Various methods of manufacturing low-cost solar-grade silicon are reviewed. The methods include refining metallurgical-grade silicon, reduction of silicon compounds by metals and non-metals, transport and thermal decomposition processes. The materials are briefly characterized by the chemical analysis, resistivity measurements and efficiency of solar cells obtained from them.

1. Introduction

Semiconductor-grade silicon is widely used to manufacture highly efficient solar cells. Silicon tetrachloride or trichlorosilane is thermally decomposed and reduced with hydrogen to produce high purity silicon [1–9]. Since this process is complex and expensive, the use of semiconductor-grade silicon has been a major factor contributing to the high cost of solar cells. In general, the purity level of silicon required for cells could be considerably less than the purity levels of semiconductor-grade silicon. Hence, the cost of manufacturing solar-grade silicon for terrestrial utilization of solar energy can be significantly lower than the semiconductor-grade silicon. In this article we have attempted to review the status of various low-cost solar-grade silicon manufacturing processes and to characterize solar cells made from solar-grade silicon.

2. History of silicon manufacturing processes

Silicon occurs in nature chiefly as silica and silicates and makes up 25.7% of the earth’s crust. In 1808, Berzelius obtained ferrosilicon by heating a mixture of silica, carbon and iron. Later, in 1811, Gray, Lussac and Thenard succeeded in preparing impure amorphous silicon by reducing silicon tetrafluoride with potassium. Soon after, Berzelius in 1824 purified amorphous silicon by removing the fluosilicates. Deville in 1854 first prepared crystalline silicon [10]. Later, silicon was produced by the thermal decomposition and reduction of silicon tetrachloride and trichlorosilane, electrolysis of a molten mixture of potassium fluosilicate and potassium fluoride or other alkali fluorides, and by the reduction of silicofluorides by sodium or aluminium. Copper has been used to obtain silicon by reaction with silica to form predominantly Cu2Si and heating this with sulphur to form CuS and free amorphous silicon [11]. The most common commercial method of producing silicon is similar to a method by Berzelius wherein silica is reduced with carbon, usually in an electric arc furnace [12–17]. Other methods include the reduction of silicon monoxide with silicon carbide and the reduction of silicates with carbon or aluminium [18–23]. The first commercial process for the production of semiconductor-grade silicon used zinc to reduce silicon tetrachloride [23, 24]. The reduction of silicon tetraiodide, and tetra-bromide, with hydrogen were also determined to be commercially feasible [25]. Currently, both silicon tetrachloride and trichlorosilane are widely used in the manufacture of hyper-pure silicon [1–9].

3. Definition of solar-grade silicon

Semiconductor-grade silicon is expensive, costing about $75/kg (US dollars) due to a number of process steps required to achieve the purity level of <1 ppb metallic impurities. Although an unequivocal definition of solar-grade silicon does not exist to date, based on various investigations,
some guidelines have been drawn. Wakefield et al. [26, 27] have provided a basis for the drafting of a solar-grade silicon specification. They have established that silicon raw material containing up to 120 ppm of a variety of common impurities can yield solar cells of at least 11.5% AM1* efficiency. They have listed the maximum impurity levels for solar-grade raw material silicon as follows: Al, 25 ppm; B and P, 0.01 ppm; others less than 5 ppm. They have, based on their cost analysis, obtained a linear relationship between purity and the cost as represented in Fig. 1. However, it should be remembered that the acceptable concentrations of impurities in solar-grade feedstock will depend on the growth technique as well as the cell fabrication processes involved. Hopkins et al. [28] have set a much broader range (1 to 1000 ppm) for a Czochralski growth operation. In this case, the tolerable feedstock impurity concentrations depend upon the melt recharges as shown in Table I.

As can be seen from Fig. 1, by reducing the purity requirements from <1 ppb to 10–50 ppm (semiconductor to solar grade), the cost of silicon could be reduced from $70 to $7/kg. Since it has been well recognized that low-cost solar cells suitable for large-scale terrestrial utilization can be made from slightly impure silicon at a price of about $10/kg, Wakefield et al. identify the solar-grade silicon in the shaded area of Fig. 1. In principle, this purity and price range has been well accepted as the manufacturer's criterion for solar-grade silicon [26, 28].

4. Feasible methods of manufacturing low-cost solar-grade silicon

In the United States, the Department of Energy, in collaboration with Jet Propulsion Laboratory and the National Science Foundation, has had as an objective the development of the process technology for the production of low-cost silicon for solar cells in a large commercial plant by 1986, at a price less than $10/kg (based on 1975 dollars). They have financially supported several organizations to evaluate all the possible economical means of manufacturing low-cost silicon. Under this scheme, Union Carbide, Dow Corning, Hemlock Semiconductor Corporation, SRI International Corporation, Aerochem Research Lab, Inc. and Crystal Systems, Inc. have demonstrated the feasibility of manufacturing low-cost silicon. In West Germany, Siemens and Wacker, and in Italy, Smiel, are developing processes to manufacture low-cost silicon. In Japan, under the Sunshine Project, Osaka Titanium, Komatsu Electronics and Shin Etsu Silicon are active in this development. The details of various processes are discussed in the following sections.

Graham et al. [29, 30] have made fundamental thermodynamic studies in detail to determine all the possible reactions for the reduction of silicon-bearing compounds. They have identified over 200 possible reactions, out of which about 148 reactions are thermodynamically feasible for the production of silicon. Among them, about 17 are considered to be economically suitable. The possible methods are:

(a) Pyrolysis of the compounds SiI₄, SiH₃, SiH₂X₂, SiH₃X and SiH₄ below a temperature of 1725°C (where X = F, Cl, Br and I). Due to the high cost of these compounds and problems associated with corrosion, hence sustaining purity, this approach is not considered feasible at present.

(b) Reduction of silica by carbon. Metallurgical silicon can be produced and purified by various techniques. Even more directly, purer starting materials can be used to obtain a higher purity silicon product. These methods are economically attractive for producing solar-grade silicon.

(c) Reduction of SiO₂, SiF₄, SiCl₄, or SiBr₄ by various metals and rare earths is thermodynamically...