Fabrication of ZnO nanotubes using AAO template and sol-gel method

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We report a novel method that enables the facile fabrication of highly ordered zinc oxide (ZnO) nanotubes using Anodic Aluminium Oxide (AAO) template and sol-gel method. 200 nm titanium and 3.2 μm aluminium films were deposited subsequently on oxidized silicon wafer by thermal evaporation method. AAO template was fabricated by two-step anodization. The ZnO nanotubes were then fabricated into the AAO template using sol-gel ZnO. AAO template and ZnO nanotubes were characterized by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and Energy Dispersive Spectrometry (EDS). The formation mechanism of ZnO nanotubes was also discussed. SEM micrographs show that fabricated vertically ZnO nanotubes are approximately 40 nm in diameters and 3.2 μm in lengths in a relatively large area of about 6 cm^2.

(Received March 9, 2009; accepted March 22, 2009))

Keywords: Zinc oxide, ZnO nanotubes, AAO template, Sol-gel

1. Introduction

Nowadays, self-assembly nanostructures have attracted much attention over the years as their fundamental importance and potential applications in nanodevices. Zinc oxide (ZnO) is an interesting material for optoelectronics as a transparent conductive electrode, ultraviolet (UV) light emitter and spin electronics as it is a wide band gap semiconductor with a large binding energy possessing unique optical and electronic properties [1]. As one of the major materials for chemical sensors, ZnO have been proposed for NH_3 [2], alcohol [3] and H_2 [4] sensing. Wan [5] et al. fabricated ZnO nanowire gas sensors using micro-electromechanical system technology. Also, ZnO is being intensively studied for implementing photonic devices. Photoluminescence (PL) properties of ZnO were extensively reported [6]. Strong emission peak at 380 nm due to band to band transition and green-yellow emission band were observed.

Due to these remarkable physical properties and the motivation of the device miniaturization trend, large efforts have been focused on nanostructured ZnO materials but only a few reports describe the fabrication of ZnO nanotubes. Sakohara et al. [7] fabricated ZnO nanotubes by sol-gel method using ZnO colloids composed of nano-sized wurtzite crystals on Si wafers and investigated luminescence properties of them. In order to prepare the ZnO nanotubes, it has been considered that template method is the simplest and most versatile approach since it does not utilize expensive lithographic processes. Anodic Aluminium Oxide (AAO) template is an ideal template for fabrication of nanotubes as it has good mechanical strength and thermal stability. Masuda et al. in 1995 [8] and Jessensky et al. in 1998 [9] describe how to fabricate AAO template on Al foil with ordered hexagonally parallel nanotubes. Wua et al. [10] and Wang et al. [11] fabricated ZnO nanotubes within the Al foil based AAO template by sol-gel method. Moreover, Rout et al. [12] prepared ZnO nanotubes in Al foil based AAO template using two different procedures and investigated hydrogen and ethanol sensing properties of them. Seo et al. [13] fabricated ZnO nanotubes within the Al foil based AAO template using template-wetting process, nanotube walls of the template were wetted by polymeric ZnO source. However, vertical standing ZnO nanotubes on silicon substrate have not been reported so far.

In this study, vertical ZnO nanotubes were fabricated into the AAO template on titanium coated silicon substrate by a novel sol–gel method.

2. Experimental

For AAO template fabrication, 200 nm thick pure titanium (99.99 %) and 3.2 μm thick pure aluminium (99.999 %) films were coated on the oxidized n-type (100) Si substrate subsequently using thermal evaporation system. AAO template was obtained by two-step anodization. High purity aluminium film was anodized in oxalic acid solution by applying 40 V constant voltage at 0^0 C for 30 min. Then, anodic aluminium oxide film was chemically etched away. Barrier layer of the AAO template between the ends of the template and the titanium coated Si substrate was removed electrochemically in KCl solution [14].

ZnO nanotubes were prepared into fabricated AAO template using sol-gel method. 0.45 g zinc acetate dehydrate (Zn (CH_3COOH).$2H_20$ (99.99 %)) was solved in 20 ml methanol and 0.25 ml acetyl acetone ($C_5H_80_2$) mixture at room temperature. Prepared solution was mixed with a magnetic stirrer for 4 hours at 50 ^{0}C until a transparent solution was obtained. Then the solution was aged for 24 h. For ZnO deposition into AAO, AAO template was immersed in prepared sol-gel ZnO at 65^0 C for 12 h. Then deposited sol-gel ZnO in AAO template was annealed to form vertically ZnO nanotubes at 600° C for 30 min. In order to avoid quick-cooling fractures, the sample was not taken out of the furnace abruptly; instead, it was kept inside the furnace until room temperature was reached.

