TITLE:

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AUTHOR(S):

Shinagawa, Tsutomu; Murase, Kuniaki; Izaki, Masanobu

CITATION:

Shinagawa, Tsutomu ...[et al]. Sustainable Electrodeposition of ZnO by a Galvanic Contact Method. ELECTROCHEMICAL AND SOLID STATE LETTERS 2009, 12(9): D72-D75

ISSUE DATE:

2009

URL:

<http://hdl.handle.net/2433/109929>

RIGHT:

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Sustainable Electrodeposition of ZnO by a Galvanic Contact Method

Tsutomu Shinagawa,^{a,z} Kuniaki Murase,^{b,*} and Masanobu Izaki^{c,*}

^aElectronic Materials Research Division, Osaka Municipal Technical Research Institute,
Osaka 536-8553, Japan

^bDepartment of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

^cDepartment of Production System Engineering, Toyohashi University of Technology,
Aichi 441-8580, Japan

The galvanic contact deposition of ZnO was carried out by immersing a conductive substrate short-circuited with a Zn rod into O₂-saturated aqueous Zn(ClO₄)₂ solutions, and the deposition behaviors were investigated in comparison with that in Zn(NO₃)₂. The dissolution of the Zn rod in the Zn(ClO₄)₂ solutions 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(ClO₄)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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Manuscript submitted April 13, 2009; revised manuscript received June 12, 2009. Published July 9, 2009.

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.⁷⁻⁹ 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

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

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,²³ 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

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.

* Electrochemical Society Active Member.

^z E-mail: tshina@omtri.city.osaka.jp

Figure 2. XRD patterns of deposits by 2 h galvanic contact deposition in O_2 -gas-bubbling solutions containing [(a)–(c)] $Zn(ClO_4)_2$ and (d) $Zn(NO_3)_2$ at $75^\circ C$; the concentrations of $Zn(II)$ salt are (a) 3, [(b) and (d)] 15, and (c) 75 mM.

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 $75^\circ C$. 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 $Zn(ClO_4)_2 \cdot 6H_2O$ (Sigma-Aldrich, Inc.) and $Zn(NO_3)_2 \cdot 6H_2O$ (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 $25^\circ C$. The FTO glass used was $30 \times 10 \times 1.1$ mm with a 9Ω sheet resistance (Asahi Glass Co., Ltd.), and the Zn rod used was a guaranteed reagent and $\phi 8 \times 60$ mm (Kanto Chemical Co., Inc.). During the immersion, O_2 gas bubbling at a flow rate of $10 \text{ cm}^3 \text{ min}^{-1}$ was carried out continuously, and the solution was thermostatted at $75^\circ C$. 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

Figure 3. Tilted FESEM images of deposits by 2 h galvanic contact deposition in O_2 -gas-bubbling solutions containing [(a)–(c)] $Zn(ClO_4)_2$ and (d) $Zn(NO_3)_2$ at $75^\circ C$; the concentrations of $Zn(II)$ salt are (a) 3, [(b) and (d)] 15, and (c) 75 mM.

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.^{11,13,14} 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 $\sim 0.6 \mu m$ reported by Mondal et al.²³

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

Figure 4. (Color online) Variation of (a) potential and (b) current density of an FTO glass substrate short-circuited with a Zn rod during galvanic contact deposition.

Figure 5. (Color online) LSV curves: electrode potentials of an FTO glass substrate and a Zn rod vs logarithm of current in (a) 15 mM Zn(ClO₄)₂ and (b) 15 mM Zn(NO₃)₂ solutions.

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 ($E^0 = -0.96$ V vs Ag/AgCl)³⁰ 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, which supplies electrons to an FTO glass, takes place spontaneously in the Zn(ClO₄)₂ solutions.

To investigate the origin of these differences between the two types of solution, LSV was performed cathodically on an FTO glass and anodically on a Zn rod in an O₂-gas-bubbling solution containing 15 mM Zn(ClO₄)₂ or Zn(NO₃)₂ at a sweep rate of 5 mV s^{−1}. The potential applied to the electrode was plotted against the logarithm of the detected current, as shown in Fig. 5. The polarization curves for an FTO glass were similar irrespective of the solution type. The current derived from the DO reduction emerged at potentials at around −0.6 V, and the reduction of Zn²⁺ ions took place at potentials below −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 $E^0(\text{Zn}^{2+}/\text{Zn})$. When two electrodes are short-circuited, the electrical current and potential between the electrodes naturally become almost equal. Therefore, the intersection of two curves in Fig. 5, i.e., the cathodic curve for an FTO glass and the anodic curve for a Zn rod, should signify the short-circuit condition in each solution. Indeed, the electrical current and potential values pointed by the intersections agreed well with the values under the galvanic contact deposition (Fig. 4). Because the potential at each intersection is close to each rest potential of a Zn rod, the difference in the galvanic contact deposition behavior in Fig. 4 may well be dominated by the rest potential of a Zn rod.

The time variation of the Zn-rod rest potential in 0.1 M NaClO₄ solutions with varying NaNO₃ concentrations was measured to confirm the influence of the NO₃[−] ion, as shown in Fig. 6. Whereas the Zn rod immersed into the NaClO₄ solution without NO₃[−] exhibited a constant potential close to $E^0(\text{Zn}^{2+}/\text{Zn})$, the rest potential of the Zn rod immersed in the solutions containing NO₃[−] readily shifted positively and was kept at an almost constant value. The potential shift variation increased with an increasing concentration of NO₃[−], indicating that the chemical state of the Zn-rod surface changes in the presence of NO₃[−]. Some precipitates, i.e., corrosion products, involv-

Figure 6. (Color online) Variation in the immersion potential of a Zn rod in 0.1 M NaClO₄ solutions with and without NaNO₃.

ing NO₃[−] would be formed on the Zn-rod surface. A plateau assignable to the dissolution was recognized in the LSV of the Zn rod, as shown by an arrow in Fig. 5b.

Conclusions

We have developed a synthetic method to yield ZnO based on the simple immersion of a conductive substrate short-circuited 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.

Acknowledgment

This work was supported by a grant-in-aid for Encouragement of Young Scientists (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

T. Shinagawa assisted in meeting the publication costs of this article.

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