Surfactant mediated epitaxy of Ge on Si(111): Beyond the surface

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For a characterization of interface and “bulk“ properties of Ge films grown on Si(111) by Sb surfactant mediated epitaxy, grazing incidence x-ray diffraction and transmission electron microscopy have been used. The interface roughness, defect structure, and strain state have been investigated in dependence of film thickness and growth temperature. For all growth parameters, atomically smooth interfaces are observed. For thin Ge layers, about 75 % of the strain induced by the lattice mismatch is relaxed by misfit dislocations at the Ge/Si interface. Only a slight increase of the degree of relaxation is found for thicker films. At growth temperatures below about 600° C, the formation of twins is observed, which can be avoided at higher temperatures.

The growth of germanium on silicon by conventional molecular-beam epitaxy is well known to proceed in the Stranski-Krastanov growth mode,[1] which inhibits the growth of smooth Ge layers and is accompanied by the formation of a large density of threading defects.[2] Different approaches have been used to overcome this problem. By the use of graded buffer layers with increasing Ge concentration it has been shown that Ge films of quality appropriate for device applications can be achieved.[3] An alternative approach is the use of surfactants that change the surface energy and surface kinetics, thus suppressing the three-dimensional island formation and establishing a layer by layer growth mode.[4–12] Surfactant mediated epitaxy (SME) also has the advantage that atomically sharp interfaces can be achieved. In addition, the defect structure of Ge films grown on Si(111) can be drastically improved by employing SME: The lattice mismatch of 4.2 % is accomodated by the formation of a periodic network of interfacial misfit dislocations.[6–8,13,14]

The temperature dependence of the formation of such networks has been investigated in a surface study using spot profile analysis low-energy electron diffraction (SPA-LEED).[15] In the work presented here, grazing incidence x-ray diffraction (GIXRD) and transmission electron microscopy (TEM) were used in order to investigate interface and “bulk” properties of SME-grown Ge films, such as the average interface morphology, the crystalline quality and strain state of the Ge films, as well as their defect structure on a local scale.

The preparation of Si(111) samples was performed in an UHV chamber with a base pressure in the low 10^{-10} mbar range. After being cut from Si wafers, the samples were degassed at 600° C for at least 12 h, followed by several short flashes up to ≈1200° C. Heating was performed by passing a direct current through the samples, and the temperature was monitored with an infrared pyrometer. Sb and Ge were evaporated from Knudsen cells, and the preparation was monitored with SPA-LEED. Prior to Ge deposition, the Si(111) surface was saturated with Sb, as confirmed by the change of the LEED pattern from (7×7) to $(\sqrt{3}\times\sqrt{3})$-R 30°. Subsequently, Ge was evaporated while the Sb flux was still maintained, in order to compensate surfactant desorption. During all deposition steps, the substrate temperature was kept constant at values ranging from 490° C to 720° C for the different samples. LEED growth oscillations were used to monitor the film thickness,[16] which ranged from 50 to 300 Å.

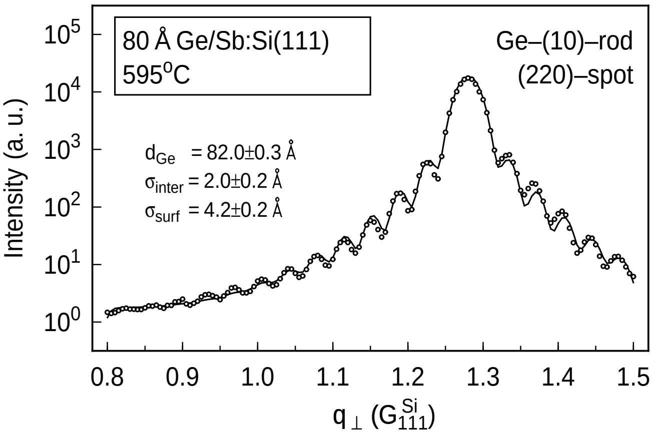

FIG. 1: Intensity along the (10) CTR of a 80 Å Ge film grown at 595° C (dots). A fit to the data according to kinematic theory is superimposed (solid line). The values shown for the film thickness d_{Ge}, as well as the interface and surface roughness σ_{inter} and σ_{surf} result from the fitting.

