MOCVD deposition of Zinc Oxide using diethylzinc and n−butanol

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Introduction

Zinc oxide (ZnO) is a wide band gap (3.3eV) II−VI semiconductor and has recently attracted much attention because of its wide range of applications for various optoelectronic devices. Many groups have reported highly conductive optically transparent ZnO thin films deposited by techniques such as Metalorganic chemical vapour deposition (MOCVD) [1−3], sputtering [4], spray pyrolysis [5], sol−gel [6] and electrodeposition [7]. In the MOCVD of ZnO Dimethylzinc (DMZn) and diethylzinc (DEZn) are the most commonly used zinc precursors with some attention now being focused on single source precursors [8].

In MOCVD these organometallics have traditionally been pyrolysed in the presence of oxygen precursors such as H_2O and O_2. However, severe premature reactions invariably occur and the use of less reactive oxygen sources including CO_2, N_2O [9] and oxygen containing heterocycles [10] have been investigated to combat this problem. The work presented here follows the approach first employed by Oda *et al.* [11] who combated the problem of premature reactions by employing the use of alcohols (R−OH) as oxidizing agents. Oda *et al.* deposited ZnO thin films using DEZn with methanol, ethanol and tertiary butanol and H_2O using a low pressure MOCVD reactor. It was shown that of the three alcohols tertiary butanol provided defect−free and highly oriented films. Hahn *et al.* [12] followed the same approach using tertiary butanol and DMZn at atmospheric pressure to deposit ZnO thin films reporting that no premature reactions were observed and that Cl−doped films had resistivities as low as 7.6×10^{-4} ohms/cm with electron mobilities of 60 $cm^2\ (Vs)^{-1}$. More recently Sallet *et al.* [13] have successfully applied the tertiary butanol approach to atmospheric MOCVD of ZnO onto sapphire (0001) substrates.

In this paper, ZnO thin films were deposited by atmospheric pressure MOCVD onto glass substrates using DEZn and a previously unreported oxygen precursor n−butyl alcohol (C_4H_9OH). The growth of the thin films was monitored using in situ laser interferometry.

Experimental

ZnO thin films have been grown at atmospheric pressure in a horizontal research MOCVD reactor. Diethylzinc and n−butanol were used respectively as zinc and oxygen sources contained in bubblers, the DEZn being kept at 0°C and the n−BuOH at room temperature. The carrier gas was high purity nitrogen dried via a molecular sieve. The substrate was heated by a resistance heater the temperature controlled by a thermocouple located in the graphite susceptor. The partial pressures of DEZn and n−BuOH transported to the reactor were set for both precursors by controlling the flow rates of the carrier gas. The zinc oxide thin film was deposited on Corning 1737 aluminosilicate glass substrates ultra sonically cleaned in deionised water for ten minutes, rinsed twice with methanol and dried with nitrogen. The growth temperature was kept constant at 270°C while the DEZn and n−BuOH partial pressure ratios were varied. The growth rates were calculated by in situ laser interferometry employing a 635nm laser. Surface morphology and grain size were analysed by scanning electron microscopy (SEM).

Results and Discussion

The growth rate of the ZnO thin films was obtained by in−situ interferometry giving information on real time growth rate and surface roughening. Figure 1 is an example of an interferogram for a ZnO growth run.

