SILICON PURIFICATION THROUGH MAGNESIUM ADDITION AND ACID LEACHING

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ABSTRACT: Silicon is the dominant material in photovoltaic devices and with regard to the PV market growth, the demand for solar grade silicon feedstock is expected to be high in the future. Although solar silicon is currently produced through both chemical and metallurgical routes, the chemical route is still the main production method, which is expensive and have environmental challenges. Acid leaching of silicon, which is a metallurgical refining process is applied for silicon purification in the present research work. In this case, magnesium in different portions is added to liquid silicon containing B, P, Fe, Al, and other trace impurities. The Si-Mg melts are solidified under a controlled cooling rate and then they are treated by acid leaching through using dilute HCl solutions. The effect of magnesium concentration on the segregation and removal of the impurities, in particular P and B, is studied by electron microscopy and chemical analysis techniques. It is indicated that the process is effective for removing the impurities, and the purification is depending on the amount of Mg added into the silicon.

Keywords: Silicon, magnesium, solar silicon, solidification, segregation, leaching, magnesium silicide

1 INTRODUCTION

Silicon is produced through carbothermic reduction of quartz in the electric arc furnace; the product being metallurgical grade (MG-Si), which is the basis of many metallurgical, chemical and electrical applications. MG-Si contains about 99wt% Si with impurities such as Fe, Al, Ti, Ca, B, and P [1]. Solar Grade Silicon (SoG-Si) with more than 6N (+99.9999) purity is produced from MG-Si and it is the feedstock for the production of silicon solar cells. Ultra-high pure silicon with around 11N purity, which is called Electronic Grade Silicon (EG-Si), is used for the fabrication of electronic devices [1]. The majority of SoG-Si and all the EG-Si existing in the market are currently produced from MG-Si through the *Siemens process* or newly developed *fluid bed reactor (FBR) technology.* In these chemical processes, pure silicon is deposited on rods or seeds from a gas phase, which is produced from MG-Si and contains gaseous compounds of silicon such as $SiHCl_3$ or SiH_4. The Siemens process in particular is an expensive process with regard to high energy consumption [2, 3]. The production of SoG-Si through *metallurgical refining processes* is more energy efficient and environmentally friendly than chemical route which in turn may encourage a faster growth of the global PV market. This has been the motivation of the development of several refining processes such as the *ELKEM Solar Silicon (ESS) process* in Norway**,** *NS Solar process* in Japan**,** *Chinese metallurgical routes s*uch as those of *Shanghai Propower* and *Ningxia,* and the *Photosil process* in France [3]**.** Solvent refining of silicon using Al as the refiner is another method as reported by *Silicor Materials* [4]. Almost all the present impurities in MG-Si except B and P can be removed by directional solidification due to large segregation is solidification[5], which is usually a final key process step in metallurgical approach. An effective process for silicon purification is acid leaching in which a metal e.g. Ca is added to silicon melt and the solidified silicon is hydrometallurgically treated by acid. The impurities are segregated during solidification and concentrated on the grain boundaries in association with a silicide phase such as $CaSi_2$ soluble in the acid. Therefore, the impurities are separated physically or dissolved chemically into the solution from the silicon grains and highly pure silicon particles are produced.

Acid leaching process for silicon purification have been studied through several studies [6,7,8,9,10,1112] and the process is effective for the removal of many impurities, in particular the elements with large segregation in solidification such as Fe, Al, Mg, Sb, Sn, Zn, Cu, Au, Ni and Ti. The process is also effective for partial removal of P. The purification of silicon is depending on the particle size of the silicon particles subject to acid leaching and better purification is obtained when smaller silicon particles are treated [6, 10]. The removal of impurities in acid leaching is higher at higher temperatures [8, 10]. And it has been observed that the purification is more effective when HCl and HF acids are used in comparison with other types of acids [6, 8, 11]. Inspecting these studies reveals that the silicon has been treated without the addition of any element to liquid silicon or through the addition of Ca into liquid silicon before solidification.

In the present study, magnesium is added into molten silicon and the effect of this element addition in silicon purification by acid leaching is investigated. Electron microscopic examination of Mg-doped silicon up to 10wt%Mg is studied using. Moreover, the purification of the samples is studied through chemical analysis study before and after leaching.

