Chapter-5
ELECTRODEPOSITION OF ZnO COATINGS ON STAINLESS STEEL SUBSTRATES

Abstract

Section-A

Cathodic reduction of zinc nitrate solution results in the deposition of ZnO crystallites with a strong c-axis orientation. The orientation of crystallites can be switched to 10l (l = 1, 2, 3) direction by varying the bath concentration (0.04 – 0.1 M) and the deposition conditions (T, 50 – 70 °C; t, 30 – 90 min). The range of concentrations yielding c-axis orientation can be widened at a high deposition temperature. At 0.1 M bath concentration and long deposition times, crystallites are oriented along 10l (l = 3) direction. At low temperature (50 °C), 100 oriented nanostructured ZnO coatings are obtained (crystallite size, 20 -35 nm). The c-axis oriented crystallites grow as hexagonal columns perpendicular to substrate and 10l oriented crystallites grow tilted at different angles to the substrate surface.

Section-B

Electroreduction of an aqueous solution of a soluble Zn salt results in the deposition of ZnO crystallites with hexagonal columnar morphology. The crystallites grow with their long axes normal to the substrate resulting in adherent coatings with a strong c-axis orientation. This phenomenon is on account of the polarity of the 001 crystal face combined with the high dielectric constant of water. When the dielectric constant of the solvent is changed by making a mixture of water and isopropanol, there is a change in the direction of orientation of the coating. The switch takes place in the sequence [001] → [102], [103] → unoriented → [100], [110] as the isopropanol concentration is raised in a step-wise manner to 60% v/v. The switch in orientation is caused by the tilt of the long axes of the hexagonal columns of ZnO with respect to the normal to the substrate. Above 60% isopropanol concentration, ZnO deposition is suppressed. This work demonstrates solution mediated control over oriented crystallization.
Section-A

Electrodeposition of ZnO coatings from aqueous Zn(NO₃)₂ baths: effect of Zn concentration, deposition temperature and time on orientation

5.1 Introduction

Oriented crystallization of inorganic materials on different substrates is a subject of contemporary interest to materials chemistry. Oriented crystallization leads to the formation of crystallites with specific morphologies and distinct $k$-dependent properties. Among various inorganic metal oxides, ZnO is of considerable interest owing to its many useful applications in the emerging field of oxide optoelectronics. ZnO is a wide band gap (3.3 eV) n-type semiconductor and crystallizes with the wurtzite structure. ZnO is also used as catalyst, phosphor and for general ceramic applications.

Deposition of ZnO on various substrates is done by using techniques such as pulsed laser deposition, rf sputtering, metalorganic chemical vapor deposition, atomic layer epitaxy, chemical vapor deposition and electrodeposition. Among all these techniques, electrodeposition is the simplest, as it obviates the need for high vacuum and high power laser/rf/ion beam sources. In addition, electrodeposition is an ambient temperature technique.

Electrodeposition of ZnO on different substrates is brought about by using different water soluble salts such as Zn(NO₃)₂, ZnCl₂ and Zn(ClO₄)₂ as source of Zn. The problem often encountered in ZnO deposition is the co-deposition of Zn metal and/or hydroxyl salts of Zn as impurity phases. The deposition of impurity phases is suppressed by an appropriate, often empirical, choice of deposition conditions comprising the deposition current/potential, temperature, concentration and composition of the bath and the pH. Izaki and Omi deposited ZnO from a Zn(NO₃)₂ solution. A switch in orientation was observed from 001 to 101 and 100 with changes in deposition potential, current and concentration. Within the matrix of synthetic conditions used by Lincot and coworkers in their series of investigations, ZnO crystallization was oriented in most instances along c-axis. The 100 orientation was observed only in ZnCl₂ baths at close to ambient temperatures (34 °C). The orientation switches to c-axis when the temperature is raised.
A common way of electrodepositing oriented films is by the use of single crystalline substrates. The substrate directs crystal growth by the deposition of specific crystal faces whose 2-D structure matches with that of the substrate surface, by a process known as “epitaxy”. Thus c-axis oriented ZnO films are grown by electrodeposition over Au(111), (110) and (100) as substrates.24, 25

Oriented crystallization can also be brought about by the addition of ionic species in the deposition bath. These ionic species adsorb on the specific crystal faces of ZnO and induce growth along other directions preferentially. For instance, in the presence of KCl as a supporting electrolyte, hexagonal columns of ZnO are electrodeposited at a low (0.001 M) Zn(NO₃)₂ concentration and disk like crystallites are electrodeposited at a high Zn(NO₃)₂ concentration (0.1 M).26

In a departure from the template-directed mechanism, oriented crystallization can be promoted on polycrystalline substrates by a solution controlled mechanism. In this process, kinetic control over crystallization is exercised, by controlling the degree of supersaturation by the use of complexing agents in the bath. The cathodic electrodeposition from ZnCl₂ bath (0.002 M)24 and anodic deposition from Zn(NO₃)₂ bath in presence of L-ascorbic acid25 on to a single crystal gold substrate yielded c-axis oriented coatings with columnar morphology. On the other hand, deposition from 0.05 M ZnCl₂ bath in presence of EDTA yielded an unoriented coating with porous morphology.27