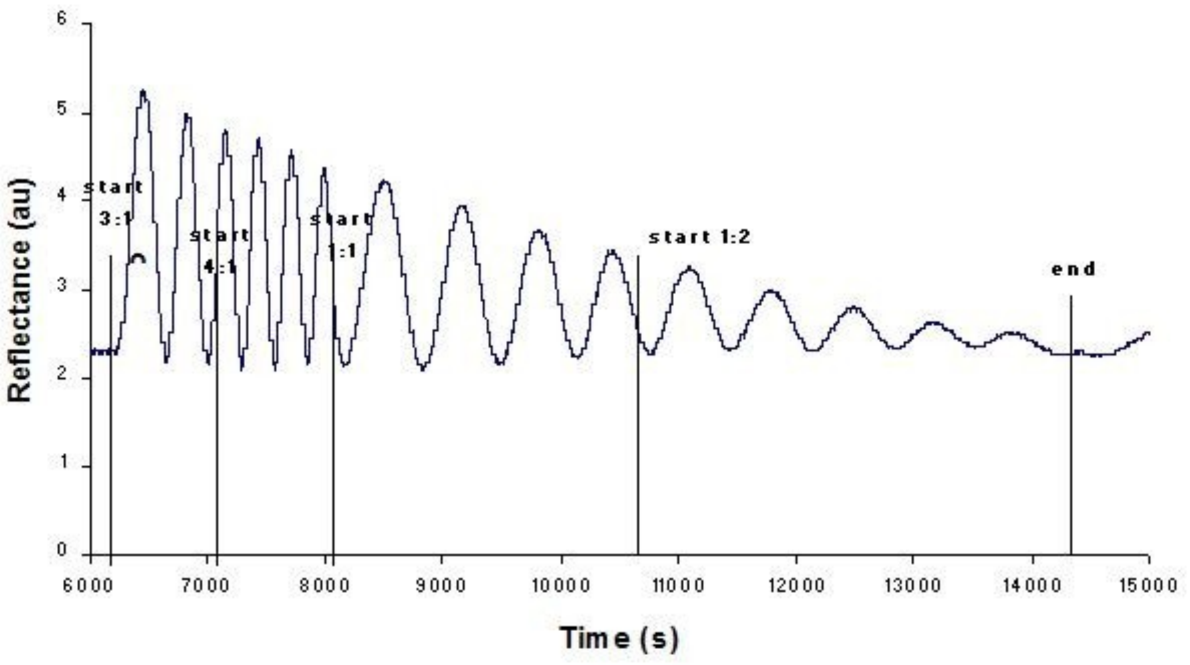

Fig. 1. Interferogram of ZnO growth run at 270°C and various II/VI ratios.

The growth rate measurements were made by measuring the time taken between interference maxima; the thickness for this half wave oscillation was 835 Å. It can be seen in figure 1 that changing the II/VI ratio at constant temperature results in different growth rates. The results of II/VI ratio experiments at 270°C are plotted in figures 2a and 2b.

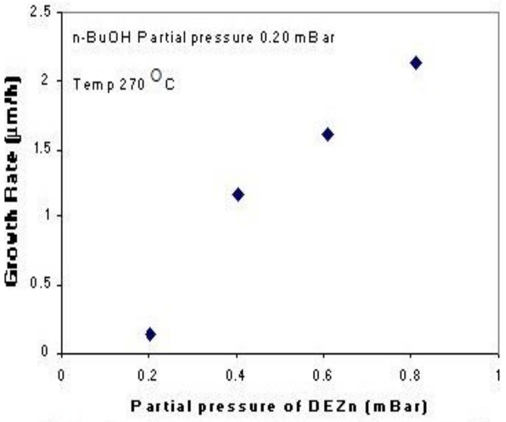

Fig. 2a. Growth rate versus DEZn partial pressure with n-BuOH fixed at 0.2mBar and glass substrate at 270°C.

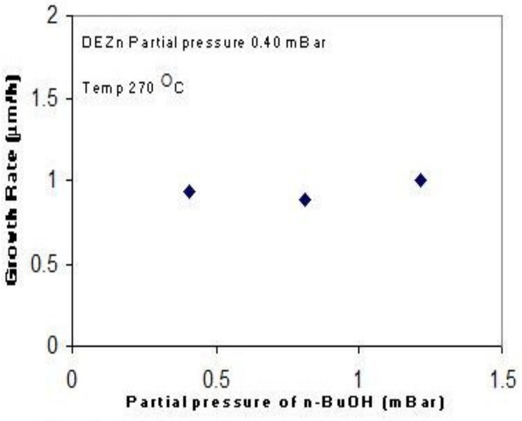

Fig. 2b. Growth rate versus n-BuOH partial pressure with DEZn fixed at 0.4mBar and glass substrate at 270°C.

