Over the past few decades, ZnO has regained its importance among numerous groups especially in the materials research and device fabrication technologies. ZnO is an n-type semiconductor with a wide bandgap (3.37 eV)\(^1\) and large exciton binding energy (60 meV)\(^1\) in hexagonal wurtzite crystal structure. It is shown to be a very promising material in a wide range of application areas from sensors\(^2\) to optoelectronic devices such as lasers,\(^3,4\) optical switches,\(^5\) light emitting diodes,\(^6\) phototransistors\(^7\) and solar cells.\(^8\) It is possible to modify electrical and optical properties of ZnO to broaden possible applications in ultraviolet optoelectronics\(^9\) and spin electronics\(^10\) through impurity incorporation. To tune these properties which are very sensitive to the shape of the particles and the preparation method, considerable attention has been paid to metal doping; a few examples are Mn\(^2+\), Cu\(^{2+}\), Cd\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Mg\(^{2+}\) and Fe\(^{2+}\).\(^10–12\) Although the origin of ferromagnetism in transition-metal doped ZnO is not yet very clearly understood and highly debatable,\(^13\) there is an increasing interest to study ZnO as a ferromagnetic material candidate.\(^14,15\) Among these materials, Mn-doped ZnO crystals receive growing attention as diluted magnetic semiconductor materials (DMS) for spintronics.\(^16,17\) Furthermore, modifying optical properties of ZnO through engineering the bandgap with Mn doping is also of interest to many groups.\(^14,18,19\) Several methodologies were employed to obtain Mn-doped ZnO particles including spray pyrolysis,\(^19\) chemical vapor deposition,\(^1\) magnetron sputtering,\(^20\) sol-gel process,\(^21\) pulsed laser deposition\(^22\) and electrodeposition.\(^23\) The first few techniques require high temperatures. Moreover, vapor-based techniques involve introduction of catalysts that might affect the physical properties of the product. Chemical synthesis, on the other hand, has emerged as a simpler alternative to produce semiconductor nanostructures. It is a cost-effective method where large area thin films on various substrates of arbitrary shapes can be produced at lower temperatures while control over growth rate, film thickness and morphology are maintained. However, there are no reports on synthesis of Mn-doped ZnO by a combination of hydrothermal techniques and electrochemistry which allows electrodeposition at higher temperatures than it is possible with air-open systems. In this present study, we report seedless electrochemical growth of Mn-doped ZnO films with this combined hydrothermal-electrochemical method for the first time and the effect of manganese ion amount on the morphology and physical properties of ZnO films were characterized.

**Experimental**

**Materials.—** All the chemicals used were of analytical grade or of the highest purity commercially available. Manganese chloride tetrahydrate (MnCl\(_2\)·4H\(_2\)O) was obtained from Merck and zinc nitrate hexahydrate (Zn(NO\(_3\))\(_2\)·6H\(_2\)O) was purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) was supplied from Alfa Aesar. Indium Tin Oxide (ITO) (\(\Omega \times 5.0 \times 10^{-4}\) ohm.cm) was purchased from Teknoma Ltd. Izmir, Turkey. Double distilled, high purity water was used from Milli-Q water (Millipore) system.

**Electrochemical Deposition of Mn:ZnO Films under Hydrothermal Conditions**

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This study demonstrated the electrochemical deposition of Mn-doped ZnO films under hydrothermal conditions at 130 °C in 50% v/v DMSO:H\(_2\)O mixture. X-ray diffraction analysis showed that the deposition of the ZnO structures was along (002) direction. However, the presence of Mn\(^{2+}\) affected the thickness of ZnO structures and we believe that the interaction of Mn\(^{2+}\) with the nonpolar surface of ZnO restricts lateral growth. Mn appears in the mixed oxide state in ZnO lattice. The photoluminescence spectra of the films show only UV emission indicating high crystal quality. The blueshift of the UV emission is observed after the introduction of Mn impurity into the ZnO lattice. The surface morphology, lattice structure, Mn content, chemical binding characteristics, and optical properties of the deposits were examined by scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and photoluminescence spectroscopy, respectively.