After preparation, the samples were investigated *ex situ* by GIXRD and TEM. The x-ray experiments were performed at the undulator beamline BW1 at HASYLAB in Hamburg, Germany. A six-circle diffractometer was used in the so-called z-axis setup[17] in order to record reciprocal space maps in the vicinity of both in-plane reflections ($q_\perp \approx 0$) as well as out-of-plane reflections ($q_\perp \neq 0$). A fixed photon energy of 10.6 keV and a fixed incident angle of 1° with respect to the sample surface was chosen for these experiments. The diffracted intensity was recorded with a one-dimensional position sensitive detector oriented parallel to the sample surface. This enables the acquisition of two-dimensional reciprocal space maps by recording one-dimensional (diffractometer) line scans. TEM investigations were performed with a Philips CM 20 at 200 kV acceleration voltage. The system is equipped with an Ultra Twin objective lens that enables imaging with a resolution of 1.9 Å.

Figure 1 shows the diffracted intensity along the Ge (10) crystal truncation rod (CTR) obtained in a GIXRD experiment from a 80 Å Ge film grown at 595° C. Because $q_{||} \neq 0$, and since the in-plane lattice constant of the Ge film is different from that of the Si substrate, only the Ge film contributes to the intensity. Around the Ge(220) Bragg spot, thickness os-

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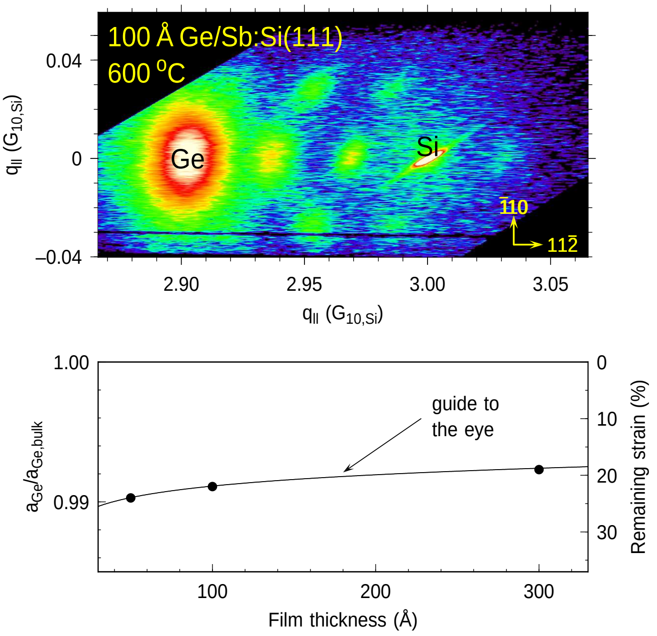

FIG. 2: Top: Reciprocal space map in the $q_{\parallel}$ plane in the vicinity of the $(22\bar{4})$ reflection (i. e. near the (30) CTR at $q_{\perp} \approx 0$), obtained from a 100 Å Ge film grown at 600° C. [Scale given in units of $G_{10}^{\mathrm{Si}} = 2\pi/(3.326\,\text{Å})$.] The positions of the Ge and Si CTRs are indicated by the labels. A hexagonal array of satellite spots is also visible. Bottom: In-plane Ge lattice constant $a_{\parallel,\mathrm{Ge}}$ as a function of film thickness for this growth temperature.

