Effect of Substrates and Film Thickness on the Properties of Zno Thin Films Grown By Chemical Bath Deposition

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ABSTRACT- Zinc oxide (ZnO) is a promising material in nanotechnology applications, for example in nano-electronics and nano-robotic technology. The objectives foe our work are to study the effect of thickness on the structural, optical, electrical and mechanical properties and various susbstrates have been investigated of ZnO thin films. ZnO thin films were coated using chemical bath technique for various thickness. All the coated films were characertized by XRD, PL and electrical measurements. The results are discussed herein. As part of our characterization process, XRD and FE-SEM were used to characterize the structural properties, current-voltage measeurements for the electrical properties, and UV-Vis spectra and photoluminescence spectra for the optical of the ZnO thin films.

Keywords: Zinc oxide (ZnO), X-ray diffraction, CBD, PL, SEM.

1. INTRODUCTION

In recent years, there is a great interest in production of transparent conducting oxide (TCO) and transparent oxide semi-conductors for the development of photonic devices and transparent conducting electrodes (TCE) for solar cells. Up to now, a number of studies on ZnO films deposited on various substrates including glass, Si, GaN, GaAs and diamond have been conducted. The substrate is very important for the growth of thin films in terms of the lattice and thermal mismatching between it and the film because it commonly leads to the development of stress in the deposited film.

2. MATERIALS AND METHOD
2.1 Substrate and its preparation
2.1.1 Choice of substrate

Thin film requires a substrate to support itself. The substrate provides the necessary mechanical strength and rigidity needed for the film and it has adequate thermal ability to ensure at room temperature and withstand at high temperature. The function of the substrate is to provide the base on to which the thin film circuits are fabricated and various thin film multi layers are deposited. To form the thin film with defined electrical parameters, the substrates must be smooth and flat otherwise electrical and optical properties may be affected. Therefore in choosing a suitable substrate, in addition to considering the need to provide the mechanical support to the deposits, due consideration must be given to the possible influence of the substrates on the properties of the deposits. Commonly used substrate materials for polycrystalline thin film circuits include alumina, glass, silicon and metals, beryllium oxide based ceramic, aluminium nitride. When the films are deposited into glass, electrical and optical measurements are not disturbed by an underlying layer and are thus easier to interpret. of all these, glass is

found to posses all the requirements and is economically and widely used.

2.1.2 Cleaning of substrate

However any type of substrate may be used in this simple growth method. Substrate cleaning in thin film technology is an important step prior to deposition. It is necessary to remove the contaminants that would otherwise affect the properties of the film. Cleaning involves the removal of contaminants without damage to the substrate. While cleaning, the bond between the substrates is broken and contaminants are set free from the substrates. The properties that can be affected by the presence of contaminants include morphology, nucleation electronic properties and the substrate film interface. Expected contaminants include fingerprints, dust, oil, and lint particles. The proper cleaning technique depends on the nature of the substrate and nature of the contaminants. The composition, physical properties such as porosity, thermal expansion, melting point, conductivity and chemistry of the substrate should be carefully considered in designing the cleaning operation. The energy required to break those bond could be supported by chemical, salvation, thermal (or) mechanical process. As the other techniques this technique also involves rigorous cleaning of the substrates.

2.2 Thickness of ZnO thin Films

A traditional method of preparing ZnO nano particles is achieved using chemical bath techniques. Zinc chloride and NaOH were used as the starting materials. Ammonium Solution was used to maintain the PH at 9.ZnO was prepared by double distilled water. Heating the liquid phase at 60oC with continuous stirring yield the ZnO particle in average nano meter size. Now the cleaned glass substrate is immersed in above processed sol to coat over the substrate. This method is based on the sequence of reaction on the substrate surface. ZnO is formed by the following reaction $(CH_3COO)_2Zn$ $2CH_3COO^-$ + $Zn^{2+}NH_2-CO=NH_2+$ H_2O O_2^- +

H_2OZn^{2+} + O_2^- ZnO The coating time is varied from 30 mins to 3 hrs in order to vary the thickness of the ZnO films. Following drying and heat treatment is to generate porous structured films on the substrate. Residual organics are removed by washing the films with acetone. This method does not require sophisticated and expensive instruments. Also by this method we have prepared pin-hole free thin films.

