The thickness effect to optical properties of SnO$_2$ thin film with doping fluorine

Susilawati$^{1,2}$, A Doyan$^{1,2}$, L Muliyadi$^1$, S Hakim$^1$ and M Taufik$^2$

$^1$Master of Science Education Program, University of Mataram, Lombok, West Nusa Tenggara, Indonesia
$^2$Physics Education, FKIP, University of Mataram, Lombok, West Nusa Tenggara, Indonesia

*susilawatiambali@unram.ac.id

Abstract. Synthesis of SnO$_2$F thin layer was grown using the sol-gel spin coating method on a glass substrate with various layers (one to four layers). The purpose of the synthesis was to determine the optical properties of thin layers including transmittance, absorbance, energy bandgap, and activation energy. The optical properties of the layers were characterized using UV-Vis spectrophotometers with a wavelength of 200-1100 nm. The results showed that at a wavelength of 300 nm the absorbance value decreased with an increasing number of layers. Absorbance values obtained for variations in layers (one to four layers) for the percentage of 95:5% and 75:25%, respectively 3.59-2.85 and 4.30-3.42, while the transmittance value decreased, namely 96.8-79.6% and 97.3-81.1%. Besides, the energy bandgap obtained decreases with an increasing number of layers. The energy bandgap decreased from 3.69-3.56 eV and 3.59-3.42 eV for direct allowed, while 4.00-3.91 eV and 3.96-3.83 eV for indirect allowed. Activation energy decreased from 0.23-0.07 eV and 4.35-1.43 eV.

1. Introduction

Tin oxide (SnO$_2$) is one of the nano-sized materials including semiconductor materials. SnO$_2$ is widely used as a base for solar cells [1] transparent conductive oxide [2] and gas sensors [3]. SnO$_2$ has several advantages, which have high transparency [4], are very sensitive to the gas presence [5] and bandgap of around 3.7 eV [6].

In its application, SnO$_2$ absorbs a lot in small waves because it has a fairly wide energy bandgap. Based on these factors, dopant substances need to be added to SnO$_2$. SnO$_2$ is usually doped with indium [7], fluorine [8], and aluminum [9]. Of the three doping elements, fluorine has the advantage of being more chemically resistant, easier to obtain so that its price is low [10], heat resistant [11] and can improve the response to gas sensors [12].

Factors that influence the quality of the thin layer produced in beside the addition of doping are the preparation methods and growth conditions of the layers. Preparation and growth methods for SnO$_2$ layers, both pure and doping additives, have been carried out by several previous researchers such as sol-gel spin coating [13], spray pyrolysis [14] and sol-gel dip-coating [15]. The method of sol-gel dip coating is the simplest technique, but the formed layer is less homogeneous. The spray pyrolysis method has several advantages, namely uniform and homogeneous size, but the morphology of the
hollow and uneven layers. Compared to the three techniques, the sol-gel spin coating has more advantages, namely effective and evenly formed and not hollow layers [16].

2. Method
Making this thin layer uses a ratio of the total mass of SnCl$_2$.2H$_2$O and NH$_4$F, namely (95:25% and 75:25%). The material is dissolved in 20 ml ethanol with a fixed concentration of 1 M using a magnetic stirrer until homogeneous, then matured for 24 hours to form sol-gel. The sol-gel was rotated using a spin coater at a speed of 2000 rpm for 3 minutes, then heated at a temperature of 100°C. The layer made consists of first until fourth layers. The formed layer was characterized using UV-Vis Thermo Scientific Genesys 150 spectrophotometer with a wavelength of 200-1100 nm.

3. Result and discussion
The optical characteristics of SnO$_2$:F thin films were carried out using UV-Vis Spectrophotometer. The results obtained from these optical characteristics include transmittance, absorbance, energy bandgap, and activation energy. Figures 1 and 2 show the shape of a SnO$_2$:F thin layer for variations in layers. Figures 1 and 2 show that as the number of layers increases, the color of the object behind the layer fades.

![Figure 1. Thin layer SnO$_2$:F (95:5%) variations of layer (a) 1 layer, (b) 2 layers, (c) 3 layers, (d) 4 layers](image)

![Figure 2. Thin layer SnO$_2$:F (75:25%) variations of layer (a) 1 layer, (b) 2 layers, (c) 3 layers, (d) 4 layers](image)

3.1. Transmittance
Graph of the relationship between the wavelength and the transmittance of the thin layer SnO$_2$:F variations of the layer are shown in the following figure.
Figure 3. Graph of wavelength relationships with a transmittance of thin layer SnO$_2$:F variation of layer (a) 95:5%, (b) 75:25%.

Figure 3 shows that the transmittance value for various layers in the wave range of 300-800 nm. The transmittance values for first until fourth layers are 95:5% and 75:25%, respectively 96.8-79.6% (figure 3a) and 98.3-81.1% (figure 3b). This means that the more the number of layers, the smaller the transmittance value produced but increases with the increase in the amount of fluorine doping. In general the greater the length of the wave causes the photons transmitted in the thin layer SnO$_2$:F to increase. This is because the larger the number of layers the larger the size of the grain, the bigger the scattered photons. Besides, the more the number of layers, the transparency level of the layer decreases [17].