2 EXPERIMENTAL PROCEDURE

2.1 Silicon doping by magnesium

A metallurgical grade silicon (MG-Si) was used in the present study. , and its chemical composition is shown in Table I.

Table I: Chemical composition of used silicon (wt%).

Mg	Al	Fe	Ca	P	B
0.005	0.16	0.17	0.014	0.0027	0.0060

Magnesium silicide (Mg_2Si) with purity above 99% was mixed with silicon in different portions and Mg-containing silicon alloys with 0.2, 0.6, 2.1, 3.6 and 4.9 wt% Mg were obtained. The mixtures were then heated and smelted in high density graphite crucibles at 1500°C in an induction furnace. The materials were then slowly cooled down and solidified with average of 10°C/min.

2.2 Leaching

The solidificed silicon samples were crushed and particles with 1-3 mm particle size were leached by hydrochloric acid solutions. The leaching was performed in two steps; first by using 15%HCl at 80°C for 3 hours, and then by 2.5%HCl at 80°C for 3 hours.

Silicon samples before and after leaching were analyzed by high-resolution Inductively Coupled Plasma-Mass Spectroscopy technique. Moreover, metallography samples were prepared and their microstructures was studied through scanning electron microscope.

3 RESULTS AND DISCUSSION

The results of the present work are presented and discussed as follows.

3.1 Microstructural analysis

The microstructure of polished solidified Mg-containing silicon samples were studied using secondary electron (SE) and backscattered electron (BSE) modes of electron microscope supported by Energy dispersive mass spectroscopy (EDS). Figure 1 shows the microstructure of the samples with different Mg concentrations. As seen in all the samples we have three phases; a grey matrix phase, a dark grey secondary phase and a bright phase. Based on the EDS results shown in Figure 2, the grey phase is silicon matrix (Fig. 2.a). In addition, some Si particles distributed in the dark grey phase. The dark grey phase is Mg_2Si phase based on the quantified EDS spectrum (Figure 3.b). Figure 1 shows clearly that the amount of Mg_2Si is increased with increasing Mg. Moreover, the shape of this phase becomes different at high Mg concentrations. According to Figure 2, the bright phase contains mainly Si, Fe, and Al and small concentrations of Ca and Mg. This phase is observed bright compared to the other phases in backscattered mode due to the existence of heavier elements in it. Since Si, Fe and Al are the main elements in the bright phase with variations in the chemical composition, we call it here Si-Fe-Al phase.

The microstructural images show that for low Mg concentrations such as images (a), (b) and (c) in Figure 1 the Mg_2Si and the Si-Fe-Al are located between the silicon grains. It was observed that for Mg concentrations lower than 2.1 wt% there is not significant Si particles together with Mg_2Si. This may be due to the growth of secondary Si phase due to a eutectic reaction over the primary Si grains. This may be due to short diffusion distances available for Si precipitation. For higher Mg concentration, in which significant amount of liquid is transformed to Si+Mg_2Si, based on the Si-Mg phase diagram, secondary silicon phase is formed through the eutectic reaction between the grains which causes the existence of Si particles together with Mg_2Si between the silicon grains as we see in image (d) in Figure 1. The Si-Fe-Al phase is obviously formed at the end of solidification and for low Mg containing melt it is located in contact with the primary silicon grains with more less the same distribution of Mg_2Si phase. In high Mg containing melts, however, the Si-Fe-Al phase is also observed in the eutectic Si+Mg_2Si phase as observed in image (d) in Figure 1.

Microscopic study shows also that there is some cracks in Si matrix and in addition significant amount of cracks in Mg_2Si phase.