2.2.1 Characterizations Made

The average thickness of the coated films were measured by Semi-Consoft in thickness measuring unit.As synthesized ZnO powder was subjected to powder X-ray diffraction (PXRD) analysis, using an X- ray powder diffractometer, PAN alytical with scintillation counter and monochromated Cu Kα (λ = 1.54056 Å) radiation.. In order to understand the chemical compositions of the prepared sample in the present study, we have carried out EDS measurements using JEOL SEM Model, JSM – 5610LV scanning electron microscope .The optical absorption spectra of coated films were recorded in the range of 200-800 nm using Consoft Inc Spectrophotometer.

2.2.2 Thickness Measurements

Thickness and coating time for all the prepared samples are tabulated in Table 2.2.2 As the time increases, the thickness also increases.

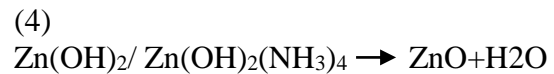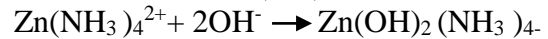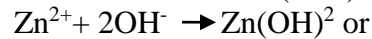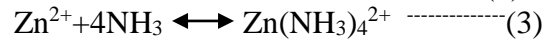| Samplecode nM	Coatingtime (min)	Thickness
Film1	25.321	30
Film2	55.525	60
Film3	78.230	90
Film4	141.615	120
Film5	161.267	150

3. EXPERIMENTAL DETAILS

CBD technique has been proven to be a good approach for synthesis of ZnO thin film with the use of ZnO seeds in the forms of thin films. Here, Si was chosen as a substrate for ZnO thin film arrays grown using a CBD technique. The Si substrates were cleaned in the ultrasonic bath with acetone, ethanol and deionized water to

remove adsorbed dust and surface contamination. In order to fabricate vertically aligned thin film, ZnO seed layer was first fabricated on the substrates by simple silar method. 100ml aqueous solutions composed of zinc acetate (Zn(CH3COO)2.2H2O) with ammonia solution were used as a precursor source for the growth of ZnO thin film. All the employed chemicals were analytical reagent grade. The concentration of Zn(CH3COO)2.2H2O was varied in the range of 0.025 to 0.075M while keeping the molar ratio of Zn(CH3COO)2 .2H2O and ammonia to be 1:1. The solution was then transferred into a sealable glass beaker in which the substrates were suspended vertically. The optimized films with precursor concentration were taken for growth temperature variation in the range of 65°C to 95°C. At the end of the growth, the substrates were taken out of the solution and rinsed several times with deionized water, and then blew dried with high purity Ar gas at room temperature. A detailed chemistry process by CBD technique can be found elsewhere. A Philips Japan MPD 1880 X-ray powder diffractometer was employed to study the crystal structure of the films. Surface morphology of the films was examined by scanning electron microscopy, SEM (JEOL, 15 kV). A Shimadzu double beam spectrophotometer was employed for obtaining absorbance in the wavelength range of 350–800 nm and to evaluate the direct band gap energies.

4.   RESULTS   AND DISCUSSIONS

4.1 Chemical process of CBD technique for the growth of ZnO thin film:

The chemical process involved in the growth of ZnO can be described as follows: Zn(CH3COO)2•2H2O provides $Zn2+$ ions required for building up ZnO thin film, water molecules in the solution provide O^{2-} ions. Even though the exact function of HMT during the growth is still unclear, it is believed to act as a weak base, which would slowly hydrolyze in the water solution and gradually produce OH^- [20]. The detailed chemical reactions were:

$$C_6H_{12}N_4 + 6H_2O + 4NH_3 + 6HCHO ----- (1)$$
$$H_2o + NH_3 \longleftrightarrow OH^- + NH^+_4 ----------- (2)$$
$$Zn^{2+} + 4NH_3 \longleftrightarrow Zn(NH_3)_4^{2+} ------------- (3)$$
$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)^2 \text{ or}$$
$$Zn(NH_3)_4^{2+} + 2OH^- \rightarrow Zn(OH)_2 (NH_3)_{4-} (4)$$
$$Zn(OH)_2 / Zn(OH)_2(NH_3)_4 \rightarrow ZnO + H2O ------- (5)$$

The growth process of CBD can be controlled through the five chemical reactions listed above. All of the five reactions can be controlled by adjusting the reaction parameters, such as precursor concentration, growth temperature and growth time. With the movement of the reaction equilibrium to the right side, ZnO will form through dehydration of Zn(OH)2 and precipitate onto the substrates.