The degree of supersaturation can be varied by the use of mixed solvents. For instance, the orientation of electrodeposited ZnO coating could be switched from c-axis to 102 and 103, merely by increasing the isopropanol content of a mixed water-isopropanol bath.28

Given the very large number and often conflicting reports on the electrodeposition of ZnO, the aim of the current work is to study a wide matrix of deposition conditions using aqueous Zn(NO₃)₂ baths. We study the effect of (1) bath concentration, (2) deposition temperature and (3) duration of deposition, on the deposition of ZnO on polycrystalline stainless steel substrates. The exact conditions which result in the deposition of micrometer thick coatings oriented along the thermodynamically stable 002 direction are determined. Conditions required to switch the orientation to other directions
such as 101, 102, 103 and 100 are reported. Further ZnO coatings obtained at low deposition temperature (< 50 °C) show broadening of the XRD profile due to small crystallite size. The crystallite size of these coatings varies in the range 19.8 – 34.8 nm.

5.2 Experimental

All ZnO coatings were deposited from aqueous solutions (0.04 – 0.1 M) of Zn(NO₃)₂ (Merck, India). All the solutions were prepared using Type-I water (Milli-Q Academic water purification system, specific resistance 18.2 MΩ cm).

Electrodeposition was carried out using an EG&G Model Versastat IIA potentiostat driven by Powersuit software. A stainless steel flag (SS 304, area 4.5 cm²) was used as a working electrode and a Pt mesh (geometric area 28 cm²) was used as the counter electrode. Deposition was carried out potentiostatically at -0.9 V with respect to a saturated calomel electrode. The deposition time was varied from 15 to 90 min. and the deposition temperature was varied from 50 to 70 °C. After deposition the coatings were rinsed with Type-I water and dried at 65 °C. Prior to electrodeposition the stainless steel electrodes were degreased with detergent and electrochemically cleaned.

All the coatings were characterized by X-ray diffraction (XRD), by mounting the electrode directly on to a Bruker axs D8 Advance diffractometer (Cu Kα source λ = 1.5418 Å). XRD profiles were fit by the Rietveld method (Fullprof suite), using the published structure of ZnO (ICSD No. cF56; P6₃mc, a = 3.2494 Å, c = 5.2054 Å). Surface morphologies were studied using a scanning electron microscope (JEOL Model JSM 6490 LV microscope, operating voltage 15 kV) by mounting the as-prepared coating on conducting carbon tape and sputter coating with Pt to improve conductivity.

Estimation of crystallite size The broadening of lines in the PXRD pattern arises due to both instrumental and sample related factors. Therefore it is customary to first correct for instrument related broadening. The residual broadening is then attributed to sample related factors. Sample related factors include broadening due to crystallite size, strain and absorption. To accomplish this, the Brass 2 Suite of programs was employed.

The Brass 2 methodology enables a rigorous separation of instrument and sample contribution to peak profiles. The instrumental contribution to line broadening is obtained by refining the parameters of the pseudo Voigt profile function to fit the line shape of a
standard microcrystalline commercial ZnO powder taken as the standard. The instrument-related profile parameters were determined using the published structure of ZnO by a Rietveld fit of PXRD profile of standard ZnO sample. This procedure obviated the need to explicitly model the sample related broadening arising due to absorption. While performing the Rietveld fit of the XRD profile of the test coating, the profile parameters are fixed at the values obtained from the standard and other parameters relating to crystallite size, microstrain and preferred orientation were refined. The crystallite size parameters were $iP_L$ and $iP_G$ which quantify the Laurentzian and Gaussian contributions respectively to particle size. Similar contributions to microstrain are given by $iS_L$ and $iS_G$.

5.3 Results and discussion

During cathodic reduction of an aqueous Zn(NO$_3$)$_2$ bath, the Zn$^{2+}$ ions present in the solution react with OH$^-$ ions produced due to the reduction of NO$_3^-$ ions and form Zn(OH)$_2$. Since zinc hydroxide is not a thermodynamically stable phase, at elevated temperatures the hydroxide quickly undergoes dehydroxylation and forms ZnO. The reactions that take place at cathode are:

$$\text{NO}_3^- + 2 \text{e}^- + \text{H}_2\text{O} \rightarrow 2 \text{OH}^- + \text{NO}_2^- \quad (1)$$
$$\text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (2)$$
$$\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (3)$$

