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Effects of Counteranions and Dissolved Oxygen on Chemical ZnO Deposition from Aqueous Solutions

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Zinc oxide (ZnO) is an n-type II-VI semiconductor oxide with a bandgap energy of 3.3 eV, which makes it transparent to visible light, and is widely used in industrial applications, such as varistors, chemical gas sensors, and surface acoustic wave devices, due to its various useful properties of semiconductivity, piezoelectricity, fluorescence, and photoconductivity.1-4 In addition, ZnO has received much attention as a transparent conductive oxide5 and a UV light-emitting material.5,6 Recent vigorous developments in optoelectronic devices, such as flat-panel displays, have heightened the demand for low-cost transparent conductive films. Because zinc is an inexpensive common metal element, ZnO is a promising candidate for alternatives to indium tin oxide, consisting of a quite expensive rare-metal element.

As one of the nonvacuum and low-temperature soft processes, the formation of a polycrystalline wurtzite ZnO film from aqueous Zn(NO3)2 solutions using an electrochemical method has been reported by Izaki and Omi,6,11 and Peulon and Lincot,12,13 respectively. The scheme of both the deposition methods is based on a local-pH increase in the vicinity of an electrode, resulting in precipitation of ZnO by the hydrolysis of Zn2+ at around pH 6.14 Because DMAB is a relatively moderate reductant, the reversible acid-base Reaction1 proceeds under near equilibrium condition.15,16 In the electrochemical route, ZnO is catalyzed by palladium nanoparticles decorated on the nonconductive substrate

\[
\text{Pd} \quad \text{(CH}_3\text{)}_2\text{NHBH}_3 + \text{H}_2\text{O} \rightarrow \text{HBO}_2 + (\text{CH}_3\text{)}_2\text{NH}_2^+ + 5\text{H}^+ + 6\text{e}^- \quad [4]
\]

and the electrons released by this reaction are used for Reaction 2, resulting in the deposition of ZnO. It should be noted that although DMAB releases five protons that decrease the pH, the six electrons released give six hydroxide ions via Reaction 2, resulting in the net reaction with one hydroxide ion generation. Furthermore, HBO2 and (CH3)2NH2+ generated from DMAB, which have acid dissociation constants, pK\text{a} of 9.2417 and 10.77,18 respectively, can release few protons below pH 8. This means that the pH in the vicinity of the Pd-catalyzed substrate can readily be raised up to pH 8. The Pd-catalyzed substrate can be prepared by a simple dipping process using three aqueous solutions; hence, this chemical solution process without an external power source is suitable for fabricating large-area ZnO films onto nonconductive substrates at lower cost. Because DMAB is a relatively moderate reductant, the reversible acid-base Reaction 1 proceeds under near equilibrium condition (i.e., under weak driving force). Such a condition, therefore, leads to the deposition of ZnO with a larger grain size and inhibits the rapid decomposition of the bulk solution.

When an aqueous Zn(NO3)2—DMAB solution is employed to deposit ZnO without deaeration, (i.e., in the presence of ambient dissolved oxygen), the electrons released by Reaction 4 can also be consumed by Reaction 3. Therefore, not only Reaction 2 but also Reaction 3 can increase the local pH. According to our in situ investigation of the ZnO deposition using an electrochemical quartz crystal microbalance with gold coating, we found some sign that DO more or less works in the initial stage of ZnO growth, while nitrate ions seem to play an important role as a counteranion of Zn2+ as well as a precursor of OH− ions.19 In the electrochemical route, ZnO has been yielded from different zinc salts as mentioned above, and the effect of their counteranions on ZnO growth was reported recently.21 Even though the counteranion is one of the major components in the deposition solution, little has been investigated in the chemical (electroless) route. Furthermore, the detailed role of DO on the chemical ZnO deposition using a conventional Pd-catalyzed
glass substrate was still unclear. In the present study, we have therefore looked deeper into the effect of counteranions (NO$_3^-$, Cl$^-$, ClO$_4^-$, and SO$_4^{2-}$) and DO on the hydrolysis behavior of Zn$^{2+}$ and the growth regime of ZnO. Significant differences based on the chemical nature of these counteranions were observed, and the negative influence of DO on the resulting ZnO was revealed.

