Fabrication of Metal Oxide Coaxial Nanotubes Using Atomic Layer Deposition

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ABSTRACT

We fabricated nanotubules of TiO_2 and ZrO_2 using atomic layer deposition (ALD) technique with polycarbonate (PC) nanoporous filters as a template. Alkylsiloxane monolayers on the both sides of PCs were formed by blanket type contact printing in order to achieve one-step process of the freestanding oxide nanotubes. TiO_2 and ZrO_2 nanotubes with 30 ~ 200 nm of diameter were successfully fabricated by ALD at 140ºC and subsequent chemical etching of the PC. Very high aspect ratio of 160:1 was achieved in both oxide nanotubes. Growth rates of the wall thickness in oxides nanotubes were 0.5 and 0.6 Å/cycles for 200 and 50 nm pore sizes of PC templates, respectively, showing ultra-precise control of the wall thickness, so as to inner diameter of the tubes. Prepared oxide nanotubes were characterized by high-resolution transmission electron microscopy (HR-TEM), field emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM). Oxide nanotubes were filled with CdS using chemical bath deposition (CBD). We successfully demonstrated formation of coaxial TiO_2/CdS nanocables. Further we developed MO-CVD processes for Cu layer. As a result, coaxial nanotubes of TiO_2/Cu and ZrO_2/Cu were successfully fabricated. Combination of the ultra-precise wall thickness control of oxide nanotube with high-aspect ratio filled Cu layer provides us a possible quantum coaxial cable for nanoelectronic applications.

Keywords: Nanotube, Self-Assembled Monolayers, Atomic Layer Deposition, Template, Wall thickness

1 INTRODUCTION

Metal oxide nanotubes as well as CNTs [1] are expected to be useful for various applications such as nanoelectronics, biological sensors, nano-fluidic devices, nano-electromechanical system (NEMS) and energy storage, etc [2]. Particularly, one-dimensional structures of inorganic materials have attracted a lot of attention because of their unique properties (e.g., electronic, magnetic, optical, etc.) and potential applications in the near future

In this study, we reported that more controllable and feasible process for nanotube of TiO_2 as well as ZrO_2 using atomic layer deposition (ALD) and nanoporous poly-carbonate (PC) membrane as a template.[3] We reported that the formation of TiO_2 and ZrO_2 nanotubes by ALD oxide thin film[4] coating on the nanoporous membranes (commercially available polycarbonate filters) as templates and subsequently removing the templates.[5] Applying this method, we successfully developed novel fabrication routes for coaxial nanotubes of metal oxides with metal oxide nanotubes with semiconducting CdS core as well as metallic Cu layer.

2 EXPERIMENTAL

Fig. 1 shows the schematic flow of the fabrication process of the oxide nanotubes in this study. Membranes used in this study as nano-templates are hydrophilic poly-carbonate (PC) filters. The PC filters are commercially available (Whatman Co., UK). PC filters used in this study have nano-pores of diameter of 200 nm, 50 nm, or 30 nm. The pores in these filters are randomly distributed across the filter, and pore densities are approximately 3×10^8 pores/cm^2.

Coatings on inner wall of PC filters were carried out using ALD up to 140 °C. Self-limiting surface reaction in our home-made ALD processes for thin films of TiO_2 and ZrO_2 were confirmed up to 200 °C. Above 140 °C, the PC filters were distorted due to the thermal stress in ALD reaction chamber. Therefore process temperatures for oxide nanotube fabrication were kept lower than 140°C. Zirconium *t*-butoxide and Titanium *iso*-propoxide were used as sources of Ti and Zr. Water vapor with the flow rate of 5 sccm was used as an oxidant. N_2 was used as a carrier gas and Ar gas was used for purging. A cycle of ALD includes Zr and/or Ti source/purging/H_2O(g)/purging (e.g. 2/80/2/240 sec., respectively, in case of ZrO_2 coating). Growth of TiO_2 thin films with 0.4 Å/cycle at 150 °C can be achieved. In a typical experiment, 100 ~ 800 cycles of ALD were performed to synthesis nanotubes of TiO_2 and ZrO_2. After the desired cyclic ALD processes, the PC filters were etched away using the solution of chloroform at 60 °C.

