The Characteristics of Silica Nano-powder and Thin Films Prepared from Rice Husk Ash

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Abstract. In this study we have conducted laboratory research on the characteristics of silicanano-powder andthin films prepared from rice husk ash by extractionmethod. Rice husk ash was obtained fromAcehBesar district, Aceh province, Indonesia. The extraction process was carried out using 1.5% KOH and 10% HCl solution. The deposition ofSiO\textsubscript{2} thin films was carried out by sol-gel method. SiO\textsubscript{2} thin films were grown on a glass substrate by a dip coating technique. The precursor solution was prepared by dissolving 1 gram of silica nano-powder into 20 ml of ethanol and stirring for 60 minutes at 50\degree C using a hot plate stirrer. The SiO\textsubscript{2} thin films were then annealed at various temperature of 450 - 600\degree C with a holding time of 60 minutes. XRD pattern showed that silica powder from rice husk ash has a nano-crystal structure. We found that there are other peaks besides SiO\textsubscript{2}. This indicated that silica nano-powder obtained by extraction method was still contains impurity elements. The characteristics of SiO\textsubscript{2} thin films strongly depend on annealing temperature. The optical bandgap of SiO\textsubscript{2} thin films varies from 3.63 - 3.68 eV.

Keywords: Rice husk ash, silicanano-powder, silica thin film, annealing temperature

1. Introduction
Rice is the main agricultural commodity in Indonesia. Rice production in Indonesia in 2016 reached 70.4 million tons and specifically in the province of Aceh, rice production in 2016 reached 2.3 million tons. For each ton of rice, there are 0.23 tons of rice husk will be produced [1]. Rice husk is a waste produced from the rice milling process. In Indonesia, rice husks are simply burned to produce rice husk ash.

The chemical composition of rice husks varies from one sample to another. This is caused by differences in climate, geographical conditions, and types of paddy [2-4]. Rice husks contain silica and organic compounds consisting of cellulose, lignin, and hemicellulose which are a mixture of D-xylene, L-arabinose, methylglucoronic acid and D-galactose [4,5]. If the organic part of the rice husk is extracted, it is likely that inorganic residues will be obtained in the form of relatively pure silica. [4,6,7]. The content of silica in rice husk ash reaches 93.54 to 98.14% [8-10]. Silica powder can be used as basic raw materials in the rubber, ceramic, electronic, pharmaceutical, and dental materials industries [11].
World attention to climate change due to global warming, one of which is caused by burning fossil fuels and increasing energy needs, has increased the interest of researchers to find alternative renewable energy sources. One of them is a solar power plant known as solar photovoltaic. One of the obstacles in developing solar cells is the high production costs caused by the high cost of raw materials. Silica from rice husk ash could be an alternative raw material for cheap solar cells. This is because the production process of silica from rice husk ash is relatively simple and inexpensive. In this study, silica (SiO$_2$) was extracted from rice husk ash and applied in the manufacture of SiO$_2$ thin films. The purpose of this study was to examine the structure and optical properties of SiO$_2$ thin films, and to analyze the effect of annealing temperature on the characteristics of SiO$_2$ thin films from rice husk ash prepared by sol-gel dip coating technique.

2. Experimental

2.1. Extraction of silica from rice husk ash
Rice husk ash used in this study was obtained from, Aceh Besar district, Aceh province, Indonesia. The silica synthesis process begins with cleaning the rice husk ash and drying. Then 50 grams of rice husk ash were put into a solution of 500 ml of 1.5% KOH and 100 ml of 10% HCl and stirred and heated for 30 minutes. Then, rice husk ash solution was filtered and the resulting silica solvent. Filtrate silica was then precipitated by adding 10% HCl solution gradually until the pH reaches 7.0, and so that it becomes gel. Then silica gel was allowed to stand for 24 hours at room temperature, then filtered and washed thoroughly using distilled water. The clean silica gel was dried using an oven at a temperature of 110°C for 24 hours. The resulting silica powder is milled using a planetary ball mill for 60 minutes.

2.2. Deposition of SiO$_2$ thin films.
Silica thin films were deposited on a glass substrate. Glass substrates were cleaned first in methanol and distilled water respectively, using ultrasonic bath before each deposition process. The precursor solution was prepared by dissolving 3 grams of silica powder into 60 ml of ethanol, then stirred and heated at 50°C for 60 minutes using a magnetic hotplate stirrer. The precursor solution was deposited on glass substrate by a dip coating technique with 30 mm/hour dipping-rising speed. In order to obtain a smooth surface and suitable thickness of the films, 3 dipping-rising cycles were realized. Samples were dried at room temperature for 10 min between each cycle. Then the deposited thin films were dried and annealed at temperature variations of 450, 500, 550 and 600°C with a holding time of 60 minutes. Structure and morphology of SiO$_2$ thin films were characterized using x-ray diffractometer.

