Effect of co doping to the optical properties of ZnO:Co Thin films deposited on glass substrate by sol-gel spray coating technique

Sinta Marito Siagian, Heri Sutanto, Anes Permatasari

Physics Department of Post Graduate Program Diponegoro University,
Jalan Prof. Soedarto, Tembalang, Kota Semarang, Jawa Tengah 50275, INDONESIA

E-mail: sintasiagian@st.fisika.undip.ac.id

Abstract. This study aims are to analyze the effect of cobalt doping concentration to the optical properties ZnO:Co thin films deposited by using sol-gel spray coating technique. Deposition of ZnO and ZnO:Co thin films has been successfully formed on a glass substrate using sol-gel method of spray coating technique with a variation of doping Co as much as 3%, 5%, 7%, 9%, and 11%. Solution of ZnO:Co synthesized by mixing zinc acetate dehydrate (Zn\((\text{COOCH}_3)_2\cdot2\text{H}2\text{O}\) into a isopropanol ((CH\(_3\))\(_2\text{CHOH}\) then monoethanolamine (MEA) and cobalt nitrate are added as a dopant at room temperature, then ZnO:Co sprayed on a glass substrate that has been heated at a temperature of 450°C. A thin film further characterized using spectrophotometer Uv-Vis to determine the value of absorbance and transmittance. Energy band gap was determined by using tauc plot that uses the absorbance value. The results show that there has been a difference in the value of the Energy band gap of ZnO with and without of Co doping. The addition of Co doping causes the decrease of small energy band gap. The magnitude of the energy band gap of thin films of ZnO is 3.337 eV and ZnO:Co 3% is 3.129 eV. Thin film that has narrower band gap was applied for material photocatalyst

1. Introduction
Semiconductors are widely used to study the photocatalysts are metal oxides such as TiO\(_2\), WO\(_3\), ZnO, CDO, In2O3, CdS, CdSe, MoS\(_2\) and WS\(_2\) [1]. Among the wide range of semiconductors, ZnO has attracted the attention of researchers because of the good chemical stability, non-toxic and low cost. Moreover, ZnO can absorb most of the solar spectrum, making it perfect as a photocatalyst [2]. ZnO is n-type semiconductor material with a band gap energy of 3.37 eV and a binding energy of 60 MeV. Narrow band gap is expected to be used as an important application is a photocatalyst [3]. Therefore, changes because of the Co doping played an important role in the photocatalysts. Cobalt (Co) is a transition metal that can be used as a dopant in ZnO having a value Eg 2.4 eV smaller than ZnO.

The Eg value corresponding to the energy at a wavelength of visible light, so it is expected the presence of Co doping on ZnO Eg value will be smaller. Various methods have been used by researchers in the deposition of a thin layer of ZnO: Co is spray pyrolysis [4], sol-gel [6] and co-precipitation [5]. Among these techniques, sol-gel method has advantages such as low cost deposition technique is simple [3], is excellent in controlling the composition, having homogeneity which is high on the molecular level, lowering the temperature of crystallization, and are capable of producing a thin layer ZnO surface area is very spacious compared to other methods [7]. One method that is more
suitable for the manufacture of thin layers is spray coating. Mechanical spray coating is a process in which the coating material (feedstock) as individual particles driven by the flow of pressurized gas to a surface (substrate).

The particles hit the substrate, paste, and forming a thin surface appropriate [8]. Advantages of spray coating technique is the deposition rate is high, it can be done on the atmospheric conditions, as well as environmentally friendly. This study will be conducted by making a ZnO:Co thin films with sol-gel method that is deposited on a glass substrate by thermal spray coating. Further research also studied the effect of the concentration of CO on ZnO to its optical properties such as transmittance, absorbance and band gap.

2. Method
Deposition of ZnO and ZnO:Co thin films has been successfully formed on a glass substrate using sol-gel method of spray coating technique with a variation of Co doping as much as 3%, 5%, 7%, 9%, and 11%. Solution ZnO:Co synthesized by mixing zinc acetate dehydrate (Zn (COOCH$_3$)$_2$.2H$_2$O into a isopropanol ((CH$_3$)$_2$CHOH) then monoethanolamine (MEA) and are added cobalt nitrate as a dopant at room temperature synthesized. The solution was stirred using a magnetic stirrer hot plate at room temperature for 45 minutes to obtain a solution that is clear and homogeneous, then ZnO:Co sprayed on a glass substrate that has been heated at a temperature of 450°C.

3. Results and Discussion
Testing characteristics of the optical properties of ZnO:Co thin films were performed using an UV-Vis spectrophotometer in the wavelength range between 300 nm to 800 nm. The data obtained from this test are processed to obtain the value of the energy band gap of each sample, which can be seen the effect of adding a dopant Co based on its concentration, respectively. To determine band gap can use tauc plot. The energy band gap of ZnO:Co plot the data obtained through direct transition absorption equation. Plot ($\alpha h\nu$)$^2$ vs $h\nu$ by extrapolating the linear part of the curve to zero absorption lines give the energy band gap for direct transitions shown in Figure 1.

