it must be mentioned that a comparison between bond lengths in unstrained Ge–Si alloys and Ge–Si dots is not necessarily straightforward. While it has been recently demonstrated[14] that strain can alter the value of the bond lengths in homogeneous 2D layers and that a linear relationship between variation of bond lengths and average strain holds to a very good accuracy[15] it must be considered that the dot samples under investigation have a relatively broad size and strain distribution; also, even for coherently strained dots the spatial distribution of strain[16] will lead to an averaging effect on the mean bond lengths measured. For these reasons, a simple relation between bond lengths and relative relaxed volume measured by AFM is not expected.

The XAFS evidence for Si–Ge intermixing is also supported by complementary data. The critical base for island formation for Ge/Si(001) increases as a function of deposition temperature in the range 600–850 °C (at constant growth rate and time), as measured by AFM;[17] since the critical base is inversely proportional to the square of the strain[18] an increase of the critical base is compatible with the presence of intermixing (see below). X-ray photoelectron spectroscopy (XPS) data on the same system detects a Si/Ge ratio which is not compatible with pure Ge dots, given the measured morphology. Finally, transmission electron microscopy (TEM) investigations on our samples show that the Ge-rich layer extends at most 2 nm below the wetting layer; this rules out the possibility that considerable Ge diffusion into the Si substrate is taking place.

In equilibrium models of dot formation,[19] since the entropic contribution to the free energy is negligible, it is the internal energy per atom which determines the state of the system.

As already remarked the important energy terms are the strain energy, the surface energy of epilayer and substrate and, in the case of relaxed or partially relaxed layers, the dislocation formation energy. Intermixing can have an important role in decreasing the strain energy. The total strain energy of an ensemble of dots is given by a volume integral in which the elements of the strain tensor appear quadratically. The magnitude of the strain tensor elements depend linearly on the difference between the local free lattice parameter (in each direction) and that imposed by the SK growth on the substrate. Since the free lattice parameter can be reduced by intermixing it follows that diffusion of Si into the Ge dots will reduce the strain energy per atom. We point out that strain-enhanced diffusion has been previously found for other systems.[20] Finally, we note that also in kinetic models of dot formation[4] the strain energy has an important role, since it determines the atomic flux on the surface of the forming SK layer and hence, ultimately, the size distribution.

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