

Preparation of ZnO Thin Films Using Zn/O-containing Single Precursor through MOCVD Method

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A new Zn/O single source precursor, TMEDA-Zn(eacac)₂, has been synthesized by using N,N,N',N'-tetramethylethylenediamine (TMEDA), sodium ethyl-acetoacetate, and ZnCl₂. From this organometallic precursor, ZnO thin films have been successfully grown on Si (100) substrates through the metal organic chemical vapor deposition (MOCVD) method at relatively mild conditions in the temperature range of 390–430 °C. The synthesized ZnO films have been found to possess average grain sizes of about 70 nm with an orientation along the *c*-axis. The precursor and ZnO films are characterized through infrared spectroscopy, nuclear magnetic resonance spectroscopy, EI-FAB-spectroscopy, elemental analyses, thermal analysis, X-ray diffraction, and field emission scanning electron microscopic analyses.

Key Words: ZnO thin film, MOCVD, Precursor, Solar cell

Introduction

Zinc oxide (ZnO), a II-VI compound semiconductor with a wide direct band gap of 3.37 eV at room temperature, is well known to have a variety of practical applications such as gas sensors,¹ acoustic devices,² transparent coatings for solar cells³ because of its large piezoelectricity, large optical refractive indices, and high optical transparency. Therefore, the ZnO thin films have been fabricated through many different techniques such as spray pyrolysis (SP),⁴ atomic-layer deposition (ALD),⁵ pulsed-laser deposition (PLD),⁶ molecular beam epitaxy (MBE),⁷ electrodeposition,⁸ chemical bath deposition (CBD),⁹ oxidation of Zinc films,¹⁰ sol-gel,¹¹ chemical vapor deposition (CVD),¹² and metal organic chemical vapor deposition (MOCVD).¹³ Among them, the MOCVD method provides with several advantages: typically, this method has been known to be very useful in producing high quality thin films with less impurities and uniform thickness under relatively milder conditions. In the MOCVD process, the most important key point is the availability of highly volatile and thermally stable single source precursors to obtain uniform and reproducible thin films. In the previous studies, ZnO thin films have been fabricated through the MOCVD method by using several precursors such as liquid dimethyl-Zn,¹⁴ diethyl-Zn complexes or solid acetate,^{15,16} alkoxide,¹⁷ and acetonate zinc complexes.^{18,19} However, these precursors have some weak points: due to the pyrophoric nature of the precursors, impurities are often found in prepared ZnO films. And also higher fabrication temperatures are required to obtain ZnO films. The most recent studies on Zn/O MOCVD precursors included the syntheses of diamine adducts of the zinc bis(2-thenoyl-trifluoroacetate)¹³ and Zn(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate)₂.²⁰ These precursors were water-free, thermally stable, and volatile. However, their ZnO film fabrications were performed at *ca.* 650 and 500 °C, respectively. Such fabrication temperatures are too high for the application to the CuInSe₂/CdS or In₂S₃/ZnO type solar cell because the absorber and/or buffer layers in CIS type solar cells might be seriously damaged with

the accompanying structural change and/or diffusion.^{21–24}

Thus, in an effort to obtain ZnO thin films through MOCVD method below 450 °C, we have synthesized and characterized a new zinc adduct, TMEDA-Zn(eacac)₂ (eacac = ethyl acetoacetate, TMEDA = N,N,N',N'-tetramethylethylenediamine). In this paper, we show that the ZnO single-crystalline films could be successfully fabricated on Si (100) substrates through the MOCVD method at relatively milder conditions. The ZnO film obtained in this work seems to be oriented along the *c*-axis on the basis of X-ray diffraction pattern. Thus, we believe the newly synthesized precursors could be used for the preparations of ZnO nanoarray as well.⁵

Experimental Details

Reagents. Most of the reagents were purchased from Sigma-Aldrich Corporation and used without further purifications. Diethyl ether was purified by shaking with an alkaline potassium permanganate and sulphuric acid solutions for several hours. Then, it was washed with water, dried with calcium chloride, and distilled. Acetone and pentane were dried over Molecular Sieves 3A and distilled prior to use.

