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New Methods for Producing Low Cost Silicon for Solar Cells

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Abstract

Growth in the solar cell industry will soon exceed the available supply of electronic grade Si from semiconductor offcuts. This is expected to lead to a significant increase in the cost of the source material, and a subsequent rise in the price of solar cells. As a result of this a number of different ways are being investigated to manufacture an alternative low-cost silicon material for solar cells. This paper discusses an investigation of several potential new processes for producing lower-cost solar cells based on the production and purification of the "volatile" chloro-silane compounds SiCl_4 and Si_2Cl_6 from naturally occurring SiO_2 . These purified compounds may then be decomposed to produce thin film Si solar cells directly, or converted to solar grade silicon for the subsequent production of conventional wafer based c-Si solar cells. The use of waste product grain husks as a new source of high grade SiO_2 feedstock for this process is also discussed. These methods offer the possibility of both new, low cost methods of producing solar-grade Si for wafer based c-Si solar cell production, as well as the direct production of inexpensive thin film Si solar cells, such as a-Si:H.

1. Introduction

With the growing interest in sustainable energy sources silicon solar cells offer opportunities to reduce greenhouse gas emissions and provide additional electricity generation capacity. The volume of solar cells produced worldwide increased by 42% from 1996 to 1997 and is expected to increase by one and a half orders of magnitude in the next 10 years from 127MW to 1920MW (Varadi, 1998). This is expected to result in a significant increase in the amount of pure silicon feedstock needed for this industry.

Crystalline silicon (c-Si) based solar cells are currently the predominant commercial solar cell technology, with 88 percent of the world market (Rannells, 1998). Most of the silicon feedstock currently used for the production of these wafer based c-Si solar cells is derived from very high purity (99.9999%) electronic grade silicon (EG-Si) offcuts from the semiconductor silicon industry. Growth in the solar cell industry will soon exceed the available supply of electronic grade Si from semiconductor offcuts. In 2010 the shortfall is expected to be about 5000 mt/year (Block and Wagner, 2000). This could lead to a significant increase in the cost of the source material and a subsequent rise in the price of solar cells. As a result of this a number of different ways are being investigated to manufacture an alternative low-cost silicon material for solar cells. The target of these efforts is to produce a bulk material characterised by the following features: abundance of resources, low cost manufacturing ($\text{US}\$10\text{kg}^{-1}$), impurity optimisation (solar grade Si) and low energy processing (Lasnier and Ang, 1990).

Amorphous silicon (a-Si:H), currently holds 11 percent of the market (Rannells, 1998), with sales of these cells expected to increase rapidly in the future. As well as a-Si:H there are a number of new thin film silicon solar cell technologies being developed (Saito *et al*, 1999; Catchpole *et al*, 1999). Unlike

the conventional wafer based c-Si technologies, a-Si:H is relatively cheap to produce, requires significantly less energy in the production process and is more tolerant to impurities in the silicon feedstock. While the wafer based c-Si technologies require the production, using high temperature melts, of crystals with high chemical and structural integrity, a-Si:H is produced at low temperatures from the gas phase decomposition of silane, SiH₄. Silane is commercially available in a gaseous form at room temperature. The use of this and other "volatile" silicon compounds offers the possibility of both new, low cost methods of producing solar-grade (sOG-Si) for conventional c-Si solar cell production, as well as the direct production of inexpensive thin film silicon solar cells.

In order to produce semiconductor grade silicon, metallurgical grade silicon MG-Si is first produced from the naturally occurring crystalline form of silicon dioxide, quartzite, with 90% or more silica (SiO₂). The quartzite is reduced in large arc furnaces by carbon to produce elemental silicon according to the chemical reaction:



The vapour reacts with impurities in the quartzite such as aluminium, carbon and magnesium, which then leave the Si as part of the waste gases. The purity of MG-Si is however still low (98-99%) owing to the low purity of the starting materials.

The Siemens C process is at present the standard method for purifying MG-Si to 99.9999% pure polycrystalline electronic grade silicon (EG-Si) for use in producing semiconductor devices and solar cells.