To avoid any subsequent processing steps – e.g. etching process of the unwanted films deposited onto both sides of PC templates – to fabricate free-standing oxide nanotubes, selective area depositions of ALD has been adopted using contact printed OTS-SAMs as passivation layers. OTS-SAMs are deposited onto the both sides of PC filter by contact printing as shown in Fig. 1(b). Micro-contact printing of OTS resulted in transition of surface characteristics of the template from hydrophilic to hydrophobic [6], which eventually caused selective deposition in hole of nanotemplate without deposition on the surface of the filters. Subsequently, ALD processes make conformal coatings of TiO_2 or ZrO_2 only onto the inner-wall of PC template. Then 2nd layer was formed either CdS using either chemical bath deposition (CBD) or Cu deposited by CVD. PC template was etched by an organic chemical etching solvent such as chloroform. Nanotubes were remained selectively without significant damaged.

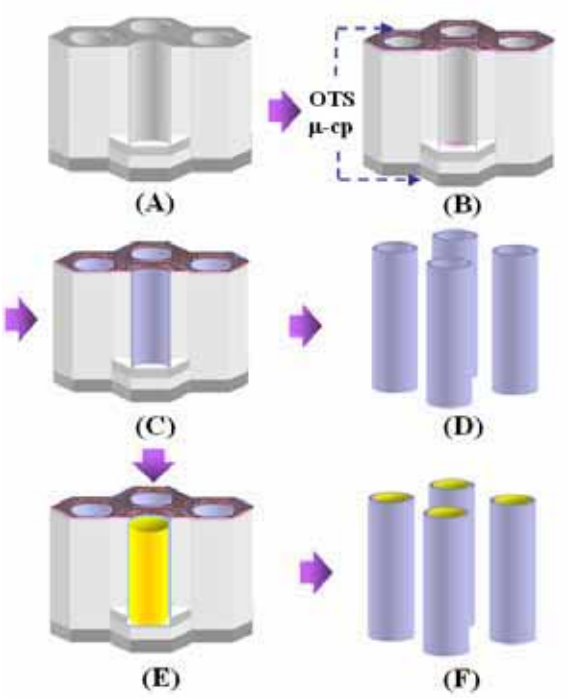


Figure 1: The fabrication processes for the oxide/semiconducting coaxial nanotubes in schematic sequence. a) PC template which has various pore size and thickness. b) Micro-contact printing with SAMs such octadesyl- tetrachlorosilane c) Selective deposition of the metal oxide layers on inner hole of nanotemplate d) Etched the PC template. Remained the metal oxide nanotubes e)Before etching the PC template, Cu was deposited by pulsed MOCVD while CdS was deposited by CBD. f) Etched the PC template. Nanocables were fabricated by the same method

As-prepared oxide nanotubular structures were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi 4500, Japan) and atomic force microscopy (AFM, SPA-400, Seiko Instruments, Japan). High resolution transmission electron microscopy (HR-TEM) was used to analyze the nanotube crystal structures and wall thicknesses. And SAED patterns were used for evaluation of crystallization of the nanotubes.

3 RESULTS & DISCUSSION

3.1 Oxide Nanotubes

Fig. 2 shows the FE-SEM image of TiO_2 nanotubes with OTS treatment after etching the polycarbonate nanotemplate in aqueous solvent. In this figure, the average diameters of the nanotubes are about 50 nm and lengths are 8 ㎛, respectively. They formed a highly ordered array over all area of nanotemplate (that is, PC filters). OTS treatment prevents the connecting the nanotubes by unnecessary deposition on nanotemplate surface. Because CH_3^- which is the head group of OTS has hydrophobic property, OTS changes surface properties from hydrophilic to hydrophobic. This results in prohibition of nucleation of TiO_2 layer because ALD mechanism is based on surface reaction on OH^- bonding layers.

By changing the precursors and reactants, various nanotube materials were made. Zr-t-butoxide, Ti-isopropoxide precursors and H_2O oxidizing agent made ZrO_2 and TiO_2 nanotubes with wall thickness of 10nm. Especially, in Fig. 3(a), SAED pattern of TiO_2 nanotube shows amorphous nanostructure, otherwise ZrO_2 nanotubes, in Fig. 3(b), have a tetragonal phase. One significant advantage of this technique is easiness of geometric of nanotubes simply choosing adequate nano-template. Through variation of pore sizes of the nanotemplates, hole sizes of nanotubes are easily controlled. Using different thicknesses of nanotemplates, lengths of nanotubes are easily varied, too.

