Optical Characterization Of Co:Zno Films Fabricated By Anodization For Photocatalytic Water Purification

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Abstract*:* While the sixth sustainable development goal to be achieved by 2030 is clean water and sanitation, there is still a global challenge in the supply of adequate clean water due to population growth and urbanization. This necessitates coming up with more affordable approaches of managing waste water. Photocatalytic degradation of pollutants has proved to be one of the promising ways of purifying water. This study aimed at preparing Cobalt doped ZnOfilms to be used in photocatalytic water purification. ZnO films were fabricated by anodization and Cobalt incorporated. Heat treatment was done at 250^0C. Optical characterization was done using a UV-VIS NIR spectrophotometer to obtain reflectance data which aided in determining the optical properties of the films. Data analysis showed a decrease in ZnO reflectance and optical band gap on incorporation of Cobalt. This implied an increase in the absorption of the films which is a fundamental property in photocatalytic water purification. Hence Cobalt doped ZnOfilms have good photocatalytic properties and can be used for photocatalytic water purification.

1. Introduction

Photocatalysishas proved to be one of the most promising techniques for purification of waste water by the chemical utilization of solar energy where hazardous organic pollutants are degraded, Hoffman *et al*., (1995).ZnOwhich is a wide band gap semiconductor with a band gap of 3.31eV has been widely used in designing of diodes, biosensors, as antibacterial agents and photocatalysts because it is cheap, readily available and non-toxic. In photocatalysisit is used to speed up the degradation rate.Its wide band gap however limits its photocatalytic activity hence the need to improve its activity. Metal ions such as Mn^{2+},Cu^{2+},Ag^{2+} and Co^{2+}have been used to alter the optical and photocatalytic properties and Cobalt ions are preferred because their ionic radius(0.745Å)is similar to that of Zinc(0.74Å), Woo *et al*., (2014).ZnO:Co films can be fabricated using different techniques such as spray pyrolysis, sol-gel, sputtering and anodization, Kulkrani and Shirsa (2015).In this study, we seek to fabricate Co:ZnO films by anodizationand characterize them optically consequently its application in photocatalytic water purification since optical properties determine the photocatalytic activity.

The problem

Water is vital for survival of all living things but its pollution is one of the major threats to life.Water pollution has resulted from rapid population growth and urbanization and this threatensthe fundamental human rights, such as the right to life, health, wellbeing, safe work, as well as protections of children and the most vulnerable. The organic pollutants in water are hazardous and cause diseases or death. Because of this global and national threat there is need for cost effective water treatment techniques such as photocatalysis. Although ZnO has been applied in photocatalysis, its band gap is wide resulting in a narrow range of the solar spectrum absorbed. This implies that there is need to narrowits band gap hence improving its photocatalytic activity.

1.1 Objectives

i) To fabricate ZnO thin films by anodization.
ii) To pigment the fabricated ZnO films with Cobalt.
iii) To determine the optical properties of pure and Cobalt pigmented ZnO films by optical characterization.

2. Literature review

In a study of the photocatalytic activity of ZnO nanoparticles synthesized by combustion method done by Nagaraju*et al.,* (2017) who showed the band gap of *ZnO* as 3.29 eV. Photocatalytic results in this study showed ZnO as a promising photocatalytic material.Kuriakose*et al.,*(2014), studied enhanced photocatalytic activity of Co doped *ZnO*nanodisks and nanaorods prepared by wet chemical method and reported that doping *ZnO*nanodisks and nanorods with Co enhanced their photocatalytic activity.Poongodi*et al.,* (2015) stated that Cobalt doped *ZnO* was seen to be more photocatalytic than the pure *ZnO*. They attributed this to the increase in ZnO crystal size when doped with Cobalt.Borhani and Amrollahi (2017) observed a shift in the ZnO band edge towards longer wavelengths on doping with Cobalt. They also reported a decrease in the absorption coefficient with increasing wavelengthand an increase with the extinction coefficient with Cobalt doping.

3. Methodology

Zinc plates of desired size were mirror polished, sonicated in ethanol, rinsed and dried in air. Pure ZnO plates were prepared by anodization method. The schematic diagram for anodization method is shown in figure 1. A constant voltage of 10V was maintained for 60 minutes using 0.5M oxalic acid as the electrolyte, zinc as the working electrode and graphite the counter electrode.This was done at room temperature after which the anodized zinc sheets were rinsed in distilled water and dried in air. Cobalt was electrodeposited in some of the anodized ZnO for 20s and 60 seconds using a 20V ac power supply. Post anodization heat treatment done by heating the plates at 523K for 2 hours.