The XRD patterns of the coating obtained at 60 °C deposition temperature from a 0.04 M Zn(NO$_3$)$_2$ solution shows only one prominent peak (Fig. 5.1a) corresponding to the 002 plane of wurtzite ZnO. As the concentration of the Zn(NO$_3$)$_2$ bath is increased, the relative intensity of the 002 reflection decreases (Fig. 5.1b) and the other reflections begin to appear. Anomalous enhancement in the intensity of the 103 reflection is observed. The XRD pattern (Fig. 5.1c) of the coating obtained from a bath containing 0.1 M Zn(NO$_3$)$_2$ solution shows all the reflections expected of ZnO but the intensity of the 101 reflection is enhanced to a great extent relative to the expected value. This kind of anomalous enhancement in the intensity of select reflections is indicative of oriented crystallization. To quantify the degree of orientation, a Rietveld fit of the profile at Fig. 5.1c was carried out (see Fig. 5.2). The Rietveld fit yields a difference profile with significant residual intensity at the 2θ value corresponding to 101 plane. When the
refinement was repeated by incorporating March function parameters to account for preferred orientation along this direction, the resultant fit was satisfactory and the difference profile was a smooth function (Fig. 5.2c). A similar analysis of the XRD profile at Fig. 5.1b (see SI. 5.1) shows that the ZnO coating obtained from a bath of intermediate concentration (0.07 M) comprises crystallites oriented along both 002 and 103 directions. We conclude that a c-axis orientation is observed in coatings obtained from low Zn(NO$_3$)$_2$ concentration and 10l ($l = 1, 3$) orientation is observed at high Zn(NO$_3$)$_2$ concentrations.

Fig. 5.1 XRD patterns of ZnO coatings obtained at 60 °C from (a) 0.04 M, (b) 0.07 M and (c) 0.1 M Zn(NO$_3$)$_2$ solutions.
Fig. 5.2 (a) XRD pattern of a ZnO coating obtained from 0.1 M Zn(NO₃)₂ bath at 60 °C compared with (b) the calculated XRD profile incorporating the effect of orientation and (c) the corresponding difference profile. (d, e) The calculated XRD profile and difference profile, respectively, obtained before the incorporation of orientation effects. Features marked by asterisks are due to the stainless steel substrate and were excluded from the Rietveld fits.

The ZnO coating obtained at a higher deposition temperature (70 °C) from 0.07 M Zn(NO₃)₂ solution, exhibits only one prominent peak corresponding to the 002 plane (Fig. 5.3a). The XRD pattern of the coating obtained from 0.1 M Zn(NO₃)₂ solution
shows all the reflections expected of ZnO, but the relative intensities of 102, 103 reflections are much greater than the expected values (Fig. 5.3b). On performing a Rietveld fit of the latter profile, the difference profile (SI. 5.2) shows residual intensity at 2θ values corresponding to 102 and 103 planes. The residual intensities were fit by incorporating orientation parameters along these two directions. A comparison of Fig. 5.3a with SI. 5.1 shows that the range of bath concentrations that yield the c-axis orientation can be extended to higher values at higher temperatures.

Fig. 5.3 XRD patterns of ZnO coatings obtained at 70 °C from (a) 0.07 M and (b) 0.1 M Zn(NO₃)₂ solutions.

XRD profiles of the ZnO coatings obtained at various deposition times at 70 °C from 0.1 M Zn(NO₃)₂ bath are shown in Fig. 5.4A. The coating obtained at 30 min. shows a strong 002 reflection (Trace a). As the duration of the deposition is increased, the relative intensities of the 10l (l = 2, 3) reflections is selectively enhanced (Trace b) and
after 90 min. of deposition the 103 reflection is the most intense (Trace c). The extent of orientation in these coatings was quantified by performing Rietveld fits of the observed profiles (see Fig. 5.4B for the Rietveld fit of Trace c). The March function orientation parameters obtained from the Rietveld fits of the XRD patterns of different coatings are listed in Table 5.1. These results show that thick coatings are more oriented than thin coatings and orientation is induced by solution controlled processes.

While depositing ZnO from Zn(NO₃)₂ baths there is a competition between hydroxylation (2) and dehydroxylation (3) reactions. When the rate of dehydroxylation is greater than the rate of hydroxylation, crystallites grow with thermodynamically stable orientation. In the present case, when the deposition was carried out at moderate temperature with low Zn(NO₃)₂ concentration (60 °C, 0.04 M), the coatings obtained show the thermodynamically stable c-axis orientation. Due to the low concentration of nitrate ions in the bath, the hydroxyl ion production is slow and the rate of hydroxylation is slower than the rate of dehydroxylation. ZnO coatings with c-axis orientation always comprise crystallites with a hexagonal columnar morphology. This kind of morphology is reported by many authors when the deposition is carried out from different Zn salt solutions and on various substrates such as ITO, single crystals of GaN and Au.¹³⁻²¹, ²², ²⁴, ²⁵ These columns grow with their long axes (also c-crystallographic axis of ZnO) normal to the substrate surface. During electrocrystallization, growth takes place by layer by layer accretion of atoms. The wurtzite crystal has hexagonal symmetry. Within the wurtzite structure the polarity of the (002) plane is very small given the small distance d₁₂ between the successive Zn²⁺ and O²⁻ layers. Consequently, the rate of growth along [010] is higher than that along [001] as accretion of atoms along [010] leads to larger enthalpy gains compared to [001]. Further within the wurtzite structure, the (010), (100) and (110) planes are crystallographically equivalent, accounting for their nearly equal incidence as faces of the hexagonal columns.
Fig. 5.4 A. XRD patterns of ZnO coatings obtained at 70 °C from 0.1 M Zn(NO₃)₂ solution with different duration of deposition (a) 30 min., (b) 60 min. and (c) 90 min. B. (a) Trace c in A above compared with (b) the calculated XRD profile incorporating the effect of orientation and (c) the corresponding difference profile. (d, e) The calculated XRD profile and difference profile, respectively, obtained before the incorporation of orientation effects. Features marked by the asterisk are due to the stainless steel substrate and were excluded for the Rietveld fits.
Table 5.1. March function parameters obtained from Rietveld fits of the observed PXRD profiles of ZnO coatings.