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uniform, well-aligned hexagonal rods strongly oriented toward the c axis were observed. Crystals smaller in the (0001) faces were grown along <0001> direction with hexagonal caps. Further addition of Mn(II) into the mixture induced further reduction in the width-to-length ratio of the particles without triggering any change in the morphological characteristics of the crystals. Diameters of the hexagonal rods decreased gradually from about 1.7–1.4 μm to 0.7 μm with increasing Mn(II) concentration. On the other hand, increase in Mn(II) concentration does not affect the thickness of the films as seen in Figure 2.

The structure of the transition metal doped ZnO films were characterized by X-ray diffraction. For the sample prepared in the absence of Mn²⁺, XRD pattern revealed typical three peaks which can be indexed to (100), (002) and (101) reflections of hexagonal wurtzite ZnO structure (JCPDS No. 0361451) without any other phase being detected (Figure 3), although (002) peak is highly intensified. The strong (002) peak observed in all of the samples indicated highly crystalline, well aligned doped ZnO particles that were preferentially grown vertically to the substrate in line with SEM images. The intensity ratio of (002) reflection to (100) reflection was 14 for the film prepared in the absence of Mn²⁺. For all other Mn-doped ZnO films the same ratio was around 100. Regardless of the concentration of Mn(II) ions, no shift in the position of (002) peak hence in the lattice parameters was observed. It can be attributed either to similar radii of the two cations (where Mn²⁺ ionic radius is 0.66 Å and those of Zn²⁺ ionic radius is 0.60 Å) or to low doping level of manganese ions. It is already established for Cd-doped ZnO films that doping levels lower than 9% does not induce a change in the lattice parameters.

Surfactants or capping agents are commonly used to modify the morphology of the particles through passivation of one or more faces selectively at the expense of the others in the colloid science. We believe capping ability of Mn(II) ions together with the high temperature are the key actors in the formation of the obtained structures. Electrodeposition from nitrate precursors is driven by the reduction of nitrate. Reduction of nitrate ions coming from the dissolution of Zn(NO₃)₂ (Eq. 1) to nitrite ions gives rise to increase in pH through formation of OH⁻ ions (Eq. 2). The hydroxide ions in turn, cause precipitation of zinc hydroxide (Eq. 3; hydroxylation) at the cathode. Zinc hydroxide is then dehydrated to generate ZnO (Eq. 4; dehydration).

\[
\text{Zn(NO}_3\text{)}_2 \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^- \quad \text{(1)}
\]
\[
\text{NO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^- \quad \text{(2)}
\]
\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad \text{(3)}
\]
\[
\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad \text{(4)}
\]

Tetrahedrally coordinated O²⁻ and Zn²⁺ ions stacked alternatively along the c axis make up the wurtzite crystal structure. Due to this arrangement of atoms, ZnO posses a negatively charged, basal
O-(001) polar plane and a positively charged Zn-(0001) plane. In addition, ZnO crystal growth rate was shown to be five times faster on the {001} planes than it is on the {1010} and {0110} planes which would yield particles with a relatively high aspect ratio. Despite of this preferential growth direction it is possible to obtain 2-D ZnO structures in the presence of KCl from highly concentrated Zn(NO$_3$)$_2$ baths (100 mM, 50 mM).$^{[27,28]}$ It is suggested that selective adsorption of Cl$^-$ ions on the polar (0001) plane is responsible for the redirected growth on the nonpolar (1010) plane. However, Pradhan and Leung observed an opposite behavior with dilute Zn(NO$_3$)$_2$ solutions.$^{[25]}$ They explained the contradictive behavior at low Zn(NO$_3$)$_2$ electrolyte concentrations with hydrolyzation kinetics. It is suggested that slower hydrolyzation reaction (formation of Zn(OH)$_2$) at low electrolyte concentrations provides time for desorption of Cl$^-$ ions from the polar surface. Since the hydrolyzation reaction is slower, as soon as zinc hydroxide is formed, it is converted to zinc oxide leading to the formation of 1-D materials. In hydrothermal-electrochemical synthesis we observed preferential growth along (0001) plane perpendicular to the substrate even at high electrolyte concentrations with or without KCl (100 Mn Zn, 100 Mn KCl). We believe this concentration independent morphology can be explained by the combined effect of desorption of Cl$^-$ at low concentrations and the increased rate of dehydrazation reaction at even higher temperature and pressure. The dehydrazation reaction, conversion of the initially formed zinc hydroxide to zinc oxide, is already shown to be increasing with deposition temperature noticeably.$^{[25]}$ Development of zinc oxide seed crystals might be even faster at 130°C. Since Cl$^-$ ions does not alter the morphology of the crystals, Mn(II) ions are responsible for the transformation from coalesced hexagonal platelets to formation of thinner rods. Being a polar basic aprotic solvent DMSO also is a major component in controlling the growth of ZnO structures obtained by electrodeposition.$^{[10,31]}$ In these studies, DMSO was shown to be also inducing anisotropic growth. A mass of DMSO is most likely absorbed on to the polar plane, hence restrains the growth along (0001) plane. Hence, ZnO particles obtained in the absence of Mn(II) ions in DMSO-H$_2$O mixture are in the form of platelets. DMSO also behaves as a reactant by increasing the OH$^-$ ion concentration according to the following equation:

