# Ga/Au Alloy Catalyst for Single Crystal Silicon-Nanowire Epitaxy

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## Introduction

One dimensional nanostructures, such as semiconductor nanowires or carbon nano-tubes, are attractive components for future applications ranging from nanoelectronics to catalysis. In particular, Si-NWs have been suggested to be used for developing high-speed field effect transistors, bio/chemical sensors, and light emitting devices with extremely low power consumption. Many of the silicon investigations have employed the vapor-liquid-solid (VLS) growth mechanism. A metal droplet catalyzes the decomposition of a Si-containing source gas, to function as a Si reservoir by eutectic liquid formation, and finally to precipitate Si-NWs due to supersaturation. Gold has been the metal catalyst of choice and is mostly used due to its favorable physical and chemical properties. We developed a method for the epitaxial growth of Si-NWs by a metal compound gallium/gold (Ga/Au) – nanoparticle-catalyzed chemical vapor deposition (CVD) from $SiH_4$ on Si (111) and Si (100) surfaces. In addition shape control of the NWs is shown to be possible [1].

## Experimental

The growth apparatus is a hot wall low pressure CVD reactor. After carefully cleaning the Si (111) and Si (100) substrates with acetone and isopropanol the samples were dipped in a buffered HF solution to remove any native oxide. Thin Ga and Au metal layers (nominally 1 – 4 nm thick) were deposited on the substrates by thermal evaporation, with the Ga layer always below the Au layer. As a reference sample, a similar 2 to 4 nm thick Au film was deposited on Si substrates pretreated in the same way. After evacuating the CVD-chamber down to $10^{-7}$ mbar the substrates were heated up in vacuum to 873 K in order to form metal droplets. The Si-NWs growth was done at a total pressure of 3 mbar using a 100 sccm flow of $SiH_4$ (2% in a He mixture) in the temperature range from 773 to 923 K.

## Results

The scanning electron microscope (SEM) image in Fig. 1 (a) shows the typical morphology of NWs grown on Si (111) substrates at 873 K for 15 min with an optimized alloy catalyst of a 2 nm thick Au layer above a 2 nm thick Ga layer. Size and length of the Si-NWs within the grass like array are very homogeneous and most of the wires are oriented along the four $\langle 111 \rangle$ directions. The wires growing perpendicularly from the substrate (top inset in Fig. 1 (a)) appear as light spots in the top-view image. Most of the remaining nanowires grow in directions such that their top-view projections correspond to the other three $\langle 111 \rangle$ directions. A closer view in the lower inset of Fig. 1 (a) shows that the NWs are highly tapered and exhibit six fold symmetry for the vertical (110) facets.

For comparison, the Si-NWs on the reference sample with the pure Au catalyst (Fig. 1 (b)) nucleate and grow in a much less controlled way, whereby the length and diameter of the NWs appears to be randomly distributed. It is also evident, that the Au droplets solidify and appear as bright spots on the tip of every nanowire. All orientations of the NWs along the four $\langle 111 \rangle$ directions could be observed. But in comparison the proportion of the NWs growing perpendicular to the substrate is much lower for the Au catalyzed growth. The NWs show a lot of kinks but have a rod-like shape (inset in Fig. 1(b)) in contrast to the tapered NWs on the Ga/Au catalyzed samples.
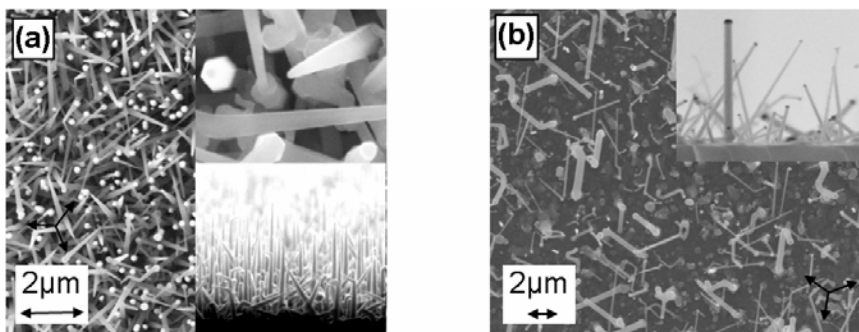


Fig. 1    (a) Top-view SEM image of Si-NWs grown at 873 K for 15 min on Si (111) with the Ga/Au catalyst. The top inset shows tapered Si-NWs exhibiting a hexagonal cross-section with six fold-symmetry and vertical {110} facets normal to the (111) direction. The inset below shows a cross-sectional view of the tapered NWs grown along $\langle 111 \rangle$ directions (b) Si-NWs grown on the reference sample with a 2 nm thick pure Au layer and identical process parameters. The cross-sectional view in the inset shows the rod-like shape of typical NWs with solidified Au droplets on top.

