Study on the structural evolution of SiO$_2$ extracted from Sidoarjo mud

Devita Rachmat$^{1,a}$ and Doty Dewi Risanti$^{1,b}$

$^1$Department of Engineering Physics, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, Sukolilo, Surabaya, Indonesia, 60111

$^a$devitarachmat@gmail.com, $^b$d.d.risanti@gmail.com

Abstract. Sidoarjo mud is known to have a large amount of silica mineral i.e 44.8% with a purity of 88.4 to 95.7%. In this study, the annealing process in extracted silica was carried out for 5 hours to observe the structural changes at 800°C, 1000°C and 1150°C. Thermogravimetric analysis of extracted silica shows that glass temperature transition (Tg) occurs at onset temperature of 800°C and crystalline phase take places at above 1150°C. The results are confirmed by X-Ray Diffraction (XRD). It indicates that there is a transformation phase of amorphous SiO$_2$ to triclinic crystalline structure with increasing amount of tridymite phase as the temperature increases from 800°C up to 1150°C. The changes in SiO$_2$ phase structure are also confirmed by FTIR results that show a transmittance shift of Si-O stretching bonds as the heating treatment temperature is increased. Based on the UV-Vis results, the optical band gap shows no dependencies on heat treatment temperature, whereas the Urbach energy is proportional to the increasing temperature, in which SiO$_2$ sample heated at 800°C has the lowest Urbach energy or the fewer defects. Urbach energy values of extracted silica are ranging from 7.91-17.33 eV. In accordance with Urbach energy, the DSSC with photoanode containing SiO$_2$ heated at 800°C shows the best performance with efficiency of 0.077 %.

1. Introduction
Silica is found in many free sources in nature, one of them is Sidoarjo mud which is known from the previous research it has silica content of 44.8% [1]. Silica extracted from Sidoarjo mud has an amorphous phase structure with a purity of 88.4 to 95.7% at pH 7 [1,2]. The previous study has been also carried out that amorphous silica extracted from Sidoarjo mud can be used as corrosion inhibitors and also as a scattering material on Dye Sensitized Solar Cell (DSSC) photoanode [3]. Amorphous silica is known to form a network of randomly interconnected tetrahedrals [4]. These tetrahedrals are composed of one silica atom at the centre and form oxygen atoms at the corners while each oxygen atom is shared by two tetrahedral atoms such that the total number of O atoms is twice that of the number of Si atoms [4]. However, the bond angle between Si and O atoms has various values allowing it to form crystalline structures in different forms such as quartz, tridymite and cristobalite and also can easily form the amorphous structures whereas amorphous SiO$_2$ is known to have more dangling bonds which further causes a localized state [5]. This localized state between conduction band and valence band causes electrons unable to move freely [5]. Hence the amorphous and crystalline SiO$_2$ have different properties such as the energy gap value of amorphous silica is 9.3 eV [6], which is higher compared to crystalline one, i.e 5.48-6.3 eV [7]. In this study silica will be
obtained by extract Sidoarjo mud using coprecipitation method. The phase transformation of the amorphous phase of silica to crystalline, was carried out through the calcination process for 5 hours at high temperature but still below its melting point of 1700°C, the corresponding properties were studied.

2. Experimental

2.1. The Preparation of silica from Sidoarjo mud

Sidoarjo mud was washed using aquadest to remove impurities. Then the mud is dried and crushed. The crushed mud is then weighed in 10 grams and washed using HCl for 12 hours. Subsequently, it was reacted with NaOH 7M and stirred for approximately 1 hour at 80°C with a speed of 2 mods. Afterwards, the slurry solution was filtered using Whatman filter paper No. 15. The filtrate solution was titrated using HCl while stirring at temperature of 40°C to obtain a pH value of 7. The extracted silica was precipitated and washed using distilled water to remove the content of acid, base and salt. Then, the silica precipitation was dried in an oven at 80°C for 12 hours. The extracted silica was heating for 5 hours at temperatures of 800, 1000 and 1150°C to ensure that the sample has fully transformed.

