Influence of Solution pH on the Electrochemical Fabrication of Functional Metal Oxides Using a Nanoporous Alumina Template

Jin-sub Choi, Eun-seong Ko*, Jin-wook Kang*, Yong-sug Tak*, and Jaeyoung Lee**†

Nanomaterials Application Division, Korea Institute of Ceramic Engineering and Technology, Seoul 153-801, Korea
* Department of Chemical Engineering, Inha University, Inchon 402-751, Korea
** Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea

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Abstract: We have investigated the influence of solution pH on the electrochemical fabrication of functional metal oxides, i.e., cuprous oxide (Cu2O) and zinc oxide (ZnO), using a nanoporous alumina template. At a low solution pH of ca. 5 ~ 7, Cu metal was preferentially filled into an alumina template; Cu2O nanorods were formed at solution pH above 8 ~ 10. In the preparation of ZnO using a zinc nitrate solution with a bulk solution pH of 4.3, a ZnO thin film prepared through remote electro-precipitation was observed on the alumina template.

Keywords: electrodeposition, alumina template, solution pH effect, Cu2O, ZnO

Introduction

The formation of nanoporous alumina templates via the electro-oxidation of aluminum is currently of great interest in relation to the fabrication of ordered nano-sized materials in biological, electronic, thermoelectric, and photonic devices [1-3]. This increasing attraction of using porous alumina as a template is mainly due to its simple and low-cost manufacturing process. Nanorods of metals [4-7], semiconductors [8,9], and polymers [10] in hexagonally ordered nanoporous alumina templates have been made by several research groups.

Electrochemical fabrication of functional metal oxides has the following advantages over conventional methods: precise control over the thickness and morphology, higher deposition rates, and simpler equipment demands because high temperatures and pressures are not required. Nickel nanorods made using a potential modulation mode [5] have potential applications in high-density magnetic memories. The preparation of metal oxide nanorods of cuprous oxide (Cu2O) in alumina templates through electrodeposition was reported recently [11].

Cu2O is a non stoichiometric p-type semiconductor with a bandgap of 2.0 eV; it has been proposed as a photocatalytic material for splitting water into H2 and O2 under visible light irradiation [12-14]. It is also a potential material for fabrication of low-cost solar cells [15,16]. Zinc oxide (ZnO) is an n-type semiconductor with a bandgap of 3.2 eV; it has transparent and conductive properties. ZnO is a promising material for use in ultraviolet-emitting diodes, piezoelectric devices, sensors, and solar cells [17-20]. ZnO films can be electrochemically deposited using the potential modulation method; the deposition process requires alkaline conditions caused by generated hydroxide ions from the electrolyte.

In this study, we compared the influence of the pH on the shape and mechanistic origins of functional metal oxides prepared from Cu2O and ZnO using a highly ordered alumina template. SEM with EDX and XRD techniques were the analysis tools of choice.

Experimental Section

Cu2O and ZnO were electrochemically deposited into/onto porous alumina templates using a conventional three-electrode system. Applying direct current through a
sputtering technique (Nuricell Inc.), Pt metal was deposited on one side of a commercial alumina template (Whatman, Anodisc 25) with a diameter of 200 nm, which was used as the working electrode. To prepare Cu$_2$O, a total of 45 g of 99.99 % CuSO$_4$ was dissolved in 75 mL of 88 % lactic acid; the Cu ions were stabilized by complexing with lactate ions. To analyze the pH effect, 5 M aqueous NaOH solution was added to adjust the pH between 5 and 12. The electrolyte for ZnO electrodeposition was 0.1 M zinc nitrate having a bulk solution pH of ca. 4.3.

A saturated calomel electrode (SCE) and Pt mesh were employed as the reference and counter electrodes, respectively. A potentiostat-galvanostat (EG&G PAR 273 A) was used to apply an optimal potential of -1.0 V and a current density of -0.5 mA/cm$^2$ for the depositions of ZnO and Cu$_2$O, respectively. The solution temperature (65 °C) was maintained during the experiments.

The surface morphology of the prepared nanorods was analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4300). The crystallinity and quantitative analysis of the metal oxides were determined using X-ray diffraction (XRD, Philips DY616) and energy dispersive X-ray spectroscopy (EDX) coupled with the SEM equipment.

Results and Discussion

We prepared five solutions of different pH for the formation of Cu$_2$O (Figure 1). The weakly acidic copper solution adjusted to pH 5 contained insoluble powder. Therefore, it could be not used for the formation of Cu$_2$O. Upon increasing the pH, the color of the solution became darker and cleared; these mixtures were used for the investigation of the pH effect on the formation of Cu$_2$O.