This is done according to the chemical reactions:



In this process, trichlorosilane (SiHCl₃) is obtained first. A bed of fine MG-Si particles is fluidized and chlorinated with hydrochloric acid in the presence of a copper catalyst to induce the reaction. The low purity MG-Si results in impure SiHCl₃, which must then undergo subsequent fractional distillation to reduce impurities by a factor of 10⁴-10⁵. A chemical vapour deposition method is subsequently used to produce the EG-Si from the very high purity SiHCl₃. Vapourized SiHCl₃ is decomposed and reduced with hydrogen at about 1000°C, resulting in the deposition of a silicon deposit on the hot surface of a bridge in the shape of an inverted U. The bridge is made of slim silicon rods and has been heated in a reactor by passing an electric current through it. This process can produce six polycrystalline rods of 1m length and 12 cm diameter simultaneously. A price increase from US\$1 kg⁻¹ for MG-Si, to more than US\$70 kg⁻¹ for EG-Si (in 1990) reflects the costliness and energy intensity of this process (Lasnier and Ang, 1990). It is the last step of this, the deposition of silicon from the gas phase (150 kWh (kgSi)⁻¹), that is the most energy intensive step.

Different ways are being investigated to manufacture an alternative low-cost silicon material suitable for the solar cell industry, solar-grade (sOG-Si) Si. Some of these processes have been reviewed by Lasnier and Ang (1990) and incorporate essentially two approaches. These are a low-purity approach where the processes start with MG-Si, or SiO₂ at a corresponding impurity level, or a high-purity approach based on an upgraded SiO₂ starting material. As well as this two types of process sequence can be distinguished, whether they are relying on SiO₂ as a primary silicon source, and volatile compounds as secondary silicon sources. All of the volatile products have the one attractive common property, namely the ease of refining either by fractional distillation or desorption. Among the volatile

halides, silicon tetrafluoride and chloride are the most economical, interesting compounds. All of the potential new processes being investigated aim to produce quantities of intermediate SOG-Si as a feedstock for manufacturing solar cells.

This paper discusses several potential new processes for producing lower-cost solar cells, based on volatile silicon halide compounds. These include using different new higher purity SiO₂ starting materials and new processes for producing SOG-Si for c-Si solar cell production from current metallurgical grade SiO₂ materials.

2. Results and Discussion

2.1. The Production of SOG-Si from MG-Si via Volatile Silicon

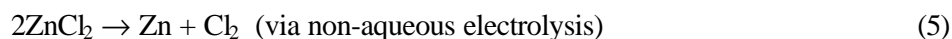
There have been several processes investigated for the production of SOG-Si via the silicon halides (halosilanes). Some of these processes are already in pilot, or production stage (Lasnier and Ang, 1990).

a) Zinc reduction of SiCl₄: Battelle Columbus Laboratories

In reviving the so-called duPont process of the early 1950's, a fluidized-bed reactor (FBR) was adapted by the Battelle Columbus Laboratories to harvest silicon. This process follows the reaction:



Furthermore a non-aqueous electrolysis step for the recovery of zinc was incorporated:



The chlorine gas produced in reaction 5 is converted to a saleable product NaOCl by reaction with caustic soda (NaOH) according to the reaction:



This process is a continuous multi-step closed-loop process in which the raw feed is MG-Si and SiCl₄ is the secondary source.

b) Silane Process : Union Carbide Corporation

The Union Carbide process under development is a multi-step continuous closed-loop process in which the raw material is MG-Si. The primary process steps are:

- (i) The preparation of chlorosilanes, predominantly HSiCl₃ by hydrogenation of a mixture of SiCl₄, which is a recycled by-product and MG-Si according to the reaction:



- (ii) The two-step disproportionation of HSiCl₃ into silane (SiH₄) with the formation of SiCl₄ as the by-product according to the reactions:



- (iii) Two deposition reactions for the conversion of the SiH_4 into silicon have been investigated, the free-space reactor and the fluidized bed reactor. The fluidized bed reactor approach is considered the most attractive for a continuous process.

c) Fluorosilicic acid (SiH_2F_6) reduction: SRI International

The SRI process under development is the reduction of SiF_4 with sodium. SiF_4 is obtained at a low cost from H_2SiF_6 , which is a by-product of the fertilizer industry.

d) Bayer AG have recently reported (Block and Wagner, 2000) research and development of a route for the production of SOG-Si with a capacity of up to 5000 mt/year and a price level of 12-15 Euro/kg. Their process consists of four steps:

1. Hydrochlorination:

Trichlorosilane (SiHCl_3) will be produced by the reaction of metallurgical silicon with recycled silicon tetrachloride (SiCl_4) and recycled hydrogen (H_2) in a fluidized-bed reactor. By-products and residues will be removed and refurbished.

