Nucleation of Ga droplets on Si and SiO\textsubscript{x} surfaces

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Abstract

We report on gallium droplet nucleation on silicon (100) substrates with and without the presence of the native oxide. The gallium deposition is carried out under ultra-high vacuum conditions at temperatures between 580 and 630 °C. The total droplet volume, obtained from a fit to the diameter–density relation, is used for sample analysis on clean silicon surfaces. Through a variation of the 2D equivalent Ga thickness, the droplet diameter was found to be between 250–1000 nm. Longer annealing times resulted in a decrease of the total droplet volume. Substrate temperatures of 630 °C and above led to Ga etching into the Si substrates and caused Si precipitation around the droplets. In contrast, we obtained an almost constant diameter distribution around 75 nm over a density range of more than two orders of magnitude in the presence of a native oxide layer. Furthermore, the droplet nucleation was found to correlate with the density of surface features on the ‘epi-ready’ wafer.

Keywords: gallium, nucleation, silicon substrate, precipitation, molecular beam epitaxy, scanning electron microscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

 Metallic nanoscale droplets provide a key ingredient for the growth of semiconductor nanowires, where they act as a catalyst in the vapour–liquid–solid (VLS) growth mode. Most commonly, Au is used as the catalyst material because of its ability to alloy with the relevant species at relatively low temperatures \cite{1}. However, traces of Au, stemming from the catalyst particle, were found along the nanowire sidewalls, which could influence material properties like carrier lifetimes \cite{2–4}. To circumvent this potential hurdle, various metals and compounds were investigated with respect to their suitability for VLS growth \cite{5, 6}. In this context, liquid Ga was also proven to work as an alternative catalyst for the epitaxial growth of III–V as well as Si nanowires \cite{7–10}. Ga droplets were also used for nanoscale droplet epitaxy \cite{11}, nanoscale etching \cite{12, 13} and to mediate the growth of III–V nanocrystals on Si substrates \cite{14}.

 A prerequisite for the device integration of nanowires is a clearly defined geometry \cite{15}. Yet, droplet nucleation and therefore nanowire growth on unpatterned substrates commonly leads to a broad diameter distribution at random positions. Figures of merit, like the density and diameter of nanowires, can be controlled through growth parameters, like substrate preparation, temperature or III–V ratio \cite{8, 16}. On the other hand, pre-patterned substrates or oxide masks for selective-area epitaxy allow uniform nanowires in well defined positions \cite{17–20}. Such processes leave a potential risk of contamination for the III–V growth facilities due to residuals from lithographic processes.

 Ga droplets also gained importance in the field of plasmonics, showing resonance effects at photon energies around 4 eV \cite{21, 22}. The low melting point of 30 °C provides a
simple method to investigate plasmonic effects at phase changes in the material.

This work presents a detailed study on Ga droplet nucleation on Si (100) substrates between 580–630 °C. Using the total droplet volume as a figure of merit allows a quantitative analysis of the Ga incorporation. Substrate temperatures above 630 °C led to cone-shaped voids in combination with Si precipitations around the Ga droplets.

2. Methods

Samples described as having have a clean Si surface were etched with buffered HF for 30 s and rinsed with de-ionized water. After this step, the samples were loaded into the vacuum loadlock within 5 min and reached $1 \times 10^{-4}$ Torr after an additional 15 min. This study was performed on quartered 3inch wafers, which were mounted to be suspended by spring taps at the edge.

The Ga droplets described in this work were fabricated under ultra-high vacuum (UHV) conditions in a molecular beam epitaxy (MBE) system. Before Ga deposition, the samples were outgassed at 200 °C and 350 °C in two subsequent steps until a pressure of below $2 \times 10^{-10}$ Torr was reached. After this preparation procedure, the substrates were brought to the desired deposition temperature without any thermal oxide desorption. The substrate temperature was measured by a pyrometer, calibrated for undoped GaAs. The Ga cell was set to an equivalent GaAs growth rate of 0.08 μm h$^{-1}$, with 1 nm GaAs corresponding to a layer thickness of 0.434 nm Ga. The growth rate was extracted from the period of GaAs/Al$_x$Ga$_{1-x}$As superlattices by high-resolution x-ray diffraction. During deposition, the substrates were rotated at 15 rpm to obtain a uniform distribution. After the deposition process, the samples were annealed at the deposition temperature for 60 s and subsequently cooled as fast as possible.