**Experimental**

**General procedures.**— Chemical deposition of ZnO films from aqueous solutions was carried out using reagent-grade chemicals and deionized (DI) water purified by a Milli-RX12 Plus system. A Corning glass (no. 1737, 20 × 40 × 0.7 mm) was used as a substrate. Prior to each chemical deposition, the substrate was rinsed with acetone and DI water and was activated using a commercialized three-step Sn/Ag/Pd dipping process (Okuno Chemical Industries, Techno Clear series). This activation process comprises a sequential immersion of the substrate into the three solutions for 1 min each, resulting in the substrate being entirely covered with Pd nanoparticles at a high density.

**pH variation of aqueous solutions.**— An aliquot of DI water (0.15 dm$^3$) was placed in an air tight glass vessel, and a sodium or zinc salt with counteranions (NO$_3^-$, Cl$^-$, ClO$_4^-$, or SO$_4^{2-}$) was added so that the resulting solution contained 0.12 M of the counteranion in question (M = mole per cubic decimeter). The pH of the solutions was roughly adjusted to 4 with a corresponding hydroacid or oxoacid solution. A conventional glass electrode or an ion-sensitive field-effect transistor electrode was used for the pH measurement. The resulting solution was bubbled with O$_2$, air, or Ar gas for 1.5 h and DMAB was added so that the concentration was 0.02 M; the bubbling was continued until the end of the experiment. The pH was then readjusted to 4.17 with the corresponding acid solution. After 10 min from the DMAB addition, a Pd-catalyzed glass substrate was immersed in the solution and the pH variation was measured at 298 K with magnetic stirring and bubbling.

**Chemical deposition of ZnO.**— In a similar manner to the above, one of the zinc salts and DMAB were dissolved into DI water (0.15 dm$^3$) bubbled with O$_2$, air, or Ar gas for 1.5 h in advance to prepare an aqueous 0.06 M zinc salt−0.02 M DMAB solution. The resulting solution in an air tight vessel was heated to 338 K, and then a Pd-catalyzed glass substrate was immersed into the solution to deposit ZnO without stirring. During the deposition, the gas was passed into the free space of the vessel instead of the bubbling. The film obtained was rinsed with DI water and dried under ambient atmosphere. For Hall coefficient measurements, ZnO films were heat-treated in advance at 723 K for 30 min under a 3% H$_2$/Ar mixed gas atmosphere.

**Characterization of ZnO.**— X-ray diffraction (XRD) patterns were measured using a Rigaku RINT2500 system with monochromated Cu Kα radiation (40 kV, 200 mA). The thickness of films was measured at three different positions by a stylus profilometer (Kosaka Lab., Surfercorder ET30000), and the three measured values were averaged. Micromorphology of films was observed with a field emission scanning electron microscope ([FESEM], JEOL, JSM-6700F). Optical transmittance spectra were recorded with a UV-visible spectrophotometer (Shimadzu, UV-3150C) with respect to air. The bandgap energy of ZnO was estimated by extrapolating the linear part of the relationship between $x^2$ and photon energy to $x^2 = 0$, where $x$ is the absorption coefficient. Electrical properties, including resistivity and carrier type, were evaluated with a van der Pauw method using a Hall coefficient analyzer (Toyo Technica, Resitex 8310).

