OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 3, No. 4, April 2009, p. 343 - 346

Formation and characterization of SiO_2 nanowire groups on Si substrate by SLS mechanism

R. KUMAR*, N. THAKUR
Department of Physics, Himachal Pradesh University, Shimla 171005 (H.P), India

SiO_2 nanowires in groups have been grown on silicon substrate by annealing SiO particles on Si substrate. The formation of nanowires has been observed trough solid-liquid-solid (SLS) mechanism. Initially using SiO on Si substrate SiO_2 nanowires were grown in groups using annealing method. These SiO_2 nanowires were etched from Si substrate using HF solution and the same Si substrate was used for second annealing without using SiO particles; again in second annealing SiO_2 nanowires have been grown. It has been observed once the nanowires are nucleated on Si substrate no supply of any precursor is necessary for the further growth of SiO_2 nanowire on Si substrate. The observed pits on the Si substrate indicate that SLS mechanism is involved in the formation of nanowires.

(Received March 04, 2009; accepted April 23, 2009)

Keywords: Nanowire; SiO_2, Si substrate, Annealing temperature

1. Introduction

One dimensional nanostructure is of high importance for applications in semiconductor industry as well as in mechanical and chemical areas. Also these are used for testing and understanding the fundamental role of small dimension and size in the different basic properties such as electrical, mechanical and optical. Nanomaterials including oxides, nitrides and carbides because of their various novel properties have been studied extensively (1-4) in the past decade. Among these materials SiO_2 has attracted considerable attention because of its potential application in nanoscale devices such as, buried oxide layer in transistors (5), nano springs (6), wave guides near field optical microscopes (7, 8), nano cables (9) and nanowires (10) etc. The SiO_2 nanowires have variety of applications in nano-scale optical devices. The nanowires have been synthesized using different techniques such as, the metallic nanoparticles-assisted technique (11-17), laser ablation technique (18, 19) and direct thermal treatment of silicon powder under the presence of graphite (20,). So far as the growth mechanism is concern, in literature only few mechanisms for SiO_2 nanowires formation have been reported, such as Zhu *at el.* (21) used a mixture of silica and silicon powders as the precursor. They have suggested the formation of SiO (g) in initial stage which decomposes to the formation of SiO_2 nanowires. Latter on they have also reported that SiO_2 nanowires can be grown only by using silicon powder instead of a mixture of silica and silicon (22). In another mechanism, it has been reported that initially Si nanowires form, which subsequently oxidize to SiO_2 nanowires. Here we have conducted two annealing experiments, in first experiment the synthesis of SiO_2 nanowires was achieved using SiO powder on the surface of Si substrate. Thus formed SiO_2 nanowires were etched from the Si substrate. In second experiment SiO_2 nanowires were grown on the same Si substrate just by annealing the substrate. In this study we have obtained two results; (I) SiO_2 nanowires grown in groups on Si substrate and (II) once the nanowires are nucleated on Si substrate no supply of any precursor is necessary for the further formation of SiO_2 nanowires. The nanowires grow through solid-liquid-solid (SLS) mechanism.

