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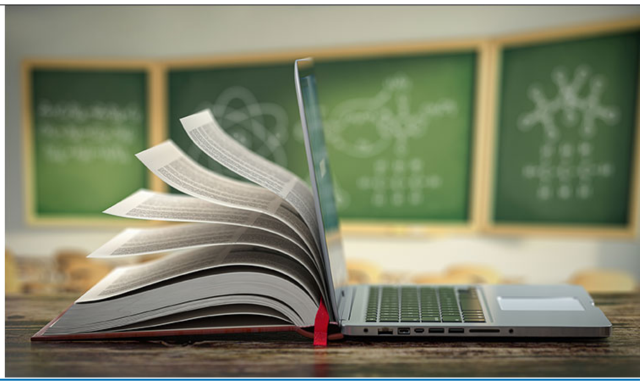

Synthesis and Characterization of TiO_2 Thin Film Based on Iron Sand of Lampung Province - Indonesia

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Abstract. This study aims to make a thin layer of TiO_2 based on ilmenite stored in iron sand of Lampung Province, Indonesia. The TiO_2 powder, which was used to make the thin layer, was obtained from the extraction of iron sand using the leaching method with a purity of 60,7%. The preparation of TiO_2 thin layers was carried out by the Chemical Bath Deposition (CBD) method with immersion time variations of 2, 3, 4, and 5 hours for samples A, B, C, and D respectively. Afterward, the samples were calcined at 500˚C for 4 hours. The characterizations involved X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), X-Ray Fluorescence (XRF), and four-point probe to measure the resistivity of the film. The XRD results in samples A (immersion time 2 hours) and D (immersion time 5 hours) show that the amorphous phase still dominates even though the diffraction peaks indicate that the presence of crystals has started to grow at several angles of scattering. The identification results of the phase presence show that the thin layer of TiO_2 at sample D is the brookite phase. The results of characterization using SEM show that the surface of the TiO_2 thin layer forms a porous structure. The average thickness of the thin film at sample B based on SEM analysis is 1.9 µm. The electrical resistivity increased with an increasing immersion time.

1. Introduction

Iron sand is sand, which in its compounds contains a lot of magnetite compounds or iron oxide which consists of iron and oxygen combination including hematite (Fe_2O_3), magnetite (Fe_3O_4) and titanium dioxide (TiO_2). The existence of iron sand as a mining material can be found in several Indonesian regions [1]. One of the iron sand ingredients is titanium dioxide. In general, titanium is rarely found in pure metal form. Most titanium is found in rutile, which consists of 95% TiO_2. TiO_2 is an inorganic chemical that can be applied mainly to manufacture the best quality white pigments, as a filler in paper mills, plastic factories, rubber factories, and as a flux in the glass industry. The pigment industry uses the enormous consumption of TiO_2, and only about 6% of TiO_2 is processed into titanium metal [2].

The advantages of TiO_2 are non-toxic, widely available and low cost of manufacturing process. TiO_2 is used in a wide variety of applications e.g., photocatalysts, supercapacitors, dye-sensitized solar cells, lithium-ion batteries, photo electrolysis, biosensors [3], as toothpaste mixtures, as skin lotions, as capacitors, food coloring [4] and gas sensors [5].

The growth of thin films for TiO_2 has been successfully carried out by various growth methods, such as electron-beam evaporation [6], sputtering [7], and sol-gel methods [8]. Another method is using Chemical Bath Deposition (CBD) method [9]. The films that have been successfully prepared by this method such as ZnO [10], IrO_2 [11], CdS [12], PbS [13], ZnS [14], and TiO_2 [3]. The CBD method is a low-cost method and can be grown on a wide substrate and produce small crystal sizes [15,16]. The thin film formed by the CBD method depends on the deposition, pH, bath temperature, and solution concentration [17]. CBD is proceeded by immersing the substrate in a solution containing metal ions and a source of hydroxide, sulfide, or selenide ions [18].

In this paper, the CBD is used to synthesize TiO2 thin films on the glass substrate. The investigations were done to know the effects of cyclic deposition on the phase composition, microstructure, and TiO2 thin film's resistivity.

