Synthesis of self-assembled iron silicon oxide nanowires onto single-crystalline Si(100)†

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Abstract:

Iron silicon oxide nanowire has been synthesized by putting single-crystalline Si(100) wafer into ammonium iron sulfate ((NH₄)₂Fe(SO₄)₂·9H₂O), hydrogen peroxide (H₂O₂) and triethylamine (TEA) solution heated to 70-100 C° in the air. The prepared iron silicon oxide nanowires with diameters of ~10nm (onto no-etched Si(100) wafer) and ~75nm (onto etched Si(100) wafer) and their self-assembling were characterized. The possible mechanism that accounted for the formation of iron silicon oxide nanowire is suggested based on experimental evidence.

Introduction

Recently, nanowires have received a lot of attention because of their nano-scale one-dimensional structure and unique mechanical, electrical, magnetic properties, as well as their potential applications for various mesoscopic electronic and optical devices.¹² Si-containing nanowires, such as amorphous and crystalline silicon oxide, silicon and doped silicon nanowires, are of great interest based on their vital roles in nanoscale electronics, sensors, optoelectronics and photoluminescent materials.³⁻⁶

There are several methods to prepare Si-containing nanowires. Among them, the traditional one is chemical vapor deposition;⁷ the others include the vapor-liquid-solution method,⁸ the laser vaporization method,⁹ and the solution growth.¹⁰ Holmes et al. have made defect-free silicon (Si) nanowires with a supercritical fluid solution-phase approach.¹⁰ Even though, there are few papers

† Electronic supplementary information (ESI) available: SEM images, EDX of Iron silicon oxide nanowires.
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reported the common solution-phase synthesis of Si-containing nanowires. In this paper, I report a new hydrothermal solution-phase preparation of iron silicon oxide nanowires and present a plausible mechanism for the formation of these nanowires.

Iron silicon oxide (Fe$_7$SiO$_{10}$) was first isolated in 1969 by Smuts et al. from a furnace refractory brick. The unit cell was monoclinic, with $a = 2.14$ nm, $b = 0.306$ nm, $c = 0.588$ nm, $\beta = 98^\circ$. The structure consisted of a stacking of FeO and Fe$_3$SiO$_6$ blocks. Later, Tilley et al. refined its composition with Fe$_7$(Si$_{0.94}$Fe$_{0.06}$)O$_{10}$ and found a paramagnetism to a weak ferromagnetism transition at ~250 K which showed that Fe$_7$SiO$_{10}$ is a ferromagnetic semiconductor below ~250 K. Bhagwat et al. have found the presence of Fe$_7$SiO$_{10}$ at the interface of Fe and SiO$_2$ interface. So far, Fe$_7$SiO$_{10}$ has potential applications as ferromagnetic semiconductors and magnetic-optical films.

**Experimental**

The iron silicon oxide nanowires were prepared onto two types of substrates: etched and non-etched p-type Si(001) wafers (Virginia Semiconductor). The etched Si(100) wafers were prepared by putting it into 30% HF solution for 24 hours and then rinsing with ethanol and deionized (DI) water. The typical procedure is as follow: 20.5 g (NH$_4$)$_2$Fe(SO$_4$)$_2$·9H$_2$O (0.05M) and 5.05g Triethylamine was dissolved into 100ml DI water, and heated the solution to 70 ºC, then the Si(100) wafer held by a PTFE clamer was put into the solution. 40ml 30% H$_2$O$_2$ was slowly drop-added into the solution within 1hr. For the etched Si(100) substrate, the reaction temperature was 96 ºC to promote the formation of SiO$_2$ layer and iron silicon oxide nanowires. The reaction was continued for another hour and some brown precipitations occured in the solution. The resulting film on the Si(100) surface was grey-brown and covered the whole wafer. The film was rinsed with ethanol and DI water several times to remove the residual TEA and dried in an oven at 60ºC. The p-type Si(001) wafers were supplied by Virginia Semiconductor, and doped with boron to a resistivity of 7.5 $\Omega$cm, and a hole density of about $2 \times 10^{15}$ cm$^3$. The sample was examined by X-ray diffraction measurements with a high-resolution Philips X'Pert MRD diffractometer. For the Bragg-Brentano scan, the primary optics module was a combination Gobel mirror and a two-crystal Ge(220) two-bounce hybrid monochromator which produces pure CuK$_\alpha_1$ radiation ($\lambda = 0.1540562$ nm) with a divergence of 25 arc sec. A 0.18º parallel plate collimator served as the secondary optics. FT-IR spectra were recorded on a Magna-IR Spectrometer 750 (Nicolet
Analyticl) with 512 scans under nitrogen at a resolution of 2 cm\(^{-1}\). The microstructures of the films were characterized by SEM micrographs with a Hitachi model S4700 cold field-emission scanning electron microscope and energy dispersive X-ray (EDX) analysis available on this SEM.