General Procedures. ¹H-NMR spectra were recorded on a Varian Gemini 2000 (300MHz) spectrometer using acetone d-6 and chloroform-d as solvents. Infrared spectra were recorded using a Jasco FT/IT-5300 spectrometer in the 400–4000 cm⁻¹ range, with a sample pressed with KBr. The instrumental resolution was 2 cm⁻¹. Mass analyses were performed at the center for research facilities of the Chung-Ang University using DIP-FAB Mass spectrometer (Micromass Autospec). Elemental micro-analyses were performed in the Korean National Center for Inter-University Research Facilities using a CE instrument elemental analyzer, EA1110. Thermogravimetric (TG) analyses were performed by Setaram LABSYS TG-DTA/DSC thermal analyzer.

Synthesis of TMEDA-Zn(eacac)₂. ZnCl₂ (273 mg, 2 mmol) and N,N,N',N'-tetramethylethylenediamine (0.303 mL, 2 mmol) were reacted in diethyl ether (30 mL) for 10 min. Resulting

TMEDA-ZnCl₂ was filtered using a glass filter, then the adduct reacted with sodium ethylacetoacetate (0.641 mg, 4 mmol) in acetone. NaCl was precipitated immediately, which was filtered off. As soon as the solvent of the filtrate was evaporated, colorless microcrystals of TMEDA-Zn(eacac)₂ have been obtained in 80% yield. Single crystals of TMEDA-Zn(eacac)₂ have been grown by a slow evaporation of the saturated pentane solution of TMEDA-Zn(eacac)₂ in the refrigerator. ¹H NMR (300 MHz, CDCl₃): δ 2.36 (s, 3H, -N-CH₃), 2.62 (s, 2H, -N-CH₂-), 4.56 (s, 1H, CO-CH-CO), 1.74 (s, 3H, -CO-CH₃), 3.98 (q, 2H, CH₃-CH₂-O-), 1.16 (t, 3H, -O-CH₂-CH₃). DIP-FAB Mass m/z: 438(M⁺). Anal. Calcd for C₁₈H₃₄N₂O₆Zn: C, 49.15; H, 7.79; N, 6.37. Found: C, 49.21; H, 7.85; N, 6.57.

Crystallographic determination. The structure of TMEDA-Zn(eacac)₂ was determined by standard crystallographic methods. A colorless plate crystal (0.02 × 0.14 × 0.18 mm³) was used for single-crystal X-ray diffraction. The intensity data were collected on a Bruker SMART APEX CCD X-ray diffractometer at 173 K using graphite monochromated Mo Kα radiation (Korea Basic Science Institute). A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in omega, and an exposure time of 5 s per frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability.

Table 1. Crystallographic data for TMEDA-Zn(eacac)₂

Empirical formula	C ₁₈ H ₃₄ N ₂ O ₆ Zn
Formula weight	439.84
Crystal system	Tetragonal
Space group	<i>I</i> 4/ <i>acd</i> (No. 142)
<i>Z</i>	16
<i>a</i> = <i>b</i> (Å)	16.798(3)
<i>c</i> (Å)	31.497(11)
Volume (Å ³)	8888(4)
Temperature (K)	173.0(2)
ρ_{calc} (g cm ⁻³)	1.315
μ (mm ⁻¹)	1.138
Crystal color	Colorless
Crystal habit	Plate
Crystal size	0.02 × 0.14 × 0.18
Reflections collected	30160
Independent reflections	2693
<i>R</i> (int)	0.0884
No. of parameters	127
Goodness-of-fit on <i>F</i> ²	1.079
X-ray radiation (λ , Å)	Mo K α (0.71073)
θ Range (°)	2.15–28.02
Limiting indices	-22 ≤ <i>h</i> ≤ 22, -22 ≤ <i>k</i> ≤ 16, -41 ≤ <i>l</i> ≤ 41
Refinement method	Full-matrix least-squares on <i>F</i> ² [SHELXL-97]
Final <i>R</i> ^{a,b} indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> (<i>F</i>) = 0.0447, <i>R</i> _w (<i>F</i> _o ²) = 0.1011
<i>R</i> indices (all data)	<i>R</i> (<i>F</i>) = 0.0910, <i>R</i> _w (<i>F</i> _o ²) = 0.1322
Largest diff. peak and hole (e Å ⁻³)	0.638 and -0.690

^a*R*(*F*) = $\sum |F_o - F_c| / \sum |F_o|$. ^b*R*_w(*F*_o²) = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

