Elaboration and characterization of metallurgical silicon for photovoltaic applications

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Abstract. There is a small quantity of participants in the global market of silicon, mainly from the developed countries. It should be noticed also that production of metallurgical silicon Mg-Si is among the most important steps to produce solar grade silicon and photovoltaic panels. Therefore, in this paper we focused on the growth of Mg-Si by carbothermal reduction of silica. An investigation was made using FT-IR characterization to study the effect of process conditions (temperature, atmosphere, duration) in Mg-Si production. Raman spectroscopy was used to investigate the produced Mg-Si. Based on these results, we established a pilot line production of metallurgical silicon at the “CRTEn” in Tunisia.

1. Introduction

Photovoltaic (PV) technology is expected to be a leading technology to solve the issues concerning the energy and the global environment that we are now facing, due to several advantages of the PV system [1]. Silicon is the most popular material for solar cells. Metallurgical silicon is produced by the reduction of silica in an electric arc furnace by means of carbonaceous materials. In the submerged arc furnace, silica and carbon raw materials react under atmospheric pressure over a range temperature of 1573 K to 2273 K (1300 °C to 2000 °C).

The upper low temperature part of the furnace is called the outer zone, whereas the hottest part of the furnace the inner zone. There is general agreement about the reactions taking place in the inner zone of the furnace.

The main reactions in the inner zone are as follows [2]:

\[ \text{SiO}_2 [s] + C [s] = \text{SiO} [g] + 2 \text{CO} [g] \]  
(1)

\[ \text{SiO} [g] + 2 C [s] = \text{SiC} [s] + \text{CO} [g] \]  
(2)

\[ \text{SiC} [s] + \text{SiO} [g] = 2 \text{Si} [s] + \text{CO} [g] \]  
(3)

2. Experimental

2.1 Sample preparation

The purity of silica used in this work is to 99.98% [3]. Common impurities in quartz, like Na, K, Al, and Fe come from minerals like mica and feldspar [4]. The carbon powder used is taken from coal. Its quantity was adjusted to obtain a nominal molar ratio C/SiO₂ = 3/1. Powders were mixed for more homogeneity.
Carbothermal reduction of the silica was performed in an electric arc furnace. The mixture loaded in the graphite crucible was placed into the hot zone of the furnace. The gas is introduced into the reaction chamber during the experiment whereas switching on the extraction system to let the exhausted gas flow into the ambient air. The temperature regulation is performed using temperature controller “OMRON E5AK”

2.2 Characterization

Synthesized samples were characterized by Fourier transform infrared spectroscopy (FTIR). The samples were ground and dispersed in a matrix of KBr at room temperature, the mixture was pressed into pellets. The spectra were saved in transmittance mode. Spectral resolution is 4 cm$^{-1}$. Prepared samples were identified also by a Raman spectrometer (LabRAM HR JOBIN YVON Technology HORIBA Scientific) to determine SiC structure.

3. Results and discussion

3.1 FTIR analyses

The FTIR spectrum of powder synthesized under air, at T=1500°C and during 120s is shown in figure 1.

![Figure 1. FTIR spectra of samples synthesized under air, at T=1500°C and during 120s.](image-url)
The FTIR spectra given in Figure 1 shows three vibrations; Two peaks around 480 cm\(^{-1}\) and 1100 cm\(^{-1}\) attributed to Si-O \([5]\) and a peak around 1385 cm\(^{-1}\) attributed to Si-CH\(_n\) bond \([6]\) which can be explained by the chemical etching realized before characterization. We increased temperature to 1700\(^\circ\)C and we obtained FTIR spectra shown in figure 2. We observed decrease of Si-O peak intensity but we have no peak of Si-Si bond which means that we have a partial deoxydation of silica.

We changed the atmosphere to work under inert gas. Figure 3 illustrates the IR spectrum of the produced samples under argon, at T=1700\(^\circ\)C and during 120s.

We notice the appearance of new peak around 810 cm\(^{-1}\) attributed to Si-C bond but we have no peak of Si-Si bond which means that we have also a partial deoxydation of silica.

We changed the atmosphere to work under CO and we increase the duration of treatment to 180s. We obtained FTIR spectrum illustrated in figure 4.

**Figure 2.** FTIR spectra of samples synthesized under air, at T=1700\(^\circ\)C and during 120s.

**Figure 3.** FTIR spectra of samples synthesized under argon, at T=1700\(^\circ\)C and during 120s.
As revealed in figure 4, a new peak around $\nu = 629 \text{ cm}^{-1}$ appears. It’s attributed to Si-Si bond. The peak around 480 cm$^{-1}$ corresponds to Si-O bond, it can be explained by rinsing the sample in pure water before characterization. On the other hand the peak associated with Si-C bond remains, which means that we obtained a mixture of peak Si+SiC.

We increase again the temperature to 1900°C and we decrease the duration of treatment to 120s and we obtain the FTIR spectra illustrated in figure 5.

![Figure 4. FTIR spectra of samples synthesized under CO at T=1700°C and during 180s.](image1)

![Figure 5. FTIR spectra of samples synthesized under CO, at T=1900°C and during 120s.](image2)
As shown in figure 5, we observe almost the same peaks of figure 4. These peaks are attributed to Si-O, Si-Si and Si-C bonds. This led us to increase the time of treatment to 180s by leaving temperature at 1900°C and under CO, we obtain then FTIR spectra shown in figure 6.

![Figure 6. FTIR spectra of samples synthesized under CO at T=1900°C and during 180s.](image)

IR analysis (figure 6) shows that the major peak is around $\nu = 629$ cm$^{-1}$ due to vibrations of the Si-Si bond. This means that we obtain silicon when we synthesize our samples under CO, at T=1900°C and during 180s.

### 3.2 Raman analyses

Figure 7 shows Raman spectra of used as raw materials in our work.

![Figure 7. Raman spectra of SiO$_2$.](image)
Figure 8 illustrates the Raman spectrum of the produced samples under CO, at T=1900°C and during 180s.

The analysis of this spectrum shows the existence of a single major peak at 517 cm⁻¹. This peak is attributed to the Si-Si bond [7]. This means that we have succeeded in producing silicon when we synthesize our samples under CO, at T=1900°C and during 180s which confirms results obtained by FTIR analyses. The cleanliness of the peak tells us that our silicon is crystallized. The other three peaks are less important and are attributed to Si-C and CC.

4. Conclusion

As a conclusion, this work allowed finding the conditions (electric power, atmosphere and duration of growth) that promote the growth of metallurgical silicon. This work enabled to set up a knowledge base for the manufacturing technology of metallurgical silicon from silica and carbon. Metallurgical silicon is well produced in Tunisia. The next step is to purify the Mg-Si to produce solar grade silicon.

References

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