**Results and Discussions**

Fig. 1 shows the FE-SEM photographs of iron silicon oxide nanowires onto a non-etched Si(100) wafer. It can be seen from the figure that iron silicon oxide nanowires with diameters of ~10nm were formed and they are self-assembled into a tree-like network. More FE-SEM pictures were given in Electronic Supplementary Information† (Fig. S1). EDX studies were performed directly on the film on the Si(100) wafer. And the ratio of Fe: Si: O are 1: 3.2: 3.4(ESI† Tab. S1). The reason for differences from the stoichiometric ratio is that the substrate was a Si wafer which will enhance the amount of Si compared with Fe\(_7\)SiO\(_{10}\) formula. The uncovered Si wafer surface and the in-situ produced O\(_2\) will also react with Si substrate to produce SiO\(_2\). The reactions accounting for the formation of Fe\(_7\)SiO\(_{10}\) and SiO\(_2\) are shown as follows:

\[
14 \text{Fe}^{3+} + 5 \text{H}_2\text{O}_2 + 2 \text{SiO}_2 + 16 \text{H}_2\text{O} \rightarrow 2 \text{Fe}_7\text{SiO}_{10} + 42 \text{H}^+ + 5 \text{O}_2\uparrow \quad (1)
\]

\[
\text{Si (wafer)} + \text{O}_2 \xrightarrow{\text{Heat}} \text{SiO}_2 \quad (2)
\]

Then the ratio of Fe: Si: O can be explained by the existence of Fe\(_7\)SiO\(_{10}\), Si and SiO\(_2\). The formation of Fe\(_7\)SiO\(_{10}\) was also examined by X-ray diffraction. Fig. 2 shows the XRD pattern of iron silicon oxide nanowires onto non-etched Si(100) wafer. Except for the peak from Si(100) substrate with 2\(\theta\) = 33.0°(Si(200)) and 2\(\theta\) = 70.3°(Si(400)), the strongest peak from the film is at 2\(\theta\) = 42.6°, and all the other peaks are not strong enough to be used to determine the compound. Through carefully checking the data with JCPDS, we think that the iron silicon oxide is Fe\(_7\)SiO\(_{10}\) (JCPDS #78-1653). The peak at 42.6° was assigned to Fe\(_7\)SiO\(_{10}\) (112). This result is consistant with that from EDX.

FT-IR spectra of iron silicon oxide nanowires, deposited onto a non-etched Si(100) wafer, are shown in Fig. 3. It can be seen in Fig. 3 that the band at 1080 cm\(^{-1}\) associated with asymmetrical stretching Si-O-Si mode (AS\(_1\)) for SiO\(_2\) did not change before and after the deposition of Fe\(_7\)SiO\(_{10}\) nanowires onto the non-etched Si(100) wafer.\(^{16-17}\) The intensity of the Si-OH stretching vibration at 950 cm\(^{-1}\) was lowered a lot after Fe\(_7\)SiO\(_{10}\) nanowires were deposited onto non-etched Si(100)
This means that because of the reaction, the amount of SiO2 decreased, which was also can be observed from SEM image of the Fe$_7$SiO$_{10}$ nanowires film (ESI† Fig. S1(a)). In Fig. S1(a), it can be seen that in the middle, there still exists a layer of SiO$_2$ with thickness of about 50nm, whereas at most surface of the Si wafer, the SiO$_2$ layer had already disappeared through the reaction (1). The Si(100) wafer used in this experiment was non-etched and has a native amorphous SiO2 layer at about 50 nm which was consistent with our SEM result. The band at 800 cm$^{-1}$ associated with symmetrical stretching Si-O-Si mode(S$_1$) for SiO$_2$ did not change before and after the deposition. The formation mechanism for this tree-like self-assemble nanowire film will be suggested at the end of the paper after the discussion of the preparation of Fe$_7$SiO$_{10}$ nanowires deposited onto an etched Si(100) wafer.

The purpose of the etching of the Si(100) wafer with 30% HF solution is to remove the native amorphous SiO$_2$ layer on the Si wafer surface and to change the Si-OH to stable Si-H group. Fig. 6 (a) shows the FT-IR spectroscopy of the etched Si(100) wafer. It is obvious that the SiO$_2$ amount drops dramatically and no vibration at 950 cm$^{-1}$ is observed from Si-OH. Many researchers have observed that after HF etching, the SiO$_2$ layer on the Si wafer surface decreased to about ~5 nm. This very thin SiO$_2$ layer will affect the resulting Fe$_7$SiO$_{10}$ nanowires’ morphology in significant way.

