Effect of oxide overlayer formation on the growth of gold catalyzed epitaxial silicon nanowires

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Effect of oxide overlayer formation on the growth of gold catalyzed epitaxial silicon nanowires

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A direct dependence between the inadvertent formation of SiO_2 on gold films deposited on silicon $\langle 111 \rangle$ substrates, and the nucleation and yield of epitaxial, gold catalyzed, silicon nanowires grown on such substrates is reported. The unintended SiO_2 layer formed due to the diffusion of silicon from the underlying substrate through the gold film is observed to be 0.5 nm with medium energy ion scattering after brief exposures of 10–15 min in air. Silicon nanowires grown at 500 °C on such samples show reduced nucleation and growth. A remarkable improvement in nanowire nucleation density and epitaxy is observed on removing the SiO_2 overlayer prior nanowire growth. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2179370]

Semiconductor nanowires have received much attention in recent years due to their interesting properties and potential applications.[1–6] The wires are typically grown using a catalyst, and gold has been the most commonly used catalyst to date since it forms eutectics at relatively low temperatures with silicon and germanium.[7–9] While gold is resistant to oxidation (a major reason for its popularity), it can catalytically oxidize silicon. The first studies of silicon migration through gold films were conducted in the early 1970s in the context of Schottky contacts between gold and silicon.[10–13] These studies describe gold catalyzed migration of silicon through the gold film, resulting in the formation of a silicon oxide overlayer. This letter investigates the effect of this overlayer formation on the nucleation of nanowires and its effect on the reproducibility and yield of epitaxially grown nanowires.

Silicon nanowire growth was performed in an UHV, hot wall, chemical vapor deposition system using 2% silane diluted in helium as the source gas. The system is load locked with a nominal base pressure below 10^{-8} Torr. Silicon $\langle 111 \rangle$ samples were hydrogen terminated using 10:1 HF followed by a minimal water rinse. The samples were then loaded into a thermal evaporator and pumped down to a base pressure of 10^{-8} Torr. A resistively heated Au cell was then used to deposit 3 nm of gold on the samples which were then left in vacuum until just prior to the nanowire growth.

In order to understand the effect of SiO_2 overlayer formation on epitaxial nanowire growth, two samples were prepared and deposited with gold. After the gold deposition, one sample was dipped in 10:1 HF for 15–30 s (HF postgold treatment). The sample was then loaded into the nanowire growth system with the second sample that did not receive any postgold treatment. The ambient exposure of both samples in the period between the unloading from the evaporator and the loading into the nanowire growth system was under 10 min. The samples were annealed at 500 °C for 10 min in helium, followed by a 10 min nanowire growth at 500 °C and 16 Torr total pressure. Figure 1 shows the scanning electron microscopy (SEM) images of the sample which

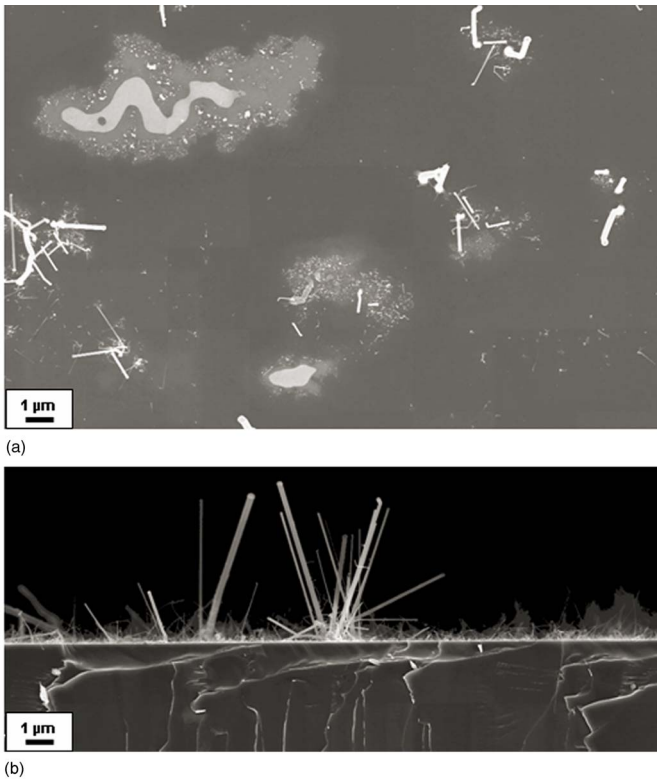

FIG. 1. (a) Plan view and (b) cross-section SEM image of the silicon $\langle 111 \rangle$ sample with 3 nm of Au, no post-Au treatment and after growth at 500 °C for 10 min at a total reactor pressure of 16 Torr. Sample shows inhibited nanowire growth due to the formation of the oxide overlayer.