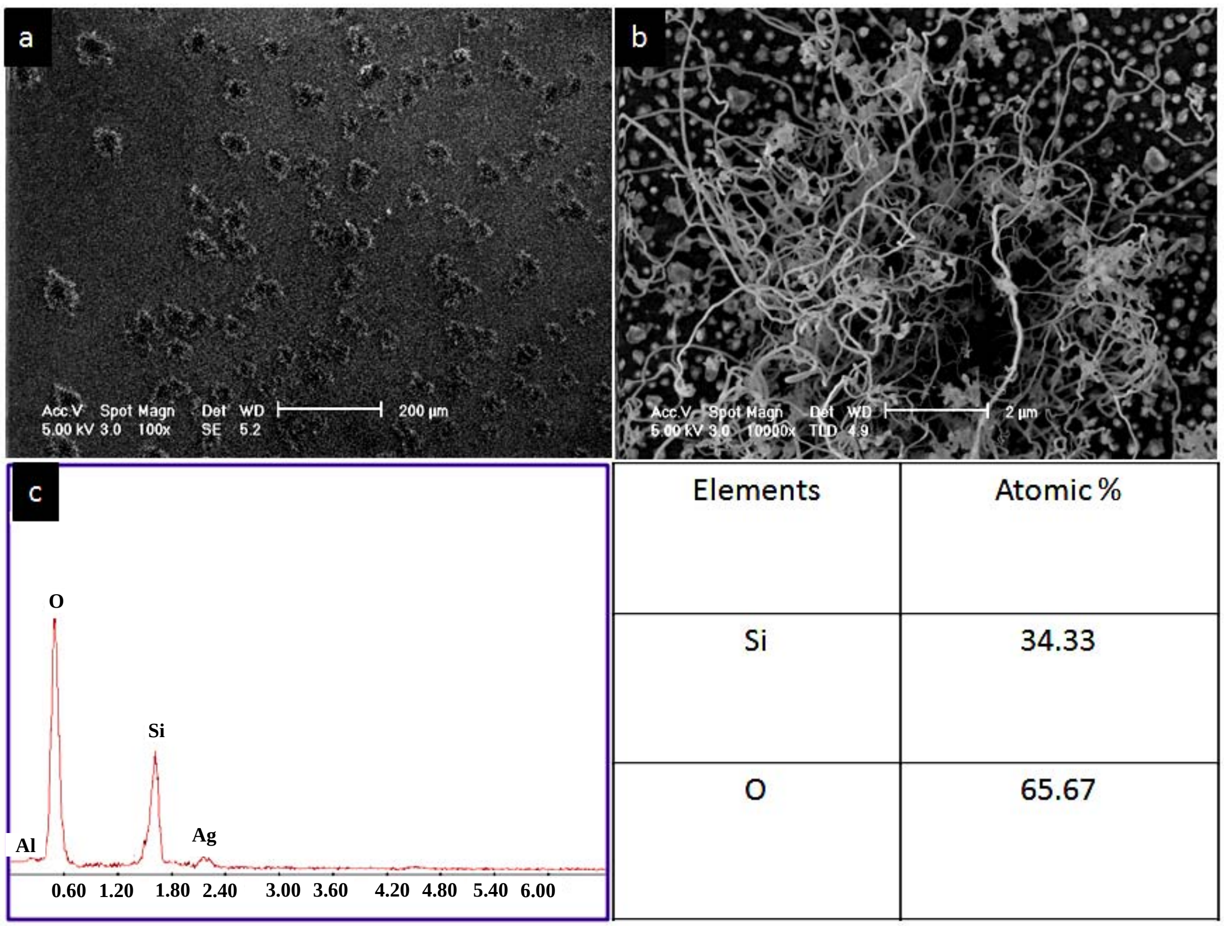
2. Experimental

The SiO_2 nanowires in groups were synthesized by thermal annealing of SiO (powder) on Si substrate at 1000 ^{o}C in a quartz tube. Boron doped p-type Si (100) substrate cleaned with acetone and diluted hydrofluoric acid, was dipped for 5 minutes into a 2 M suspension of powdered SiO (Aldrich, purity 99.99%) in ethanol. Thus prepared Si substrate was placed at the center of a horizontal quartz tube furnace. Ar gas was allowed to flow at the rate of 100 ml/min to make the environment inert inside the reaction chamber before raising the temperature. After 30 min of Ar flow, H_2 was introduced inside the reaction chamber at 80 ml/min, meanwhile the temperature of the furnace was raised to 1000^{o}C at a heating rate of 16.66 ^{o}C/min. The reaction was carried out at 1000^{o}C for 1 hour. After cooling down the furnace, sample was taken out and the nanowires grown in groups on the Si substrate were characterized by field emission scanning electron microscopy (FESEM) installed with energy dispersive x-ray spectroscopy (EDX) and the transmission electron microscopy (TEM: 200 kV, JEOL-JEM 2100).

These SiO_2 nanowires were removed from Si substrate by etching the substrate in HF (10%) solution for 10 min. The etched Si substrate after confirming through FESEM was further placed inside the reaction chamber and the temperature of the furnace was raise to 1000^{o}C. Again the annealing reaction was performed for 1 hour in the presence of H_2 (80 ml/min) and Ar (100 ml/min) without using SiO powder. The grown nanowires were further characterized.

