International Journal of Advanced Technology in Engineering and Science
Vol. No.3, Issue 08, August 2015
www.ijates.com
ijates
ISSN 2348 - 7550

THIN FILM GROWTH TECHNIQUES: IMPORTANCE OF THIN FILMS

Sumati Pati

Vikram Dev (A) College, Jeypore, (India)

I. INTRODUCTION

The effect of growth technique on thin film growth is of considerable significance, as films grown by two different growth techniques using same precursor materials usually have different properties. This is attributed to the fact that the properties of the grown films depends on a great extent on their structure, micro structure and the type of impurities present. In addition, films grown using the same growth technique but variant process parameters, show different properties due to the variation of the process parameters. Therefore, controlling the process parameters is the key way to tailor the properties of the grown films. In this chapter, therefore, it is important and necessary to make a detailed investigation on the techniques used for the deposition of thin films.

It is known that, the improved performance of the thin films in various fields of application is directly related to their exposed surface-to-volume ratio and therefore films made using high surface area often exhibits dramatically improved performance [1-2]. The majority of the nano-material was tested in thick film form synthesized by screen-printing technique. Proper control of the grain size of these thick films remains one of the major research issues. The thick film devices must be heated to sufficiently high temperature for film integrity as well as grain-to-grain connectivity. At the same time the processing temperature should not be too high so that rapid grain growth takes place with rapid decrease of the open porosity. Therefore, the material fabrication process needs to be directed towards the thin film technology (with appropriate microstructure control) rather than adopting the traditional thick film technology starting from powders. The stability of nano-crystalline thick films also remains one of the major research issues. The stability problem can be partially circumvented by fabricating thin film sensing materials.

The above advantages of thin films have boosted the growth of high quality thin films (ZnO thin film in the present work). ZnO thin films can be grown by various techniques, such as: metal organic chemical vapor deposition (MOCVD) [3], pulsed-laser deposition (PLD) [4], molecular beam epitaxy (MBE) [5], sputtering [6], chemical spray pyrolysis [7], screen printing [8], chemical solution deposition (CSD) technique [9], chemical vapor deposition (CVD) [10], sol gel spin coating technique [11] and so on. Using some of these growth techniques it is possible to control the thickness, micro structure and grain size of the films precisely.

Out of the above cited deposition techniques MOCVD is one of the most important techniques for proper control of the deposition parameters. It is a vapor-phase deposition process in which organometallic precursors are used. Despite of a number of factors that is to be optimized during the growth, following are the advantages of MOCVD growth technique: (i) material can be grown at atmospheric pressure (ii) low growth temperature can be achieved (iii) thickness and microstructure can be controlled precisely (iv) uniform deposition can be done (v) high growth rate can be achieved, and so on [3]. Viewing in light of the above description, in this Chapter the details of the MOCVD growth procedure for the growth of ZnO thin films is illustrated.

II. GROWTH OF ZNO THIN FILMS USING MOCVD

As ZnO is prone to form in various types of structures, growth of ultra thin ZnO film requires a suitable technique where high deposition rate can be achieved. For high deposition rate the flow rate of zinc precursor should be high and there should be appropriate oxygen flow rate. MOCVD is proved to be a promising method for controlling this flow rate of the precursors, thus controlling the rate of deposition and hence the quality of the films. Therefore, in this section the growth of ultra thin ZnO thin films using MOCVD technique is described in details. It begins with the results of the MOCVD growth of ZnO that are already reported in the literature. Next, the effects of various parameters such as substrate, temperature, and flow rate on the growth of ZnO thin films are depicted. There follows the optimization of ZnO thin films.