Scanning electron microscope (SEM) images for the curve fits were taken from more than ten independent spots on each sample. The position of these spots was chosen to be 1 cm from the sample edge, along a line, parallel to one of the cleave facets of a quarter wafer, in order to avoid distortion of the results due to a temperature gradient. The Gwyddion scanning probe analysis software was later used to extract droplet densities and diameter distributions, based on Gaussian fits to the raw data [23]. All length scales were calibrated using another SEM machine with a laser interferometry stage. The topography of the substrates was recorded by atomic force microscopy (AFM), using Si tips in tapping mode.

3. Results and discussion

The Ga droplets discussed in this work were deposited under UHV conditions. Typical background pressures during Ga deposition were below $2 \times 10^{-9}$ Torr, mainly caused by residual hydrogen and nitrogen. Two series of samples were fabricated, where in one case the native oxide was left untreated, while for the second it was removed wet-chemically. In both cases, the substrate temperature was varied between 580 and 630 °C. The equivalent Ga layer thickness was set between 1.4 and 17.9 nm, while keeping a constant Ga deposition rate around 0.08 μm h$^{-1}$ and a constant annealing time of 60 s.

The samples were then analysed by SEM images. Droplet distributions for the different amounts of Ga, deposited at a substrate temperature of 600 °C, are shown in figures 1(a)–(d). An increase of the droplet diameter with the equivalent Ga layer thickness is evident.

Figure 1. SEM images of Ga droplets nucleated on clean Si surfaces at 600°C with varying Ga thicknesses. Higher equivalent layer thicknesses of Ga mainly result in increased droplet diameters between 250 and 1000 nm.

Figure 2. Ga droplets on Si surfaces with the native oxide, recorded by SEM. The droplets were fabricated at different temperatures between 580 and 630°C at a constant Ga thickness of 11.9 nm. The droplet density is inversely proportional to the substrate temperature.
droplet densities due to the variation of the substrate temperature on Si wafers with native oxide for a constant deposited Ga thickness of 11.9 nm, thus comparable to figure 1(d).

3.1. Substrate-roughness independent analysis

All samples showed pronounced differences in the droplet distributions between the center and edge of the wafer. In particular the droplet density was found to be up to one order of magnitude higher at the original wafer edge compared to the center. Nevertheless, the amount of Ga per unit area was constant over the whole sample. To account for differing droplet distributions, we fitted the obtained data with equation (1), which expresses the diameter \(d\) of \(n\) spheres with a volume \(V\) per unit area.

\[
d(n) = 2 \eta \sqrt[3]{\frac{3V_{\text{tot}}}{4\pi n}}.
\]  

This function is shown to match the experimentally obtained distributions using the volume as the only fit parameter. The total volume of droplets \(V_{\text{tot}}\), given in equation (2), corresponding to the deposited Ga thickness remains constant.

\[
V_{\text{tot}} = \sum_n V_n.
\]  

The fact that the Ga droplets are not perfect but truncated spheres is taken into account through the parameter \(\eta\), which gives the ratio between the volume of a truncated sphere with respect to an ideal one. The factor was determined from SEM images via the aspect ratio of droplets close to the cleaved edges. The data of all samples were corrected with a factor of 0.34, insensitive to substrate temperature or equivalent Ga layer thickness. This corresponds to a wetting angle of 73.9° for Ga on Si(100), which is significantly larger than the contact angle of Ga droplets on Si(111) nanowire sidewalls (17.74°)\(^\text{[24]}\), however if the reported angle reference was to the surface normal of the sidewall, then the values (90° – 17.74° = 72.26°) would be in excellent agreement.

3.2. Nucleation on Si surfaces

The fitting method, as described above, was applied to a set of samples with differing equivalent layer thicknesses of Ga between 1.4 and 11.6 nm. Resulting droplet diameter versus density distributions, including the corresponding fits according to equation (1), are plotted in figure 3. Each sample shows a distribution of data points, obtained from different positions on the quartered wafers, where higher droplet densities were found closer to the original wafer edge. Despite the broad distribution of densities, between 0.07 and 0.7 \(\mu\)m\(^2\), spanning approximately one order of magnitude, the fits are proven to be a valid approximation.

The data points in figure 3 show a clear correlation between the amount of Ga and the droplet diameter. By changing the equivalent layer thickness of Ga from 1.4 to 11.6 nm, the droplet diameter can be tuned from approximately 250 to 1000 nm. The droplet density on the other hand remains unaffected, which suggests that this quantity is controlled by other growth parameters in combination with the substrate morphology. Potential causes of the surface morphology are a rough starting Si surfaces, or the onset of native oxide formation between wet-chemical preparation and the point when the substrates reach UHV conditions in the MBE system.

