

Factors Influencing the Chemical Vapor Deposition of Oriented ZnO Films Using Zinc Acetate

G. L. Mar, P. Y. Timbrell, and R. N. Lamb*

Surface Science and Technology, School of Chemistry, University of New South Wales, Sydney NSW 2052, Australia

Received March 30, 1995. Revised Manuscript Received July 12, 1995*

c-axis-oriented zinc oxide (ZnO) films have been grown on silicon (100) substrates by low-pressure chemical vapor deposition using zinc acetate as the metal–organic source. The chemical transformations of the zinc acetate during sublimation and the subsequent pyrolysis on the substrate were examined. The influence of substrate temperature and water ambient during deposition on the resultant properties of the ZnO films were systematically investigated. The ZnO films were analyzed by X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, UV–visible absorption, X-ray diffraction and scanning electron microscopy. The deposition rate, level of carbon contamination, *c*-axis orientation, and bandgap of the films were found to be strongly dependent on both the substrate temperature and water ambient pressure. The optimal deposition conditions were obtained using a water ambient pressure of 3×10^{-3} mbar and substrate temperature of 400 °C which produced highly *c*-axis-oriented ZnO films with minimal (<2.0%) residual carbon contamination.

Introduction

Many chemical vapor deposition (CVD) methods based on the use of separate group II and VI sources have been developed to deposit zinc oxide semiconductor films. A major problem associated with a large number of these methods is the precise control of the reaction between highly reactive zinc sources such as dimethyl- and diethylzinc with oxidants such as oxygen and water. Single-source metal–organic precursors offer an elegant alternative method for the CVD of ZnO films. The basis of this approach is the facile pyrolysis of a single zinc- and oxygen-containing metal–organic compound to form ZnO films at a suitable substrate temperature. Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$, (ZA)) was first suggested as a potential single-source precursor by Tammenmaa et al.¹ for ZnO film growth by atomic layer epitaxy.

In this study we examined the species produced by the sublimation of anhydrous zinc acetate in high vacuum and its subsequent deposition and pyrolysis on heated silicon substrates. An important step was to identify the actual precursor species involved in the film growth process. This would allow for the introduction of an oxidizing or reducing gas as a means of facilitating the thermal decomposition. In this respect we investigated the role of a water vapor ambient during deposition as well as the effect of substrate temperature on the resultant ZnO film properties. The preferred axis of orientation, residual carbon contamination, and bandgap were used to determine the optimal deposition conditions for the growth of high-quality films. The amount of residual carbon contamination in the film that results from the pyrolysis of the metal–organic precursor was quantified in order to ensure that the films are suitable for device applications.

When anhydrous ZA is sublimed in vacuum, it is believed to form tetrameric basic zinc acetate ($\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$) by gas-phase oligomerization.² The model of the basic zinc acetate (BZA) molecule is shown in Figure 1 and the tetrahedral Zn_4O core structure illustrates the features that make it a favorable single-source precursor for ZnO film growth. The crystal structure and intermolecular distances of the Zn–O core of the BZA molecule³ closely resemble that of crystalline ZnO.⁴ The BZA core structure has also been found to be a well-tailored molecular model for crystalline ZnO.⁵ Khan et al.⁶ and Gyani et al.⁷ suggested that BZA is the important species in the CVD of ZnO using ZA as the source material. Other researchers considered only ZA as the important species in the reaction scheme, and no emphasis was given to the role of BZA in the film deposition process.^{1,8–10}

Experimental Section

The film depositions were performed in a high-vacuum (base pressure $\sim 5 \times 10^{-9}$ mbar) CVD system (Figure 2) specifically developed for chemical vapor deposition using solid-phase precursors. The substrates are mounted on a resistively heated sample stage and positioned at 50° tilt to horizontal (i.e., direction of source flux). The zinc acetate dihydrate (99.5%, BDH Ltd) was contained in a resistively heated, dual zone, Knudsen cell. Both the sample stage and Knudsen cell

(2) Koyama, H.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1954**, *24* (2), 112.

(3) Hiltunen, L.; Leskela, M.; Makela, M.; Niinisto, L. *Acta. Chem. Scand. A* **1987**, *41*, 548.

(4) Abrahams, S. C.; Bernstein, J. L. *Acta. Crystallogr.* **1969**, *B25*, 1233.

(5) Bertonecello, R.; Bettinelli, M.; Casarin, M.; Gulino, A.; Tondello, E.; Vittadini, A. *Inorg. Chem.* **1992**, *31*, 1558.

(6) Khan, O. F. Z.; O'Brien, P. *Thin Solid Films* **1989**, *173*, 95.

(7) Gyani, A. K.; Khan, O. F. Z.; O'Brien, P.; Urch, D. S. *Thin Solid Films* **1989**, *182*, L1.

(8) Kobayashi, K.; Matsubara, T.; Matsushima, S.; Okada, G. *Thin Solid Films* **1993**, *235*, 20.

(9) Kim, J. S.; Marzouk, H. A.; Reucroft, P. J.; Hamrin, C. E. *Thin Solid Films* **1992**, *217*, 133.

(10) Maruyama, T.; Shionoya, J. *J. Mater. Sci. Lett.* **1992**, *11*, 170.

* Abstract published in *Advance ACS Abstracts*, August 15, 1995.

(1) Tammenmaa, M.; Koskinen, T.; Hiltunen, L.; Niinisto, L.; Leskela, M. *Thin Solid Films* **1985**, *24*, 125.

