

# Single-Source Chemical Vapor Deposition Growth of ZnO Thin Films Using $Zn_4O(CO_2NEt_2)_6$

A. J. Petrella, H. Deng,<sup>†</sup> N. K. Roberts, and R. N. Lamb\*

Surface Science & Technology, School of Chemical Sciences, The University of New South Wales, Sydney 2052, Australia

Received May 3, 2002. Revised Manuscript Received July 30, 2002

A novel precursor, hexakis[ $\mu$ -(diethylcarbamato-O:O')]- $\mu_4$ -oxotetrazinc, ( $Zn_4O(CO_2NEt_2)_6$ ) (1), for the single source chemical vapor deposition (SSCVD) growth of ZnO films has been developed. The structure and chemistry of resultant films were characterized using photoemission spectroscopy and diffraction techniques as well as electron microscopy. The polycrystalline films are of relatively dense columnar structure and have preferred *c*-axis orientation. Their morphology is very similar to that of RF sputtered films, but with the significant difference that they do not exhibit the strain and stress usually inherent in as-deposited RF sputtered films. Film preparation using  $Zn_4O(CO_2NEt_2)_6$  is therefore a simple one-step process with a lower overall production temperature required to produce high-quality films. Additionally, piezoelectric measurements of the films indicated piezoelectric responses close to that of single-crystalline ZnO.

## Introduction

Zinc oxide films have various applications that exploit their electrical, optical, and piezoelectric properties. Thin films of zinc oxide have been prepared using various deposition methods, including RF sputtering,<sup>1,2</sup> pulsed laser deposition,<sup>3</sup> atomic layer epitaxy,<sup>4</sup> and chemical bath deposition.<sup>5</sup>

Thin films have also been fabricated using chemical vapor deposition methods, using volatile metal-organic reactants. For ZnO deposition this typically involves the use of metal alkyls, usually dimethyl- or diethylzinc in combination with a separate source of oxygen such as  $H_2O$  or  $O_2$ .<sup>6–8</sup> Due to the high reactivity of metal alkyl precursors with  $O_2$  or  $H_2O$ , reactions may occur prematurely in the gas phase, resulting in the formation of solid particles. This limits the quality of films produced and the area that can be coated uniformly. Difficulties with this method have been addressed by use of less reactive alkyl adducts<sup>9,10</sup> or by careful reactor de-

sign;<sup>11,12</sup> however, the methods remain complicated and require the use of expensive equipment.

The thin film deposition methods currently available concentrate on improving either deposition apparatus or precursor chemistry. For a deposition method to be widely applicable, it should be relatively inexpensive and simple and produce a good quality product. The scope for chemistry-based methods to improve the quality of products, minimize costs, and simplify the deposition process has led to an increased interest in understanding how fundamental aspects of precursor chemistry relate to resultant film properties. In particular, there has been increasing interest in the synthesis and study of volatile single-source metal-organic precursors that can be used to deposit a variety of thin film materials.<sup>13–16</sup>

The single-source chemical vapor deposition (SSCVD) technique promises to provide deposition at moderate temperatures and with significant simplification of deposition apparatus since the technique essentially involves precursor vaporization followed by precursor decomposition/deposition.

The viability of single-source film deposition is dependent on the chemistry of the precursor. Thus, precursor design and synthesis underpin this technique. The precursor must provide the reactants needed for film growth within a single molecule, while maintaining the volatility and thermal stability needed for reactant transport to the site of film deposition. Upon arrival at the substrate, which is usually heated, the precursor must then decompose cleanly, leaving behind the de-

\* To whom correspondence should be addressed. E-mail: r.lamb@unsw.edu.au.

<sup>†</sup> School of Microelectronics and Solid State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, China.

(1) Maniv, S.; Westwood, W. D.; Columbini, E. *J. Vac. Sci. Technol. B* **1982**, 20 (2), 162.

(2) Kim, Y. J.; Kim, Y. T.; Yang, H. K.; Park, J. C.; Han, J. I.; Lee, Y. E.; Kim, H. J. *J. Vac. Sci. Technol. B* **1997**, A15 (3), 1103.

