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Materials

Effect of Fe metal on the growth of silicon oxide nanowires

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Abstract: Silicon oxide (SiO_x) nanowires are generally grown on Si substrate under the catalysis of Au in N_2 atmosphere at elevated temperatures. Because the price of Au metal is quite high, Fe metal is then used to replace a part of Au for catalyzing the growth of SiO_x nanowires. The results show that the Fe film can be used as the diffusion barrier of Au. SiO_x nanowires are grown on Au/Fe/Si substrate at 1030°C. Under the catalysis of Fe/Au, the efficiency for the growth of SiO_x nanowires is promoted.

Key words: silicon oxide ; nanowires; Au catalyst; Fe substitution; Si substrate

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1. Introduction

Because silicon oxide (SiO_x) nanowires possess some particular physical properties and have much potential for applications as blue light emitters, optical sensors [1], and reinforcing composites [2], they have greatly attracted the attention of the researchers. Zhang *et al*. prepared aligned SiO_x nanowires on anodic alumina by a sol-gel method [3]. Zhang *et al*. prepared ordered amorphous SiO_x nanowires on a Ga ball placed on top of a Si wafer [4]. Park *et al*. synthesized amorphous SiO_x nanowires on NiO-catalyzed silicon substrate [5]. Jiang *et al*. produced SiO_x nanowires by using Fe-Co-Ni alloy nanoparticles as catalyst and showed that they had a strong blue-green emission at 525 nm, which might be related to oxygen defects [6]. Zhang *et al*. displayed that SiO_x nanowires could be formed on tin balls by chemical vapor deposition *via* a vapor-liquid-solid (VLS) process [7]. Wang *et al*. reported that amorphous SiO_x nanowires could be grown on silicon wafers by using Pt as catalyst [8]. Park *et al*. used Au and Pd-Au thin films as catalysts to grow amorphous SiO_x nanowires on Si substrate *via* a solid-liquid-solid (SLS) mechanism [9]. Lin *et al*. synthesized amorphous SiO_x nanowires from silicon monoxide powder under supercritically hydrothermal conditions [10]. Wang *et al*. fabricated SiO_x nanowires on patterned nanodots containing exposed hydrogen silsesquioxane (HSQ)/Fe-SiO_2 nanocomposites [11]. Zhang *et al*. used low melting point metal Pb as catalyst for the large-scale growth of highly aligned SiO_x nanowires *via* VLS process [12].

In the present work, the Au and Fe/Au films were used as catalysts for the growth of SiO_x nanowires. Due to the expensive price of Au, a part of Au catalyst was replaced by Fe in order to reduce the cost of SiO_x nanowire preparation. The growth behavior of SiO_x nanowires using the Au film as catalyst was compared with that using the Fe/Au film as catalyst. The effect of Fe metal on the growth of SiO_x nanowires was further studied.

2. Experimental

N type silicon wafer with (100) surface and 4-7 Ω·cm resistivity was used as substrate for the growth of SiO_x nanowires. Before being coated with the catalyst films of Au and Au/Fe, the substrate surface was successively cleaned in the following solutions: acetone with ultrasonic vibration for removing the dust and organic substance, a mixture solution of H_2SO_4 and H_2O_2 for removing the grease and inorganic impurities, and 10% HF solution for removing the native SiO_x.

The Fe film was coated on the silicon surface in an electron beam evaporation deposition chamber at a vacuum pressure of 1×10^{-6} torr with a voltage of 6.5

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kV, a current of 27 mA, and a deposition rate of about 0.1 nm/s. The Au film was coated on the surface of Fe film or silicon substrate under the condition of 6.5 kV, 130 mA, and about 0.1 nm/s deposition rate. The SiO_x nanowires were grown on the substrate of Au (20 nm)/Si or Au (10 nm)/Fe (10 nm)/Si in a tube furnace. After the substrate was put into the tube furnace at 600°C, the furnace temperature was then increased up to about 1050°C and kept for a period of time in the N_2 gas with a flow rate of 1600 cm^3/min. The sample was finally taken out when the furnace temperature was decreased down to 600°C.

