Active-oxidation of Si as the source of vapor-phase reactants in the growth of SiO_x nanowires on Si

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Gold-coated silicon wafers were annealed at temperatures in the range from 800–1100 °C in a N₂ ambient containing a low (3–10 ppm) residual O₂ concentration. A dense network of amorphous silica nanowires was only observed on samples annealed at temperatures above 1000 °C and was correlated with the development of faceted etch-pits in the Si surface. Comparison with known thermodynamic data for the oxidation of Si and vapor-pressures of reactants shows that nanowire growth is mediated by a vapor-liquid-solid mechanism in which the dominant vapor-phase source of reactants is SiO produced by the active oxidation of Si. © 2010 American Institute of Physics. [doi:10.1063/1.3488882]

Amorphous silica nanowires (NWs) can be grown by a range of techniques^{1,2} and have great potential as biological and environmental sensing elements due to their large surface-to-volume fraction, excellent physical and chemical stability, and the well-established protocols for coating silica with bioselective coatings.^{3,4} Silica nanowires can also be doped^{5–8} or coated with secondary materials⁹ to extend their functionality to other areas of application, such as microcatalysis. Of particular relevance to the present study is the fact that recent reports have shown that dense arrays of SiO_x NWs can be grown by a relatively simple technique that requires no toxic gas source, such as silane.^{10–14} Instead, nanowire growth is achieved by depositing a thin metal film on Si and annealing the resulting heterostructure to temperatures close to 1100 °C in a high purity Ar or N₂ purging ambient. In this case the NW growth process has been attributed to a vapor-liquid-solid (VLS) mechanism as first described by Wagner and Ellis¹⁵ but the source of the Si and O gas-phase reactants has been mostly speculative. Some authors have identified the active oxidation of Si as a possible source of Si (Ref. 16) while others have variously attributed the source of Si to the dissolution and/or evaporation of the Si substrate or its native oxides, with and without the action of a metal catalyst, and the source of oxygen to the decomposition of the native oxide, the contaminants in the annealing ambient, the silica furnace tube, or leaks into the furnace gas supply.

In this study we show unambiguously that the growth of SiO_x nanowires is the direct result of a reaction between the Si substrate and residual oxygen in the annealing ambient and confirm the vapor-phase transport mechanism for nanowire growth. This understanding naturally leads to alternative approaches for the growth of SiO_x NWs, including the use of a silicon capping layer as a secondary source of reactants to promote SiO_x nanowire growth on substrates other than silicon.

To study nanowire growth, commercially prepared (100) Si wafers (p-type, B-doped, 10–20 Ω cm) and fused silica slides were coated with 10 nm of Au by sputter deposition. Individual samples were then annealed for 1 h at 800, 900, 1000, and 1100 °C in a quartz-tube furnace flushed with flowing N₂ gas at a flow rate of 1650 mL/min. Separate samples were annealed at 1100 °C for 2, 5, 10, and 60 min to study the temporal evolution of the samples. In all cases the annealing gas was dried prior to entering the furnace by passing it through a laboratory drying canister filled with anhydrous CaSO₄ but had a specified O₂ content of 3–10 ppm. The furnace tube was sealed from the atmosphere by passing the N₂ gas through an oil-filled backflow preventer at the tube exit. The Au-coated silica plate was also annealed at 1100 °C for 1 h with and without a Si-capping layer. In the latter case the Au-coated silica plate was placed face down on a Si wafer during annealing. All samples were characterized by scanning electron microscopy (SEM) using either a Hitachi 4300 Schottky field emission scanning electron microscope (FESEM) or a Zeiss UltraPlus analytical FESEM, with secondary or backscattered electron imaging modes. Sample cross-sections were fabricated by cleaving along a <011> direction of the Si substrate.

Figure 1 shows SEM images of Au-coated Si samples after annealing at temperatures of 800, 900, 1000, and 1100 °C. Samples annealed in the temperatures range from 800 to 1000 °C were found to be covered with Au-rich islands but showed no evidence of nanowire growth [Figs. 1(a)–1(c)]. In contrast, samples annealed at 1100 °C were found to be covered in a dense network of nanowires having lengths exceeding 100 μm and diameters in the range from 50 nm to 2 μm, as shown in Fig. 1(d). High-resolution transmission electron microscopy and energy dispersive x-ray spectroscopy analysis of similar samples showed that the nanowires are composed of amorphous silica with an average composition of SiO_x with x close to 1.8.