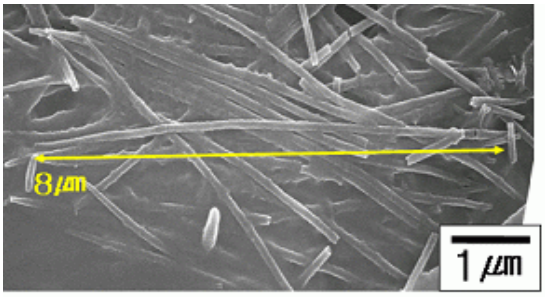
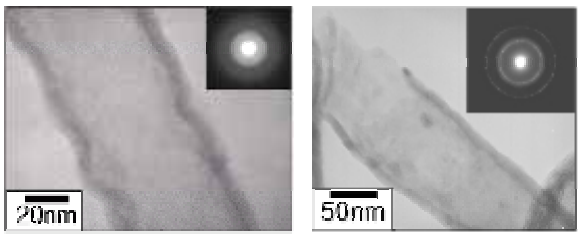


Figure 2 : FE-SEM image of TiO_2 nanotube which has the hole size of 50nm and length of 8 ㎛ with 1:160 aspect ratio



(a)TiO_2 Single Wall (b)ZrO_2 Single Wall

Figure 3: HR-TEM images of the oxide single wall nanotubes

3.2 Oxide and Semiconductor Layers Nanotubes

Cadmium sulfide (CdS) is an important II-VI semiconductor material compound which a good transparency in region of visible light and excellent photoconductive property.[7] CdS has been used in opto-electronic devices, window layer of thin film solar cells based on CdTe or $CuInSe_2$ or Cu_2S, SO_x gas sensor, optical memories and photoconductive cell. It can be applied widely in the development of other functional devices. In this fabrication, CdS was filled into metal oxide nanotubes using chemical bath deposition(CBD).

To fabricate TiO_2/CdS nanocables, nanotemplate surface was treated with SAM(OTS) by micro contact printing as we mentioned above. After oxide deposition by ALD, CdS was deposited by ammonia free chemical bath deposition technique. In ammonia free CBD condition, KOH, NTA acid, $CdSO_4$ and Thiourea are mixed in DI water and stirred. CdS was deposited about 100nm at pH 9 in 20 minutes. Unnecessary CdS removed by sonification. Then PC deposited TiO_2 / CdS was etched with Chloroform heated 60°C about 30minutes. Nanocables were chracterized by FE-SEM, HR-TEM and an energy dispersive spectroscopy (EDS) analysis. Fig.4 (a) shows a FE-SEM image and fig.4 (b) shows a HR-TEM micrograph. They show that outlet hole is TiO_2 nanotube and inlet hole is CdS nanowire, which is deposited uniformly on TiO_2 nanotube wall. Fig. 4 (c) shows EDS data of the TiO_2/CdS nanocable confirming chemical nature of the cable.

As increasing the deposition times, thickness of CdS was increased monotonously. Using this result, we could control the inner wall thickness easily. Fig. 5(a) is the TiO_2/CdS double wall nanotube that CdS was deposited for 20 minutes. It has that the outer TiO_2 thickness is 15nm, inner CdS thickness is 30nm and inner hole diameter is about 50nm. Otherwise, deposition times were increased for 40 minutes, CdS was jammed in TiO_2 nanotubes. As this result Fig. 5(b), TiO_2/CdS formed the nanocables. In the TiO_2/CdS nanocable, SAED pattern in Figs.5 show the inner CdS tube was polycrystal tetragonal structure.

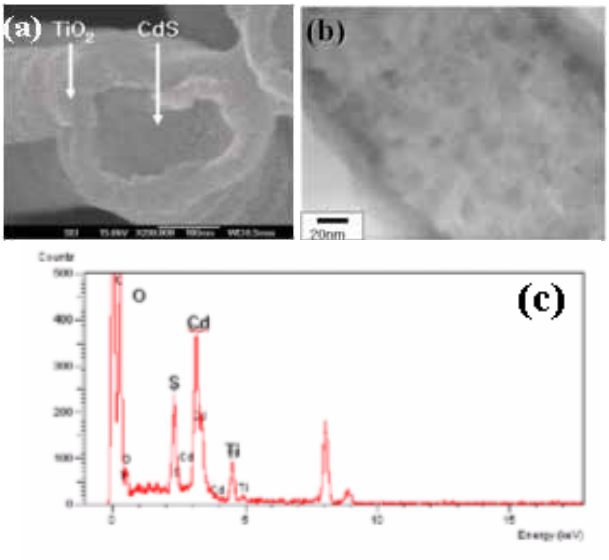


Figure 4: (a) FE-SEM and (b) HR-TEM images (c) EDS analysis of TiO_2/CdS nanotube