2. Experimental Method

2.1. Glass Substrate Preparation

The glass substrates were washed using soap and rinsed with water. Then the distilled water was boiled.

2.2. Solution Preparation

An amount of 0.3 grams of TiO_2 powder was dissolved in 20 ml of HNO_3 and 10 ml of ethanol. Then they were stirred using a magnetic stirrer for 24 hours. After that, a 7% of $NaHCO_3$ solution was made using 7 g of $NaHCO_3$ then mixed into a volumetric flask containing 100 ml of distilled water [16]. The $NaHCO_3$ solution was dropped into the TiO_2 solution which has been stirred for 24 hours until it reached a pH of 1-3.

2.3. Thin Film Growth and Characterization

The glass substrates were hung using a stative and then inserted vertically into the beaker glass containing the TiO_2 solution. The thin films were formed at room temperature (27 ^oC) with a constant magnetic stirring rate. The growth of TiO_2 thin films was carried out by varying the immersion time, i.e., 2,3,4, and 5 hours in 2 depositions. Then the glass substrates were removed from the beaker glass and drained until there was no solution dripping. Then the films were heated at 100 ^oC for 1 hour. After that, the glass substrates were calcined at 500 ^oC for 4 hours [16]. Afterward, The TiO_2 thin films were characterized by SEM (ZEISS/EVO MA 10) and XRD (PanAnalytical: E'xpertPro with CuK α-radiation = 1.540598 Å, and 2θ in the range of 10˚– 80˚), then measured their resistivity. The resistivity measurement was carried out by a modified four-probe method by bolting an ohmic contact to the surface of the film.

3. Results and Discussion

3.1. XRF Analysis of TiO_2 Powder

The XRF results (Table 1) show the purity of the TiO_2 powder, which would be used for synthesizing the thin film, is 60.701%. This TiO_2 powder was obtained from the HCl leaching process with 2 hours of time duration at 110 ^oC.

Table 1. XRF analysis of TiO_2 powder extracted at 110˚C for 2 hours.

Compound	Concentration (%)
MgO	0.167
Al_2O_3	0.182
SiO_2	15.106
P_2O_5	0.687
CaO	1.071
TiO_2	60.701
V_2O_5	0.574
MnO	0.221
Fe_2O_3	19.273
ZrO_2	0.641

3.2. XRD Analysis of TiO_2 Films

XRD characterization of the TiO_2 films was carried out on films that were produced by immersing for (film A) 2 hours and (film D) 5 hours (Figure 1). Figure 1 shows that the films are generally still dominated by the amorphous phase even though the diffraction peaks indicating a crystalline phase's presence have started to grow in several scattering angles. The amorphous phase at film A still exists because the TiO_2 film formed on the glass substrate is still too thin so that X-ray emerges from the film and hits the amorphous glass substrate. Then, according to film D analysis, brookite peaks were observed at an angle of 2θ around 31.695º (JCPDS 29-1360). The sample preparation can influence the rutile phase formation in this study. The samples are not in powder form but thin films. So when they are dried, heat quickly emerges into the samples, and the formation of the rutile phase occurs earlier than in powder form.

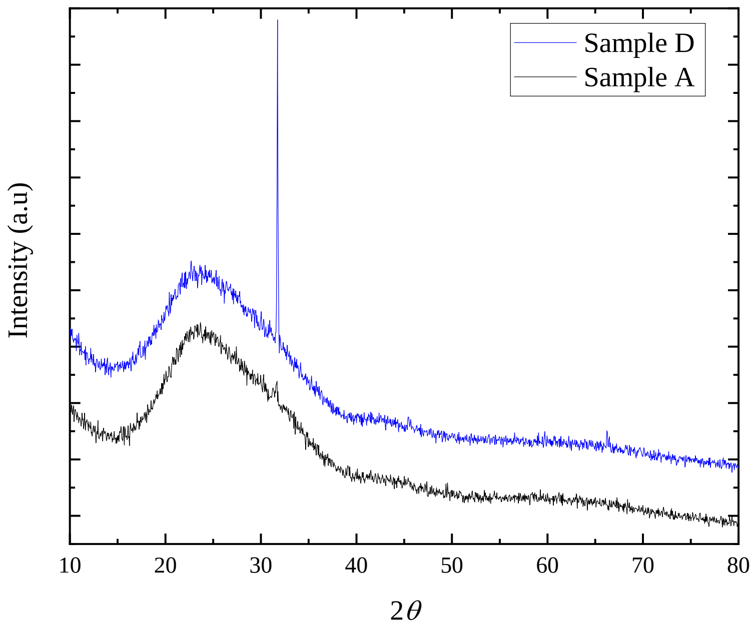

Figure 1. XRD analysis of TiO_2 films which were produced by immersing for (A) 2 hours and (D) 5 hours.