4.2 Effects of substrate on structure characters and morphology of ZnO thin film:

Figure 1 shows the XRD patterns of ZnO thin film grown on three kinds of substrates, (a) quartz glass substrate, (b) Si substrate and (c) ITO glass substrate. All diffraction peaks are consistent with the wurtzite structure, which can be indexed to a standard spectrum of JCPDS (No, 36-1451). For all the samples, the (002) diffraction peak in XRD patterns is dominant, yet other peaks are nearly invisible, which reveals the preferentially oriented growth in the c-axis direction. In addition, it can be found that the (002) peak intensity for the samples deposited on quartz glass and Si substrates are much higher than that of samples deposited on ITO glass substrate, which was suggested to be caused by the less amount of ZnO thin film grown on the ITO glass than that on the quartz and Si substrates.
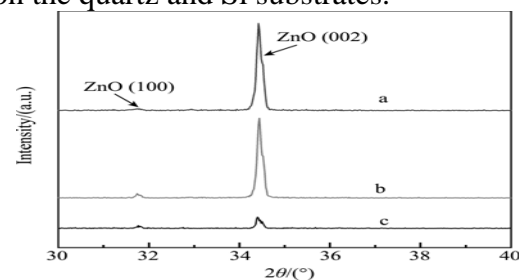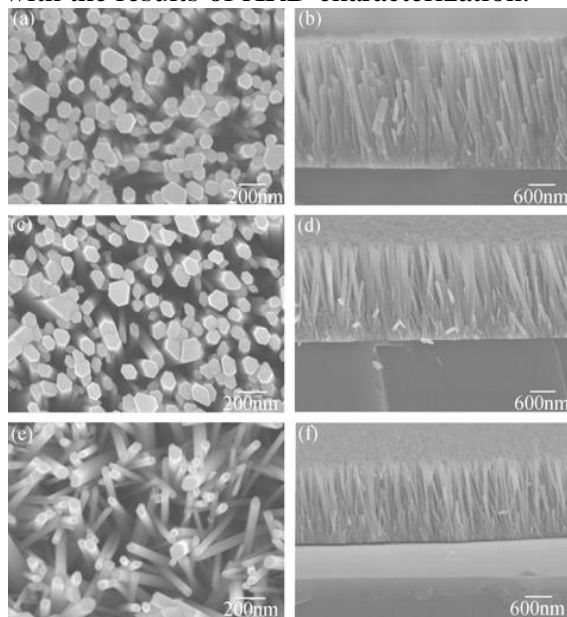

Figure 1 XRD patterns of ZnO thin film grown on different kinds of substrates (a).Quartz glass; (b) Si; (c) ITO glass

Figure 1.a shows the SEM images of as-grown samples grown on three kinds of substrates. It can be clearly observed from the figures that the ZnO well-defined thin film arrays were successfully grown densely and vertically on all the substrates. However, the average diameter and length of the ZnO thin film array were closely related to the substrate nature. The length and average diameter of the ZnO thin film on the quartz glass, Si and ITO glass were 3.3um (120nm in average diameter), 2.5um (105nm in average diameter), and 2.3um (60nm in average diameter), respectively. Thus, the aspect ratios on the quartz glass, Si and ITO glass were calculated to be 27.5, 23.5, and 38.3, respectively. It has been well established that the higher average density and length of the thin film will lead to higher intensity of the (002) diffraction peak. Therefore, the SEM results were in well agreement with the results of XRD characterization.

