Selectivity and Reactivity of the Trichlorosilane Process

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1 ABSTRACT

The influence of different intermetallics in metallurgical grade silicon (M-Si) on the reaction of M-Si with HCl-gas was investigated. Surface studies of M-Si samples as well as batch reactor studies were performed. All M-Si samples used were synthetic qualities with controlled amounts of impurities.

The reactor studies indicate that Al and Fe in M-Si decrease the reaction start temperature, whereas calcium seems to increase it.

Fe rich AlFeSi-phases produce $FeCl_2$, which accumulates in the reactor. Al rich AlFeSi-phases are consumed and form gaseous products. The $FeSi_2$ phase seems to be inert in the HCl atmosphere. Al_2CaSi_2 influence the surface of the surrounding silicon, thus increasing the reaction start temperature.

2 INTRODUCTION

Electronic grade silicon is produced from metallurgical grade silicon (M-Si) via the Siemens process.The raw material for this process is trichlorosilane (TCS), which is produced from M-Si and HCl gas.

$$M\text{-}Si + 3\ HCl = SiHCl_3 + H_2 \qquad (1)$$

Reaction 1 produces tetrachlorosilane (STC) as a byproduct. Usually, TCS is isolated from the product stream by distillation, and then decomposed back into silicon. Thus, increasing the yield of TCS (TCS selectivity of the reaction) is crucial. The selectivity depends on several parameters: reaction temperature, contact time and the properties of, and impurities in, the M-Si employed. The first two factors have to be considered by the TCS producers, while the properties of the M-Si are dependent on what the M-Si producers can supply.

According to Ehrich et.al.[1], a minimum temperature is needed for reaction 1 to start. They found that the minimum reaction start temperature was strongly influenced by impurities in the silicon, especially copper. A vibrating glass reactor was employed in these experiments.

STC is the thermodynamically stable product of reaction 1, while TCS is kinetically favored. Thus, one can expect that with increasing temperature, TCS selectivity will decrease (Bade and Hoffmann)[2]. Work done by Lobreyer et al[3] confirms this, but the temperature dependence of the different silicon samples differs. They found that M-Si impurities raised the reactivity of M-Si towards HCl gas and lowered the TCS selectivity of the reaction. They concluded that M-Si impurities act as a catalyst for a temperature dependent reaction to STC.

Wakamatsu et.al.[4] used a fixed bed microreactor to investigate the influence of iron and phosphorous on the TCS process. They found that Fe and P have a cooperative effect to lower the TCS selectivity.

Samori et al[5] used a fluidized bed reactor to figure out the the roles of aluminium and iron in the TCS process. They found that Al increase TCS selectivity, and $FeCl_2$,which is formed during the process, decrease TCS- selectivity.

In most of the works described above industrial M-Si samples was employed. As observed by Wakamatsu[4] some of the elements in M-Si exhibit cooperative effects. Thus, to rule out any uncontrolled factors, all the samples used in this work were synthesized from high purity electronic grade silicon. The goal was to get a basic understanding of the roles of different intermetallic phases in the TCS production.

3 EXPERIMENTAL

3.1 PREPARATION OF SAMPLES

All the samples were prepared from high purity silicon, mixed with the appropriate amount of different pure metals. The mixture was heated to 1500°C in a Balzers induction furnace under argon atmosphere. The melt was then cast in a graphite crucible.

The cast was cut in suitable pieces (roughly 23x6x4 mm) with a diamond saw. One surface was polished on a Struers RotoPol polisher. The surface was characterized with respect to intermetallic phases in a scanning electron microscope (SEM) using energy dispersive X-ray analysis (EDX).

The leftovers of the cast were ground in a BICO grinder to a powder (<1 mm), and sieved into narrow particle size fractions. (–50, 50-90, 90-125, 125-180, 180-250 and +250 μm). The fraction 180-250 μm was chosen as a standard.