The growth of SiO_x nanowires is generally believed to proceed via a VLS or vapor-solid-solid growth mechanism depending on the catalyst employed. In the present case,

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FIG. 1. SEM images of Au-coated Si samples after a 1 h anneal at (a) 800, (b) 900, (c) 1000, and (d) 1100 °C. Samples annealed at temperatures in the range 800–1000 °C show only gold islanding. No nanowires are observed. The sample annealed at 1100 °C is covered in a dense network of SiO_x nanowires.

growth proceeds by a VLS mechanism in which liquid Au:Si eutectic droplets, such as those evident Figs. 1(a)–1(c), serve as the catalyst. Theoretical analysis suggests that the catalytic activity of Au-based nanoparticles is size dependent, with smaller particles (<10 nm) showing enhanced activity for oxidation reactions.^{17–19} Nanowire growth is, therefore, expected to be dominated by smaller catalyst particles. To gain further insight into the nanowire growth mechanism, sample cross-sections were examined by SEM at various stages of growth.

Figure 2 shows SEM images of sample cross-sections taken at various times during annealing at 1100 °C. During the first few minutes of annealing the thin Au film coalesces into islands on top of the native oxide, while the native oxide itself begins to decompose via the reaction $\text{Si(s)} + \text{SiO}_2\text{(s)} \rightarrow 2\text{SiO(g)}$,²⁰ where (s) and (g) denote the solid and gas phases, respectively. This occurs heterogeneously and is nucleated and catalyzed by Au, perhaps via diffusion to the Si–SiO₂ interface through microchannels within the oxide.²¹ Although this decomposition reaction produces volatile SiO the amount produced is insufficient to account for the observed SiO_x nanowire growth. [This is readily confirmed by a simple calculation, i.e., a native oxide of thickness 5 nm and bulk density ($\sim 6 \times 10^{22}$ atoms cm⁻³) contains around 4×10^{16} oxygen atoms cm⁻². By comparison, the number of oxygen atoms in a typical nanowire layer consisting of 100 μm long nanowires with a 1% volume fraction is

FIG. 2. Temporal evolution of SiO_x nanowire growth. (a) Initial stages of Au reaction with Si substrate to form Au:Si eutectic and enhance etching, (b) nanowire growth and etch-pit evolution, (c) interface void formation caused by etching of Si substrate underneath nanowire layer, and (d) final stages of etching prior to film delamination.

FIG. 3. A phase diagram showing the oxidation of Si as a function of O₂ concentration and temperature. The boundary between passive and active oxidation is fitted from experimental data by Smith and Ghidini (Ref. 26) for a Si(100) surface. The hashed area represents the 3–10 ppm of O₂ in the annealing ambient and the labeled points represent the annealing conditions employed for the samples in Figs. 1(a)–1(d), respectively. This clearly shows that annealing temperatures in the range 800–1000 °C correspond to passive oxidation, while annealing at 1100 °C corresponds to active oxidation.

around 1.0×10^{19} oxygen atom cm⁻². For a 10% volume fraction, which is closer to that observed experimentally, this increases to around 1.0×10^{20} oxygen atom cm⁻². The amount of oxygen contained within the nanowires is therefore between 10^3 and 10^4 times the amount available from the native oxide.] As time progresses, Au is observed to react with the Si substrate to form a liquid eutectic (363 °C) and to produce faceted etch-pits in the Si substrate, such as those evident in the SEM images of Figs. 2(b) and 2(c). Further annealing eventually produces a continuous network of etch-pits at the NW-substrate interface, as seen in Figs. 2(c) and 2(d), and can lead to complete delamination of the NW layer from the substrate.