Figure 2a shows the growth rate of the ZnO films as a function of the partial pressure of DEZn when n−BuOH partial pressure was fixed and substrate temperature was 270°C. The growth rate increased linearly as the partial pressure of the DEZn increased. Figure 2b shows the growth rate as a function of the partial pressure of n−BuOH when DEZn partial pressure was fixed and substrate temperature was 270°C. The growth rate did not significantly change when the partial pressure of n−BuOH was increased from 0.4mBar up to 1.2mBar.

From the growth rates of ZnO for various partial pressures of precursors at this temperature the kinetics appear to be 1^{st} order with respect to DEZn partial pressure and zero order for n−BuOH partial pressure. This data is not consistent with the previously reported literature by Auld *et al.* [8] which states that for similar precursors of DMZn and isopropanol the formation of an alkylzinc alkoxide in the gas phase was shown. This active precursor species proceeds to decompose into ZnO in the hot boundary layer above the substrate, or more likely, during heterogeneous pyrolysis of the alkylzinc alkoxide on the substrate surface. Increasing the II/VI ratio above 1 would not be likely to produce more alkylzinc alkoxide or increase its decomposition into ZnO. Another possible explanation of the results is that in this system the ZnO is formed on the substrate surface by reaction between adsorbed DEZn and adsorbed n−BuOH via an ethyl radical reaction. Kim *et al.* [14] report that isopropanol chemisorbed into isopropoxy and atomic hydrogen on the surface of Si (100) between 550K and 650K, n−BuOH could reasonably be expected to behave in a similar manner on a glass substrate. If the n−BuOH was preferentially adsorbed onto the substrate it would form an effective monolayer on the substrate surface. The rate of reaction would then be determined by how much DEZn was able to adsorb onto the substrate and react with the adsorbed n−BuOH. This mechanism is a surface catalyzed reaction and therefore a change in growth rate could be expected from the initial nucleation where the surface is changing from aluminosilicate glass to ZnO.

The surface morphology was analyzed by scanning electron microscopy (SEM), all ZnO films were sputtered with gold to give clearer images of both the ZnO and Glass substrate.