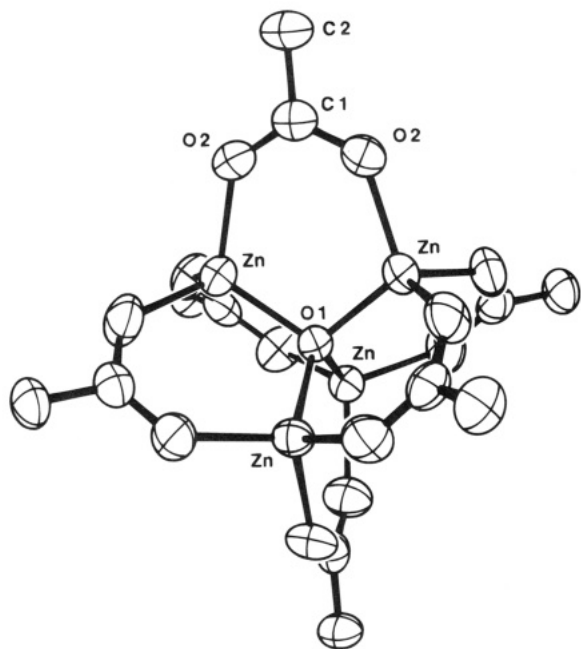


Figure 1. Model of the basic zinc acetate molecule ($\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$), from Hiltunen et al.³

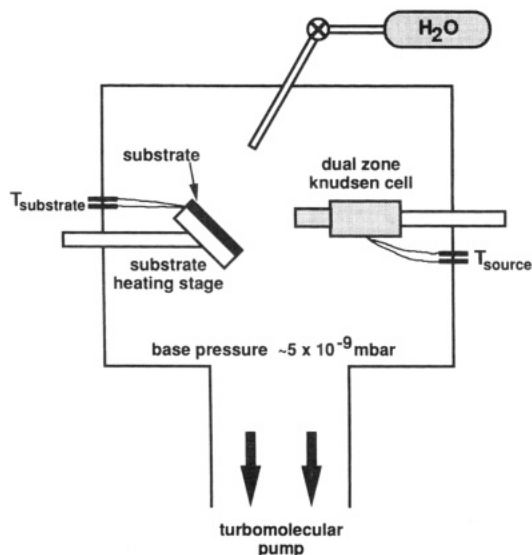


Figure 2. Schematic diagram of the chemical vapor deposition setup showing the dual zone Knudsen cell doser, substrate heating stage, and gas inlet.

temperatures were monitored using Al/Cr thermocouple wires. Distilled water was stored in a glass vial connected to a leak valve attached to the reaction chamber. The CVD system was pumped by a rotary-backed turbomolecular pump.

Zinc Acetate Sublimation in High Vacuum. To investigate the effect of the ZA sublimation temperature and the nature of the species produced in high vacuum, films were deposited onto room-temperature (25 °C) spectroscopic-grade potassium bromide (KBr) and silicon (100) substrates using Knudsen cell temperatures of 180, 200, 230 and 250 °C. The ZA dihydrate was initially dried at 110 °C for 2 h to remove the water of crystallization. The anhydrous ZA was then heated to the required temperature using a slow heating rate of <5 °C/min and held constant at the desired temperature for 20 to 30 minutes for each deposition. It is believed that a slow heating rate is necessary for the complete sublimation of ZA without decomposition.^{3,11} Films were also deposited onto room temperature substrates in the presence of a water

ambient to investigate the effect of H_2O on the oligomerisation reactions believed to occur during sublimation. X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared spectroscopy (FTIR) were used to examine the nature of the film. The spectra of the ZA dihydrate source compound and BZA synthesized by vacuum distillation of ZA were also recorded for comparison.

A consideration in the pyrolysis of the metal-organic to ZnO is the incorporation of involatile carbon groups into the films. To investigate the possible role of H_2O in facilitating the decomposition of the BZA and minimizing the residual carbon contamination, depositions were carried out in the absence of water ($\sim 1 \times 10^{-8}$ mbar), at 6×10^{-4} and 3×10^{-3} mbar H_2O ambient pressure for 2 h on 400 °C Si(100) substrates. The influence of substrate temperature on the film growth was also examined by performing the depositions at a constant water ambient and at 350, 400, 450, and 500 °C substrate temperature for 2 h.

ZnO Film Properties. The zinc and oxygen stoichiometry and residual carbon contaminant levels (in atomic percent) of the deposited films were determined by XPS. The XPS data were acquired using a Kratos XSAM 800 spectrometer with Al K α (1486.6 eV) source and 40 eV pass energy, which gives an overall energy resolution of 1.1 eV at $E_B = 84$ eV (Au 4f_{7/2} photoelectron). A ZnO single crystal was used as a reference to provide a standardized curve fitting and Zn/O normalization procedure for the XPS data analysis. The ZnO crystal was etched for 5 min using a 4 keV ion beam and $\sim 6 \mu\text{A}$ sample current to remove surface contamination before analysis. The O 1s and Zn 3s photoelectron peaks were found to best fit a 50/50 Gaussian/Lorentzian line shape and a Shirley background subtraction. The binding energies (E_B) of the Zn 3s and O 1s photoelectrons in the ZnO crystal spectrum were determined to be 140.2 and 531.1 eV, respectively. The O 1s region also showed the presence of a surface hydroxide¹² species at $E_B = 533.0$ eV and was measured to be $\sim 10\%$ of the oxide peak intensity. The sum of both peaks was used to calculate the Zn/O ratios in all cases. The ZnO films were also argon ion etched with a 4 keV beam and $\sim 6 \mu\text{A}$ sample current for 5 min prior to analysis to remove any postdeposition surface contamination. The XPS spectra presented are not corrected for sample charging.