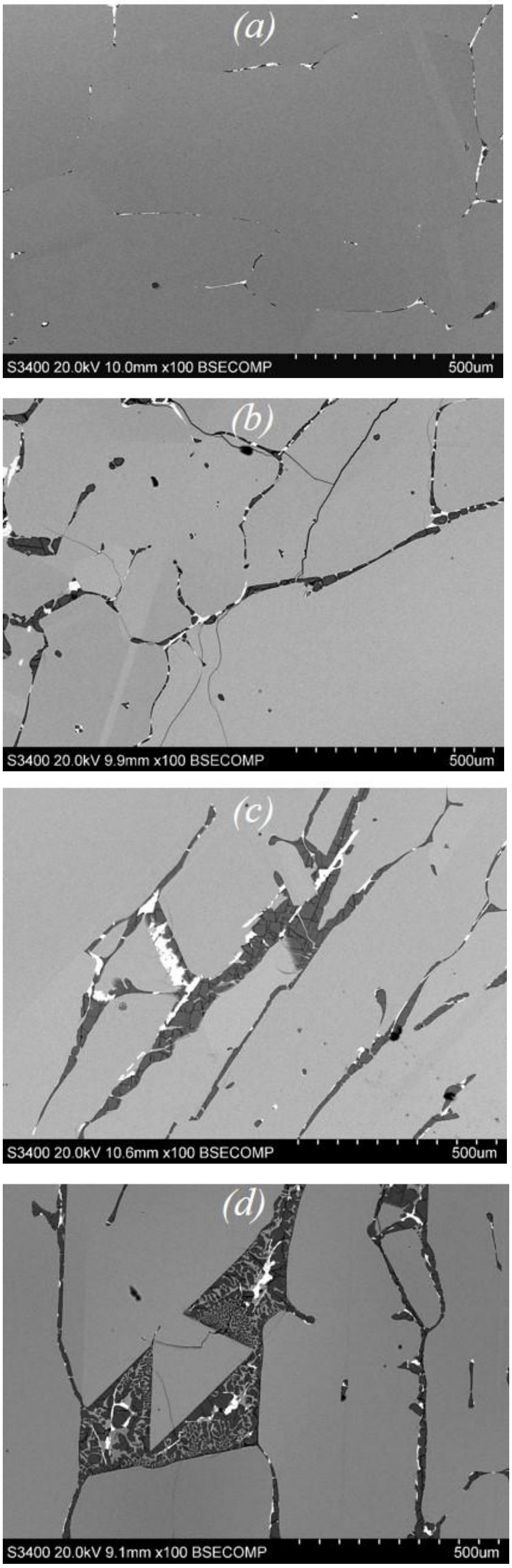

Figure 1: DSED images of (a): 0.2 wt%, (b): 0.6wt%, (c): 2.1wt%, (d): 3.6% Mg-containing silicon.

