

INVESTIGATION ON THE QUALITY OF SILICON EXTRACTED FROM THE PADMA RIVER SAND USING MAGNESIO-ALUMINOTHERMIC PROCESS

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ABSTRACT

Investigation on the quality of the extracted Silicon (Si) from the sand of the Padma river of Bangladesh using the Magnesio-Aluminothermic process has been presented in this work. Magnesio-Aluminothermic process, which is low-energy, low-cost and CO₂ free compared to conventional carbothermic process, was used for the extraction of Si from the sand. By performing the thermite process, Si was extracted as a eutectic mixture of Aluminium and Si, following that, several cycles of acid leaching were used to obtain highly pure polycrystalline silicon. After grinding the cleaned sand and making a homogeneous mixture with associated chemicals and ignition materials, modified Aluminothermic reaction was performed to produce a eutectic mixture of Si and Al. Grinded eutectic mixture of Si and Al was then purified with acid leaching and finally above 97% pure crystalline Si was extracted. XRD (X-ray diffraction) and Raman Spectroscopy confirmed the polycrystalline nature of Si where XRF (X-ray fluorescence) and EDX (Energy Dispersive X-ray Spectroscopy) corroborated the high purity of extracted Si describing the chemical composition.

Keywords: Magnesio-Aluminothermic extraction, Polycrystalline Si, Acid Leaching, XRD, EDX.

1. INTRODUCTION

The development of clean energy sources as an alternative to fossil fuels has become a major concern in the world today. In Bangladesh, we get abundant solar energy throughout the year that can be a source of renewable energy [1]. This solar energy can be converted into electricity by the use of solar cells. But, today prices of solar cell modules are high in the world due to the high-cost contribution from the production of polysilicon [2]. Siemens process one of the expensive processes due to significant wastage of about 50% during ingot slicing using wire saw [3]. Silicon is the second most abundant element in the earth's crust (27.7 %), only oxygen beats it and can easily be extracted from white sand (SiO₂) in a spectacular reaction [4-6]. Sand usually contains Silicon (Si) as the major element as its constituents [7]. It is a metalloid with a divided metallic cluster and it is quite brittle and crystallizes in the diamond lattice with a specific gravity of 2.42 at 20 °C [8-11]. Silicon is found in nature in several forms, including, flint, quartz, and opal. In fact, about 35 crystalline forms have been identified [12]. Conventionally, silicon extraction is done by a carbothermic process, where silica is reduced in the form of coal, charcoal heating with 1500-2000 °C in an electronic arc furnace. This carbothermic process produces >95% pure Si [13]. But this process is very energy-intensive and liquefies the silicon, thus destroying any original morphology of the SiO₂ and Single crystal silicon is not possible, comparatively high cost, furnace operating temperature above 2000 °C [13]. Due to considerably increased in the cost of the source materials of the solar cells, a number of different ways are being investigated to manufacture semiconductor device in the ongoing days [14]. The target of these efforts is to produce a bulk

material characterized by an abundance of resources, impurity optimization, low energy processing, and low-cost manufacturing. Magnesium-Aluminothermic reaction was used to extract silicon from the sand of the Padma river. In Magnesium-aluminothermic reaction, metal oxides react with the aluminum to produce the molten metal [15, 16]. To upgrade of elemental silicon from the Silicon eutectic mixture of Si and Al, acid leaching process was used from three generally used methods: Acid leaching, molten-salt electrolysis, Fractional crystallization [17-21]. In this contribution, we report, the easiest, environmentally benign and cost-effective way to extract Si from river sand instead of SiO_2 to observe the influence as well as the applicability of extracted Si nanoparticles in photovoltaic for harvesting the solar energy by using as promising dopant for solar cell active materials. First, Si with additive elements was extracted using Magnesium-aluminothermic process and then acid leaching process was used to extract pure silicon. Finally, investigation on the quality like purity, crystallinity, chemical compositions has been investigated.

2. EXPERIMENTAL

2.1 Sample preparation

The sand was collected from the upper surface of the Padma river in BGB area of Rajshahi. The collected sand was cleaned by normal water about 10 times and then with distilled water about 7 times and then, sand was cleaned by acetone 5 times to remove chemical impurities. The cleaned sand was dried at 100°C for about 6 hours by a furnace (Carbolite CWF). Dry sand was grinded to form fine powder with wood mortar & pestle. Since, finer the sand, faster the reaction, hence sand was done very fine powder. A homogenous mixture was made with dry powder of sand, Aluminum (Al) and Sulfur (S) with specific weight ratio 7:8:6 respectively. Regents, Aluminum and Magnesium were collected from Qualikems Fine Chem Pvt. Ltd. and Loba Chemie Pvt Ltd. respectively those were used without further purification. The prepared mixture was transferred to a small clay flower pot. A small cone-shaped indentation at the top was formed and then it was filled with (1g) magnesium powder to facilitate ignition and magnesium ribbon ($\sim 4\text{-}5$ cm) was used as fuse wire. The reaction was performed in an open place for 40-50 seconds. Finally, the residue (shown in Fig. 1) was collected after cooling down about 30-40 minutes.