<table>
<thead>
<tr>
<th>Figure</th>
<th>March function paramètres</th>
<th>Orientation</th>
<th>Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig.2</td>
<td>0.30 0.81</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>Fig.4B</td>
<td>0.32 0.66</td>
<td>103 002</td>
<td>0.35 0.81</td>
</tr>
<tr>
<td>SL.1</td>
<td>0.20 0.92</td>
<td>103 002</td>
<td>0.39 0.66</td>
</tr>
<tr>
<td>SL.2</td>
<td>0.40 0.38</td>
<td>103 102</td>
<td>0.73 0.32</td>
</tr>
<tr>
<td>SL.3</td>
<td>0.52 0.54</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Orientation along 10l is observed when the deposition is carried out from a bath of high Zn(NO₃)₂ concentration (0.1 M). Due to the high concentration of nitrate ions in the bath, rate of hydroxyl ion production is higher than that of dehydroxylation due to which there is a competition between growth along thermodynamically stable [002] direction and other directions. Accretion of atoms takes place along the less thermodynamically stable faces 10l (l = 1, 2, 3) faces as well. The 10l planes are present at different angles to the c-crystallographic axis. Because of competition between different 10l planes for accretion of atoms the hexagonal columns grow with their long axes tilted at different angles to the normal to the substrate. The intensity of different 10l reflections depends on the tilt angle and the number density of crystallites. Typical SEM images of coatings oriented along 002 and 10l directions are given in Fig. 5.5. The c-axis oriented coating shows the end faces of the hexagonal columnar crystallites of ZnO are parallel to the substrate. The 10l oriented coatings show the hexagonal end faces tilted to the substrate surface. A schematic of the different tilt angles is shown in Fig. 5.6.
Fig. 5.5 SEM images of ZnO coatings oriented along (a) c-axis and (b) 10l direction.

Fig. 5.6 A schematic of a hexagonal columnar crystal of ZnO with its long axis tilted at different angles with respect to the surface of the substrate.
**Synthesis of nanostructured ZnO coatings**

Entirely different phenomena were observed when the electrodeposition was carried out at low temperatures (< 60 °C). Representative XRD profiles (Fig. 5.7) of the coatings obtained at 50 °C from baths of different Zn(NO₃)₂ concentrations (0.04 – 0.1 M) show Scherrer broadening of peaks. Scherrer broadening decreases as the concentration of the electrolyte decreases. The coating obtained from a bath of 0.07 M concentration shows all the reflections expected of ZnO with a high relative intensity of the 100 reflection. On performing the Rietveld fit of observed profile (see SI 5.3) the difference profile shows residual intensity at 2θ value corresponding to the 100 reflection. On repeating the refinement by incorporating the orientation parameters (see Table 5.1) the difference profile was a smooth function.

![XRD patterns](image)

**Fig. 5.7 XRD patterns of ZnO coatings obtained at 50 °C from (a) 0.04 M, (b) 0.07 M and (c) 0.1 M Zn(NO₃)₂ solution.**
The crystallite sizes of coatings obtained at 50 °C deposition temperature was analyzed by employing Brass 2 Suite of programs. In order to determine the instrument-related broadening, a Rietveld fit of the XRD profile of a microcrystalline commercial ZnO powder (Fig. 5.8) was carried out. When the profile parameters (Table 5.2) obtained from this fit were used to obtain a Rietveld fit of the profile shown in Fig. 5.7c, by refining only scale and background parameters, the resulting mismatch (Fig. 5.9a) clearly shows the sample related broadening. On refining crystallite size and microstrain parameters, the resulting difference profile (Fig. 5.9b) was a smooth function. In the same manner the crystallite sizes of other coatings were also analyzed. The results of Brass 2 analysis of all the samples are given in Table 5.3.

Fig. 5.8 Rietveld fit of the powder XRD pattern of microcrystalline ZnO sample used as a standard.
Fig. 5.9 Rietveld fit of profile shown in Fig. 5.7c by refining only the background and scale parameters (a) and after refining the contributions of microstrain and crystallite size parameters (b). Profile parameters are as in Fig. 5.8. Features excluded from the refinement are due to the stainless steel substrate.
Table 5.2 Profile parameters obtained by the Rietveld fit of the PXRD pattern of microcrystalline commercial ZnO used as the standard.