3.2 THE REACTOR

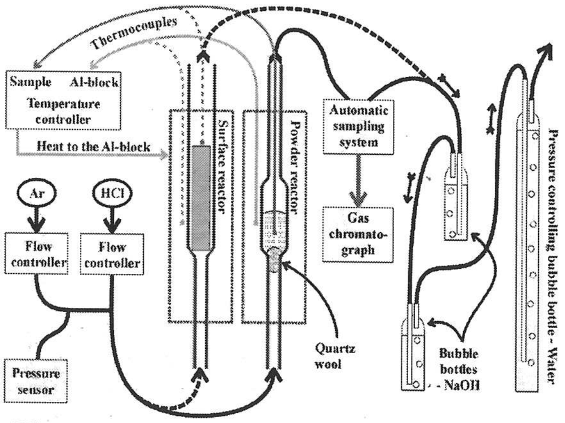

Figure 1 - The powder reactor was similar to Wakamatsu's batch reactor.[4]

The two interchangeable reactors for surface and powder studies respectively are shown in figure 1. Surrounding the reactor is an aluminium block serving as a heating element as well as a heat buffer. The temperature difference between the Al-block and the reactor gives information about the heat evolution of the reaction.

3.3 RECORDING OF DATA

All parameters like pressure, Argon-flow, HCl-flow, reactor - and Al-block - temperature were measured and recorded continuously throughout the experiment using a Hewlett Packard DataLogger.

3.4 REACTION START TEMPERATURE

The ignition temperature or, as defined in this paper, the reaction start temperature, was measured by increasing the temperature in the reactor at a constant rate (2°C/min), and with a constant HCl flow (10ml/min), until an increase in the temperature difference between the reactor and the aluminium block was observed.

3.5 SELECTIVITY

The amounts of the different products were measured with an online gas chromatograph (GC). Every 13 minutes a new sample was automatically injected into the GC column. Based on these measurements, the selectivity was calculated using the definition in equation 2.

$$\text{TCS-Sel} = \frac{n_{TCS}}{n_{TCS} + n_{STC}} \qquad (2)$$

3.6 SURFACE STUDIES

The polished and characterized samples were put into the surface study reactor, and subjected to HCl gas for 3 – 8 min. The surface was then studied in the SEM/EDX to detect changes in the elemental composition and topography of the sample.

4 RESULTS AND DISCUSSION

The method of preparing the synthetic silicon qualities produced no slag and the amount of impurities was easily controlled. See table 1.

Sample	**Fe 0.2, Al 0.1**	**Fe 0.2**
Si	99.39 %	99.46 %
Al	0.11 %	0.02 %
Fe	0.20 %	0.22 %
Ca	0.002 %	0.005 %

Table 1 – XRF-analysis of two synthetic silicon batches. The numbers in the sample names refers to weight %.

4.1 REACTOR STUDIES

The reaction start temperature was strongly influenced by the type of intermetallic phases present in the silicon.

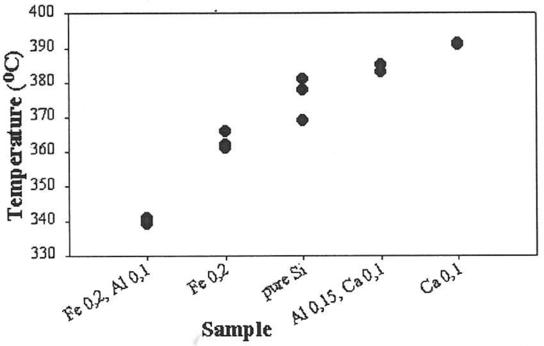

Figure 2 - Reaction start temperatures for the different synthetic silicon samples. The numbers refer to weight%. Grain Size: 180-250 μm.

As can be seen from figure 2, the reaction start temperature was high for the high purity silicon sample (~375°C). The reaction start temperature was lowered by the presence of aluminium – iron and iron phases, while calcium raised the reaction start temperature.

As figure 3 shows, the selectivity varied throughout the experiment. Why the selectivity drops at around 50% is still uncertain. One explanation might be that channels are formed through the silicon mass. As a standard, the measured selectivity when 30 % of the silicon had been consumed was compared. At 30 % Si consumption, the system, in most cases, was in a steady state.

The selectivity of the process showed only small variations with the different synthetic silicon qualities used, as well as with temperature.

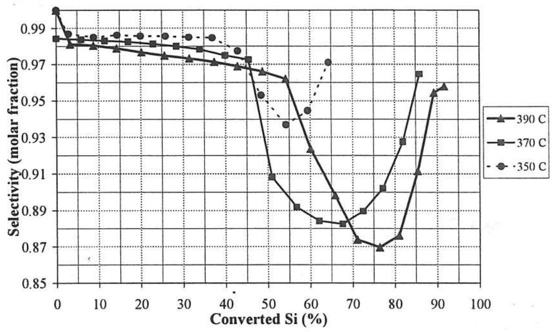

Figure 3 - Selectivity of the reaction during the experiment at three different temperatures Sample: Fe 0.2, Al 0.1.