2.1 History of Growth

In the past decades, good quality ZnO thin films have been grown using MOCVD technique by optimizing different parameters. In 1980, Lau *et al*. [12] have grown ZnO thin films on sapphire substrate using diethyl zinc (DEZn) as zinc precursor, H_2O, CO_2, and N_2O as oxygen precursor and H_2 as carrier gas. They recorded a maximum growth rate of 5.1µm/hr at 400^oC in presence of DEZn and H_2O, but explained that in order to retain epitaxy the growth rates had to be kept low. They showed H_2 to be a poor carrier gas for ZnO growth. In 1981 Roth and Williams [13] have grown ZnO thin films using DEZn and O_2 on Pyrex glass substrates, by varying the deposition rate and substrate temperature. They also encountered similar problems as Lau *et al.*, as DEZn and O_2 react spontaneously even at room temperature, causing the deposition of white ZnO powder on the reactor walls. They observed an increase in growth rate above 370^oC, which reaches a maximum value of 2.4 mm/hr at 450^oC. Wright *et al*. [14] in 1984 deposited ZnO thin films on GaP and glass slides using oxygen-containing heterocycle compounds such as furan, tetrahydrofuran, and tetrahydropyran to avoid the premature reactions observed with H_2O and O_2. They got promising results regarding the quality of the film, however the growth rate decreased to 1.9 mm/hr which they thought may be due to the reaction between dimethyl zinc and these heterocyclic compounds. Finally, these problems were overcome in 1985 when Oda et al. [15] used alcohols like methanol (MeOH), ethanol (EtOH), or *tert*-butanol as oxygen precursors. By adjusting the flow of carrier gas (He) through the bubblers, they set their DEZn and alcohol flow rates at 54 and 1300~9000 mmol/min, respectively, and studied the growth from 200 to 400^oC. Of all the alcohols tested, they observed a crystalline layer of ZnO and the highest degree of *c*-axis orientation, at lowest temperature (200^oC) using *tert*-butanol. They also reported that the *n*-type conductivity of the grown ZnO films was related to the presence of donor levels resulting from oxygen vacancies. Then after thirteen years, in 1998, Hahn *et al.* [16] reported MOCVD growth of ZnO using alcohol (*tert*-butanol) as the oxygen precursor. Keeping the horizontal reactor chamber at atmospheric pressure, they varied the temperature from 260 to 410^oC and the VI: II ratio between 2 and 18:1 during growth. They have noticed that the grown films become brownish at a substrate temperature of 360^oC and at VI: II ratios less than 2:1 and reported that the oxygen deficiencies are responsible for the brownish color of the films. They also observed the *c*-axis orientation of ZnO thin films with grain sizes averaging 100 nm.

After that numbers of researches [17-18] were carried out focusing on various aspects such as cleanness of the reactor tube, growth temperature, chamber pressure, flow rates of precursors and so on. From the history of growth it is also observed that the growth of ZnO were aimed at various applications such as, solar cell transparent electrodes, piezoelectric devices or SAW filters and specially at photonic devices. Eriksson et al. [19] in 2009 have studied the oxygen gas sensitivity of electrochemically produced ZnO nanoparticles and PE–MOCVD grown ZnO films.

2.2 Effect of Substrate on the Growth of ZnO thin Films

Though using MOCVD it is possible to grow very good quality of films but the quality of the film depends strongly on the quality of the substrate. It is reported that a low lattice mismatch between the film and substrate improves the film quality and large mismatch usually leads to structural defects and larger strain on the film surface [20]. As stated by G. Korotcenkov [20] selection of substrates with corresponding lattice parameter and thermal expansion coefficient, can reduce the strain and at suitable conditions it is also possible to grow epitaxial metal oxide thin films. Hence proper selection of the substrates is one of the key issues for the growth of good quality thin films. For the growth of ZnO thin films a large number of substrates are available, such as GaN, sapphire, fused quartz, Si, and so on. GaN is an ideal substrate for the growth of ZnO, being similar lattice constants and having wurtzite structure. However, it does not have a native substrate. So first the buffer layers of GaN are grown for the growth of ZnO [21]. Sapphire (a = 4.75 Å, c = 12.99 Å) is also used largely for the growth of ZnO thin films.

Besides this, the most important point that is taken into consideration while choosing a substrate is that for certain characterization of the grown films certain substrates are needed; e.g. for Hall measurements of ZnO thin films one needs a non-conducting substrate and for optical characterization a transparent substrate (like fused silica) is needed. In our work we have used fused silica as the substrate for the growth of ZnO thin films.

2.3 Influence of Temperature on the Properties of ZnO thin Films

Out of all the parameters that affect the quality of the thin films, one of the most important is the growth temperature. This growth temperature affects quite a bit on the properties of the grown thin films. To study the influence of growth temperature on the quality of the film, we have grown a number of ZnO thin films in the temperature range 400-500°C, keeping the other parameters constant. Each film is grown for one hour duration keeping the flow rates of the diethyl zinc (DEZn) and *tert*-butanol at 20 and 60 sccm, respectively. The influence of flow rate will be discussed in the next section. The structural and micro structural properties are studied in terms of X-ray diffraction pattern and FESEM micrographs respectively [22]. Fig. 1 (a-c) shows the XRD pattern of the grown films in the said temperature range.