Fig. 4 shows the FE-SEM photographs of the as-prepared Fe$_7$SiO$_{10}$ nanowires film. It can be seen from the figure that nanowires with diameter of ~ 60nm were formed and were connected to form a network. More SEM images are available from ESI† Fig. S3. EDX data was also shown in ESI† Fig. S4 and Tab. 2. The ratio of Fe: Si: O in this film is 1:39.4:3.4, which suggested a very small amount of Fe$_7$SiO$_{10}$ nanowires in the film. Most of the Si came from the Si(100) wafer. This situation is different from that of the non-etched Si(100) wafer in which half of Si came from SiO$_2$. The thin layer of Fe$_7$SiO$_{10}$ nanowires film was also verified by Fig. 7. This will be discussed later. The X-ray diffraction is shown in Fig. 5. The XRD pattern is almost the same as that of the Fe$_7$SiO$_{10}$ nanowires film deposited onto non-etched Si(100) wafer. As presented before, this pattern was assigned to Fe$_7$SiO$_{10}$ (112).

FT-IR spectra of Fe$_7$SiO$_{10}$ nanowires film (b) with the etched Si(100) wafer (a) are presented in Fig. 6. As discussed above, the etched Si wafer has a low amount of SiO$_2$ and Si-OH was effectively absent, which means the Si-OH group was not present in the SiO$_2$ layer surface, while the Si-H group was. After deposition of the Fe$_7$SiO$_{10}$ nanowires, the intensity at 1080 cm$^{-1}$
associated with the asymmetrical stretching of the Si-O-Si mode (AS₁) for SiO₂ increased dramatically, and there was the same trend in the 800 cm⁻¹ associated with the symmetrical stretching Si-O-Si mode for SiO₂. This suggests that a new SiO₂ layer is formed during the process via reaction (2). The band at 950 cm⁻¹ associated with Si-OH stretching vibration appeared in the Fe₇SiO₁₀ nanowires film, which also suggested the formation of a new SiO₂ layer. The excess amount of H₂O₂ in the solution produced excess amount of O₂ either through oxidation by Fe(III) ions or its own disproportionation which will easily react with the Si-H or Si wafer to generate the SiO₂ layer.

To understand the mechanism of the growth of Fe₇SiO₁₀ nanowires, a high magnification FE-SEM image was analyzed in Fig. 7. It can be observed from that figure that a SiO₂ layer with a thickness about ~20 nm deposited onto the Si(100) substrate, and within and above the SiO₂ layer, a Fe₇SiO₁₀ nanowire network formed. The diameter of the Fe₇SiO₁₀ nanowires was about 60 nm, which is much higher than that of Fe₇SiO₁₀ nanowires deposited onto non-etched Si(100) wafer. The reason for this is that in the etched Si(100) wafer, the SiO₂ layer is very thin, higher temperature (96ºC) was used to perform the reaction than was used for the non-etched Si(100) wafer (70ºC). It is understandable that in the previous conditions, much thicker Fe₇SiO₁₀ nanowires were obtained than the latter.

Based on all the experiment evidence, we propose a growth model to account for the formation of iron silicon oxide nanowires, as shown in Fig. 8. As seen in the model for non-etched Si wafers, Fe(III) and H₂O₂ reacted with the SiO₂ layer to form nanowires within the layer by using triethylamine as a template, and most of the SiO₂ in the layer gradually reacted with the solution to form brown Fe₂Si₂O₆ precipitation. At the end, only the tree-like Fe₇SiO₁₀ nanowires cluster onto the Si(100) wafer surface remained, just as shown in the Fig. 1. For the etched Si wafer, the SiO₂ layer was first formed with a thickness of about ~20 nm, which takes much time. Then the next step is the same as with the non-etched Si(100) wafer situation. But in this situation the Fe₇SiO₁₀ nanowires just formed the network and there is no enough time for the new-formed SiO₂ layer to react with the Fe(II) produced by reduction reaction of the Fe(III) to form Fe₂Si₂O₆, then at the same reaction time, in this situation, ended with Fe₇SiO₁₀ nanowires within and above the SiO₂ layer, as shown in Fig. 7. If the reaction lasted for long time for the etched Si wafer, it will be supposed to get the same result with the non-etched Si wafer. The formation of the highly-ordered
Fe$_7$SiO$_{10}$ nanowires structures could be driven by triethylamine, which is well known as a self-assemble template.$^{20}$

In conclusion, Fe$_7$SiO$_{10}$ nanowires self-assemble films have been deposited onto etched and non-etched Si(100) wafers. The SiO$_2$ layer is critical to form Fe$_7$SiO$_{10}$ nanowires, and triethylamine also plays a vital role for both the formation of the Fe$_7$SiO$_{10}$ nanowires and their self-assembling. The magnetic properties and its potential applications in ferromagnetic semiconductors and other areas will be examined in our future research.

