Morphology and Optical Properties of Zinc Oxide Films Grown on Metal Coated Glass Substrates by Aqueous Chemical Growth

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Abstract. Zinc oxide films were deposited on three different metal coated substrates (gold, nickel and platinum) by aqueous chemical growth method. This paper discusses the effect of metal coated substrates on the morphology and optical properties of grown ZnO films. X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and UV-visible spectroscopy (UV-vis) were employed to characterize the samples. All the as-deposited ZnO films exhibit crystalline hexagonal wurzite structure. The crystallite size of the ZnO films were in the range of 29 to 32 nm. FESEM micrographs revealed hexagonal rod, oval-like and flower-like ZnO structures formed on all metal coated substrates. The Pt coated film contains higher density hexagonal rod as compared to others metal coated substrate. Most probably the Pt lattice parameter is the nearest to ZnO compared to nickel and gold. The optical band gap energy, $E_g$ of ZnO films were estimated to be 3.30 eV which is near to bulk $E_g$, 3.37 eV. This indicates that the ZnO grown by aqueous chemical growth is able to produce similar quality properties to other conventional method either films or bulk size.

1. Introduction
Zinc oxide has been recognized as a promising semiconductor for various applications in electronics because of its wide band gap (3.37 eV at room temperature) and large exciton binding energy of 60 meV [1]. Recent research developments have revealed that the morphology of the films plays a key role in the application of ZnO in specific fields [2]. Via the chemical solution route, tube-, wire-, and flower-like ZnO nanostructures can be obtained [3]. The aqueous chemical growth has been widely proved for the large scale production of nano/microscale materials because it is less expensive, simple, fast, and requires a low growth temperature [4].

In the present work, we investigate the effect of different metal coated glass substrate on ZnO films growth by aqueous chemical growth method. These three metal coatings; gold (Au), nickel (Ni) and platinum (Pt) are selected since these metals are often used in electronic devices. The morphology of ZnO growth on each substrate and potential growth mechanisms are proposed. It is believed that the type of metal coating on the substrate plays a role in the morphology, shape and size and optical properties of ZnO. The ZnO films grown on the metal coated glass substrates (gold, nickel and platinum) could be used in various applications such as as solar cell, optical coatings, sensors, ultraviolet optical detectors and etc.
2. Materials and Method

ZnO films were grown on metal coated glass substrates by the aqueous chemical growth method. This method is based on heating the aqueous solution which containing the substrate immersed in the solution. All chemicals were used in the as-received form with no further purification. 100 ml aqueous solution with concentration of 0.05 M was prepared using 0.74 g of zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O) and 0.35 g hexamethylenetetramine (C$_6$H$_{12}$N$_4$). The chemicals were dissolved in deionized water. The aqueous solution was magnetically stirred until complete dissolution for 1 h. The glass substrates used for this experiment were ultrasonically cleaned with acetone and ethanol, followed by deionized water, for 15 mins. The cleaned glass substrates were then dried in the air. The three glass substrates were coated with different metals, namely gold (Au), nickel (Ni) and platinum (Pt), using a sputter coater for 2 mins with a current of 30 mA. Each of metal coated glass substrate was placed horizontally at the bottom of a sealed beaker. The samples were then heated at 90 °C for 3 hours in an oven without any stirring. Subsequently, the samples were removed and washed thoroughly with deionized water, to eliminate any residual salts, and were then dried in air.

The morphology and film thickness of the deposited ZnO films were analyzed using field emission scanning electron microscopy (FE-SEM-SUPRA 55VP). Crystal phase and orientation were determined by X-ray diffractometer (XRD, BRUKER D8 ADVANCE) with CuKα radiation source (40 kV, 40 mA, λ = 0.15406 nm). The optical transmittances of the ZnO thin film were measured using UV/VIS/NIR spectrometer (LAMBDA 900).

3. Results and Discussion

X-ray diffraction (XRD) patterns of ZnO films deposited on different metal coated glass substrates at 90 °C for 3 h is shown in Figure 1. All of observed peaks indicated that ZnO were successfully grown on all substrates. The XRD patterns of the ZnO films shows the characteristic peaks corresponding to planes (100), (002), (101) with high intensities and (102), (110) with low intensities planes, which matched well with reference data (JCPDS No. 36-1451). All of characteristic peaks are assigned to hexagonal ZnO wurtzite structure with cell constant of $a = 3.24982$ Å and $c = 5.20661$ Å, indicating the product is pure ZnO. Moreover, there are no other visible peaks or impurities from other phases were detected implying the pure ZnO were grown on the substrates. The average crystallite size, $D$ is estimated using Scherrer’s equation [5], $D = 0.9 \lambda / \beta \cos \theta$. Where $\lambda$ is the X-ray wavelength (0.154056 nm), $\beta$ is FWHM (in radians) of the diffracted peak 2$\theta$ and $\theta$ is the Bragg diffraction angle (in radians). The calculated crystallite size is about 29 nm for ZnO film deposited on Au and Ni coated glass substrates and 32 nm is for Pt coated glass substrates.
Figure 1. XRD patterns of ZnO films grown on: (a) Au, (b) Ni and (c) Pt coated glass substrates at 90 °C for 3 h.

