Al_2O_3 Nano-Coating by Atomic Layer Deposition

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Aluminum oxide (Al_2O_3) materials were coated conformally on ZnO nanorods by atomic layer deposition (ALD). The ZnO nanorods were first synthesized on a Si(100) substrate from ball-milled ZnO powders by a thermal evaporation procedure. Al_2O_3 films were then deposited on these ZnO nanorods by ALD at a substrate temperature of 300℃ using trimethylaluminum (TMA) and distilled water (H_2O). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of the deposited ZnO nanorods revealed that amorphous Al_2O_3 cylindrical shells surround the ZnO nanorods. These TEM images illustrate that ALD has an excellent capability to coat any shape of nanorods conformally.

Keywords: ZnO nanorod, Atomic layer deposition, Al_2O_3, Coating, TEM

1. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs)[1], the study of syntheses and applications for one-dimensional nanostructured materials has become a new generated trend in the branches of researching semiconductors. Recent research trend leads to conveying semiconducting materials to nanorods for optoelectronic and nanoelectronic devices[2, 3]. In particular, the nanomaterials of metal-oxide-related wide bandgap semi-conductors including ZnO and Ga_2O_3 have been a matter of concern due to their excellent crystalline quality, chemical stability, and wide bandgap. They have been synthesized by the thermal evaporation of semiconductor powders. In the thermal evaporation, ball-milling of crystalline powders that lowers their melting point leads to the synthesis of nanomaterials at relatively low temperatures[2, 4].

To realize optoelectronic and nanoelectronic devices utilizing nanorods, the protection of the nanorods from contamination and from oxidation is of crucial importance[5, 6]. Conformal coating of nanorods is required to retain their optical and electrical properties. Moreover, the three dimensional geometry of nanorods requires high degree of control of the coating layers[7]. Atomic layer deposition (ALD) is one of adequate techniques satisfying these requirements because of its nature of surface controlled process, such as atomic layer control, thickness controlled by the number of reaction step and perfect control of growth rate. ALD is expected to be the ideal candidate of powerful growth methods of achieving conformal coating layers.

Aluminum oxide (Al_2O_3) has been widely applied as corrosion resistant coating films[8]. And this oxide material has been also utilized as dielectrics of capacitor and gate oxides in memory devices due to its high dielectric constant, very low permeability, and high thermal conductivity[9]. Especially, precise control in the thickness of Al_2O_3 films by ALD has been focused in the field of ultra thin memory devices[10, 11]. Moreover, step coverage of Al_2O_3 films on patterned substrates has been recently investigated by ALD to develop conformality on films[11, 12]. Nevertheless, conformal coating of nanomaterials (including nanorods) by ALD has not been investigated yet.

In this study, ALD growth method has been applied to the deposition of Al_2O_3 layers on ZnO nanorods. ZnO nanorods were first grown on a Si (100) substrate from ball-milled ZnO powders by a thermal evaporation procedure, and then Al_2O_3 material was deposited on these ZnO nanorods by ALD. The chemical components and structural properties of the deposited Al_2O_3 films were investigated by energy-dispersive X-ray (EDX) spectroscopy and transmission electron microscopy

(TEM).

2. EXPERIMENTAL PROCEDURE

ZnO powders were used for synthesizing ZnO nanorods. The ZnO powders were milled for 20 hours in the mechanical ball mill system. The thermal evaporation of the ball-milled ZnO powders was performed at 1380℃ for 3 hours with an argon flow rate of 500 sccm. ZnO nanorods were formed on a silicon substrate from the evaporation of the ball-milled ZnO powders [2]. Al_2O_3 were deposited on the synthesized ZnO nanorods at a temperature of 300℃ by using ALD technique. Trimethylaluminum (TMA) and distilled water were utilized as the precursors for the deposition. The process pressure was 280 and 250 mTorr for the dosing of chemical precursors and the Ar gas purging, respectively. One cycle for the deposition of Al_2O_3 is composed of TMA dosing, Ar purging, H_2O dosing and Ar purging. Dosing and purging times were 2 and 20 sec, respectively.