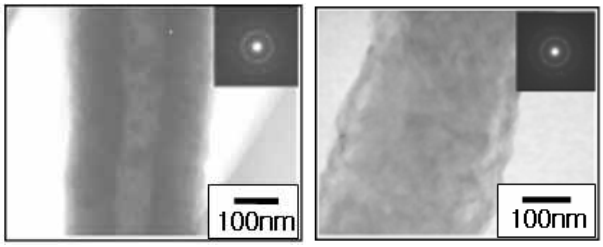
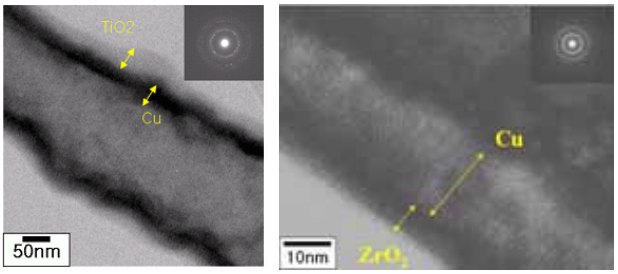
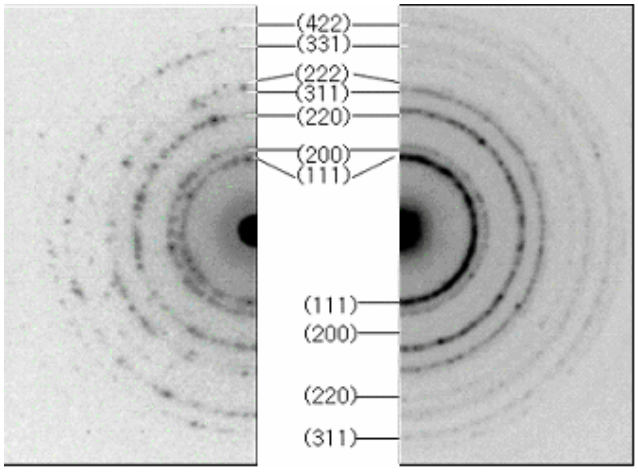


Figure 5: TiO_2/CdS nanotubular structures (a) Double wall nanotubes (b) Nanocable



(a)TiO_2/Cu Double wall (b)ZrO_2/Cu Double wall

Figure 6: HR-TEM images of the copper metal and oxide double wall nanotubes



(a) ZrO_2 (b) ZrO_2/Cu

Figure 7: Diffraction pattern of the ZrO_2/Cu nanotubes

3.3 Oxide and Metal Layers Nanotubes

After TiO_2 layer was deposited on PC template, Cu layer was deposited by pulsed MOCVD by alternating the supply of the (hfac)Cu(DMB) and H_2 reactant. A typical pulsed deposition cycle consisted of 3 sec of (hfac)Cu(DMB) cycle, then a 6 sec of Ar purging time, followed by 3 sec long H_2 reactant pulse, and finally, a 6 sec of Ar purge cycle. The Cu source was heated at 30 ^oC, with the gas delivery line maintained at 40 ^oC. Then PC deposited TiO_2/ Cu was etched with Chloroform as the same method.

Fig 6. shows the metal copper and oxide double wall nanotubes. Cu layers were deposited on both oxide tube walls. And figs. 7 are the selective area electronic diffraction patterns of the ZrO_2 single wall and ZrO_2/Cu double wall nanotubes. In the case of ZrO_2/Cu double wall nanotubes, we clearly observed (111), (200), (220), (311) patterns of Cu as well as ZrO_2 patterns. In Fig. 7, SAED pattern of ZrO_2 nanotubes shows polycrystalline nanostructure which has tetragonal structure. Even though equilibrium phase of zirconia is monoclinic, tetragonal phase may results from nano-scale geometric effects, which cause high material pressure at tube-wall because of extremely high curvature.

4 SUMMARY

In this study, nanotubes which have various hole sizes, lengths and wall thicknesses were fabricated on PC nanotemplates by atomic layer deposition. SAMs treatment on the PC filters effectively reduced cross-link between oxide nanotubes because the treatment inhibited nucleation of oxide films. 30 ~ 200 nm in diameter of TiO_2 and ZrO_2 nanotubes were successfully fabricated by ALD at 140 °C and subsequent chemical etching of the PC. Very high aspect ratio of 160:1 was achieved in both oxide nanotubes. Growth rates of the wall thickness in oxides nanotubes were 0.5 and 0.6 Å/cycles for 200 and 50 nm pore sizes of PC templates, respectively, showing ultra-precise control of the wall thickness, so as to inner diameter of the tubes. After metal oxide nanotube was made, CdS could be filled into metal oxide nanotube by method of CBD. It was confirmed by FE-SEM and HR-TEM. In addition, we successfully fabricated nanotubes with double walls of metal and oxide layers.

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