The maximum correction applied to the intensities was <1%. The data were integrated using the Bruker SAINT program, with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. Ψ -scan was used for the absorption correction on the hemisphere of data. The data were solved and refined using SHELXS-97 and SHELXL-97, respectively.^{25,26} All of the atoms were refined with anisotropic displacement parameters and converged for *I* > 2(*I*). All calculations were performed using the WinGX-98 crystallographic software package.²⁷ Crystallographic data, atomic coordinates and displacement parameters, and selected bond distances and angles for TMEDA-Zn(eacac)₂ are given in Table 1-3.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for TMEDA-Zn(eacac)₂

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a (Å ²)
Zn(1)	0.78721(2)	0.46279(2)	0.125	0.02775(18)
O(1)	0.69688(13)	0.38625(14)	0.10942(8)	0.0320(6)
O(2)	0.71054(13)	0.50522(16)	0.17322(7)	0.0333(6)
O(3)	0.59252(14)	0.54926(14)	0.19651(8)	0.0340(6)
N(1)	0.84737(17)	0.38339(17)	0.17067(9)	0.0306(7)
C(1)	0.5677(2)	0.3568(2)	0.08473(12)	0.0383(9)
C(2)	0.6229(2)	0.4014(2)	0.11421(10)	0.0285(8)
C(3)	0.5906(2)	0.4541(2)	0.14320(11)	0.0294(8)
C(4)	0.6367(2)	0.5019(2)	0.17052(10)	0.0291(7)
C(5)	0.6365(2)	0.6019(2)	0.22404(12)	0.0364(9)
C(6)	0.5773(2)	0.6499(2)	0.24856(13)	0.0453(10)
C(7)	0.8721(2)	0.4265(2)	0.20908(11)	0.0411(9)
C(8)	0.7933(3)	0.3191(2)	0.18367(12)	0.0458(10)
C(9)	0.9174(2)	0.3528(2)	0.14795(11)	0.0421(10)

^a*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3. Selected bond distances (Å) and bond angles (°) for TMEDA-Zn(eacac)₂

Bond distances			
Zn(1)–O(1) × 2	2.048(2)	N(1)–C(8)	1.468(5)
Zn(1)–O(2) × 2	2.115(2)	N(1)–C(9)	1.469(4)
Zn(1)–N(1) × 2	2.207(3)	N(1)–C(7)	1.470(4)
O(1)–C(2)	1.278(4)	C(1)–C(2)	1.511(5)
O(2)–C(4)	1.244(4)	C(2)–C(3)	1.382(5)
O(3)–C(4)	1.362(4)	C(3)–C(4)	1.410(5)
O(3)–C(5)	1.442(4)	C(5)–C(6)	1.496(5)
		C(9)–C(9)#1	1.523(7)
Bond angles			
O(1)–Zn(1)–O(1)#1	170.83(13)	O(1)–Zn(1)–N(1)#1	90.24(10)
O(1)–Zn(1)–O(2)	86.13(9)	O(1)#1–Zn(1)–N(1)#1	96.66(10)
O(1)#1–Zn(1)–O(2)	87.74(10)	O(2)–Zn(1)–N(1)#1	172.09(11)
O(2)–Zn(1)–O(2)#1	96.04(14)	O(2)#1–Zn(1)–N(1)#1	90.83(10)
		N(1)#1–Zn(1)–N(1)	82.60(15)

Symmetry transformations used to generate equivalent atoms: #1-*y*-5/4, -*x*-5/4, -*z*+1/4

MOCVD experiment and film characterization. The ZnO thin films were prepared through the MOCVD method and all processes were handled under vacuum. A detailed description of the equipment and methodology used has been published previously.²²⁻²⁴ In deposition process using TMEDA-Zn(eacac)₂, bubbler temperature was controlled to 110 °C and ZnO thin films were deposited in the temperature range of 390-430 °C for 1hr on Si (100). The resulting thin films were characterized by powder X-ray diffractometer (Scintag XDS-2000) and fieldemission scanning electron microscope (Hitach S-4700).