The SiO_x nanowires, Fe/Au and Au catalysts, and Si substrates were characterized using scanning electron microscopy (SEM, JEOL-JSM-6380) and transmission electron microscopy (TEM, JEOL-JEM 2010). The procedure of preparing the sample for TEM cross-section view consists of the following steps: (1) the as-plated samples were cut into 2 mm×3 mm pieces and were glued on a glass plate by thermoplastic resin for grinding the Si substrate; (2) several pieces of ground samples were stuck together by AB adhesive, and their two lateral sides were thinned by grinding; (3) the samples were stuck to a Cu ring with 3 mm diameter by AB adhesive and put into an ion thinning machine for further thinning the lateral thickness of samples; (4) after the samples were broken through by ion beams, they then could be observed for TEM cross-sectional views. Most of the micrographs were taken under two-beam diffractions with deviation parameter s_g slightly positive.

3. Results and discussion

Fig. 1 shows the SEM views of the samples at 1000°C for 30 min in N_2 gas with a flow rate of 1600 cm^3/min for Au (20 nm)/Si and Au (10 nm)/Fe (10 nm)/Si substrates, respectively. It can be seen that no SiO_x nanowires are grown on the two substrates. Fig. 1(a) shows that the Au (20 nm) film has agglomerated into many nanosized particles. Fig. 1(b) reveals that only the Au (10 nm) film agglomerates into nanosized particles and the Fe (10 nm) still keeps at film state.

Fig. 2 shows the SEM views of the samples at 1030°C for 30 min in N_2 gas with a flow rate of 1600 cm^3/min for Au (20 nm)/Si and Au (10 nm)/ Fe (10 nm)/Si substrates, respectively. Fig. 2(a) reveals that there are SiO_x wires grown on Au (20 nm)/Si substrate, in which the diameter of SiO_x wires is about 500 nm and the length of SiO_x wires is not uniform, a part of them being very short and some of them being several μm. Fig. 2(b) reveals that the SiO_x nanowires grown on Au (10 nm)/Fe (10 nm)/Si substrate are quite long and tangled with each other.

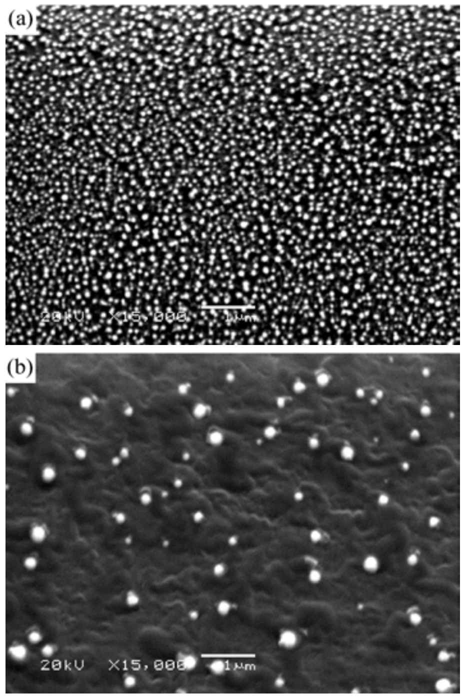


Fig. 1. SEM views of samples at 1000°C for 30 min in N_2 gas with a flow rate of 1600 cm^3/min: (a) Au(20 nm)/Si substrate; (b) Au(10 nm)/Fe(10 nm)/Si substrate.

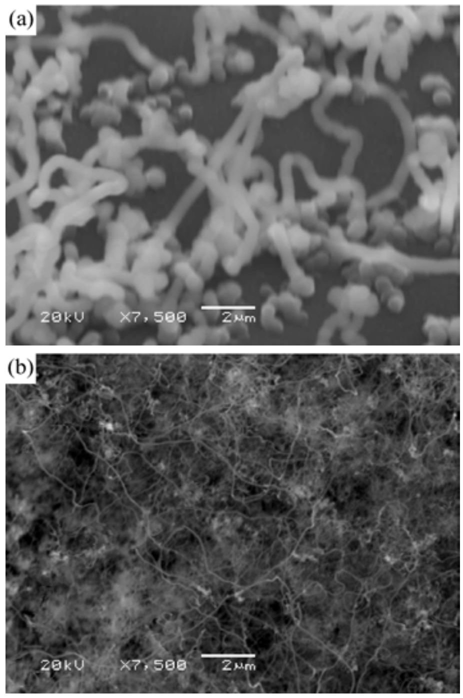


Fig. 2. SEM views of samples at 1030°C for 30 min in N_2 gas with a flow rate of 1600 cm^3/min: (a) Au(20 nm)/Si substrate; (b) Au(10 nm)/Fe(10 nm)/Si substrate.