Fig. 1. (a) Eutectic mixture of Si and Al (b) Grinded eutectic mixture of Si and Al.

2.2 Silicon from a eutectic mixture

Hydrochloric acid (HCl) 46% was added with grinded eutectic mixture of Al and Si (Fig. 1) in a glass beaker at a constant temperature of 50°C on a hot plate for 20 minutes for each leaching cycle then washed by distilled water (Fig. 2b). After repeating this process three times, the solid residue which is mainly elemental silicon was found in the form of pea-size, hard, black, crystalline globules (Fig. 2b). In this process, Sulfur was removed as the following reaction:

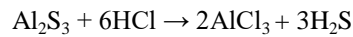
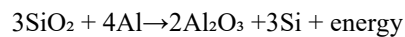
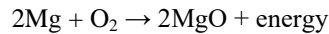


Fig. 2. (a) Acid leaching of grinded eutectic mixture of Si and Al (b) Pea-size Silicon (Si)

3. RESULTS AND DISCUSSION

3.1 Optical microscopy and X-ray Fluorescence

The average particle size of sand of Padma river near BGB area that was used to extract Si-NPs was 75.57 μm (Fig. 3a) was found from simple optical microscopy. The magnesio-aluminothermic reaction of sand provides residue that consists of primary silicon and aluminum as a simple eutectic aluminum-silicon mixture. The eutectic mixture is a mechanical mixture, not a compound, therefore, aluminum can be easily removed by acid leaching. XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays ("a fingerprint") that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition. XRF result (Fig. 3b) shows that above 97% purity was obtained after 3-cycle acid leaching of grinded eutectic mixture of Al and Si.

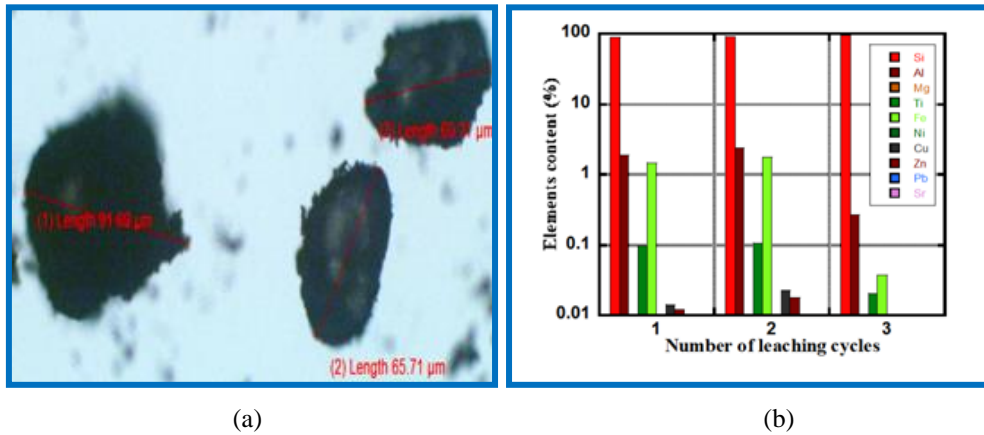


Fig.3. (a) Microscopy of the sand particle (25 x mag.) and (b) Effect of leaching on the removal of residue from the eutectic mixture of Al-Si in XRF

3.2 Energy-dispersive X-ray spectroscopy and Photo Luminescence

Energy-dispersive X-ray spectroscopy is a characterization technique that provides an elemental composition of various constituent elements in the sample. The abscissa of the EDX spectrum indicates the ionization energy and ordinate indicates the counts. Higher the counts of a particular element, higher will be its presence at that sample. EDX spectrum with Atom% and Weight % (Fig.-4b) shows the purity of Si increases with increasing the number of cycles and Al and O₂ decrease. Fig. 4 shows that after three cycles of acid purification high-quality silicon (above 97%) was found. It is noted that after the third cycle another new element Sr is seen in very small amount.

