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Morphological Characterization and Optical Properties of CIGS/TiO_2 Thin Films Using Sputtering Technique

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ABSTRACT

Solar energy as a renewable energy source, is currently an important alternative to meet energy needs because of its unlimited amount and environmentally friendly. Almost the entire surface of the earth receives sunlight optimally, so breakthroughs are needed to transform the solar energy into electricity. In the research development process that was to develop advanced materials to support the development of alternative energy. Thin film synthesis was carried out using the Physical Vapor Deposition (PVD) of Direct Current (DC) Sputtering method on Indium Tin Oxide (ITO) substrates using Copper Indium Gallium Selenide (CIGS) and TiO_2 with deposition time variations of 30, 45, and 60 minutes. Based on the test results, thin film surface with the largest grain size is 266.75 nm at CIGS/TiO_2 45 minutes. This shows that more CIGS and TiO_2 atoms are released from the target surface, forming clumps that cover the substrate surface along with the addition of deposition time. The longer the deposition time shows the higher the absorbance value. The highest absorbance value is 4.60873, which was achieved by 60 minutes CIGS/TiO_2 sample with wavelength of 271 nm.

KEYWORDS: *CIGS, TiO_2, PVD Sputtering, Thin Film, Solar Cell.*

NOMENCLATURE

PVD	Physical Vapor Deposition
DC	Direct Current
ITO	Indium Tin Oxide
CIGS	Copper Indium Gallium Selenide
TiO_2	Titanium Dioxide
DSSC	Dye-Sensitized Solar Cells
SEM	Scanning Electron Microscopy
UV-Vis	Ultraviolet Visible

1.0 INTRODUCTION

Solar energy can be converted into electrical energy through a device called solar cells. Solar cells convert solar energy into electrical energy following the photovoltaic principle, by absorbing photon energy at a certain wavelength that will excite some electrons in a material to the outermost energy band [1]. There are several types of solar cells including silicon solar cells, thin film combinations of groups I-III-IV such as CIGS, and solar cells made of organic materials or dye sensitized solar cells (DSSC) [2].

Silicon-based solar cells have a 23% efficiency, but this material is ecologically unfriendly and has significant production costs. DSSC is more environmentally friendly, but has limited efficiency and has not been mass produced [3]. Meanwhile, CIGS solar cells have high efficiency and absorption capacity, durable, can be made on a large scale, and more cost-effective than silicon solar cells [4]. Copper Indium Gallium Selenide (CIGS) is a semiconductor used as a light-absorbing agent in solar cells and has a direct band gap of 1.04-3.50 eV [5]. CIGS also has a high absorption coefficient, good radiation levels and properties. In addition, CIGS with stable characteristics against photo degradation makes CIGS a candidate that can be mass-produced [6].

Currently, various methods have been developed in the manufacture of CIGS films such as co-evaporating, sputtering, electrodeposition, spin coating and heating [7]. Based on these methods, sputtering is the most superior method because it produces efficiency, uniformity of microstructure and good electrical properties [8]. A research that researcher have done previously was using the sputtering method for different time variations and it showed that the longer the deposition time, the larger the grain size produced. This was because more particles were distributed over the surface of the substrate, so clumps were formed covered the surface and produced good adhesion from the layer to the substrate [9]. Heating during sputtering facilitates the adhesion of CIGS particles to the substrate and promotes the production of CIGS crystalline particles [10]. Besides, titanium dioxide (TiO_2) is frequently employed in solar energy applications. This material's advantages include high efficiency, ease of manufacture, low cost, non-toxicity, and long-term durability [11]. TiO_2 has a higher photocatalytic activity than other photocatalysts like ZnO, CdS, WO_2, and SnO_2. This is due to its suitable band gap, which allows electrons to be excited into the conduction band and holes to form in the valence band when exposed to ultraviolet light. This material is resistant to photodegradation and can effectively absorb light and UV rays [12].

This study aims to obtain a thin layer of solar cells on the morphology and optical properties of ITO substrates with CIGS and TiO_2 with variations in TiO_2 deposition time of 30, 45, and 60 minutes.

2.0 RESEARCH METHOD

2.1 ITO Substrate Preparation and Deposition Process

The preparation to testing process in this study is outlined in Figure 1. This flow diagram illustrates the sequential steps involved, from the initial stage to the final testing phase. By following this process, a systematic and efficient approach is ensured for conducting the research.