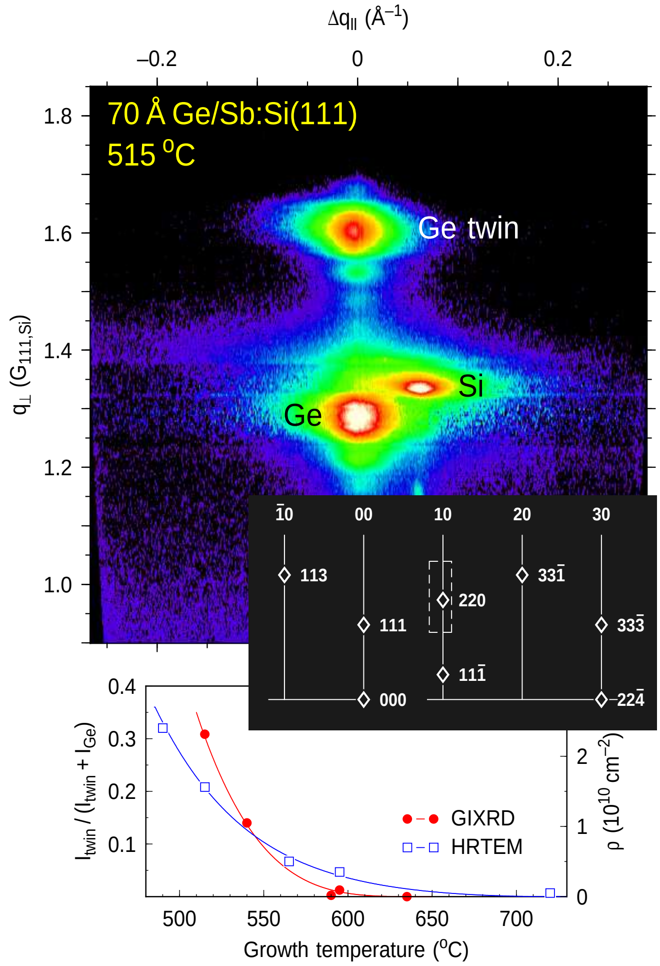

FIG. 3: Top: Reciprocal space map around the (10) CTR of a Ge film grown at 515° C. The vertical direction of the map points along $q_{\perp}$ (scale given in units of $G_{111}^{\mathrm{Si}} = 2\pi/d_{111}^{\mathrm{Si}}$), whereas the horizontal direction lies in the (111) plane. Middle: schematic cross-section through the reciprocal space of the Si substrate. The map shown above is inclined ($\approx 16°$) with respect to the plane of this schematic. Its projection is indicated by the dashed box. Bottom: Growth temperature dependence of the normalized intensity of the peak originating from twinned Ge (red dots), and the density ρ of twins and stacking faults estimated from high resolution TEM (blue squares). The solid lines are guides to the eye.

cillations are clearly visible over the whole displayed q-range, indicative of a smooth Ge film. This is confirmed by the results of a numerical fit that has been performed with an approach very similar to that described in an earlier letter.[11] For all films investigated, we find surface and interface roughnesses of a few Angströms, independent of film thickness and growth temperature. It should be noted that such values for the interface roughness is compatible with typical surface roughnesses of the bare substrates. This confirms that smooth Ge films of uniform thickness can be grown by SME, and interdiffusion at the interface is suppressed by the surfactant, resulting in atomically sharp interfaces.

The strain state of the Ge films has been investigated by recording in-plane RSMs in the vicinity of the $(22\bar{4})$ Bragg reflection, like the one shown in Fig. 2. In addition to the (30) CTRs of Ge and Si, a hexagonal array of satellite spots is clearly visible, which can be attributed to a periodic lattice distortion induced by the misfit dislocation network.[13] It should be noted, however, that these satellite spots become broader and less intense for lower growth temperatures and are hardly detectable below approximately 500° C, in agreement with a previous SPA-LEED study of the surface morphology.[15]

From the position of the Ge CTR, the in-plane lattice constant $a_{\parallel,\mathrm{Ge}}$ can be determined. The result of this evaluation is also shown in Fig. 2. With increasing film thickness d_{Ge} (at a constant growth temperature of 600° C), there is a slight increase of $a_{\parallel,\mathrm{Ge}}$ towards the bulk value. This is expected, because for infinitely large d_{Ge} the film must show bulk properties. This relaxation, however, proceeds very slowly: From 50 to 300 Å film thickness, the remaining strain drops only from 24 % to 19 %. This indicates that during progressive Ge deposition only few defects are introduced into the Ge films, and the main part of the lattice mismatch (about 75 %) is already accomodated by the introduction of misfit dislocations during the early stages of Ge growth. The residual strain obtained from our x-ray diffraction analysis is in agreement with results from *in situ* stress-induced optical deflection measurements.[18] This strain might have interesting implications on the electronic structure of the Ge films. For example, for Ge grown in the [001] direction, a direct band gap has been predicted in case of *tensile* strain.[19] Although in the present case the Ge is *compressively* strained, a different strain dependence might be found due to the *rhombohedral* distortion for the case of (111), in contrast to the *tetragonal* distortion induced for the (001) orientation, with possible consequences on band gap and carrier mobilities.

