Silicon nanowhiskers grown on ⟨111⟩Si substrates by molecular-beam epitaxy

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Silicon nanowhiskers in the diameter range of 70 to 200 nm were grown on ⟨111⟩-oriented silicon substrates by molecular-beam epitaxy. Assuming the so-called ''vapor–liquid–solid'' (VLS) growth process to operate, we initiated the growth by using small clusters of gold at the silicon interface as seeds. The *in situ* generation of the Au clusters as well as the growth parameters of the whiskers are discussed. The experimentally observed radius dependence of the growth velocity of the nanowhiskers is opposite to what is known for VLS growth based on chemical vapor deposition and can be explained by an ad-atom diffusion on the surface of the whiskers. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1762701]

Small whiskers (also called nanorods or nanowires) and nanotubes are of increasing interest due to their physical properties as well as their potential for new nanodevices.[1–4] Comprehensive studies on the vapor–liquid–solid (VLS) growth of whiskers of silicon and other materials with sizes down to the 100 nm range already started in the 1960's and 1970's.[5–7] However, their fabrication with defined radius, position, length, and technological applications turned out to be elusive at that time. During recent years, remarkable progress has been achieved. Several growth concepts have been developed for semiconductors, ceramics, and metals allowing the fabrication of whiskers with diameters <100 nm and a length of several micrometers.

Silicon whiskers are normally grown by chemical vapor deposition (CVD)[8,9] and gas-source molecular-beam epitaxy (GS-MBE).[10–13] In the case of the CVD method, small droplets of metals, such as gold, are forming low-temperature eutectic liquids with silicon acting as a seed for the whisker growth. The silicon is preferentially incorporated via the liquid silicon–metal droplet. This technique is referred to as the VLS mechanism.[5–7,14] It is characterized by silicon whisker growth at the whisker/droplet interface by the incorporation of Si atoms coming from the liquid droplet.

Three main models have been discussed concerning the different incorporation processes of atoms. In the first VLS model, the semiconductor vapor (precursor) reaches the liquid droplet surface, reacts, and semiconductor atoms are incorporated into the droplet, where an alloy is formed. A further supply of the semiconductor from the vapor phase leads to a supersaturation of the semiconductor atoms in the droplet. The interface acts as a sink causing a Si incorporation into the lattice and, thereby, the growth of the whisker with the alloy droplet riding on the top. The second model is similar to the first one. However, it is assumed that in this case the semiconductor atoms diffuse on the droplet surface to the metal/semiconductor interface, where they are incorporated.[7,15] In the third model discussed,[16] it is assumed that semiconductor atoms impinge on the whole wafer surface, where they diffuse also along the surface of the whisker to the liquid/alloy interface.

For the growth of semiconductor whiskers CVD has been used. Successfully in comparison, the GS-MBE technique was applied only for a limited number of III–V whiskers, such as InAlAs[17] and to the growth of silicon whiskers with solid titanium silicide catalysing the growth.[3] However, the molecular-beam epitaxy (MBE) technology allows to study basic growth steps in more detail and can be used as a model system. As a distinction to CVD, here the metal droplet does not act as a catalyst for the precursor gas, since Si atoms are directly offered in the molecular beam.

In this letter, we present a study of the growth of Si nanowhiskers by MBE and its dependence on the nanowhisker diameter. We especially investigated the influence of the following parameters on the initial morphology of Si whisker growth: Amount of deposited gold, growth temperature, and Si flux during the growth. In our experiments, ⟨111⟩-oriented 5 in. Si wafers were used as substrates. Before the growth, the wafers were cleaned by the conventional RCA procedure. Our MBE system (UHV chamber RIBER SIVA 45) included electron-beam guns for the evaporation of Au and Si as well as a substrate heater. The substrate temperature T_S was controlled by a thermocouple as well as a pyrometer. We started the experiments in the MBE chamber with a desorption of the oxide layer by a thermal annealing at 850 °C. Afterward, a thin Au film was deposited at a substrate temperature of 525 °C with thicknesses between 1.5 nm and 2 nm measured by a quartz monitor. The size of the thereby generated droplets could be chosen between 70 and 200 nm. During the subsequent whisker growth the constant Si flux amounted to 0.5 Å/s. A set of samples were grown at $T_S = 525\,°\mathrm{C}$. Afterward, the samples were investigated by transmission electron microscopy (TEM) and high-resolution scanning electron microscopy (SEM).