The FTIR analysis was performed in transmission mode on a Bomem MB100 spectrometer with a MCT detector scanning at 4 cm^{-1} resolution from 400 to 4000 cm^{-1} .

The crystallinity and *c*-axis orientation in the ZnO films were examined by X-ray diffraction (XRD) using a Siemens D500 diffractometer with a unmonochromated Cu K α source. A measure of the *c*-axis orientation in the films was determined by the (002)/(101) peak intensity ratio which was calculated to be 0.37 for a randomly oriented ZnO powder reference. The average diameter (D) of the oriented ZnO crystallites was estimated using the Scherrer formula:¹³

$$D = 0.94\lambda/B \cos \theta$$

where λ is the Cu K α wavelength (1.5418 Å), B is the fwhm of the (002) diffraction peak in radians, and θ is the diffraction angle of the (002) peak in degrees.

The film morphology and thickness were examined by field emission scanning electron microscopy (FE-SEM) using a Hitachi S-900 Microscope and beam energy of 5 keV. The samples were coated with 3 nm of chromium to minimize surface charging and images were taken at sample tilt angles of 0 and 40°.

The optical properties of the films were characterised by its absorption in the UV-visible range using a Cary 5 spectrometer. In this case the films were grown on silicon substrates, and the analysis was performed in reflectance mode with a Teflon-coated diffuse reflectance sphere. The reflectance spectrum of the ZnO powder reference was also acquired. The optical bandgap of the ZnO powder and films were determined

(12) Au, C. T.; Roberts, M. W.; Zhu, A. R. *Surf. Sci.* **1982**, *115*, L117.

(13) Cullity, B. D. *Elements of X-ray Diffraction*, 2nd ed.; Addison-Wesley: Reading, MA; 1978, p 102.

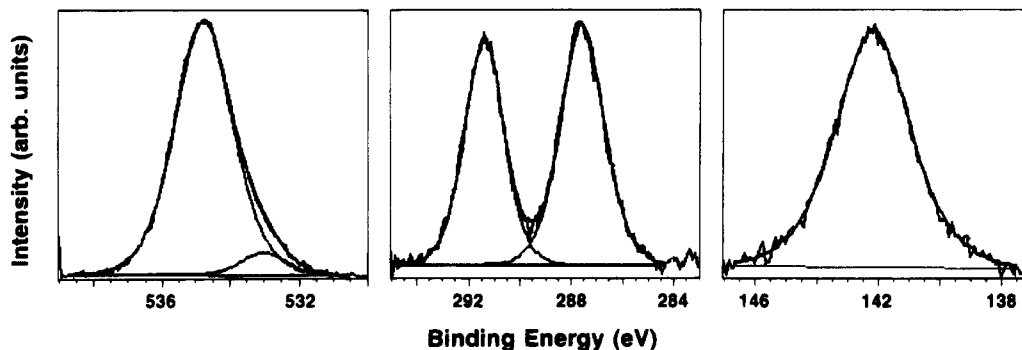


Figure 3. Deconvoluted XPS spectra of the Zn 2p_{3/2}, O 1s, and C 1s regions of a basic zinc acetate film deposited on room temperature Si(100) substrate by the vacuum sublimation of anhydrous zinc acetate.

by applying the following relationship¹⁴ in the high absorbance region:

$$\alpha(\omega) = B(h\nu - E_{\text{opt}})^n/h\nu$$

where $\alpha(\omega)$ = absorption coefficient, B = constant, $h\nu$ = photon energy, E_{opt} = optical bandgap, and n has the value 1, 2, 3, or $1/2$. $n = 1$ was found to be most suited for ZnO films, in agreement with previous work.¹⁵ The linear region of the absorption edge in the plot of $\alpha h\nu$ vs $h\nu$ was extrapolated to the photon energy to estimate the bandgap. The bandgap of the ZnO powder reference was determined to be 3.19 eV.

Results

Thermal Properties of the Zinc Acetate. The XPS spectra of the Zn3s, O 1s, and C 1s photoelectron regions of a film deposited by the sublimation of anhydrous zinc acetate (ZA) on a room temperature Si(100) substrate is shown in Figure 3. The charge corrected binding energy positions ($E_B = 532.7$ and 531.0 eV) and separation (1.7 eV) of the O 1s peaks are in good agreement with those reported by Bertonecello et al.⁵ The smaller peak at lower binding energy may be attributed to the central oxygen in the μ_4 -oxo core structure of basic zinc acetate (BZA). The C 1s region shows two peaks attributed to the "methyl" ($E_B = 285.6$ eV) and "carboxyl" ($E_B = 289.3$ eV) carbons present in BZA or ZA. The XPS data suggest that BZA is present in the film deposited on the room-temperature Si substrate but does not provide unambiguous evidence of the presence of BZA. There is no clear distinction between the spectrum of BZA in either the crystal form or as-deposited film from that of ZA. The position of the O 1s peak at lower binding energy (531.0 eV), though consistent with the results predicted by Bertonecello et al.⁵ could also be related to the presence of adsorbed water on the sample or water of crystallization in zinc acetate dihydrate crystals.