![Figure 1](image1.png)  
**Figure 1.** Plot ($\alpha h\nu$)$^2$ vs $h\nu$ for undoped  

![Figure 2](image2.png)  
**Figure 2.** Plot ($\alpha h\nu$)$^2$ vs $h\nu$ for ZnO:Co 11%

The excitation of electrons from the valence band to the conduction band need an energy, energy for excitation through the band gap is the one who called the band gap energy. Cobalt has Eg 2.4 eV smaller than ZnO and these values correspond to the wavelength of visible light energy, so that with the addition of Co dopants Eg value will be small.
Table 1. Values energy band gap undoped and ZnO:Co Thin films

| Thin films   | Band gap (eV) |
|--------------|---------------|
| ZnO:Co (0%)  | 3.337         |
| ZnO:Co (3%)  | 3.129         |
| ZnO:Co (5%)  | 3.125         |
| ZnO:Co (7%)  | 3.117         |
| ZnO:Co (9%)  | 3.108         |
| ZnO:Co (10%) | 3.099         |

Based on the data above was obtained that the higher the concentration of the dopant cobalt energy band gap is getting narrower, with a maximum reduction currently on ZnO: Co (11%) which is 3.099 eV. Narrow band gap is expected to be used for photocatalytic applications [3]. The decline in energy band gap because of their long shifts hypercromic wave in an optical absorption of ZnO [9]. The energy band gap shrinks the less photon energy required to excite the electron. The electrons are generated that has the important role in the application of photocatalysts.

Absorbsivitas molar is characteristic of a substance that informs how much light is absorbed by the dye molecules at specific wavelengths. The greater the value of molar absorptivity of a substance, the more light is absorbed by it, or in other words, the greater the absorbance value.

Figure 3. absorption spectra of ZnO and ZnO:Co thin films with different concentrations

The figure shows the absorbance spectrum of ZnO:Co thin films with different variation of dopan concentration. value is measured using a spectrophotometer obtained without doping 0.2090 at a wavelength of 350 nm, for the increase in doping 3% obtained value of its absorbance was 1.2757 at a wavelength of 362 nm, to 5% obtained value 1.1938 in the wavelength range of 360 nm, for the addition of dopants 7% obtained value 0.9065 in the wavelength range 352 nm, while the concentration of 9% while the observed value is approximately 1.1307 nm, and for the highest concentration of 11% was obtained absorbansi its value is 1.1135 at a wavelength of 350. The different wavelength of absorption caused by increasing dense and regular arrangement of atoms which resulted in the higher value. The highest absorbance peaks were observed in the spectrum at maximum wavelength of 362 nm in exist the blue-shift area, these materials have characteristics could absorb at the wavelengths in this area. Absorbance values were high due to the number of atoms involved in the process of absorption of the light beam with a maximum absorbance value of 1.2757 at
a wavelength of 362 nm to a concentration of 3%. This shows that the concentration of the sample can absorb these higher UV rays. The higher value of the material absorption and more light is absorbed. Transmittance of ZnO:Co thin films can be shown in the figure below.

![Transmittance Uv-Vis of ZnO:Co thin films](image)

**Figure 4.** Transmittance Uv-Vis of ZnO:Co thin films

Based on the picture above can be seen that the highest transmittance in the region of a wavelength of 466 nm with a transmittance value is 83.5% at a concentration 7% is higher than 70% ZnO value.

| Thin Film     | Transmittance (%) |
|---------------|-------------------|
| ZnO:Co (0%)   | 68.5 %            |
| ZnO:Co (3%)   | 74.5 %            |
| ZnO:Co (5%)   | 83 %              |
| ZnO:Co (7%)   | 83.5 %            |
| ZnO:Co (9%)   | 76.3 %            |
| ZnO:Co (10%)  | 70.6 %            |

The transmittance is expected to decrease due to the three factors: oxygen deficiency, surface roughness and impurity centers. Thus, these transitions suggest that Co$^{2+}$ ions are substituted at the Zn$^{2+}$ ions in the ZnO lattice [10].

4. **Conclusions**

Based on the data was obtained that the higher the concentration of the dopant cobalt energy band gap is getting narrower, with a maximum reduction currently on ZnO:Co (11%) which is 3.099 eV. The energy band gap shrinks the less photon energy required to excite the electron. The electrons are generated that has the important role in the application of photocatalysts. Absorbance values were high due to the number of atoms involved in the process of absorption of the light beam with a maximum absorbance value of 1.2757 at a wavelength of 362 nm to a concentration of 3%, This shows that the concentration of the sample can absorb these higher UV rays.

**References**

[1] Djarwanti., Cholid, S., Yuniati, A., 2009, journal of research industry 3 (2), 109-117.
[2] Kaur J, Singhal S, 2013, *Ceramics International* **40**, 7417–7424.
[3] Poongodi G, Anandan P, Kumar R M, Jayavel R, 2015, *Molecular and Biomolecular*
Spectroscopy 148, 237–243.

[4] Benramache S, Temam H B, Arif A, Guettaf A, Belahssen O, 2014, Optik 125, 1816-1820
[5] Kumar S, Song T K, Gautam S, Chae, K H, Kim S S, Jang K W, 2015, Material research 66, 76-82.
[6] Ashraf R, Riaz S, Bashir M, Naseem S, 2013, Advance in nano biomechanics robotics and energy research (ANBRE 13).
[7] Efendi N H, Sutanto H, 2014, Youngster Physic Journal 3 (2), 135-142.
[8] Surono, A T, Sutanto, 2014, Youngster Physics Journal 2 (1), 7-14.
[9] Ullah R, Dutta J, 2008, Journal of Hazardous Materials 156, 194–200.
[10] Rajendar V, Dayakar T, Shobhan K, Srikanth I, Venkateswara R, 2014, Superlattices and Microstructures 75, 551-563