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Production and purification of silicon by calcium reduction of rice-husk white ash

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Polycrystalline silicon of reasonable purity has been prepared by metallothermic reduction of purified rice-husk white ash (amorphous silica) by using calcium. The mechanism of reduction of the silica with calcium was investigated using simultaneous thermogravimetric analysis and differential thermal analysis, which revealed the reduction temperature to be around 720° C. The paper also discusses the method of preparation of silicon and its purification procedure. Characterization of the silicon sample thus prepared was made by X-ray diffraction, scanning electron microscopy and emission spectrography.

1. Introduction

The conventional process of manufacturing silicon of reasonable purity involves a very high cost of production [1]. Therefore world-wide efforts are being directed to develop a low-cost, high-volume and commercially feasible process for production of high purity silicon to be used in solar cells for photovoltaic power generation [2–7]. One such process involves reduction of rice-husk ash to produce silicon [8–9]. Rice husk is a by-product of the rice milling industry. It is an attractive source of high-grade amorphous silica [10], which contains metallic impurities at very low concentrations [11] and can be further purified by a simple acid leaching process [8, 12]. This rice-husk silica can be reduced to polysilicon of reasonable purity by a metallothermic process. Extensive study on reduction of this silica by magnesium to produce silicon of reasonable purity has been successfully conducted [8–9].

A research project on the reduction of amorphous silica (obtained from rice husk) to silicon of reasonable purity by a metallothermic process using calcium instead of magnesium has been undertaken. Calcium was selected because it is a stronger reducing agent [13] and naturally more abundant than magnesium.

2. Experimental details

2.1. Purification of rice-husk silica

The white ash (containing 98% silica), obtained by burning rice husk at less than 500° C, was leached with moderately hot (50 to 60° C) concentrated hydrochloric acid for 2 h to remove most of the soluble impurities present in it. The material was then thoroughly washed with warm distilled water and dried.

2.2. Thermogravimetric and differential thermal analysis of purified rice-husk silica with calcium

The purified rice-husk silica and commerical grade calcium were mixed thoroughly in stoichiometric proportions. A small quantity (about 30 mg) of the mixture was placed in a platinum crucible in a thermal analyser (Mettler TA 2000) and the differential thermal (DTA) and thermogravimetric (TGA) curves were recorded simultaneously along with the rate of temperature change. Heated Al_2O_3 was used as the reference sample.

2.3. Reduction of rice-husk silica

Purified rice-husk silica was thoroughly mixed with granular calcium in stoichiometric proportions. The mixture was packed in a sillimanite

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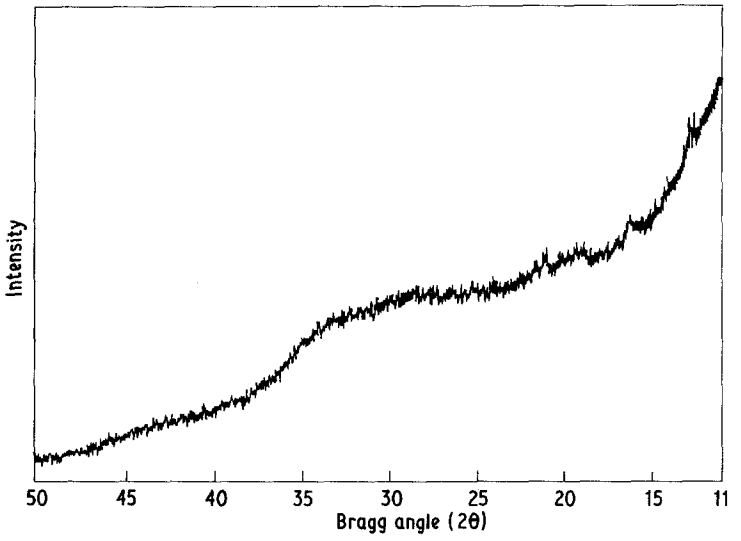

Figure 1 X-ray diffractogram of purified rice-husk white ash prepared at less than 500° C.

crucible of approximately 150 ml capacity and covered in such a way that there was no air space left inside the crucible. The silica in the mixture was then reduced inside an electrically heated muffle furnace at around 720° C. The reduced mass after being cooled to room temperature was taken out of the crucible and ground to fine particles.

2.4. Purification of silicon

The well-ground reaction product was leached with concentrated nitric acid. Intermittent stirring was necessary for effective leaching to take place. The acid-leached product was washed thoroughly with distilled water and dried. The unreacted silica in the material was then allowed to react with concentrated hydrofluoric acid for about 4 h. Finally all the acid was removed by repeated washing with warm distilled water.