The FTIR spectra of the ZA dihydrate source compound and vacuum distilled BZA crystals (KBr disks) and a film of BZA deposited on a room temperature KBr disk by ZA sublimation are shown in Figure 4. The infrared data are unambiguous concerning the actual species that was sublimated and deposited on the substrates. The carboxylate symmetric stretch ($\nu_{\text{sym}} \text{COO}^-$) and asymmetric stretch ($\nu_{\text{asym}} \text{COO}^-$) modes of the ZA dihydrate are observed at 1448 and 1558 cm⁻¹, respec-

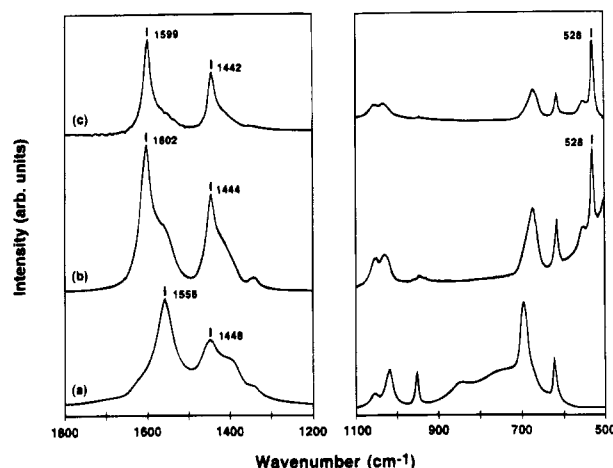


Figure 4. FTIR spectra of (a) zinc acetate dihydrate crystals, (b) vacuum distilled basic zinc acetate crystals, and (c) film of basic zinc acetate deposited on room-temperature KBr disk by the vacuum sublimation of anhydrous zinc acetate.

tively, and are consistent with those observed from chelating acetate ligands.¹⁶ For the BZA crystals the main $\nu_{\text{sym}} \text{COO}^-$ and $\nu_{\text{asym}} \text{COO}^-$ modes were observed at higher frequencies of 1444 and 1602 cm⁻¹ and correspond to those of bridging acetate ligands. The shoulders seen at lower frequencies in both bands indicate that some chelating acetates may be present. The film deposited by ZA sublimation under the CVD conditions shows only well-resolved bridging acetate stretching bands with no evidence of the chelating acetates. The most distinguishing feature, however, is the presence of the Zn₄O core asymmetric stretch ($\nu_{\text{asym}} \text{Zn}_4\text{O}$) appearing at 529 cm⁻¹ for the BZA crystal sample and deposited film. This vibrational mode is associated with the Zn₄O framework of the BZA molecule and is not present in ZA. The FTIR data are in good agreement to those previously obtained^{17,18} and confirm that BZA is formed when ZA is sublimated in high vacuum. The presence of water vapor during sublimation of ZA had no observable effect on the formation of BZA, and spectra similar to that shown in Figure 3c were obtained. The sublimation of ZA occurs at temperatures as low as 180 °C up to the melting point of 252 °C. The effect of increasing the source temperature was to

(16) Johnson, M. K.; Powell, D. B.; Cannon, R. D. *Spectrochim. Acta* **1981**, *37A*, 899.

(17) Berkesi, O.; Dreveni, I.; Andor, J. A.; Goggin, P. L. *Inorg. Chim. Acta* **1991**, *181*, 285.

(18) Johnson, M. K.; Powell, D. B.; Cannon, R. D. *Spectrochim. Acta* **1982**, *38A*, 125.

(14) Abeles, F. *Optical Properties of Solids*; North-Holland: Amsterdam, 1972; p 132.

(15) Ogawa, M. F.; Natsume, Y.; Hirayama, T.; Sakata, H. *J. Mater. Sci. Lett.* **1990**, *9*, 1354.

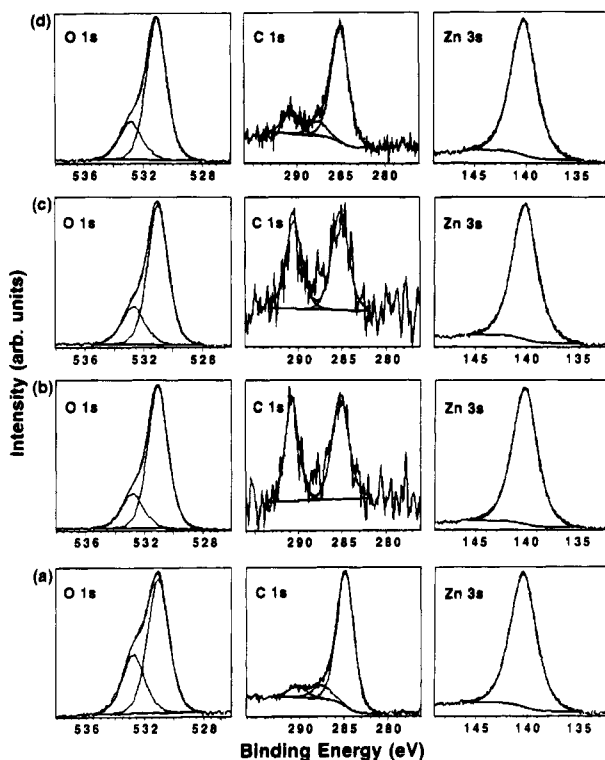


Figure 5. Deconvoluted XPS spectra of the Zn $2p_{3/2}$, O 1s, and C 1s regions of ZnO films deposited on 400 °C Si(100) substrates in (a) no H_2O , (b) 6×10^{-4} , (c) 3×10^{-3} mbar H_2O ambient, and (d) on 500 °C Si(100) substrate in 3×10^{-3} mbar H_2O ambient.

increase the rate of sublimation of the ZA source. The sublimation temperature subsequently used for film growth was ~ 240 °C and gave a stable and reproducible source dosing pressure of $\sim 4 \times 10^{-5}$ mbar.

