Atomic layer deposition of ZnO:Al on PAA substrates

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Abstract. In this work the ZnO:Al films of different thickness are grown on the Porous Anodic Alumina (PAA) and p-Si (100) substrates by Atomic Layer Deposition. The ZnO:Al films thicknesses are chosen appropriately in order to obtain complete filled pores as well as pores with a thin covering on the surface. The obtained structures are investigated with spectroscopic ellipsometry and Scanning Electron Microscopy (SEM) techniques.

1. Introduction
In last decades the interest in nanomaterials increases rapidly due to their profound implications for many sectors of the electronics [1]. Two principal factors cause the properties of nanomaterials differ significantly from other materials: increased relative surface area, and quantum effects. The unusual properties of nanomaterials give their rich variety of applications: nanoelectronics, optoelectronics, spintronics, sunscreens and cosmetics, paints, displays, batteries, catalysis, medicine, sensors, food, construction, agriculture, energy and many others [1]. Therefore, a lot of companies and scientific laboratories all over the world are involved in development and investigation of nanomaterials. One of the easiest techniques for obtaining of cost-less templates for construction and designing different nanostructures is Porous Anodic Alumina (PAA) or Anodic Aluminum Oxide (AAO). PAA is a self-organized material with honeycomb-like structure formed by high density arrays of uniform and parallel nanopores with controlled diameter of the pores (from a few nm to several hundreds nanometers) formed by electrochemical oxidation (anodization) of aluminum in different electrolytes [2–5]. The deposition of nanofilms on 3D substrates like Porous Anodic Alumina (PAA) is of great interest from fundamental point of view as well as for practical applications. The best technique for covering such complicated substrates is the Atomic Layer Deposition (ALD) method because of its perfect 3D conformability, uniform covering on ultra-high aspect ratio (>2000:1) features, large area thickness uniformity, atomically flat and smooth coatings and possibility to control the thickness at the nanometer scale. Depending on the PAA substrate properties (pores dimensions, distance between pores, one or double side opened structures), deposition conditions (type of precursor, pulse duration, repetition, substrate temperature, etc.), chemical and thermal treatment different nanostructures could
be obtained such as nanorods, nanotubes and nanodots. These nanostructures could consist of single or multi shell constructions in which each shell could be formed from different material (conducting, insulating or magnetic) which gives a rich variety of possibilities. Such structures could be used as magnetic, gas, chemical and biological sensors, as well as for catalytic converters, medical applications, Solid Oxide Fuel Cells (SOFCs), supercapacitors, batteries, magnetic, nanoelectronic, spintronic and magnonic devices.

In this work the ZnO:Al films of different thickness were grown on the PAA substrates by Atomic Layer Deposition. The thicknesses were chosen appropriately to obtain completely filled pores and pores with a thin covering on the surface. The structures were investigated by plan- view and cross-section Scanning Electron Microscopy (SEM).

2. Experimental

AAO templates were prepared by two-step anodization of 38 μm 99.9995% Al foil (Alfa Aesar). The first anodization of the Al plate was performed at a constant voltage of 40 V for 30 min after degreasing of the Al plate in 40 g/L NaOH followed by electropolishing for 60 and 30 seconds in specimens B1601-3 and B1601-4, respectively. Then the anodic oxide was removed in a solution of phosphoric and chromic acids at 80 °C for 70 min. The second anodization then was carried out to the complete transformation of Al to Al2O3. Furthermore, a pore widening step was done for samples B1601-1 and B1601-2 in the same electrolyte (4% (COOH)2), 40 °C, 40 min.

Atomic Layer Deposition (ALD) was used to deposit ZnO:Al films of different thickness. Thermal ALD with a Beneq TFS-200 reactor at 200 °C in nitrogen flow of 600 sccm was used. To obtain the ZnO:Al films the TMA (trimethylaluminium) with H2O and DEZ (diethylzinc) with H2O precursors at 1:24 ratio for Al2O3 and ZnO sublayers respectively were used. The duration of the precursor pulses and purging were 200 ms and 2 s respectively. The covering of PAA templates with different thicknesses was obtained by varying the repetition of full cycles (ZnO:Al2O3= 24:1 denotes one full cycle). The repetition of full ZnO:Al2O3 cycles 56; 4; and 2 times were done. In all processes the p-Si(111) substrate as a reference sample was loaded together with PAA templates. The samples were denoted as 28, 29 and 31 for 56, 2 and 4 full cycles repetition, respectively.

