Investigation of the chemical composition profile of SiGe/Si(001) islands by analytical transmission electron microscopy

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The authors have determined the composition profile within individual $Si_{1-x}Ge_x$ nanoscale islands on Si(001). Samples have been grown by means of liquid phase epitaxy in the Stranski-Krastanov mode. By applying electron energy loss spectroscopy, the intensities of Si *K* and Ge *L* edges have been measured to determine the relative atomic concentration of germanium. The quantification of the composition suggests a profile comprising of two regions with different linear concentration gradients. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2751598]

In the past two decades low-dimensional structures, such as quantum dots (QDs), have attracted a tremendous interest in basic and application researches.[1] A very promising attempt toward perfectly ordered monodisperse ensembles of QDs relies on the Stranski-Krastanov growth mode. Therein dislocation-free three-dimensional islands laterally self-assemble on top of a thin wetting layer. The shape transition from a planar toward a three-dimensional mode increases the free-surface energy. However, the energy gain due to elastic relaxation overcompensates this energetical drawback. It has been found that the final island size inversely scales with the lattice mismatch applied,[2] indicating the key role of strain for preventing Ostwald ripening. The growth of $Si_{1-x}Ge_x$ islands on Si substrates has been widely used as a model system to obtain a more comprehensive description of the underlying mechanisms.[3–5] In particular, the chemical composition profile incorporated in the islands, i.e., the variation of the germanium content x, may serve as a sensitive fingerprint of the detailed growth scenario. On the other hand, the variation of the composition within QDs distinctly influences their electro-optical properties.[6] In this letter, we report on direct measurements of the chemical composition profile in individual $Si_{1-x}Ge_x$/Si(001) islands by applying analytical transmission electron microscopy (AEM), more precisely by electron energy loss spectroscopy (EELS).

The samples were grown by liquid phase epitaxy (LPE) on (001) silicon substrates using a slide-boat reactor. To ensure a high purity of the epitaxial layers, the entire growth process was performed in pure hydrogen atmosphere. In a first step, the components silicon and germanium were solved in liquid bismuth, which has been homogenized for 2 h at the growth temperature of 973 K to equilibrate the system. After *in situ* desorption of the natural oxide layer at 1200 K, the Si–Ge–Bi solution was brought into contact with the substrate. To initialize the growth, an oversaturation was established by choosing a growth temperature of up to 2 K below the saturation temperature.

LPE operates close to the thermodynamic equilibrium, in contrast to other rather kinetically controlled techniques, e.g., molecular beam epitaxy. Consequently, LPE-grown islands exhibit a similar (equilibrium) shape over an extended composition range. It is characterized by truncated pyramids with {111} side facets and a (001) top facet, see Fig. 1. Under these conditions, the aspect ratio $w/h^*=2$ (island base width along the [110] over island height) minimizes the free-surface energy.[7] Since scattering methods generally suffer from averaging over spacially extended island ensembles,[8,9] a more direct access to individual objects appears to be highly desirable.

By applying AEM, the standard preparations of mechanical grinding, polishing, dimpling, and Ar ion milling were carried out in order to obtain electron-transparent cross-section samples. Using EELS, the atomic concentration ratio of the two elements silicon and germanium can be calculated by dividing their integral intensities I_{Si} and I_{Ge} via

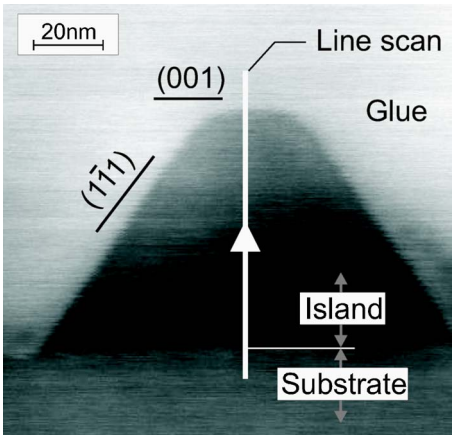

FIG. 1. Bright field scanning transmission electron microscopy image of a (110) cross section through a $Si_{0.7}Ge_{0.3}$ island with the position of the AEM line scan indicated.