**Results and Discussion**

Figure 1 shows a potential–pH diagram of the Zn–H$_2$O system, calculated using a set of thermochemical data cited in the paper by Goux et al. Here, the activity of Zn$^{2+}$ ($a_{Zn^{2+}}$) was set at 0.06, which corresponds approximately to the present ZnO deposition condition, 0.06 M Zn$^{2+}$. The boundary pH between Zn$^{2+}$ and ZnO (Reaction 1) is 6.2 at 298 K and 5.8 at 338 K. Because the initial pH of the 0.06 M Zn(NO$_3$)$_2$−0.02 M DMAB solution was 6.0 at 298 K, spontaneous hydrolysis of Zn$^{2+}$ ions is thermodynamically supposed to take place at 338 K, if the pH is kept constant through the heating. However, the fact is that the initial solution was stable and no precipitation was recognized at 338 K for over 3 h in the absence of a Pd-catalyzed glass substrate under ambient atmosphere, suggesting that the solution was in a supersaturated state of, for example, dissolved Zn(OH)$_2$ species. Therefore, a local pH increase in the vicinity of a Pd-catalyzed glass substrate via the redox reactions (Reactions 2-4) can be a trigger to deposit ZnO on the glass without precipitation in the bulk solution.

**Effect of counteranions on pH increase.**— To examine the effect of the counterions on the pH increase induced by the DMAB oxidation (Reaction 4) and subsequent dissolved oxygen reduction (Reaction 3), oxygenated aqueous 0.02 M DMAB solutions containing a sodium salt of major strong acids (i.e., NaNO$_3$, NaCl, NaClO$_4$, or Na$_2$SO$_4$) were prepared in such a way that the concentration of the counterion was 0.12 M. The pH of each solution was adjusted to 4.17, and then a Pd-catalyzed glass substrate was immersed into the solution at 298 K with continuous magnetic stirring. The pH variation of the bulk solution after the immersion is given in Fig. 2a and the apparent generation rate of OH$^-$ calculated from the early-stage pH variation is in Table 1. Here, the data recorded for a sodium salt-free solution are included for reference. The pH of the aqueous solution containing NO$_3^-$ or ClO$_4^-$ as a counteranion increased readily like a neutralizing titration curve of an acidic solution. This trend is similar to that of the sodium salt-free solution, indicating that these counterions have little influence on the redox reactions (Reactions 3 and 4) causing a pH increase. Actually, the OH$^-$ generation rate for the NO$_3^-$ solution was calculated to be 6.1 μmol min$^{-1}$, the highest among them. The rapid pH increase was then buffered at pH over 8 by HBO$_2$ ($pK_a$ = 9.24) generated from DMAB (Reaction 4), as mentioned above and also demonstrated in Fig. 2c. In contrast, the addition of Cl$^-$ or SO$_4^{2-}$ ion inhibited a rapid pH increase. The pH increase rate of the solution containing SO$_4^{2-}$ was <1/10 that of the NO$_3^-$ solution, and pH was 8.8 even after 2 h. The exact reason for the difference in pH increase is still unclear at this time. We, however, have an impression that the
behavior is related to the strength of anion as a Lewis base. The acid dissociation constant for HNO₃ is −1.43 (pKₐ), while that for HSO₄⁻ is 1.99, suggesting that SO₄²⁻ ions have relatively stronger coordination ability toward H⁺, Na⁺, and some other species in the solution. This might affect the rate of Reaction 3 or 4. Alternatively, SO₄²⁻ ions adsorbed to the surface of the Pd particles can inhibit the decomposition of DMAB. These noticeable differences in pH increase in terms of counteranions are attributed to their multiple interactions between the counteranion and H⁺, Zn²⁺ ions, and the Pd catalyst, as discussed in the next section. Note that such slow pH increase does not necessarily follow the inability of ZnO deposition because the net OH⁻ ions required for the ZnO generation in the vicinity of a substrate should not be essential, in itself, but only from the solution by the oxidation of DMAB.