Results and Discussion

Crystal structure of TMEDA-Zn(eacac)₂. The crystal structure of TMEDA-Zn(eacac)₂ (Figure 1) has been determined by X-ray single-crystal diffraction technique. TMEDA-Zn(eacac)₂ is a zero-dimensional molecular organometallic compound, which crystallizes in the tetragonal space group *I4₁/acd* (No. 142). As can be seen in Figure 1, TMEDA-Zn(eacac)₂ can be described as having a distorted octahedral geometry around the unique six-coordinate Zn²⁺ cation. Four oxygen atoms from two asymmetric bidentate ligands, eacac, and two nitrogen atoms from a bidentate ligand, TMEDA, are surrounding the Zn²⁺ cation to form the distorted octahedral environment. The Zn-O distances are ranging from 2.048(2) to 2.115(2) Å, while the bond length of Zn-N is 2.207(3) Å. The bond angles for O-Zn-O, O-Zn-N, and N-Zn-N are ranging 86.13(9)-170.83(13), 90.24 (10)-172.09 (11), and 82.60 (15), respectively. Bond valence calculation^{28,29} resulted in 1.98 for Zn²⁺ cation. Selected bond lengths and angles are presented in the Table 3.

Physicochemical properties of TMEDA-Zn(eacac)₂. The infrared spectrum of the TMEDA-Zn(eacac)₂ shows the β -diketonate ligand peaks at 1645 and 1617 cm⁻¹ (C=O stretching vibrations), and 1516 cm⁻¹ (C=C stretching vibrations). The other peaks at 1253 and 1059 cm⁻¹ can be assigned to the C-N stretching vibrations of the TMEDA ligand and C-O stretching vibration of the ethylacetoacetate ligand, respectively.^{13,30}

The ¹H NMR spectrum of the TMEDA-Zn(eacac)₂ shows a singlet at δ = 4.56 ppm whose integration accounts for two protons between diketonate in the eacac ligand. Another sin-

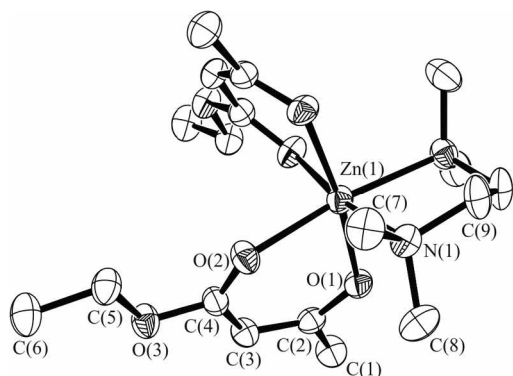


Figure 1. ORTEP (50% probability ellipsoids) drawing for TMEDA-Zn(eacac)₂. H atoms are omitted for clarity

glet of eacac ligand at δ = 1.74 ppm is associated with three protons of methyl group. And a triplet and a quartet at δ = 1.16 and 3.98 ppm, respectively, could be the ethyl moiety of the ether group. In addition, singlets at δ = 2.36 and 2.62 ppm represent the resonances of the six and four protons of the methyl and ethylene groups of the TMEDA, respectively.

The thermal behaviour of the synthesized precursor was investigated using thermogravimetric analysis. The precursor is quite stable in ambient conditions³¹ and has a low melting point of 82-83 °C at 760 Torr with a decomposition temperature of 205 °C in comparison to the known similar precursors^{13,32} suggesting that it can be used in the MOCVD process under relatively milder conditions. Powder XRD measurement on the calcined material revealed the precursor decomposed to ZnO.

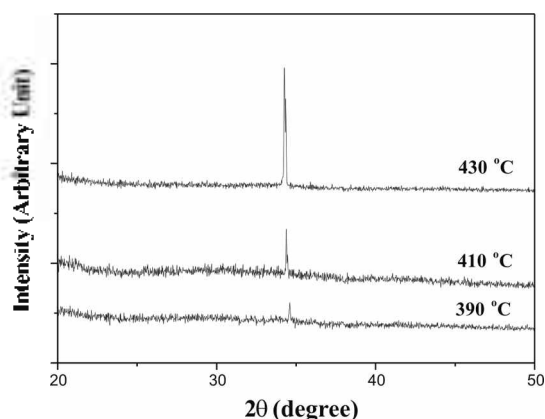


Figure 2. Powder X-ray diffraction patterns of ZnO films at different temperatures