In order to identify the mechanism causing the tapering we grew NWs for different times and growth temperatures. Up to a growth time of 240 min, the length of the NWs was found to depend directly on the growth time. While the tip diameters of the NWs grown for a long time are the same as those grown for a short time and are determined by the catalyst diameter, the foot prints of the NWs increased during the course of the growth. This fact indicates that the NW tapering is caused primarily by sidewall deposition (radial growth) of silicon. For the longest NWs the diameter at the foot print was 1500 nm, while the diameter of the tip was less than 70 nm over a length of 15 µm. The experiments carried out for different growth temperatures clearly indicated that radial growth dominated at high growth temperatures.

The assumption that "unanalyzed" deposition of Si on the sidewalls of the NWs causes the tapering can not be sustained as NWs on the reference samples (Au catalyzed) show no tapering (see Fig. 1). Therefore, we suppose that this growth morphology results from a Ga enhanced deposition at the (110) facets of the Si-NWs. Fig. 2 (a) shows the temperature dependences of the axial NWs growth rates ($R_{ax}$) and the radial growth rate ($R_r$) for the tapered NWs. The growth rate data in the Arrhenius plot falls on straight lines, showing that all of the growth processes were done in reaction limited regimes. The value of the calculated activation energy for the Ga enhanced deposition at the (110) facets of the Si-NWs of 266 kJ/mol is close to the activation energy of the decomposition of a $SiH_4$ gas, which is about 234 kJ/mol. The activation energy for the axial growth on the samples with the pure Au film was found to be 89 kJ/mol. Remarkably, for 773 K no NW growth was observed for these reference samples under the given experimental conditions.
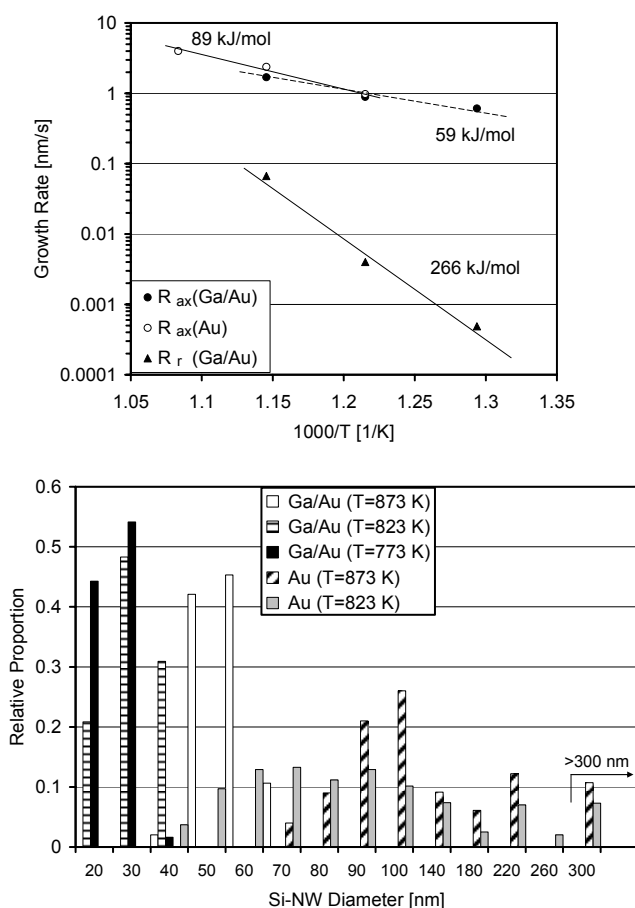
Fig. 2 (a) Temperature dependence of the axial ($R_{ax}$) and radial ($R_r$) growth rate for the Ga/Au and Au catalyzed samples at SiH4 partial pressure of 3 mbar and 30 min growth time. (b) Histogram, showing the relative proportion of the Si-NW diameters for the Ga/Au and Au catalyzed growth process as a function of the growth temperature.