2. Pre- and fine Purification:

Discharging of impurities takes place at different parts of the process. The over all approach and process simulation will be validated by further experimentation.

3. Redistribution:

In this catalysed reaction step trichlorosilane (SiHCl_3) is converted via dichlorosilane (SiH_2Cl_2) and monochlorosilane (SiH_3Cl) to monosilane (SiH_4). Resulting silicon tetrachloride (SiCl_4) will be fed to the hydrochlorination reaction. Suitable catalysts are aminofunctional ion exchange resins.

4. Pyrolytic Decomposition of Monosilane:

The decomposition of monosilane (SiH_4) occurs in a fluid-bed reactor preferably as a heterogeneous reaction at temperatures at above 600°C . To avoid homogeneous decomposition of monosilane, the reaction conditions must be optimized, particularly the temperature, partial pressure of the silane, gas velocity and bed particles.

In addition to the desired product of SOG-Si this process delivers further products suitable for different markets such as the chemical industry and the photovoltaic electronic market.

e) Potential route via SiCl_4 and Si_2Cl_6

The possibility of producing SOG-Si from MG-Si via the chlorosilanes SiCl_4 and Si_2Cl_6 is another possible process that is investigated in this work. Gatterman and Weinlig in 1894 (as reported in Hegge, 1967) proposed a mechanism for the production of SiCl_4 and Si_2Cl_6 from silicon according to the reactions:



Based on this postulation, it is possible to produce Si_2Cl_6 through reaction (11) and utilise the decomposition reaction (12) to obtain silicon at 350°C (Hegge, 1967).



The product SiCl_4 in equation (12) can be recycled for the production of Si_2Cl_6 by equation (11).

However, Martin (as reported in Hegge, 1967) has given evidence that Gattermann and Weinlig's postulation expressed by equations (10) and (11) was not correct. According to Martin the sequence of the products formed by the reaction between Si and Cl_2 is in the order:



Therefore, according to Martin Si_2Cl_6 is an intermediate product rather than a final product during the reaction. Instead, SiCl_4 is the final product. Therefore, Si_2Cl_6 can only be obtained as a by-product with a 20% yield under well-controlled conditions through reactions (10) and (11) with an 80% yield of SiCl_4 . Furthermore Si_2Cl_6 is unstable in the presence of Cl_2 at temperatures near 300°C and burns to form SiCl_4 according to the equation:



In this study, the reaction between MG-Si and Cl_2 at temperatures below 250° was investigated using a visible glass tube furnace. It was observed that the initiation of the reaction between MG-Si and Cl_2 below 250°C did not depend much on temperature, but on the pre-treatment of the feed MG-Si and the presence of impurities. Finely ground MG-Si and the presence of antimony shorten the induction period. However, it appeared that control of the temperature to as low a value as possible after the initiation of the reaction was important to obtain a higher proportion of Si_2Cl_6 in the product. It is believed that the presence of antimony catalysed the reaction through the formation of a reactive complex between Si, Sb and Cl_2 . The mechanism of the reaction catalysed by Sb and a route for the catalysed conversion of SiCl_4 to Si_2Cl_6 is under further investigation. The development of a direct conversion of SiCl_4 to Si_2Cl_6 would form a new route for production of SOG-Si via Si_2Cl_6 at lower temperatures according to reaction (12). Nevertheless, Si_2Cl_6 as a by-product is readily separable from SiCl_4 by fractional distillation due to the large difference in their boiling points (SiCl_4 : 57°C , Si_2Cl_6 : 145°C). In commercial production the Si_2Cl_6 could then be converted to Si and SiCl_4 according to equation (12).