<table>
<thead>
<tr>
<th>Space group</th>
<th>Shape and width parameters</th>
<th>Goodness of fit parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>P6₃mc</td>
<td></td>
<td>R_p</td>
</tr>
<tr>
<td></td>
<td>( U_L )</td>
<td>( W_L )</td>
</tr>
<tr>
<td></td>
<td>0.1417</td>
<td>0.05819</td>
</tr>
<tr>
<td>Cell parameters (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( a )</td>
<td>( c )</td>
</tr>
<tr>
<td></td>
<td>3.249 (5)</td>
<td>5.205 (8)</td>
</tr>
</tbody>
</table>

Table 5.3 Results of Brass 2 analysis of the ZnO coatings obtained at 50 °C deposition temperature

<table>
<thead>
<tr>
<th>[Zn(^{2+})]</th>
<th>Crystallite size parameters</th>
<th>Microstrain parameters</th>
<th>Goodness of fit parameters</th>
<th>Apparent crystallite size D(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( iP_L )</td>
<td>( iP_G )</td>
<td>( iS_L )</td>
<td>( iS_G )</td>
</tr>
<tr>
<td>0.04 M</td>
<td>0.02210</td>
<td>0.05841</td>
<td>0.2628</td>
<td>0.1981</td>
</tr>
<tr>
<td>0.07 M</td>
<td>0.07356</td>
<td>0.06948</td>
<td>0.1397</td>
<td>0.3155</td>
</tr>
<tr>
<td>0.1 M</td>
<td>0.06931</td>
<td>0.16620</td>
<td>0.3011</td>
<td>0.4763</td>
</tr>
</tbody>
</table>
The scanning electron microscopy images of the coatings obtained from a 0.1 M Zn\textsuperscript{2+} solution at 50 °C deposition temperature are shown in Fig. 5.10. Generally ZnO crystallites are well faceted hexagonal columns, but in the present case there are no faceted crystallites. Aggregates of small grains are observed and the substrate is completely covered.

![SEM images](image)

**Fig. 5.10** SEM images of the ZnO coatings obtained at 50 °C.

During electrodeposition the growth temperature also plays an important role on the hydroxylation and dehydroxylation reactions. When the deposition was carried out at 50 °C, rate of hydroxylation is faster than that of dehydroxylation. Production of large amount of OIF might suppress the faceted crystal growth by adsorbing on all possible crystal faces and this leads to the formation of crystallites with smaller size. Our results shows that as the concentration of the Zn(NO\textsubscript{3})\textsubscript{2} increases the crystallite size decreases due to increase in the rate of hydroxyl ion production.

**5.4 Conclusions**

In conclusion, electrodeposition of c-axis oriented ZnO crystallites is promoted at low zinc nitrate concentrations, high temperatures and low deposition times. Such
crystallites exhibit hexagonal columnar morphology and grow normal to the substrate. At high concentrations the crystallites are oriented along 101, at high temperatures and high deposition times the crystallites are oriented along 102 and 103 directions. The 10l (l = 1, 2, 3) orientations arise due to the increasing tilt of the columnar crystallites with respect to the substrate. At low temperature the ZnO crystallites are not facetted and the crystallite size is in the nanometer range.
References
SI. 5.1 (a) XRD pattern of a ZnO coating obtained from 0.07 M Zn(NO₃)₂ bath at 60 °C compared with (b) the calculated XRD profile incorporating the effect of orientation and (c) the corresponding difference profile. (d, e) The calculated XRD profile and difference profile, respectively, obtained before the incorporation of orientation effects. Features marked by the asterisk are due to the stainless steel substrate and were excluded for the Rietveld fits.
SI. 5.2 (a) XRD pattern of a ZnO coating obtained from 0.1 M Zn(NO₃)₂ bath at 70 °C compared with (b) the calculated XRD profile incorporating the effect of orientation and (c) the corresponding difference profile. (d, e) The calculated XRD profile and difference profile, respectively, obtained before the incorporation of orientation effects. Features marked by the asterisk are due to the stainless steel substrate and were excluded for the Rietveld fits.
SI. 5.3 (a) XRD pattern of a ZnO coating obtained from 0.07 M Zn(NO₃)₂ bath at 50 °C compared with (b) the calculated XRD profile incorporating the effect of orientation and (c) the corresponding difference profile. (d, e) The calculated XRD profile and difference profile, respectively, obtained before the incorporation of orientation effects. Features marked by the asterisk are due to the stainless steel substrate and were excluded from the Rietveld fits.
Section-B

Electrochemical synthesis of ZnO coatings from water-isopropanol mixed baths: control over oriented crystallization

5.5 Introduction

ZnO is a n-type semiconductor with wurtzite structure and a band gap of 3.3 eV at ambient temperature.\textsuperscript{1} ZnO is of considerable interest in contemporary materials science because of its many useful applications in the emerging field of oxide optoelectronics.\textsuperscript{2} In addition, it is used as a phosphor,\textsuperscript{3} catalyst\textsuperscript{4} and a general ceramic.\textsuperscript{5} Thin films of ZnO are transparent and conducting.\textsuperscript{6}

ZnO films and coatings are generally made by rf sputtering,\textsuperscript{6} metalorganic CVD,\textsuperscript{7} atomic layer epitaxy,\textsuperscript{8} CVD\textsuperscript{9} and electrodeposition.\textsuperscript{10-23} Among all these techniques, electrodeposition is the simplest, as it obviates the need for high vacuum and high power laser/rf/ion beam sources. In addition, electrodeposition is an ambient temperature technique.