2.2. Characterizations

Thermogravimetric Analysis (TGA) was carried out on 14.9 mg Sidoarjo mud and 16.3 mg silica extracted from Sidoarjo mud using Linseis STA PT 1600 thermal analyzer in a temperature range of 0°C to 1200°C with a heating rate of 10°C/minute. Identification of transformation in crystalline phase was observed by X-Ray Diffractometer (Philips X’pert MPD 30 kV, 40 MA). Fourier Transform InfraRed (FTIR) test was performed using a Thermo Nicolet i510 Spectrometer. Subsequently, the absorption of silica in visible light (200 nm - 800 nm) was characterized using a UV-Vis Spectrometer (Lambda 750 UV/VIS/NIR spectrophotometer). Furthermore, to find out the effectiveness of silica extracted from Sidoarjo mud as scattering material in the DSSC photoanode, the I-V test was done in Photonics Material Laboratory, Department of Physics, ITB.

3. Results and discussion

3.1. TGA Analysis

Figure 1. shows the TGA curves of pristine Sidoarjo mud and SiO\textsubscript{2} extracted from Sidoarjo mud. Weight loss stage of pristine Sidoarjo mud take places in two steps. The first stage occurs at temperature below 100°C, which should be due to the evaporation of physically adsorbed water molecules and the second was between 400 – 600°C, that is attributed to dehydroxylation process or hydroxyl groups (water crystal) releases process. The two weight loss stages are also observed in SiO\textsubscript{2} extracted from Sidoarjo mud with its pronounced decrease up to 400°C as indicative of the presence of water evaporation and melting of some impurities. Our silica TG curve indicates two distinct phase transformations, i.e. glass transition onset temperature is at 800°C and crystallization at about 1150°C. The larger temperature gap of the two processes may result in the more stable glass phase obtained [8]. According to the phase diagram of silica the glass transition is related to β tridymite[9]. These two transformation cannot be seen in TGA curve of pristine Sidoarjo mud, since there exists a more complex compounds in it.

3.2. XRD Analysis

X-ray powder diffraction (XRD) studies were performed on all samples studied to confirm their amorphous and crystalline states (Figure 2). SiO\textsubscript{2} extracted from Sidoarjo mud without heat treatment has the amorphous phase as shown from the broad peak at 20 value of 22° [11,12]. The transition from amorphous to crystalline silica of Sidoarjo mud takes place further as the temperature increases [9].
SiO$_2$ in triclinic structure is obtained for all heat treated samples. However, the tridymite structure is also observed and its fraction is increased. This result indicates that extracted silica undergoes a very slow transformation towards a stable tridymite structure starting from 1000°C. This is also supported by the TGA results (Figure. 1) showing the larger gap between glass transition and crystalline temperatures.

![Figure 1](image1.png)

**Figure 1** TGA curves of pristine Sidoarjo mud and SiO$_2$ extracted from Sidoarjo mud

![Figure 2](image2.png)

**Figure 2** XRD spectra of extracted SiO$_2$ heated at various temperatures

### 3.3. FTIR Analysis

In the IR spectra of silica extracted from Sidoarjo mud as illustrated in Figure 3. The rocking, bending, and stretching vibrational bands of Si-O can be observed at ~450 cm$^{-1}$, ~800 cm$^{-1}$, and ~1073 cm$^{-1}$, respectively [8]. There are two typical features for each sample, namely, a shift in the transmittance band of Si-O bending bond to a slightly lower wave numbers and an increase in transmittance intensity of Si-O stretching bond as heat treatment temperature was increased [8]. The strong absorption bands in the region of ~3400 cm$^{-1}$ and 1650 cm$^{-1}$ which only appears in silica without heat treatment indicates the stretching vibrations between hydrogen and some other atoms as the existence of water content [9]. The presence of water content in silica extracted from Sidoarjo mud is related to TGA curve in Figure. 1, i.e. a continuous decrease up to 400°C, and it is confirmed by the loss of hydrogen from the surface that is observed by IR spectroscopy.