The structure and chemical components of Al_2O_3 layer were analyzed by transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) spectroscopy, respectively. The thickness of the Al_2O_3 layers was determined by TEM, and the interface between the ZnO nanorods and the Al_2O_3 layers was examined by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3000F).

3. RESULTS AND DISCUSSION

Figure 1 is a TEM image of a nanorod selected from ZnO nanorods grown on a Si(100) substrate; the diameters of ZnO nanorods are within the range of 50~200 nm, their cross section is circular, and their lengths are 20~30 ㎛. The selected area electron diffraction (SAED) pattern in the inlet of Fig. 1 indicates that the growth direction of the ZnO nanorod grown on a Si (100) substrate is normal to the (001) plane. SAED patterns obtained from several different parts along the selected nanorod without rotating the nanorod are nearly identical, indicating that the nanorod is single crystalline.

Figure 2 is a TEM image of one selected from single-crystalline ZnO nanorods [grown on a Si (100) substrate] deposited with Al_2O_3 materials by ALD. The TEM image illustrates that a cylindrical Al_2O_3 shell with the cap surrounds the ZnO nanorod. The Al_2O_3 shell is 46nm in thickness; its thickness is quite uniform along the nanorod. The inset of Fig. 2 shows the SAED pattern of the Al_2O_3-coated ZnO nanorod. This pattern shows the rings overlapped with regularly positioned spots, while that of the bare ZnO nanorod shows only the spots (see the inset of Fig. 1). The presence of the rings in the SAED pattern indicates that the Al_2O_3 layer coated on the ZnO nanorod is amorphous. The TEM image and SAED pattern illustrate that the ZnO nanorod is coated conformally with amorphous Al_2O_3 material.

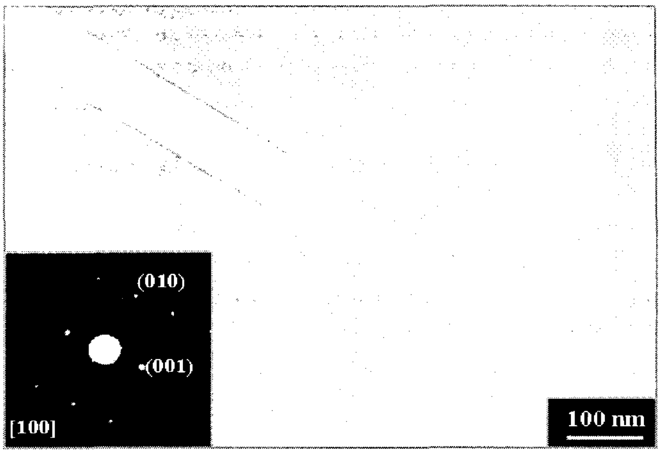

Fig. 1. A TEM image of a nanorod selected from ZnO nanorods grown on a Si(100) substrate.

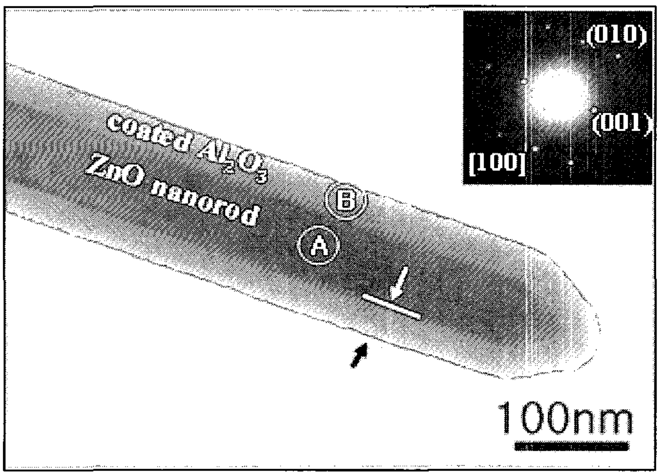

Fig. 2. A TEM image of an Al_2O_3-deposited ZnO nanorod. The central part (A) is the ZnO nanorod and the outer part (B) is the deposited Al_2O_3 layer.

