Sustainable Electrodeposition of ZnO by a Galvanic Contact Method

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The galvanic contact deposition of ZnO was carried out by immersing a conductive substrate short-circuited with a Zn rod into an aqueous solution of Zn(NO3)2. The solution of the Zn rod in the Zn(NO3)2 solution supplied a continuous and almost constant current to the substrate, allowing the cathodic electrodeposition of ZnO without an external power and by-products. The morphology of the resulting ZnO depended on the Zn(NO3)2 concentration. In contrast, a much smaller current was observed in the Zn(NO3)2 solution, and little ZnO was deposited.

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Zinc oxide (ZnO) is an n-type semiconducting oxide with a wide bandgap energy of 3.3 eV and a high exciton binding energy of 59 meV, which make visible transparency and room-temperature UV emission possible. Thin ZnO layers including various nanostructures have received increasing attention for a wide range of applications such as chemical sensors,1-3 electrodes in solar cells,4-6 and UV emitting devices.7,8 Among the many physical and chemical processes to grow ZnO, electrochemical deposition from aqueous solutions is a powerful technique to give high quality ZnO and offers a large-scale synthetic route with low cost. Since the electrodeposition technique of ZnO was established by Izaki and Omi10 and Peulon and Lincot in 1996,11 ZnO with a variety of structures, including pillar,12-14 tube,15,16 flower,17,18 and sheet,19 has been synthesized by applying the technique. Moreover, the epitaxial growth of ZnO has also been attained by using lattice-matched substrates.20-22 In these ZnO electrodepositions, cathodic electrolysis is employed in an aqueous Zn(NO3)2 or ZnCl2 solution, and the deposition mechanism is based on the increase in local pH in the vicinity of an electrode, followed by hydrolysis of zinc ions to give ZnO

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \]  

Such a local deposition fashion can, therefore, prevent precipitation in the bulk of solution unlike chemical bath deposition and hydrothermal synthesis. To raise the local pH, the cathodic reduction of dissolved oxygen (DO) and nitrate ion, which gives hydroxide ion, is generally utilized

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]  

and an external power, i.e., potentiostat/galvanostat, is employed to control the electrolysis.

Recently, Mondal et al.23 reported a unique electrochemical process to deposit ZnO without external power through a “galvanic contact method,” also referred to as the “contact immersion method.” In this method, a working substrate is short-circuited to an auxiliary electrode, of which the potential when immersed into the deposition bath is negative to the Nernst potential of the cathodic reaction desired on the working substrate. The galvanic contact method is, therefore, a kind of “short-circuited galvanic cell” and generally offers a “semipotentiostatic condition” without a set of potentiostat and reference electrodes. So far, metals, alloys, and metallic calcogenides, such as Cu–Sn,24 CdTe,25-28 and CdSe,29 have been synthesized by using galvanic contact methods. In the literature, a metallic zinc rod as an anode and transparent conductive oxide-coated (TCO) glass substrate as a cathode were immersed into a 10 mM (M = mol dm−3) Zn(NO3)2 solution at 60–80°C, and then the two electrodes were just short-circuited to deposit ZnO. The driving force to promote the ZnO deposition is the dissolution of zinc ions from metallic zinc, which supplies electrons to the TCO glass, reducing nitrate ions. However, Mondal et al.23 reported that the growth of ZnO stopped at a layer thickness of ~0.6 μm due to the electrical resistance of ZnO, which becomes higher with increasing thickness.

Nonetheless, this system is potentially interesting because one can obtain an external power-free solution process. Furthermore, by not using nitrate ion but using DO to raise the local pH, the following overall reaction is given

\[ \text{Zn} + \frac{1}{2}\text{O}_2 \rightarrow \text{ZnO} \]  

resulting in a no-by-product process that keeps the Zn2+ concentration constant (Fig. 1). Therefore, the development of a galvanic contact method affording a continuous ZnO growth offers a useful tool to yield ZnO. Here, we demonstrate the continuous galvanic contact deposition of ZnO by using simple Zn(ClO4)2 solutions with O2 gas bubbling, and the deposition behavior in the Zn(ClO4)2 solution is discussed in comparison with that in the Zn(NO3)2 solution.

Figure 1. Schematic view of the galvanic contact deposition of ZnO using a Zn-bar anode immersed in an oxygenated aqueous solution.

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Experimental

To deposit ZnO, an aqueous solution containing 3–75 mM Zn(ClO$_4$)$_2$ or 15 mM Zn(NO$_3$)$_2$ was bubbled with O$_2$ gas in advance for 1 h and heated at 75°C. Then, a F-doped SnO$_2$ (FTO) coated glass substrate short-circuited with a Zn rod was immersed into the solution for 2 h. To prepare the solutions, reagent grade chemicals of Zn(ClO$_4$)$_2$·6H$_2$O (Sigma-Aldrich, Inc.) and Zn(NO$_3$)$_2$·6H$_2$O (Nacalai Tesque, Inc.) and deionized water purified by a Milli RX12 Plus system were employed. The pH of the solutions were 5.3 and 5.4 for Zn(ClO$_4$)$_2$ and Zn(NO$_3$)$_2$, respectively, at 25°C. The FTO glass used was 30 × 10 × 1.1 mm with a 9 Ω sheet resistance (Asahi Glass Co., Ltd.), and the Zn rod used was a guaranteed reagent and φ8 × 60 mm (Kanto Chemical Co., Inc.). During the immersion, O$_2$ gas bubbling at a flow rate of 10 cm$^3$ min$^{-1}$ was carried out continuously, and the solution was thermostatted at 75°C. After the immersion, the deposit on the FTO glass was rinsed with deionized water and dried under ambient atmosphere. The characterization was performed with an X-ray diffractometer (XRD, Rigaku RINT2500) and a field-emission-scanning electron microscope (FESEM, JEOL JSM6700F).