Referring to our previous studies [11], we applied a current density of -0.5 mA/cm$^2$ to the Pt substrate for fabrication of a homogeneous and compact nanorod of cuprous oxide. Figure 2 displays XRD data of the materials deposited into the alumina template at different values of solution pH. (a) pH 6, (b) pH 8, (c) pH 10. Cu$_2$O preparation in CuSO$_4$ + 5H$_2$O + Lactic acid + 5 M NaOH at -0.5mA/cm$^2$ for 4 h.
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Figure 3. (a, b) SEM images of Cu$_2$O nanorods in an alumina template. (c, d) EDX data of region (spectrum) 1 and 2, respectively. The preparation conditions for Cu$_2$O were the same as those described in Figure 2(c).

solved oxygen in the solution enhance the local surface pH, it is not enough to make appropriate alkaline conditions to prepare Cu$_2$O. At solution pH of 8.0, we clearly observe various Cu$_2$O peaks, which became dominant compared with the Cu peak formed at pH 6.0. A solution pH of 8.0 consecutively forms Cu$_2$O (111), (200), (220), and (311). Figure 2(c) shows very distinct Cu$_2$O peaks without detecting any Cu into the alumina template. At a solution pH of 10.0, Cu$_2$O (200) was formed preferentially. At a solution pH of 12, we did not observe any formation of Cu complex into the alumina template; this result might be due to complete dissolution of the alumina template (not shown here).

By analysis of previous studies [22], the orientation of Cu$_2$O films is related to the solution pH; Cu$_2$O [100] and [111] forms appear at pH 9 and 12. In this study, Cu$_2$O (200) and (111) were mainly formed at values of solution pH of 10.0 and 8.0, but these results are not in good agreement with those reported by Golden and coworkers [22]. Exact understanding of the mechanistic origins of the formation of the crystal patterns is still unclear; further precise measurements of the relationship between the solution pH and the orientation of the Cu$_2$O crystals should be performed.

Figure 3 presents the cross-section view and EDX data of Cu$_2$O deposited into alumina template structure at a current density of -0.5 mA/cm$^2$ and a solution pH of 10. Figure 3(a) shows three distinct regions: the alumina template area, the nanorod area, and the compact thin film layer. The first region is the alumina template (indicated as spectrum 1) and the third region is the platinum layer formed using the DC sputtering method. The second region (see spectrum 2) corresponds to the Cu$_2$O nanorods formed within the alumina template. The Cu$_2$O nanorods grew homogeneously until they reached a length of ca. 4 µm, presenting an aspect ratio of 20. Figure 3(b) displays only the Cu$_2$O nanorods after selective dissolution of the alumina template in NaOH solution. EDX observation of Figures 3(c) and (d) clearly support the morphological observations.

Figure 4(a) displays a top-view of the alumina template when a potential of -1.0 V was applied for 30 s in 0.1 M Zn(NO$_3$)$_2$ solution. Bulky precipitated species (zinc hydroxides) cover the nanoporous alumina template. Figures 4(b) and 4(c) are a cross-sectional view and top-view of the alumina template at an electrolysis
time of 2 h. Although a much larger cathodic charge applies, nanorods were not formed into the alumina template and the pores were destroyed by hydroxide ions. Figure 4(c) presents a top-view of the material deposited onto the alumina template; we clearly observe a hexagonal structured material. Figure 4(d) displays the EDX data of Figure 4(c); it indicates that ZnO is distributed on the alumina template. Analyzing and understanding Figure 4, we conclude that ZnO was deposited onto the alumina template and not into the alumina pores. The generation of hydroxide ions, reduced from nitrate, increased the local pH both inside and on the surface of the alumina template [11,23]. In aqueous solutions, the most stable form of zinc ions, the tetra-coordinate ion $\text{Zn(H}_2\text{O)}_4^{2+}$, reacts with hydroxide ions only near the top of the alumina template [21]. Zinc hydroxide precipitated on alumina template and became ZnO through a dehydration reaction.

Conclusions

Electrochemical deposition and precipitation are appropriate techniques for preparing highly ordered and/or thin film structured functional metal oxides using an alumina template. Cu$_2$O nanorods were formed in the presence of a critical concentration of hydroxide ions, i.e., in a pH-dependent process. Thus, precise control of the solution pH and temperature were important for the preparation of the Cu$_2$O nanorods. A thin film of ZnO was only remote-deposited onto the non-conducting alumina template in medium pH by two subsequent electrochemical and chemical reactions. Because of deformation of the alumina template near the Pt substrate and inhomogeneous distribution of hydroxide ions, the ZnO nanorods could not form. Further understanding of the mechanistic origin of the ZnO thin film, i.e., the role of hydroxide ions, might make it possible to determine appropriate conditions to prepare ZnO nanorods within the alumina template. We expect that this work will be a reference for the development of such systems as small-scale piezoelectric devices, sensors, and solar cells.

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References