Figure 2 illustrates the FESEM micrographs of ZnO films grown on different metal coated glass substrates at 90 °C for 3 h. Multiple type of ZnO structures have been observed grown on the different metal coated glass substrates such as hexagonal rods, flower-like, oval-like and special feature of nanorod array. This may due to the metal coated substrate (Au, Ni and Pt) act as catalyst for the growth site of ZnO. Furthermore the lattice difference between ZnO and each metals may results in different ZnO morphology that obtained. Figure 2 (a) shows the morphology of ZnO film grown on Au coated glass substrate. A mix of flower-like and oval-like morphologies were grown on the substrate with specific direction. Similar morphologies were also found in ZnO film grown on Ni coated glass substrate (Figure 2 (b)). The oval-like structure was most likely as a result of coalescence between small hexagonal structures. The flower-like structure are seen to be grown on top of oval-like structure which suggests secondary growth are preferred only on ZnO rather than metal substrate.

Figure 2(c) shows hexagonal rods, oval-like structure and nanorod arrays coexisting on Pt substrate. Higher magnification in Figure 2(d) shows ZnO nanorod arrays structure directly grown on metal substrate which typically are observed grown using ZnO seed layer or substrate. According to Yamada et al. [6], the existence of this nanorod-array is because of a small lattice mismatch that exists between ZnO and Pt-substrate, ~1.4%, which allows this structure to be formed. This type of structure was not observed on both ZnO film grown on Au- and Ni-coated substrate. It is also can be seen that not all ZnO nanorod array region provide secondary growth site as indicated by flower-like structures selectively growth on nanorod region.
The average of film thicknesses were measured from the cross-sectional view of ZnO film micrographs using FE-SEM. The average thicknesses of ZnO films were found to be ~8.3 µm, ~8.2 µm and ~8.7 µm for Au, Ni and Pt coated glass substrates, respectively.

The proposed growth mechanism of flower-like structures of ZnO is shown in Scheme 1. Step (a) is the growth process of hexagonal rods that bundle together. Step (b) is the hexagonal rods coalescence become a single oval-like structure; step (c) is the oval-like structure rapidly grow and become branching out structures and step (d) is the flower-like structure from hexagonal rods begins to grow at the top of the oval-like structure. These is in good agreement with Li et al. [7] who observed that nanorods grow initially as a bundle but in an independent way and then coalesce, thus finally becoming a single nanorod.

![Scheme 1](image1.png)

**Scheme 1.** Growth mechanism of ZnO flower-like structures: (a) hexagonal rod structures grow as a bundle, (b) oval-like coalescence, (c) oval-like branching out and (d) flower-like structure begins to grow on the top of oval-like structure.

The transmittance spectra are recorded over 300-800 nm. The variations of transmittance with wavelength for ZnO films deposited on different metal coated glass substrates are shown in Figure 3. It is clearly seen that the transmittance value are vary with the different metal coated glass substrate. This is corresponding to the substrate colour appearance as the Au coated glass substrate is yellow in
appearance; Ni coated glass substrate is transparent while Pt coated glass substrate is dark grey in appearance. Low transmittance value is observed for Pt coated glass substrate, 30-54% compared to Au coated, 31-60% and Ni coated with higher transmittance value, 40-79%. It is found that substrate colour appearances are strongly influenced the transmittance values.

The optical band gap energy ($E_g$) can be determined by calculating the absorption coefficient, $\alpha$. It is related to the band gap energy, $E_g$ and photon energy, $h\nu$ as follows, $\alpha = \alpha_o (h\nu - E_g)^n$. Where $\alpha_o$ is a constant, and the exponent of $n = \frac{1}{2}$ is for ZnO which have direct allowed transition. The values of band gap energy ($E_g$) is obtained by extrapolating the linear potion of the curves to $(ah\nu)^2 = 0$. The $E_g$ values for ZnO film were found to be 3.30 eV for Ni coated and 3.29 eV for Au and Pt coated glass substrate. The differences of $E_g$ values obtained were attributed to the changing in their surface microstructures, morphologies of the grown samples and crystallite size [8].

**Figure 3.** A typical transmittance spectra of ZnO films deposited on different metal coated glass substrates at 90 °C for 3 h.

**Figure 4.** Plot of $h\nu$ vs. $(ah\nu)^2$ of ZnO films deposited on different metal coated glass substrates at 90 °C for 3 h.
4. Conclusion
In this work, pure zinc oxide films were successfully produced by aqueous chemical growth method on different metal coated glass substrates at relatively low temperature, 90 °C. XRD patterns show well-defined ZnO peaks without any visible impurities for all samples proved the as-synthesized product is pure. The calculated crystallite sizes are found to be in between 29-32 nm. The results presented in this paper revealed that different types of metal coating have a profound effect on the morphology of ZnO growth using this technique. It has been observed that the as-synthesized ZnO present various interesting morphologies of such as hexagonal rods, flower-like, oval-like and nanorod array. Moreover, the ZnO nanorod array is only observed for Pt coated glass substrate which prove the metal coating have influence on the ZnO morphology. The optical band gap, $E_g$ for ZnO films are found to be around 3.29-3.30 eV which is in good agreement with bulk value of ZnO, 3.37 eV.

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