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X-ray diffraction analysis of silicon prepared from rice husk ash

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Polycrystalline silicon has been prepared by metallothermal reduction of rice husk ash, which contains a considerable amount of amorphous silica. Acid-leached rice husk was burnt at a temperature of 620° C to obtain rice husk ash (RHA). RHA was then reduced with magnesium and major impurities were minimized or removed by an acid leaching process. The end-product was analysed using X-ray diffraction and mass spectrometric techniques. It was found that the powdered silicon obtained from magnesium reduction of RHA had a very low impurity concentration indicating that rice husk, which is an agricultural waste, is a potential source of metallurgical and solar-grade silicon.

1. Introduction

Low-cost solar-grade silicon is needed for the promotion of solar cell technology. At present, solar cells are manufactured using semiconductor-grade silicon [1]. This makes them very expensive. Since the purity level of solar-grade silicon is considerably less than that of semiconductor-grade silicon, the cost of manufacturing solar cells can be considerably reduced by investigating new and inexpensive source materials.

At present, different methods are used to obtain silicon from various silicon compounds such as quartz (SiO_2), flourosilicic acid solution (H_2SiF_6), silicon tetrachloride ($SiCl_4$) and trichlorosilane ($SiHCl_3$) [2]. Rice husk is also found to have a high content of hydrated silica from which silicon can be extracted. Rice is cultivated on a large scale in many countries of the world and sufficient amounts of husk can be easily collected at a low cost. The husk, after cleaning, is burnt in air in order to obtain a white ash. This ash contains 90 to 98% amorphous silica depending on the variety of the rice [3, 4]. The major impurities in rice husk ash (RHA) are potassium, sodium, calcium, magnesium, iron, phosphorus and aluminium which occur in the form of oxides or silicates. Silicon can be prepared from RHA by reducing it with carbon, calcium, barium, aluminium and magnesium and acid-leaching the end-product in order to minimize the impurity concentration [1]. Recently the conversion of RHA into silicon tetrachloride by chlorination and the extraction of silicon by rice-hull cooking in a nitrogen atmosphere has been reported [5].

In this paper, we report the preparation of polycrystalline silicon from the magnesium reduction of rice husk ash. The reduced sample is acid-leached with HCl, HF and H_2SO_4. The composition of the end-product is determined using X-ray diffraction and spark-source mass spectrometric techniques. The powdered silicon thus extracted from RHA is found to have a low impurity concentration and seems to be a suitable raw material for the preparation of solar-grade silicon.

2. Experimental procedure

Rice husk, obtained from local rice fields, was washed with distilled water in order to remove dirt. It was then boiled in a mixture of HCl and distilled water in the ratio 1 : 10 for 15 min and was subsequently washed with distilled water and dried. After that the rice husk was burnt in air to get a black ash. The black ash was then put into an alumina crucible in a muffle furnace at a temperature of 620° C in order to obtain a white ash. The X-ray diffraction intensity of this ash was recorded as a function of Bragg angle 2θ in the angular range of 10 to 100° on a Rigaku powder diffractometer (Geigerflex D-Max/11-A) at a scanning speed of 2 deg min^{-1}, using nickel-filtered Cu$K\alpha$ radiation. The divergency of the X-ray beam was kept at 1°, the receiving slit width was 0.3 mm and the ratemeter time constant was 1 sec. The X-ray diffraction pattern of this ash showed that it was amorphous (Fig. 1). When the ash was heated to 900° C or above, X-ray diffraction peaks corresponding to different phases of SiO_2 appeared indicating that the RHA was rich in silica [6]. Qualitative elemental analysis of RHA using a Jeol JMS-01-BM-2 spark-source mass spectrometer was also performed and it was found that the RHA sample contained sodium, magnesium, aluminium, potassium, calcium and iron as major impurities.