3. Results and discussion

Fig. 1(a) shows FESEM image of nanowires grown while using SiO (powder) suspension in ethanol on the surface of Si substrate. This image shows the formation of SiO_2 nanowires in groups on the Si substrate. This group is composed typically of several nanowires varying in diameter from 40 nm to 70 nm and height up to 10 µm. From the high magnification FESEM image in Fig. 1(b), the nanowires can be seen coming out from a pit at the surface of Si substrate. Therefore the group of nanowires grows from a pit i.e. with each group a pit is associated. To determine elemental composition of these nanowires, EDX spectroscopy study was performed. The EDX spectrum is shown in Fig. 1(c). The measured atomic % of elements is found nearly in ratio 1:2 for Si and O respectively. These EDX results are shown in table of Fig. 1.



Elements	Atomic %
Si	34.33
O	65.67

Fig. 1 (a). It shows the FESEM image of the nanowires grown group wise on Si surface, (b) is a high magnification FESEM image of a group of wires, (c) shows the EDX spectrum of SiO_2 nanowires and in table is the elemental composition of nanowires.

In second experiment, the SiO_2 nanowires were removed from the surface of Si using 10% HF solution. The FESEM image of the Si substrate after removing SiO_2 nanowires is shown in Fig. 2(a). This image clearly shows that the nanowires are completely removed from the surface of Si substrate. Only the pits consisting roots of SiO_2 nanowire grown in the first experiment are observed clearly. In high magnification FESEM image shown in Fig. 2(b) a nanowire is shown to be etched from the surface level while actually it exists inside the pit. These FESEM images in Figs. 2(a) and 2(b) show that no nanowire exists outside the pit after etching through HF solution, except the roots inside the pit. This Si substrate was placed inside the quartz tube for second annealing without using SiO powder suspension on its surface. We found that the nanowires grow again from the pits, as shown in Fig. 2(c). Also it has been observed that the nanowires grow only from the pit rather than the rest surface of Si substrate. Again the EDX characterizations revealed the atomic % of Si and O for second time grown nanowires in ratio 1:2 which again composes SiO_2.

Fig. 2(d) shows the TEM images of the SiO_2 nanowires. It can be seen that the diameter of these SiO_2 nanowires is about 40 nm.

The upper right inset of Fig. 2(d) shows a selected area electron diffraction pattern (SADP), which indicates that the SiO_2 nanowires are amorphous.

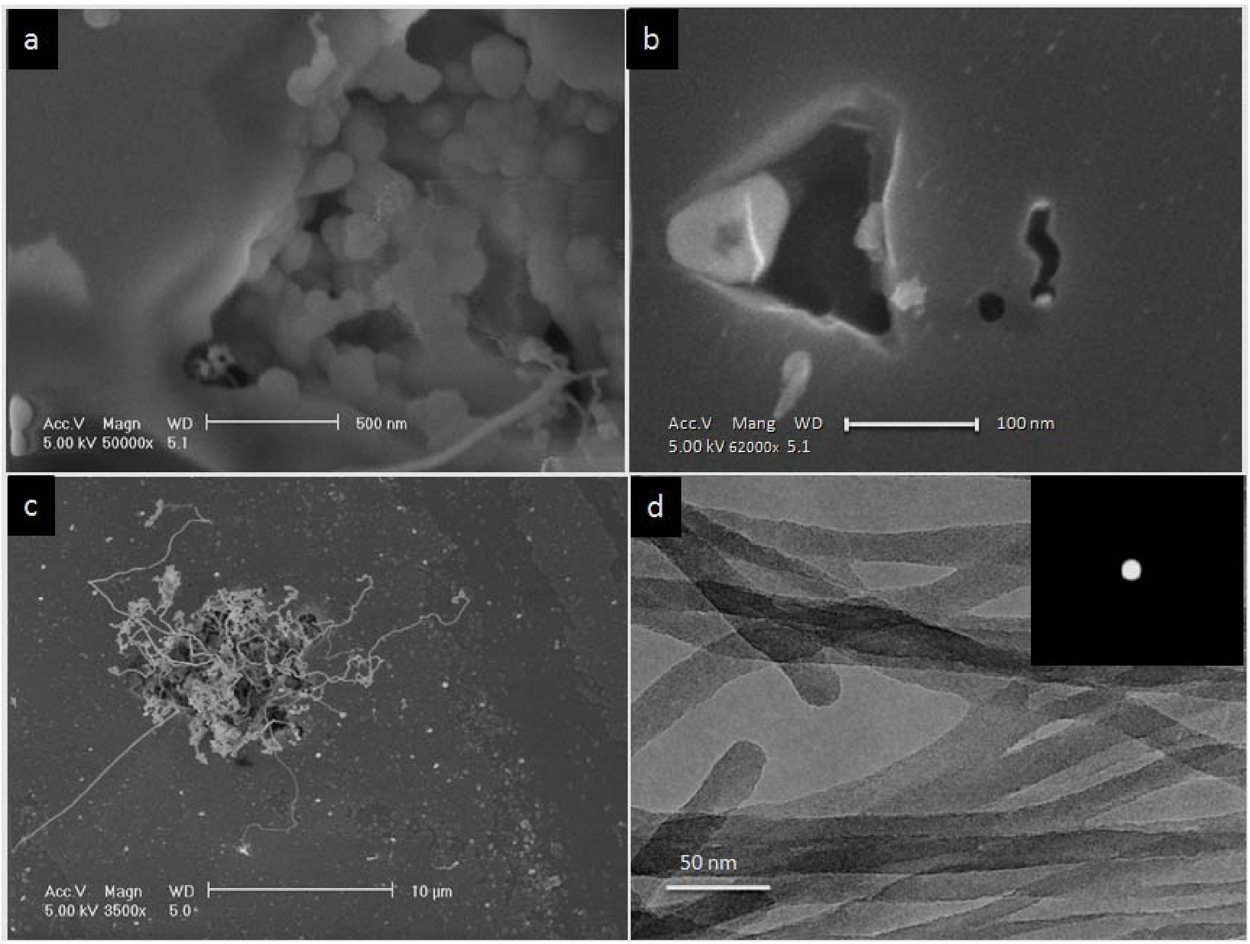
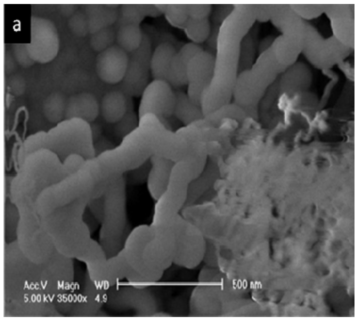