Effect of counteranions on ZnO growth. — The influence of the multiple interactions between the counteranion and H⁺, Zn²⁺ ions, and the Pd catalyst on the ZnO growth under a typical deposition condition was examined using the same series of oxygenated solutions containing the zinc salts. Figure 3 shows XRD patterns of the deposits obtained by immersing a Pd-catalyzed glass substrate for 1 h at 338 K. Wurtzite ZnO was obtained only from the solution containing a NO₃⁻ or ClO₄⁻ ion. Deposits obtained from the Cl⁻ and SO₄²⁻ solutions had XRD peaks at 2θ of 11.2 and 8.0°, respectively, and they were identified as Zn₅Cl₂(OH)₆·5H₂O (JCPDS no. 07-0155) and Zn₄(SO₄)(OH)₆·5H₂O (JCPDS no. 39-0688). It is thought that, because Cl⁻ and SO₄²⁻ ions have relatively high stability constants with Zn⁵⁺ (Zn⁵⁺ + Cl⁻ = ZnCl⁺, log K_{Cl⁻} = 0.11; Zn⁵⁺ + SO₄²⁻ = ZnSO₄, log K_{SO₄²⁻} = 0.89), such double salt hydrates are liable to form in the neutral pH region. Even in the case of Cl⁻ and SO₄²⁻ solutions, ZnO could be formed if the pH increased to a higher level. In fact, ZnO have successfully been obtained by an electrochemical method from aqueous ZnCl₂ and ZnSO₄ solutions, where an external power source forcibly supplies a cathodic current to a substrate. In the present case, however, the moderate hydrolysis

Table I. Apparent generation rate of OH⁻ ions in aqueous 0.02 M DMAB solutions with Pd-catalyzed glass and various salts. These values were calculated from Fig. 2a and b, 4, a, and 5.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Cation</th>
<th>O₂ bubbling rate (μmol/min)</th>
<th>Ar bubbling</th>
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<tr>
<td>NO₃⁻</td>
<td>Na⁺</td>
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<tr>
<td>Cl⁻</td>
<td>Zn⁺²</td>
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<td>Zn⁴⁺</td>
<td>Na⁺</td>
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<td>Na⁺</td>
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<td>SO₄²⁻</td>
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</tr>
<tr>
<td>No additive</td>
<td>No additive</td>
<td>0.085a</td>
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* Without Pd-catalyzed glass.

Figure 3. Normalized XRD patterns of deposits obtained by immersing Pd-catalyzed glass into (a) O₂- or (b) Ar-bubbled aqueous 0.06 M zinc salts-0.02 M DMAB solutions for 1 h at 338 K. JCPDS (no. 36-1451) data of wurtzite ZnO is also indicated.
condition leads to the deposition of the double salt hydrates on the glass in preference to ZnO or Zn(OH)₂. In consequence, a counteranion having low stability constants with a Zn²⁺ ion such as NO₃⁻ (Zn²⁺ + NO₃⁻ = ZnNO₃, log K_{ZnNO₃} = −0.2) and ClO₄⁻ ions is indispensable for the chemical (electroless) ZnO deposition from the DMAB solutions. (Note that, as well-known among electrochemists, the interaction between ClO₄⁻ anions and metal cations is negligible, while the log K_{ClO₄} for the reaction Zn²⁺ + ClO₄⁻ = ZnClO₄ is not reported.)

The reduction of NO₂⁻ ions gives OH⁻ ions through Reaction 2, as mentioned above. Similarly, it is thermodynamically possible that ClO₄⁻ ions are reduced to yield OH⁻ ions, while the redox potential is nobler than that of NO₃⁻.

\[
\text{ClO}_4^- + H_2O + 2e^- \rightarrow \text{ClO}_3^- + 2OH^- \quad E^0 = 0.374 \text{ V vs NHE}
\]