3.2. Absorbance

Graph of the relationship between wavelength and absorbance of SnO$_2$:F variations of the layer is shown in Figure 4.

Figure 4. Graph of the relationship of wavelengths with the absorbance of thin layers of 2: F variations of the layer. (a) 95: 5%, (b) 75: 25%.
In this picture, we can see the difference in the absorbance value of SnO$_2$:F thin layer for variations in layers. The maximum absorbance values for coating variations are first until the fourth layers for the percentage of 95:5% and 75:25% in the ultraviolet region with a wavelength of 300 nm, respectively 3.59-2.85 (figure 4a) and 4.30-3.42 (figure 4b). Based on figure 4, it is clear that the more the number of layers, the absorbance value produced is smaller, especially in the ultraviolet region with a wavelength of 300 nm, but increases with the increase in the amount of fluorine doping. In general, the absorbance value decreases with an increasing number of layers [18].

3.3. Bandgap energy
The energy bandgap is obtained by making a linear line from the graph of the relationship between a photon ($h\nu$) and $(a(h\nu))^{n}$, with $n = \frac{1}{2}$ for direct allowed and $n = 2$ for indirect allowed [19]. The absorption coefficient value ($a(\nu)$) and the energy bandgap value can be obtained from equations 1 and 2.

\begin{align*}
\alpha(\nu) &= \frac{2.303A}{t} \tag{1} \\
\alpha(\nu)h\nu &= B(E_f - E_g)^n \tag{2}
\end{align*}

Where: $A =$ absorbance, $t =$ thickness, $B =$ A constant, $E_f =$ Energy photon, $E_g =$ energy bandgap, $h =$ Planck’s constant. Based on equation 2 obtained energy bandgap direct and indirect allowed layer SnO$_2$:F with the Tauc plot method such as figures 5 and 6.

**Figure 5.** Energy bandgap direct allowed thin-film SnO$_2$:F. (a) 95:5%, (b) 75:25%.

**Figure 6.** Energy bandgap indirect allowed thin-film SnO$_2$:F. (a) 95:5%, (b) 75:25%.
The value energy bandgap direct and indirect allowed is shown in Figure 7 below.

![Figure 7. Relationship between layers variation with SnO$_2$:F thin band energy bandgap. (a) 95:5%, (b) 75:25%.

Figure 7 above shows that the bandgap energy value for layer variations. The value of the bandgap energy values for first until fourth layers for the percentage of 95:5% and 75:25% respectively 3.69-3.56 eV (figure 7a) and 3.59-3.42 eV (figure 7b) for direct allowed, while 4.00-3.91 eV and 3.96-3.83 eV for indirect allowed. The obtained energy bandgap has decreased with an increasing number of layers and the percentage of fluorine doping [20, 21].

3.4. Activation energy
Activation energy is the minimum energy needed by SnO$_2$ and Fluorine for chemical reactions. Activation energy is determined by the slope of the straight line ln ($\alpha$) versus photon energy ($h\nu$). The value of ln ($\alpha$) is obtained from equation 3.

$$\alpha(\nu) = \alpha_0 \exp \left( \frac{E_f}{E_u} \right)$$  \hspace{1cm} (3)

Where $E_f$ = photon energy, $\alpha_0$ = constant, and $E_u$ = Urbach energy. The values of Ln ($\alpha$) and activation energy are shown in figures 8 and 9.

![Figure 8. Graph of the relationship between photon energy and ln ($\alpha$) SnO$_2$:F variation of the layer. (a) 95:5%, (b) 75:25%.

\[ R^2 = 0.0182 \]
\[ R^2 = 0.9187 \]
Based on figure 9 the activation energy was obtained for first until fourth layers percentage 95:5% and 75:25%, respectively 0.23-0.07 eV and 4.35-1.43 eV. In general, activation energy decreased with an increasing number of layers and the percentage of fluorine doping. This shows that the electron mobility increases which causes the electron transfer from the valence band to the conduction band to increase [22].

4. Conclusions
The optical properties of SnO$_2$:F thin layers include absorbance, transmittance, energy bandgap, and activation energy. In the ultraviolet region with a wavelength of 300 nm the absorbance value increases with the addition of fluorine doping but decreases with increasing number of layers, while the transmittance value increases at a wavelength of 350 nm up to 800 nm (ultraviolet-visible) as the amount of fluorine doping increases and decreases along with the increasing number of layers. Besides, the energy bandgap and activation energy obtained decrease with an increasing percentage of fluorine doping and the number of layers.

5. References
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\[ y = 0.0494NL + C \quad R^2 = 0.9258 \]

\[ y = 0.9477NL + C \quad R^2 = 0.9733 \]
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