Silicon nanowires

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Gold-Enhanced Low-Temperature Oxidation of Silicon Nanowires**

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The thermal oxidation of silicon is one of the major processes in Si device fabrication. Silicon dioxide is widely used as an excellent insulator both in active devices, such as metal–oxide–semiconductor field-effect transistors (MOSFETs), and in the region between active devices. Wet oxidation and dry oxidation of silicon have been well studied both experimentally and theoretically for more than 40 years. As the ultra-large-scale integration (ULSI) dimension approaches the nanoscale, the interest in the fabrication of silicon nanowires (SiNWs) typically surrounded by SiO2 has increased enormously due to potential device applications and novel physical properties.[1]

However, there are hardly any results available in the literature on the thermal oxidation of epitaxial SiNWs perpendicular to the substrate surface. In recent years, SiNWs grown by the vapor–liquid–solid (VLS) mechanism[2][3] have been proposed as building blocks for single-electron transistors, optoelectronic devices, and sensors.[4–11] During VLS growth, gold has been the most commonly used catalyst to date, since it forms a convenient low-temperature eutectic with silicon (melting point of 363 °C at 19.5 at.% Si and 80.5 at.% Au). Si atoms resulting from decomposition of the vapor-phase source materials, SiCl4 or SiH4, for example, are absorbed by the Au particle, which is presumably a liquid droplet at the SiNW growth temperature. Upon supersaturation of the liquid alloy, a solid precipitate of the source material (silicon) is generated. The epitaxial nanowire perpendicular to the Si surface thus obtained is of high crystalline quality. There is direct contact between the single-crystal SiNW and Au hemispherical particle at its apex. This simple one-dimensional (1D) structure offers a model system for the study of thermal oxidation. At the same time, interfacial reactions between silicon and gold can also be investigated in this special structure, which is very important for improving our knowledge of the reaction between metals and semiconductors in the fabrication of electronic devices.

Concerning the high-temperature oxidation (875 °C) of SiNWs, Westwater et al. found that the Au droplet at the apex of the wire plays an important role.[2] Low-temperature oxidation of silicon assisted by gold had already been reported by Hiraki et al. in 1971.[13] They covered a clean surface of a Si crystal with an evaporated Au layer (with a thickness in the order of 100 nm) and heated the sample in an oxidizing atmosphere at temperatures (100–300 °C) that were lower than the Si–Au eutectic point. They found that Si atoms migrate through the Au film to its surface, which resulted in the formation of a silicon oxide overlayer. The growth stopped after a saturated thickness was reached. The saturated SiO2 thickness was proportional to (and about double) the original Au thickness. Later, Popović et al. explained this saturation effect by the formation of SiO2 at grain boundaries of the polycrystalline Au thin film.[14] This kind of metal-enhanced oxidation of silicon has also been reported for other Si–metal systems and attracted much interest at the end of the last century.[15,16] However, all of the low-temperature oxidation studies considered 2D systems in which a thin film of the metal covered a flat Si crystal surface.

Herein, we report the gold-enhanced low-temperature oxidation of SiNWs (1D structures) grown by the VLS process with liquid gold droplets as catalyst. Unexpected results, which are very different from the oxidation behavior found in 2D film systems,[14–16] and the high-temperature oxidation of SiNWs[2] were observed by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM).

SiNW growth was achieved by ultrahigh-vacuum (UHV) chemical vapor deposition (CVD) using diluted silane as a precursor gas. The experimental process was as follows: 1) the Si(111) wafer was quickly transferred into a UHV chamber after its cleaning by the standard RCA method followed by a HF dip; 2) a gold film of 1-nm thickness was deposited onto the Si(111) surface, which was annealed afterwards at 600 °C for 20 min to form small Au–Si droplets, and 3) the SiNWs were grown at 500 °C and a silane partial pressure of 10 Pa for 20 min. After CVD growth, the sample was cooled to room temperature (RT), removed from the UHV chamber, and inspected by SEM. Figure 1 shows an SEM image of a SiNW sample with a surface tilt angle of 60° from the horizontal. We observed SiNWs with an average diameter of 100 nm and a length of about 1 μm.

The sample was placed in a furnace for low-temperature oxidation in ambient air after storage in air at RT for about one year. In all of the experiments, the sample was heated to 250 °C, which was well below the eutectic temperature (363 °C) of the Au–Si system. Then the sample was cooled slowly to RT.