Figure 2 SEM images of as-grown samples grown on three kinds of substrates (a) (b) Quartz glass; (c) (d) Si; (e) (f) ITO glass

## 4.3 Effect of substrates on optical properties of ZnO thin film:

Optical properties of thin film are important for many of their technological applications. Figure 4.3 shows the room temperature PL spectra of ZnO thin film grown on different substrates with the same condition.
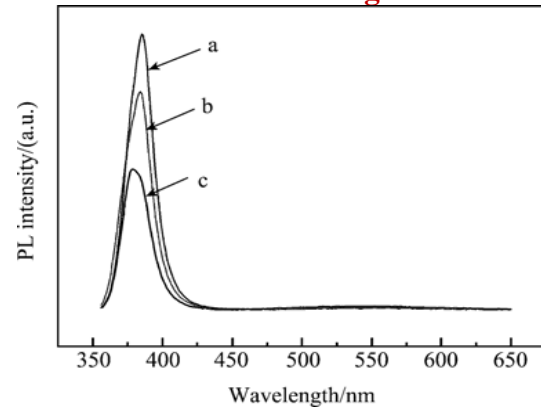
Figure 3 PL spectra of ZnO thin films grown on different substrates with the same condition (a) Quartz glass; (b) Si; (c) ITO glass

The UV emission in ZnO PL spectra is well accepted as the nearnband edge emission which has an exciton nature. Meanwhike, the visible emission band in ZnO PL spectra is usually observed for most ZnO thin film reported in literature, which is believed to be closely related to the defect level induced by the defects of O vacancies, Zn interstitials or their complexes. In our case, however, it should be noted that only strong near-band edge UV emission peak at about 380nm were observed for the ZnO thin film arrays on all substrates regardless of crystalline or amorphous, yet the usually observed defect related deep level emissions were nearly undetectable, indicating high optical quality ZnO thin film arrays were successfully achieved via this low temperature easy process chemical approach. It is also shown from Fig.3 that the UV peak intensity of sample (c) is remarkably lower than sample (a) and (b), indicating relatively poor optical quality for the ZnO thin film grown on ITO glass substrate. Compared with the samples on ITO substrates, a slight red shift in UV emission is observed for ZnO thin film grown on quartz and Si substrates, which is assumed to be associated with the different compress stress in the ZnO thin film. That is, a big compress stress will result in the narrowing of the band gap and further lead to the red shift of near band edge emission.This assumption will be demonstrated by Raman spectra measurements.
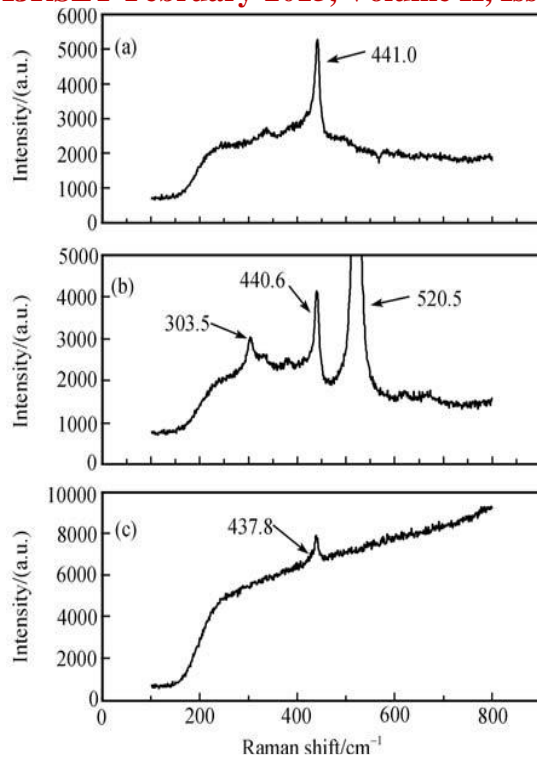
Figure 4.a Raman spectra of ZnO thin films grown on different Substrates (a) Quartz glass substrate; (b) Si substrate; (c) ITO glass

CONCLUSION

ZnO thin film were successfully synthesized on different substrates by the chemical bath deposition (CBD) method. Effects of the substrate on the structure, morphology and optical properties of ZnO thin film were studied. XRD and SEM results demonstrate that the ZnO thin film arrays with a hexagonal wurtzite structure were grown densely and vertically on all the substrates, whereas the average diameter and length were found to be closely related to the substrates nature. The high optical quality ZnO thin film presented here was very prospective for its applications in optoelectronic nanodevices, such as UV lasers, light-emitting diodes.

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