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The Preparation of SiO_2 Nanotubes with Controllable inner/outer Diameter and Length using Hydrothermally Grown ZnO Nanowires

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1. Introduction

Recently, one-dimensional (1-D) inorganic nanotubes, such as ZnO, TiO_2, Al_2O_3, ZrO_2, and SiO_2 etc., have attracted a lot of attention due to their unique properties, structural versatility, specific chemical and physical properties, which make much potential applications in nanoelectronic and optoelectronic devices [1]. Among various inorganic nanotubes, SiO_2 nanotubes (SiO_2-NTs) have attracted considerable interests owing to their hydrophilic nature, easy colloidal suspension formation, and surface functionalization accessibility for both inner and outer walls. Furthermore, silica nanotubes have the characteristic of their room-temperature light-transmission properties in the visible range, and possible usage for hosting materials in bioanalysis and bioseparation and potential applications in optoelectronic nanodevices [2-3]. The SiO_2-NTs can be fabricated by various approaches such as surfactant intercalation method, electroless deposition, sol-gel technique, templated-assistance method, MOCVD method and thermal evaporation method [4-7]. However, these techniques are less suitable for commercial applications because of the high cost of equipments, small-scale production, long processing time, and requiring working in an ultra-high vacuum. To overcome these drawbacks, the synthesis of vertically aligned SiO_2-NTs by deposition of SiO_2 on hydrothermally grown Zinc-Oxide nanowires (ZnO-NWs) and then removal of the ZnO-NWs were reported in this study. The optical properties of the SiO_2-NTs with superior transmittance performances were also investigated and discussed.

2. Experiments

Figure 1 illustrates the flowchart of SiO_2-NTs fabrication. In experiments, ITO-glass was used as the substrate which was cleaned ultrasonically using acetone, methanol, rinsed in DI water, blown dry with N_2, and then dipped into chemical solution ($HCl:H_2O$ = 3:1) for 10 min to remove the surface particle; and a 100 nm thick aluminum-doped-zinc-oxide (AZO) film was sputtered on ITO-glass substrates to serve as a seed layer for the growth of Zinc-Oxide nanowires (ZnO-NWs) by hydrothermal growth (HTG) method. (Fig. 1(a) - 1(b)). Then the samples were then placed in a mixed solution of 0.07 M $Zn(NO_3)_2{\cdot}6H_2O$ and 0.09 M $C_6H_{12}N_4$ at 90°C for 2 hour for the synthesis of ZnO-NWs (Fig. 1(c)). Well-ordered and vertically-aligned ZnO-NWs were grown horizontally on the AZO substrate. Note that both the length and diameter of the ZnO-NWs can be well controlled by the HTG duration. After HTG growth, the hexagonal ZnO-NWs were used as templates for deposition of SiO_2. The surface of ZnO-NWs were covered with low temperature (200°C) chemical vapor deposition (CVD) SiO_2 (Fig. 1(d)). It was then followed by ICP etching to unveil the top portion of the ZnO-NWs arrays for synthesizing SiO_2-NTs (Fig. 1(e)). Finally, the samples were placed into a mixture chemical solution ($H_3PO_4:HCl:H_2O$ = 1:1:10), and ZnO-NWs were removed by the chemical treatment and SiO_2-NTs formed (Fig. 1(f)). According to the growth of ZnO-NWs and ICP dry-etching process, the SiO_2-NTs with tunable inner and outer diameters and lengths can be synthesized readily. The morphology and chemical components of the grown ZnO-NWs and the fabricated SiO_2-NTs were characterized by scanning electron microscopy (SEM, Hitachi S4700) and energy dispersive spectroscopy (EDS), respectively. The optical transmittance characteristics of the prepared ZnO-NWs and SiO_2-NTs were measured by UV/Vis Spectrophotometer (Hitachi model U-3010).

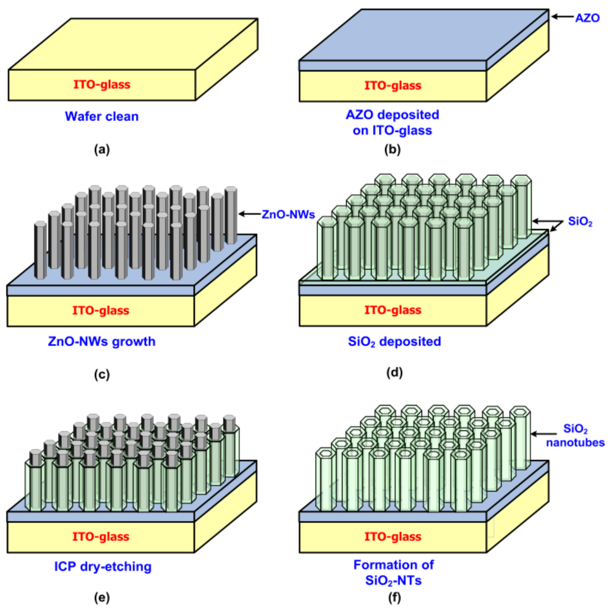

Fig. 1 The flowchart of the synthesis of SiO_2-NT arrays.