(3) Ryu, Y. R.; Zhu, S.; Wrobel, J. M.; Jeong, H. M.; Miceli, P. F.; White, H. W. *J. Cryst. Growth* **2000**, 216 (1–4), 326.

(4) Yousfi, E. B.; Fouache, J.; Lincot, D. *Appl. Surf. Sci.* **2000**, 153, 223.

(5) Mane, R. S.; Lokhande, C. D. *Mater. Chem. Phys.* **2000**, 65, 1.

(6) Lau, C. K.; Tiku, S. K.; Lakin, K. M. *J. Electrochem. Soc.* **1980**, 127 (8), 1843.

(7) Ghandhi, S. K.; Field, R. J.; Shealy, J. R. *Appl. Phys. Lett.* **1980**, 37 (5), 449.

(8) Wenas, W. W.; Yamada, A.; Konagai, M.; Takahashi, K. *Jpn. J. Appl. Phys.* **1991**, 30 (3B), L441–L443.

(9) Hahn, B.; Heindel, G.; Pschorr-Schoberer, E.; Gebhardt, W. *Semicond. Sci. Technol.* **1998**, 13, 788.

(10) Kaufmann, T.; Funchs, G.; Webert, M.; Frieske, S.; Gaeckle, M. *Cryst. Res. Technol.* **1989**, 24 (3), 269.

(11) Smith, F. T. *J. Appl. Phys. Lett.* **1983**, 43 (12), 1108.

(12) Gorla, C. R.; Emanetoglu, N. W.; Liang, S.; Mayo, W. E.; Lu, Y. *J. Appl. Phys.* **1999**, 85 (5), 2595.

(13) Veith, M. *Mater. Sci. Forum* **2000**, 343–346, 531.

(14) Gleizes, A. N. *Chem. Vap. Deposition* **2000**, 6, 155.

(15) Bochmann, M. *Chem. Vap. Deposition* **1996**, 2 (3), 85.

(16) Senzaki, Y.; Gladfelter, W. L. *Polyhedron* **1994**, 13 (8), 1159.

sired material in the stoichiometry and structure required for the application of interest. There have been a number of reports on the deposition of II/VI materials from single-molecule sources such as thiophosphinates,<sup>17–19</sup> thiocarbamates,<sup>20–22</sup> and selenocarbamates.<sup>23,24</sup>

In this article we report the growth of *c*-axis oriented ZnO films using the volatile carbamate precursor  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  (**1**).<sup>25</sup>

## Experimental Section

Films were generally deposited on silicon (111) substrates. Substrates were rinsed with acetone and air-dried in preparation for deposition. Deposition experiments were performed in a high-vacuum deposition chamber, base pressure  $\approx 5 \times 10^{-6}$  Torr, and also in low-vacuum systems with base pressures ranging from  $1 \times 10^{-2}$  to  $10^{-1}$  Torr. Film growth was carried out using a constant source temperature of  $\approx 185$ – $195$  °C and substrate temperatures of 350, 400, and 450 °C. The substrate was aligned perpendicular to effusing precursor vapor, separated typically by 3–5 cm. For purposes of comparison, some films were also grown from **1** in the presence of water vapor ( $\approx 10^{-2}$  Torr).