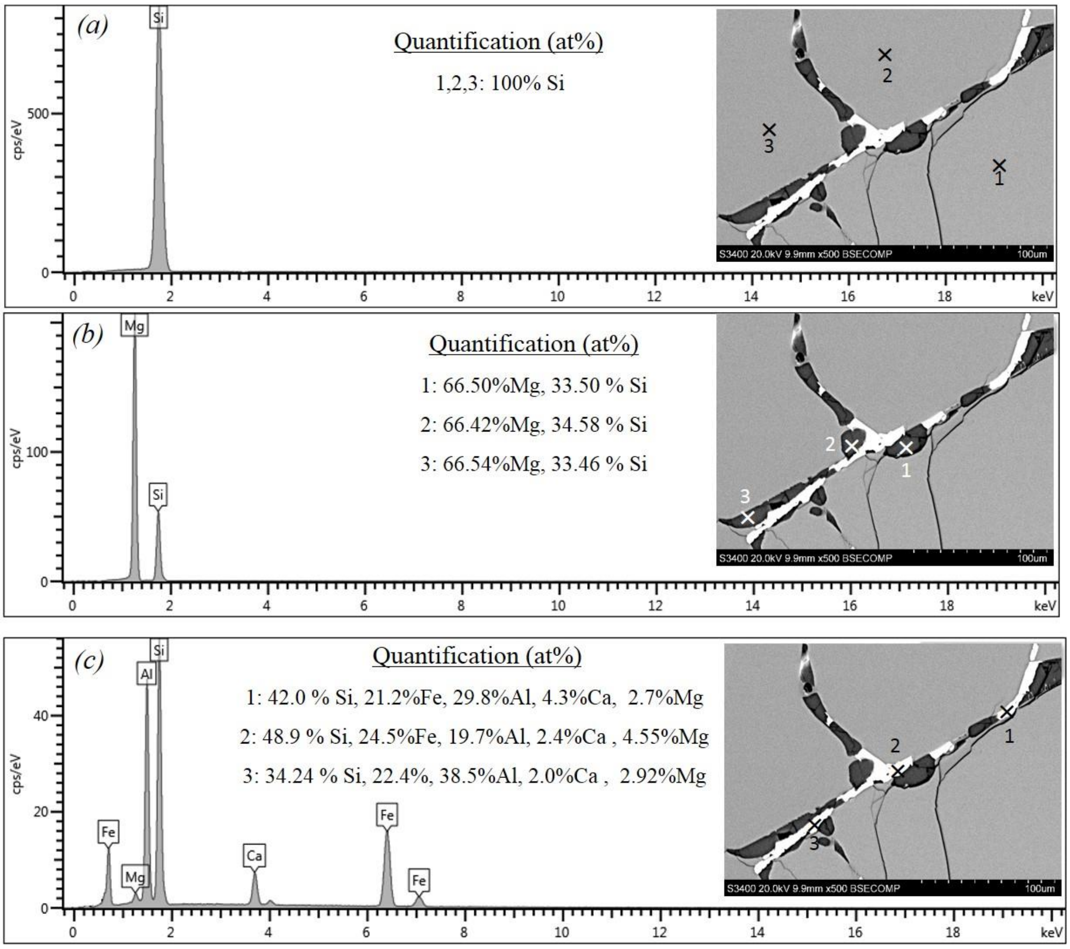

Figure 2: EDS analysis of coexisting phases in samples.

3.2 Leaching effect

Electron microscopy of specific locations of some samples after leaching in different durations indicated the effect of leaching on the removal of Mg_2Si phase adjacent to the silicon grains (Figure 3).

The solution of Mg_2Si causes the physical separation of intermetallic phases as observed in Figure 3. All the impurities, in particular trace elements such as P and B in the both phases are therefore removed from the silicon.

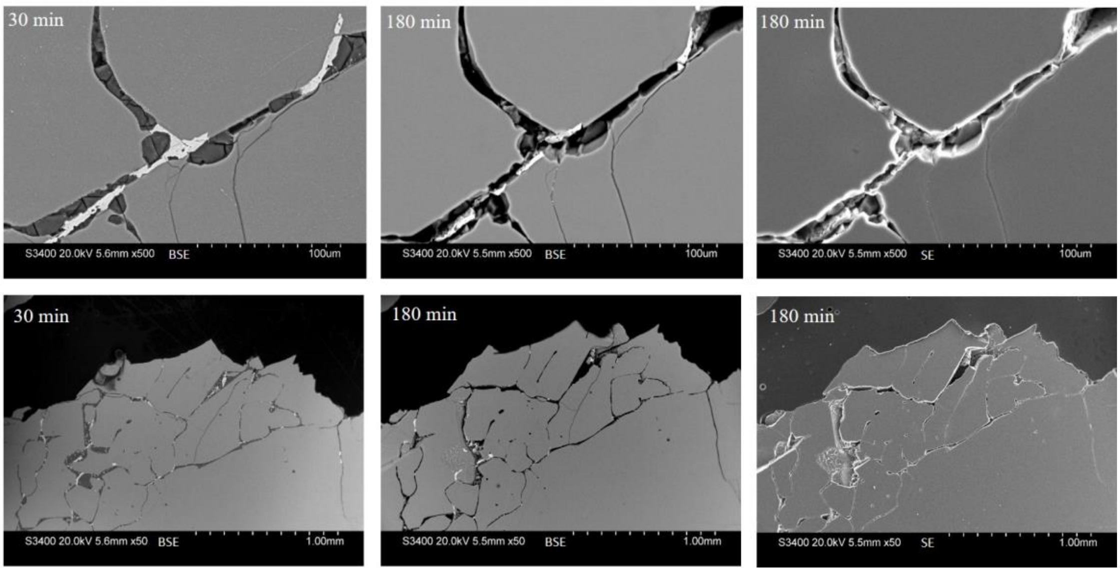

Figure 3: SE and BSE images of 2.1%Mg-containing sample during different durations of leaching.