In the absence of a catalyst, such as Sb, the reaction between MG-Si and Cl_2 readily occurs at temperatures above 500°C and the reaction rate increases with an increase in the flow rate of Cl_2 over the MG-Si powder. In fact, the Si powder became red hot when the supply of Cl_2 increased at a higher flow rate. When the reaction was completed, only white ash was left in the sample boat with the conversion of MG-Si to silicon chloride compounds being about 92%. The proportion of Si_2Cl_6 in the product is very small due to the decomposition of Si_2Cl_6 at higher temperature in the presence of Cl_2 . The volatile compounds obtained in this work have not yet been analysed to determine their purity. It is expected however that using repeated fractional distillation they can be easily purified as feed materials for the production of SOG-Si.

2.2. The production of SOG-Si directly from metallurgical grade SiO_2 via volatile halides

It has been suggested (Hengge, 1967) that SiCl_4 can be produced directly from SiO_2 using carbon (as a reducing agent) and chlorine gas as feedstock according to the reaction:



It was found that no appreciable amount of SiCl_4 was produced at temperatures less than 1100°C using the feedstock $\text{SiO}_2 + \text{C} + \text{Cl}_2$. By heating the SiO_2 , C and Cl_2 in a furnace to 1220°C , SiCl_4 was readily obtained as a stable liquid at room temperature with a yield of about 85% of total Si input, but with little production of Si_2Cl_6 . Therefore it has been shown that it is possible to produce SiCl_4 directly from SiO_2 by this process. This SiCl_4 could then be converted directly to SOG-Si via processes such as those of Battelle Columbus or Union Carbide described above. Alternatively the SiCl_4 could be reacted with white-hot MG-Si and by cooling the products rapidly to give Si_2Cl_6 according to equation (11) (Trooste and Hautefeuille, 1871) that would then be purified by fractional distillation, before decomposition to Si and SiCl_4 according to equation (12). We are also currently investigating some potential methods of producing Si_2Cl_6 directly from SiCl_4 .

2.3. The Production of Thin Film a-Si:H Solar Cells from MG-SiO₂

Most thin film a-Si:H solar cells are currently produced commercially by the use of glow discharge (GD) chemical vapour deposition of silane. Because of its gaseous nature, and the fact that it is pyrophoric (combusts spontaneously on contact with air), silane is potentially dangerous to use, and requires complex safety procedures for its handling, transport and use. The chloro-silanes, such as SiCl_4 and Si_2Cl_6 on the other hand are stable liquids at room temperature and are easily refined by partial distillation. Unlike their hydrogen equivalents the chloro-silanes can then be easily and safely stored and transported ready for use at a later stage. As such these compounds offer the potential of a new method of more safely producing a-Si:H and other thin film silicon solar cells.

Nakata and Wagner (1994) have used a glow discharge containing dichlorsilane (SiH_2Cl_2) with small additions of silane to produce a-Si:H material that was close to device quality. Byun *et al* (1995) have deposited a-Si:H films with a hydrogen content of 6 at.% and an optimum chlorine concentration of 10^{19} cm^{-3} . They found that the degradation in photoconductivity on initial illumination normally associated with a-Si:H solar cells was very small. This shows that it is possible to produce good quality a-Si:H solar cell material which contains a small amount of chlorine. Byun *et al* (1995) suggest that these cells may in fact be more electronically stable than a-Si:H samples produced by the conventional method. Therefore it should be possible to use the chloro-silanes, produced using the methods discussed above, as the source gas for producing a-Si:H solar cells. To the knowledge of the authors no one has yet reported the use of the glow discharge of SiCl_4 or Si_2Cl_6 to produce a-Si:H solar cell material. It should be possible to do this by doing using a feedgas containing the SiCl_4 or Si_2Cl_6 in a hydrogen carrier gas in the glow discharge.

A promising new method of depositing a-Si:H from disilane is the hot-wire deposition technique, which is much simpler to use, and therefore likely to be less expensive (Molenbroek, Mahan and Gallager, 1997; Martins *et al*, 1998). Instead of using glow discharge of a chloro-silane hydrogen mixture to produce a-Si:H a potential new, less expensive, method of producing a-Si:H may be to use the hot-wire deposition of SiCl_4 or Si_2Cl_6 with hydrogen as a carrier gas. Our results so far have shown that it is possible to produce a thin film of silicon from SiCl_4 using a hot wire filament. The structure, chemical composition and purity, and electronic quality of the films produced have not yet been thoroughly tested, and this method is currently being investigated further. If successful this method, coupled with the processes described above for producing SiCl_4 and Si_2Cl_6 , would enable a much less expensive and safer method of producing a-Si:H and other thin film solar cell material directly from SiO_2 . This in turn could be expected lead to a significant decrease in the production cost of thin film silicon solar cells.