The TCS-selectivity was as high as 99.2% for some of the synthetic silicon qualities employed in the reactor studies. This is a very high selectivity compared to what is obtained in industrial processes, where the usual selectivity is around 80 - 90%.

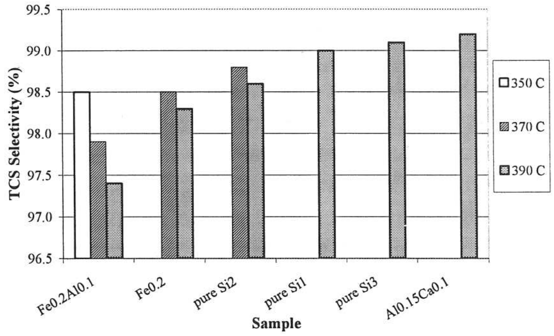

Figure 4 - Selectivity of the process using different silicon samples. Grain Size: 180-250 μm.

Figure 4 shows that all the samples tested so far gave selectivities between 97.4 and 99.2 % TCS. The TCS selectivity was expected to decrease with increasing temperature because STC is the thermodynamically stable compound. This was

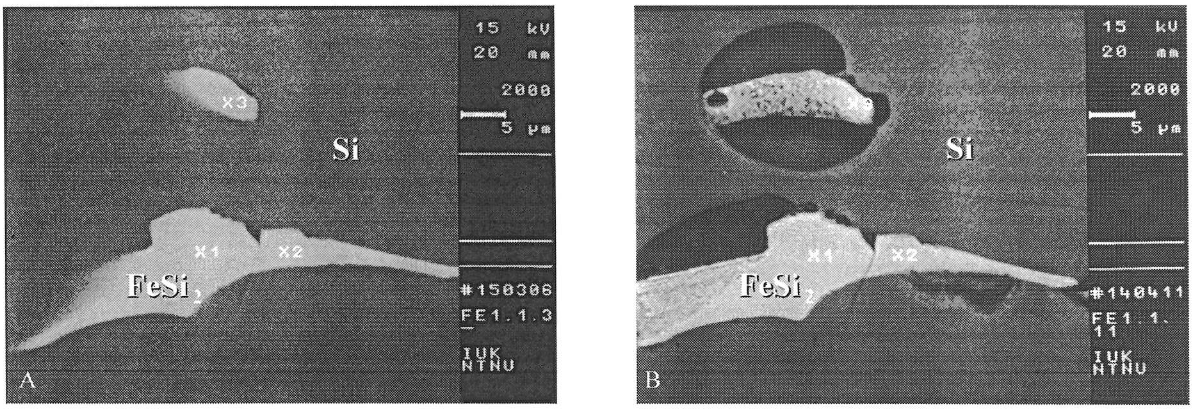

Figure 5 - SEM image of sample Fe0.2. A: Before HCl exposure. B: after 3 min. HCl gas exposure. $FeSi_2$ is left untouched by HCl gas.