2.5. Characterization of silicon

2.5.1. X-ray analysis

The X-ray diffraction spectra of the purified rice-husk silica, reduced material obtained after calcium reduction, and acid-purified reduced material, were taken at a chart speed of $2° \text{ min}^{-1}$ with the help of an X-ray diffractometer (Model CCON–1500, made in USSR) using MoK_α radiation.

2.5.2. Scanning electron microscopic analysis

The scanning electron microscopic (SEM) study of silicon after acid leaching was conducted with Model ISI 60 (Akashi Seisakusho Ltd, Japan).

2.5.3. Emission spectrographic analysis

The emission spectrographic analysis of the purified rice-husk silica and silicon was carried out at the National Physical Laboratory, New Delhi, India to detect the presence of impurity. This analysis was performed by subjecting the material to a high d.c. arc source and then photographically recording the emission from the sample with the help of a quartz spectrograph. The concentrations of the impurities in the material were determined by measuring the intensity of the lines emitted by the impurities as compared to the standard 100% pure element.

3. Results and discussion

The X-ray diffractogram of purified rice-husk silica is shown in Fig. 1. The diffraction pattern indicates the amorphous nature of the silica in rice-husk.

To determine the exact reduction temperature of silica and calcium and to obtain an approximate idea of the reaction mechanism involved in the process, DTA and TGA studies of this mixture were conducted. The sample was heated at a uniform rate of $10° \text{ C min}^{-1}$. Fig. 2 shows a typical simultaneous DTA and TGA record of the experiment. The reduction temperature was 720° C, where a sharp exothermic peak occurred. The sharp exothermic peak at around 500° C may be due to the burning of greasy material on the surface of the calcium. The two endothermic peaks occurring at around 220 and 320° C may be attributed to the removal of some volatile material during firing of the mixture. There is a broad exothermic peak at around

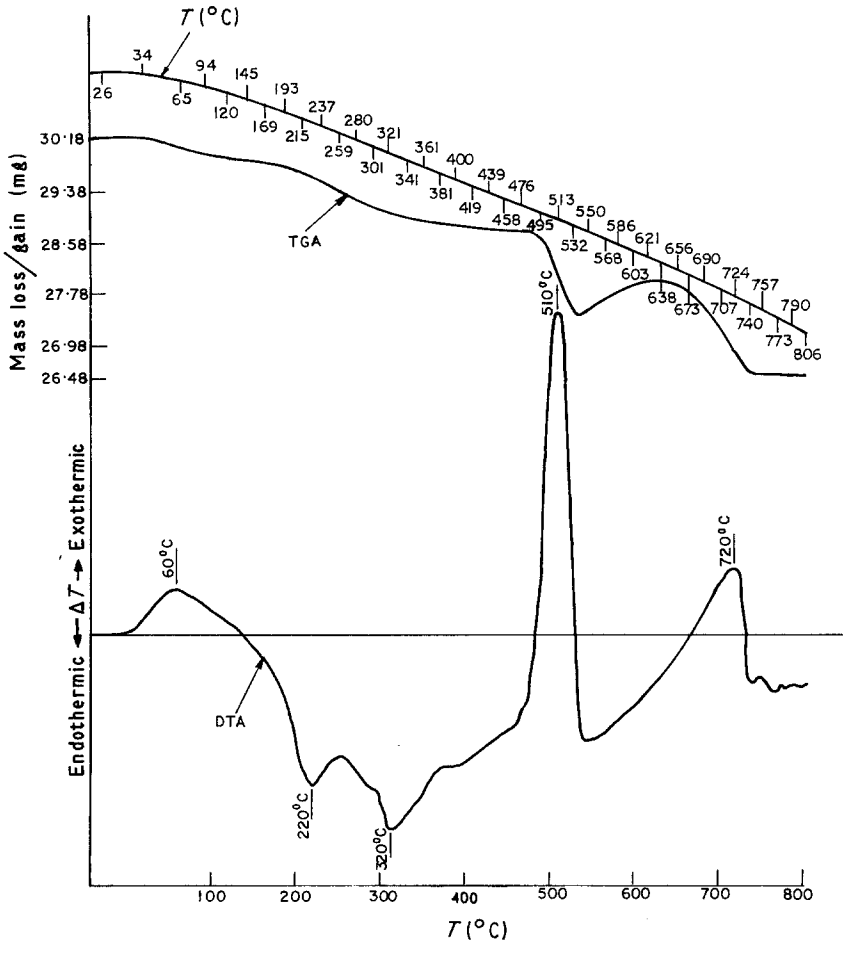

Figure 2 Simultaneous TGA and DTA curves for a mixture of rice-husk white ash and calcium. Sample weight 30.18 mg, heating rate 10° C min^{-1}, in a static air atmosphere.