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Figure captions

Figure 1. FESEM of iron silicon oxide nanowires deposited onto non-etched Si (100) wafers with low (a) and high (b) magnification.

Figure 2. XRD of iron silicon oxide nanowires deposited onto non-etched Si (100) wafer.

Figure 3. FT-IR spectrum of non-etched Si(100) wafer (a) and iron silicon oxide nanowires grown on it.

Figure 4. FESEM of iron silicon oxide nanowires deposited onto etched Si(100) wafer with low (a) and high (b) magnification.

Figure 5. XRD of iron silicon oxide nanowires deposited onto etched Si(100) wafer

Figure 6. FT-IR spectrum of etched Si(100) wafer (a) and iron silicon oxide nanowires grown on it.

Figure 7. FESEM of iron silicon oxide nanowires deposited onto etched Si(100) wafer with high magnification.

Figure 8. Proposed growth model based on the results presented in this paper.
Fig. 1 FESEM of iron silicon oxide nanowires deposited onto non-etched Si (100) wafer with low (a) and high (b) magnification.
Fig. 2 XRD of iron silicon oxide nanowires deposited onto non-etched Si(100) wafer.
Fig. 3 FT-IR spectrum of non-etched Si(100) wafer (a) and iron silicon oxide nanowires gown on it.
Fig. 4 FESEM of iron silicon oxide nanowires deposited onto etched Si(100) wafer with low (a) and high (b) magnification.
Fig. 5 XRD of iron silicon oxide nanowires deposited onto etched Si(100) wafer.
Fig. 6 FT-IR spectrum of etched Si(100) wafer (a) and iron silicon oxide nanowires grown on it.
**Fig. 7** FESEM of iron silicon oxide nanowires deposited onto etched Si(100) wafer with high magnification.
Fig. 8 Proposed growth model based on the results presented in this paper.
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Fig. S1 presented the FE-SEM photographs of the as-prepared Fe$_7$SiO$_{10}$ nanowires self-assemble films deposited onto a non-etched Si(100) wafer. Please note Fig. S1(a), where there still existed some the SiO$_2$ layer with thickness of about ~50nm and the other parts there just left Fe$_7$SiO$_{10}$ nanowires film.

Fig. S2 presented the EDX spectrum of the film based on directly measuring the film on Si substrate and Tab. S1 showed the composition of the film. The carbon shown in Fig. S2 and Tab. S1 is from triethylamine which is either adsorbed in the Fe$_7$SiO$_{10}$ nanowires surface or residual inside the film.

Fig. S3 presented the FE-SEM photographs of the as-prepared Fe$_7$SiO$_{10}$ nanowires self-assemble films deposited onto etched Si(100) wafer.

Fig. S4 presented the EDX spectrum of the film based on directly measuring the film on Si substrate and Tab. S2 showed the composition of the film. The carbon is from triethylamine which is either adsorbed in the Fe$_7$SiO$_{10}$ nanowires surface or residual inside the film. Here the carbon containing is much higher than that of non-etched Si wafer situation, which may be explained as during the formation of the SiO$_2$ layer and much large amount of triethylamine was trapped inside it.
**Fig. S1** FESEM of iron silicon oxide nanowires onto non-etched Si(100) wafer from low to high magnification.
**Fig. S2** EDX of iron silicon oxide nanowires deposited on non-etched Si(100) wafer.

**Table S1** EDX result of iron silicon oxide nanowires onto non-etched Si(100) wafer

| Element | Wt %  | At %  |
|---------|-------|-------|
| C K     | 2.51  | 5.26  |
| O K     | 26.9  | 42.4  |
| Fe L    | 27.6  | 12.5  |
| Si K    | 42.99 | 39.84 |
| Total   | 100.00| 100.00|
Fig. S3 FESEM of iron silicon oxide nanowires onto etched Si(100) wafer from low to high magnification.
**Fig. S4** EDX of iron silicon oxide nanowires deposited onto etched Si(100) wafer.

**Table S2** EDX result of iron silicon oxide nanowires onto etched Si(100) wafer

| Element | Wt %  | At %  |
|---------|-------|-------|
| C K     | 7.51  | 15.76 |
| O K     | 5.38  | 8.48  |
| Fe L    | 5.52  | 2.49  |
| Si K    | 81.59 | 73.26 |
| Total   | 100.00| 100.00|