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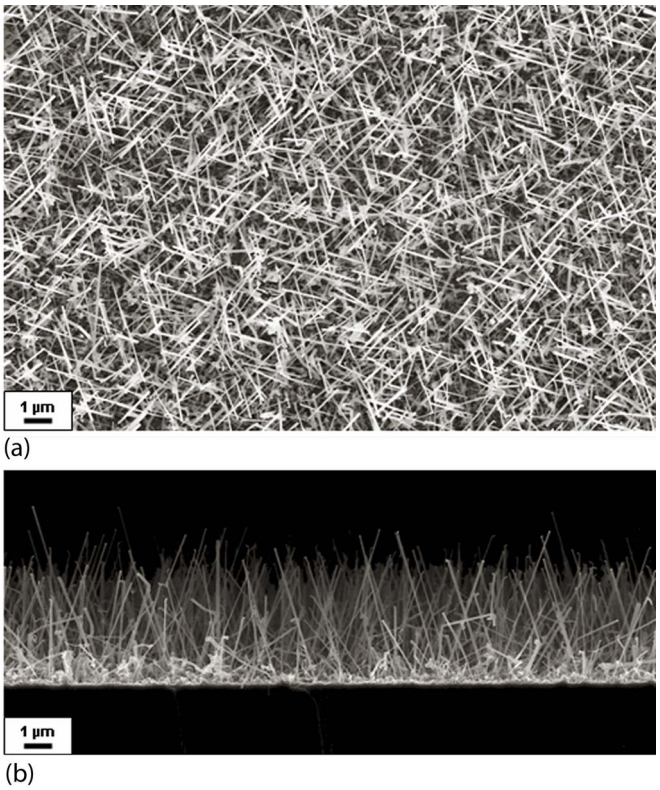

FIG. 2. (a) Plan view and (b) cross-section SEM image of the silicon ⟨111⟩ sample with 3 nm of Au, with post-Au treatment in 10:1 HF and after growth at 500 °C for 10 min at a total reactor pressure of 16 Torr. Sample shows dense epitaxial nanowire growth due to the removal of the oxide overlayer.

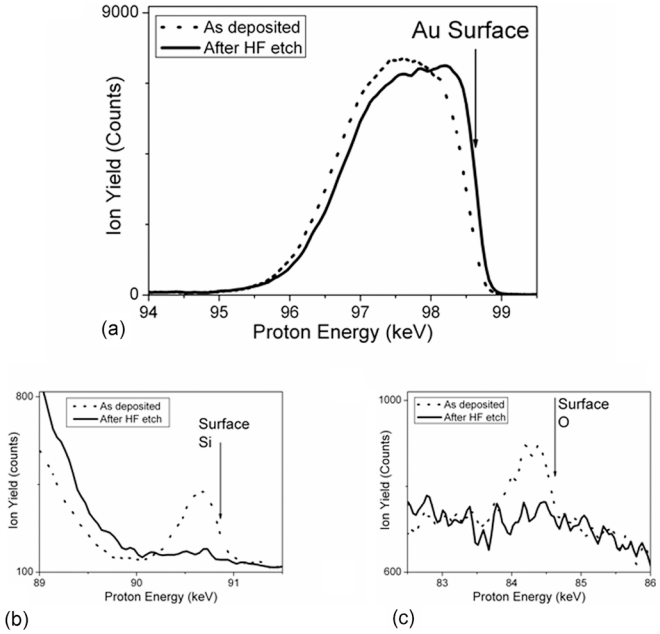

FIG. 3. MEIS spectra showing the presence of an oxide overlayer on top of an as-deposited gold catalyst film and its absence upon HF treatment: (a) gold spectra, (b) silicon spectra, and (c) oxygen spectra.

did not receive any HF postgold treatment. Due to the presence of the oxide overlayer, the sample shows suppressed growth of nanowires. The cracks and discontinuities in the poor quality oxide overlayer expose the gold below resulting in short nanowire growth at these locations.