Fig. 3 shows the SEM views of the samples at 1050°C for 30 min in N_2 gas with a flow rate of 1600 cm^3/min for Au (20 nm)/Si and Au (10 nm)/Fe (10 nm)/Si substrates, respectively. Fig. 3(a) shows that only a little amount of SiO_x nanowires are grown on Au (20 nm)/Si substrate and their length is about 1 μm.

Fig. 3(b) shows that the SiO_x wires grown on Au (10 nm)/Fe (10 nm)/Si substrate are above 1 μm in length and have diameter roughly ranging from 50 to 300 nm.

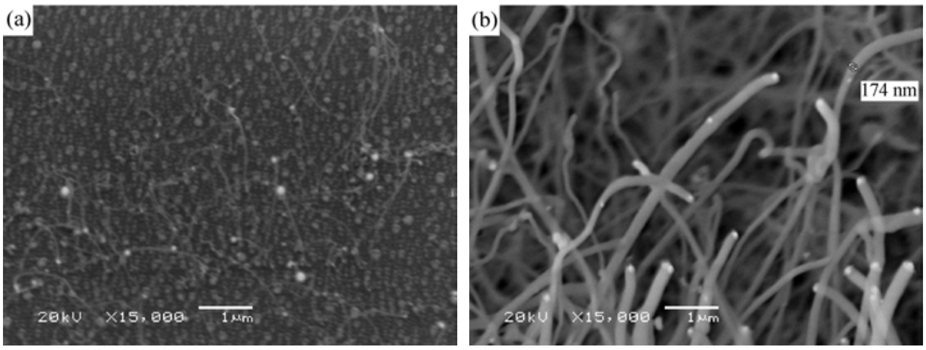
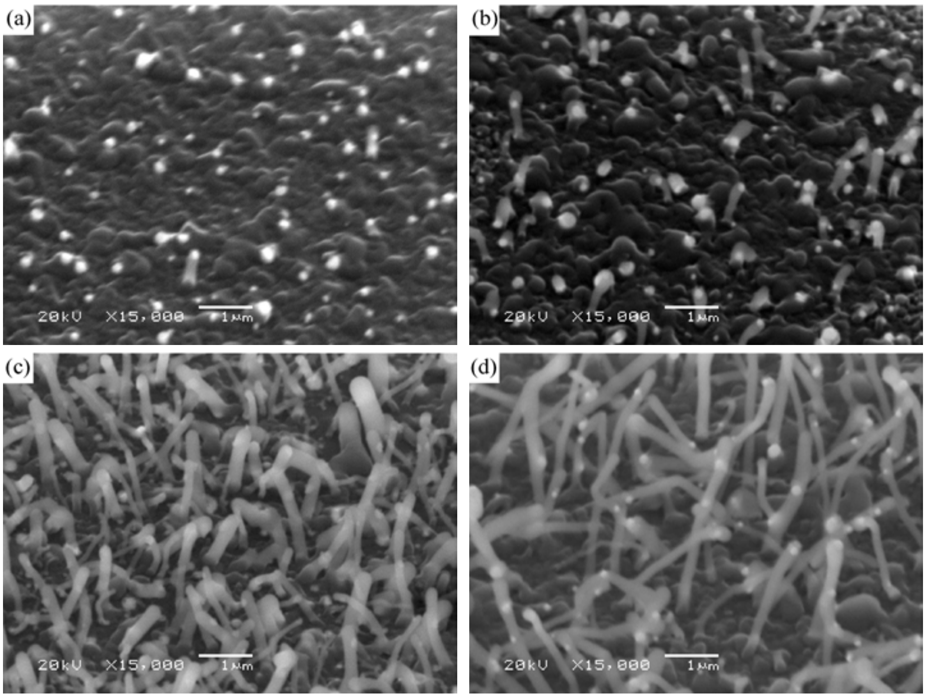


Fig. 3. SEM views of samples at 1050°C for 30 min in N_2 gas with a flow rate of 1600 cm^3/min: (a) Au(20 nm)/Si substrate; (b) Au(10 nm)/Fe(10 nm)/Si substrate.

