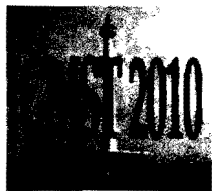


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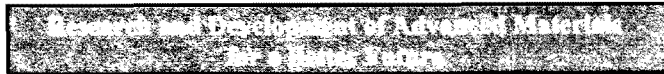
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PRODUCTION OF SEMICONDUCTOR MATERIALS SILICON FROM SILICA RICE HUSK WASTE AS ALTERNATIVE SILICON SOURCES

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ABSTRACT

Rice is one of the most important cultivated plants in human civilization. Rice production ranks third in the world of all cerealia after maize and wheat. According to Central Agency Statistics of Indonesia, production of rice in 2010 would reach 54 million tons. Hence, it would appear that the main agricultural waste generated from rice is the rice husk. Rice husk waste has been widely used as an alternative energy source; one of them is as a fuel. Since 1997 IPB has produced rice husk stove that burned fuel from rice husk. Utilization of rice husk was producing other wastes, namely charcoal husk. According to the research before, this waste contains 80% - 90% of silica, and thus has the potential to produce silicon that can be used as a semiconductor material. This research used dry and wet chemistry method to produce silicon. First step involved is ashing of the charcoal husk at four temperatures i.e. 700°C, 800°C, 900°C, and 1000°C, leaching the ash with HCl 3% for 2 hour, reducing silica with Mg at the temperature of 650°C and continued with leaching the residue using HCl, H₂SO₄, HF. Analysis methods used were the XRD, and SEM-EDS. According to XRD Analysis, hkl silicon appears in (111) (220) (311) (400) (331). This study succeeded in producing silicon from waste rice husk with high degrees of crystallinity i.e. 98.31%, 96.82% with purity of 67.82% and 79.17% respectively.

Keywords: silicon, silica, rice husk waste, semiconductor, X-ray diffraction, SEM, EDX.

INTRODUCTION

Rice is one of the most important cultivated plants in human civilization; this is because rice is the main carbohydrate source of the majority population in the world, especially in Indonesia. Indonesia is one of the largest rice producing nations in Southeast Asian region, especially among the countries that joined into Associations of South East Asian Nations (ASEAN), and in 2010 rice production expected will reach 54 million tons [1].

Each ton of paddy contains 72% rice, 5%-8% bran, and 20%-22% ash [2]. It would appear that the process produced quite a lot of agricultural waste, one of them is rice husk. Rice husk is a waste material of rice cultivation which is very hard and rough, weather-resistant, of low nutritional values, and do not possess high economical values [3].

Utilization of rice husk as alternative energy sources (biomass energy) since 2007 has been developed by the University of Agriculture Bogor (IPB), namely rice husks stove. This stove

is using rice husks waste as fuel [4]. After rice husks waste was used as an energy, rice husk would appear as ash waste. Rice husk ash contains silica at 72.1% and will be increased to 94.95% when it burned at a temperature of 700°C for six hours [5]. This condition makes rice husk ash can be used as alternative sources to produce silica and finally can become source of silica for cheap and economical production of silicon semiconductor.

This research aims to produce silicon powder from rice husk charcoal waste which is produced by rice husk stove at IPB, using chemical reduction method, and using magnesium powder as reducing agent. The residue of reactions is leaching using HCl, H₂SO₄ and HF. Analytical method used in this research is XRD and SEM-EDX.

EXPERIMENTAL METHOD

Equipment and Materials

This research was using equipment based in porcelain, glassware, plastics and alumina. Type of hot plate and furnace which is used is MSH-20D and NDI Vulcan 3-130. To determine the degree crystallinity of silica or silicon was done using Shimadzu XRD and the composition of silicon is using a Zeiss SEM-EDX Ivo Bruker 133 eV made by Germany's, both of them belongs to Center of Forest Products - Research and Development Department of Forestry Bogor.

Rice husk charcoal waste used in this research taken from rice husk stove IPB fuel burning. While the chemicals used are generally derived from Darmstant Merck, contain of hydrochloric acid (HCl) pa, sulfuric acid (H₂SO₄) pa, hydrofluoric acid (HF) technical, magnesium (Mg) powder, and distilled water.