$$ \text{(CH}_3)_2\text{SO} + \text{HOH} \rightarrow \text{(CH}_3)_2\text{SOH}^+ + \text{OH}^- \quad [5] $$

Higher OH$^-$ concentration also accelerates the hydroxylation reaction (Eq. 3) as well as nucleation rate. However, Mn(II) addition stimulates formation of hexagonal rods. It is very important to note that although the mixture contains high amount of DMSO, the final product is the film composed of rods. Presence of Mn$^{2+}$ in the mixture together with the reasons given above results in the formation of rod structures. It is most likely that the Mn(II) species in the deposition solution are adsorbed onto the nonpolar surfaces of ZnO parallel to the $c$ axis and hence preventing the growth in the lateral direction. Below 20 mM Mn(II) ions are not sufficient to induce thinner rod formation (Figure 1b). As Mn(II) concentration increases above 20 mM, lateral growth is far more restricted hence diameter of hexagonal rods decreases as it is observed for Cr$^{3+}$-doped ZnO particles before.$^{[33]}$ Similar observation was also reported by Lincot et al.$^{[34,35]}$ In their manuscripts related with ZnO deposition in the presence of lanthanide ions, they have reported that increase in the lanthanide concentration and formation of hydroxide layer resulted in lower rod density. Formation of Mn related species in between the rods during the deposition might be responsible for thinner rods in our films. We have not, however, found any evidence of hydroxide layer beneath the ZnO layers when we analyze the films with electron microscope and Energy Dispersive X-ray Fluorescence (EDX). On the other hand, SEM and EDX investigations revealed the presence of Mn containing precipitates on small areas, particularly at the edges, on some films (data not shown) and this could be the evidence for the growth of thinner ZnO rods on the surface as a result of the absorption of Mn-species on lateral surface of ZnO structures.