Fig. 4 shows the SEM views of the samples on Au (10 nm)/Fe (10 nm)/Si at 1050°C in N_2 gas with a flow rate of 1600 cm^3/min for 5, 10, 15, 20, and 30 min, respectively. These views reveal that the SiO_x nanowires cannot grow up till the growth time is increased up to about 10 min, and the length of SiO_x nanowires is increased with the increase in growth time as shown in Figs. 4(c)-4(e). These views also show that there is a nanoparticle, which is confirmed as Au, on the top of each SiO_x nanowire.



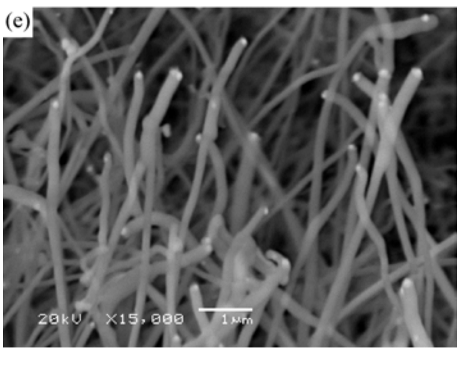


Fig. 4. SEM views of samples on Au(10 nm)/Fe(10 nm)/Si substrates at 1050°C in N_2 gas with a flow rate of 1600 cm^3/min for different time: (a) 5 min; (b) 10 min; (c) 15 min; (d) 20 min; (e) 30 min.

Fig. 5 shows the SEM views of the samples at 1050°C for 30 min in N_2 gas with a flow rate of 1600 cm^3/min for Fe (20 nm)/Si and Fe (10 nm)/Si substrates, respectively. There are no any SiO_x nanowires grown on the two substrates. However, the Fe (10 nm) and Fe (20 nm) films both have agglomerated into particles and the size of the Fe particles is directly proportional to the thickness of the Fe film. Fig. 6

shows the SEM view of the sample on Au (10 nm)/Si substrate at 1050°C for 30 min in N_2 gas with a flow rate of 1600 cm^3/min. Only very little quantity of SiO_x nanowires are grown on this substrate, which is similar to those in Fig. 3(a) for the substrate of Au (20 nm)/Si under the same growth condition.

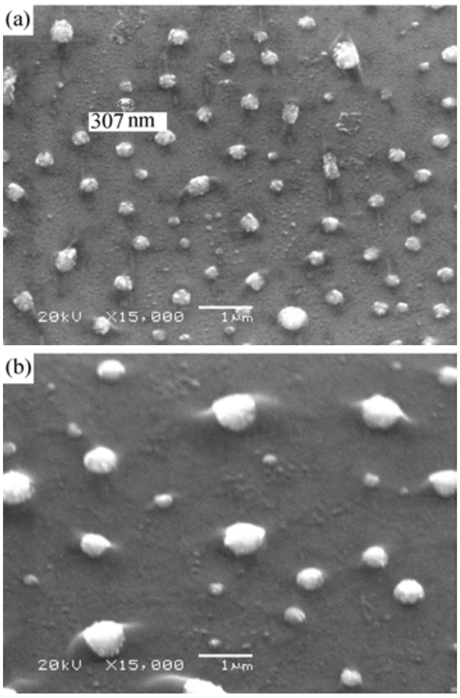


Fig. 5. SEM views of asamples at 1050°C for 30 min in N_2 gas with a flow rate of 1600 cm^3/min: (a) Fe(10 nm)/Si; (b) Fe(20 nm)/Si.

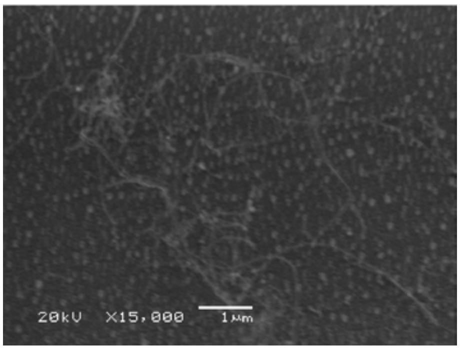


Fig. 6. SEM view of a sample on Au(10 nm)/Si substrate at 1050°C for 30 min in N_2 gas with a flow rate of 1600 cm^3/min.

Fig. 7 shows the TEM cross-section views of samples at 1050°C for 5 min in N_2 gas with a flow rate of 1600 cm^3/min for Au(20 nm)/Si and Fe(10 nm)/Si substrate, respectively. In Fig. 7(a), a large part of Au diffuses downward into Si substrate; meanwhile, the other Au becomes relatively small particles and catalyzes the growth of SiO_x nanowires, which look like spheres. In Fig 7(b), the Fe film still keeps at film state.