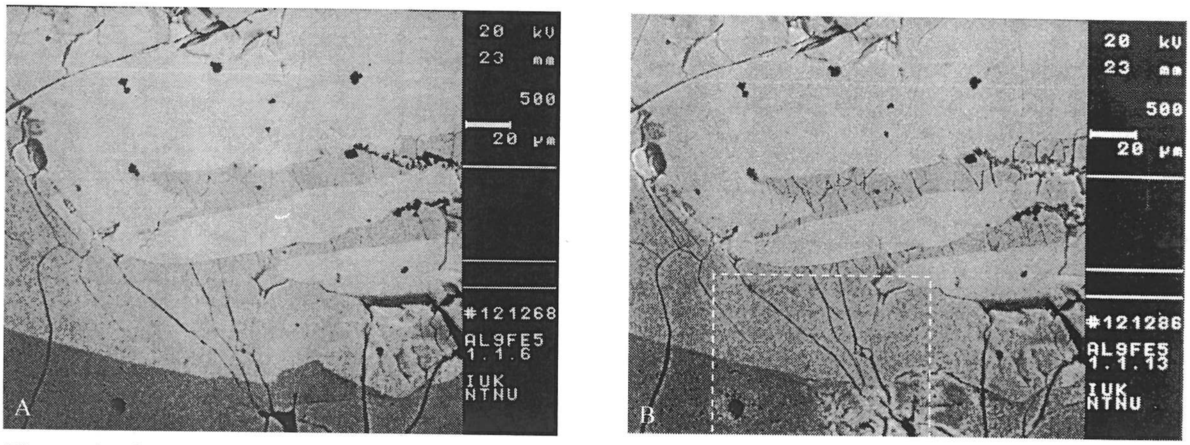

Figure 6 – SEM images of sample $Al_9Fe_5Si_8$. A: Before HCl exposure. B: After 3 min. HCl exposure. White square: Enlarged in figure 7.

indeed observed for all the synthetic samples. When all experiments run at 390°C are compared, it is observed that the selectivity is higher for samples with higher reaction start temperature (compare figures 2 and 4). This indicates that the reaction should be run at as low temperature as possible above the reaction start temperature.

Since the selectivity is very high for all the samples compared with the industrial process, some, so far unknown, parameter must reduce the selectivity in industrial processes. This might be different trace elements in, or the morphology of the M-Si, or an effect of the different reactor design.

4.2 SEM STUDIES

The SEM studies uncovered some basic differences in the way different silicon samples react with HCl gas. In all the samples the intermetallic phases seemed to have strong influence on the process.

The reaction always started at the boundary between the intermetallic phase and the silicon matrix, but the shape of the pits formed by the consumption of silicon, and the state of the intermetallic phase after reaction varied.

Figure 5 shows SEM images of the sample Fe 0.2 before and after reaction with HCl gas. The silicon was consumed from the edges of the $FeSi_2$ phase, but the phase itself was left untouched in the process.

Figure 6 shows SEM images of the sample $Al_9Fe_5Si_8$ before and after reaction. In this sample there is no surrounding matrix of pure silicon. The image shows three different phases. All the phases contain iron, aluminium and silicon, but in different ratios. The brightest areas have most iron, the darkest areas have most aluminium.

EDX analysis of the phases showed that the phase richest in aluminium was chlorinated, while the other phases remained more or less intact. Only very shallow pits were formed on the surface of these phases. The aluminium rich phase on the other hand, formed deep pits and cracks. Figure 7 shows the difference between two of the phases.

In other parts of the sample, deposited particles of $FeCl_2$ were observed. This indicates, as suggested by Bade and Hoffman[2], that $FeCl_2$ indeed is accumulated in the reactor if iron rich phases are present.

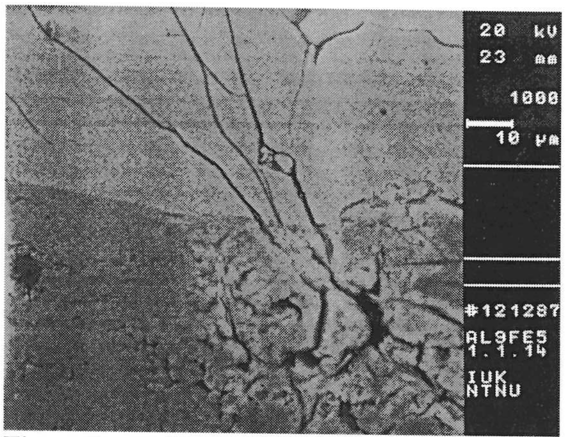

Figure 7 – One enlarged segment of figure 6B.

The sample in Figure 8 (Fe 0.2, Al 0.1) does have a surrounding silicon matrix. It is observed that silicon is consumed from the edge of the intermetallic phases. The intermetallic phases are also chlorinated and consumed in the process.