The current and electrode potential during the immersion were measured with a digital multimeter (Yokogawa 7552) and a double-junction-type Ag/AgCl reference electrode (DKK-TOA HS-305D). The double-junction electrode was composed of an inner (Ag/AgCl electrode immersed in a saturated KCl solution) and an outer compartment divided by a glass frit. To prevent the precipitation of low solubility KClO$_4$ at the solution junction, the outer compartment was filled with a 10 wt % NaCl aqueous solution. Linear sweep voltammetry (LSV) was carried out using an automatic polarization system (Hokuto Denko HSV-100) and a Pt-sheet counter electrode. The LSV was started from each steady rest potential at a sweep rate of 5 mV s$^{-1}$.

Results and Discussion

Figure 2 shows normalized XRD patterns of deposits by 2 h galvanic contact deposition from the 3, 15, and 75 mM Zn(ClO$_4$)$_2$ and 15 mM Zn(NO$_3$)$_2$ solutions. All deposits obtained from the Zn(ClO$_4$)$_2$ solutions were identified as c-axis-oriented ZnO with a wurtzite structure (JCPDS no. 36-1451), and no other phases such as zinc hydroxides and metallic zinc were recognized. In the pattern for the Zn(NO$_3$)$_2$ solution (Fig. 2d), only a slight peak assignable to ZnO 0002 was observed in addition to strong diffractions from the FTO glass substrate. Figure 3 shows FESEM images of the deposits corresponding to Fig. 2. Whereas dense ZnO nanopillars of 2–2.5 μm length and 0.15–0.3 μm diameter were observed after the galvanic contact deposition using 3 and 15 mM Zn(ClO$_4$)$_2$ solutions, a 1.6 μm thick ZnO layer composed of hexagonal columnar grains with a diameter of about 0.5 μm grew from the 75 mM Zn(ClO$_4$)$_2$ solution. Such Zn$^{2+}$-concentration-dependent morphology change in electrodeposited ZnO has been reported elsewhere. In contrast, considerably sparse and small ZnO grains of about 0.3 μm length and 50 nm diameter were seen in the deposit from the 15 mM Zn(NO$_3$)$_2$ solution. These results clearly indicate that the galvanic contact method using the Zn(ClO$_4$)$_2$ solutions enables the continuous growth of ZnO beyond the thickness limit of ~0.6 μm reported by Mondal et al.

The deposition behavior of ZnO, including current density and electrode potential, during the galvanic contact deposition is shown in Fig. 4. The rest potentials of an FTO glass in the Zn(ClO$_4$)$_2$ and Zn(NO$_3$)$_2$ solutions were 0.2–0.4 and 0.07 V (vs Ag/AgCl), respectively, and then dropped sharply to ~0.95 and ~0.62 V immediately.
after the short circuiting. This value (−0.95 V) for the Zn(ClO₄)₂ solution was close to the standard electrode potential of Zn²⁺/Zn (E° = −0.96 V vs Ag/AgCl) and then slightly and gradually drifted 40–100 mV within 3 h. In contrast, the cathode potential in the Zn(NO₃)₂ solution shifted positively within 10 min and remained at a constant value of −0.53 V for at least 3 h. In the variation in the current density (Fig. 4b), it was seen that the currents for the Zn(ClO₄)₂ and Zn(NO₃)₂ solutions differed by 1 order of magnitude. The current density in the Zn(ClO₄)₂ solution was kept at almost constant values ranging from 0.2 to 0.5 mA cm⁻² up to at least 3 h with a Zn²⁺ concentration dependence. This indicates that the stable and continuous dissolution of the Zn²⁺ ion from the Zn rod immersed into the NaClO₄ solution without NO₃⁻ ion, as shown in Fig. 5. Whereas the potential of a Zn rod in 0.1 M NaClO₄ solution shifted positively within 10 min and remained at a constant value of −1.1 V . In contrast, there is a considerable difference in the polarization curves for the Zn rod. The rest potential of the Zn rod in the Zn(ClO₄)₂ solution was 0.4 V negative to that in the Zn(NO₃)₂ solution, which is near the value of E°(Zn²⁺/Zn). When two electrodes are short-circuited, the electrical current and potential values pointed by the intersections signify the short-circuit condition in each solution. Indeed, the electrical current and potential values pointed by the intersections in each solution are close to the standard electrode potential of Zn²⁺.

Conclusions

We have developed a synthetic method to yield ZnO based on the simple immersion of a conductive substrate short-circuiting with a metallic zinc into Zn(ClO₄)₂ aqueous solutions bubbled with O₂ gas and have also revealed the negative influence of the NO₃⁻ ion. Using the Zn(ClO₄)₂ solution made an external power-free and by-product-free process possible. This galvanic contact method offers great potential for the external power-free electrodeposition technique of oxides.

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