3.3. SEM Analysis

Based on the surface structure image from the SEM photos as shown in Figure 2, there is no difference in the samples' surface structure between the samples produced with an immersion time of 2, 3, 4, and 5 hours. However, a porous structure has begun to form.

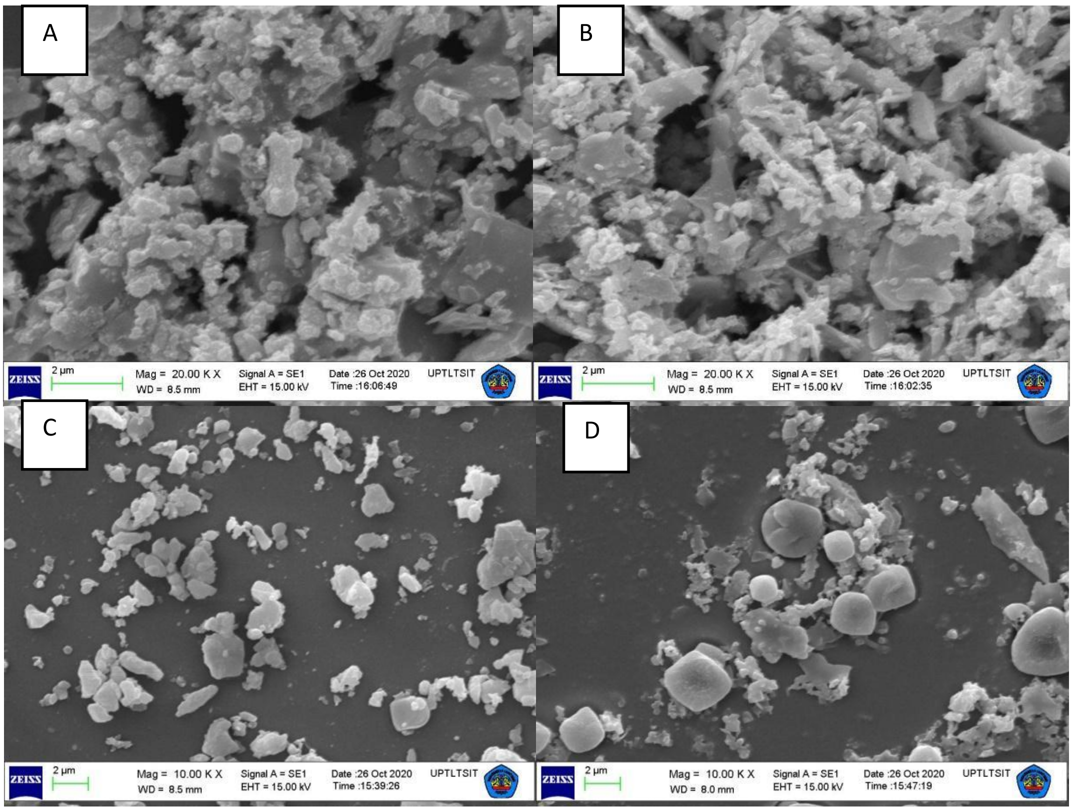

Figure 2. Surface morphology of TiO_2 films which were produced by immersing for (A) 2 hours, (B) 3 hours, (C) 4 hours, and (D) 5 hours.