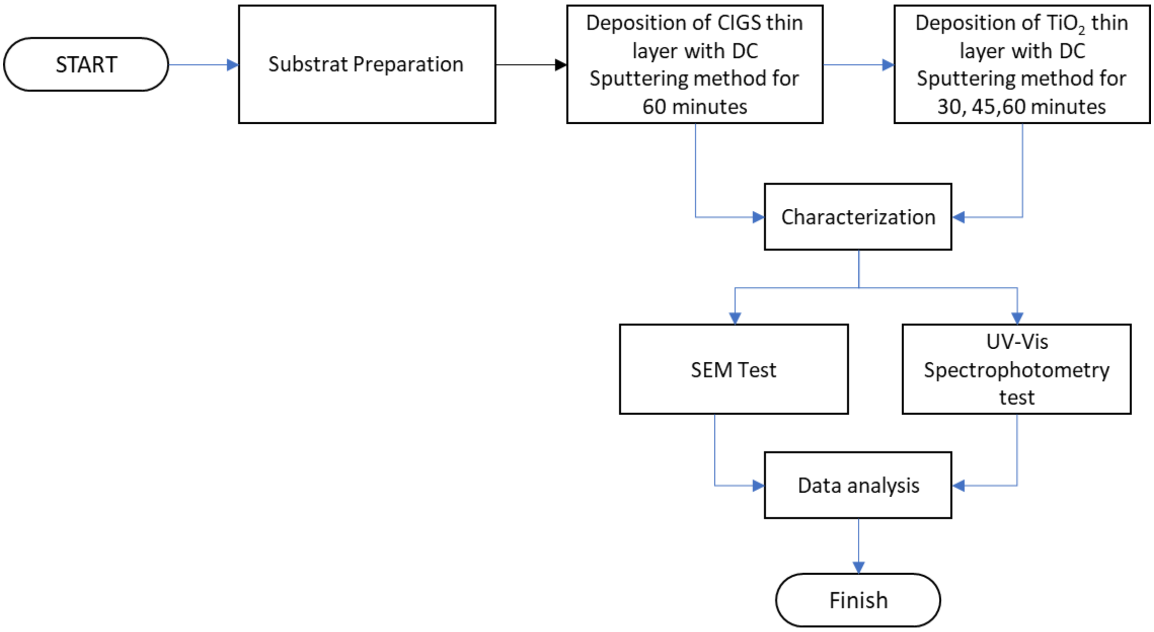

Figure 1: Research flow diagram

The deposition process commenced with the meticulous preparation of the ITO substrate. To eliminate any contaminants, the substrate was subjected to an alternating cleaning process using an alcohol solution. This cleaning process was further enhanced by immersing the substrate in an ultrasonic cleaner bath for the duration of 5 minutes. The substrate was then thoroughly dried using a clean, dry tissue to ensure a pristine surface for subsequent deposition steps.

The deposition process began with the meticulous preparation of the device. To ensure a clean environment, the device was subjected to a pre-vacuum stage, where the pressure was set to 2 x 10^{-2} torr for 15 minutes. Following this, argon gas was introduced into the chamber, maintaining a pressure of 2.5 x 10^{-2} torr. The subsequent deposition process utilized PVD DC Sputtering. Initially, a CIGS target material was deposited for 60 minutes, forming the first layer. This deposition was carried out at the energy of 5 kV and a current of 20 mA. After the formation of the first layer, the deposition process continued with a TiO2 target material. To investigate the impact of deposition time, three variations were implemented: 30, 45, and 60 minutes. The visual results of this deposition process are presented in Figure 2.

The deposition process resulted in a matte black coloration of the substrate. A notable observation was that as the deposition time increased, the resulting substrate exhibited a darker and shinier appearance. This trend is visually depicted in Figure 3.