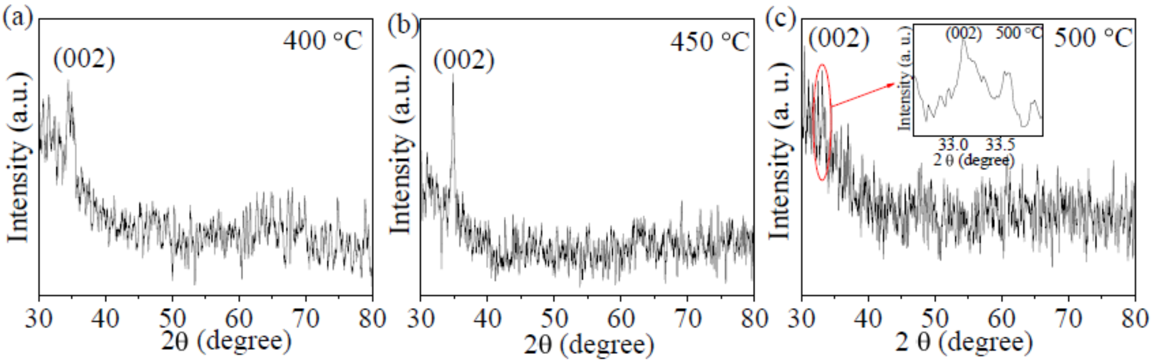

Fig.1: XRD pattern of the ZnO thin films grown at different temperatures (a) 400°C, (b) 450°C, and (c) 500°C. Inset of figure (c) shows the (002) peak of the corresponding pattern [Reproduced from Ref. 22]

As demonstrated from the XRD pattern all the grown films are textured along (002) plane. However, the intensity of the (002) oriented peak differs significantly. The XRD pattern of the sample grown at 400°C (Fig.1 (a)) shows a weak (002) peak. This lower intensity may be attributed to the low growth temperature. Now increasing temperature from 400°C to 450°C, as shown in Fig.1 (b), leads a significant enhancement in the intensity of (002) diffraction peaks. This shows the preferential orientation of the ZnO grains along (002) planes. However, further increase in temperature reduces the preferential orientation in ZnO grains, as observed from Fig. 1 (c). This may be due to the faster reaction rate at higher growth temperatures which hinders the crystallization reaction [23].

Fig. 2 (a-c) shows the FESEM images of the grown ZnO thin films in the temperature range 400- 500°C.

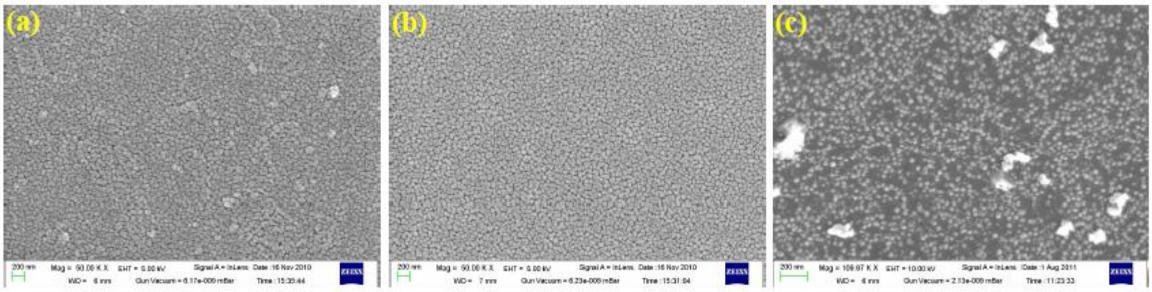

Fig.2: FESEM images of the ZnO thin films grown at different temperatures, (a) 400°C, (b) 450°C, and (c) 500°C [Reproduced from Ref. 22].