These mobilities are also affected by the presence of defects, which we address in the following. A RSM in a $q_{\perp}$-$q_{\parallel}$ plane in the vicinity of the (10) CTR is shown in Fig. 3. In addition to the Ge (220) and a tail of the Si(220) Bragg reflection (the latter does not lie exactly in the plane represented

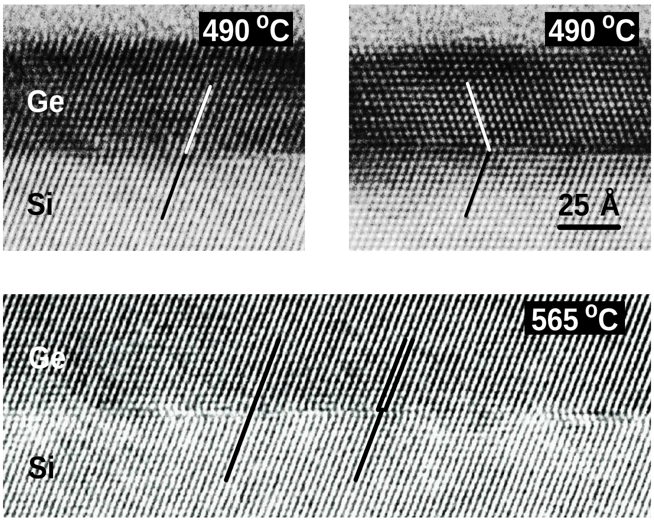

FIG. 4: High resolution cross-sectional TEM images obtained from Ge films grown at different temperatures. In the upper images (490° C), the direction of the $(11\bar{1})$ planes is indicated by straight lines. In the right image, a twinned regioned of the Ge film is shown. In the lower image (565° C), black lines indicate the registration of the net planes in Ge and Si with respect to each other.

by the RSM), thickness fringes are easily recognized along the Ge (10) CTR. Moreover, a quite strong maximum is observed on the Ge CTR at higher $q_\perp$ values. It originates from regions within the Ge film which are twinned; that is, B-type domains are formed, which are rotated by 180° around the (111) direction with respect to A-type (regular) domains. The $(\bar{1}0)$ CTR of the twins coincides with the regular (10) CTR. From the schematic cross-section through the reciprocal space shown in Fig. 3, it follows that the observed additional peak in the RSM is the (113) Bragg reflection of the twinned material. The intensity of this peak ($I_{\rm twin}$) strongly decreases with growth temperature, whereas the intensity from the regularly oriented Ge regions ($I_{\rm Ge}$) increases with temperature. The ratio $I_{\rm twin}/(I_{\rm twin} + I_{\rm Ge})$, which is an estimate for the volume fraction of the twinned material, is shown at the bottom of Fig. 3. Although, as mentioned earlier, the Ge films show a smooth morphology in the whole temperature range, these results imply that a temperature of $\gtrsim$600° C is required to produce Ge films with excellent single crystalline quality.

This is confirmed by cross-sectional high-resolution TEM images obtained from samples grown at different temperatures, as shown in Fig. 4. For 490° C, twinned areas are found in agreement with the GIXRD results. In the film grown at 565° C, hardly any twins can be found with TEM. Due to the high structural order at higher temperatures, however, interfacial misfit dislocations can be easily identified with TEM, as shown in Fig. 4 for the high temperature sample.

Apart from twins, a major defect type observed with TEM are stacking faults (not shown here). The density of stacking faults and twins, as estimated from high resolution TEM images is depicted at the bottom of Fig. 3 as a function of growth temperature. In agreement with the GIXRD results, this indicates a drastical improvement of the crystalline quality at higher temperatures.

It is noteworthy, that the results described here are not limited to Sb as a surfactant. We obtained similar GIXRD results for Ge films grown by Bi-mediated epitaxy, and the presence of a dislocation array has been reported previously.[11,20] However, the approach used in this paper is not viable for Bi SME, since temperatures above 600° C are not accessible due to strong thermal desorption of the surfactant species. Moreover, the observation of twins in Ge films grown by SME is not unique to group V elements. Using ion scattering, it was shown that, apart from Ga incorporation, twins are a major defect type in Ge films grown on Ga-terminated Si(111),[21] although an ordered misfit dislocation network has not been reported for this system. The suppression of twin formation at high temperature points to a kinetically limited process. The fact that twin formation occurs for different surfactant species with different adsorption geometries and different binding energies indicates that the energy barrier to be overcome is related to “bulk” processes occuring during the transition of Ge from B-type to A-type orientation at initial growth stages.

In summary, we have demonstrated that Ge films with smooth surfaces and atomically sharp interfaces can be grown by Sb surfactant-mediated epitaxy, independent of growth temperature in the whole investigated range from 490° C to 720 ° C. For low temperatures, however, large volume fractions of the Ge films grow in B-type orientation. The crystalline quality improves drastically above 550° C, and high-quality Ge films are obtained at higher temperatures, which show a large degree of relaxation due to misfit dislocations at the interface.

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