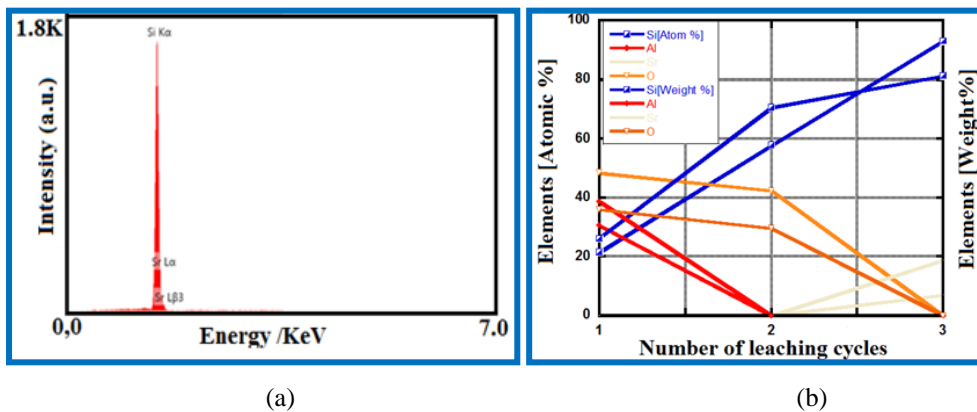


Fig. 4. (a) EDX spectrum of extracted Si-Al mixture after three times acid leaching; (b) EDX spectrum of extracted and three times acid leached Si-Al eutectic mixture at atomic % and weight %.

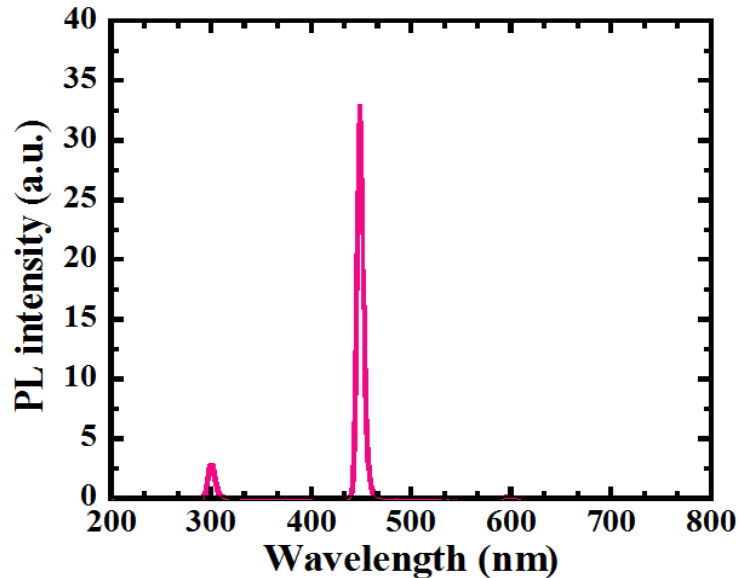


Fig. 5. Photoluminescence (PL) of Si particles extracted from river sand.

Fig. 5 shows the photoluminescence (PL) study of extracted Si from sand that well-matched with the standard spectra of Si-wafer as a reported article [22]. Ultra-sonication to make nanoparticles was performed after collecting the Si from sand dispersed in 2-propanol. The PL peak intensity strongly depends on the particle size, smaller size offers the greater intensity of the peaks corresponding to the higher absorption of the light having comparable wavelength with the particles size [23, 24]. The PL peak energy exhibit a blue shift with decreasing the size of the Si nanostructures along with increasing the peak intensity resulting from size-dependent widening of the energy gap. Since the prepared sample of Si dispersed in 2- Propanol contains different size and shape (~100-450 nm), the intensity of the PL peak is lower than the slandered Si nanoparticles. This result reveals that the prepared sample contains large size of Si particles extensively.

3.3 X-ray diffraction and Raman study

The x-ray powder diffraction (XRD) method was used to phase analysis to determine the presence of silicon. The shift of diffraction peaks towards higher diffraction angle means crystal lattice is compressed and if the peaks are shifted towards lower diffraction angle that means lattice is expanded and conversely stress due to impurities decreased. The XRD peak shift is a result of a change in the lattice parameters owing to some reasons such as crystallize size and lattice strain, Thermal annealing, changes in stoichiometric composition by doping, doppler effect during counts, etc [25-27]. Fig. 6 shows, XRD peaks are shifted towards lower angle with acid leaching that indicates the crystal lattice relaxation for removing the stressing elements those were a presence into the Si crystal such as Al, Mg, Ti, Ni, Fe, Cu, Zn, Pb, Sr. The XRD patterns of acid-treated silicon depict the presence of polycrystalline silicon.