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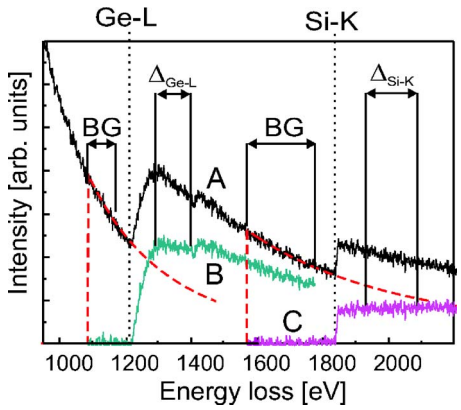

FIG. 2. (Color online) Electron energy loss between 900 and 2200 eV covering the Ge *L* and the Si *K* absorption edges. In the interval, labeled BG, the background signal (dashed lines) has been fitted to the measured data (plot A) separately for both edges. After background subtraction the energy windows, indicated $\Delta_{Ge\ L}$ and $\Delta_{Si\ K}$, were set both for Ge *L* (plot B) and for Si *K* (plot C) above the respective edge. The corresponding integral intensities I_{Ge} and I_{Si} have been subsequently determined within these windows $\Delta_{Ge\ L}$ and $\Delta_{Si\ K}$.

$$\frac{n_{Si}}{n_{Ge}} = \frac{\sigma_{Ge}}{\sigma_{Si}} \frac{I_{Si}}{I_{Ge}},$$

where σ_{Si} and σ_{Ge}, are the partial ionization cross sections for the corresponding elements.[10] Thus, the germanium content x can be calculated via $x=1/(1+n_{Si}/n_{Ge})$. For this purpose, a VG HB 501 UX scanning transmission electron microscope, equipped with a Gatan ENFINA 1000 parallel electron energy loss spectrometer, has been used. The accelerating voltage has been set to 100 keV. In order to ensure an intense signal along with a high spatial resolution, a convergence semiangle of 28 mrad and a collection semiangle of 24 mrad have been used. For the numerical data treatment, the Gatan *Digital Micrograph* program has been applied.

We have measured the electron energy loss spectrum between 900 and 2200 eV, thus simultaneously covering the Ge *L* edge at 1217 eV and the Si *K* edge at 1839 eV (Fig. 2). In order to quantitatively evaluate the exact integral intensities, we have to consider exclusively the intensities just due to the ionization for each element. The continuously decreasing background components at both edges have been removed by fitting a power law. Generally, the intensity measured in an energy loss spectrum decreases $\propto 1/q^4$, where q is the momentum transfer. Thus, the integration windows for the integral intensities (Δ_{Ge} *L* and Δ_{Si} *K*) have been set to a minimum width of 100 eV, beginning at least 80 eV above the ionization edges. In that way, the contributions to the integral intensities due to multiple scattering effects and random noise could be minimized.

For the determination of the ratio of the partial cross sections σ_{Si} and σ_{Ge} (the so-called *k* factor), we performed under identical experimental conditions multiple measurements at a standard consisting of a 200 nm thick $Si_{1-x}Ge_x$ layer grown on a Si substrate. By applying Rutherford backscattering, the nominal germanium content inside the $Si_{1-x}Ge_x$ layer could be determined to $x=0.215$. A dependence of the elemental quantification from the sample thickness could be excluded for the probed $Si_{1-x}Ge_x$ islands due to the uniformity of the quantification at different thicknesses of the $Si_{1-x}Ge_x$ layer.