The contribution of these two counteranions to the pH increase was then examined by using an Ar-bubbled aqueous DMAB solution. Figure 4 shows the pH variation after the immersion of a Pd-catalyzed glass substrate into an Ar-bubbled aqueous 0.02 M DMAB solution containing 0.12 M NaNO₃ or NaClO₄. The pH variations for sodium salt-free Ar-bubbled DMAB solutions with and without the Pd-catalyzed glass substrate are examined for comparison, and the results are also plotted in Fig. 4. A time-dependent pH increase was found in each case, while the increment was much smaller than that observed in the presence of dissolved oxygen (see Fig. 2a). The apparent generation rate of OH⁻ calculated from the pH variation is listed in Table I. Although the pH increments are generally small in the Ar-bubbled solutions, it is important that NaNO₃ solution showed the largest pH-increase rate (0.21 μmol min⁻¹) among the four conditions in Fig. 4. In contrast, the pH-increase rate of NaClO₄ solution (0.15 μmol min⁻¹) was almost the same as that for the sodium salt-free, suggesting that ClO₄⁻ ions have, contrary to the expectation, a poor ability to generate OH⁻ ions, even though the ClO₄⁻/NO₃⁻ pair has a nobler redox potential \(E^0 = 0.374 \text{ V vs NHE}\) than NO₃⁻/NO₂⁻ redox pair \(E^0 = 0.01 \text{ V}\). This is probably because the reduction of ClO₄⁻ is kinetically hindered, just as SO₄²⁻ ions are virtually stable in aqueous solutions in spite of the noble redox potential of the SO₄²⁻/S²⁻ pair.

Similar results regarding ClO₄⁻ ions have also been reported for the electrodeposition of metal oxides. Note that a pH increase with the apparent OH⁻ generation rate of 0.085 μmol min⁻¹ was also recognized without the immersion of the Pd-catalyzed glass substrate. This indicates that a spontaneous decomposition of DMAB gradually takes place without the catalysis. Figure 3b shows XRD patterns for the Pd-catalyzed glass substrate after immersing in an Ar-bubbled aqueous 0.02 M DMAB solution containing 0.06 M Zn(NO₃)₂ or ZnClO₄ for 1 h at 338 K. Wurtzite ZnO was deposited from the Ar-bubbled Zn(NO₃)₂ solution even with the quite low pH-increase rate. In contrast, no peak for ZnO was observed for the ZnClO₄ solution, demonstrating that the deposition does not take place. From the above results, it was revealed that Zn(NO₃)₂ is the only salt that provides ZnO independently without DO.

Effect of DO on pH increase.— The influence of DO, which accelerates the pH increase, on the chemical ZnO deposition was examined by preparing an O₂-, air-, or Ar-bubbled aqueous 0.06 M Zn(NO₃)₂-0.02 M DMAB solution. The concentrations of DO in these three solutions are −1.25 mM (O₂), −0.28 mM (air), and −0 (Ar) at room temperature. Figure 5 shows the pH variation of the solutions after the immersion of a Pd-catalyzed glass substrate at 298 K with magnetic stirring. As expected, the order of the pH-increase rate depended on the DO concentration, \(O_2 > \text{air} > \text{Ar}\). As an independent experiment, ZnO films were deposited on the Pd-catalyzed glass substrate from each aqueous 0.06 M Zn(NO₃)₂-0.02 M DMAB solution at 338 K. The concentration of DO at 338 K can be estimated from the Bunsen absorption coefficients to be −0.83 mM (O₂) and −0.15 mM (air). Figure 6 shows the thickness variation of ZnO obtained from the three solutions as a function of deposition time. All the curves showed rapid growth within the first 10 min [deposition rates in nanometers per minute were 14.3 (O₂), 12.4 (air), and 10.1 (Ar)], followed by gradual increases in thickness toward 3 h. Corresponding top- and tilted-

\[\text{The DO concentration under air- and Ar-bubbling conditions was measured with a conventional DO meter (HORIBA 9520-10D), and under O}_2\text{-bubbling was the saturation value at 298 K.}\]
DMAB solution bubbled with O\textsubscript{2} at a remarkable rate on the order of O\textsubscript{2} from the Ar-bubbled solution. These results indicate that ZnO grows from the ZnO surface becomes moderate but continuously proceeds. Furthermore, the rapid growth caused by DO results in defective crystal nuclei probably including some Zn(OH)\textsubscript{2} due to imperfect dehydration.

