Patterned growth of silicon oxide nanowires from iron ion implanted SiO$_2$ substrates

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Abstract

We demonstrate experimentally a simple and efficient approach for silicon oxide nanowire growth, by implanting Fe$^{+}$ ions into thermally grown SiO$_2$ layers on Si wafers and subsequently annealing in argon and hydrogen to nucleate the nanowires. We study the effect of implantation dose and energy, growth temperature, H$_2$ gas flow, and growth time on the silicon oxide nanowire growth. We find that sufficiently high implant dose, high growth temperature, and the presence of H$_2$ gas flow are crucial parameters for silicon oxide nanowire growth. We also demonstrate the patterned growth of silicon oxide nanowires in localized areas by lithographic patterning and etching of the implanted SiO$_2$ substrates before growth. We propose a simple physical model to explain the growth results. This work opens up the possibility of growing silicon oxide nanowires directly from solid substrates, controlling the location of nanowires at the submicron scale, and integrating them into nonplanar three-dimensional nanoscale device structures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One-dimensional (1D) nanostructures, such as nanotubes and nanowires, have attracted significant research attention in recent years due to their unique structural and electronic properties. Controlled growth and synthesis of such 1D nanostructures remain an active research area. SiO$_2$ is a material which is of great technological importance in silicon VLSI technology. Nanowires of silicon oxide have a great potential in applications such as low-dimensional waveguides, scanning near-field optical microscopy, blue light emitters, nanoscale optical devices and sensors, sacrificial templates, and biosensors [1–3].

Several methods have been used to grow silicon oxide nanowires, such as laser ablation [2], thermal evaporation [4], and chemical vapor deposition (CVD) [5]. In most of these cases, a growth model based on the vapor–liquid–solid (VLS) growth mechanism [6] has been used to explain the observed results.

An essential component of the VLS growth process is the nanoscale catalyst particles required to nucleate the growth of nanowires. For example, several recent studies have demonstrated the growth of silicon oxide nanowires from a variety of different catalyst nanoparticles, including sputtered or evaporated metal thin films (such as Pt [1, 7], Au [8], Pd [8], and Ni [9]), molten Ga [5, 10–12], and Sn powder [13, 14]. In some of these studies, Si was supplied as a powder [2, 4] or in gaseous phase as silane (SiH$_4$) [5]. In a number of other studies, on the other hand, the catalyst material was deposited directly on the Si substrate [1, 7–14]. In these studies, the Si reactant is supplied by the solid Si substrate during growth, and the oxygen is supplied in gaseous form either intentionally by introducing oxygen or air into the chamber or unintentionally as a residual gas due to leakage or impurities in the carrier gases used.

In order to control the origin of nanowires during growth, the catalyst is typically patterned by lithography into small ‘islands’ [7, 9]. Nanoscale catalyst particles formed from deposited thin films and powders are typically...
difficult to pattern into very small dimensions or into nonplanar three-dimensional (3D) device structures, such as the sidewalls of high aspect ratio trenches [15]. An alternative catalyst deposition technique, which has not been studied as much [3, 15–18], is to use ion implantation and subsequent annealing to create catalyst nanoparticles. Ion implanted catalyst is much easier to pattern into very small features and over high aspect ratio topography compared to other types of catalyst, and it offers extremely accurate control of the dose of atoms introduced into the substrate. Since ion implantation is a well-established technique in silicon microfabrication, which is very reproducible and easily scalable, it could offer significant technological advantages as a method to form catalyst nanoparticles for nanowire growth.

A few previous experiments have shown that ion implantation and subsequent annealing can create catalyst nanoparticles for nucleating the growth of multi-walled carbon nanotubes (MWNTs) [15–17]. More recently, the growth of silicon nanowires by CVD on gold (Au) implanted Si substrates was demonstrated [19, 20]. In another recent work, palladium (Pd) ion implantation into bare Si wafers was used to grow silica nanowires [3]. Furthermore, we have recently shown that single-walled carbon nanotubes (SWNTs) [18], GaN nanowires, and Ga2O3 nanowires and nanoribbons [21] can be produced by the process of iron (Fe) ion implantation into thermally grown SiO2 layers, subsequent annealing, and CVD growth. However, the patterned growth of silicon oxide nanowires from Fe ion implanted SiO2 substrates has not been demonstrated previously.

In our experiment, 500 nm thick SiO2 layers were first thermally grown on silicon (100) substrates by wet oxidation. Fe+ ions were implanted into these layers, as depicted in figure 1(a), at an energy of 60 keV with three different doses (1014, 1015, and 1016 cm−2) and at a dose of 1015 cm−2 with three different energies (25, 60, and 130 keV). The projected range $R_p$ of the 25, 60, and 130 keV energy implants in SiO2 are 24, 50, and 103 nm, respectively, based on SRIM [22] calculations. The implant energies were chosen such that most of the as-implanted Fe atoms are confined close to the substrate surface. The depth profile of the 60 keV, 1015 cm−2 implant calculated by SRIM simulations is shown in figure 1(b), where the peak concentration $C_p$ is $\sim 1.5 \times 10^{18}$ cm−3. The implant doses were chosen based on our previous results for carbon nanotube, and GaN and Ga2O3 nanowire growth [18, 21].