60° C which is possibly a change in the baseline of the recorder pen. It may be noted that the phenomenon observed in the DTA studies is well supported by TGA of the material. The continuous loss of mass from 60 to 420° C occurs in two stages. The first stage (from 60 to 190° C) corresponds to the removal of moisture, whereas the second stage (from 190 to 420° C) corresponds to the removal of some volatile material. Burning of the greasy material from the surface of calcium, as indicated by the exothermic peak at around 500° C, is also shown by an associated loss of mass in the TGA record at the same temperature. The loss of mass was also observed in the TGA record at 720° C, corresponding to the reduction peak in the DTA curve.

Fig. 3 shows the X-ray diffractogram of the reaction products obtained from reduction of white ash by calcium at 720° C. The *d* spacings corresponding to various diffraction peaks have been identified. The pattern reveals the presence of all the strong intensity lines of silicon, resulting from the reduction process. In addition, diffraction lines due to calcium oxide, calcium silicate and α-quartz are also observed. When the reduced mass is purified by treating the product with concentrated HNO_3 and subsequently with concentrated HF, the removal of most of the impurities in the reaction products takes place (Fig. 4). This indicates that acid leaching of the reduced mass can upgrade the reaction products. The presence of α-quartz in Fig. 3 may be due to the higher reduction temperature required for calcium reduction of white ash, as compared to its magnesium reduction at around 650° C [8], where the presence of α-quartz was not observed.

The emission spectrographic analysis of a

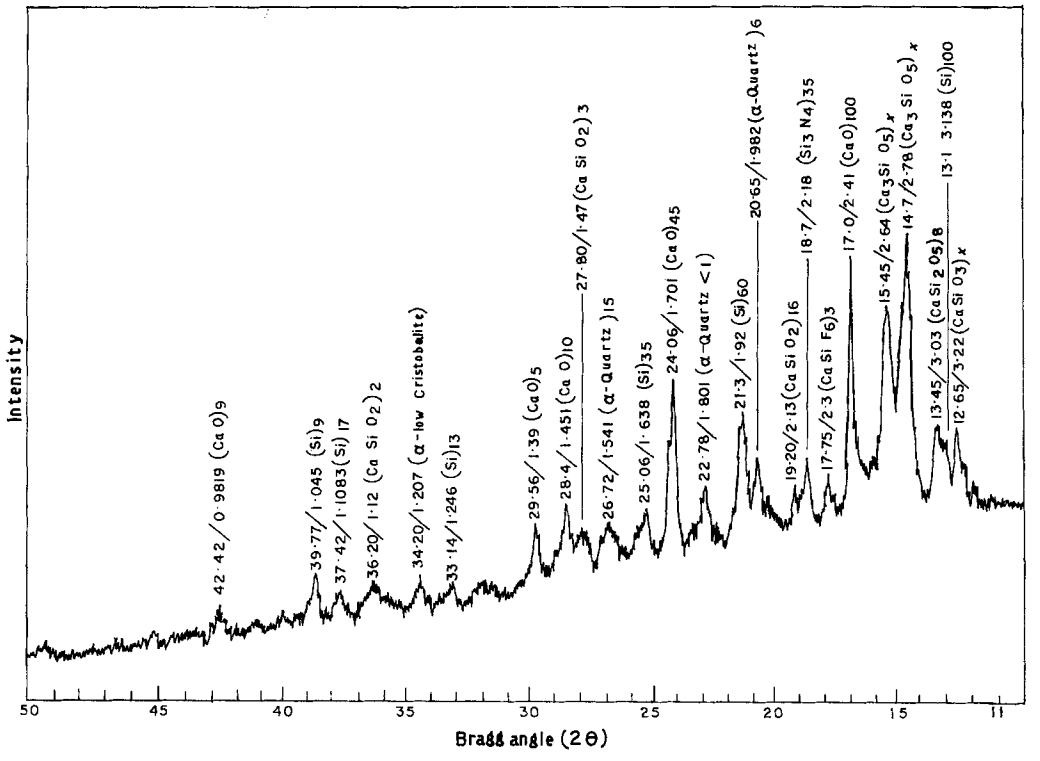

Figure 3 X-ray diffractogram of the reaction products obtained from calcium reduction of rice-husk white ash at 720° C.