The morphology of the deposited ZnO nanotubes was studied mainly by Scanning Electron Microscopy (SEM). SEM investigations were performed on a Jeol JSM 6335-SEM instrument operating at 20 kV. Before SEM analysis each samples were coated gold film with ca. 30 nm thickness using sputtering technique. The surface of ZnO nanotube deposited AAO template was magnified 50,000 times. Further structural characterizations were performed by X-Ray Diffraction (XRD, Cu K_α, λ = 0.154 nm), Energy Dispersive X-Ray (EDX) analysis.

3. Results and discussion

The morphologies of the AAO template and ZnO nanotubes were characterized by SEM. Figure 1 shows typical top view and cross-sectional view of the AAO template. AAO template observed was hexagonally straight, approximately 50 nm in diameters and 3.2 μm in lengths with 80 nm interpore distances.

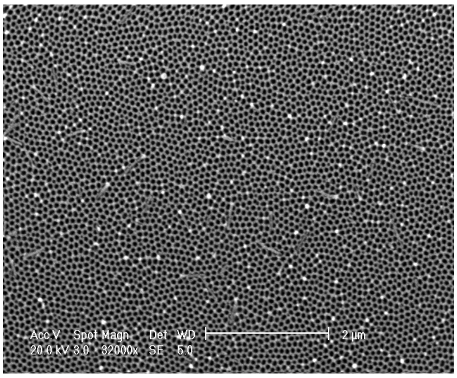
The formation process of ZnO nanotubes within fabricated AAO template using sol-gel process was described as follows: Unlike a traditional sol–gel process, the AAO template was dipped into the methanol solution containing zinc acetate and acetyl acetone. Because of the lower viscosity of obtained solution than that of traditional sol; this solution is easier to fill into the AAO template. After filling, when the sol-gel was heated, the OH^- ions released from hydrolysis reaction of system's water combine with zinc ions to form Zn $[(OH)_x](H_2O)_y$ sol as follows:

$$(Zn\,(CH_3COO)_2 + 2CH_3OH \longrightarrow Zn\,(OH)_2 + 2\,CH_3\,CH_3COO$$

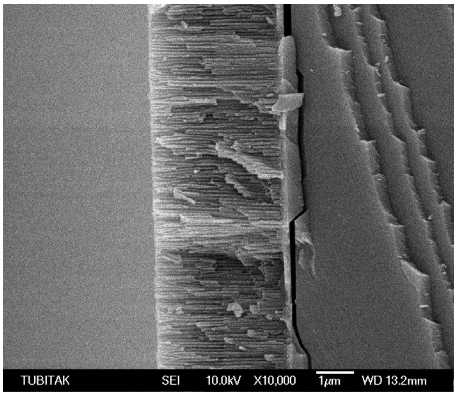
The formed Zn $(OH)_2$ is in colloidal particulate diamension and form Zn $[(OH)_x](H_2O)_y$ sol. During this process, the sol particles were negatively charged; meanwhile, the nanotube walls of the AAO template were positively charged. As a result of this, the density of sol particles was larger near the wall of template, thus it was reasonable that the ZnO nanotubes first formed in the wall area of the AAO template and then extended to the centre area gradually, until the AAO template was filled completely to form nanowires, it was controlled with process time to form nanotubes or nanowires. AAO template was taken out of the sol and annealed in a tube furnace. After covering of this sol on the inner wools of AAO template it need to convert Zn $[(OH)_x](H_2O)_y$ to the ZnO by annealing:

$$Zn\,[(OH)_x](H_2O)_y \longrightarrow ZnO + (y+x-2)H_2O$$

Low-energy sol-gel spreads rapidly on high-energy surfaces. Therefore, the walls of the AAO template were covered with ZnO film if they exhibit a high surface energy. The underlying driving forces are due to short-range as well as long-range Van der Waals interactions between the sol-gel and the walls of the AAO template [13]. After sol-gel process and annealing, the ZnO formed a thin film covering the walls of the AAO template thus; ZnO nanotubes filled the AAO template. Figure 2 shows typical top view and cross-sectional view of the ZnO nanotubes within the AAO template.