In the course of the chemical ZnO deposition, slight bath decomposition, (i.e., precipitation of ZnO in the bulk solution) was observed at ~2 h or later, and the growth of ZnO concomitantly slowed down. Although the initial order of the thickness (O\textsubscript{2} > air > Ar) depended on the DO concentration, the thickness order became air > Ar > O\textsubscript{2} after 2 h deposition, suggesting less influence of DO on the ZnO growth on the ZnO surface and an increase in the relative contribution of NO\textsubscript{3}\textsuperscript{−} in the deposition process. The chemical ZnO growth on a ZnO surface was investigated by immersing a ZnO-coated glass substrate into three 0.06 M Zn(NO\textsubscript{3})\textsubscript{2}−0.02 M DMAB solutions each treated with the following bubbling gases: (i) O\textsubscript{2}, (ii) Ar, and (iii) Ar-bubbling with additive 0.12 M NaNO\textsubscript{3}. The ZnO-coated glass employed was prepared by immersing a Pd-catalyzed glass substrate into an air-bubbled 0.06 M Zn(NO\textsubscript{3})\textsubscript{2}−0.02 M DMAB solution at 338 K for 1 h. The increased thicknesses of the ZnO resulting from 2 h deposition in the above three solutions were (i) 119, (ii) 100, and (iii) 107 nm, corresponding to the deposition rates of (i) 0.99, (ii) 0.83, and (iii) 0.89 nm min\textsuperscript{−1}, respectively. These values are <1/10 of those for the initial 10 min deposition on the Pd-catalyzed glass substrate, and it turned out that the neither DO nor additional NO\textsubscript{3}\textsuperscript{−} ions (as NaNO\textsubscript{3}) had a remarkable effect on the ZnO growth here. These findings may well be attributed to the difference in catalytic activity and concomitant rate-determining step of the chemical redox reactions (Reactions 2-4) between on the Pd catalyst and on the ZnO surface; the reduction of DO and NO\textsubscript{3}\textsuperscript{−} is the rate-determining step on the Pd catalyst, while the further growth of ZnO on the ZnO surface is limited by the oxidation of DMAB because the ZnO surface has less catalytic activity toward it.

Effect of dissolved oxygen on ZnO growth.— Although wurtzite ZnO generally exhibits a spontaneous c-axis preferred growth orientation since the (0001) basal plane has a higher surface energy, the difference in the initial nucleation process can affect the subsequent ZnO growth regime. This was investigated by XRD measurements. Figure 8 shows XRD patterns of ZnO films obtained from 1 and 3 h deposition in an aqueous 0.06 M Zn(NO\textsubscript{3})\textsubscript{2}−0.02 M DMAB solution bubbled with O\textsubscript{2}, air, or Ar gas. The intensity of XRD patterns was normalized in terms of film thickness for ease of comparison between the bubbling gases. Although all ZnO films had a (0001) preferred growth orientation, the Ar-bubbled solution gave a superior (0001) orientation. Independent of the bubbling gases, the in-

### Figures

**Figure 6.** ZnO film thickness as a function of deposition time. The ZnO was deposited on Pd-catalyzed glass from an aqueous 0.06 M Zn(NO\textsubscript{3})\textsubscript{2}−0.02 M DMAB solution bubbled with O\textsubscript{2}, air ( ), or Ar ( ) gas.

**Figure 7.** Top-view and tilted-view FESEM images of ZnO deposited on Pd-catalyzed glass for 1 and 10 min at 338 K from an aqueous 0.06 M Zn(NO\textsubscript{3})\textsubscript{2}−0.02 M DMAB solution bubbled with O\textsubscript{2}, air, or Ar gas.