Izaki and Omi\textsuperscript{10-12} reported the electrodeposition of ZnO by cathodic reduction of an aqueous solution of a soluble salt of Zn. They explored empirically, the various deposition conditions that yielded oriented, highly conducting micrometer-thick coatings of ZnO on transparent conducting glass substrates. However it was Lincott and coworkers\textsuperscript{14, 16, 19, 21} who in a series of papers, investigated the kinetics and mechanism of ZnO electrodeposition. They obtained by experiment and theory, the conditions required for the nucleation of ZnO in preference to other competing phases such as Zn(OH)\textsubscript{2} and the basic salts of Zn. They also used a variety of substrates, such as oriented GaN(0002),\textsuperscript{15, 16, 20} Au\textsuperscript{14} and spray pyrolyzed SnO\textsubscript{2}.\textsuperscript{17} A number of precursors for the oxide ion as well as Zn\textsuperscript{2+} ion were explored.\textsuperscript{16-19} Two features are common to all these studies:

(1) The ZnO coatings are all oriented strongly along the [001] direction.
(2) In all cases, the crystallites have a columnar morphology, the cross section of the columns are hexagonal. The strong out-of-plane orientation is the result of the long axis of the columns, also the c-crystallographic axis of ZnO, being perpendicular to the substrate.
The results remain unchanged even when single crystalline substrates of GaN\textsuperscript{15, 16},\textsuperscript{20} or Au\textsuperscript{22, 23} were used. Single crystalline substrates facilitate in-plane orientation as well, by virtue of which the hexagonal columns are rotated to minimize the strain due to lattice mismatch.\textsuperscript{22} Anodic deposition from an alkaline zincate bath also yielded a strong [001] out-of-plane orientation and columnar morphology. These observations indicate that the [001] oriented crystallization under the potential gradient of the double layer is driven by the factors inherent to the structure of ZnO, rather than experimental factors such as bath composition or deposition conditions. Indeed the (001) plane of ZnO has a low surface energy, as a result of which crystallite growth takes place in-plane rather than along the direction normal to it.\textsuperscript{23} This kind of growth is thermodynamics driven. At high deposition currents, when the growth is kinetically driven,\textsuperscript{12} the orientation is lost, as the hexagonal columns grow with a random tilt of their long axes to the substrate surface.

One of the problems confronting the electrodeposition of ZnO, is co-deposition of zinc hydroxide or the basic salts of Zn.\textsuperscript{14} This can generally be avoided by using a nonaqueous bath such as DMSO, where dissolved O$_2$ reduction can be used to generate the oxide ion. Formation of Zn(OH)$_2$ can be suppressed by carrying out the electrodeposition at an elevated temperature (100 °C).\textsuperscript{24} These films were also textured along the [001] direction.

Since the photoluminescence of ZnO is $k$-dependent,\textsuperscript{25} there is interest in the growth of ZnO coatings with different orientations. In this study we use a mixed H$_2$O/isopropanol bath and report differently oriented ZnO coatings.

### 5.6 Experimental

ZnO coatings, were deposited from Zn(NO$_3$)$_2$ baths (0.04 M) prepared using water-isopropanol (IPA) mixed solvent (0-60% v/v IPA). Zn(NO$_3$)$_2$ and IPA were purchased from Merck, India and used as such. All the solutions were prepared using ion-exchanged Type-I water (Milli-Q Academic water purification system, specific resistance 18.2 MΩ cm).

Electrodeposition was carried out using an EG&G Versastat IIA scanning potentiostat driven by Powersuite software. A stainless steel flag (SS 304, area 4.5 cm$^2$) was used as cathode and a cylindrical Pt mesh (geometric area 28 cm$^2$) was used as the
counter electrode. Deposition was carried out potentiostatically at -0.9 V with respect to saturated calomel electrode. The deposition time was varied from 60 to 90 minutes and deposition temperature was maintained at 60 °C. After deposition, the coatings were cleaned with water and dried at 65 °C. Prior to electrodeposition, stainless steel electrodes were degreased with detergent and electrochemically polished by polarizing them anodically (30 s) and then cathodically (30 s) in 1 M KOH solution, and again anodically (30 s) in 1 M HCl (current density 20 mA cm⁻²).⁵⁶

Mass of the coatings, was determined by weighing the stainless steel flags before and after deposition. Thickness of the coatings, was estimated using the density of ZnO (5606 kg m⁻³). The mass and thickness of the coatings are given in Table 5.4. As the observed coatings are porous, the thickness in Table 5.4 is only an approximate estimate of the average value.

All coatings were characterized by X-ray diffraction (XRD), by mounting the electrode directly onto a Bruker aXS D8 Advance diffractometer (Cu Kα source λ = 1.541 Å). XRD profiles were fit by the Rietveld method (FullProf suite), using the published structure of ZnO (ICSD No.cF56) (P6₃mc, a = 3.2494 Å, c = 5.205 Å). The quality of the fit was judged from the R values and also by an examination of the difference profile. The observation of systematic residual intensities in the difference profile at positions corresponding to the different Bragg reflections is indicative of oriented crystallization.⁷ In such cases the Rietveld refinement was repeated by the inclusion of the modified March function to account for the orientation. The March function has two refinable parameters, G₁ and G₂. Of importance in the present context is G₂. G₂ = 0 corresponds to a fully oriented coating, while G₂ = 1 to a coating without any preferred orientation. Reflections due to the substrate were excluded in the refinement process.