Figures 3(a) and 3(b) show the EDX spectra taken for the central and edge parts (marked by A and B, respectively, in Fig.2) of the coated ZnO nanorod. The EDX spectrum taken for the edge part exhibits that the Al-related peak is much stronger in intensity than the Zn-related peak, which indicates that the deposited part is indeed Al_2O_3; the Cu-related peaks in the spectra come from the Cu grids. Additionally, an Al_2O_3 film was deposited on a plain Si substrate by ALD under the same deposition condition as the nanorods under study. In a

Fourier transform infrared (FTIR) spectrum taken for this Al_2O_3 film grown on Si substrate (not shown here), a broad absorption band associated with amorphous Al_2O_3 was observed. These EDX and FTIR results support our argument that the coating material of the ZnO nanorod is amorphous Al_2O_3.

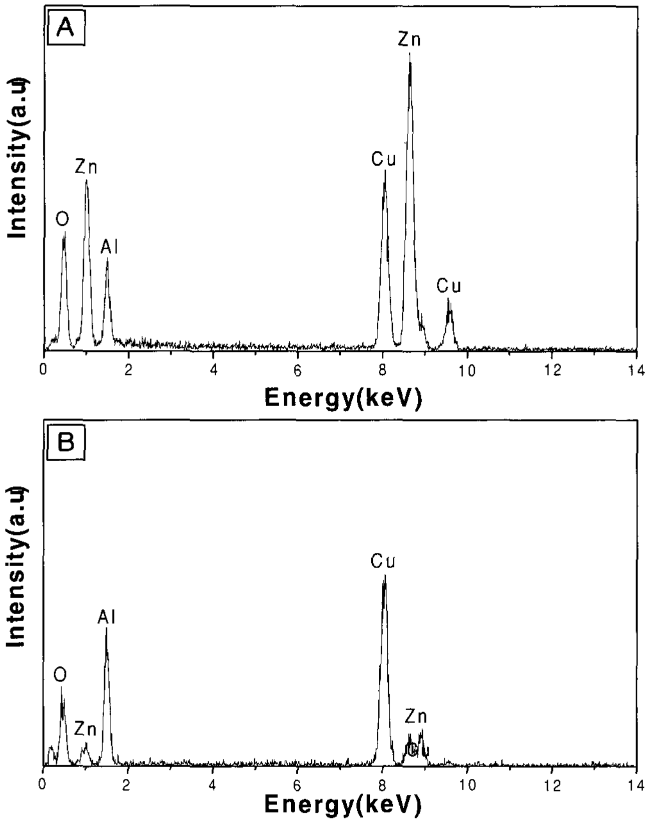

Fig. 3. EDX spectra taken for the central part A (a) and the outer part B (b) (in Fig.2) of the Al_2O_3-deposited ZnO nanorod.

Figure 4 shows a HRTEM image of an Al_2O_3-coated ZnO nanorod. The HRTEM image illustrates the periodic array of atoms in the ZnO nanorod and the randomly positioned atoms in the Al_2O_3 shell. The HRTEM confirms that the ZnO nanorod is single crystalline and that the coating Al_2O_3 material is amorphous. However, the HRTEM image does not show any interfacial alloy layer between the ZnO and Al_2O_3 layers. The absence of the interfaces in our Al_2O_3-coated ZnO nanorods is consistent with the ZnO/Al_2O_3 nanolaminate structures reported by Elam et al; these nanolaminate structures do not show any interfacial alloy layers [13].