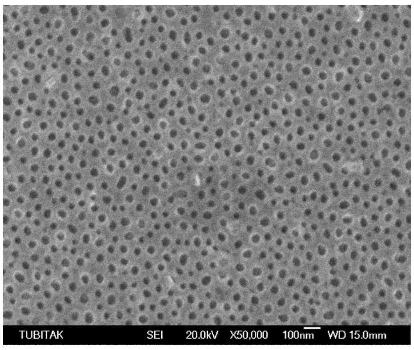


(a)



(b)

Figure 1. SEM micrographs of the AAO template: (a) Cross-sectional view (b) Top view



(a)

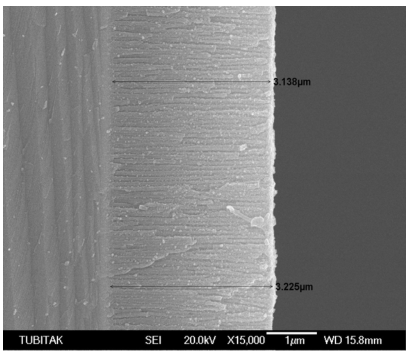


Figure 2. SEM micrographs of the ZnO nanotubes within AAO template: (a) Top view; (b) Cross-sectional view.

Figure 2 shows that the ZnO nanotubes are roughly parallel to each other, vertically aligned to form an array. Fabricated vertically ZnO nanotubes are approximately 40 nm in diameters and 3.2 μm in lengths with 100 nm interpore distances. Therefore, deposited ZnO nanotube density is approximately 10^{10} cm^{-2}. (Nanotube density (ρ) = $(2/\sqrt{3}D_{int}^2)\text{x}10^{14}$ cm^{-2}, where D_{int} is the interpore distance).

As the end of AAO template is opened (barrier layer of the AAO template between the ends of the AAO nanotubes and the titanium coated Si substrate was removed) deposited ZnO nanotubes were connected to the titanium coated Si substrate. For future studies, AAO template will be removed by dissolving the AAO in dilute NaOH solution, thus expected free-standing ZnO nanotubes on titanium coated Si substrate will be obtained. Figure 3 shows XRD spectra of ZnO nanotubes within AAO template.

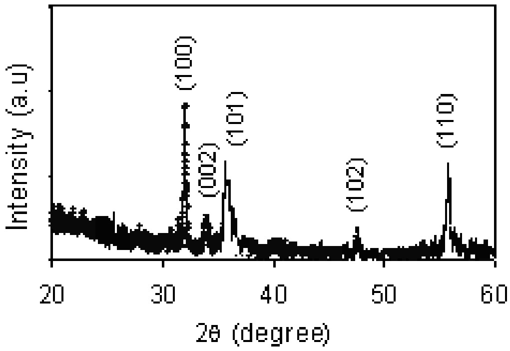


Figure 3. XRD spectra of ZnO nanotubes within AAO template.

The structure of the fabricated ZnO nanotubes was investigated using X-ray diffraction spectra. The peak positions and their relative intensities are consistent with those of a standard wurtzite-type structure, which proves that there is no preferred orientation and that the ZnO nanotubes are polycrystalline. All diffraction peaks are indexed as hexagonal wurtzite structure ZnO.

Figure 4 shows the Energy Dispersive Spectrometry (EDS) spectra from the surface of ZnO deposited AAO template. The EDS spectra clearly show Zn signals from ZnO nanotubes, O signal from AAO template, ZnO nanotubes and the oxidized Si substrate. Al signal from AAO template, Ti signals from titanium film as opened ends of the ZnO nanotubes were connected to titanium film, Si signals from the Si substrate. The EDS spectra indicated that ZnO nanotubes into the AAO template and the interface between the AAO template and the Si substrate consists of Ti interconnected openings.

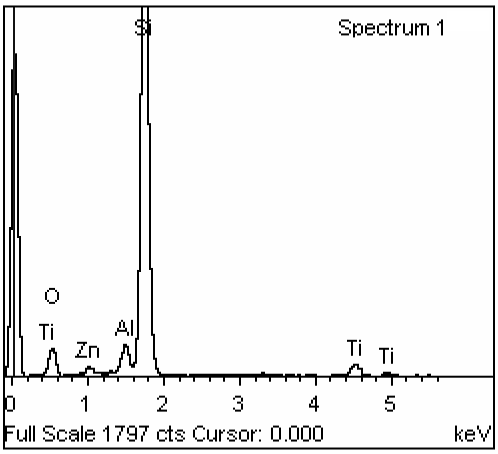


Figure 4. EDS spectra from the surface of ZnO deposited AAO template.

4. Conclusions

We have successfully fabricated ZnO nanotubes within AAO template on titanium coated Si substrate using sol-gel method. Fabricated well-ordered ZnO nanotubes have hexagonal wurtzite structure approximately 40 nm in diameters and 3.2 μm in lengths with 10^{10} cm^{-2} density. Obtained ZnO nanotubes offer potential for optoelectronic, photonic devices and chemical sensors.

Acknowledgements

This study was supported by Grant No. 106T546 from The Scientific and Technological Research Council of Turkey. The authors would like to thank Dr. Hayrettin Yüzer for valuable discussion and technical help.

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