To observe the initial oxidation state of the SiNWs, we used a short heating time of t = 80 min. The TEM images in Figure 2 clearly show the main results of the oxidation experiment. At first glance, we find that most SiNWs with gold caps start to be oxidized dramatically along their axes, while there is almost no change for the radial directions of the SiNWs. A close view shows that only a very thin oxida-
tion shell, which is not much thicker than the native oxide layer, forms around each nanowire. Compared to this predicted phenomenon, the unexpected oxidation process along the axes of the SiNWs is more interesting. Insets a–c of Figure 2 show close-up views of three different results for SiNWs having undergone the same oxidation procedure. In inset a, we observe a direct contact between the gold cap and the SiNW under it. The interface between them is flat. The gold particle shows a trend to be divided into two or more parts. The oxide (gray contrast) covers the elongated part of the former gold hemisphere. The oxide thickness is inhomogeneous with some tendency to form lamellae. Inset b shows a SiNW that was apparently oxidized faster. The original gold particle was separated into two parts due to the oxidation process. The upper part looks like a pear, while the lower part more or less has the shape of a nanocone. From Figure 2 and insets a and b we can see that these SiNWs, although exposed to the same oxidation conditions, show different oxidation rates. No direct relationship between the diameters of the SiNWs and their oxidation rate was found in our experiments. Compared with the process demonstrated in insets a and b, a totally different oxidation behavior is shown in inset c of Figure 2. We observe an almost intact SiNW without obvious oxide product. A thin oxide layer with a thickness of a few nanometers between the Au cap and the SiNW was detected for a similar nanowire by energy-dispersive X-ray (EDX) analysis line scan (see Figure 7). Furthermore, a thin oxide layer is also visible covering the whole Au cap of each SiNW.

Figure 3 shows TEM images of nanowires after a longer oxidation period of 4 h. We observe a pronounced oxidation along the axes of most SiNWs while keeping the shape of the Au nanocone at the interface to Si. A further check by increasing the time of heat treatment showed that the oxidation process continues until the nanocone arrives at the substrate surface. We also observed some partially oxidized SiNWs with only Au nanocones remaining at their tops. The chemical bonds between the Au metal and the Si oxide nanowires are weak. If the Si oxide grows without contact to the Si oxide covering the SiNW, the Si oxide nanocone sits on top of the Au nanocone in an unstable way. An example is given in the inset of Figure 3, which shows a short and heavily bent Si oxide nanowire. This oxide nanowire shows a white-line contrast along its center, which can be attributed to a hollow core of the oxide nanowire.

Figure 4 shows an SEM image of nanowires after a 12 h heat treatment. We observed a striking increase in the length of most nanowires due to oxidation except for a few intact ones, which is consistent with the TEM image shown in inset c of Figure 2. The oxidized products are marked in yellow for better identification in the picture. A careful check shows that many oxide nanowires have a length of several micrometers after oxidation of the SiNWs. The compositions of the oxide nanowires and the nanoparticles on top were determined by analytical microscopy at RT. Figure 5 shows STEM images of nanowires after low-temperature oxidation (80 min at 250 °C). From the EDX spec-
tra shown in Figure 5b, we confirmed that the two nanoparticles are Au crystals separated by silicon oxide.

To understand the different types of oxidation behavior described above, let us discuss the mechanism behind the associated phenomena. The formation of the oxidation shell around the nanowires occurred as expected for the thermal oxidation of single-crystalline Si, which has been described, for example, in the appropriate handbook.\cite{17} The oxidation of silicon by molecular oxygen proceeds according to the overall reaction $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$. This process is called dry oxidation. The oxidation of silicon by $\text{H}_2\text{O}$ occurs by the reaction $\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2$. This oxidation process, based on a mixture of $\text{O}_2$ and $\text{H}_2\text{O}$ as oxidants, is called wet oxidation. It has the advantage of oxidizing at a much higher rate than dry oxidation. A comprehensive comparison between dry and wet oxidation was carried out by Deal and Grove.\cite{18} High temperatures are not necessary to grow an oxide. Silicon will oxidize in air at RT. Once an oxide forms, however, with either oxygen or water, silicon must diffuse through the oxide to continue the reaction. The diffusivity of Si in SiO$_2$ is many orders of magnitude smaller than the diffusivity of O$_2$ or H$_2$O. As a result, the chemical reaction occurs at the Si/SiO$_2$ interface. The volume of the SiO$_2$ is larger than the volume of the reacted silicon by a factor of 2.2. This volume increase leads to a continuous oxide film on silicon. At RT and at 250°C, neither water nor oxygen is sufficiently mobile to diffuse through the thin (native) oxide. After a short while, the oxidation reaction effectively stops and the oxide will not get much thicker than about 2 nm. This is the reason for the formation of only a thin oxidation shell for the SiNWs in our experiment.