Fig. 2 (a). It is FESEM image a large pit containing roots of etched nanowires, (b) shows a single nanowire root inside a pit, (c) shows nanowires growing out of a pit in second time annealing and (d) is TEM image of nanowires showing amorphous structure with inset.

By considering the above results, a mechanism involved in the formation of SiO_2 nanowires is proposed. The pit formation at Si substrate clearly indicates that the nanowire formation is through SLS mechanism. Silicon from the substrate diffuses to the wire form and a pit is formed in Si substrate as shown in Figs. 2(a) and 2(b). It is also clear that only the roots of the nanowires exist while rest part of nanowires above the Si surface has been etched by HF solution. A part of root of nanowires inside the pit as shown in Fig. 2(b) could not be etched by HF solution.

This confirms the fact that initially Si nanowire grow from the Si substrate, which gets subsequent oxidization after formation or emerging out of the pit. These oxidized part of the Si nanowires has been etched away by HF solution leaving behind the unoxidized Si root inside the deep pit. The oxygen inside the reaction chamber responsible for the oxidation is expected to come either from degassing the quartz tube or the tube end cap leakages.



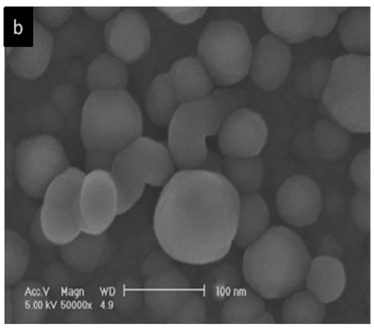


Fig. 3. FESEM images of nanowires growing out of a pit after second time annealing. (a) Shows a large nanowire formation and (b) shows t he nucleation of nanowire by aggregation of particles.

In the first experiment we used SiO suspension. The SiO particles accumulated at different positions at Si surface when it was dipped in suspension, which decomposed to Si and O at high temperature. These Si atoms from SiO interact with the underlying Si atoms on the Si surface and form Si nanowire consuming the Si from the Si substrate. This observation can be verified from Fig. 1(a) as the nanowires are grown only at certain positions on Si substrate in group form. It is inferred that these are the positions where SiO particles accumulate. From the high magnification FESEM image in Fig. 3 of the nanowires growing out from the pit in second experiment the aggregation of nanoparticles in the form of nanowire is clearly shown. It can be inferred that Si particles left behind inside the pit after etching by HF solution work as the precursor for nanowire formation during second experiment. These nanoparticles interact with the Si nanoparticles inside the substrate and form nanowire through SLS mechanism. The nanowire growing up from the pit is clearly shown in Fig. 3(b) where the nanowire is in aggregation form of nanoparticles, which is grown by consuming Si through SLS mechanism from the substrate. The formation of SiO_2 nanowires is caused by SiO precursor in first experiment and by Si nanoparticles itself in second experiment.