Influence of H_2O on Film Growth. The results of the film depositions carried out in various ambient pressures of H_2O and at a constant substrate temperature of 400 °C indicate that H_2O has a great influence on the level of carbon contamination and the physical properties (e.g., c -axis orientation, crystallite diameter, and bandgap) of the ZnO films. The XPS spectra of the O 1s, C 1s, and Zn 3s regions of these films are shown in Figure 5 and indicate that ZnO films were formed. The Zn 3s peaks in all the films are observed at $E_B \sim 140$ eV. The oxide peak is observed at $E_B = 530$ eV and the peak at higher E_B (533 eV) is attributed to surface hydroxide species.

The film deposited in the absence of H_2O (Figure 5a) was found to have a high level (>10 at. %) of residual carbon contamination. The C 1s region exhibits a large peak at $E_B = 284.8$ eV, which is consistent with the presence of involatile hydrocarbon groups resulting from the pyrolysis of the BZA precursor. The broad shoulder observed at higher E_B suggests other possible oxygen-bonded species. The Zn/O ratio for this film was calculated to be 0.87.

A partial pressure of H_2O (6×10^{-4} mbar) during deposition was sufficient to drastically reduce the concentration of the carbon detected and significantly alter the C 1s line-shape as shown in Figure 5b. Two low-intensity peaks are observed in the C 1s region which represents ~ 2.0 at. % carbon in the film. At a higher H_2O ambient of 3×10^{-3} mbar (5c) the carbon level is reduced to below 2.0 at. %. With increasing

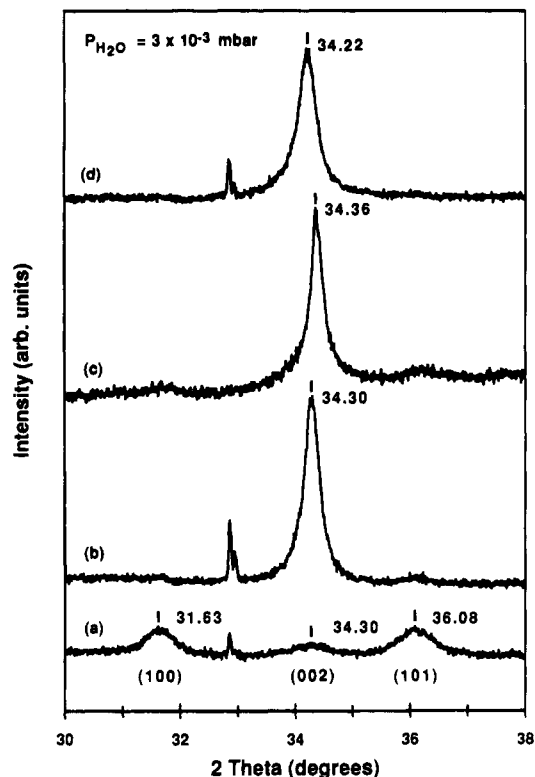


Figure 6. XRD θ - 2θ scans of (a) ZnO powder reference sample and ZnO films grown on 400 °C Si(100) substrates in (b) no H_2O , (c) 6×10^{-4} and (d) 3×10^{-3} mbar H_2O ambient.

H_2O , the XPS data indicate that fewer involatile hydrocarbon groups were being incorporated in the film, and the narrow C 1s peak widths show that there are fewer carbon species present. The spectra of a film deposited in 3×10^{-3} mbar H_2O ambient but at 500 °C substrate temperature are also shown in Figure 5d. The C 1s region scan shows an increase in the level of hydrocarbon species to ~ 6.0 at. %, which clearly demonstrates that substrate temperature is also an important deposition parameter and will be discussed in greater detail later. Though the depositions were carried out in various pressures of H_2O vapor, all the films were found to contain a similar Zn/O ratio of ~ 0.88 (excess oxygen) which suggests that the amount of oxygen in the films was not dependent on the amount of H_2O present but rather on the substrate temperature.

The XRD θ - 2θ scans of a ZnO powder reference and films grown in the various ambient pressures of H_2O are presented in Figure 6 with the positions of the (100), (002), and (101) peaks indicated. The peak present at 33° is attributed to the underlying Si(100) substrate, and its intensity is critically dependent on the exact alignment of the silicon substrate in the XRD instrument. Corresponding SEM images of these films are shown in Figure 7. In the absence of a H_2O ambient during deposition, the growth rate was low (~ 50 nm/h), and the resultant ZnO films showed no signs of crystallinity (Figure 6b) and scanning electron microscopy reveal a 90 nm thick film with no defined structure (Figure 7a).