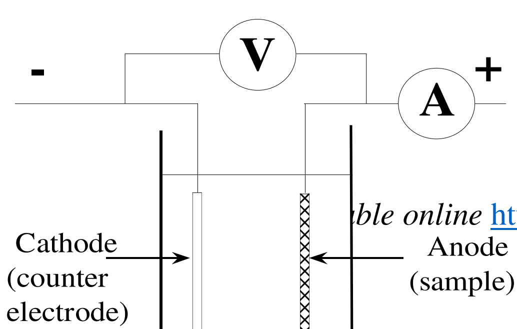

Figure 1: Schematic diagram for anodizationmethod. Nemes*et al.,* (2011)

Optical characterization was done using a perkinelmerUV/VIS/NIR Lambda 19 spectrophotometer equipped with an integrating sphere to evaluate the optical properties of the pure and Cobalt pigmented ZnO films. Reflectance measurement was done in the solar range 300nm < λ < 2500nm. Further data analysis was done using the SCOUT software which aided in the determination of the optical properties of the fabricated films.

4. Results

4.1 Reflectance

Figure 2 shows the spectra for the measured reflectance for the polished Zinc metal before anodization and the as deposited ZnO and Co:ZnO films.

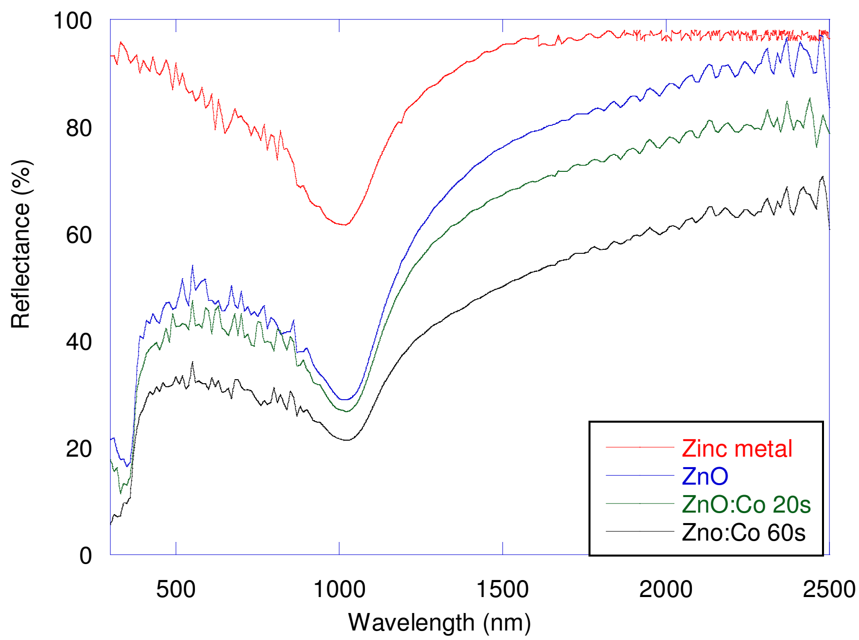

Figure 2: Measured reflectance spectra for polished zinc metal, pure ZnO and Co:ZnO

Polished zinc metal has a higher reflectance more than 60% because of its shiny nature. The reflectance for pure ZnOis higher thanfor Co:ZnO. This can be attributed to the darkening of the ZnO films when they are pigmented with Cobalt. A sharp decrease in the pure and Co:ZnOreflectance is observed at low wavelengths about 348nm. This decrease gives the absorption edge of the films which is agreement with the fact that ZnO absorbs in the UV region of the solar spectrum. The decrease in reflectance of the Cobalt pigmented ZnO films is indicative of an increase in the absorption.

4.2 Absorption coefficient

Figure 3 shows the absorption coefficient as a function of wavelength.