Figure 5 shows a TEM image of some Al_2O_3-coated ZnO nanorods. The TEM image demonstrates that a necked ellipsoid nanorod is coated conformally with Al_2O_3. This TEM images shows that ALD has an excellent capability to coat any shape of nanorods conformally (see also the conformal coating of the conical already shown in Fig. 2).

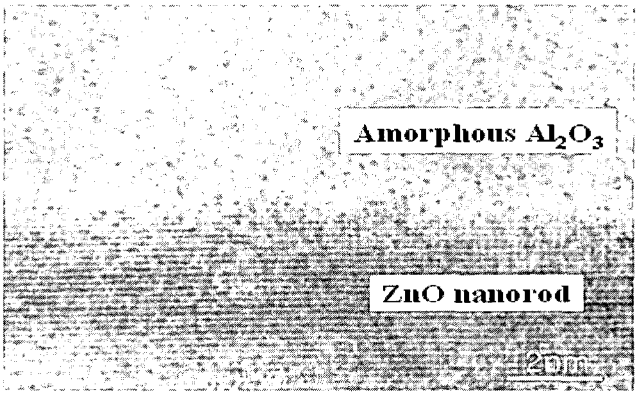

Fig. 4. A HRTEM image of an Al_2O_3-deposited ZnO nanorod.

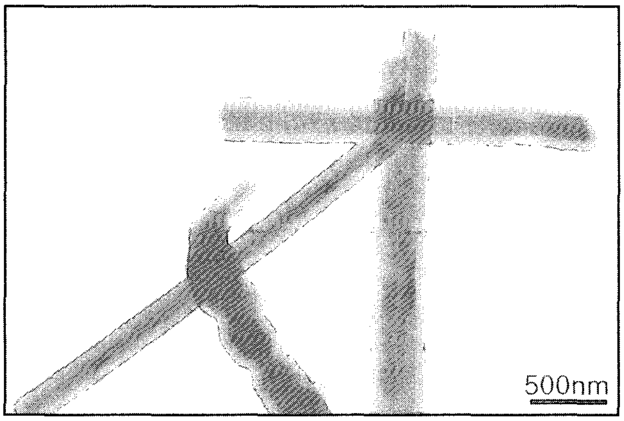

Fig. 5. A TEM image of some Al_2O_3-deposited ZnO nanorods.

The thicknesses of Al_2O_3-coating layers were precisely measured by TEM. The deposition rate of the Al_2O_3 coating may be determined in a straight way from the plot to be 0.19nm/cycle. This value agrees with that of deposition rate for flat surfaces [9]. We suggest here that the coating method using nanorods can be applied as a convenient technique to measure the thicknesses of plain layers grown by ALD method; during the growth of plain layers by ALD method, nanorods are put together. Notice that the growth rate of the Al_2O_3 film by ALD does not depend on the substrate materials as well as the crystal structures. The thickness and deposition rate of plain layers grown by ALD have been conventionally measured by vertical (side-view) TEM or by elliposometry. Vertical TEM analysis requires the complicated procedure for preparing TEM specimens, and elliposometry analysis is an indirect method that is dependent significantly on refractive indexes of deposited layers and substrates. Our suggested coating method using nanorods is a straight and convenient method to measure precisely the nanoscale thicknesses for the plain layers through the measurement of the thickness of the coated layers deposited on nanorods. The coated layers on the nanorods can play a role as an indicator of the growth rate of the ALD system.

4. CONCLUSION

In summary, conformal Al_2O_3 layers were deposited on ZnO nanorods by ALD, after the synthesis of ZnO nanorods from ball-milled ZnO powders by a thermal evaporation procedure. TEM and HRTEM images of the deposited ZnO nanorods revealed that amorphous Al_2O_3 cylindrical shells wrap the ZnO nanorods, but they did not show any interfacial alloy layer between the ZnO and Al_2O_3 layers. The deposition rate of the Al_2O_3 coating may be determined in a straight way to be 0.19nm/cycle. And we suggested that the coated layers on the nanorods can play a role as an indicator of the deposition rate of the ALD system.

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