Preferred c -axis orientation in the crystal structure of the films, evident by the increase in the (002) peak intensity with respect to the other peaks (i.e. (100) and (101)), was observed to increase with H_2O ambient pressure. ZnO films were deposited at a higher rate

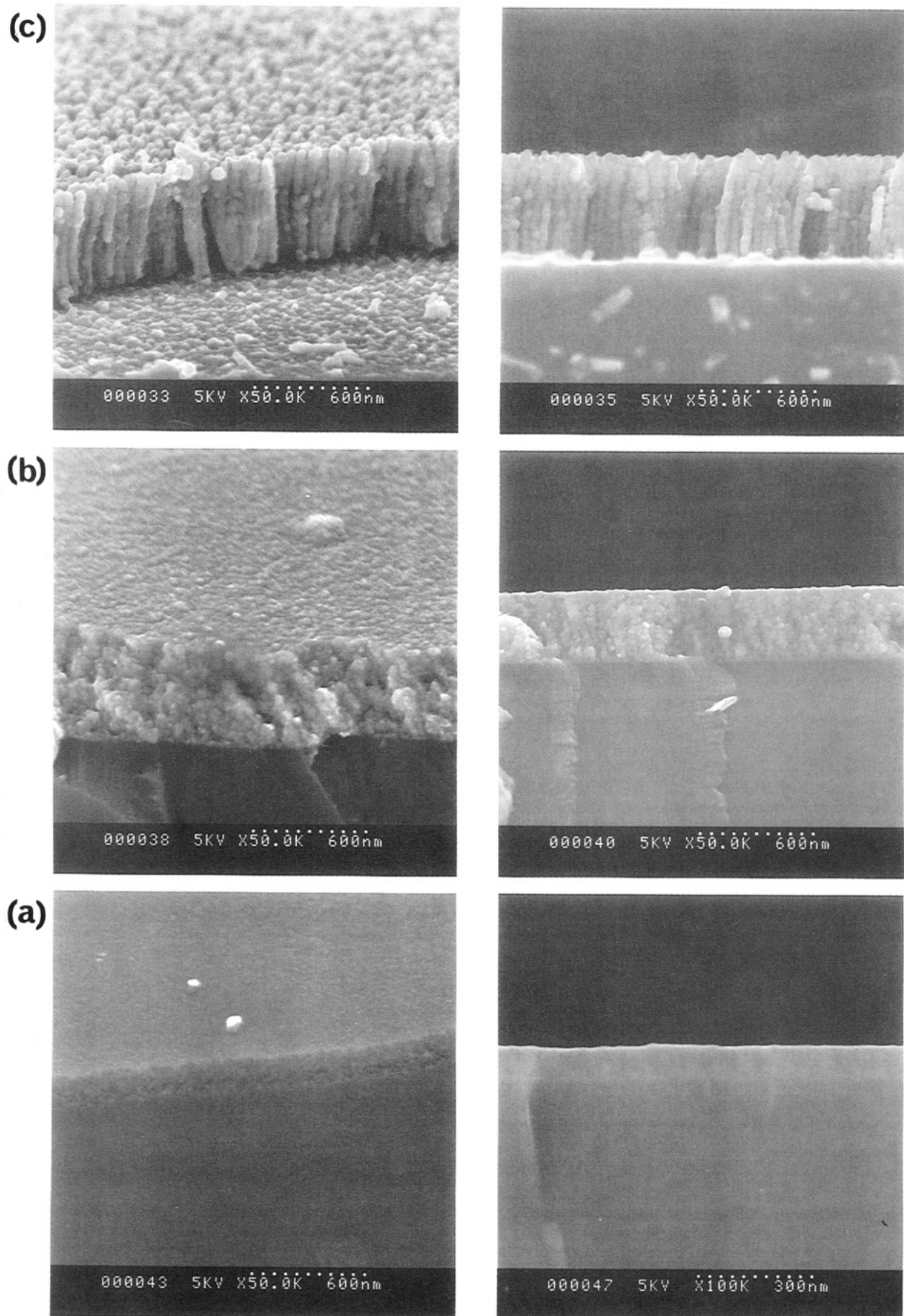


Figure 7. SEM micrographs showing an edge and perspective (40° to film surface) view of the cleave edges of the ZnO films grown on 400°C Si(100) substrates in (a) no H_2O , (b) 6×10^{-4} and (c) 3×10^{-3} mbar H_2O ambient.

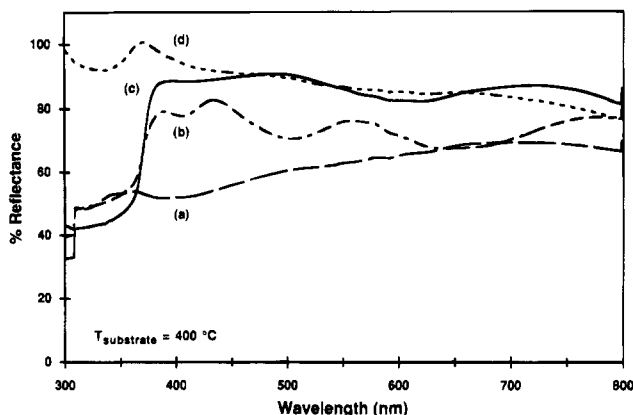


Figure 8. UV-vis diffuse reflectance spectra of ZnO films grown on 400 °C Si(100) substrates in (a) no H₂O, (b) 6×10^{-4} , and (c) 3×10^{-3} mbar H₂O ambient. The reflectance spectrum of a clean Si(100) substrate is also shown (d).