As observed from the figure the microstructure of the grown samples depends strongly on the growth temperatures. At 400°C (lowest growth temperature in the present study) the microstructure reveals presence of individual grains separated by voids. No prominent grain boundaries are observed. This is attributed to the fact that at lower growth temperatures the surface adatoms may not have sufficient mobility. Now with increasing growth temperature, at 450°C, the surface morphology shows distinct grains separated by grain boundaries without the presence of voids. However, with further increase in temperature the morphology becomes sparse, which may be due to the sintering and grain growth at higher temperature. In view of the structural and micro structural characterization of the samples, it appears that 450°C is the optimum temperature for the growth of ZnO thin films.

2.4 Influence of Flow Rate on the Properties of ZnO thin Films

The VI: II ratio during growth is a measure of the O-to-Zn ratio in the gas phase during the film deposition process, which has a significant effect on the properties of ZnO. A low VI: II ratio will create oxygen vacancies in the crystal lattice, while a high VI: II ratio will cause an abundance of oxygen producing various defects in the material. These defects in turn affect the properties of the material to a large extent [24-25]. Pagni et. al. [24] studied the effect of flow rate on the structural and optical properties of the ZnO thin films. They found that decreasing the VI: II ratio from 60:1 to 10:1 lead the (002) XRD peak position to shift to higher values, which is due to the generation of oxygen vacancies in the crystal as less oxygen enters the reactor tube. They have also reported the largest optical band gap (3.24 eV) and the lowest Urbach tail E_0 parameter (254 meV) for the sample deposited at a VI: II ratio of 18:1. They reported an increase in carrier concentration from 5.2×10^{17} to 9.4×10^{19} with a decrease of flow rate from 60:1 to 10:1, which is also due to the creation of oxygen vacancies with lower flow rate. Choopun *et al.* [25] reported the layers of well-faceted hexagons at low oxygen pressures. They also reported a transition pressure (10^{-2} Torr) at which the samples showed smooth surfaces, and after which they have high nucleation densities, irregular grains of different sizes, and increased surface roughness. In our work we have kept a lower VI: II ratio (3:1) to enable the formation of oxygen vacancies in the ZnO thin films, as presence of oxygen vacancies will promote the use of ZnO thin films in various fields like gas sensor.

III. ACKNOWLEDGEMENT

The author gratefully acknowledged IIT Kharagpur for providing the experimental facility.

REFERENCES

[1]. N.S. Ramgir, Y.K. Hwang, S.H. Jhung, I.S. Mulla, and J.S. Chang, Effect of Pt concentration on the physicochemical properties and CO sensing activity of mesostructured SnO_2, Sensors and Actuators B, 114, 2006, 275-282.

[2]. N. Yamazoe, G. Sakai and K. Shimanoe, Oxide semiconductor gas sensors, Catalysis Surveys from Asia, 7, 2007, 63-75.

[3]. S. Pati, S. B. Majumder, and P. Banerji, MOCVD grown ZnO ultra thin film gas sensors: Influence of microstructure, Sensors and Actuators A, 213, 2014, 52–58.

[4]. S. Majumdar and P. Banerji, Growth and characterization of urea doped p-type ZnO thin film grown by pulsed laser deposition, Advanced Materials Research, 67, 2009, 127-130.

[5]. C.-Y.J. Lu, L. Chang, K. H. Ploog and M. M. C. Chou, Epitaxial growth of nonpolar ZnO on MgO (1 0 0) substrate by molecular beam epitaxy, Journal of Crystal Growth, 378, 2013, 172-176.

[6]. S. Elmas and S. Korkmaz, Deposition of Al doped ZnO thin films on the different substrates with radio frequency magnetron sputtering, Journal of Non-Crystalline Solids, 359, 2013, 69–72.

[7]. P. S. Shewale, G. L. Agawane, S. W. Shin, A. V. Moholkar, J. Y. Lee, J.H. Kim and M. D. Uplane, Thickness dependent H_2S sensing properties of nanocrystalline ZnO thin films derived by advanced spray pyrolysis, Sensors and Actuators B, 177, 2013, 695–702.

[8]. S. Akbar, P. Dutta and C. Lee High temperature ceramic gas sensors: A review, International Journal of Applied Ceramic Technology, 3, 2006, 302-311.