An example of the grown whiskers is presented in Fig. 1,

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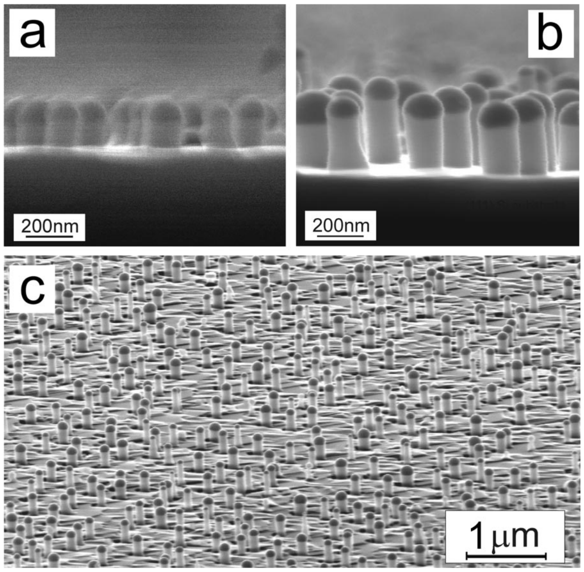

FIG. 1. SEM cross section images of Si whiskers grown on a $\langle 111\rangle$ Si substrate at 0.5 Å/s for 60 min (a) and 120 min (b) growth time at $T_S = 525\,^\circ\mathrm{C}$. The sample (b) was tilted to get an overview on the arrangement of the whiskers (c).

where a total growth time of 60 min [Fig. 1(a)] and 120 min [Figs. 1(b) and 1(c)] was chosen. Both experiments are characterized by a homogeneous distribution of $\langle 111\rangle$-oriented whiskers of cylindrical morphology, partly hexagonal facetted (see Fig. 2). They have a diameter in the range from 100 nm to 160 nm, which is determined by the Au droplet sizes. Their average lengths amount to about 95 nm [Fig. 2(a)]. and 210 nm [Figs. 2(b) and 2(c)], respectively. TEM investigations showed that only a few whiskers have defects, such as stacking faults and, quite rarely, microtwins. The Au/Si droplets on top have a semispherical shape.

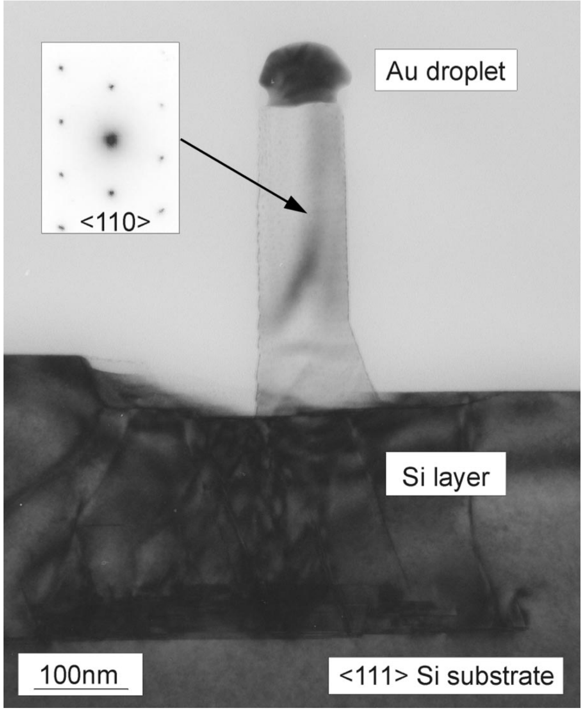

FIG. 2. TEM cross section image of a Si whisker with a length of about 300 nm and a diameter of 95 nm on a $\langle 111\rangle$ Si substrate. Dislocations are visible within the Si layer at the location of the whisker. The sample is related to Fig. 1(b).

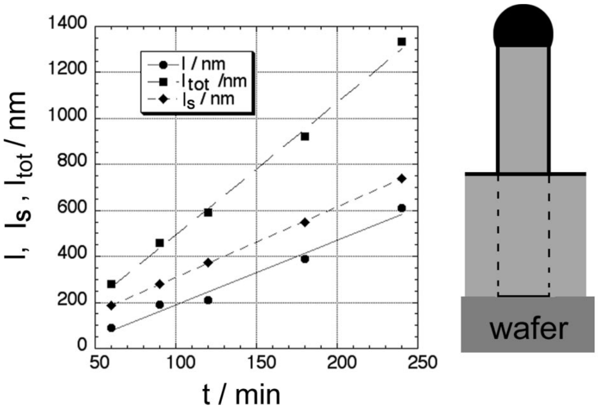

FIG. 3. Time dependence of the length of whiskers as a function of growth time t between 60 and 240 min (left). l denotes the length of the whiskers measured from the Si base layer; l_S relates to the grown Si layer, and l_{tot} corresponds to the total length of whiskers including the base layer as schematically, shown on the right side.

During the growth of the whisker a Si layer is formed on the wafer as well. Its thickness is nearly equal to the nominal amount of deposited silicon, as will be described below in more detail. This is a fact which is not often discussed in literature for the case of CVD-grown samples. Figure 2 shows a corresponding cross section TEM micrograph of a whisker. The epitaxial Si layer contains a high density of crystal defects at the location of the whisker, whereas at other locations the defect density is very low. The defects are mostly dislocations and stacking faults. The whisker seems to reside in a flat groove, which can also be seen in Fig. 1(c). We measured the diameter and the length of the whisker as a function of the growth time. The result of the length measurements is given in Fig. 3 for five different times t between 60 min and 240 min. The size ℓ denotes the length from the base to the top of the whisker, ℓ_S the thickness of the grown Si layer and $\ell_{\mathrm{tot}}=\ell+\ell_S$ is the total length of the whiskers including the base layer, respectively. The observed growth is nearly linear in time. The length of the whiskers is increasing with time from about 100 nm for 60 min to 600 nm for 240 min, respectively.

