Characteristics and Optical Properties of Fluorine Doped SnO$_2$ Thin Film Prepared by a Sol–Gel Spin Coating

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Abstract. This study aims to determine the optical properties of thin films which include absorbance, transmittance, energy band gap, and activation energy characterized by UV-Visible spectrophotometer (UV-vis) with a wavelength of 200-1100 nm. Tin dioxide (SnO$_2$) films are prepared by doping various Fluoride ion (F$^-$) concentrations (0, 5, 10, 15, 20 and 25%) on glass substrates using the sol-gel spin coating method. The absorption edge of SnO$_2$ thin films was found to accrue from 2.90 to 4.41 at 300 nm wavelength when the F$^-$ doped concentration increased from 0 to 25%. Furthermore, the transmittance also increased from 65.5 to 97.8% towards the wavelengths from 300 to 350 nm. However, the band gap and activation energies obtained decreased with a percentage increase in fluorine doping. The energy band gap decreased from 3.55-3.41 eV and 3.90-3.84 eV for direct as well as indirect allowed respectively, while the activation energy decreased from 4.04-1.99 eV. The band-gap energy of SnO$_2$ thin films also decreased, and the electrons adjustment from the valence to conduction band caused the conductivity of the film to increase.

1. Introduction

Tin Oxide (SnO$_2$) is a semiconductor material with high conductivity [1], with its optical transparency high in invisible regions [2] and an energy band gap of 3.7 eV [3]. The substance is widely used as a base for the manufacture of gas sensors [4], transparent conductive oxide (TCO) [5], solar cells [6], touch screens [7], and transistors [8]. In its application, SnO$_2$ only absorbs small waves [9] due to its large energy gap. To reduce this, it was necessary to add dopant ingredients such as zinc [10], indium [11], aluminium [12], and fluorine [13]. However, of these doping elements, fluorine is the best of all as it is widely abundant in nature [14] resistant to heat [15], structural change and reduces energy band gap [16].

Various method has been previously used to grow SnO$_2$ thin films by researchers such as sol-gel spin coating, spray pyrolysis [17], and magnetron sputtering [18]. However, out of these three techniques, the excess spin coating sol-gel was the most effective and able to form a homogeneous film [19].
thin layer of SnO$_2$ with doping fluorine grown with the spray pyrolysis method has the disadvantage that the formed layer is not homogeneous and cracks occur after being heated. Based on this description, research on the thin film of fluorine-doped SnO$_2$ was carried out using the sol-gel spin coating technique.

2. Experimental

SnO$_2$ thin films were obtained by sol-gel spin coating on glass substrates using Tin (II) Chloride Dehydrate (SnCl$_2$.2H$_2$O) as the base, Ammonium Fluoride (NH$_4$F) as a doping material and Ethanol (C$_2$H$_5$OH) was the solvent. Glass measures 10 × 10 × 3 mm was used to grow layers or substrates, while other materials such as distilled water and Ethanol were used for cleaning substrates. The ratio of the total mass of SnCl$_2$.2H$_2$O to NH$_4$F was 100:0 to 75:25% [20] after both were mixed and dissolved in 20 ml ethanol under a magnetic stirrer for two days to form a gel. Furthermore, the total mass of SnCl$_2$.2H$_2$O was kept between 4.515 to 3.386 g, while the amount of NH$_4$F was kept between 0 to 0.185 g. A spin coater was then used to properly mix the gel at 3000 rpm for 3 minutes and dried at room temperature. The layer formed was characterized by UV-Visible Thermo Scientific Genesys 150 spectrophotometer with a wavelength of 200-1100 nm.

3. Result and Discussion

The optical characteristics of SnO$_2$ and SnO$_2$: F thin films were carried out using UV-Vis Spectrophotometer. The results obtained include absorbance, transmittance, energy band gap, and activation energy. While the wavelength range from 200 to 1100 nm. Figure 1 shows the thin film variation of SnO$_2$:F 100:0, 95:5, 90:10, 85:15, 80:20 and 75:25 %.

![Figure 1. Thin film of SnO$_2$:F (a) 100:0%, (b) 95:5%, (c) 90:10%, (d) 85:15%, (e) 80:20%, (f) 75:25 %](image)

![Figure 2. Spectra of absorbance of SnO$_2$ and SnO$_2$:F for different doping concentration.](image)

![Figure 3. Spectra of transmittance of SnO$_2$ and SnO$_2$:F for different doping concentration.](image)

3.1. Absorbance

Graph of the wavelength relationship and difference with the absorbance of thin films SnO$_2$ and SnO$_2$:F is shown in Figure 2. Furthermore, the maximum absorbance value for doping percentage of fluorine 0,
5, 10, 15, 20, and 25% in the ultraviolet region with a wavelength of 300 nm of 2.90-4.41 was also displayed. Based on Figure 2, it was clear that the higher the doping percentage, the greater the absorbance value produced, especially in the ultraviolet region with 300 nm waves. In general, the absorbance value increases with rising in fluorine doping value. This result was consistent with the study [21], which states that fluorine doping increases the absorbance value of thin films. This is because, in the fundamental transition area, photons were absorbed by electrons and moved from the valence to the conduction band [22].