The substrate temperature was found to have a pronounced effect on the droplet density. As plotted in figure 4,
the density can be reduced by almost one order of magnitude for a substrate temperature of 630 °C, compared to samples fabricated at 580 or 600 °C. Using the Ga amount as an additional degree of freedom, as shown for equivalent layer thicknesses of 2.8, 5.7 and 11.4 nm, respectively, allows for individual diameter and density combinations.

### 3.3. Incorporation of Ga into droplets

Fits to the total Ga volume, condensed in droplets, allow an analysis of the adsorption of Ga atoms to Si surfaces and the incorporation into droplets. The relation between nominally deposited Ga and the total volume of truncated spheres is shown in figure 5. The data points for 580 and 600 °C can be fitted with a slope of 1.25. For the highest temperature of 630 °C a falloff, resulting in a slope of 0.84, from this characteristic can be observed.

A priori, a slope of one or below would be expected, if all Ga atoms reaching the surface are condensed into droplets. However, all SEM images were taken ex situ, which despite a fast transfer, allowed the formation of some oxide skin around the Ga droplets. An energy dispersive x-ray (EDX) analysis revealed an oxygen content of up to 10% within the droplets, which would translate into 33% volume growth. Although the presence of As could be expected from the deposition in a III–V MBE chamber, no traces could be found within the droplets or on the sample surface by EDX scans. The presence of an additional Ga wetting layer or Si:Ga surface reconstruction patterns, as characterized by several other groups, can not be excluded with the available analysis techniques [25, 26].

### 3.4. Droplet volume reduction through annealing

Material loss through re-evaporation or diffusion into the substrates was studied through a variation of the post-deposition annealing time. Samples with a constant equivalent Ga layer thickness of 11.6 nm and annealing times between approximately 1 and 20 min exhibited a clear decrease of the total droplet volume, plotted in figure 6.

One possible reason for this decrease is re-evaporation of Ga from the sample surface. However, a maximum temperature of 630 °C, leading to a Ga vapor pressure of $1 \times 10^{-8}$ Torr, could not account for a volume reduction of 35% within 20 min. Yet, desorption of Ga can not be neglected since the vapor pressure was measured for a bulk quantity at atmospheric pressure [27]. The behavior of nano-scale droplets is expected differ and lead to some thermal desorption of Ga. The desorption characteristics were found to be non-trivial due to the different contributions from Ga droplets and wetting layer [28]. Calculated desorption of Ga from Si(100) surfaces exceeds the deposited thickness for substrate temperatures of 600 and 630 °C, indicating that Ga atoms within the wetting layer are re-evaporated at these temperatures [29]. Migration between the droplets therefore also leads to a volume loss despite the low desorption rate of Ga from Ga surfaces [28]. Additionally, some amount of Ga is expected to diffuse into the Si substrates, as discussed in the following.

Gallium droplets which were annealed at substrate temperatures of 630 and 650 °C were surrounded by bright rings which typically extend over a 100 nm wide region. These features are shown in figure 7(a) for a temperature of 630 °C and an annealing time of 20 min. A view on the cleaved edge, shown in figure 7(c), reveals that these ring-shaped features are bulges around the Ga droplets, which can be attributed to Si interdiffusion and precipitation upon cooling. An EDX analysis, performed ex situ at room temperature, did not indicate Ga atoms outside the actual droplet. The binary

**Figure 5.** Total Ga droplet volume with respect to the equivalent layer thickness of Ga. The data points obtained at 600°C were fitted with a linear slope of 1.25. The volume gain can be attributed to an oxidized skin, surrounding the Ga droplets. No significant amount of Si was found within the droplets. While this linear relation seems to be valid for substrate temperatures of 580 and 600°C. There is a pronounced falloff for the samples fabricated at 630°C, for which the slope was fitted to be 0.84.

**Figure 6.** Total volume as a function of annealing time at a substrate temperature of 630°C for an initially constant equivalent Ga layer thickness of 11.6 nm. Annealing for 20 min leads to a reduction by 35% in the volume.
diagram allows a liquid solution of Si and Ga with an onset around 530 °C. Due to the absence of any other element, we conclude that these precipitations are formed from the solution within the droplets.

Droplets which were annealed at 650 °C showed cone-shaped voids at the initial droplet positions, as depicted in figures 7(b) and (d). The Ga appears to etch into the Si substrates, resulting in a Si precipitation around the droplets. Similar behavior was observed for Ga-mediated epitaxy of GaAs rings on GaAs substrates [30, 31]. The onset of this behavior most likely also accounts for the apparent volume reduction in samples fabricated at 630 °C. Apart from traces, visible as bright spots near the top edge of the cones, we could not find significant amounts of Ga. Since Ga acts as p-type dopant in Si, atoms most probably diffuse into the substrate, reaching concentrations below the 1–2% detection limit of EDX. Ga diffusion into the substrate was also observed for metal-organic chemical vapor deposition of Ga on Si(100) substrates, although the lower growth temperature and different growth kinetics due to the organic precursors only caused the formation of pyramidal structures beneath the droplets [32].