(~ 180 nm/h) with a H₂O ambient of 6×10^{-4} mbar and were found to be polycrystalline but with some preferred orientation. The (100), (002), and (101) peaks are present in the θ - 2θ scan (Figure 6c), and the measured (101)/(002) peak ratio was 0.82, compared to 0.37 for the ZnO powder. This indicates that there was preferred *c*-axis growth in the film structure. The SEM micrographs (Figure 7b) show a 360 nm film of granular structure that exhibits signs of columnar growth. The average diameter (*D*) of the oriented crystallites in the film was calculated to be 16 nm. With a higher H₂O vapour pressure of 3×10^{-3} mbar present during the deposition, the growth rate was seen to increase further (~ 220 nm/h; Figure 6(d) and only the (002) peak was observed, indicating a highly *c*-axis-oriented crystal structure. The diameter of the ZnO crystallites in the film was also found to increase in size to 34 nm. The SEM micrographs (Figure 7c) clearly show a 550 nm film with the columnar structure characteristic of *c*-axis oriented ZnO.

The UV-visible reflectance spectra of ZnO films grown on 400 °C Si(100) substrates as a function of H₂O ambient pressure and a clean Si(100) substrate are shown in Figure 8. There was no evidence of a bandgap for the film grown in the absence of H₂O. This film also reduces the reflectivity of the Si. In contrast the film deposited in 6×10^{-4} mbar H₂O ambient had a measured bandgap of 3.27 eV with similar results (3.28 eV) for the film deposited at a higher H₂O ambient (3×10^{-3} mbar).

Influence of Substrate Temperature on Film Growth. The substrate temperature also plays a significant role in determining the resultant properties of the ZnO films, apart from providing the necessary energy for the thermal decomposition of the BZA precursor. A minimum temperature of 400 °C was found to be required for the complete decomposition and formation of the ZnO in the absence of H₂O,¹⁹ but a lower substrate temperature of 350 °C was sufficient if the film was deposited in a high H₂O ambient (3×10^{-3} mbar). XPS analyses of the film indicate that with substrate temperatures above 350 °C the thermal decomposition is complete and the C 1s regions are similar to Figure 5c. The residual carbon contaminant

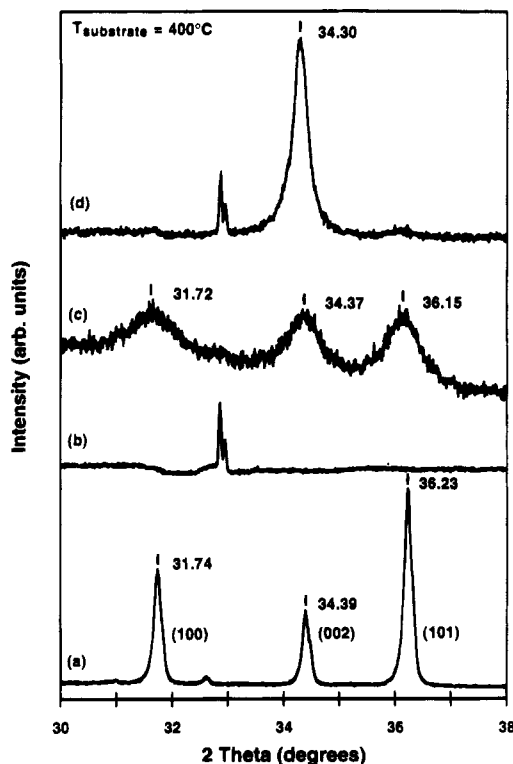


Figure 9. XRD θ - 2θ scans ZnO films grown at 3×10^{-3} mbar H₂O ambient at Si(100) substrate temperatures of (a) 350, (b) 400, (c) 450, and (d) 500 °C.

level in the film deposited at 350 °C was calculated to be < 2.0 atomic %. Figure 9 is the XRD scans of films deposited in a 3×10^{-3} mbar H₂O ambient as a function of substrate temperature. At 350 °C the θ - 2θ scan of the film (Figure 9a) shows the presence of the (100), (002), and (101) peaks. The (002)/(101) peak intensity ratio was calculated to be 0.34, which is comparable to the value obtained for the ZnO powder reference sample, indicating the crystallites in the film are randomly oriented. At substrate temperatures above 350 °C, all the films were found to be highly *c*-axis oriented as evident by the presence of only an intense (002) peak (Figure 9b-d). The average crystallite size for the oriented films was calculated to be 34, 40, and 29 nm for substrate temperatures of 400, 450, and 500 °C, respectively. The SEM images of these highly oriented films are similar to that of Figure 7c showing a well-defined columnar structure.

The measured Zn/O ratios in the films were found to be dependent on the substrate temperature. A substrate temperature of 350 °C resulted in films with a significant excess of oxygen, Zn/O ratio = 0.88. This ratio is observed to increase to 0.90, 0.93, and 0.96 for substrate temperatures of 400, 450, and 500 °C, respectively. The level of carbon contamination detected in the films deposited at 350-450 °C varied between 1.5 and 2.5 at. % but was observed to significantly increase to ~ 6.0 at. % at 500 °C. Similarly, the UV-vis reflectance spectra of the ZnO films (Figure 10) shows small but measurable changes in the bandgap of the corresponding films as a function of substrate temperature. The bandgap of the films grown at 350-450 °C varied between 3.21 and 3.28 eV. There appears to be a relationship between the carbon levels above ~ 2.0 at. % and the measured bandgap, as reduction in the

(19) Mar, G. L.; Timbrell, P. Y.; Lamb, R. N. *Thin Solid Films* **1993**, 223, 341.