Making Silica

Preparation of silica is through two stages, first stage is of the ashing of the charcoal rice husk, and in second stage is leaching of the ash. In first stage, first of all the charcoal rice husk waste is weighed with an analytical balance, and then put it in a porcelain cup, it is arranged to have the same thickness. After that, burnt it in a furnace using a rate of temperature rise 5°C/minutes with initial temperature detention is 400°C for 2 hours then continuing burnt it by varying the temperature of 700°C, 800°C, 900°C, or 1000°C for 1 hour.

After process of ashing is finished, it is continued with leaching process. This process is intended to eliminate existing impurity in rice husk ash, so pure silica will be resulted. This process is using hydrochloric acid (HCl) 3%. First of all, husk ash is inserted in a glass cup, then mixed with 3% HCl, then heated to 70°C while stirring by magnetic stirrer with speed of 240 rpm for 2 hours. Then the sample is washed using hot aquades repeatedly until it is free of HCl, then it was filtered with ash-free filter paper. The result of filtering (residue + filter paper) is then heated in a furnace at a temperature that is same as previous ashing process, until the remnant became white silica. The sample was then chilled in the furnace.

Making Silicon

The making of silicon is through two stages, first stage is to reduce silica of the leaching results using Mg powder, the second stage is leach residue of reduction result. At first, size of Silica and Mg is equated, then mixed using Mg powder with comparison in accordance with stoichiometric rules. Then burnt in a furnace at a rate of 5°C /minutes at 650°C for 1 hour.

Silicon purification process is required to eliminate impurity of existing other metals. This purification was done using hydrochloric acid (HCl). At first, the sample is inserted in a glass cup, then mixed with HCl, then closed using a watch glass and then heated with a hot plate at 70°C while stirring by magnetic stirrer at a speed of 240 rpm for 1 hour. Then the

sample was initially leached with HCl 3% for 1 hour, followed by leaching for 1 hour with 3 kinds of variations, namely A (leached with 60 ml HCl 15%), B (leached with 300 ml HCl 3%), and C (leached with 60 ml HCl 3% as much as 5 times), while stirring by a magnetic stirrer with speed and heated as foregoing. The sample is filtered and washed with hot aquades until the free acid, then dried.

To eliminate the unreacted silica, the residue of reduction result is washed with sulfuric acid (H₂SO₄) p.a. 95 % - 98 % (1:1) and hydrofluoric acid (HF) 70% technical. At first, 1 gram of sample was inserted into a glass plastic cup or platinum, then aquades was poured until wet. Then added H₂SO₄ (1:1) as much as 6 drops and HF 70% as much as 25 drops. Then fumes in the steambath for 2 hours. After that, add the HF 70% as much as 25 drops, heat until dry. The residue is washed using hot aquades, then filtered, and the residue is dried in a furnace at a temperature of 110°C for 12 hours.

RESULT DAN DISCUSSION

Making Silica

The process of making silica through two stages, which are ashing charcoal rice husk waste was then followed by leaching of waste rice husk ash. Ashing process of waste charcoal rice husk was by burning in the furnace at 400°C for 2 hours followed by four different temperature variations, which are 700°C, 800°C, 900°C and 1000°C each for 1 hour. Followed by washing using 3% HCl for 2 hours. XRD test results of this process then is equated with the database PCPDF 1997 win of the ICCD. Figure 1 shows the X-ray diffraction pattern of this process for each variation of heating, it shown silica peak appears at the point angle 2θ = 21.8°. The difference of heating in producing rice husk ash affect produced silica phase, as seen from the top of the X-ray diffraction patterns of silica on heating 700°C and 800°C produces amorphous silica phase. each degree of crystallinity reached 48.92% and 52.58%.