Fig. 8 shows the TEM cross-section view and diffraction pattern for the sample on Au (10 nm)/Fe (10 nm)/Si substrate in N_2 gas with a flow rate of 1600 cm^3/min. Fig. 8(a) reveals that the Fe film has agglomerated into particles on the Si surface and the Au film has also become particles, which catalyzes the growth of SiO_x nanowires and exists on the top of SiO_x nanowires. The electron diffraction pattern of SiO_x nanowires of Fig. 8 (b) reveals the SiO_x nanowires are amorphous.

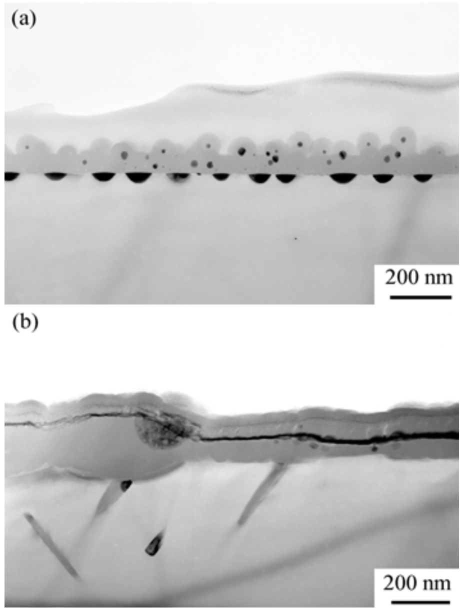


Fig. 7. TEM cross-section views of samples at 1050°C for 5 min in N_2 gas with a flow rate of 1600 cm^3/min: (a) Au(20 nm)/Si substrate; (b) Fe(10 nm)/Si substrate.

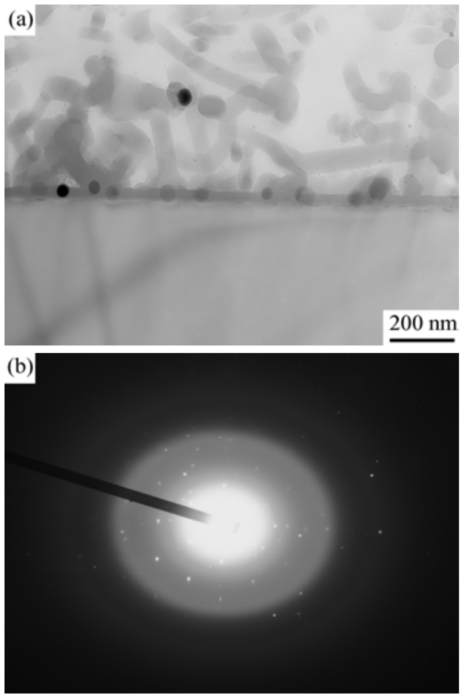


Fig. 8. TEM cross-section view (a) and electron diffraction pattern (b) of a sample on Au(10 nm)/Fe(10 nm)/Si substrate at 1050°C for 5 min in N_2 gas with a flow rate of 1600 cm^3/min.

From the results stated above, the growth behavior of SiO_x nanowires can be described as the following. For the catalyst of Au in N_2 gas with a flow rate of 1600 cm^3 /min, if the growth temperature is 1000°C, no SiO_x nanowires are grown on Au/Si substrate; if the growth temperature is 1030°C, SiO_x nanowires can be grown on Au/Si, which have the thickness of about 500 nm and nonuniform in length. If the growth temperature is 1050°C, only a little amount of SiO_x nanowires can be grown on Au/Si substrate. A large part of Au can diffuse downward into Si at elevated temperatures. When the thickness of Au film in Au/Si substrate is decreased from 20 nm to 10 nm, the amount of SiO_x nanowires grown on Au/Si is then reduced due to the decrease of Au particles.

For the catalyst of Au/Fe in N_2 gas with a flow rate of 1600 cm^3/min, if the growth temperature is 1000°C, no SiO_x nanowires can be grown on Au/Fe/Si substrate; if the growth temperature is 1030°C, thin and long SiO_x nanowires can be grown on Au/Fe/Si substrate; if the growth temperature is 1050°C, the SiO_x nanowires grown on Au/Fe/Si substrate are relatively short and thick, they cannot grow up till the growth time is increased up to about 10 min and their length increases with the increase of growth time.