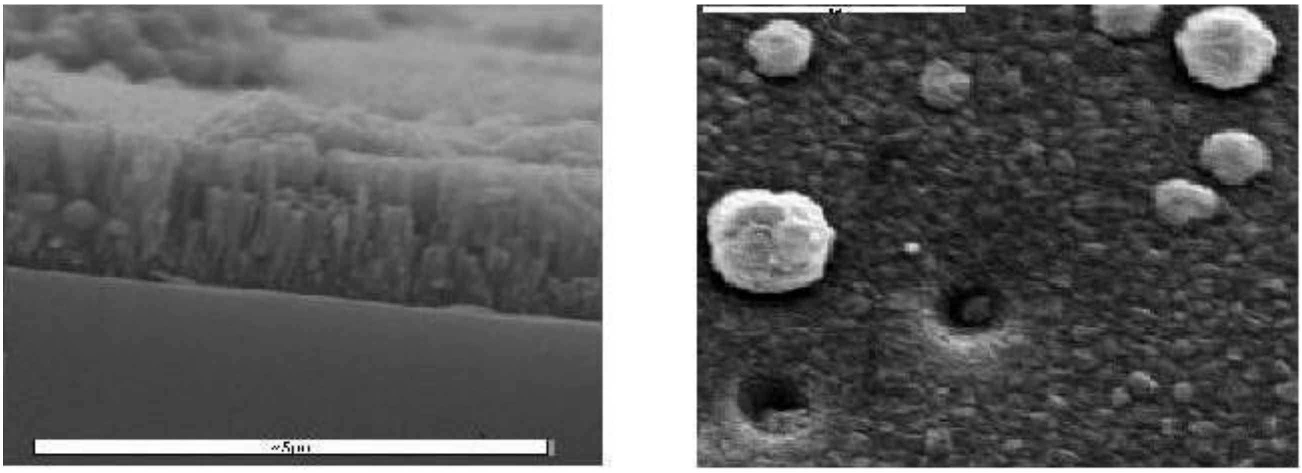

Fig. 3. SEM images of ZnO/glass films grown at 270°C and a II/VI ratio of 4:1; cross section of cleaved film showing columnar grain structure scale bar = 5 µm (left) surface morphology of film scale bar = 5 µm (right)

Figure 3 shows SEM images of a ZnO film (1.5 µm thick) grown with DEZn and n−butanol on a glass substrate at 270 °C. In the cross sectional image on the left an observed columnar structure normal to the substrate may indicate *c*−axis orientation of the film. The right hand image shows the surface of the same ZnO film with an average grain size of 250 nm. The large macro defects and holes distributed across the film may be further evidence of the surface catalyzed growth mechanism whereby morphological defects and impurities on the substrate surface, not removed during preparation, have acted as preferential nucleation sites leading to a faster growth rate than the rest of the film. The holes may be explained in the same manner whereby impurities on the substrate surface have inhibited the growth of the ZnO.

References

[1] S. Oda, H. Tokunaga, N. Kitajama, J. Hanna, I. Shimizu and H. Kokado, Jap. J. App. Phys. 24, 12, (1985) 1607−1610.
[2] M. Yoshino, W. W. Wenas, A. Yamada, M. Konagai, and K. Takahashi, Japan. J. Appl. Phys. 32 (1993) 726−730.
[3] S. Y. Myong, S. J. Baik, C. H. Lee, W. Y. Cho and K. S. Lim, Japan. J. Appl Phys 36 (1997) L1078−L1081.
[4] J. F. Chang and M. H. Hon, Thin Solid Films 386 (2001) 79−86.
[5] T. Y. Ma and S. S. Lee, J. Mat. Sci. Mat. In Elec. 11 (2000) 305−309.
[6] Y. S. Choi, C. G. Lee and S. M. Cho. Thin Solid Films 289 (1996) 153−158.
[7] E. A. Dalchiele, P. Giorgi, R. E. Marotti, F. Martin, J. R. Ramos−Barrado, R. Ayouci and D. Leinen, Sol. Energy Mat. & Sol. Cells 70 (2001) 245−254.
[8] J. Auld, D. J. Houlton, A. C. Jones, S. A. Rushworth, M. A. Malik, P. O’Brien and G. W. Critchlow, J. Mater. Chem 4 (1994) 1249−1253.
[9] C. K. Lau, S. K. Tiku and K. M. Lakin, J. Electrochem. Soc. 127 (1980) 1843.
[10] P. J. Wright, R. J. M. Griffiths and B. Cockayne, J. Crystal Growth 66 (1984) 26.
[11] S. Oda, H. Tokunaga, N. Kitajama, J. Hanna, I. Shimizu and H. Kokado, Jap. J. App. Phys. 24, 12, (1985) 1607−1610.
[12] B. Hahn, G. Heindel, E. Pschorr−Schoberer and W. Gebhardt, Semicond. Sci. Technol 13 (1998) 788−791.
[13] V. Sallet, C. Thiandoume, J. F. Rommeluere, A. Lusson, A. Riviere, J. P. Riviere, O. Gorochov, R. Triboulet and V. Munoz−Sanjose, Mat. Letters 53 (2002) 126−131.
[14] J. Kim, K. Kim and K. Yong, J. Vac. Sci. Technol. A29(5) (2002) 1582−1586.