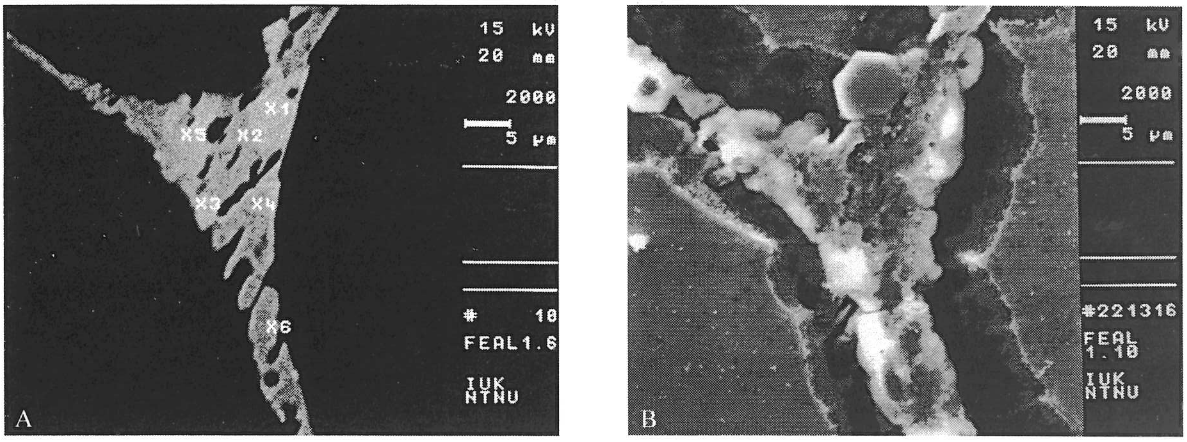

Figure 8 – SEM images of the sample Fe0.2Al0.1. **A:** Before HCl exposure. EDX analysis in the marked spots reveal a mixture of the same three phases as in figure 6. **B:** After 3 min. of HCl exposure. The iron-aluminium-silicon phases are chlorinated by contact with HCl gas.

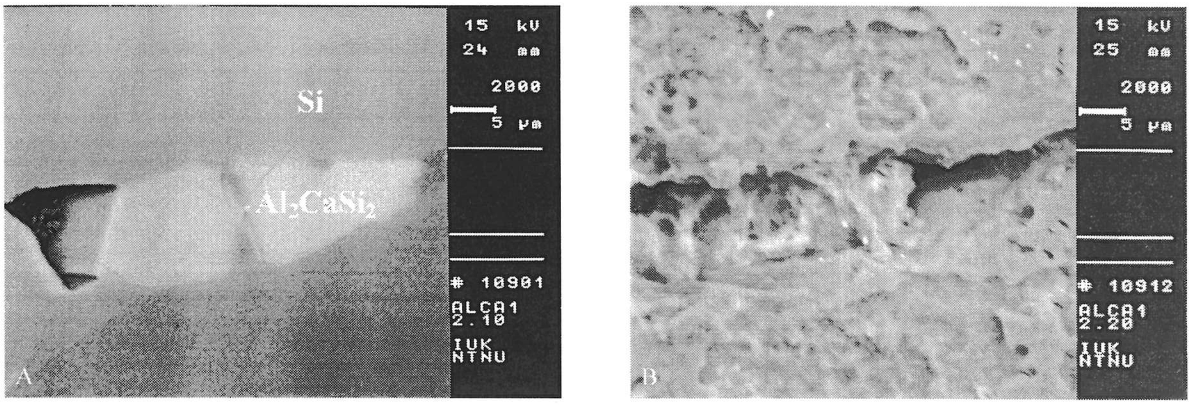

Figure 9 – SEM images of the sample Al0.15Ca0.1. A: Before HCl exposure. B: After 3 min. of HCl exposure. Al_2CaSi_2 is totally consumed by HCl gas.

Figure 9 shows before and after images of the sample Al 0.15, Ca 0.1.

Again it is observed that silicon is consumed from the edge of the intermetallic phase (Al_2CaSi_2), though in a bit different manner. The deep ditches formed in the other samples are shallower, and spread more evenly across the silicon surface. The figure also shows that the Al_2CaSi_2 phase is completely consumed in the process.

CONCLUSIONS

Aluminium and iron in M-Si decrease the reaction start temperature, whereas calcium seems to increase it.

Selectivity varies only slightly for the synthetic samples used in this project. The cause of the low selectivity in the industrial process is still to be uncovered. The results show that it is indeed possible to increase the TCS selectivity.

SEM images reveal that different intermetallic phases behave very differently when subjected to HCl gas.

Iron rich aluminium-iron-silicon phases produce $FeCl_2$ which accumulates in the reactor. Aluminium rich aluminium-iron-silicon phases are consumed and form gaseous products. The $FeSi_2$ phase seems to be inert in the HCl atmosphere. Al_2CaSi_2 influence the surface of the surrounding silicon, thus increasing the reaction start temperature.

In all the samples, the consumption of the main matrix of silicon starts at the edges of the intermetallic phases.

ACKNOWLEDGEMENTS

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