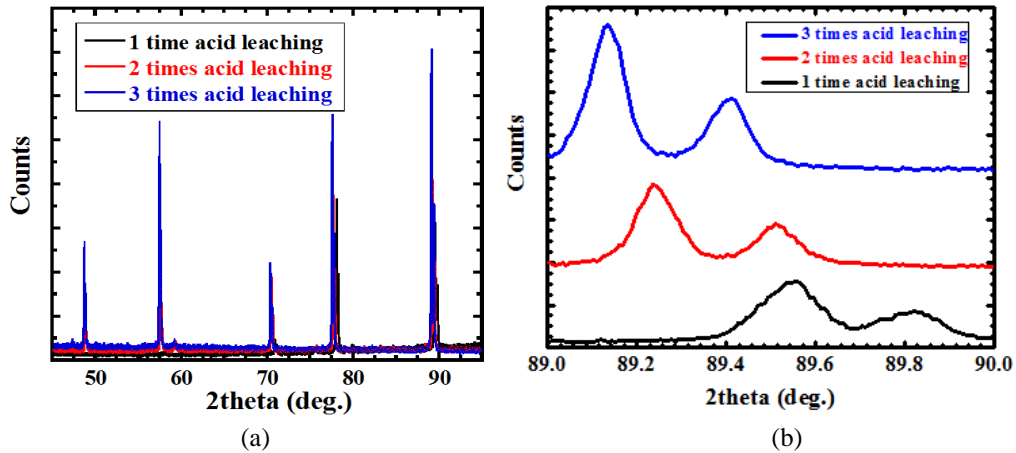


Fig. 6. (a) XRD (counts vs 2Θ) of eutectic mixture of Al and Si at different leaching cycles and (b) Zoom view for left peak shift at $2\Theta \sim 90$.

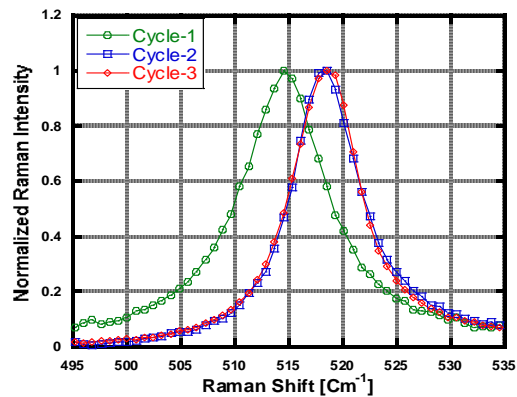


Fig. 7. Raman spectra of eutectic mixture of Si-Al at different leaching cycles

The Raman spectra show the high crystalline nature of extracted silicon from river sand. Fig. 7. shows that with increasing the number of acid leaching cycles, the shifting of peaks towards higher wave-numbers and peak was reached at 519 cm^{-1} through accomplishing the three removal cycles which is the nearest of the crystalline Si peak at 520 cm^{-1} [28]. In Raman spectra, shifting of peaks towards lower or higher wave-numbers is related to the chemical bond length of molecules. If the chemical bond length of molecules changes due to any internal or external effects, then it may cause to shift wave-number. The shorter bond length causes to shift higher wave-number. Fig. 6. shows the shift toward higher wave-numbers hence bond length be shorter than previous that refers to the purity of high crystalline Si with acid leaching cycles.

4. CONCLUSION

Microscopy of sand clearly indicates the particle size of sand 75.57 μm . XRF shows the amount of Si increases while the amount of Aluminum decreases with acid leaching cycles. After three cycles of purification, Si above 97 % in purity was found with no Aluminum. An EDX spectrum shows that no Aluminum and Oxygen are present after three removal cycles. EDX atom% and weight% results also show that the amount of Aluminum is zero and only presence Silicon (Si) with a very small amount of Sr after the 3rd cycle of acid leaching. In addition, the peak shift of XRD toward a lower angle that refers to the purity of polycrystalline Si increases till the 3rd cycle. These results also revealed by Raman Spectra. The Raman shift toward higher wave-numbers indicates bond length be shorter than previous removal cycles that refer to high-quality polycrystalline Si. This paper reports, high-quality polycrystalline silicon (Si) can be extracted using a very simple, cost-effective and environmental benign Magnesio-aluminothermic process from the river sand that may offer promising advancement in photovoltaic technology with accomplishing by the further investigations.

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