Although the faceted etch-pits depicted in Fig. 2 could arise from alloying between Au and Si they are similar to those observed during high-temperature annealing of Si under conditions of low O₂ partial pressure. The oxidation of Si is known to fall within two distinct regimes depending on the annealing temperature and oxygen partial pressure (see, for example, early work by Lander and Morrison²² and reviews by Engstrom *et al.*,²³ and Engel²⁴). At a given temperature, the dominant oxidation mechanism is controlled by the O₂ partial-pressure; At “high” partial pressures oxidation proceeds via the reaction $\text{Si(s)} + \text{O}_2\text{(g)} \rightarrow \text{SiO}_2\text{(s)}$ to form a passivating SiO₂ layer, while at “low” partial pressures it proceeds via the reaction $2\text{Si(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{SiO(g)}$. In the latter case the substrate surface becomes pitted due to the production of volatile SiO vapor via the active oxidation reaction.^{22,25,26} Although most active-oxidation studies have been performed in vacuum, similar behavior is observed during annealing at atmospheric pressure when the residual O₂ concentration is comparable to that employed in the vacuum studies. This residual O₂, estimated to be 3–10 parts per million (ppm) in commercially available “high-purity” processing gases is believed to be responsible for Si etching²⁷ and surface roughening during rapid thermal annealing²⁸ and for the etch-pits observed in Fig. 2.

Figure 3 shows a phase diagram for the oxidation of Si as a function of temperature and oxygen concentration in which the solid line represents the transition from stable

FIG. 4. Schematic diagrams of the sample configurations used to anneal Au-coated silica samples and SEM images of the resulting nanostructures. Part (a) depicts a Au-coated SiO_2 slide during annealing at 1100°C without a Si capping layer, and an SEM image of the sample surface after annealing showing the presence of Au nanoparticles. Part (b) depicts a Au-coated silica slide covered with a Si proximity cap during annealing at 1100°C together with SEM images of the capping wafer surface and the silica surface after annealing. In this case the silica slide is covered with a low density of nanowires and the capping layer is covered in etch-pits.

passive-oxidation, $\text{Si(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{SiO}_2(\text{s})$, to active oxidation, $2\text{Si} + \text{O}_2 \rightarrow 2\text{SiO}$, as determined from a fit to the data of Smith and Ghidini²⁶ for Si(100) under ultrahigh vacuum conditions. The annealing conditions employed in the current experiments are shown for reference. Specifically, the shaded area represents an oxygen concentration of 3–10 ppm present in the N_2 annealing ambient, while the points labeled (a)–(d) correspond to the annealing conditions for the samples depicted in Fig. 1, i.e., to annealing temperatures of 800, 900, 1000, and 1100°C . From this data it is clear that nanowires only form when samples are annealed within the active oxidation regime. Of the various species produced in this reaction, SiO is the most abundant and has the highest vapor pressure.²⁹ This strongly suggests that nanowire growth is mediated by SiO vapor produced during the active oxidation reaction and that this reaction is responsible for the observed substrate etching.

To test of this model and confirm the vapor-phase transport of the primary reactants, a Au-coated silica sample was annealed at 1100°C with and without a silicon capping layer. The results are summarized in Fig. 4. Without a capping layer there is no source of Si to produce SiO vapor and the silica surface is found to be covered with Au islands, as shown in Fig. 4(a). In contrast, a similar sample annealed face-down on a (100) silicon wafer to provide a source of reactants was found to be covered in SiO_x nanowires, as shown in Fig. 4(b). These nanowires were shorter and straighter than those grown on Si substrates, with lengths typically less than $1\text{ }\mu\text{m}$ and diameters ranging from 50 to 200 nm. Significantly, the Si capping layer used to anneal the silica sample was heavily etched following nanowire growth, as shown in Fig. 4(b) (upper right). This is consistent with the model in which nanowire growth is mediated by SiO vapor produced via the reaction between silicon and oxygen at low concentrations.

Active oxidation of the Si substrate is enhanced by the presence of metallic catalysts (Au in this case) as bare wafers do not exhibit significant etching when annealed under identical conditions at 1100°C . When used as a capping layer for the silica samples, the Si wafer Au is evaporated onto the Si capping layer surface from the silica substrate during annealing at 1100°C . This acts to enhance the active oxidation reaction and also leads to the growth of a low density of nanowires on the capping layer surface, as shown in Fig. 4(b) (upper right).

In summary, we have shown that the growth of SiO_x NWs during high temperature annealing of Au-coated silicon substrates is mediated by the active oxidation of Si due to trace concentrations (3–10 ppm) of O_2 in the annealing ambient, and that SiO produced by the reaction $2\text{Si} + \text{O}_2 \rightarrow 2\text{SiO}$ is the likely source of Si. We have further shown that the SiO is transported from the substrate to the catalyst in the vapor phase thereby confirming the VLS growth mechanism. Finally, we demonstrated that a sacrificial Si wafer can be used as the source of SiO vapor to grow SiO_x nanowires on substrates other than Si without the need for toxic reactants such as SiH_4 .