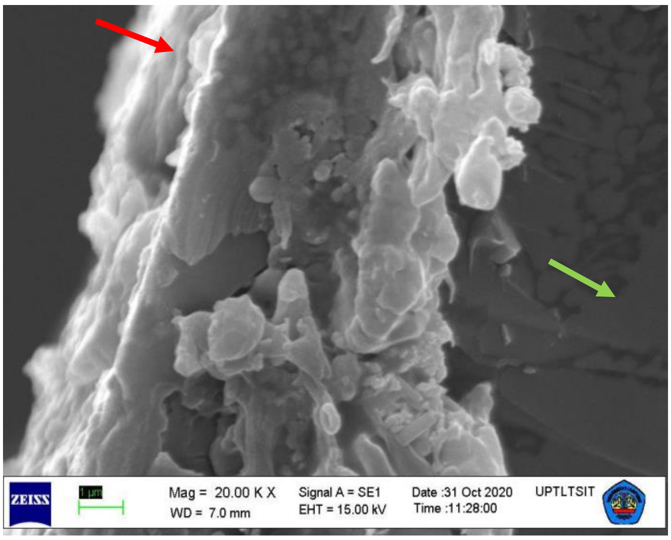

Figure 3. A cross-section of TiO_2 thin film and the glass substrate on sample B. The TiO_2 thin film's thickness is pointed by the red arrow and the glass by the green arrow.

Then, to estimate the thickness of the TiO_2 thin film on the glass substrate, a cross-sectional SEM analysis was performed on one of the samples. The cross-sectional SEM image is shown in Figure 3. Figure 3 shows the boundary between the TiO_2 thin film sample and the glass substrate. By referring to the scale stated in the figure, the thickness of the film can be calculated. The average thickness of the thin film in sample B is 1.9μm.

3.4. Resistivity

The electrical resistivity of TiO_2 films was measured using four-point probes. Based on the resistivity, it can be determined whether the film is a semiconductor or a conductor. The conductors' resistivity is less than 10^{-3} Ωcm, and semiconductors are $10^{-3} – 10^{7}$ Ωcm [19]. The resistivity of the TiO_2 thin film with variations of immersion time is shown in Figure 4.

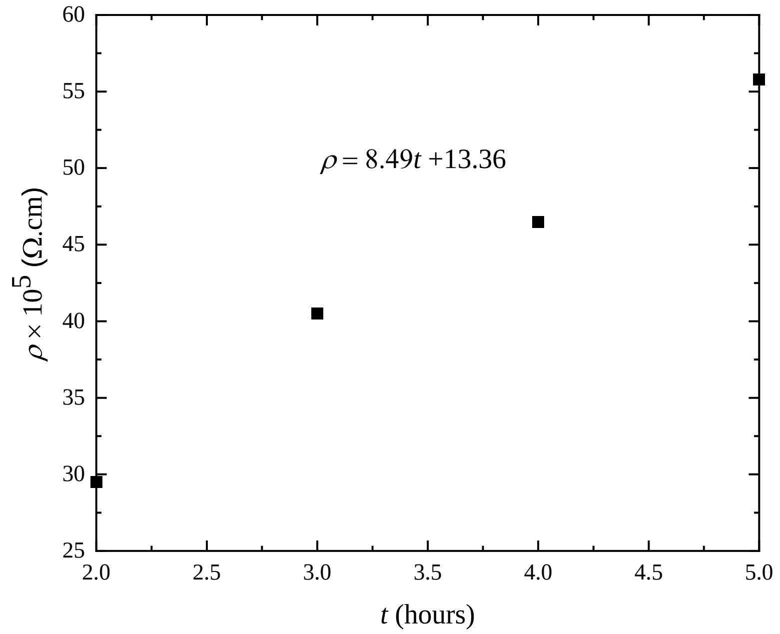

Figure 4. The resistivity (ρ) of TiO2 thin films with variations of immersion time (t).

Based on Figure 4, the resistivity of the TiO2 thin films in this study can be classified as semiconductors. The increase in resistivity value is influenced by the thickness of the layer [16]. Therefore, the resistivity value increases with the time of immersion.

4. Conclusion

The identification results of the phase presence show that the thin layer of TiO_2 for sample D (with 5 hours time immersion) is the brookite phase. The results of characterization using SEM show that the TiO_2 thin layer's surface forms a porous structure. The thin film's average thickness at sample B (with 3 hours time immersion) based on SEM analysis is 1.9 μm. The electrical resistivity increases with an increase in immersion time.

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