On the other hand, the sample with the HF postgold treatment shows dense epitaxial nanowire growth as shown in Fig. 2. The wires are much longer compared to that in Fig. 1 indicating that the HF removed the oxide overlayer resulting in a cleanly exposed gold surface. Similar experiments were repeated by depositing gold using electron beam evaporation and produced the same results and conclusions. The degree of suppression was found to vary with the change in the substrate orientation. This effect can be explained by studies showing the difference in the rate of overlayer formation on different orientations of silicon surfaces. This in turn can be attributed to the relative strengths of the bonds holding the silicon atoms on different surface orientations.[14]

In order to understand the formation of the oxide layer and the surface passivation with HF after gold deposition, samples were prepared in the identical manner as for the nanowire growth experiments and were then analyzed using medium energy ion scattering (MEIS) with 100 keV protons. A sample with 3 nm of gold and another with the same thickness of gold with an additional HF dip after the gold deposition were measured. Similar to the nanowire growth experiments, the ambient exposure of the samples during the transfer from the evaporator to the vacuum of the MEIS system was kept under 10 min. Figures 3(a)–3(c) show the MEIS spectra for these two samples. The data are consistent with the growth of 0.5 nm of silicon oxide on the sample with no postgold HF etch. On the other hand, the sample with the postgold clean showed no formation of oxide within the detection limits of the technique. It is important to note that Figs. 3(b) and 3(c) clearly indicate the disappearance of both the surface silicon and the surface oxide as a result of the HF dip. This rules out the possibility that the observations in Fig. 3(a) are simply gold islands on a silicon surface, with the silicon oxide signal arising from the exposed regions of the substrates. If that were the case, the silicon peak would not have disappeared in Fig. 3(b). The fact that it does demonstrates that the as-deposited gold film is continuous on the silicon substrate. The HF treated sample stored in UHV for 1 week and remeasured showed no overlayer formation while samples left in air for 48 h after gold deposition grew a thick oxide of 0.8 nm. Samples treated with HF and exposed to air for 40 min before the MEIS measurement, however, showed no formation of SiO_2. It is difficult to conclude at this point whether the migration of silicon through the gold film (causing the oxide to form) takes place at room temperature or during the evaporation of the gold.

Note that the effect of the silicon oxide overlayer is more apparent for short growth times for the nanowires. Extended growth times allow the reduction and eventual disappearance of the silicon oxide overlayer with prolonged exposure to silane at the growth temperature. An example is shown in Fig. 4 where an extended growth on samples with no HF postgold treatment for an hour resulted in a dense growth of nanowires. As the silicon oxide overlayer degrades, eventually nucleation across the wafer is seen to occur. A strongly reducing environment may ensure the quicker removal of this surface oxide layer and offer an advantage in this regard.

In summary, this letter reports on the formation of an oxide overlayer on gold catalyst films, and its effect on the nucleation and yield of epitaxial nanowire growth. In the absence of knowing this phenomenon, the reduced growth of nanowires has been attributed to either low temperatures of growth or to the delayed nucleation of nanowires. The un-

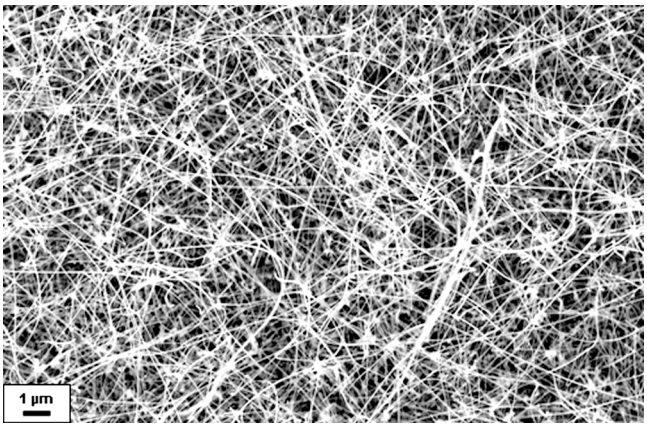

FIG. 4. SEM image of the silicon ⟨111⟩ sample with 3 nm of Au, no post-Au treatment, and after growth at 500 °C for 1 h at a total reactor pressure of 16 Torr. Sample shows dense growth of nanowires.

derstanding of this overlayer formation, and its effect on the growth of epitaxial nanowires from our study, would be crucial in obtaining repeatable, low temperature, ordered and high density synthesis of nanowires.

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