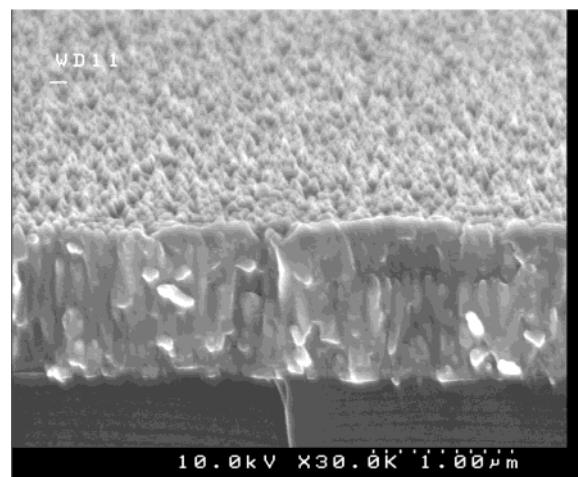
Film chemistry was monitored using X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB 220iXL instrument with a monochromated Al K $\alpha$  X-ray source. XRD scans in the  $\theta$ – $2\theta$  mode were performed using a Siemens D-500 Kristalloflex diffractometer with unmonochromated Cu K $\alpha$  radiation ( $\lambda = 1.54179$  Å). The topography of the films was examined using a Hitachi S-4500 scanning electron microscope (SEM).

For piezoelectric measurements films were grown on a 100-nm layer of chromium (deposited onto Si(100) wafers by dc sputtering) and coated with a 100-nm chromium top electrode. An interferometer setup configured from a Michelson interferometer (see ref 26) was used. X and Y cut quartz was used for calibration and ac voltages of 0.25–5.0 V were applied across the films at frequencies ranging from 1 kHz to 50 MHz.

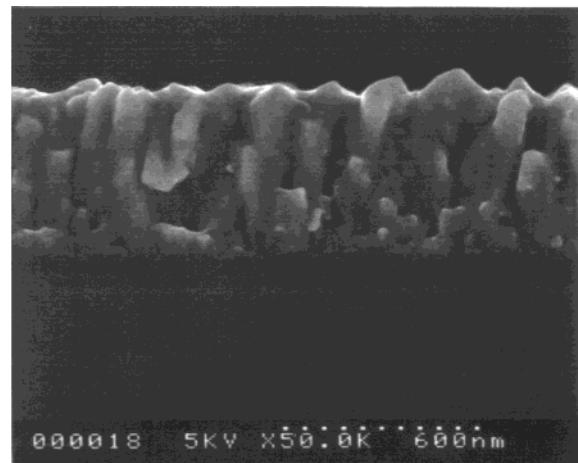
## Results and Discussion

Figure 1 shows two cross-sectional SEM micrographs of a typical film grown at 400 °C using  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  as the sole deposition source. No significant differences were observed in the morphologies of films grown at different substrate temperatures in the range of 350–450 °C or in the different pressure regimes. It was found that growth rates did not vary with substrate temperature. Optimum source temperatures ranged between 185 and 195 °C, producing a growth rate of  $\approx 300$  nm/h. Although growth rates increased with increasing source temperature, it was found that substantial decomposition of the precursor also occurs. Keeping the source temperature below 195 °C allowed repeated cycling of the source material.

- (17) Takahashi, Y.; Yuki, R.; Sugiura, M.; Motojima, S.; Sugiyama, K. *J. Cryst. Growth* **1980**, *50*, 491.
- (18) Byrom, C.; Malik, M. A.; O'Brien, P.; White, A. J. P.; Williams, D. J. *Polyhedron* **2000**, *19*, 211.
- (19) Evans, M. A. H.; Williams, J. O. *Thin Solid Films* **1982**, *87*, L1–L2.
- (20) Frigo, D. M.; Khan, O. F. Z.; O'Brien, P. *J. Cryst. Growth* **1989**, *96*, 989.
- (21) Hursthouse, M. B.; Malik, M. A.; Motevali, M.; O'Brien, P. *Organometallics* **1991**, *10*, 730.
- (22) Malik, M. A.; Saeed, T.; O'Brien, P. *Polyhedron* **1993**, *12* (12), 1533.
- (23) Malik, M. A.; O'Brien, P. *Chem. Mater.* **1991**, *3*, 999.
- (24) Hursthouse, M. B.; Malik, M. A.; O'Brien, P. *J. Mater. Chem.* **1992**, *2* (9), 949.
- (25) Belforte, A.; Calderazzo, F.; Englert U.; Stahle, J. *Inorg. Chem.* **1991**, *30*, 3778–3781.
- (26) Muensand, S.; Guy, I. L. *Appl. Phys. Lett.* **1998**, *72*, 1896.