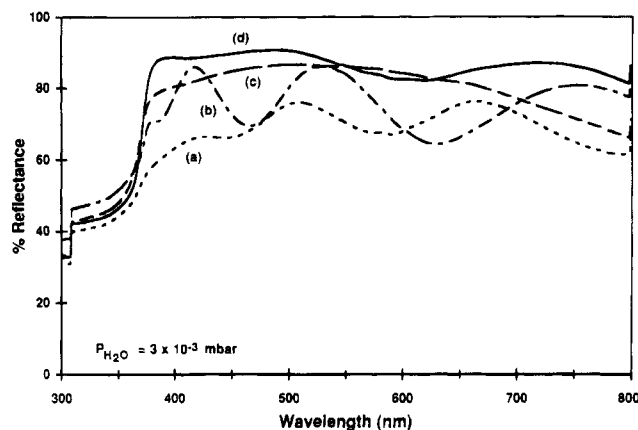
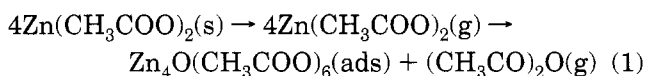


Figure 10. UV-vis diffuse reflectance spectra of ZnO films grown at 3×10^{-3} mbar H_2O ambient at substrate temperatures of (a) 350, (b) 400, (c) 450, and (d) 500 °C.

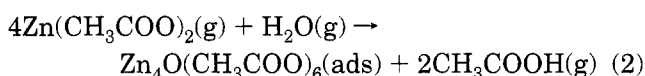
bandgap to 3.13 eV was observed for the film grown at 500 °C.

Discussion

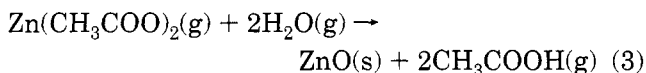
The presence of a gas ambient such as water vapor during deposition has been shown to be an important factor for the formation of highly oriented ZnO thin films by single-source CVD. A possible explanation for this effect is that the water facilitates the thermal decomposition by producing volatile byproducts. To understand how a gas ambient could improve the deposition, it was crucial to identify the actual precursor species involved in the film growth. We have shown that under CVD conditions BZA was produced by the sublimation of ZA as in eq 1¹¹ and adsorbed on the substrates. The



presence of H_2O vapor during the sublimation of ZA had no observable effect on the formation of BZA and could in fact aid its production by



There was no evidence of other reactions such as the hydrolysis of ZA occurring in the vapor phase or on the substrate at room temperature to hinder the formation of BZA, i.e.

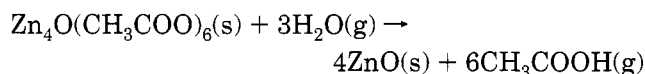


Therefore, the subsequent growth of ZnO films is believed occur by the decomposition of the BZA molecules impinging on the hot substrate. In vacuum and in the absence of water, it has been suggested that the pyrolysis of BZA to ZnO occurs between 350 and 400 °C by a decarboxylation reaction:^{3,11}



This has been shown not to be a favorable method of producing high-quality ZnO films. Films produced in this way did not exhibit any signs of crystallinity and

were found to contain high levels (>10 at. %) of residual carbon contamination. The presence of water vapor drastically reduces the amount of residual involatile carbon groups detected in the ZnO film. The water is believed to facilitate the decomposition reaction by the formation of acetic acid at 350 °C in a hydrolysis reaction analogous to eq 3:



In summary, BZA appears to be the actual precursor species that impinges upon the heated substrate when ZA was sublimed. The role of the water ambient is to provide an energetically more favorable reaction pathway by the formation of acetic acid during the pyrolysis of BZA, which leads to the formation of ZnO with very favorable physical characteristics.

Conclusion

Highly oriented ZnO thin films with minimal residual carbon contamination (<2.0 at. %) have been successfully grown on silicon(100) substrates by single-source CVD. Though zinc acetate was used as the metal-organic source compound, the results indicate that basic zinc acetate was the actual precursor for ZnO film growth. This illustrates the potential for single-source precursors, such as basic zinc acetate, to be used in the fabrication of high-quality ZnO films. The resultant film properties (*c*-axis orientation, crystallite diameter, and bandgap) were found to be strongly dependent on the ambient water vapor pressure and substrate temperature.

The results indicate that in the case of basic zinc acetate, water aids the formation of oriented films by providing (i) an energetically favored decomposition mechanism and (ii) volatile byproducts (acetic acid) which are less likely to interfere with the growth process or be incorporated in the film as contaminants. The pyrolysis of BZA in the presence of water was observed to be complete at of 350 °C compared to a temperature of at least 400 °C in the absence of water. At a substrate temperature of 350 °C there was insufficient energy to produce a preferred *c*-axis orientation in the crystal structure in the film. Beyond 450 °C, the residual carbon concentration in the film increases substantially with substrate temperature, which suggests the higher temperature was causing heterogeneous reactions to occur.

In summary, the optimal conditions for the growth of high quality, *c*-axis-oriented ZnO thin films by CVD using the basic zinc acetate precursor are a high H_2O vapor pressure of 3×10^{-3} mbar and a substrate temperature between 400 and 450 °C.

Acknowledgment. The authors would like to acknowledge the financial support of the Australian Research Council and the Department of Industry, Science and Technology.