The composition of the Mn-doped ZnO films and the chemical bonding states of the metals were examined by studying the Zn 2p and Mn 2p core level XPS spectra. The peak positions were same for all of the films. Figure 4a displays Zn 2p XPS spectrum of the film prepared with lowest [Mn(II)]/[Zn(II)] feed ratio. There appear two peaks centered around 1022.45 and 1045.38 which corresponds to Zn 2p$_{3/2}$ and 2p$_{1/2}$ respectively matching the binding energy of Zn$^{2+}$ in ZnO. The Zn 2p binding energies are very similar for all of the films. The position of the Zn 2p$_{1/2}$ peak does not vary with etching time indicating good chemical stability of Zn through the film. Mn 2p core level XPS spectrum of the same film is shown in Figure 4b. It can be seen that there are three peaks appearing at 641.62, 652.91 and 655.46 eV which are obtained similarly for all other samples. The peak centered at 641.62 eV is at higher binding energy than Mn$_{2+}$ (2p$_{3/2}$) ($\sim$ 641 eV) found in Mn-doped ZnO samples earlier and at lower binding energy than the value which is commonly observed for Mn$^{3+}$ (2p$_{3/2}$) ($\sim$ 642 eV) in literature.$^{[11,16,19,36]}$ Nesbitt and Banerjee proposed 640.8 ±0.3 eV as the binding energy of Mn$^{3+}$ (2p$_{3/2}$) after a detailed study and literature search on XPS spectra of Mn$^{2+}$.$^{[37]}$ Plus, they determined that the position of the Mn$^{3+}$ (2p$_{3/2}$) peak of oxides range between 641.7 and 641.9 eV. An earlier study on the transition metal oxide spectra assigns 641.7 eV to the 2p$_{3/2}$ peak to manganese 3+ oxidation state both in Mn$_2$O$_3$ and mixed metal oxide Mn$_3$O$_4$.$^{[38]}$ In addition, the 11.29 eV spin orbit splitting between the Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ is in agreement with previous reports on XPS spectrum of Mn$_3$O$_4$.$^{[39,40]}$ Hence, the peaks at 641.62 and 652.91 can be attributed to 2p$_{3/2}$ and 2p$_{1/2}$ orbitals in the mixed valence oxide. Furthermore, presence of Zn (L$_2$M$_2$M$_3$) Auger transition (around 655 eV) besides confirming strong interaction between Zn and Mn, also implies oxidation state higher than 2+ for Mn.$^{[41]}$ Metallic manganese formation

![Figure 4](ecsdlsite/terms_use)
was not observed (637.7 eV). According to the XPS results, the real manganese content in the films is around 3% regardless of the Mn(II) concentration in the deposition solution (Table I).

Figure 5 shows the room-temperature photoluminescence (PL) spectra of the doped and undoped ZnO films prepared by the hydrothermal-electrodeposition. All the films show strong near-band-edge (NBE) emission around 375–385 nm due to the transitions of the excited electrons from conduction band to valence band but almost no visible emission. Emission in the visible region is generally attributed to excited electrons from conduction band to valence band but almost no visible emission. Emission in the visible region is a sign of crystal quality. Since, high intensity ratio implies high crystal quality. Photoluminescence spectra of undoped and Mn-doped ZnO films. Figure 5.

<table>
<thead>
<tr>
<th>Mn(II)/Zn(II)</th>
<th>Mn%</th>
<th>Zn%</th>
<th>Mn(II)/Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the deposition bath</td>
<td>In the film</td>
<td>In the film</td>
<td>In the film</td>
</tr>
<tr>
<td>0.2</td>
<td>3.3</td>
<td>96.7</td>
<td>0.03</td>
</tr>
<tr>
<td>0.4</td>
<td>3.26</td>
<td>96.74</td>
<td>0.033</td>
</tr>
<tr>
<td>0.6</td>
<td>2.88</td>
<td>97.12</td>
<td>0.029</td>
</tr>
<tr>
<td>0.8</td>
<td>3.83</td>
<td>96.17</td>
<td>0.039</td>
</tr>
<tr>
<td>1</td>
<td>3.64</td>
<td>96.34</td>
<td>0.037</td>
</tr>
</tbody>
</table>

The fact that UV emission does not shift further with increasing Mn(II) concentration suggests the level of manganese that can be incorporated to ZnO is limited which is in line with XPS results.

Conclusions

Hydrothermal-electrodeposition at 130°C was successfully employed to produce Mn-doped ZnO films. Hexagonal wurtzite ZnO structure growing toward (002) direction was obtained with no impurity phases. Obtained particles were of high crystal quality indicated by high intensity ratio of UV emission to visible emission. The lattice parameters are not altered on addition of Mn. Mn-doping affected the crystal growth enhancing formation of particles with high aspect ratio. As concentration of Mn(II) in the deposition bath increased, coalesced platelets were transformed into hexagonal particles of smaller diameter. XPS results display that Mn is present both in divalent and trivalent state in ZnO lattice. Presence of manganese induced a shift in UV emission toward lower wavelength by introducing excessive carriers into the lattice.

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