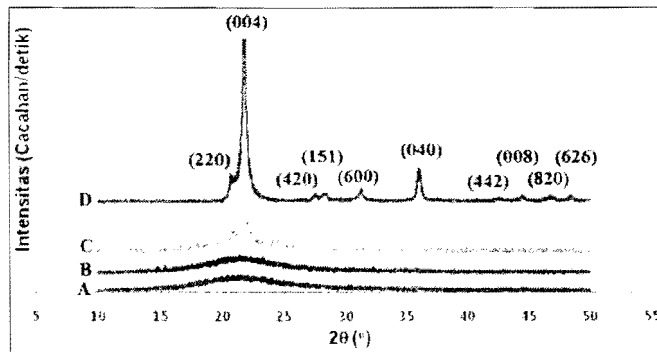


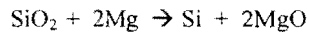
Figure 1: X-ray diffraction pattern of rice husk ash at temperature A (700°C), B (800°C), C (900°C), D (1000°C). Silica peaks appear in each sample

The crystallinity degree of silica at 900°C heating appear in two points 2θ, which are point 21.8° hkl (004) and 36.1° hkl (040), the crystallinity degree reached 54.55%. Meanwhile, at a temperature of 1000°C the crystallinity degree increases until it reaches 93.13%, as shown by the appearance of silica on top of the peak X-ray diffraction pattern in a lot of points 2θ, which are points 20.86° hkl (220), 21.86° hkl (004), 27.62° hkl (420), 28.46° hkl (151), 31.3° hkl (600), 36.12° hkl (040), 42.6° hkl (442), 44.72° hkl (008), 46.8° hkl (820), and 48.66° hkl (626).

The process of heating in a furnace at a certain temperature and rice husk ash leaching using 3% HCl for 2 hours able to eliminate impurity of rice husk ash waste, resulting pure silica, as seen on the top of the X-ray diffraction pattern, there were no other peaks other than silica.

Making Silicon

To produce silicon, silica from purified rice husk ash is mixed with Mg powder. Comparison between silica and magnesium powder ash in accordance with the rules stoichiometric, with the rate of increasing temperature 5°C/minutes. It is expected that the process of heating a mixture of rice husk ash and Mg powder occurs reaction as follows:



Then the residue from reduction result is washed using HCl. At first the residue is washed with HCl 3% for 1 hour, followed by washing for 1 hour with the variation, A, B, and C.

X-Ray Diffraction Pattern Test

Figure 2 shows the X-ray diffraction pattern of residue reduction result for the source of silica 700°C after washing with treatment A, B and C. From X-ray diffraction pattern which produced, indicate that the reaction between silica and magnesium has occurred and produced silicon at point $2\theta = 28.42^\circ$ hkl (111), 47.32° hkl (220), 56.1° hkl (311), 69.16° hkl (400) and 76.38° hkl (331). From this diffraction pattern is not contain peak of MgO, but there is silica peak although on amorphous phase at point $2\theta = 22.8^\circ$ hkl (004). The leaching process with HCl has able to eliminate the element of MgO, but not for silica. X-ray diffraction pattern from the three leaching treatment A, B and C, is shown in treatment B, the peak of silica is smaller than the treatment A and C. Leaching with treatment B can reduce the intensity of silica.

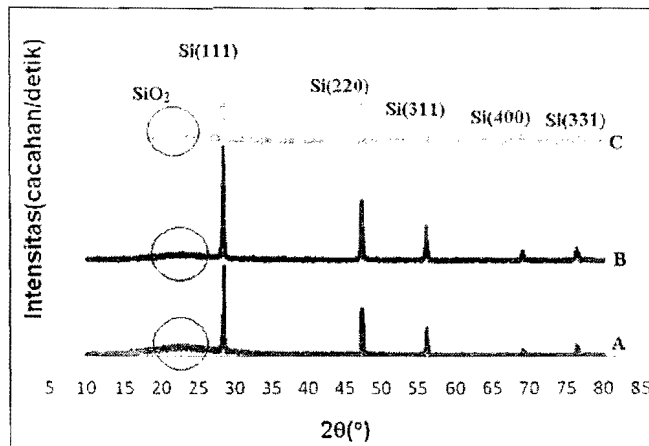


Figure 2: X-ray diffraction pattern leach residue from reduction silicon for source of silica 700 °C with treatment A, B, and C.