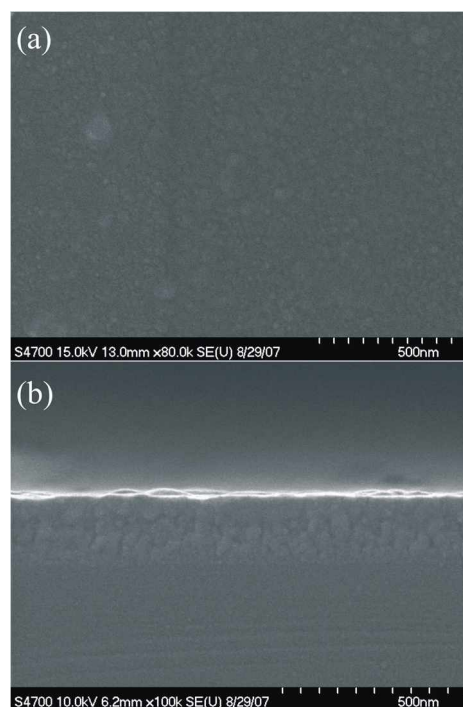


Figure 3. SEM images of ZnO thin films grown on Si (100) using TMEDA-Zn(eacac)₂: (a) surface image, (b) side view grown at 410 °C

Table 4. Characteristics of the ZnO thin film deposited at 410 °C

Theta(θ) [$\times 10^{-3}$] (radian)	0.3304
FWHM [$\times 10^{-3}$] (radian)	2.00
Crystallite size (nm)	70
<i>c</i> -lattice constant (Å)	5.210
Stress [$\times 10^8$] (Pa)	-7.69

MOCVD depositions from the TMEDA-Zn(eacac)₂ precursor. The suitability of an organometallic compound as a proper precursor for the MOCVD process might be best verified when it is applied to the real fabrication for a film containing a specific metal center. In this case, the TMEDA-Zn(eacac)₂ precursor has been tested whether it could be successfully fabricated to the ZnO film. Several deposition experiments from the TMEDA-Zn(eacac)₂ precursor to the ZnO films have been made on Si (100) substrates. The precursor has been heated to 110 °C at the bubbler, while the substrate temperatures have been kept at 390~430 °C during the 1 hour deposition time. The powder X-ray diffraction patterns for the ZnO films can be found in Figure 2. As can be seen in Figure 2, a diffraction peak around 34.4° is observed at each temperature. The peak can be indexed to the (002) of the ZnO film. Unlike the randomly oriented bulk samples, only one peak is observed from the deposited ZnO film due to the preferred orientation. This is consistent with the fact that the ZnO film grows along the *c*-axis. The (004) peak, which is expected around 73.35°, was overlapped with a strong Si substrate peak. However, in order to confirm the successful preparation of ZnO film, SEM/EDX analysis has been performed. EDX analysis for the film provided a Zn:O ratio of 1:1. It has been reported that the orientation of the deposited ZnO film might be closely related to the types of used substrates.³³ Although the film has been grown along one direction, the lattice constant *c* for the hexagonal close packed ZnO could be obtained from the relationship between the interplanar spacings and Bragg's equation.^{31,33} Based on the powder diffraction pattern in Figure 2, the lattice parameter *c* is calculated to 5.210 Å. The biaxial stress also can be calculated from the parameter *c* by using $\sigma = -453.6 \times 10^9 ((c - c_0) / c_0)$, where *c*₀ is the strain-free lattice parameter (*c*₀ = 5.205 Å) measured from a ZnO powder sample.³⁴ The biaxial stress is -7.69×10^8 Pa at 410 °C. All the calculation data obtained from the powder XRD are summarized in Table 4.

Figure 3 shows the SEM images of the ZnO films deposited on the Si (100). The ZnO films present very uniform morphologies, with coalesced grains of about 70 nm in diameter (see Table 4), which are in good agreement with the calculated crystallite sizes from the powder XRD. The growth rate of these films is 3.3 nm/min at 410 °C.

Conclusions

ZnO thin films through the MOCVD method using TMEDA-Zn(eacac)₂ single source precursor are successfully deposited on Si substrate below 450 °C and the deposition rate is relatively quite good under mild conditions. The ZnO grain size is about 70 nm and the range of biaxial stress is -7.69×10^8

Pa. Thus, it is expected that the CIS type solar cells, including CuInSe₂/CdS or In₂S₃/ZnO layers, could be built through complete MOCVD processes below 450 °C.

Supporting information available. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC674028. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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