**Figure 8.** Normalized XRD patterns of ZnO films deposited on Pd-catalyzed glass for (a) 1 and (b) 3 h at 338 K from an aqueous 0.06 M Zn(NO\textsubscript{3})\textsubscript{2}−0.02 M DMAB solution bubbled with O\textsubscript{2}, air, or Ar gas.
tensity of 0002 diffraction increased with increasing deposition time, while other diffraction peaks such as 1013 showed little dependence on the deposition time. This indicates that the initial growth (i.e., nucleation) on the Pd catalyst involves some randomly oriented ZnO and then c-axis growth progresses exclusively on the initial ZnO surface. Such phenomena can be attributed to the rapid nucleation on the Pd catalyst and the moderate growth, near the chemical equilibrium, on the ZnO surface. The variation of peak intensity ratio of 0002 and 1013 diffractions for the ZnO films deposited for 1–3 h at 338 K from an aqueous 0.06 M Zn(NO$_3$)$_2$-0.02 M DMAB solution bubbled with O$_2$ (□), air (○), or Ar (□) gas.

In contrast, there was a clear difference in electrical properties. Here, the electrical property of the ZnO films obtained by 3 h deposition was investigated using a Hall coefficient analyzer. Because the as-deposited ZnO films had high resistivity of >10$^5$ Ω cm due to extremely low carrier concentration, films were heat-treated at 723 K for 30 min under a 3% H$_2$/Ar mixed gas atmosphere in order to increase the carrier concentration. These heat-treated ZnO films showed XRD patterns with somewhat wider fwhm without peak shifts compared to those before the heating. The results are summarized in Table II. All the ZnO films exhibited n-type conductivity as expected from the following well-known carrier-generation mechanisms: (i) ZnO $\rightarrow$ Zn$^+$ + e$^-$ + 1/2O$_2$ or (ii) O$_2$ $\rightarrow$ $\Delta_{\sigma}$ + e$^-$ + 1/2O$_2$. Resistivity was drastically decreased to a measurable level by the heat-treatment, and of importance to note here is that the ZnO film obtained from the Ar-bubbled solution showed resistivity as low as 2.67 $\times$ 10$^{-2}$ Ω cm, which is one-half that for the O$_2$-bubbled solution. The order of carrier density was Ar > O$_2$ = air, and that of mobility was air > Ar > O$_2$, suggesting that the dense columnar grains and higher crystallinity of ZnO contribute to the higher carrier concentration, and larger columnar diameter contributes to higher mobility.

Figure 9. XRD peak intensity ratio of 0002 to 1013 diffraction for the ZnO films deposited for 1–3 h at 338 K from an aqueous 0.06 M Zn(NO$_3$)$_2$-0.02 M DMAB solution bubbled with O$_2$ (□), air (○), or Ar (□) gas.

Effect of dissolved oxygen on the optical and electrical properties of ZnO.—Visible transparency and bandgap energy were evaluated on 240 nm thick ZnO films deposited from the three different solutions by the same method as mentioned above (Fig. 11). The spectra were taken with respect to air and hence involve contribution from a Corning glass as well as ZnO films deposited on both its sides. All the ZnO films exhibited high visible transparency of >80% and a critical absorption edge at 367.5 nm corresponding to a bandgap energy of 3.37 eV. Thus, no significant difference in optical properties was recognized among these ZnO films grown from the O$_2$-, air-, or Ar-bubbled solutions in the present experimental conditions.