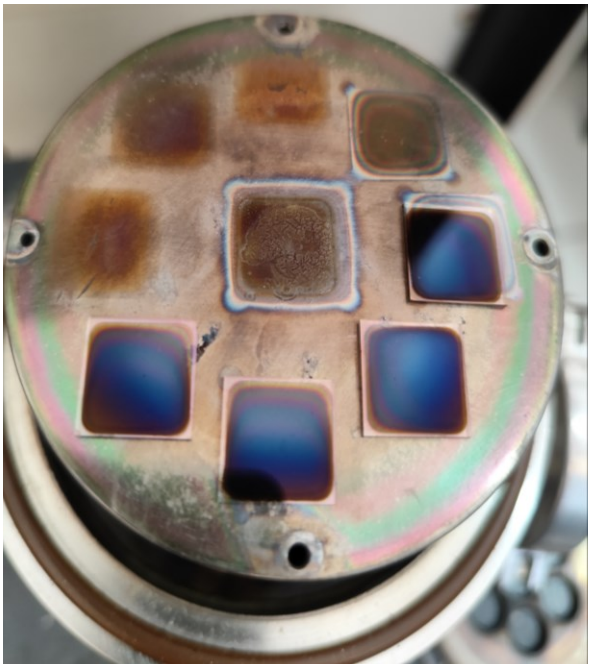

Figure 2: Results of the deposition process on the substrate

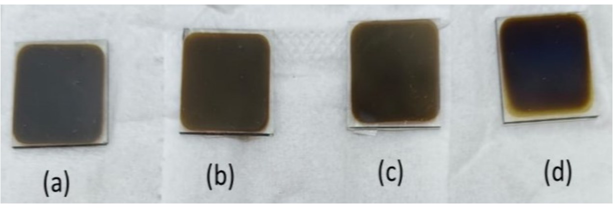

Figure 3: (a) CIGS layer, (b) 30 min CIGS/ TiO_2 layer, (c) 45 min CIGS/TiO_2 layer, and (d) 60 min CIGS/ TiO_2 layer.

2.2 Testing Process

The testing stage on the substrate that has been coated with CIGS and TiO_2 is carried out using Scanning Electron Microscopy (SEM) and UV–Vis Spectrophotometry tests.

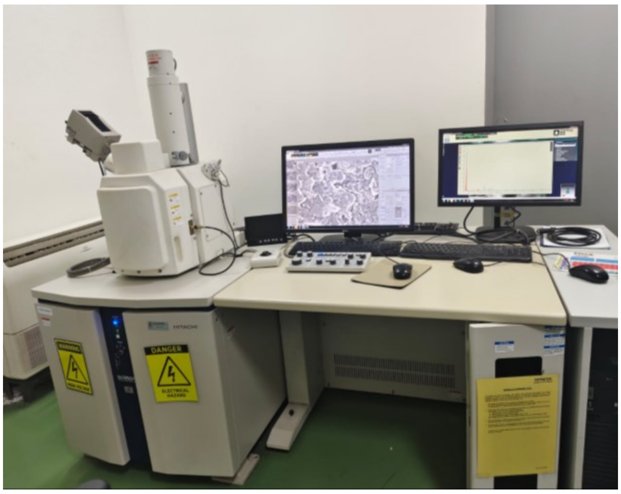

Figure 4. Testing process using SEM

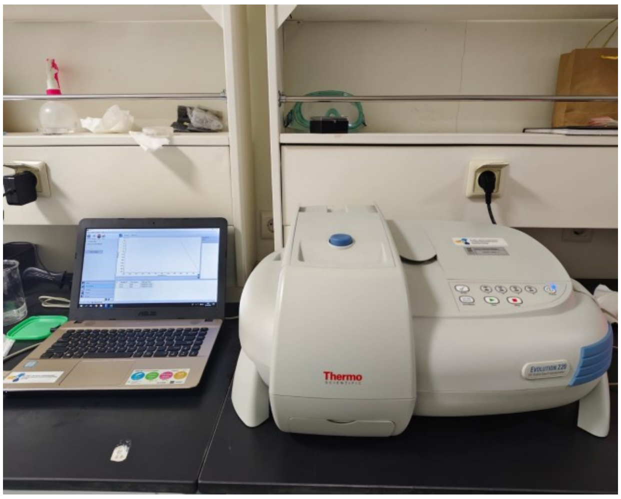

Figure 5: Testing process using UV-Vis Spectrophotometry

SEM testing was conducted using Scanning Electron Microscopy (SEM) type SU3500. The basic principle of SEM is to shoot an electron beam through an electron gun towards the sample and detect the interaction between the specimen and the electron beam in order to determine the surface morphology as shown in Figure 4. The sample used was an ITO sample measuring 1.5 x 1.5 cm which had been coated with CIGS and TiO2. The sample's surface was observed to determine the morphology, grain size and composition of the layer. The calculation of grain measurements was carried out using a magnification of 20,000x. Furthermore, from the visible image, the composition calculation was carried out using EDX (Energy Dispersive X-Ray) to determine the composition of the elements produced from the layer on the substrate surface.