3.5. Nucleation on SiOx surfaces

Droplet distributions nucleated on Si wafers with the native oxide could not be fitted with equation (1). Instead, a mean diameter of 75.3 nm, insensitive to variations in the substrate temperature, was found for an equivalent Ga layer thickness of 11.9 nm, as shown in figure 8. A variation of the Ga thickness between 5.8 and 17.9 nm showed a linear relationship with the droplet diameter, with a slope of 3.3 nm per deposited nm of Ga. Statistical data related to this set of samples can be found in table A2. The growth temperature mainly influenced the density of droplets, where values between 580 and 630 °C led to an indirectly proportional range of approximately 0.1–30 μm².
3.6. Density correlation with substrate roughness

The surface morphology of the Si wafers was analyzed by AFM images in order to identify the origin of the observed density gradient. Figures 9(a) and (b) show the topography of the untreated substrates with the native oxide. There is an obvious gradient in the density of features, which are typically 4.0 nm high, from 0.3 μm⁻² in the center to 9.36 μm⁻² close to the wafer edge. The common shape of these elevations in the figures stems from the topography of the AFM tip, which indicates that the features are sharper than the measurement probe. Similar features were recently observed on Si (100) surfaces with SiC nanoparticles acting as a catalyst [33]. The resulting RMS roughness was calculated to be 1.69 and 2.17 nm for regions in the wafer center and close to the edge, respectively. Comparing the droplet densities from figure 8 with figures 9(a) and (b), the density of nucleated Ga droplets on SiO₂ surfaces can be correlated with surface defects by orders of magnitude.

Figures 9(c) and (d) present topographic data from similar regions on the substrate but recorded after wet-chemical removal of the native oxide. Both wafer center and edge appear as flat surfaces with a measured RMS roughness of 0.36 and 0.23 nm, respectively. Some fraction of the surface features seems to remain after HF-etching, showing up as bright spots in both scans. Nevertheless, a comparison with 9(a) and (b) reveals a clear improvement.

4. Conclusions

This work provides a detailed analysis of the formation of Ga droplets on Si (100) wafers. Experimentally obtained droplet distributions are described via the total volume of truncated spheres, which allows a quantitative analysis in the presence of a density gradient over the wafers. AFM scans indicate that this gradient can be correlated with the density of spiked features, which are initially present on the wafers.

The droplet formation on clean Si surfaces follows nucleation theory with an indirect relation between substrate temperature and droplet density. A variation of the equivalent Ga layer thickness by a factor of four leads to droplet diameters, scaled by a factor of two for a given density. Annealing of the droplets at a temperature of 630°C for a duration of 20 min, led to a volume reduction by 35% and resulted in the formation of Si precipitation around the Ga droplets. The Ga droplets were found to disappear for a substrate temperature of 650°C, where void cones indicate that liquid Ga dissolved the Si substrates locally.

The nucleation on Si wafers with their native oxide generally results in droplet distributions with smaller diameters around 50–100 nm, but with densities which are higher by one order of magnitude compared to samples with clean Si surfaces. Again the ratio between the deposited amount of Ga and the droplet diameter is found to be around two.

The tunability of Ga droplet nucleation on Si substrates, as spanned by this comprehensive study, can be applied in different research fields, for example in the Ga-catalyzed growth of semiconductor nanowires or for nano-plasmonic applications.

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Appendix. Statistical Data

Table A1 contains sample size and standard deviations of the samples with clean Si surfaces, discussed in section 3. Table A2 contains the corresponding data for Si surfaces with the native oxide.
| Ga thickness (nm) | Temp. (°C) | No. of droplets | Analysed area (μm²) | Mean diameter (nm) | Std. Err. (nm) |
|------------------|------------|-----------------|---------------------|-------------------|---------------|
| 11.9             | 580        | 7173            | 280                 | 74.25             | 4.34–5.28     |
| 5.8              | 600        | 3152            | 280                 | 55.61             | 4.52–8.73     |
| 11.9             | 600        | 3656            | 471                 | 76.05             | 5.07–14.56    |
| 17.9             | 600        | 5089            | 421                 | 90.34             | 4.46–8.61     |
| 9.5              | 630        | 933             | 446                 | 74.89             | 3.15–12.14    |
| 11.9             | 630        | 3958            | 421                 | 72.18             | 6.26–13.09    |
| 17.9             | 630        | 219             | 210                 | 89.67             | 8.83–11.48    |

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