For metallothermic reduction we used the RHA sample prepared at 620° C, as it was amorphous, easy to grind and more amenable to reduction. First, RHA was leached with dilute HCl at 100° C to remove any soluble impurities, then it was washed with distilled water, dried and ground into a very fine powder. It was then reduced with magnesium of 4 N purity at a temperature of 620° C in a muffle furnace. Fig. 2 shows the X-ray diffraction pattern of the reduced sample taken under the same diffraction conditions. At this stage, the major impurities in the sample were magnesium oxide and magnesium orthosilicate, $2(Mg_{0.96}Fe_{0.04})O \cdot SiO_2$. These are soluble in acids. Now, the reduced sample was acid-leached with HCl in order to remove MgO and other impurities which

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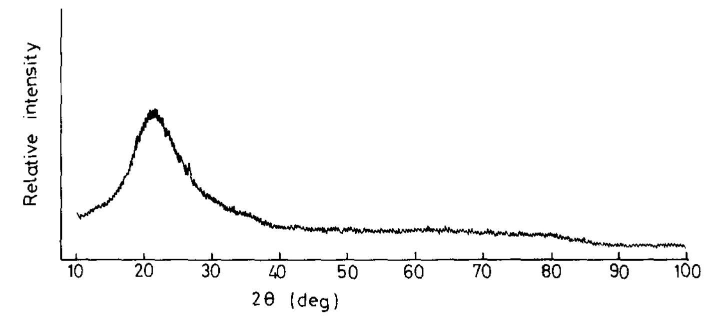

Figure 1 X-ray diffraction pattern of RHA at 620° C using Cu$K\alpha$ radiation.

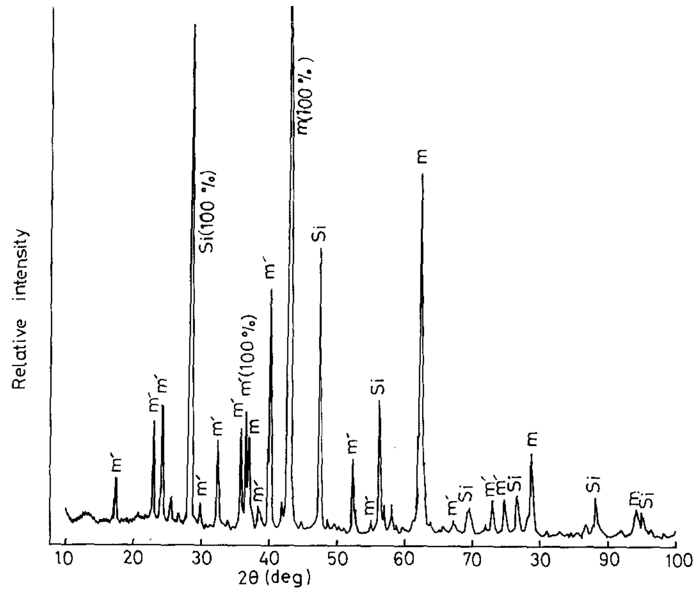

Figure 2 X-ray diffraction pattern of RHA reduced with magnesium. Major peaks corresponding to silicon (Si), magnesium oxide (m) and magnesium orthosilicate (m′) are indicated on the pattern.

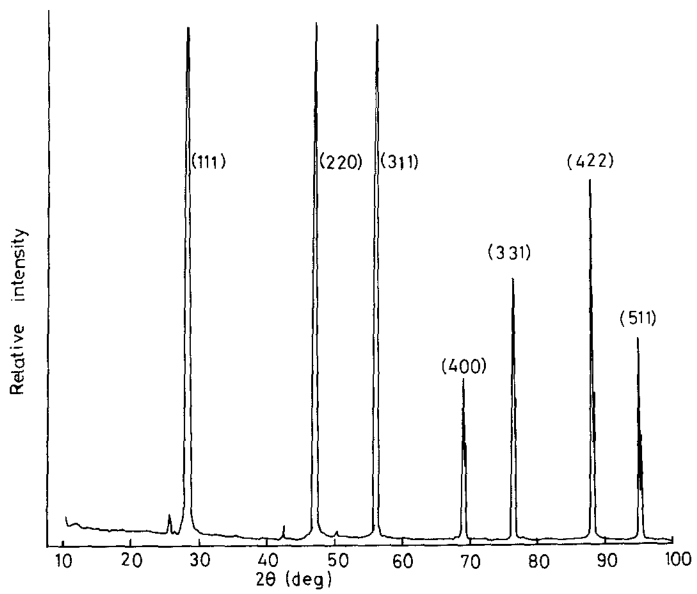

Figure 3 X-ray diffraction pattern of silicon extracted from RHA.