The UV-Vis spectrophotometry testing was carried out at the Nanoscience and Nanotechnology Research Center, Bandung Institute of Technology (ITB), utilizing a UV-Vis spectrophotometer model 220. This instrument operates within the ultraviolet and visible light (UV-Vis) regions of the electromagnetic spectrum. For this study, absorbance measurements were performed across a wavelength range of 200-800 nm, ensuring comprehensive data capture within the specified spectral range

The testing procedure involved systematic calibration and sample preparation to ensure precise measurements. As illustrated in Figure 5, the process included the alignment of the sample within the spectrophotometer and the acquisition of absorbance spectra over the designated wavelength interval. This approach facilitated the accurate determination of material properties based on their interaction with UV-Vis light.

3.0 RESULT AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM) Test Results

Scanning electron microscope (SEM) is a tool used to analyze the surface or morphology of samples with a certain magnification. In this study, a magnification of 20,000x was used. The results of the CIGS morphological structure appear as in Figure 6.

Based on the results of the top view morphology analysis, it shows different CIGS/ TiO_2 coating results. The results are distinguished based on the TiO_2 deposition time at 30, 45, and 60 minutes. Figure 5 (a), (b), (c), (d) shows that the CIGS coating without TiO_2 shows an inhomogeneous surface. While the CIGS/TiO_2 coating with a deposition time of 30 minutes produces a denser, smoother and more homogeneous sample surface. This condition indicates that small particles stick together tightly [13]. Then for the CIGS/ TiO_2 layer with a deposition time of 45 minutes shows that CIGS and TiO_2 nanoparticles were successfully deposited on the sample surface and more CIGS and TiO_2 atoms were released from the target surface, forming clumps that cover the substrate surface [9]. On the substrate surface with a CIGS/ TiO_2 layer with a deposition time of 60 minutes, larger clumps of CIGS and TiO_2 atoms appeared. As previously reported [14] defects in the CIGS layer will decrease when large crystals are formed.

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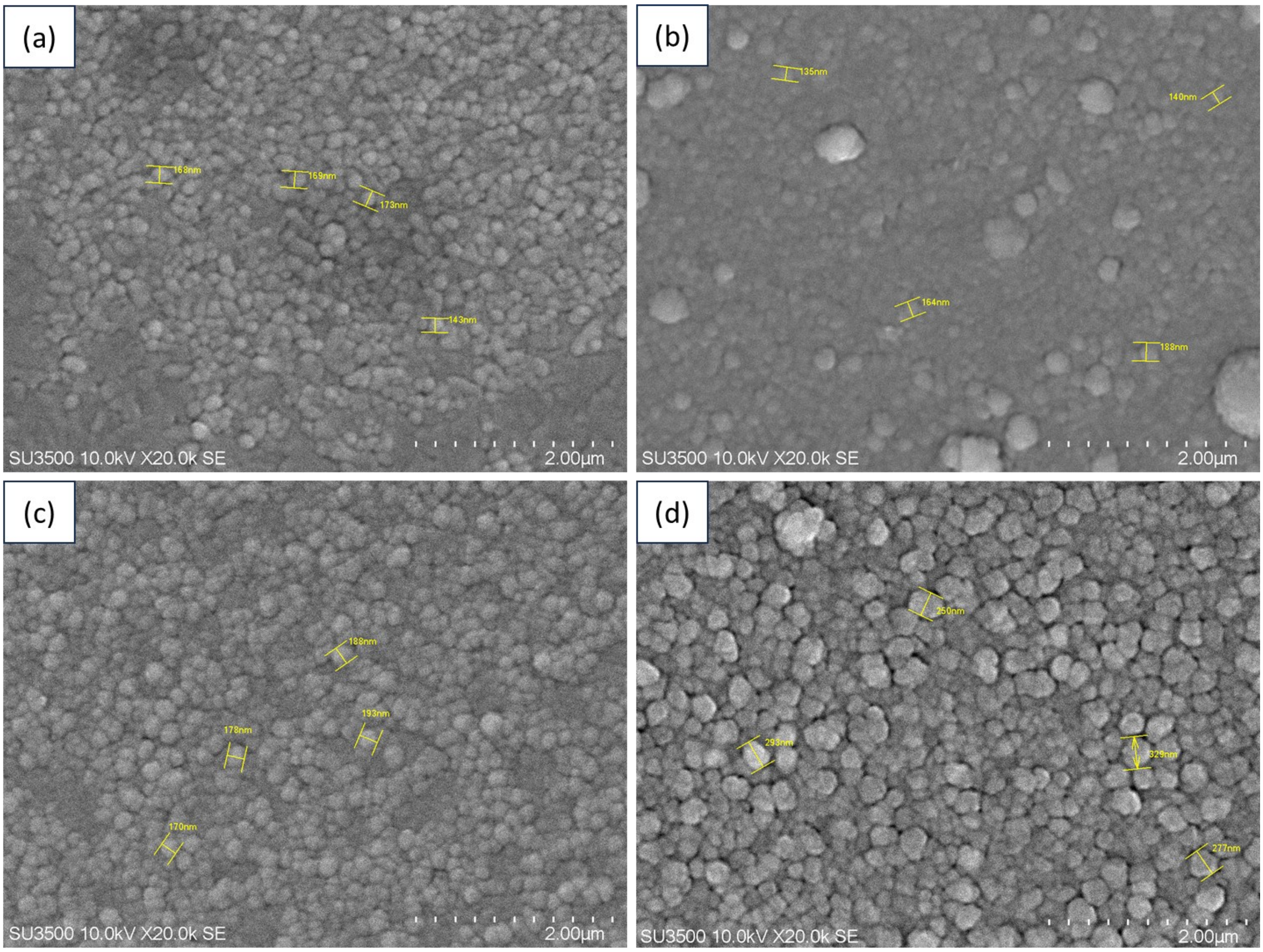