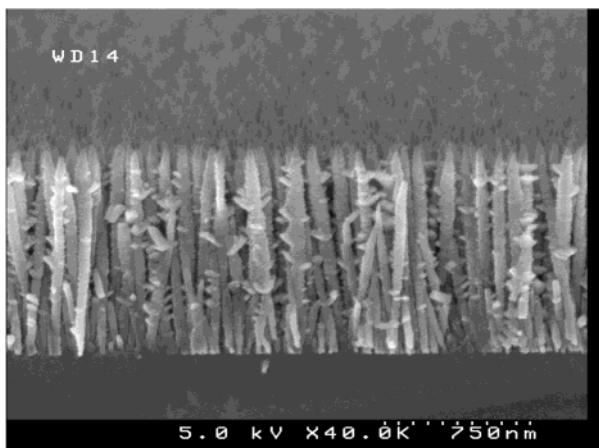
**Figure 1.** SEM micrograph a typical film grown using  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  at a substrate temperature of 450 °C, while the vapor source temperature was kept at 185–195 °C.



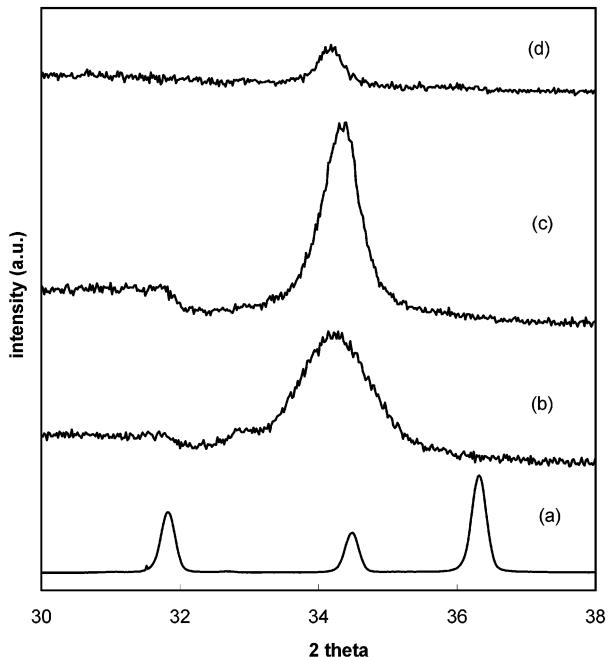
**Figure 2.** SEM micrograph of a typical film grown using RF sputtering.

For comparison, Figure 2 shows a typical SEM micrograph of a ZnO film grown by RF sputtering.<sup>27</sup> Notably, the SEM micrographs of the films grown using the carbamate  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  (Figure 1) are very similar to those grown using RF sputtering. Both are of relatively high density with a grainy, columnar morphology. These films contrast with those grown using an isostructural ZnO precursor, basic zinc acetate ( $\text{Zn}_4\text{O}(\text{CO}_2\text{CH}_3)_6$ ) (**2**). Both basic zinc acetate<sup>28</sup> and  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$ <sup>25</sup> feature a tetrahedral arrangement of four zinc atoms around the central oxygen; however, it has been found that  $\text{Zn}_4\text{O}(\text{CO}_2\text{CH}_3)_6$  does not independently deposit crystalline ZnO. For crystalline ZnO film growth using basic zinc acetate, the deposition must be carried out in the presence of water vapor (essential for effective film deposition<sup>29</sup>). Moreover, basic zinc acetate produces ZnO films of much lower density than the carbamate does (see SEM, Figure 3). This result emphasizes that both structure and chemistry of precursors determine final film properties.

- (27) Puchert, M. Ph.D. Thesis, UNSW, Sydney, Australia, 1996.
- (28) Hiltunen, L.; Leskela, M.; Makela, M.; Niinisto, L. *Acta Chem. Scand.* **1987**, *A41*, 548.
- (29) Marr, G. L.; Timbrell, P. Y.; Lamb, R. N. *Chem. Mater.* **1995**, *7* (10), 1890.