TABLE I Mass spectrometric analysis of silicon sample extracted by magnesium reduction of acid-leached RHA

Impurity element	Concentration (p.p.m.)
B	2
Na	50
Mg	58
Al	5
P	Not detected
K	144
Ca	76
Mn	4
Fe	50
Cu	10
Ti	2

existed in the oxide form. Next, the sample was leached with HF and then with HF + H_2SO_4. During this step many impurities which were present in the form of silicates were removed more or less completely. The sample was then washed with distilled water and dried. Fig. 3 shows the diffractograph of the acid-leached sample. It was found that the pattern closely resembled that of a polycrystalline silicon sample (Fig. 4) of 5 p.p.m. total metallic impurities which we are using as a standard for comparison. The mass of the sample at various stages of treatment was also noted and it was observed that from 100 g of rice husk, 17.06 g of white ash was obtained, from which after

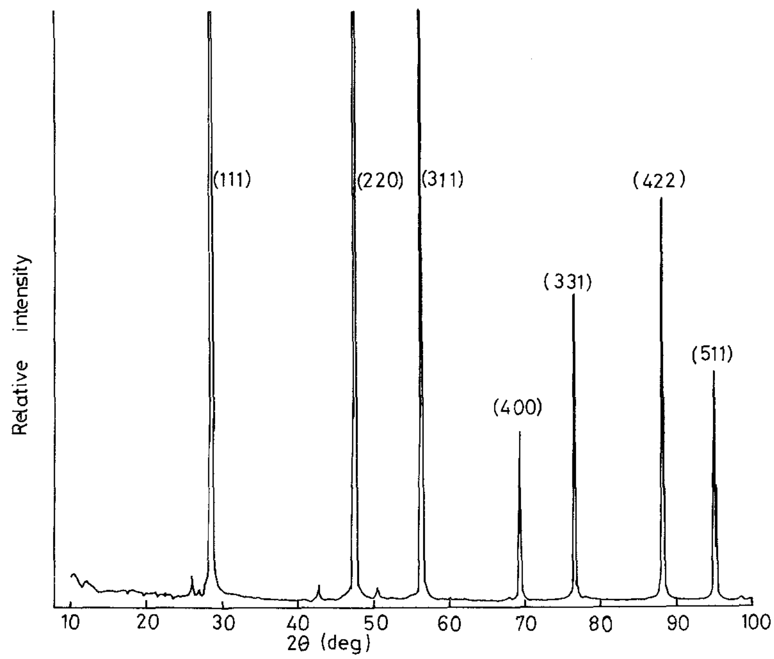

Figure 4 X-ray diffraction pattern of standard silicon sample.

magnesium reduction and acid-leaching, 4.7 g of silicon powder was prepared. The final sample had a grey colour with a brownish tint.

Quantitative elemental analysis of silicon prepared from RHA was also performed using the spark-source mass spectrometer (Table I). Sodium, magnesium, potassium, calcium and iron were found to be present in the range 50 to 150 p.p.m. Boron, aluminium manganese and titanium were present in very low concentrations, each being less than 10 p.p.m. Phosphorus was not detected in the sample, though its presence has been reported by some other authors [1, 5] in their silicon samples extracted from RHA. In fact, the impurity contents of different samples would vary slightly according to the type of rice husk and the fertilizer used for the crop.

3. Summary and conclusion

The work described in this paper for the preparation of silicon differs from conventional processes in two ways:

(i) the starting material is an agricultural waste and
(ii) purification through halogenation followed by fractional distillation and cracking is avoided.

Rice husk contains 40% cellulose, 30% lignin and 25 to 30% hydrated silica [7]. Although cellulose and lignin can be separated from silica by chemical methods, combustion is more economical and was employed in this work. Rice husk was burnt at a temperature of 620° C and the amorphous RHA thus acquired was reduced with magnesium and acid-leached to obtain silicon. The structure of the end-product was analysed using X-ray diffraction and quantitative elemental analysis was performed using a mass spectrometric technique. It was found that the total impurity content of silicon extracted from RHA was less than 500 wt p.p.m. Further, there were no lifetime-killing impurities in the sample such as molybdenum, tantalum, nickel, vanadium and chromium except for a very small amount of titanium ($\sim$ 2 p.p.m). Metallic impurities were also considerably reduced during acid-leaching. Boron was however present in a low concentration.

We conclude that the purity of silicon extracted from RHA is 99.95% and can be upgraded by using various conventional purification techniques [2] to obtain solar-grade silicon. Further, the impurity content of the silicon prepared from rice husk taken from the local fields is quite comparable to similar extractions reported by authors in other countries [1–4]. Therefore, rice husk which is an agricultural waste can be used as a raw material for the production of metallurgical and solar-grade silicon.

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