In contrast, there was a clear difference in electrical properties. Here, the electrical property of the ZnO films obtained by 3 h deposition was investigated using a Hall coefficient analyzer. Because the as-deposited ZnO films had high resistivity of >10$^5$ Ω cm due to extremely low carrier concentration, films were heat-treated at 723 K for 30 min under a 3% H$_2$/Ar mixed gas atmosphere in order to increase the carrier concentration. These heat-treated ZnO films showed XRD patterns with somewhat wider fwhm without peak shifts compared to those before the heating. The results are summarized in Table II. All the ZnO films exhibited n-type conductivity as expected from the following well-known carrier-generation mechanisms: (i) ZnO $\rightarrow$ Zn$^+$ + e$^-$ + 1/2O$_2$ or (ii) O$_2$ $\rightarrow$ $\Delta_{\sigma}$ + e$^-$ + 1/2O$_2$. Resistivity was drastically decreased to a measurable level by the heat-treatment, and of importance to note here is that the ZnO film obtained from the Ar-bubbled solution showed resistivity as low as 2.67 $\times$ 10$^{-2}$ Ω cm, which is one-half that for the O$_2$-bubbled solution. The order of carrier density was Ar > O$_2$ = air, and that of mobility was air > Ar > O$_2$, suggesting that the dense columnar grains and higher crystallinity of ZnO contribute to the higher carrier concentration, and larger columnar diameter contributes to higher mobility.

Figure 10. Top-view FESEM images of ZnO deposited on Pd-catalyzed glass for 1 and 3 h at 338 K from an aqueous 0.06 M Zn(NO$_3$)$_2$-0.02 M DMAB solution bubbled with O$_2$, air, or Ar gas.

Figure 11. Transmittance spectra of 240 nm thick ZnO films deposited on Pd-catalyzed glass at 338 K from an aqueous 0.06 M Zn(NO$_3$)$_2$-0.02 M DMAB solution bubbled with O$_2$ (□), air (○), or Ar (□) gas. Inset is dependence of $\alpha^2$ (α: absorption coefficient) on photon energy.
Table II. Electrical properties for ZnO films deposited from an aqueous 0.06 M \( \text{Zn(NO}_3\text{)}_2 \)-0.02 M DMAB solution bubbled with \( \text{O}_2 \), air, or Ar, and heat-treated at 723 K for 30 min under a 3% \( \text{H}_2/\text{Ar} \) mixed gas atmosphere.

<table>
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<th>Bubbling-gas</th>
<th>Resistivity (( \Omega \text{ cm} ))</th>
<th>Carrier density (( \text{cm}^{-3} ))</th>
<th>Mobility (( \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 )</td>
<td>( 4.57 \times 10^{-2} )</td>
<td>( 1.22 \times 10^{19} )</td>
<td>11.2</td>
</tr>
<tr>
<td>Air</td>
<td>( 3.26 \times 10^{-2} )</td>
<td>( 1.21 \times 10^{19} )</td>
<td>15.8</td>
</tr>
<tr>
<td>Ar</td>
<td>( 2.67 \times 10^{-2} )</td>
<td>( 1.70 \times 10^{19} )</td>
<td>13.8</td>
</tr>
</tbody>
</table>

Conclusions

The effects of various counteranions (\( \text{NO}_3^- \), \( \text{Cl}^- \), \( \text{ClO}_4^- \), and \( \text{SO}_4^{2-} \)) and DO on the ZnO growth regime, including a series of redox reactions in DMAB solutions, were investigated using the Pd-catalyzed glass substrate, corresponding sodium and zinc salts, and \( \text{O}_2 \), air, or Ar bubbling. Whereas the counteranions of \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \) affected the Zn\(^{2+}\) hydrolysis-causing pH increase of an \( \text{O}_2 \)-bubbled DMAB solution, it was found that only \( \text{NO}_3^- \) can raise the pH of a DMAB solution independently without DO. The influence of DO on the ZnO growth rate is predominant over that of \( \text{NO}_3^- \) at the initial growth on the Pd catalyst, while the influence becomes comparable to that of \( \text{NO}_3^- \) at the subsequent growth on the ZnO surface, due to the difference in their catalytic activity toward the oxidation of DMAB. The ZnO nucleation rate depending on the DO concentration affects the resultant ZnO structure in terms of crystallinity, growth orientation, and surface morphology. The control of the nucleation rate by eliminating DO in the aqueous \( \text{Zn(NO}_3\text{)}_2 \)-DMAB solution was found to give ZnO films with higher conductivity.

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References