3.2. Transmittance
Graph of the relationship of wavelength with the transmittance of the films of SnO$_2$ and SnO$_2$:F shown in Figure 3. Based on it, the transmittance value for doping percentage of fluorine was 0, 5, 10, 15, 20 and 25% in the wave range of 300-350 nm (ultraviolet region) and 65.5-97.8%, respectively. This means that the higher the doping percentage, the greater the transmittance value in the area. However, in the wavelength range of 350-800 nm (ultraviolet-visible), the transmittance was constant, because the photons with energy smaller than the band gap, was unable to excite electrons, therefore, the photons were only transmitted [23]. Furthermore, in the fundamental transition area, photons were absorbed by electrons and moved from the valance to the conduction band. The transmittance value of a film was also related to its crystal quality. The sharp plot of the transmittance chart edge shows that the crystal quality of the film was getting better. Besides being influenced by the quality of the crystal film, the transmittance value was also influenced by doping or impurity, which was the presence of fluorine as doping [24].

3.3. Energy Band Gap
The amount of energy band gap is obtained by making a linear line from the graph of the relationship between photon ($h\nu$) as the X and ($a(h\nu)$)$^m$ axis as Y, with $m = \frac{1}{2}$, 3/2 for direct forbidden, and 2 indirect allowed with values of 1/3 for indirect allowed [25]. The absorption coefficient value ($a(\nu)$) and the energy band gap value are obtained from the following equations 1 and 2.

$$a(\nu) = 2.303 \frac{A}{d}$$

$$a(\nu)h\nu = B(E_f - E_g)^m$$

Where $A$ is absorbance, $B$ is a constant, $d$ is sample thickness, $E_f$ is the energy of the photon, $E_g$ is energy band gap, and $h$ is Planck's constant. Based on equation 2, the obtained energy band gap direct allowed by thin films of SnO$_2$ and SnO$_2$: F with the Tauc plot method is shown in Figure 4.
Figure 4. Energy band gap direct allowed by SnO$_2$ and SnO$_2$:F. (a) 100:0, (b) 95:5, (c) 90:10, (d) 85:15, (e) 80:20, and (f) 75:25%.
Figure 5. Energy band gap indirect allowed SnO$_2$ and SnO$_2$:F. (a) 100:0, (b) 95:5, (c) 90:10, (d) 85:15, (e) 80:20, and (f) 75:25%.

The energy band gap value of the direct and indirect allowed obtained shown in Figures 6 and 7.
Based on Figures 6 and 7, the concentrations of fluorine doping (0, 5, 10, 15, 20 and 25%), and energy band gap were 3.55, 3.50, 3.47, 3.45, 3.44 and 3.41 eV respectively for direct allowed, while 3.90, 3.89, 3.88, 3.87, 3.85 and 3.85 eV were for the indirect. The energy band gap obtained has decreased along with the addition of fluorine doping. This means that the higher the percentage of fluorine doping, the smaller the energy band produced which accelerates the electrons to move from the valence to the conduction band so that the conductivity of the film increases and used as a semiconductor material. Also, the added fluorine doping tends to affect the optical properties of SnO\textsubscript{2} thin films by reducing the value of the energy band gap. This is caused by the width of the band built by the localization state in each film. This means that the more doping used, the growing film causes the greater randomness fraction of the structure and content of the constituent impurity elements [26].

3.4. Activation Energy

The activation energy is the minimum energy needed for chemical reactions to occur. It is shown in figures 8 and 9 along with \(\ln(\alpha)\).

The activation energy was determined by the slope of the straight line \(\ln(\alpha)\) versus photon \((h\nu)\). The value of \(\ln(\alpha)\) is obtained from equation 3.

\[
\alpha(\nu) = \alpha_0 \exp\left(\frac{E_f}{E_u}\right)
\]  

\(\text{Figure 6. Relationship between percentage of dopants with energy band gap direct allowed}\)

\(\text{Figure 7. Relationship between percentage of dopants with energy band gap indirect allowed}\)

\(\text{Figure 8. Relationship between percentage of dopants with } \ln(\alpha)\)

\(\text{Figure 9. Relationship between percentage of dopants with activation energy}\)
Where the photon, $\alpha_0$ was a constant, and $E_u$ was Urbach energy. The activation energy values obtained for fluorine doping concentrations were 0, 5, 10, 15, 20 and 25%, which was 4.04, 3.71, 2.96, 2.66, 2.23 and 1.99 eV, respectively. In general, it decreased with increasing value of fluorine doping. This means that the energy needed to carry out a chemical reaction was smaller as the percentage of fluorine doping increases. Furthermore, the energy required to create a reaction between SnO$_2$ and fluorine was smaller. This shows that the rate of electrons from the valence band to the conduction band, thereby increasing the conductivity of the films, which is also used as a semiconductor material.

4. CONCLUSION

The optical properties of SnO$_2$ and SnO$_2$:F thin films with spin coating sol-gel method include absorbance, transmittance, energy gap band, and activation energy. In the ultraviolet region using a wavelength of 300 nm, the absorbance value increases with the addition of fluorine dopants, while the transmittance value increases at a wavelength of 350 to 800 nm area (ultraviolet-visible). Also, the band gap and activation energies obtained decreases with an increase in the percentage of dopant fluorine. The decreasing energy gap accelerates the electrons to move from the valence to the conduction band, thereby increasing the conductivity of the films, which is also used as a semiconductor material.

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