Effect of substrates on Zinc Oxide thin films fabrication using sol-gel method

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Abstract. The properties of ZnO thin films were deposited on three different substrates via dip coating method was investigated. The films were prepared on glass, ITO and p-type silicon. Characterization of the film revealed that the properties of the dip coated ZnO thin films were influenced by the type of substrates. The grains on ITO and glass were ~10 nm in size while the grains on wafer agglomerate together to form a denser film. Studies of the optical properties using UV-VIS-NIR of the fabricated films demonstrated that glass has the highest transmittance compared to ITO.

1. Introduction

Zinc Oxide (ZnO) is a very important II-VI group of semiconductor material with a direct bandgap of 3.37 eV at room temperature, excellent chemical and thermal stability, non-toxicity and has a large exciton binding energy (60 meV) [1]. Researches on ZnO thin films have gained a lot of attention due to its unique physical properties such as structural, optical and morphological as well as its wide range of applications. ZnO films have been studied for diverse of applications such as optoelectronic devices [2], solar cells [3,7], gas sensors [4], varistors [5], surface acoustic wave devices [6], and field effect transistors [8-10].

ZnO thin films can be prepared by various methods including chemical vapor deposition [11], sputtering [12], pulsed laser deposition [13], sol-gel [14, 15], thermal evaporation [16], anodization [17] and oxidation [18]. However, among these methods, sol-gel dip coating method has several advantages such as low fabrication costs, simple process, large area of substrate coating, allows control over the composition and dopant incorporation. In this work ZnO thin films deposited on different type of substrates which are glass, ITO and silicon wafer by the sol–gel dip-coating technique. The influence of different substrates on the properties of ZnO thin films was investigated. The characterization of the ZnO thin films is performed by field emission scanning electron microscope (FESEM) to study the morphological properties, X-ray diffractometer (XRD) for crystallinity properties and UV-VISS for optical properties.
2. Experimental Procedure

Fabrication of nanoporous Nb$_2$O$_5$

In this experiment, zinc acetate dihydrate (Zn.2O) was used as a precursor while 2-methoxyethanol (MO) and monoethanolamine (MEA) (NO) were used as the solvent and the stabilizer respectively. To prepare the ZnO thin films, zinc acetate dihydrate was dissolved in a mixture composed of 2-methoxyethanol and MEA. The zinc acetate dihydrate and MEA molar ratio was kept at 1:1, while the concentration of zinc acetate was 0.4M. The solution was stirred and heated at 80 °C on the hot plate for 1 hour until it become clear and homogeneous. Then, the solution was sonicated at 50 °C for 1 hour by using an ultrasonic water bath. Afterwards, the solution was being stirred without any heat for 24 hours before the deposition process. In this experiment, dip-coating method was used to obtain the ZnO thin films on the substrates.

The glass and ITO substrates were cleaned ultrasonically twice in acetone, methanol and deionized water for 5 minutes before the deposition process. As for silicon substrates, before continuing with the normal cleaning process, we need to soak the substrates with a solution of hydrofluoric acid (HF) and deionized water (DI) with a ratio of 1:10. The substrates were dipped and withdrawn from the precursor solution at a withdrawal speed of 1.0mm/s under ambient conditions. Immediately after the coating process, the thin films were heated to 300 °C for 10 minutes to evaporate the solvent. The final coatings were obtained after repeating this process for five times. After coating, the thin films were annealed for 1 hour at 500 °C under ambient condition.

The structural properties of the ZnO thin films were characterized by using a field emission scanning electron microscope (FESEM) for surface morphology and surface profiler to calculate the thickness of the thin film for calculations of band gap energy. The optical properties were characterized by UV-VIS-NIR to investigate the transmittance and absorption of the thin films.

3. Results

FESEM images Structural properties

Fig. 1 shows the FESEM images of ZnO films fabricated under identical conditions on (a) glass, (b) ITO and (c) silicon. Each transparent substrate has unique surface conditions. Therefore, the deposited ZnO thin films on the different transparent substrates will have different morphology. The SEM images revealed that the fabricated thin films generally consist of grains with varied sizes and dimensions. The ZnO films appeared to have about the same grains size on glass and ITO substrates. However the films fabricated on glass has more voids. The ZnO films become more dense and tend to agglomerate on silicon wafer leaving large grain boundaries. Generally, ZnO thin films on all substrates appeared to be in porous structures.
The optical properties such as transmittance and absorption coefficient were investigated by analyzing the UV-Vis-NIR patterns of ZnO thin films in the wavelength range of 300-800 nm depicted in Fig. 2 and Fig. 3. The transmittance of ZnO thin films on glass substrate increased abruptly from 10%-85% in the visible range (380-800 nm). Furthermore, the optical transmission for ZnO thin films on ITO substrate also increased rapidly in the visible range but only until 80%. It is suggested that the presence of voids around the grains is greater on glass compared to ITO that makes the light to transmit higher on glass, which was previously discussed in the FESEM results. In addition, silicon has 0% optical transmission since it is not transparent substrate.

Many electrons or disordered lattice structures in the ZnO thin films were scattered by incident light, thus decreasing the transparency of ZnO thin films [19]. Furthermore, the difference of optical transmittance between substrates was due to optical scattering at the grain boundaries. It is suggested that the transmittance of the ZnO thin films depends on films structure and uniformity [20]. Fig.3 shows the absorption coefficient of ZnO thin films in three different substrates that were calculated by using Lambert’s Law, where $\alpha$ is the absorption coefficient, $t$ is the thin film’s thickness and $T$ is the transmittance of the thin film, as shown in Equation 1.

$$\alpha = \frac{1}{t} \ln \left( \frac{1}{T} \right)$$

(1)

ITO has larger absorption coefficient compared to glass substrate in the UV region (<400 nm) that might be due to the amount of zinc species within the films and the density of the ZnO thin films on the ITO substrate that can cause an improvement in the light absorption in the visible region. The band gap energy of the thin films has been determined by using the Equation 2 and Equation 3 [22, 23] below:

$$\alpha hv = B(hv - E_g)^{1/2}$$

(2)

$$(\alpha hv)^{1/2} = B(hv - E_g)$$

(3)

Where $\alpha$ is the absorption coefficient in Fig. 3, $hv$ is the photon energy, $E_g$ is the band gap energy and $B$ is an energy-independent constant [23, 24]. The $E_g$ is obtained by crossing the line of the function of $hv$. From the Tauc’s plot, the band gap energy of ZnO thin films on glass substrate is approximately 3.17 eV while for ITO substrate is 3.00 eV. These results are valid since it is consistent with published
values of the ZnO transition band gap data [25]. The difference of band gap energy between different substrates is influenced by the optical scattering between grain boundaries and the grains that agglomerates together in the thin films. The difference between the band gap energy of each substrate may be beneficial in many applications such as sensors, solar cells and many more.

CONCLUSION

We have investigated the properties of ZnO thin films deposited using dip coating method on three different substrates which are glass, ITO and silicon. The ZnO thin films on glass were less dense as compared to ITO and silicon based on their grain boundaries and uniformity. In terms of optical properties, the ZnO thin films showed a 95% transmittance on glass in visible region (380-800 nm) which was higher than ITO. In addition, the band gap of ZnO thin films was higher on glass compared to ITO because of the larger grain boundaries. It can be concluded that structural and optical properties of the ZnO thin films were influenced by the different substrates.

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