3. Results and Discussion

Figure 2 shows SEM images of the key fabrication processes of SiO_2-NTs as shown in Fig. 1(c) - 1(f). From Fig. 2(a), it can be observed that the hexagonal ZnO-NWs with an average length of 2 μm, average diameter of 20-200 nm, and high density of 2×10^8 cm^{-2} were grown vertically-aligned on the AZO layer. Figure

2(b) shows the ZnO-NWs were firmly covered with CVD SiO_2. Figure 2(c) shows the SEM image of ZnO-NWs after CVD SiO_2 coating and ICP etching with the top view shown in the inset. As shown in Fig. 2(c), the top portion of the ZnO-NW arrays (~0.5 μm) was unveiled after the ICP dry-etching. In Fig. 2(d), it shows that SiO_2-NTs with inner diameter/length and thickness of the tube wall determined by the diameter/length of ZnO-NWs and thickness of the CVD SiO_2, respectively, were synthesized successfully after the removal of ZnO-NWs. SiO_2-NTs were observed anchoring firmly on AZO layer during measurements. Note that in the present case, the inner diameter, length, and thickness of the tube wall were 20-200 nm, 2 μm, and 10-100 nm, respectively.

Figure 3 show the EDS analyses of the ZnO-NWs, ZnO-NWs after CVD SiO_2 coating and ICP etching, and the SiO_2-NTs. The chemical components of the grown ZnO-NWs were confirms mainly comprising of pure metallic Zinc and oxygen. After ICP treatment and the removal of ZnO-NWs, the EDS analysis shows that the prepared NTs were mainly comprised of silica and oxygen without any residual ZnO.

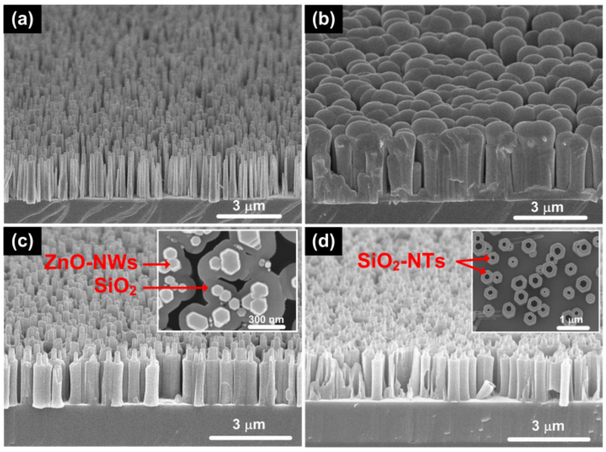

Fig. 2 The SEM images of the sample at key fabrication step: (a) ZnO-NWs on AZO layer, (b) ZnO-NWs covered with CVD SiO_2, (c) the sample after ICP etching, (d) SiO_2-NTs formed after the removal of ZnO-NWs.

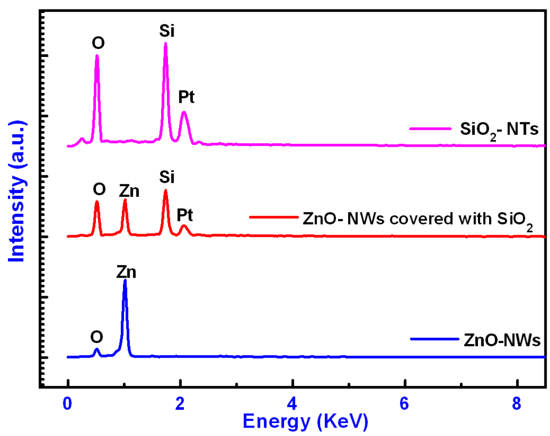

Fig. 3 The EDS analyses of ZnO-NWs, ZnO-NWs after CVD SiO_2 coating and ICP etching, and the SiO_2-NTs, respectively.

Figure 4 shows the transmittance of the prepared SiO_2-NTs grown on AZO film. The prepared SiO_2-NTs was seen having a superior transmittance (92%) compared with that of ZnO-NWs (80%) in the visible light spectrum ranging from 400 to 800 nm. The room-temperature transparent properties would have great potential in optics, optoelectronics, and bio devices. Applications of SiO_2-NTs on the surface of solar cells to increase their light collection efficiency are now under way.

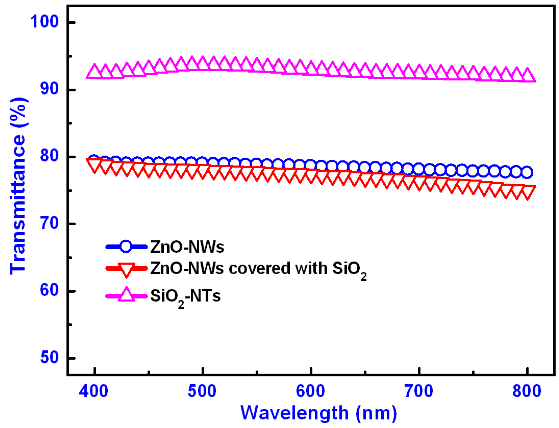

Fig. 4 The transmittance of the ZnO-NWs, ZnO-NWs after CVD SiO_2 coating and ICP etching, and the SiO_2-NTs, respectively.

4. Conclusion

In summary, the fabrication and optical properties of SiO_2-NTs have been demonstrated. The SiO_2-NTs with tunable inner and outer diameters and lengths have been synthesized successfully by a simple method using SiO_2 deposition on a hydrothermally grown ZnO-NWs template and then followed by the removal of the ZnO-NWs. A superior transmittance of around 92% of SiO_2-NTs in the visible light spectrum, which is higher than that of ZnO-NWs of the same geometry by about 12%, was reported in this study. The proposed SiO_2-NTs fabrication method would provide a simple and low-cost building block for future applications and developments of optic and optoelectronic devices.

Acknowledgments

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