For unpatterned (i.e. blanket) growth of silicon oxide nanowires, the as-implanted samples were placed in a one inch quartz tube furnace. The quartz tube was then purged at room temperature with 350 sccm flow rate of Ar and 200 sccm flow rate of H2 for 15 min. After purging the tube, the temperature was increased to 1100 °C and the samples were annealed for 30 min under the same gas flow rates (350 sccm Ar and 200 sccm H2) to grow the silicon oxide nanowires. The system was then cooled down to room temperature under the same gas flow rates and the samples were taken out of the furnace and characterized.

For patterned growth, the 60 keV, 1015 cm−2 as-implanted samples were patterned by standard photolithography and
FIGURE 2. Scanning electron microscopy (SEM) images of silicon oxide nanowires grown from Fe catalyst ion implanted into thermally grown SiO₂ layers. The implant energies and doses are (a) 60 keV, 10¹⁴ cm⁻², (b) 60 keV, 10¹⁵ cm⁻², (c) 60 keV, 10¹⁶ cm⁻², (d) 25 keV, 10¹⁵ cm⁻², and (e) 130 keV, 10¹⁵ cm⁻², respectively. The inset of part (b) shows the close-up of nanowires with diameters of ∼40 nm. The scale bar in the inset is 100 nm.

The as-grown samples were characterized by a JEOL JSM-6335F field emission gun scanning electron microscope (SEM) operating at 10 kV, a JEOL 2010F high resolution transmission electron microscope (HRTEM) operating at 100 kV equipped with selected area electron diffraction (SAED) and energy dispersive x-ray spectroscopy (EDS) capability, and a Digital Instruments Nanoscope III atomic force microscope (AFM) operated in the tapping mode. For the HRTEM characterization, the as-grown nanowires were dispersed in 2-propanol, the solution was sonicated, and...
3. Results and discussion

The SEM images of figures 2(a)–(c) show the unpatterned growth results from 60 keV implants with $10^{14}$, $10^{15}$, and $10^{16}$ cm$^{-2}$ dose, respectively. As seen in figure 2(a), no nanowires were grown on the low dose sample, whereas the $10^{15}$ and $10^{16}$ cm$^{-2}$ dose samples showed dense growth of long and interwoven nanowires. Using a simple model, the flux of Fe atoms diffusing to the oxide surface is proportional to the dose of the implant; as a consequence, a low dose results in insufficient size and density of catalyst nanoparticles and no nanowire growth. The SEM images of figures 2(d), (b), and (e) show the unpatterned growth results from $10^{15}$ cm$^{-2}$ dose implants with 25, 60, and 130 keV energy, respectively. Nanowire growth is observed for all energies; however, the nanowires on the 130 keV sample look more straight, most likely due to the lower nanowire density caused by the deeper location of catalyst in the SiO$_2$ layer (i.e. larger $R_p$) for that case. Furthermore, based on the analysis of SEM and TEM images, the diameters of the as-grown silicon oxide nanowires were found to be in the range between 10 and 50 nm (see inset of figure 2 (b)).

The as-grown nanowires from the 60 keV, $10^{15}$ cm$^{-2}$ implant were also characterized by HRTEM. Figures 3(a) and (b) show low resolution and high resolution TEM images, respectively, of the silicon oxide nanowires. The inset of figure 3(b) shows the SAED pattern of an individual silicon oxide nanowire. The high resolution TEM image and the SAED pattern confirm that the as-grown silicon oxide nanowires are amorphous. Figure 3(c) shows the EDS spectrum of an individual silicon oxide nanowire. The copper and carbon peaks in the spectrum come from the TEM grid that the nanowires are deposited on. The only other visible peaks are oxygen and silicon, confirming that the as-grown nanowires are indeed silicon oxide. Furthermore, quantitative EDS analysis revealed an atomic ratio of Si to O of 1:2.6.
Figure 4. (a) HRTEM image of a ∼30 nm diameter catalyst nanoparticle at the end of a nanowire. (b) Spot EDS spectrum of the nanoparticle. In addition to the peaks observed in figure 3(c), the spot EDS spectrum of the nanoparticle also shows Fe peaks, confirming that the seed contains Fe.

The as-grown samples were also characterized by cross-sectional TEM analysis. The cross-sectional TEM samples were prepared using a focused ion beam (FIB). Figure 5(a) shows the cross-sectional TEM image of the 60 keV, 10^{15} cm^{-2} implant sample after nanowire growth. A thick interwoven mesh of nanowires is visible at the top of the image. Below this interwoven mesh, a ∼480 nm thick SiO₂ layer is visible, demonstrating that most of the original 500 nm thick SiO₂ substrate still remains unconsumed after growth. Figure 5(b) shows a close-up cross-sectional TEM image of the near surface region of the sample, where the dark patches are the agglomerated Fe distributed within the SiO₂ layer.