2.4. The use of High Purity SiO₂ from Grain Husks

As well as the conventional sources of cheap silica such as sand, bentonite and diatomaceous earth another potential source of cheap high-grade silica is as a by-product of the burning of waste rice husks in cogeneration plants. Apart from the energy derived from direct burning in cogeneration plants, rice husks are also known to have reasonably high silica content of approximately 18% (Riveros and Garza, 1986). Rice husks heated in an oxidising atmosphere can be transformed into a white ash, which is almost pure silica. Furthermore the amount of deleterious contaminants effecting solar cell or semiconductor performance, such as B, As and F are generally very low compared to the other mineral based sources of silica.

Several authors (Riveros and Garza, 1986; Basu, 1972; Archarya, Dutta and Banerjee, 1980; Amick, 1982; Hunt *et al.*, 1984) have reported studies of the use of rice husks for the production of high purity SiO₂. Hunt *et al.* (1984) have studied the use of rice hulls (husks) as a raw material for producing silicon. Impurity analyses undertaken as part of their work indicated that rice hulls from various sources are compositionally similar and have low concentrations (10-20 ppm) of aluminium and iron, the major impurities in conventional raw materials used to prepare MG-Si. Their studies also show that the levels of the major impurities (Ca, K, Mg and Mn) in the rice hulls can be reduced by about a factor of 100 to around 20 ppm by hot hydrochloric acid leaching. The doping impurities boron and phosphorus, important in silicon intended for solar cells, were less affected by acid leaching, with concentrations of 1 and 40ppm respectively in the leached hulls. Therefore it is possible using small amounts of inexpensive reagents, very simple equipment and a minimum of manipulation to produce from rice husks a source of SiO₂ of much higher purity than conventional mineral based sources. This much higher purity feedstock will result in a reduced need for purification in the subsequent processing stages, and a corresponding reduction in the cost of the final SOG-Si.

One rice mill in Thailand, with a 2.5 MW cogeneration plant, produces and uses for power generation 100 tonnes of rice husks daily (Pennington, 1998). This mill alone is therefore a potential source of approximately 18 tonnes a day of high grade silica suitable for use in the production of a-Si:H solar cells, or semiconductor grade silicon. This silica can be purified using simple low cost acid leaching. The subsequent conversion of this purer starting resource directly to chlorosilanes, using the methods developed in this work, before decomposition into SOG-Si for solar cell production can be expected to result in a significant reduction in cost.

In 1990 the amount of electronics waste Si used to manufacture 50MW_p year⁻¹ of silicon solar cells was about 400 mt/year (Lasnier and Ang, 1990). This is now close to 1050 mt/year to produce the current 130MW_p year⁻¹ (Rannells, 1998) of solar cells. The rice husks from the one Thai rice mill described above could potentially produce 17520 mt/year of SOG-Si, or fifteen times that needed to meet this market. This is also significantly higher than the amount of 7500 mt/year predicted by Block and Wagner (2000) to be needed in 2010. There are a number of such rice mills throughout the world. Furthermore our investigations have shown that the husks and straw from other grain crops such as oats, wheat and barley also contain reasonable amounts of high quality silica. Therefore the potential for the use of grain husks as a source of high purity SiO₂ feedstock for the production of low cost solar-grade silicon is enormous. The use of these husks, which would otherwise be a waste byproduct that must be disposed of, for co-generation then the production of solar cells, therefore has the potential to also lead to significant economic and environmental benefits.

3. Conclusions

It has been shown that it is possible, with good yields, to produce the volatile chlorosilanes SiCl₄ and Si₂Cl₆ from metallurgical grade Si, and SiCl₄ from SiO₂. Methods for the production of thin film silicon

solar cells such as amorphous silicon, or solar-grade silicon for conventional solar cell production, by the subsequent fractional distillation and decomposition of these compounds is discussed. The use of grain husks as a new source of high grade SiO₂ feedstock for this process has also been discussed. These methods promise less expensive and safer ways of producing thin film and conventional silicon solar cells from SiO₂.

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