This activation energy is much smaller than the one found for Si-CVD from $SiH_4$ sources (144 – 167 kJ/mol), which is attributed to the catalytic decomposition of $SiH_4$ at the surface of the Au droplets and explains the higher growth rate of Si-NWs by VLS growth. The even lower activation energy on the Ga/Au catalyzed sample of 59 kJ/mol indicates that the addition of Ga influences the $SiH_4$ decomposition and/or the crystallization at the liquid-solid interface. The NW grow very dense and show a much higher proportion of epitaxially oriented NWs and in case of Si (111) substrates, even perpendicular grown nanowires. Because of the lower melting point of Ga/Au alloys the addition of Gallium is already active for the formation of the catalytic droplet. Despite the fact that the Ga/Au film has two times the thickness of the pure Au film on the reference sample, the average diameter of the grown NWs is smaller, and the diameter and length distribution is narrowly dispersed at any growth stages and growth temperatures. The relative proportions of the NWs diameter obtained at different temperatures are plotted in Fig. 2 (b). The average diameter of NWs grown with the Ga/Au catalyst at 873 K is about 60 nm and decreases with temperature down to about 30 nm for 773 K. The dispersion of the diameters becomes significantly narrower for 773 K. The histograms of the NW diameter obtained on the Au catalyzed reference samples at 873 K and 823 K show a much broader dispersion with an accumulation cluster at about 70 nm and 100 nm respectively. As shown in Fig. 1, NWs with diameters of more than

300 nm were also observed on these samples. The addition of Ga might change the de-wetting behavior of the deposited metal film during the annealing. This results in smaller catalytic alloy particles with a much narrower distribution of the diameters.

Si-NWs of uniform diameter and length while preserving epitaxy were obtained by adding an additional annealing step at 873 K for 30 min in vacuum. The SEM image in Fig. 3 shows the top-view of self oriented rod-like Si-NWs grown for 15 min at 823 K on Si (100) and Si (111) substrates.

NWs with their orientation controlled by the crystal orientation of the substrate grow along any one of the four ⟨111⟩ directions, thus the visible orthographic projections forms either rectangular or triangular networks. For the (111) substrate the NWs which grow vertically from the substrate appear as light spots in the top-view image.
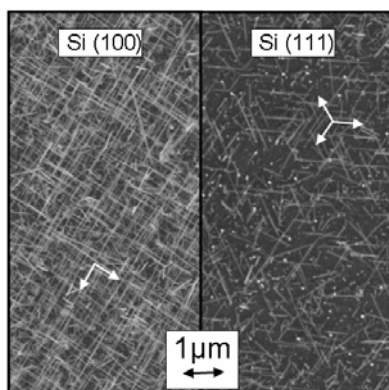


Fig. 3:  Plane-view SEM images of Si-NWs forming regular networks on Si (100) and Si (111) substrates.

## Conclusion

The effect of reaction conditions on the growth of Si-NWs via well defined Ga/Au nano-clusters as catalysts for VLS growth from $SiH_4$ source was investigated. HRTEM demonstrates that these high quality NWs grow mainly along the (111) direction with a large proportion of them even perpendicular to the substrate. The diameter and length distribution are narrowly dispersed at any growth stages and growth temperatures. The Si-NWs growth rate follows an Arrhenius law within the temperature range of 723 – 873 K with an activation energy of 59 kJ/mol. For our materials system, the tapering observed at higher temperatures is caused by a Ga catalyzed two-dimensional deposition of Si on (110) facets as the NWs continue to grow along the axial direction. By making a particular choice of growth conditions, it is possible to realize either rod-like or tapered silicon nanowires, which may be desirable for applications as field emitters.

## References

[1]  A. Lugstein, M. Steinmair, Y. J. Hyun, E. Bertagnolli, and P. Pongratz,  "Ga/Au alloy catalyst for single crystal silicon-nanowire epitaxy", Appl. Phys. Lett. 90, 023109 (2007).