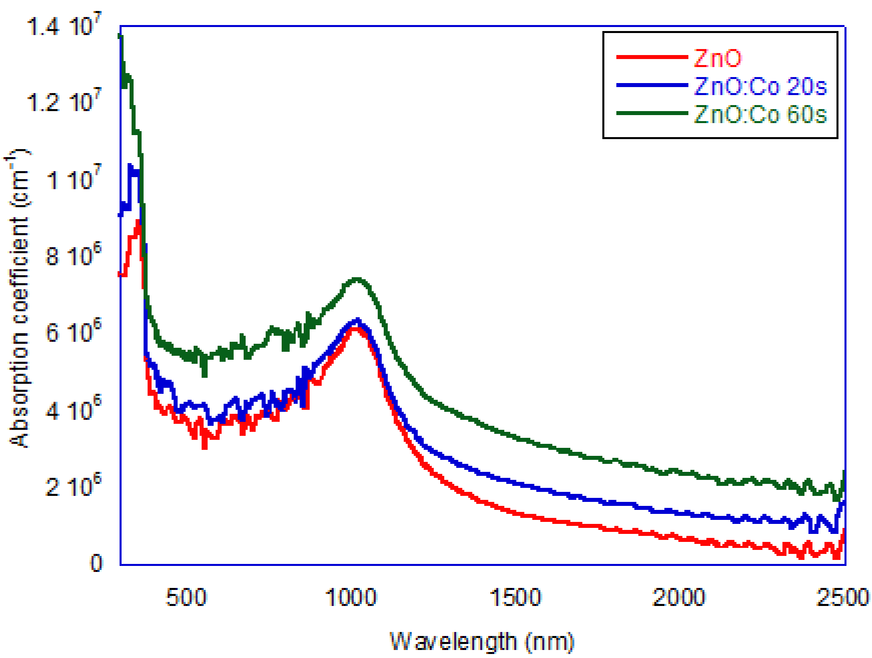

Figure 3: Absorption coefficient as a function of wavelength

The absorption coefficient for the pure and Cobalt pigmented ZnO films is observed to sharply increase at low wavelengths representing the UV region of the solar spectrum. This also further explains the high absorption of ZnO in the UV region due to its wide band gap. Cobalt pigmented ZnO has a higher absorption coefficient in the lower wavelengths than pure ZnO. This is attributed to the decrease in reflectance on pigmenting hence an increase in absorption. At higher wavelengths, the absorption coefficient remains low showing low absorption by the films.

4.3 Band gap

The optical band gap for ZnO which is a direct band gap semiconductor is as shown in figure 4.

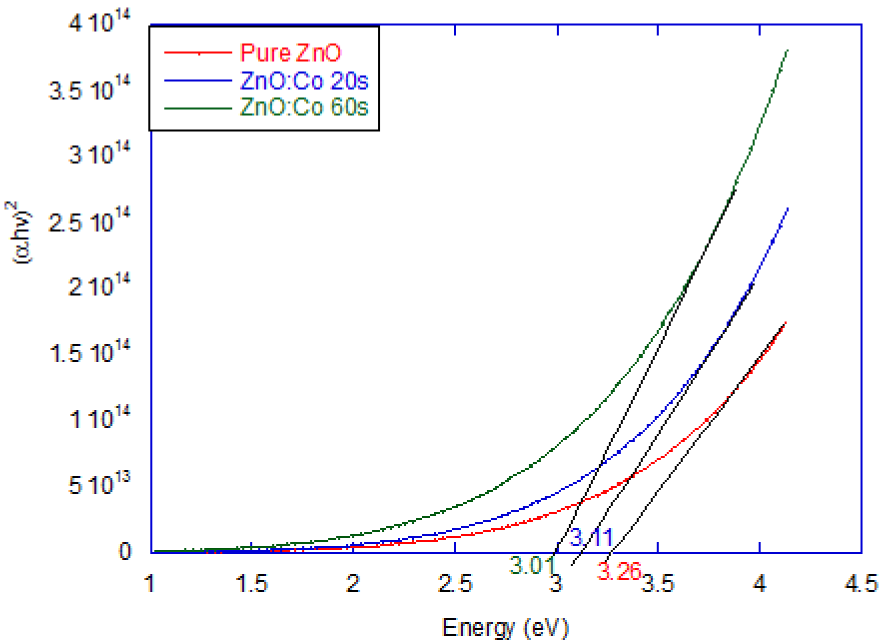

Figure 4: Graph showing the optical band gap of the fabricated films

The optical band gap of pure ZnO is 3.26e V. A decrease in the band gap is observed as the ZnO films are pigmented with Cobalt. The decrease in band gap is an indication of an increase in the absorption of the films as confirmed by the reflectance and absorption coefficient. This is attributed to the red shift in the absorption edge of the ZnO films which results from the Cobalt ions being incorporated into the ZnO crystal structure. This leads to the formation of impurity levels between the ZnO band gap hence narrowing it.

Recommendations

The results obtained and reported in this work show a clear influence of the Cobalt pigmenting on ZnO optical properties. This study was confined to a narrow study of the optical properties. Photocatalysis is also influenced by other factors like the structure and surface morphology. It is therefore recommended that structural characterization of the films be done to confirm the surface morphology and the crystal structure and orientation. This can be studied using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD).

Conclusion

Pure and Cobalt doped ZnO films were successfully fabricated by anodization.Cobalt pigmenting decreases the reflectance of ZnO films hence an increase in absorption while absorption coefficient increases with Cobalt pigmenting and decreases at higher wavelengths.Band gapZnO is narrowed by pigmenting it with Cobalt. The more the Cobalt deposited in ZnO films the more the decrease in band gap.The optical properties of the Cobalt doped ZnO show that ZnOphotocatalysis can be enhanced by pigmenting it with Cobalt.

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