Ellipsometric measurements for Si reference substrates were performed using a Woollam M2000D rotating compensator spectroscopic ellipsometer with a wavelength range from 193 to 1000 nm. The film thickness and the optical constants were determined by fitting the experimental \( \Psi \) and \( \Delta \) data.

SEM (Scanning Electron Microscope) investigations were carried out with the Hitachi SU-70 equipment using 15 kV of electron beam accelerating voltage and upper SE (Secondary Electron) detector, sensitive to the surface topography.

3. Results and discussion

3.1. Morphology of porous anodic alumina templates

Four different double-side Porous Anodic Alumina (PAA) templates (see figure 1) were obtained by a two-step anodization in the way described above. The main parameters of these templates are summarized in table 1. In our previous SEM investigations [6] it was determined that at similar experimental conditions (as in samples B1601-3 and B1601-4) the diameters of the pores were about 30-40 nm and grew up to 60-70 nm after their widening (samples B1601-1and B1601-2). Polishing was used to reduce the Al foil thickness and thereby obtain anodic oxide of different thickness. The final thickness of PAA templates was measured using optical microscopy technique (figure 2).
Figure 1. Sketch of double side PAA.

Figure 2. Optical microscopic image (cross-section) of the B1601-1 sample.

Table 1. Parameters of PAA templates.

| Pore diameters, nm | Total thickness of PAA templates, μm |
|--------------------|--------------------------------------|
| B1601-1            | 22                                   |
| B1601-2            | 30.5                                 |
| B1601-3            | 17                                   |
| B1601-4            | 22                                   |

3.2. Parameters of ALD thin films deposition

Thermal ALD depositions of the ZnO:Al thin films of different thickness on PAA templates and p-Si(111) substrates were done. In order to obtain conformal films, the Al2O3 monolayer was grown first (1 cycle) from the TMA and H2O precursors. Then, 24 monolayers of ZnO were deposited (24 cycles) from the DEZ and H2O precursors. The full cycle (ZnO:Al 24:1) was repeated 56, 4 and 2 times to obtain different thickness. The deposition rates of pure ZnO and Al2O3 sublayers were obtained from thick films (1010 and 880 cycles respectively) grown on Si substrates at 200 °C and the thicknesses were extracted from the Ellipsometric measurements [7]. Deposition rate for ZnO and Al2O3 films are 2 and 1.14 Å/cycle respectively. Therefore, for full cycle (ZnO:Al 24:1) with repetition 56, 4 and 2 the obtained thicknesses correspond to 275, 19.7 and 9.8 nm. Moreover, the volume percentage of Al2O3 content in ZnO:Al films evaluated from the formula of $a = \frac{mA}{mA + nB}$, given in [7] should be about 2.3 %, where the $m$ and $n$ are the numbers of TMA and DEZ cycles and $A$ and $B$ are the growth rates of Al2O3 and ZnO, respectively. It should be noted that in thinner films (with 2 and 4 repetition of full cycles) the growth rate is supposed to be lower due to the interphase interactions and surface initialization for conformal deposition. As the repetitions number increases the surface conformality improves and growth rate becomes more uniform. These factors also should lead to the Al content decrease in the ZnO:Al films for their lower thicknesses.

3.3. Ellipsometric study

The spectroscopic ellipsometry data of $\Psi$ and $\Delta$ were taken in the wavelength range from 193 to 1000 nm on ZnO:Al (24:1) films grown on p-Si(111) with repetition of full cycles 56, 4, and 2, respectively. The experimental $\Psi$ and $\Delta$ were analyzed using a three-layer model consisting of a silicon substrate with SiO2 native oxide as a first layer, a ZnO layer as a second layer and a roughness layer as a third layer. For the Si substrate and the native oxide, the data from the database of CompleteEASE Woollam data analysis software was used. The ZnO:Al layer was modeled using a PSemi-M0 and two Gaussian oscillators. The roughness layer for all samples is modeled by Bruggeman’s EMA (Effective
Medium Approximation) of 50 % voids and 50 % bulk material [8]. The thicknesses of the ZnO:Al layers on Si substrates as determined from the fits are as follows: 262.46 nm for sample 28, 8.11 nm for sample 29 and 16.54 nm for sample 31. These results are in agreement with the thicknesses obtained from the growth rate discussed above.