The oxidation at the apex of the nanowire is strongly modified by the influence of the gold particle. The basic process is similar to the phenomenon discovered by Hiraki et al.\cite{13} when describing their gold-assisted low-temperature silicon oxidation experiments. Ishikawa et al. reported that AuSi$_x$ grains could be formed in Si wafers by annealing at 310°C after a 100-nm-thick Au film was evaporated onto thin silicon oxide insulator (SOI) structures with Si pillars in the SiO$_2$ layer,\cite{19} which was later investigated in detail by in situ TEM.\cite{20} In this work, we did not observe any evidence for silicide formation by our RT TEM investigations.

Figure 6 shows a schematic diagram of the process of gold-enhanced low-temperature oxidation as proposed by us. At the Si/Au interface, silicon is dissolved and diffuses through the gold to the gold surface, which was modeled by Kuo and Clancy using a modified embedded-atom method (MEAM).\cite{21} Reaction with oxygen or water occurs at the gold surface, and a silicon oxide layer is formed. The diameter of this initial oxide shell is a few percent larger than the diameter of the gold particle. This oxide layer exerts pressure on the gold particle and the gold responds by plastic deformation. The gold particle is elongated and constricted. During further growth the shape of the lower part of the particle changes to a nanocone, while the higher part is separated by an intermediate oxide. The shape of the nanocone does not change during further oxidation and remains in this steady-state shape. The reaction requires diffusion of water or oxygen to the
water to the gold surface. One reason for the formation of lamellae of the oxide, which allows easy access of oxygen or process continued. An important point is the formation of the surface of the gold particle was possible and the oxidation of the Au, continuous diffusion of silicon towards the out-diffusion of silicon.\cite{14} In our case without grain boundaries of Au, which finally stopped the oxide at grain boundaries of Au, which finally stopped the oxidation process.

In conclusion, we have shown two kinds of oxidation behavior during heat treatment at 250°C along the axes of SiNWs grown by the VLS process using Au droplets as catalyst. In a few cases, the presence of a thin silicon oxide layer between the Au particle and the single-crystal SiNW prevents the interaction of Au with Si and hence the Si out-diffusion, and oxidation stops. However, in most cases, Si out-

where $\rho$ is the density of Si ($5 \times 10^{22}$ cm$^{-3}$), $v$ the growth speed of the oxide (0.1 nm s$^{-1}$), $x$ the mean diffusion distance (10 nm), and $\Delta C$ the concentration difference of Si in Au ($5 \times 10^{19}$ cm$^{-3}$). The equilibrium solubility of Si in Au at 250°C seems to be unknown. Johnson et al.\cite{23} published a measurement of the solubility just below the eutectic temperature and obtained a value of 0.27 at. % with a large estimated error. The solubility decreases with lower temperature and we assume a value of 0.1 at. % at 250°C. Using the above values, an estimate of \[ D = \frac{\rho \times v \times x}{\Delta C} \] (1)

is obtained. This value is a lower limit of the diffusion coefficient.

Figure 6. Schematic diagram of the gold-enhanced low-temperature oxidation of a SiNW. I) SiNW before heat treatment. II) Si out-diffusion is promoted by the interaction of Si with Au, which forms Si atoms in a metallic state in the Au particle. Hence, Si migrates through the Au particle and is finally oxidized at its surface to produce a silicon oxide nanowire. The thin arrows mark the diffusion paths of Si and O$_2$. III) The Au particle changes its shape to a nanocone. The excess part of the former Au particle is trapped by the Si oxide nanowire. IV) Almost complete conversion of the SiNW into an oxide nanowire.

Figure 7. STEM image and EDX analysis spectrum (inset, scanning from A to B) of a SiNW after heat treatment. Heating temperature $T_{\text{heating}} = 250^\circ\text{C}$, heating time $t_{\text{heating}} = 80$ min.
diffusion is promoted by the interaction of Si with Au due to the direct Si/Au contact. Si atoms can readily migrate through the Au particle and be oxidized at its surface. Unlike 2D oxidation for Si covered with an Au film, for these 1D structures the oxide is observed to form lamellae. These are hypothesized to cause cracks in the oxide, thereby allowing O\textsubscript{2} to continue to migrate to the Au surface for continued oxidation of the Si atoms as they diffuse through to the Au surface, which results in continued oxide growth and the eventual consumption of the SiNW. Within the special 1D structure, the Au particle is elongated and constricted. During further growth the shape of the lower part of the particle changes into a nanocone. The two gold-containing parts of the resulting nanostructures are separated by an intermediate Si oxide nanowire.

**Experimental Section**

SiNW growth and low-temperature oxidation were performed as described in the text. For the TEM investigations, the samples were mounted in a reflection holder but tilted to allow transmission through nanowires close to the sample edge. The STEM samples were prepared by collecting nanowires with a thin carbon film on a TEM grid. The instruments used were a JEOL JSM-6300F scanning electron microscope, a Philips CM20 twin transmission electron microscope, and a Philips CM20 FEG scanning transmission electron microscope.

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