Surface morphologies were studied using a scanning electron microscope (JEOL Model JSM 6490LV microscope, operating voltage 15 kV) by mounting the as-prepared coatings on conducting carbon tape and sputter coating with Pt to improve the conductivity.
5.7 Results and discussion

The XRD pattern of a ZnO coating obtained from an aqueous bath (Fig. 5.11a) has only one prominent peak at 34.4°2θ (d = 2.603 Å) corresponding to the (002) plane of ZnO. Two minor peaks appear at 2θ values corresponding to the (101) and (103) planes. To facilitate phase identification many such coatings were ground together. The XRD pattern of this polycrystalline powder sample exhibits all the reflections expected of wurtzite ZnO and a Rietveld fit of the profile (Fig. 5.11b) yields the structure of ZnO (space group P6₃mc, refined parameters a = 3.2506(2) Å, c = 5.2079(5) Å). We conclude that Fig. 5.11a corresponds to a coating of ZnO with a strong c-axis orientation. These results are in keeping with numerous previous reports.

The nature of the coating remained unchanged at low (10-30% v/v) IPA concentrations. When the IPA content was raised to 35-40% (v/v), a dramatic change in the XRD pattern was observed. Although the pattern exhibits all the reflections expected of ZnO, the intensity of the reflection due to the (103) plane at 62.9°2θ (d = 1.477 Å) is enhanced greatly relative to that of the (110) plane (see Supporting Information SI. 5.4; Fig. 5.12a). The reflection due to the (002) plane is progressively attenuated (compare Fig. 5.11a with SI. 5.4). On performing a Rietveld fit of the profile shown in Fig. 5.12a, residual intensities were seen in the difference profile at 2θ values corresponding to the (102) and (103) planes (Fig. 5.12e). The refinement was repeated by incorporating March function parameters to account for preferred orientation along these directions. The resultant fit was found to be satisfactory (Fig. 5.12b) and the difference profile (Fig. 5.12c) was a smooth function. The preferred orientation parameters are given in Table 5.4.
Fig. 5. 11 XRD pattern of a ZnO coating obtained from (a) an aqueous bath and (b) Rietveld refinement of the structure of a powder sample of ZnO obtained by grinding many coatings of the type shown in (a).
Fig. 5.12 (a) XRD pattern of a ZnO coating obtained from 40% (v/v) isopropanol bath compared with (b) the calculated XRD profile incorporating the effect of orientation and (c) the corresponding difference profile. (d) and (e) are respectively the calculated XRD profile and difference profile obtained before the incorporation of orientation effects. Features marked by the asterisk are due to the stainless steel substrate and were excluded for the Rietveld fits.
Table 5.4 Characteristics of ZnO coatings obtained with baths of different compositions

<table>
<thead>
<tr>
<th>Bath Composition (% v/v)*</th>
<th>Mass (mg)</th>
<th>Approximate average thickness (µm)</th>
<th>March function parameters G₁</th>
<th>G₂</th>
<th>Orientation</th>
<th>Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>16.7</td>
<td>6.6</td>
<td></td>
<td></td>
<td>001</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>17.8</td>
<td>7.04</td>
<td>0.56</td>
<td>0.42</td>
<td>102</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>103</td>
<td>0.38</td>
</tr>
<tr>
<td>50</td>
<td>19.1</td>
<td>7.5</td>
<td></td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>20.7</td>
<td>8.2</td>
<td>0.28</td>
<td>0.96</td>
<td>100</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>110</td>
<td>0.74</td>
</tr>
</tbody>
</table>

*% of Isopropanol
The ZnO coatings obtained at still higher IPA concentrations (~50% v/v) yield unoriented coatings with no reflection appearing with anomalous intensity (Fig. 5.13a). At 60% v/v IPA concentration, anomalous growth in the intensity of the peak due to the (100) plane was observed (Fig. 5.13b). This anomalous growth is evident in the residual intensities observed in the difference profile obtained at the end of the Rietveld refinement procedure (Supporting Information SI. 5.5). Incorporation of a bi-axial orientation in the [100] and [110] directions led to a smooth difference profile (SI. 5.5 and Table 5.4).

![XRD patterns](image)

**Fig. 5.13 XRD patterns of ZnO coatings obtained from (a) 50% (v/v) and (b) 60% (v/v) isopropanol baths. Features marked by the asterisk are due to the stainless steel substrate.**
The SEM image of the ZnO coating obtained from an aqueous bath reveals the cross-section of hexagonal columnar crystallites (Fig. 5.14a). The long axis of the hexagonal column, also the c-crystallographic axis, is normal to the substrate accounting for the observed [001] orientation (XRD in Fig. 5.11a).