4. Conclusions

The SiO_2 nanowires grow from the points where SiO particle exists on the surface of Si substrate during the annealing process. The SiO particle acts as the precursor for the formation of the SiO_2 nanowires in first experiment; once the nanowire is formed the formation of SiO_2 nanowire does not require SiO presence. The Si nanoparticle formed inside the pits itself works as the precursor and wires grow up through SLS mechanism.

References

[1] S. Iijima, Nature **354**, 56 (1991).
[2] H. Dai, E. W. Wong, Y. Z. Lu, S. Fan, C. M. Lieber, Nature **375**, 769 (1995).
[3] Z. L. Wang, Adv. Mater. **15**, 432 (2003).
[4] W. S. Shi, Y. F. Zheng, N. Wang, C. S. Lee, S. T. Lee, Adv. Mater. **13**, 591 (2001).
[5] E. Alice, White, K. T. Short, Science **241**, 930 (1988).
[6] H. Zhang, C. Wang, E. Buck, L. Wang, Nano Letters **3**, 577 (2003).
[7] J. Hwang, L. K. Tamm, C. Bohm, T. S. Ramalingam, E. Betzig, M. Edidin, Science **270**, 610 (1995).
[8] J. R. Guest, T. H. Stievater, G. Chen, E. A. Tabak, B. G. Orr, D. G. Steel, D. Gammon, D. S. Katzer, Science **293**, 2224 (2001).
[9] Y. Zhang, K. Suenaga, C. Colliex, S. Iijima, Science **281**, 973 (1988).
[10] K. Saulig-Wenger, M. Bechelany, D. Cornu, S. Bernard, F. Chassagneux, P. Miele, J. Mater. Chem. **13**, 3058 (2003).
[11] Y. Q. Zhu, W. K. Hsu, M. Terrones, J. P. Hare, H. W. Kroto, D. R. M. Walton, J. Mater.Chem. **8**, 1859 (1998).
[12] Z. Q. Liu, S. S. Xie, L. F. Sun, D. S. Tang, W. Y. Zhou, C. Y. Wang, W. Liu, Y. B. Li, X. P. Zou, G. Wang, J. Mater. Res. **16**, 683 (2001).
[13] X. C. Wu, W. H. Song, K. Y. Wang, T. Hu, B. Zhao, Y. P. Sun, J. J. Du, Chem. Phys. Lett. **336**, 53 (2001).
[14] B. Zheng, Y. Wu, P. Yang, J. Liu, Adv. Mater. **14**, 122 (2002).
[15] Z. W. Pan, Z. R. Dai, C. Ma, Z. L. Wang, J. Am. Chem. Soc. **124**, 1817 (2002).
[16] C. H. Liang, L. D. Zhang, G. W. Meng, Y. W. Wang, Z. Q. Chu, J. Non-Cryst. Solids **277**, 63 (2000).
[17] S. Jin, Q. Li, C. S. Lee, Phys. Status Solidi (a) **188**, R1 (2001).
[18] D. P. Yu, L. Hang, Y. Ding, H. Z. Zhang, Z. G. Bai, J. J. Wang, Y. H. Zou, W. Qian, G. C. Xiong, S. Q. Feng, Appl. Phys. Lett. **73**, 3076 (1998).
[19] S. T. Lee, Y. F. Zhang, N. Wang, Y. H. Tang, I. Bello, C. S. Lee, J. Mater. Res. **14**,, 4503 (1999).
[20] K. Saulig-Wenger, D. Cornu, F. Chassagneux, G. Ferro, T. Epicier, P. Miele, Solid State Commun. **124**, 157 (2002).
[21] N. Wang, Y. H. Tang, Y. F. Zhang, C. S. Lee, I. Bello, S. T. Lee, Chem. Phys. Lett. **299**, 237 (1999).
[22] Y. Zhang , N. Wang, S. Gao, R. He, S. Miao, J. Liu, J. Zhu, X. Zhang, Chem. Mater. **14**, 3564 (2002).

*Corresponding author: rajeshkumarf11@gmail.com