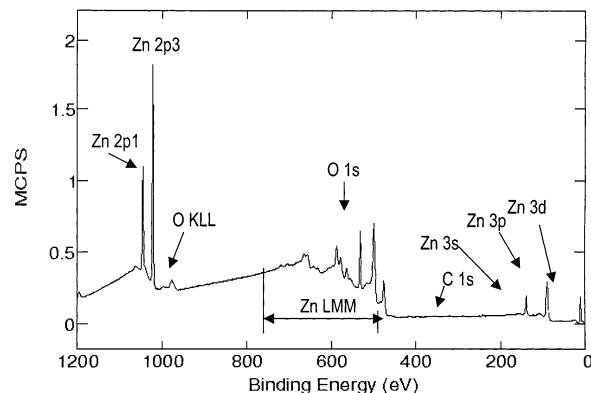
**Figure 3.** A typical film grown using  $Zn_4O(CO_2CH_3)_6$ .



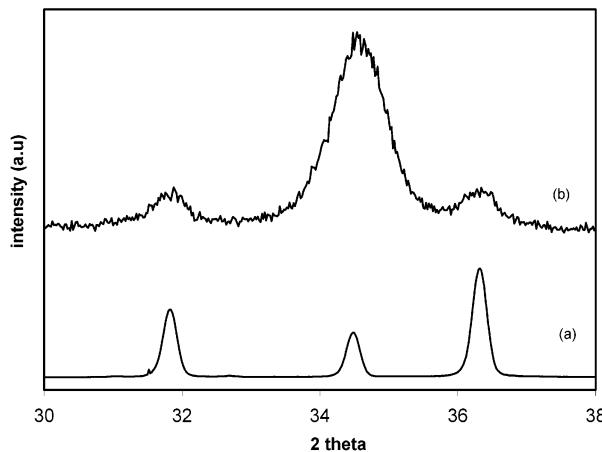
**Figure 4.** XRD spectra for films grown at substrate temperatures of 350 °C (Figure 4b), 400 °C (Figure 4c), and 450 °C (Figure 4d), while the vapor source temperature was kept at 185–195 °C. For comparison an XRD scan for ZnO powder is also shown (Figure 4a).

The crystallographic properties of the films, such as size of the crystallites and orientation, are determined by kinetic and thermodynamic factors during deposition. Under equilibrium conditions ZnO tends to grow *c*-axis orientated since the (001) plane has the lowest surface free energy.<sup>30</sup> Figure 4 shows the XRD spectra obtained for the films grown at substrate temperatures of 350 °C (Figure 4b), 400 °C (Figure 4c), and 450 °C (Figure 4d), while the vapor source temperature was kept at 185–195 °C. For comparison an XRD scan for ZnO powder is also shown (Figure 4a). In all three scans taken of the films only the (002) reflection is detectable, which indicates that the hexagonal films are *c*-axis orientated. Their crystallite sizes ranged approximately from 8 to 20 nm.

Surprisingly, the carbamate was found to deposit only *c*-axis orientated films in the substrate temperature



**Figure 5.** XPS survey scan for film grown at 450 °C.



**Figure 6.** XRD for film grown using  $Zn_4O(CO_2NEt_2)_6$  in the presence of water vapor.

range investigated. The absence of random orientation, at all three substrate temperatures, indicates that  $Zn_4O(CO_2NEt_2)_6$  (**1**) deposits ZnO without the introduction of additional reagents or stringent control of deposition conditions. Evidently, in the temperature range 350–450 °C, there is sufficient thermal energy available for decomposition of the precursor molecules and nucleation and subsequent growth of the film crystallites.