Crystal growth during electrochemical deposition takes place under the potential gradient in the double layer presumably by the layer-by-layer accretion of atoms from solution. The (001) plane of ZnO is polar and crystal growth takes place by the accretion of alternative layers of Zn$^{2+}$ and O$^{2-}$ ions. Generally growth normal to the polar planes is very high, causing them to disappear. But within the wurtzite structure, the polarity of the (001) plane is very small given the small distance $d_{12}$ (see ref. 28) between the successive Zn$^{2+}$ and O$^{2-}$ layers. Consequently growth rate along [010] is higher than that along [001].$^{29}$ Further within the wurtzite structure, the (010), (100) and (110) planes are crystallographically equivalent,$^{30}$ accounting for their nearly equal incidence as faces of the hexagonal columns (Fig. 5.14b). Similar morphologies are widely reported in earlier papers.$^{11-18,20,22,23}$

The (102)/(103) orientation of the coatings is obtained when the crystallites are tilted to bring the [102]/[103] directions normal to the substrate surface (Fig. 5.15). This requires a rotation of the hexagonal columns about the $b$-axis. The SEM images clearly show the tilt of the faces of the hexagonal columns with respect to the substrate surface. By the same argument, loss of orientation of coatings obtained at 50% v/v IPA, arises due to the random tilt of crystallites with respect to the normal to the surface. The SEM image of the unoriented coating shows clusters of well faceted crystallites, which appear to be products of gregarious secondary crystallization (Fig. 5.16a). Even in regions where outgrowths due to secondary crystallization are not there, the crystallites grow with their vertices rather than their faces protruding out of the substrate surface. The biaxial orientation along [100] and [110] observed in coatings deposited at 60% v/v IPA orientation is expected if the hexagonal columns are rotated about the $b$-axis by 90°. However degree of orientation is very small (Table 1: $G_2 \approx 0.7$) and the SEM image of the coating (Fig. 5.16b) shows a few scattered rectangular faces of the supine hexagonal columns.
Fig. 5.14 (a) SEM image of end faces of hexagonal columns of ZnO deposited from an aqueous bath. (b) A schematic showing the crystallographic planes forming the six faces of the ZnO columns.
Fig. 5.15 (a) SEM image of a ZnO coating oriented along [103] obtained from 40% (v/v) IPA bath. Schematics (b) and (c) represent hexagonal columns of ZnO oriented along [001] and [103] directions respectively.
Fig. 5. 16 SEM images of (a) an unoriented ZnO coating obtained from 50% (v/v) IPA bath and (b) a ZnO coating with a bi-axial orientation obtained from 60% (v/v) IPA bath.

The question arises as to why the direction of orientation changes with increasing IPA content. One possible reason could be the change in the dielectric constant of the bath. A polar crystal face would be stabilized in a bath with a high dielectric constant and specially so when it is polarized by an external field as in an electrochemical cell. These forces are considerably reduced when the dielectric constant of the solvent is decreased, thereby enabling the accumulation of crystal faces of lower polarity. A convenient way of changing the dielectric constant of the bath in a continuous manner is by making a mixture of two miscible liquids having different dipole moments. The dielectric constant of the mixed water-IPA solvent changes from 66.62 to 28.9 as the IPA concentration is raised from 0 to 60% (v/v) at the deposition temperature (60 °C).³¹
Many parameters affect the outcome of an electrodeposition process. These include the interfacial pH, diffusion controlled mass transport as well as mechanical transport in stirred solutions, equilibria and reaction kinetics of chemical and electrochemical processes. Both thermodynamic and kinetic factors are involved, making the theoretical modelling of electrodeposition a complex process. Mandin and coworkers\textsuperscript{32-33} have extensively modelled the electrodeposition process to numerically evaluate the interfacial pH and reactant concentrations and applied their model to understanding the deposition of ZnO. These models\textsuperscript{32} predict speciation, porosity and morphological microstructure, but not the crystal structure and film texture. Developing a complete theoretical model to predict film texture and relate it to the dielectric constant of the solvent is outside the scope of this paper. Nevertheless, this study generates the possibility of exploring a variety of mixed baths to tailor oriented crystallization of different semiconducting oxides.

5.8 Conclusion

In conclusion, the orientation of an electrodeposited ZnO coating could be switched from the commonly observed [001] to other directions by varying the solvent composition. This is an illustration of solution mediated control over oriented crystallization in contrast with the better known substrate controlled orientation by epitaxy. Solution mediated crystallization provides a way of growing oriented coatings on polycrystalline substrates for a variety of possible applications.
References


Supporting Information

SI. 5.4 XRD patterns of ZnO coatings obtained from (a) 35\% (v/v) and (b) 40\% (v/v) isopropanol baths. Features marked by the asterisk are due to the stainless steel substrate.
SI. 5.5 (a) XRD pattern of a ZnO coating obtained from 60% (v/v) isopropanol bath compared with (b) the calculated XRD profile incorporating the effect of orientation and (c) the corresponding difference profile. (d) and (e) are respectively the calculated XRD profile and difference profile obtained before the incorporation of orientation effects. Features marked by the asterisk are due to the stainless steel substrate and were excluded for the Rietveld fits.