### 3.4. UV-Vis Analysis

UV-vis characterizations results were used to determine the optical band gap (E$_g$) using Tauc plot. E$_g$ is determined by extrapolation of a linear part of the curve to intercept the energy axis ($a(h\nu) = 0$)$^{[10]}$. Figure. 4 shows that the increase in heat treatment temperature tends to increase the optical band gap values as written in Table 1. Moreover, Urbach energy (E$_{\alpha}$) which can be obtained from the reciprocal of the slope of ln $\alpha$ against photon energy ($h\nu$) is shown in Figure. 5 and listed in Table 1. It is known that Urbach energy (E$_{\alpha}$) value represents structural defect. Urbach energy of heat treated silica are getting higher as the temperature increases. Whereas E$_{\alpha}$ is constant or weakly dependent on temperature $^{[11]}$.

### 3.5. J-V Curves Analysis

In general, all photounode samples containing SiO$_2$ show higher efficiency compared to that of without SiO$_2$ addition (see Table 2.). Since the amount of silica heated at 1150°C is not sufficient for DSSC fabrication, therefore we cannot measure its J-V characteristics. There exists a so-called parasitic effects in DSSC that caused by internal resistances, i.e. series resistance (R$_{S}$) and shunt resistance (R$_{SH}$). Those resistances may lead to power loss in DSSC. As illustrated in Figure 6, SiO$_2$
heated at 800°C has higher series resistance compared to that of SiO$_2$ heated at 1000°C. All samples studied show a non ideal J-V curve, which is attributed to the presence of those resistances. Photoanode containing extracted silica can enhance the performance of TiO$_2$ photoanode in DSSC up to 0.055%. Extracted silica is beneficial for improving open circuit voltage. On the other hand, its effect on the short circuit current is somewhat complex. This is because of the presence of particularly series resistance which becomes more obvious for silica heated at 1000°C. It is likely that extracted SiO$_2$ in the form of triclinic structure results in an almost ideal J-V curve. This is also supported by the fact that the Urbach energy of this condition is the lowest.

Table 1. Urbach energy values of SiO$_2$ extracted from Sidoarjo mud

| Sample                  | Urbach energy (eV) | Optical gap (eV) |
|-------------------------|--------------------|-----------------|
| SiO$_2$ without heat treatment | 7.91               | 2.55            |
| SiO$_2$ 800°C           | 7.43               | 2.875           |
| SiO$_2$ 1000°C          | 14.39              | 2.7             |
| SiO$_2$ 1150°C          | 17.33              | 2.55            |
Table 2. Efficiency of DSSC

| Photoanode sample                  | Efficiency (%) |
|-----------------------------------|----------------|
| TiO₂                              | 0.022          |
| TiO₂/SiO₂ without heat treatment  | 0.062          |
| TiO₂/SiO₂ 800°C                   | 0.077          |
| TiO₂/SiO₂ 1000°C                  | 0.064          |

4. Conclusions
SiO₂ extracted from Sidoarjo mud heated at 800 – 1150°C undergoes structural transformation: amorphous to triclinic to tridymite with hexagonal structure. Extracted silica has glass transition temperature at 870°C which corresponds to the formation of tridymite. It is known that the rise in Urbach energy (E_u) of extracted silica is proportional to the increasing temperature. DSSC photoanode containing extracted silica can enhance the performance of TiO₂ photoanode in DSSC up to 0.055%.

5. Acknowledgments
The authors gratefully thanks to the Ministry of Research Technology and Higher Education of Republic Indonesia through Penelitian Terapan Unggulan Perguruan Tinggi 2018 for supporting the financial aid during this project

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