In order to gain a further understanding of the effect of growth parameters on the silicon oxide nanowire growth, the effect of growth temperature, H₂ gas flow, and growth time was also investigated for the 60 keV, 10^{15} cm^{-2} implant sample. First, we report on the effect of temperature. The unpatterned growth was repeated by lowering the temperature to 1000°C, keeping all the other parameters constant. However, no nanowire growth was observed at 1000°C and lower temperatures could be explained by two factors: First, the diffusion rate of implanted Fe atoms towards the surface depends exponentially on temperature. As a result, the density
and size of catalyst nanoparticles formed on the SiO$_2$ surface by the out-diffusion of Fe atoms could be too low to nucleate nanowire growth at lower temperatures. Secondly, as it will be mentioned later, the proposed growth model involves the formation of droplets containing Fe, which then nucleate the silicon oxide nanowires. Nanowires cannot be nucleated if the temperature is not high enough to form these droplets.

Next, we investigate the role of hydrogen gas flow in the nanowire growth process. For this case, the growth temperature was kept at 1100 °C, but no H$_2$ gas was supplied during the growth process, keeping all the other parameters the same. No nanowire growth was observed in the absence of H$_2$ flow. Figure 6 shows the AFM image of the sample surface after growth without any H$_2$. In this case, it is clear from the AFM image that catalyst nanoparticles of sufficient size have not been formed in the absence of H$_2$. Hydrogen is known to enhance the diffusion of impurities in SiO$_2$ [23, 24]. The increase in the catalyst nanoparticle size and density when H$_2$ is flown during the growth can be explained by a similar enhancement of Fe diffusion in SiO$_2$ in H$_2$ ambient. Furthermore, SiO$_2$ can be reduced by hydrogen, which supplies more reactants of Si and O to the nanowire. As a result, the presence of H$_2$ gas flow is also a crucial factor for silicon oxide nanowire growth.

We have also investigated the effect of growth time. Nanowire growth was performed at 1100 °C for times between 5 and 30 min, keeping all the other parameters the same. The SEM images of the as-grown nanowires showed similar results, indicating that a dense mesh of silicon oxide nanowires can form even in 5 min growth.

Finally, we present the results of patterned growth from the 60 keV, 10$^{15}$ cm$^{-2}$ implant sample. After implantation, the SiO$_2$ layer was patterned by photolithography and etched by BOE, as explained previously. The sample was then grown at 1100 °C using the same standard recipe as in the unpatterned case (see figure 2(b)). The SEM images of figures 7(a) and (b) show the growth results. It is clear from figure 7 that the silicon oxide nanowires have grown selectively only from the unetched areas of the patterned sample. These results demonstrate that ion implantation-based nucleation methods can be used for patterned growth of silicon oxide nanowires in localized areas on a silicon substrate.

The vapor–liquid–solid (VLS) growth mechanism [6] has been commonly used to explain the growth of nanowires from catalyst nanoparticles. In VLS growth, the precursor is initially provided in gas phase and forms a liquid alloy with the catalyst nanoparticles. In our silicon oxide nanowire growth process, silicon and oxygen are provided directly from the solid SiO$_2$ substrate. The physical model for the growth of silicon oxide nanowires can be proposed as follows: first, the as-implanted Fe (figure 8(a)) out-diffuses during the annealing to form catalyst nanoparticles on the SiO$_2$ surface (figure 8(b)). The catalyst nanoparticles from which nanowire growth has not yet nucleated could also get larger by a surface diffusion and Ostwald ripening process. Droplets containing Fe form from these catalyst nanoparticles. When these droplets become supersaturated in silicon and oxygen, silicon oxide nanowires nucleate and precipitate out of these droplets (figures 8(c) and (d)).
4. Conclusions

In conclusion, we have experimentally demonstrated the patterned growth of silicon oxide nanowires from Fe$^+$ ions implanted into thermally grown SiO$_2$ layers. We have also studied the effect of implantation dose and energy, growth temperature, the presence of H$_2$ gas flow, and growth time on the silicon oxide nanowire growth. TEM, SAED, and EDS characterization revealed that the as-grown nanowires are amorphous silicon oxide with a Si:O ratio of 1:2.6. Furthermore, sufficiently high implant dose, high growth temperature, and the presence of H$_2$ gas flow were found to be crucial parameters for silicon oxide nanowire growth. We also demonstrated the patterned growth of silicon oxide nanowires in localized areas by lithographic patterning and etching of the implanted SiO$_2$ substrates before growth. We proposed a simple physical model to explain the growth results. This works opens up the possibility of growing nanowires directly from solid substrates, controlling the origin/location of nanowires at the submicron scale, and integrating them into nonplanar three-dimensional device structures with precise dose control. This method of nucleating nanowire growth is not limited to silicon oxide nanowires; it could also be generally applied to the growth of other types of nanowires for potential nanoscale device applications.

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References