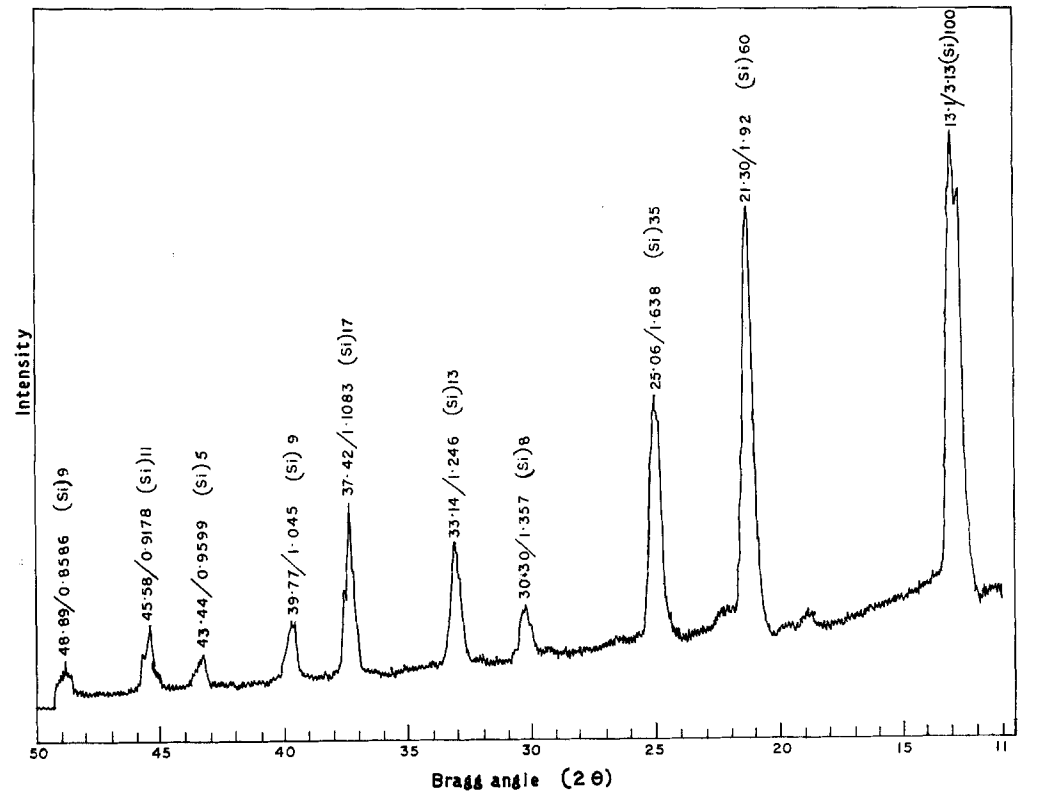

Figure 4 X-ray diffractogram of the purified polycrystalline silicon obtained by calcium reduction of rice-husk white ash.

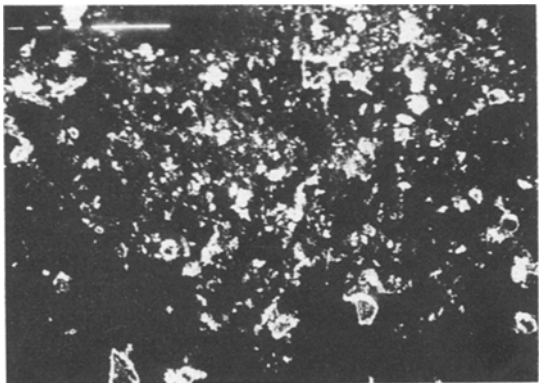

Figure 5 Scanning electron micrograph of purified polysilicon obtained by calcium reduction of rice-husk white ash. Long marker size 100 μm.

typical silicon sample obtained after acid purification indicates the absence of impurities such as vanadium, zirconium, nickel, sodium, potassium and cobalt. The presence of boron of the order of 10 ppm in the purified silicon sample may be due to contamination from glassware used in the acid-leaching process. However, if adequate care is taken and silica vessels are used, the presence of boron may be eliminated. It may be noted that the detection limit of the instrument used in this analysis is 3 ppm. Overall the sample was 99.9% pure. The material can be further upgraded by using quartz vessels, an MgO-coated sillimanite crucible, and high-purity chemicals.

A representative scanning electron micrograph of the fine powder of purified silicon is shown in Fig. 5. The photograph shows that the average particle size is of the order of 5 μm. The photograph also indicates etching of the silicon particles by the acid-leaching steps.

4. Conclusions

(a) White ash obtained from complete combustion of rice husk at a temperature of 500° C is an excellent source of high-grade amorphous silica.

(b) It is possible to reduce this amorphous silica to silicon by calcium at 720° C.

(c) A purity of 99.9% of the reduced product may be achieved by leaching with concentrated HNO_3 and HF.

(d) X-ray diffraction, SEM and emission spectrographic studies indicate that the silicon product is of reasonable purity.

(e) Use of high-purity finely powdered calcium, an MgO-coated sillimanite crucible, and high-purity chemicals may lead to the production of solar grade silicon.

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