Then treatment B is tested to other sources of silica, which is heated at temperature of 800°C (B2), 900°C (B3) and 1000°C (B4). X-ray diffraction pattern shows the peaks of silica

and silicon. For sample B1, B2, and B3 peak silica with amorphous phase, while for sample B4 silica peak crystalline phase.

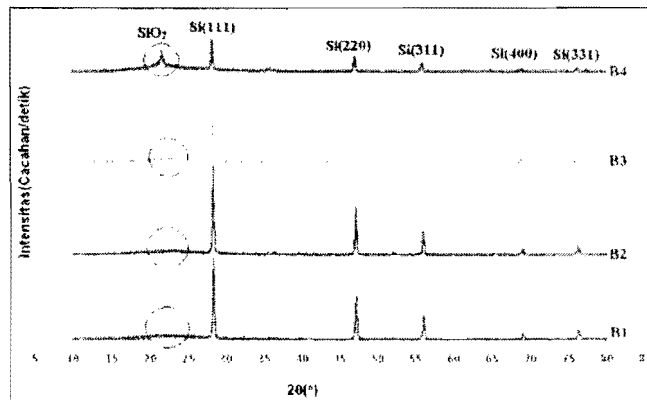


Figure 3: X-ray diffraction pattern leached by sample B1, B2, B3 and B4

Then the samples B1, B2, B3, and B4 are leached using H_2SO_4 and HF . Figure 4 X-ray diffraction pattern only show peak of silicon in point $2\theta = 28.42^\circ$ hkl (111), 47.32° hkl (220), 56.1° hkl (311), 69.1° hkl (400) and 76.38° hkl (331).

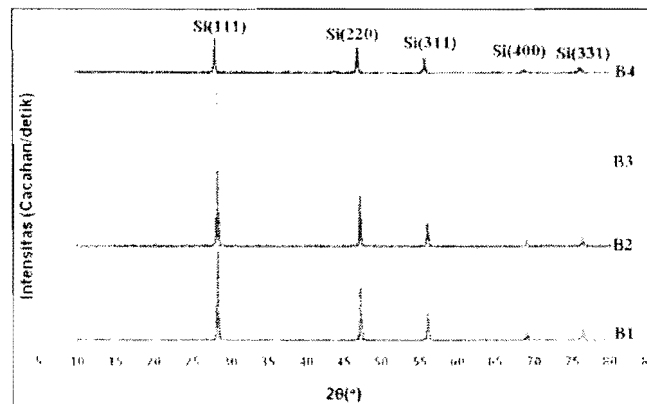


Figure 4: X-ray diffraction pattern sample B1, B2, B3 and B4 after HF.

Leaching with 3% HCl , H_2SO_4 and HF , is able to eliminate the silica thus produce silicon with the degree of crystallinity up to 98.31%.

SEM-EDS Test

As a comparison, the results of the study in SEM-EDS test was also done using silicon wafer semiconductor p type. The result of EDS shows purity of silicon on p type semiconductor silicon wafer reaches 86.26%. In addition to silicon, containing impurities F (1.99%), C (7.06%), O (4.35%), Mg (12.38%).

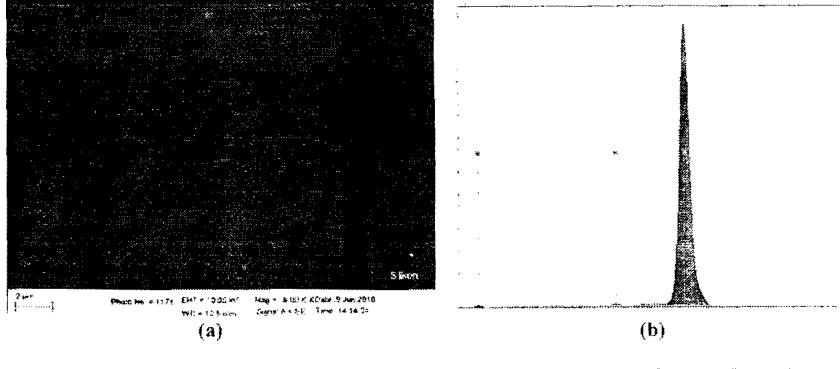


Figure 5: (a) SEM result with 5000x magnification, (b) EDS result of silicon wafer surface