The chemical analysis of the samples before and after leaching shows that there is significant decrease in the concentrations of the impurities in silicon. Figure 4 shows the removal degree of the impurities calculated based on the chemical composition analysis by the following equation:

$$Removal\ degree = \frac{C_i - C_f}{C_i} \times 100$$

Where C_i and C_f are concentrations of the impurity before and after leaching, respectively. Figure 4 shows that all the impurities are removed to some degree through acid leaching. The removal degree is increased with increasing the amount of the added Mg into silicon for the majority of the impurities. However, the addition of Mg in higher than 2.1% does not show a significant effect in terms of B removal. It may however be generally concluded that the segregation of the impurities and their separation through acid leaching is improved with increasing the amount of Mg in silicon.

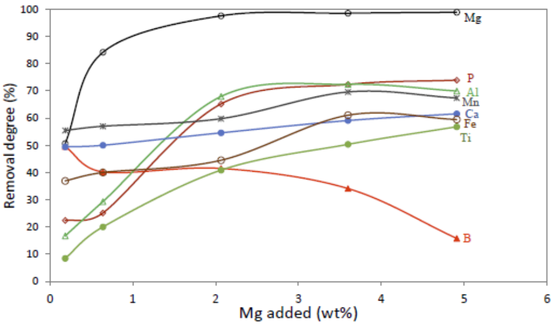

Figure 4: The removal degree of the impurities for different concentrations of Mg in silicon.

The chemical analysis measurements show that the removal of P is significantly improved with increasing the concentration of Mg in silicon as clearly shown in Figure 5. This may indicate that the segregation of P is better when more Mg exist in the silicon melt.

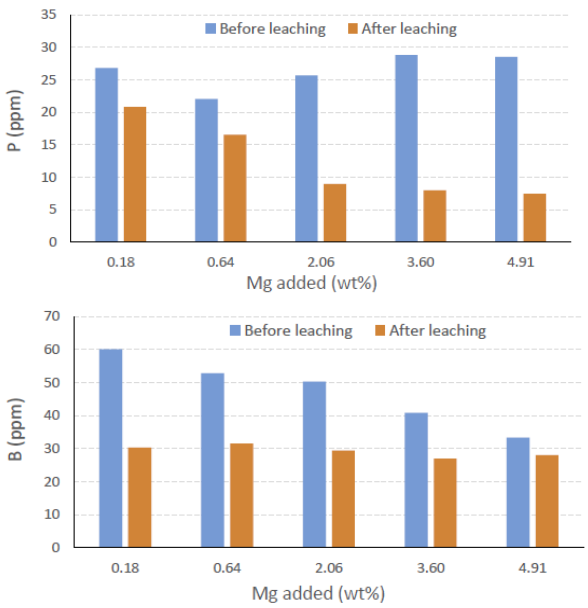

Figure 5: The concentrations of B and P before and after acid leaching of different Mg-containing silicon samples.

The B removal results in Figure 5 show that the B segregation and separation is minimally increased with Mg addition in small amount to 2.1wt%, and higher Mg concentrations do not affect B removal significantly. Figure 5 shows that B is removed around 50% in low Mg concentrations, and this may indicate that the segregation of B during solidification is improved.

The presented data in this research are based on selected leaching conditions and optimal purification conditions may be obtained through more experimental work.

4 CONCLUSIONS

- The alloying of molten silicon with magnesium followed by slow cooling and solidification shows the precipitation of Mg_2Si and Fe-Al-Si-Ca intermetallic phases between silicon grains.
- The leaching of silicon samples by 15%HCl solution is effective for dissolving Mg_2Si phase.
- The removal of Mg_2Si phase causes significant removal of the Fe-Al-Si-Ca intermetallic particles due to their sizes and distribution along Mg_2Si particles.
- The ICP-MS results show that all types of the impurities are removed from silicon through Mg addition followed by acid leaching.
- Phosphorous in particular shows better segregation with increasing the amount of the added Mg to silicon.

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[13] SFI Norwegian acronym for Centre for Research driven Innovation (CRI).