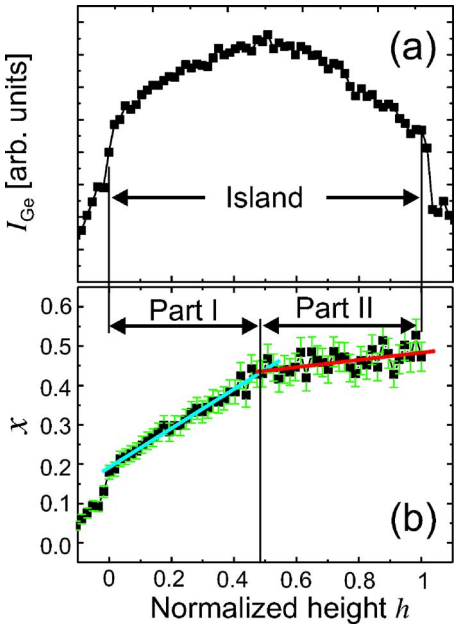

FIG. 3. (Color online) Results of the EELS measurements at an individual $Si_{1-x}Ge_x$ island. The integral intensity of the germanium EELS signal I_{Ge} (integrated over $\Delta_{Ge\ L}$, Fig. 2) and the corresponding germanium content x are plotted against the normalized height h in (a) and (b), respectively. The error bars given arise from the error propagation of the standard deviation, which was calculated by the determination of the mean *k* factor.

EELS measurements have been carried out on $Si_{1-x}Ge_x$ islands with base widths between 110 and 130 nm. To obtain a spatially resolved germanium content profile, several line scans at the position indicated in Fig. 1 have been performed accounting an average time of 4 s per data point. The line scans typically consist of 80 equidistantly spaced data points. The scans started in the substrate to minimize the contamination with carbon released from the glue during the electron irradiation. Since scattering results have indicated a constant germanium content in the [110] direction,[11] only line scans along the [001] growth direction through the center of the island have been performed.

The EELS signal integrated within the Δ_{Ge} *L* energy window (Fig. 2) and the resulting germanium content as a function of the normalized island height are given in Fig. 3. The slope of the flanks of the integral intensities of the Ge signal has been used to determine the position when the electron beam completely probes the island. The boundary between the substrate and the island is set to $h=0$; the top of the island corresponds to $h=1$. Due to the effective spot diameter of 4 nm of the electron beam, the expected concentration change at the substrate-island interface from pure Si to $Si_{1-x}Ge_x$ is blurred. We deduce that the Ge content x abruptly changes from 0 to nearly 0.2 at this interface. The concentration profile in Fig. 3(b) exhibits two island regions (parts I and II), which can be characterized by two separate linear concentration gradients: a steep increase of germanium at the island bottom (part I) followed by a comparatively flat plateau above (part II). Measurements at other islands exhibit a very similar behavior. Comprising all investigated islands, the transition between the two parts occurs at $h=0.5\pm0.1$. At the island bottom the germanium content x linearly changes between 0.2 and 0.45, whereas toward the apex it only further increases to about 0.5. For each part, a linear fit was added in Fig. 3(b) to emphasize the described behavior.

The data obtained at the island top are more affected by fluctuations, since the sample thickness varies over the cross section. By getting thinner at the apex, the number of scattering events and thus the intensity for both germanium and silicon decrease. This leads to a decreased signal to background ratio, and it increases the impact of random noise toward the apex. Although the nominal germanium content of the topmost part is based on a reduced statistics, a flat plateau is clearly visible.

We have probed the chemical composition in self-organized $Si_{1-x}Ge_x/Si(001)$ islands by electron energy loss spectroscopy. Since the islands can certainly elastically relax during their formation a larger lattice constant, and hence a higher germanium content, toward the apex appears energetically reasonable.[11] EELS proves an increasing germanium content along the [001] growth direction. The germanium content x increases from about 0.2 to 0.45 within part I, while a comparatively flat plateau in part II is found. This observation is in a good agreement with different growth scenarios for the two parts, as observed by atomic force microscopy (not shown). Very shallow surface undulations initially form flat pyramids with a fourfold symmetry and subsequently steeper $\{11m\}$ side facets up to an inclination angle of about 16°, which corresponds to {115} facets. As deduced from x-ray measurements near the (004) reciprocal lattice point together with scattering simulations,[11] the island shape changes abruptly at about one-third of the final island height toward truncated pyramids with {111} side facets and an (001) top facet, indicating different chemical compositions at the island bottom and apex.

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