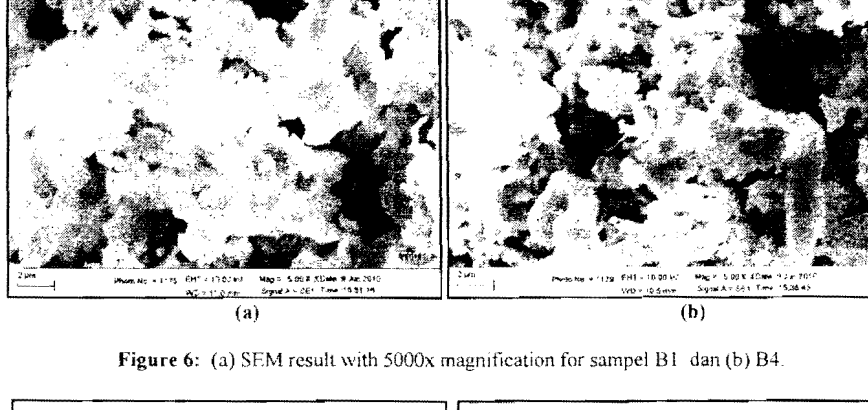


Figure 6: (a) SEM result with 5000x magnification for sampel B1 dan (b) B4.

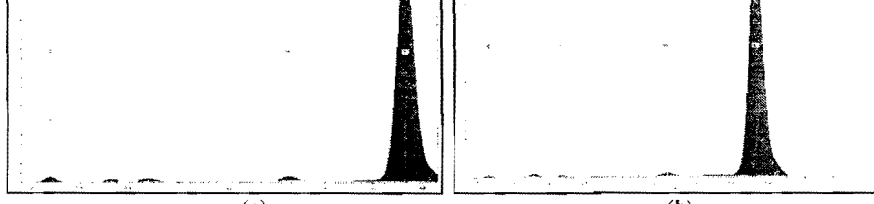


Figure 7: EDS result of samples silicon (a) B1 and (b) B4

Purity of silicon for the samples B1 and B4 reaches 67.82% and 79.1%. Both of them containing same impurities with silicon wafer there is F, C, O and Mg. B1 sample containing impurities F (13.22%), C (9.88%), O (7.47%), Mg (1.61%), whereas the B4 containing impurities F (6.55%), C (4.30%), O (9.02%), Mg (0.96%). When compared with the results of EDS silicon wafer the levels of purity of the sample B4 has a difference of 7.09%, while sample B1 at 18.44%. A difference between the levels of purity silicon wafer is not too many visible with sample B4.

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Table 1: Composition of silicon according to EDS analysis for silicon wafer. silicon from silica 700°C(B1) and silicon from silica 1000°C (B4)

Elements	Silicon wafer	B1	B4
Silicon	86.26 %	67.82 %	79.17 %
Fluorine	1.99 %	13.22	6.55 %
Carbon	7.06 %	9.88 %	4.30 %
Oxygen	4.35 %	7.47 %	9.02 %
Magnesium	0.34 %	1.61 %	0.96 %

CONCLUSION

This study showed that charcoal rice husk, which is a waste produced by the IPB rice husks stove, can be used to produce silica. By burning this silica and using magnesium as reducing agent in accordance with stoichiometric rules at temperature of 650°C in furnace, the waste can be used to produce silicon. By leaching the residue of silicon with HCl 3%, H₂SO₄ 98% (1:1), and HF 70 % impurity can be eliminated, and improved purity residue of silicon.

Analysis methods used were the XRD, and SEM-EDS. According to XRD Analysis, hkl silicon appears in (111) (220) (311) (400) (331). This study succeeded in producing silicon from waste rice husk with high degrees of crystallinity i.e. 98.31%, 96.82% with purity of 67.82% and 79.17% respectively.

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