Growth of 3C-SiC phase on silica-carbon composite with the carbothermal reduction method

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Abstract. Growth of 3C-SiC phase on silica-carbon composites has been conducted. Silica (95.48%) was obtained from rice husk purified using HCl then characterized with X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Fourier Transform Infra-Red (FTIR). The carbon source was from activated carbon. Silicon carbide formation was synthesized using the carbothermal reduction method at temperature 1150 °C, 1300 °C, and 1450 °C. Characterization of silicon carbide phase was performed by X-Ray Diffraction (XRD) and UV-Vis Spectrophotometer. The increased temperature on carbothermal reduction process related to the intensity improvement of 2θ phase 3C-SiC(111) which indicates that the 3C-SiC phase is increasingly formed. The 3C-SiC(220) phase crystallite size increased from 20.37 nm to 22.66 nm. The formation of 3C-SiC phase and crystallite size affected on the electronic properties of the synthesized material. The band gap decreased by the increased of 3C-SiC phase formed from ~3.2 eV (1150 °C) to ~2.7 eV (1300 °C) and ~2.7 eV (1450 °C).

1. Introduction

In recent decades, silica carbide (SiC) has generated much interest due to their unique properties. Silicon carbide is a wide band gap semiconductor with excellent thermal stability and high breakdown field that make it be a promising material for high temperature, high frequency and high power electronic devices [1,2]. Their excellent properties make SiC could be potential applications for composites, field emitters, FETs, sensors, nanoelectromechanical devices, catalyst, super-capacitors, bio imaging probes and wave absorbers [3].

There are more than 200 polytypes of silica carbide and the most common polytypes are cubic 3C (β-SiC), hexagonal 4H and 6H (α-SiC), and rhombohedral 15R, which are differentiated by the repeated stacking sequences of the bottom layers of SiC structure [4]. The β-SiC exhibits mechanical strength, high ionic mobility, thermal stability, chemical inertness, and high saturation electron drift velocity, furthermore, β-SiC is an eco-friendly semiconductor material with a band gap of 2.4 eV [5,6].

Many researchers have synthesis SiC with various different methods such as Chemical Vapour Deposition (CVD) [7], Physical Vapor Transport (PVT) [8], Electrochemical etching [9], and Carbothermal Reduction [5,10,11,12]. The carbothermal reduction is the most used method for synthesis SiC due to simple and economical preparation method [5,2,13]. Most of the other methods involved complex processes and manipulation [2]. Moreover, most of the other method used two-step templating synthesis using preceramic polymer which makes it costly and long processes [14]. As we know silicon carbide can be obtained from SiO2 reduced carbon via carbo thermal reduction method wherein through the formation of the intermediates of gaseous silicon monoxide. The kinetics of SiC
formation is influenced by several things such as the ratio of mole Si/C, temperature and gas atmosphere [11,15].

The use of rice husk as a starting material for SiC formation has been widely discussed in the last few decades. Rice husk (RH) is the by-product of rice which is abundant and low-cost. Rice husk is potential as starting material because the silica content in rice husk up to 16-26 % depends on organic content in rice husk [16]. Furthermore, SiO, in rice husk has high reactivity making it a good candidate for carbo thermal synthesis of SiC [17,18,19].

In this paper, we have grown 3C-SiC via carbo thermal reduction processes. The mixture of silica-rice husk and activated carbon was pressed into a hard pellet in 1: 3-mole ratio. Silica from rice husk can be obtained by calcination of rice husk at a temperature of 700 °C for 2 hours.

2. Experimental

2.1. Preparation of SiO₂ from rice husk
The rice husk was collected from a rice mill in Gemolong, Srage City, Central Java, Indonesia. Preparation of silica was made by grinding of the rice husk (RH) followed by chemical treatment with HCl 3 N, in the ratio RH: HCl 1:10 (w/v) for one hour with constant stirring. The RH was washed with aquadest and it was filtered obtaining a pulp (PRH). The PRH is then calcined using a tubular furnace for 2 hours at 700 °C. The combustion products were rice husk ash, hereafter denoted as RHA. RHA then washed with HCl 2 N for 2 hours in constant stirring and then neutralized with aquadest followed by aquabidest until neutral. X-ray diffraction (XRD) patterns of the RHA were recorded using an X-ray diffractometer BRUKER D8 type with Cu-Kα radiation. The chemical composition was analyzed by X-ray fluorescence (XRF, Model S2 Ranger, BRUKER). Vibrational spectra were recorded on Fourier Transforms Infra-Red (FTIR) spectrophotometer (Shimadzu IR Prestige-21).

2.2. Synthesis and electronic properties of 3C-SiC from SiO₂, rice husk and activated carbon
Synthesis of 3C-SiC in various temperature was conducted in Carbolite Vacuum Furnace at Ar atmosphere with 0.5 L/min flow rate. The mixture of Silica from rice husk and activated carbon was prepared by grinding in a mortar in 1: 3-mole ratio then the mixture pressed to form a pellet. The mixture pellet then heated at 1500, 1300 and 1450 °C for 2 hours. Synthesized products were examined by X-ray powder diffraction (XRD) using CuKα (Copper-Kα) radiation and the crystallite size was determined by the Debye-Scherrer equation. The energy band gap of the synthesized product determined by Tauc plot method in ethanol solution. The mixture of synthesized product and 10 ml ethanol solution then sonication for 6 hours and the absorbance analyzed with UV-Vis spectrophotometer (Lambda 25 Pelkin Elmer).