We estimated the optical bandgap $E_g$ of the ZnO:Al from the equation

$$\alpha = \frac{(h \nu - E_g)^2}{h \nu},$$

by plotting the absorption coefficient squared $(\alpha h \nu)^2$ versus photon energy, as shown on figure 3. The dispersion of the absorption coefficient $\alpha$ was determined from the dispersion of the extinction coefficient $\kappa(\lambda)$ using the equation $\alpha = 4 \pi \kappa / \lambda$. The extinction coefficient $\kappa$ was estimated by fitting the experimental data $\Psi$ and $\Delta$.

Figure 3 shows a comparison of the squared absorption coefficient $(\alpha h \nu)^2$ versus photon energy for 207 nm thick undoped ZnO layer and a 262.46 nm thick ZnO:Al (sample #28) layer of similar thicknesses. The estimated optical bandgap of the aluminum doped zinc oxide layer is about 210 meV larger than the optical bandgap of the undoped ZnO layer. This is supposed to be due to the Burstein-Moss effect. The samples #29 and #31 were omitted because of the band gap expansion due to the quantum confinement effect as described in (Ref. [9, 10]).

![Figure 3](image-url)

**Figure 3.** Square of absorption coefficient $(\alpha h \nu)^2$ for undoped and Al-doped ZnO layers vs. photon energy. Solid lines show linear fits to the experimental data. The intercept at $(\alpha h \nu)^2 = 0$ shows the bandgap of ZnO.

3.4. **SEM observations**

The SEM images show an extremely conformal coverage of the PAA matrix by ZnO:Al layer deposited by ALD (figures 4 and 5). This layer fills the pores even up to a depth of several micrometers (which is unattainable with other deposition methods). The ZnO:Al layer is polycrystalline (as shown on SEM images) and pore-free (dense material, which is characteristic for the materials obtained by ALD).

On the figure 4, plan- view and cross- section SEM images of ZnO:Al films on PAA templates for two different thicknesses corresponding to full cycle repetition of 4 and 56 are presented.
Figure 4. SEM images of ZnO:Al with 4 times repetition on PAA template (a) top-view and (b) cross-section of sample B1601-2 2/31

At 4 repetitions (around 16 nm ZnO:Al on Si substrate according to the ellipsometry data) of full cycle very thin film of ZnO:Al covers the walls of pores and decreases the pores diameters. For sample B1601-2 2/31 (with 60-70 nm pores) the pores diameters decrease to 30-40 nm (figure 4). At lower magnification the typical honeycomb-like structure of PAA template can be observed (figure 4a). On higher magnification (not shown here) it should be seen the grains 20×10 nm. The higher repetition (56 full cycles) fill up the pores and dense ZnO:Al films (~270 nm) start to grown on the top (figure 5) with the typical for ZnO sticks-like structure (200×20 nm elongated grains). The obtained thickness from SEM images 270 nm is a little bit higher than the thickness of 260 nm obtained by ellipsometric measurements on a Si substrate because of the higher deposition rate on PAA due to already saturated the Al2O3 surface.

Figure 5. SEM images of ZnO:Al with 56 time repetition on PAA template (a) top-view and (b) cross-section of sample B1601-2 3/28

4. Conclusions
ZnO:Al (24:1) films with different thicknesses were grown by Atomic Layer Deposition on Porous Anodic Alumina templates and p-Si(100) substrates. An extremely conformal coverage of the PAA templates with a ZnO:Al layer is obtained as shown by SEM analysis. The layers fill the pores even up to a depth of several micrometers which is unattainable with other deposition methods. The deposited ZnO:Al layer is polycrystalline and pore-free dense material. Ellipsometry analyses on Si substrates confirm the thickness of ZnO:Al films obtained from the SEM. It was found that the estimated optical bandgap from the Ellipsometric measurements of the thicker Al doped ZnO layer is about 170 meV larger than the optical bandgap of the undoped ZnO layer due to the Burstein-Moss effect.

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