The optical characteristics of SiO$_2$ thin films were analyzed from ultraviolet-visible (UV-Vis) spectrometer measurement. The optical bandgap was determined using Touch’s plot method $h\nu$ versus $(\alpha h\nu)^{1/2}$, where $\alpha$ and $h\nu$ denote the optical absorption coefficient and photon energy, respectively [12]. The optical absorption coefficient ($\alpha$) were calculated from transmittance spectra obtained by UV-Vis measurement using the relation: $\alpha = -\frac{1}{d}\ln T(\lambda)$, where $d$ is the thickness and $T$ is optical transmittance of the films.

3. Results and Discussion
Although synthetic silica has been produced commercially, but the production of silica from rice husk ash has several advantages, including the stages of processing steps are relatively simple and do not require expensive equipment and costs. Silica powder from rice husk ash has high purity with a little metal oxide impurity. Figure 1 showed the x-ray diffraction (XRD) patterns of silica powder from rice husk ash. It can be seen that there are diffraction peaks with relatively low intensity at the Bragg angle of 20 29.1, 30.2, 35.5, 40.3, 48.8 which correspond to the Bragg 2θ angle of ICSD powder diffraction file (PDF). The above diffraction peaks look good on silica powder before and after being milled for 60 minutes. However, a wide 2θ angle at a range of 18 - 29° which is characteristic of an amorphous structure was also still found.
Silica (SiO$_2$) thin films could be deposited by various techniques, including sol electrophoretic deposition [13], plasma enhanced chemical vapor deposition (PECVD) [14,15], sol-gel spin coating [16], and sol gel dip coating [17]. In this study, the sol-gel dip coating method was used. The choice of this method is based on several advantages including, it can produce a homogeneous film with a uniform particle size. Besides that, the films can be grown on a wide surface and growth process is relatively easy and fast. In the sol-gel dip coating technique, annealing process is one of the most important parameters that determines the characteristics of the film.

Figure 2 showed the XRD pattern of SiO$_2$ thin films from rice husk ash extract annealed at varying temperatures. It can be seen that there is no significant difference in the diffraction pattern of SiO$_2$ thin films annealed at different temperatures. We also found that the temperature annealing affects the high of peak diffraction intensity. It can be seen that the higher the annealing temperature, the higher the intensity of the diffraction peak.
Figure 3. Optical transmittance of SiO$_2$ thin films annealed at various temperatures.

Optical properties measurement using ultraviolet-visible (UV-Vis) spectrometers showed that SiO$_2$ thin films annealed at temperature of 400$^\circ$C has a relatively high optical transmittance value of 80% as shown in Figure 3. The higher the annealing temperature, the transmittance value of SiO$_2$ thin films was getting lower. Annealing temperature also affects the optical response of thin layers of SiO$_2$. The higher of annealing temperature, the optic response of SiO$_2$ thin film shifts to the right towards a greater wavelength. The optical response of the SiO$_2$ thin film occurs at wavelengths between 300 - 360 nm.
**Figure 4.** Determination of the optical band gap of SiO$_2$ thin films annealed at different temperature 
(a) 400$^\circ$C, (b) 450$^\circ$C, (c) 500$^\circ$C, (d) 550$^\circ$C, and (e) 600$^\circ$C using Touc’s plot method.

Figure 4 showed determination of the optical band gap of SiO$_2$ thin films using Touc’s plot method. The optical band gap of the SiO$_2$ thin film also depends on the annealing temperature, as shown in Figure 5. The optical band gap of the SiO$_2$ thin film decreases from 3.68 – 3.63eV as the annealing temperature increases from 400 – 600$^\circ$C.

Figure 6 showed the optical absorption coefficient of SiO$_2$ thin films from rice husk ash annealed at different temperatures. The optical absorption coefficient of SiO$_2$ thin films reaches the order of $10^3$ cm$^{-1}$. This indicates that of SiO$_2$ thin films from rice husk ash could be one of the potential candidates for optical absorbent material to be applied to photonic devices. Annealing temperature did not significantly affect the absorption coefficient of SiO$_2$ thin films extracted from rice husk ash.
Figure 5. The effect of annealing temperature on the optical bandgap of SiO$_2$ thin films.

Figure 6. The optical absorption coefficient of SiO$_2$ thin films from rice husk ash annealed at different temperatures.
4. Conclusion
Silica (SiO$_2$) nano-powder has been successfully extracted from rice husk ash. XRD pattern of SiO$_2$ nano-powder showed that diffraction peaks of SiO$_2$ with relatively low intensity were observed, but a wide peak which was a characteristic of amorphous still also appeared. The XRD patterns of SiO$_2$ thin film from rice husk ash annealed at temperatures of 400 – 600 $^\circ$C did not show a significant difference. It could be seen that the higher annealing temperature, the higher intensity of diffraction peak SiO$_2$. The annealing temperature was also affects the transmittance, optical response, optical absorption coefficient and band gap of SiO$_2$ thin films. In this study, we obtained that band gap of SiO$_2$ thin films decreased from 3.68 - 3.63eV with increasing annealing temperature from 400 - 600 $^\circ$C.

Acknowledgements
The authors wish to thank the Laboratory of Chemical Research for the assistance in the extraction process of silica from rice husk ash in this study and the Laboratory of Materials the University of Syiah Kuala for analytical techniques of XRD analysis.

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