Figure 6: (a) CIGS morphology, image (b) CIGS/ TiO_2 30 min morphology, image (c) CIGS/ TiO_2 45 min morphology, and image (d) CIGS/ TiO_2 60 min morphology

In the surface morphology of the layer, the calculation of the apparent grain size of the layer on the substrate surface is also carried out. The average grain size on the substrate is shown in Table 1.

Table 1: Grain size of CIGS and CIGS with TiO_2 coatings

No	Sample	Grain size (nm)
1.	CIGS	163.25
2.	CIGS/TiO_2 30 minutes	157.00
3.	CIGS/TiO_2 45 minutes	182.25
4.	CIGS/TiO_2 60 minutes	266.75

Table 1 shows the grain size difference in the resulting layers. The substrate with CIGS coating produced a surface with small grains of around 163.25 nm. The decrease in grain size to 156.75 nm was found on the substrate with CIGS/ TiO_2 coating with a deposition time of 30 minutes. CIGS/ TiO_2 with a deposition time of 45 minutes showed a larger grain size of 182.25 nm. Furthermore, for CIGS/ TiO_2 with a deposition time of 60 minutes showed the largest grain size of 287.25 nm. This showed that the addition of deposition time increase the grain size.

The white granules on the substrate surface as shown in Figure 6 also indicate that the CIGS and TiO_2 atoms released on the substrate surface undergo an increasing nucleation process and then experience growth so that clumps are formed on the surface which results in the addition of more TiO_2 content [9]. Based on the SEM results, we can conclude that from a morphological point of view, sputtering in Ar atmosphere seems to be an effective way to form CIGS thin films because it shows flat and balanced particles [15].

Table 2: Thin Film Composition of CIGS and CIGS with TiO_2 using EDX

Sample	Composition (%)					
	Cu	Ga	In	Se	Ti	O_2
CIGS	8.13	8.43	43.5	39.44	0	0
CIGS/ TiO_2 30 minutes	7.52	8.04	45.76	36.06	0.26	2.36
CIGS/ TiO_2 45 minutes	7.66	7.53	46.39	32.47	0.31	5.53
CIGS/ TiO_2 60 minutes	13.42	6.53	47.5	22.09	0.83	9.63

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Table 2 shows the differences in the content of the layer elements on each substrate along with the addition of deposition time for TiO_2. Deposition time also causes more O_2 composition to be deposited on the surface of the substrate which causes the formation of nanoparticle agglomerates or cauliflower-shaped grains [16]. Clear morphological differences are also shown on the surface of the TiO_2 layer with increasing O_2 concentration, where the size of the grains formed is also larger as shown in Figure 6.

3.2 UV-Vis Spectrophotometry Test Results

UV-Vis Spectrophotometry test on CIGS/TiO_2 thin layer was conducted to determine the absorption spectrum of the film. The absorption spectrum in this study was measured in the range of 200-800 nm. Where the spectrum 200-400 nm is UV light and the spectrum 400-800 nm is visible light. The test results are shown in the following graphic image.