3. Result and Discussion

3.1. Characteristics of Silica From Rice Husk

| Element | SiO₂ | P₂O₅ | SO₃ | Cl  | CaO | TiO₂ | Fe₂O₃ | CeO₂ |
|---------|------|------|-----|-----|-----|------|-------|------|
| Content (%) | 95.48 | 1.67 | 1.11 | 1.09 | 0.39 | 0.05 | 0.11  | 0.03 |

Composition of rice husk ash from XRF analysis is shown in Table 1. It can be seen that the extraction methodology provided SiO, with a purity of about 95.48 %. Rice husk ash still contains a small amount of metallic impurity. The generated SiO from rice husk has amorphous characteristics which can be seen in Figure 1a. The diffractogram XRD of SiO from rice husk shown a broad peak located approximately at 2θ = 15-35°, agrees with the reported JCPDS data (card No. 01-086-1561).
Figure 1. (A) Diffractogram and (B) Infrared spectra of SiO$_2$ from rice husk.

The major functional group on silica are identified by FTIR. FTIR spectra of silica from rice husk present in Figure 1b. From figure 1b, there is four major and the typical peak of silica. The broadband in 3400 cm$^{-1}$ are correlated to the O-H stretching of hydroxyl group [20] and the band at 1100 cm$^{-1}$ indicated the asymmetric stretching vibration of Si-O-Si group [21]. The band at 460 and 800 cm$^{-1}$ are respectively to a vibrational mode of O-Si-O bending and symmetric stretching of Si-O-Si group [22].

3.2. Characteristic and electronic properties of the synthesized material

Silicon carbide was synthesized by carbothermal reduction of amorphous SiO$_2$ from rice husk with activated carbon at various temperature 1150 °C, 1300 °C, and 1450 °C in atmosphere gas argon. The growth of the silicon carbide phase can be seen from the XRD-ray diffraction pattern in Figure 2. XRD analysis shows that the silicon carbide phase formed is 3C-SiC phase according to JCPDS no. 75-0254 with the three major peaks at 2θ = 35.6°, 59.9°, 71°. The 3C-SiC phase is formed at 1300 °C and then increases at temperature 1400 °C which can be determined from the increased intensity of the XRD peak of 3C-SiC phase. At temperature 1100 °C, a 3C-SiC phase has not formed but at that temperature, the unreacted SiO$_2$ undergoes crystallization which forms the crystalline phase of SiO$_2$ in the form of cristobalite (JCPDS no 71-0785) and quartz (JCPDS no 86-1630) phases.

From XRD analysis we could determine the crystallite size of using the Scherrer equation [Eq. (1)] [5].

$$D = \frac{K \lambda}{\delta W \cos \theta}$$  

where K is a constant (K = 0.99), $\lambda$ is the X-ray wavelength ($\lambda$ = 1.5418 Å) and $\delta W$ is the line broadening at half the maximum intensity (FWHM). The recapitulated crystallite size of the synthesized material at different temperature can be seen in Table 2. It could be seen that the crystallite size of 3C-SiC phase increased with increasing temperature.
Figure 2. Diffractogram peak of synthesized material in (a) 1150 °C (b) 1300 °C and (c) 1450 °C.

Table 2. Crystallite size of cristobalite, quartz, and 3C-SiC phase in various synthesized material temperature.

| Temperature (°C) | D (nm) | Cristobalite(101) | Quartz(101) | 3C-SiC(220) |
|-----------------|--------|------------------|-------------|-------------|
| 1150            | 36.45  | 44.205           | -           |
| 1300            | 33.95  | 37.39            | 20.37       |
| 1450            | 35.72  | 40.98            | 22.66       |

Figure 3. (A) Absorbance spectra and (B) Tauc plot of synthesized material in (a) 1150 °C (b) 1300 °C and (c) 1450 °C.
The electronic properties of the sample could be determined by the energy band gap value. The UV-Vis Spectrophotometer was used to calculate the band gap of the synthesized material from various temperature. The band gap of the sample was determined using the Tauc plot method as equation 2.

\[
(\alpha h\nu) = C(h\nu - E_g)^n
\]

The value of the optical band gap was calculated by extra plotting the straight line portion of \((\alpha h\nu)\) vs \(h\nu\) graph to \(h\nu\) axis [23].

The UV-Vis absorbance spectra and Tauc plot of the material with various temperature can be seen in Figure 4. The result of the absorbance measurement shows that there is 1 peak of the absorption on each material of the synthesized material and from Tauc plot method could be seen that presence of 3C-SiC phase generates the decreasing of energy band gap value. The energy band gap of synthesized material at 1100 °C is 3.2 eV decreased to 2.7 eV at temperature 1300 and 1450 °C. The value of the band gap energy of the synthesis material is influenced by the 3C-SiC phase formation and the crystal size of the material [24,25].

4. Conclusion

Growth of 3C-SiC phase on silica-carbon has been conducted at various temperature. 3C-SiC phase formed at temperature 1300 °C and increased at temperature 1450 °C. At the 1100°C 3C-SiC phase not formed because of the temperature didn’t enough to reduction of SiO, therefore, SiO undergoes to crystallization generate cristobalite and quartz phase. The energy band gap of the synthesized material at 1100 °C is 3.2 eV decreased to 2.7 eV at temperature 1300 and 1450 °C cause of the present 3C-SiC phase.

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