The effect of Au/Fe catalyst on the catalysis of SiO_x nanowires growth is larger than that of Au catalyst. This phenomenon can be ascribed to that the Fe film can be used as the diffusion barrier of Au. Due to the existence of Fe film between Au and Si, the Au atom cannot diffuse into Si; therefore, all Au can act as catalyst for the growth of SiO_x nanowires. Because the melting point of Au is lower than that of Fe, the Au film agglomerates into particles more easily than Fe film. In the growth process of SiO_x nanowires, if the temperature is appropriate, the Au film can all agglomerate into particles at relatively early time and the Fe film successively agglomerates into particles. After the Si atom diffuses outward through the boundary between Fe particles and goes into the Au particles, the SiO_x nanowires are then formed due to the supersaturation of Si in Au and the oxidation of Si with O.

4. Conclusion

Under the atmosphere of N_2 gas with a flow rate of 1600 cm^3/min, amorphous SiO_x nanowires can be grown on Au/Si and Au/Fe/Si substrates at appropriate growth temperature. The effect of Au/Fe catalyst on the catalysis of SiO_x nanowire growth is larger than that of Au catalyst. In the growth process of SiO_x nanowires on the Au/Si substrate, a large part of Au would diffuse downward into Si and only the other part of Au agglomerated to particles could be used as catalyst to catalyze the SiO_x nanowire growth. In the growth process of SiO_x nanowires on the Au/Fe/Si substrate, the Fe film can be used as diffusion barrier of the Au atom into Si at relatively early time and all the Au can then act as catalyst for the growth of SiO_x nanowires. Therefore, using the Au/Fe/Si substrate, the SiO_x nanowires can be grown better than that of Au/Si substrate.

References

[1] L. Tong, J. Lou, R.R. Gattas, *et al.*, Assembly of silica nanowires on silica aerogels for microphotonic devices, *Nano Lett.*, 5(2005), p.259.

[2] X.Q. Yan, W.Y. Zhou, L.F. Sun, *et al.*, The influence of hydrogen on the growth of gallium catalyzed silicon oxide nanowires, *J. Phys. Chem. Solids*, 66(2005), p.701.

[3] M. Zhang, Y. Bando, K. Wada, and K. Kurashima, Synthesis of nanotubes and nanowires of silicon oxide, *J. Mater. Sci. Lett.*, 18(1999), p.1911.

[4] B. Zhang, Y. Wu, P. Yang, and J. Liu, Synthesis of ultra-long and highly oriented silicon oxide nanowires from liquid alloys, *Adv. Mater.*, 14(2002), p.122.

[5] B. Park and K. Yong, Characterization of silicon oxide nanowires directly grown from NiO/Si, *Surf. Rev. Lett.*, 11(2004), p.179.

[6] Z. Jiang, T. Xie, B.Y. Yuan, *et al.*, Synthesis of core-shell nanowires of FeCoNi alloy core with silicon oxide layers, *Appl. Phys. A*, 81(2005), p.477.

[7] J. Zhang, B. Xu, Y. Yang, *et al.*, Catalyzed-assisted growth of well-aligned silicon oxide nanowires, *J. Non Cryst. Solids*, 352(2006), p.2859.

[8] C.Y. Wang, L.H. Chan, D.Q. Xiao, *et al.*, Mechanism of solid-liquid-solid on the silicon oxide nanowire growth, *J. Vac. Sci. Technol. B*, 24(2006), p.613.

[9] H.K. Park, B.L. Yang, S.W. Kim, *et al.*, Formation of silicon oxide nanowires directly from Au/Si and Pd-Au/Si substrates, *Phys. E*, 37(2007), p.158.

[10] L.W. Lin, Y.H. Tang, X.X. Li, *et al.*, Water-assisted synthesis of silicon oxide nanowires under supercritically hydrothermal conditions, *J. Appl. Phys.*, 101(2007), p.014314.

[11] F. Wang, M. Malac, R.F. Egerton, *et al.*, Controlled growth of silicon oxide nanowires from a patterned reagent, *J. Phys. Chem. C*, 111(2007), p.1865.

[12] J. Zhang, F.H. Jiang, Y.D. Yang, and J.P. Li, Molten Pb as a catalyst for large-scale growth of highly aligned silicon oxide nanowires, *J. Cryst. Growth*, 307(2007), p.76.