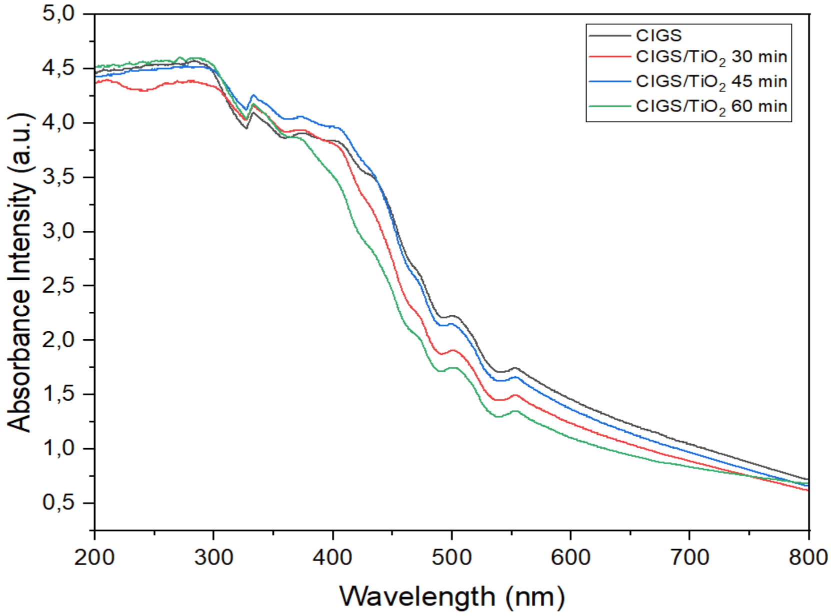

Figure 7: Results of UV-Vis Spectrophotometer CIGS and CIGS testing with TiO_2

The peak absorbance results obtained from Figure 7 reveal significant differences between the CIGS layer without TiO2 and those with varying TiO2 deposition times. These variations in peak absorbance indicate the influence of TiO2 on the optical properties of the CIGS layer. The absorbance value data is shown in the Table 3.

Table 3: Absorbance values of CIGS and CIGS thin films with TiO_2

No	Sample	Wavelength (nm)	Absorbance
1	CIGS	283	4.5784
2	CIGS/ TiO_2 30 minutes	209.5	4.39866
3	CIGS/ TiO_2 45 minutes	274	4.52745
4	CIGS/ TiO_2 60 minutes	271	4.60873

Based on the data in Table 3, the deposition time when making a thin layer affects the absorbance value. The longer the deposition time, the higher the absorbance value [17]. At the maximum absorbance point, it shows that electrons cannot absorb energy at that wavelength so that the energy given is only passed through. The diffraction pattern of the CIGS layer on the substrate with different variations has a relatively the same absorption value. This shows that the excitonic absorption peak in the CIGS film is identified as having good optical properties and strong exciton energy [18].

Based on table 3. on CIGS without TiO_2, the absorbance peak was 4.5784 at a wavelength of 283 nm. After the addition of TiO_2 with a sputtering time of 30 minutes, the absorbance value was 4.39866. Then, the TiO_2 deposition for 45 minutes showed a value of 4.52745, and the TiO_2 coating for 60 minutes showed the highest absorbance value of 4.60873. This shows that with the addition of deposition time, the absorption power increases. The increase in the absorbance peak also shows a shift to the left with the addition of the TiO_2 layer, so that its absorbance to ultraviolet light also increases.

4.0 CONCLUSION

In this study, it was shown that the CIGS layer without TiO_2 produced a surface with small grains of around 163.25 nm and the surface appeared less homogeneous. Then for the CIGS/TiO_2 layer with a longer deposition time, it showed that CIGS and TiO_2 nanoparticles were successfully deposited on the sample surface and more CIGS and TiO_2 atoms were released from the target surface. The lumps covering the substrate surface showed a flatter and more balanced morphology with the largest grain size being 266.75 nm at CIGS/ TiO_2 45 minutes. The deposition time during the manufacture of thin layers also affected the absorbance value. The longer the deposition time, the higher the absorbance value. Where the highest absorbance value was achieved by the CIGS/ TiO_2 60 minute sample of 4.60873 with a wavelength of 271 nm. It shows that the 60-minute CIGS/TiO2 sample has good light absorption capacity and can be used as an absorber layer in solar cells.

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