¹S. Kuchibhatla, A. S. Karakoti, D. Bera, and S. Seal, *Prog. Mater. Sci.* **52**, 699 (2007).

²N. Wang, Y. Cai, and R. Q. Zhang, *Mater. Sci. Eng. R.* **60**, 1 (2008).

³N. S. Ramgir, P. K. Sekhar, A. Zajac, L. Lee, T. Zhukov, and S. Bhansali, *Sens. Lett.* **5**, 608 (2007).

⁴N. S. Ramgir, A. Zajac, P. K. Sekhar, L. Lee, T. A. Zhukov, and S. Bhansali, *J. Phys. Chem. C* **111**, 13981 (2007).

⁵R. G. Elliman, A. R. Wilkinson, T. Kim, P. Sekhar, and S. Bhansali, *Nucl. Instrum. Methods Phys. Res. B* **266**, 1362 (2008).

⁶R. G. Elliman, A. R. Wilkinson, T. H. Kim, P. K. Sekhar, and S. Bhansali, *J. Appl. Phys.* **103**, 104304 (2008).

⁷P. K. Sekhar, A. R. Wilkinson, R. G. Elliman, T. H. Kim, and S. Bhansali, *J. Phys. Chem. C* **112**, 20109 (2008).

⁸A. Shalav, T. H. Kim, and R. G. Elliman, *J. Appl. Phys.* **107**, 046101 (2010).

⁹A. Shalav, D. K. Venkatachalam, F. Reichardt, F. Fischer, and R. G. Elliman, *Mater. Res. Soc. Symp. Proc.* **1206**, M16 (2010).

¹⁰C. Y. Wang, L. H. Chan, D. Q. Xiao, T. C. Lin, and H. C. Shih, *J. Vac. Sci. Technol. B* **24**, 613 (2006).

¹¹D. Bahloul-Hourlier and P. Perrot, *J. Phase Equilib. Diffus.* **28**, 150 (2007).

¹²H. W. Kim, S. H. Shim, M. H. Kong, and H. H. Yang, *Phys. Status Solidi A* **205**, 2002 (2008).

¹³Y. Choi, J. L. Johnson, and A. Ural, *Nanotechnology* **20**, 135307 (2009).

¹⁴P. K. Sekhar and S. Bhansali, *Mater. Lett.* **64**, 729 (2010).

¹⁵R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964).

¹⁶A. S. Ferlauto, S. Oliveira, E. E. Silva, R. Magalhaes-Paniago, L. O. Ladeira, and R. G. Lacerda, *J. Nanosci. Nanotechnol.* **6**, 791 (2006).

¹⁷Y. Chen, P. Crawford, and P. Hu, *Catal. Lett.* **119**, 21 (2007).

¹⁸M. B. Cortie and E. van der Lingen, *Mater. Forum* **26**, 1 (2002).

¹⁹M. M. Schubert, S. Hackenberg, A. C. van Veen, M. Muhler, V. Plzak, and R. J. Behm, *J. Catal.* **197**, 113 (2001).

²⁰R. Tromp, G. W. Rubloff, P. Balk, F. K. Legoues, and E. J. Vanloenen, *Phys. Rev. Lett.* **55**, 2332 (1985).

²¹H. Dallaporta, M. Liehr, and J. E. Lewis, *Phys. Rev. B* **41**, 5075 (1990).

²²J. J. Lander and J. Morrison, *J. Appl. Phys.* **33**, 2089 (1962).

²³J. R. Engstrom, D. J. Bonser, M. M. Nelson, and T. Engel, *Surf. Sci.* **256**, 317 (1991).

²⁴T. Engel, *Surf. Sci. Rep.* **18**, 91 (1993).

²⁵C. Gelain, A. Cassuto, and P. Legoff, *Oxid. Met.* **3**, 139 (1971).

²⁶F. W. Smith and G. Ghidini, *J. Electrochem. Soc.* **129**, 1300 (1982).

²⁷C. J. Frosch and L. Derick, *J. Electrochem. Soc.* **104**, 547 (1957).

²⁸B. Mohadjeri, M. R. Baklanov, E. Kondoh, and K. Maex, *J. Appl. Phys.* **83**, 3614 (1998).

²⁹T. Suzuki, *J. Appl. Phys.* **88**, 6881 (2000).