On one hand, each data point in Fig. 3 represents the maximum of a length distribution of whiskers grown during a particular experiment. On the other hand, each length distribution correlates to a specific distribution of the whisker diameters d. As an example, Fig. 4 presents the situation for a growth time of 240 min in a linear scale. It is obvious that for a given growth time the length of the whiskers is systematically longer for whiskers with smaller diameters, which is opposite to what has been found for CVD grown whiskers.[7] A simple fit based on a power-law $\ell = Cd^m$ leads to $m \approx -1$.

For the CVD growth by the VLS mechanism, it is well established[7] that whiskers with a larger diameter should grow faster than those with a smaller diameter due to the Gibbs–Thomson effect as already pointed out in 1975 by Givargizov.[7] In contrast, in our specific MBE experiments, we observed the opposite result: Thinner whiskers grow faster than thicker ones as shown in Fig. 4. No diameter dependence of the whisker growth was reported in the available published MBE experiments. In Fig. 3, the data points correspond to an average length as mentioned above. Based

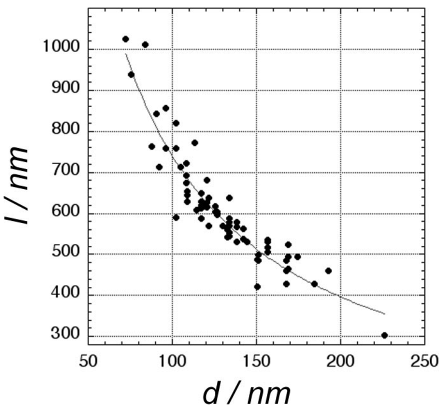

FIG. 4. Correlation between the length l and diameter d of Si whiskers. In this specific case, the growth experiments were performed at 525 °C for 240 min. The data fit correlates to the relation: $l = Cd^m$, $m \approx -1$.

on our experimental observations, this particular MBE whisker growth can not be described in a satisfying manner by a simple VLS process. In the following, we will discuss a growth mechanism, which not only includes the incorporation of Si atoms by a direct impingement into the eutectic droplets, but also by the Si ad-atom diffusion on the surface of the wafer and on the surface of the whiskers. Such ad-atoms are the result of impingement of Si atoms on the whole wafer surface.

The experimentally observed constant growth rate dl/dt as a function of time and the inverse dependence on the diameter d (or Radius $R = d/2$) restricts the possible transport mechanisms to those which approximately obey the following relation

$$\pi R^2 dl/dt = \gamma R. \tag{1}$$

The expression on the left-hand side is proportional to the total flux of silicon atoms incorporated into the whisker. On the right-hand side, γ is a constant independent of time and the radius of the whisker. Integration of Eq. (1) leads then to the observed radius and time dependence

$$l = (\gamma/\pi) t/R. \tag{2}$$

Let us now consider various atomistic transport and incorporation processes and their time and radius dependence.

(i) The rate of direct impingement of the molecular beam is time independent but should be proportional to the whisker area πR^2 and thus would lead to no dependence on the growth rate on the whisker radius.

(ii) A diffusion of silicon atoms on the surface of the whisker from the base of the whisker to the liquid droplet would give the observed radius dependence but also lead to a time dependence $l \propto \sqrt{t}$ which is not observed experimentally.

(iii) If the diffusion on the silicon surface including the surface of the whiskers is so fast that the flux of silicon atoms is limited by the incorporation rate at the boundary of the cylindrical whisker and the liquid droplet, then a radius dependence and time-independence of the growth rate as described in Eq. (1) can be expected.

Only the last process (iii) can explain the observed kinetics and radius dependence of whisker growth. We therefore consider this process involving fast surface diffusion and incorporation of silicon into the droplet as the rate limiting step as the most likely growth process. In this context, it is worth mentioning that during VLS growth by CVD, the rate limiting process is also not the diffusion of silicon precursors (in the vapor) but their incorporation into the droplet. The required fast diffusion of silicon on the silicon surface may possibly be influenced by the presence of a certain concentration of gold atoms at the wafer surface and the cylindrical surface of the whisker which were detected as nanoscopic solidified gold droplets, Au:Si eutectica after cooling down the wafers.

Our results support the assumption that as in the case of CVD-grown whiskers, the incorporation of Si ad-atoms is preferred at the Si/Au droplet interface. However, the whisker growth by MBE has a strong surface-related Si diffusion component, which leads to a larger growth rate for nano-whiskers with a smaller radius. This is just opposite to what is well established in the case of CVD-grown nanowhiskers. One has to take into account that we investigated the MBE growth via a gold/silicon eutectic. The use of other metals/silicon eutectic systems might show a different behavior.

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