[9]. M. Wang, S. H. Hahn, E. J. Kim, J. S. Kim, S. Kim, C. Park and K.-K. Koo, Chemical solution deposition of ZnO thin films with controlled crystallite orientation and intense ultraviolet emission, Thin Solid Films, 516, 2008, 8599–8603.

[10]. D. Kim, I. Yun and H. Kim, Fabrication of rough Al doped ZnO films deposited by low pressure chemical vapor deposition for high efficiency thin film solar cells, Current Applied Physics, 10, 2010, S459–S462.

[11]. S. Pati, P. Banerji and S. B. Majumder, Properties of indium doped nanocrystalline ZnO thin films and their enhanced gas sensing performance, RSC Advance, 5, 2015, 61230-61238.

[12]. C. K. Lau, S. K. Tiku and K. M. Lakin, Growth of epitaxial ZnO thin films by organometallic chemical vapor deposition, Journal of Electrochemical Society, 127, 1980, 1843-1847.

[13]. A.P. Roth and D.F. Williams, Semiconducting Zinc Oxide films prepared by organic chemical vapor deposition from diethyl zinc, Journal of Electrochemical Society, 128, 1981, 2684-2686.

[14]. P.J. Wright, R. J. M. Griffiths and B. Cockayne, The use of heterocyclic compound in the organometallic chemical vapor deposition of epitaxial ZnS, ZnSe and ZnO, Journal of Crystal Growth, 66, 1984, 26-34.

[15]. S. Oda, H. Tokunaga, N. Kitajima, J. -I. Hanna, I. Shimizu and H. Kokado, Highly oriented ZnO films prepared by MOCVD from diethyl zinc and alcohols, Japanese Journal of Applied Physics, 24, 1985, 1607-1610.

[16]. B. Hahn, G. Heindel, E. Pschorr-Schoberer and W. Gebhardt, MOCVD layer growth of ZnO using DMZn and butanol, Semiconductor Science and Technology, 13, 1998, 788-791.

[17]. N. Oleynik, M. Adam, A. Krtschil, J. Blasing, A. Dadgar, F. Bertram, D. Forster, A. Diez, A. Greiling, M. Seip, J. Christen and A. Krost, Metal organic chemical vapor phase deposition of ZnO with different O-precursors, Journal of Crystal Growth, 248, 2003, 14–19.

[18]. C. Kirchner, Th. Gruber, F. Reub, K. Thonke, A. Waag, Ch. Gieben and M. Heuken, MOVPE growth of ZnO using various oxygen precursors, Journal of Crystal Growth, 248, 2003, 20-24.

[19]. J. Eriksson, V. Khranovskyy, F. Soderlind, P.-O. Kall, R. Yakimova and A. L. Spetz, ZnO Nanoparticles or ZnO films: A comparison of the gas sensing capabilities, Sensors and Actuators B, 137, 2009, 94–102.

[20]. G. Korotcenkov, Gas response control through structural and chemical modification of metal oxide films: State of the art and approaches, Sensors and Actuators B, 107, 2005, 209–232.

[21]. B. M. Ataev, W. V. Lundin, V. V. Mamedov, A. M. Bagamadova and E. E. Zavarin, Low-pressure chemical vapor deposition growth of high-quality ZnO films on Epi-GaN/α-Al_2O_3, Journal of Physics Condensed Matter, 13, 2001, L211–L214.

[22]. S. Pati and P. Banerji, Effect of temperature on the structural and morphological characteristics of ZnO thin films grown by MOCVD, International Journal of Computer & Mathematical Sciences, 3 (7), 2014, 76-83.

[23]. B. S. Li, Y. C. Liu, D. Z. Shen, J. Y. Zhang, Y. M. Lu and X. W. Fan, Effects of RF power on properties of ZnO thin films grown on Si (0 0 1) substrate by plasma enhanced chemical vapor deposition, Journal of Crystal Growth, 249, 2003, 179–185.

[24]. O. D. Pagni, On the MOCVD growth of ZnO, Ph. D. Thesis, Faculty of Science at the University of Port Elizabeth (2004).

[25]. S. Choopun, R. D. Vispute, W. Noch, A. Balsamo, R. P. Sharma, T. Venkatesan, A. Iliadis and D. C. Look, Oxygen pressure-tuned epitaxy and optoelectronic properties of laser-deposited ZnO films on sapphire, Applied Physics Letters, 75, 1999, 3947-3949.