The results of XPS studies indicated no significant difference in the stoichiometry of films grown in the experimental temperature range we employed. As an example, an XPS survey scan for a film grown at 450 °C substrate temperature is shown in Figure 5. The C 1s core level feature was below the limit of detection. The density and relative purity of the films grown from **1** indicate that, under these conditions, organic fragments are being removed efficiently (it has been observed previously for other precursors that incomplete precursor decomposition results in the formation of randomly oriented or even amorphous films<sup>29</sup>). This in turn implies that the precursor satisfies both kinetic and thermodynamic demands for the deposition of ZnO films using this vapor phase process.

In contrast, the deliberate introduction of  $H_2O$  vapor while growing a film using  $Zn_4O(CO_2NEt_2)_6$  at 400 °C gives a film with random orientation, as indicated by the XRD measurement shown in Figure 6b. (Figure 6a shows the ZnO powder reference for comparison.)

(30) Fujimura, N.; Nishihara, T.; Goto, S.; Xu, J.; Ito, T. *J. Cryst. Growth* **1993**, *130*, 269.

Separate chemical tests, *in vitro*, show that  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  in toluene solution is quite susceptible to hydrolysis by water, to give amorphous  $\text{ZnO}$ . Hence, it is likely that the deposition of  $\text{ZnO}$  from gaseous  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  proceeds through a different mechanism in the presence of water vapor.

Piezoelectric measurements found the films grown using **1** to have excellent piezoelectric properties. The piezoelectric coefficients  $d_{33}$  for films grown at 400 °C were found to be as high as  $10 \pm 2 \text{ pm/V}$ , a value which approaches that expected for single-crystal  $\text{ZnO}$ . These results indicate that the film crystals are not only aligned with respect to their crystallographic axis but also that the polar axes are aligned.

The piezoelectric properties of the  $\text{ZnO}$  films prepared in our work are comparable to those of sputtered films. With  $\text{ZnO}$  powder as a calibration reference,<sup>31</sup> it can be calculated<sup>32</sup> from the shift of the (002) XRD reflections (data displayed in Figure 4) that the biaxial compressive stresses are 1.28, 0.83, and 1.64 GPa, respectively, for the films grown at substrate temperatures of 350, 400, and 400 °C. The biaxial compressive stresses in as-deposited sputtered films typically range from 6 to 11 GPa<sup>33</sup> and postdeposition annealing is generally required to reduce film stress. Films grown

using  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  do not require postdeposition annealing.

The self-sufficiency of  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  as a precursor simplifies film fabrication. Deposition of a useful film requires only the sublimation of the precursor onto a hot substrate. Since no additional reagents are required, no strict control of vapor pressure is necessary; consequently, a very rudimentary deposition apparatus may be used. In addition, although the precursor is somewhat moisture-sensitive, it is kinetically stable, so there are no problems with pre-reactions of the precursor with residual amounts of reactive gases (e.g.,  $\text{H}_2\text{O}$ ) in the deposition apparatus. As a result, high-vacuum systems are not necessary and the use of vacuum simply facilitates sublimation of the precursor. The reaction of  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  to form  $\text{ZnO}$  is only significantly activated by the temperature (i.e., at least 350 °C). While both  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  and  $\text{Zn}_4\text{O}(\text{CO}_2\text{CH}_3)_6$  can be easily and safely handled in air and pose little risk to the user, the deposition of  $\text{ZnO}$  using  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  does not require the controlled introduction of water vapor. Therefore, deposition of quality  $\text{ZnO}$  films using  $\text{Zn}_4\text{O}(\text{CO}_2\text{NEt}_2)_6$  is a simple one-step procedure, without the complexities/difficulties and safety issues associated with alternative procedures.<sup>6–12,29</sup>

CM0204324

(31) Hellwege, K. H.; Hellwege, A. M. *Numerical Data and Functional Relationships in Science and Technology*; Springer-Verlag: Berlin, 1964; group III, Vol. 2, p 58.

(32) Hoffman, R. W. *Physics of Non Metallic Thin Films*; Plenum: New York, 1976; p 273.

(33) Puchert, M. K.; Timbrell, P. Y.; Lamb, R. N. *J. Vac. Sci. Technol. A* **1996**, 14, 2220.