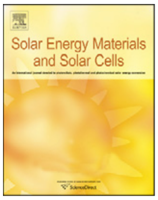
Solar Energy Materials & Solar Cells 107 (2012) 188–200

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Review

Chemical vapor deposition of silicon from silane: Review of growth mechanisms and modeling/scaleup of fluidized bed reactors

W.O. Filtvedt [a,*], A. Holt [a], P.A. Ramachandran [b], M.C. Melaaen [c]

[a] IFE Kjeller, Norway
[b] Washington University, MO, USA
[c] Telemark University College, Tel-Tek, Porsgrunn, Norway

ARTICLE INFO

Article history:
Received 12 April 2012
Received in revised form
10 August 2012
Accepted 21 August 2012
Available online 24 September 2012

Keywords:
Polysilicon
Fluidized bed
FBR
Silicon

ABSTRACT

For an installed silicon based solar cell panel, about 40% of the energy costs involved in the production of the panels can be attributed to the production of the silicon feedstock itself (poly production and crystal growth). Hence reducing the energy consumption in these steps is crucial in order to minimize the energy payback time of installed capacity. For the first step, viz., the poly production, the most promising cost reduction alternative is the fluidized bed reactors (FBR) using silane as a precursor rather than trichlorosilane (TCS) since for TCS the reverse reactions makes the theoretical trichlorosilane conversion substantially lower. Use of silane has, however, many challenges and scaleup to larger capacity can be achieved if associated risks are properly dealt with. This paper outlines some of these challenges and provides a detailed survey of the current status on the growth mechanism and kinetics of silane pyrolysis. The paper also provides a summary of modeling of fluidized bed reactors (FBR) in some depth and give some empirical insight to key aspects in FBR scaleup design.

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[*] Corresponding author. Tel.: +47 63 80 64 01; fax: +47 63 81 63 56.
E-mail address: Werner.Filtvedt@ife.no (W.O. Filtvedt).

0927-0248/$ - see front matter
http://dx.doi.org/10.1016/j.solmat.2012.08.014

1. Introduction and scope

Solar cells is an increasing consumer of polysilicon in the world market. Although the rapid expansion in world production capacity have presently made the silicon prices drop, the long term expectations are still growing in PV energy demand and thereby significant growth in polysilicon consumption can be expected in the future [1–3].

The most commonly used method for production of polysilicon is decomposition of a silicon containing reactant gas through heating.

Understanding of the fundamental reactions and how they influence product quality is important in order to aid further development. Substantial research has been done by various groups on both decomposition, deposition, product characterization and ultimately reactor design. Monosilane based fluidized bed reactors appear to give the lowest possible cost of operation over the established methods. There are however many challenges with porosity, and impurity encapsulations that one need to overcome if the method is to be become dominant. A second problem is fine formation due to homogeneous reaction in preference to deposition on feed particles. Finally the fluid bed reactor (which currently has the best potential for the silane process) involves complex interaction of hydrodynamics and hence is difficult to scaleup. Hence the use of monosilane in a fluid bed reactor has additional challenges and complexities. In order to advance the technology further and to move to larger scales, a critical review and evaluation of the current knowledge in this field is needed and this is the main scope of this paper. This paper aims to provide an insight to what topics have been examined earlier, where the research stands today and what elements that needs further research to continue the development.

A brief background information and references to some earlier review papers is first provided.

1.1. Silicon CVD precursors

In the early days of silicon CVD several gases were explored for the purpose, but in today's reactors monosilane SiH_4 (silane) and trichlorosilane $SiHCl_3$ (TCS) are the ones frequently used. Upon being heated to the decomposition temperature, the gases undergo the following reactions:

$$SiH_4 \longrightarrow Si + 2H_2 \tag{1}$$

$$SiHCl_3 + H_2 \rightleftharpoons Si + 3HCl \tag{2}$$

The decomposition temperature for silane is about 420 °C [4]. However, at this temperature the kinetic energy of the individual silicon atoms is too low to form crystalline structures. Low temperature atmospheric pressure decomposition will therefore cause amorphous structures [5]. Silane based CVD reactors are therefore often operated at temperatures in the range 650–800 °C. Some designs utilize after treatment of the beads at even higher temperatures to assure a crystalline structure and complete release of bonded hydrogen.

The decomposition temperature of TCS is about 468 °C [4]. Also the reaction is equilibrium limited and thermodynamic conversions are in the range of 25% or so depending on the TCS to hydrogen ratio which necessities TCS recovery and recycle [6]. The CVD reactors utilizing TCS are however often operated at higher temperatures than 468 °C because some intermediate silicon chlorides have higher decomposition temperatures and since low temperature amorphous structures might cause chlorine encapsulation. These chlorine encapsulations will cause defects and reduce the quality of the material. Typical temperature range for TCS reactors is 850–1200 °C. The lower temperature range for silane and the absence of reverse reactions are the primary reason for switching to silane as the precursor.

A detailed understanding of the kinetics and the growth mechanism and the quality of the product is needed for further advances in this technology.

1.2. Fluidized bed reactor

The workhorse of today's industry is the Siemens reactor where either TCS or silane is deposited on silicon rods. Several improvements have been made to the design resulting in a substantial reduction in energy consumption [7]. However, the need for maintaining large temperature differences between the deposition surfaces and the reactor wall, as well as the limited deposition surface area will cause a limit to theoretical reactant yield and lowest energy consumption. TCS has proven successful for these reactors, among several reasons because some reverse reactions will remove loosely bound solid silicon and thereby continuously assure high quality of the deposited material. The drawback is that the product of some of these reactions may form gaseous species that are not decomposed by the reactor operating temperature and this causes a lower reactant gas yield. The yield is defined as the fraction of the introduced reactant gas that becomes solid silicon at the desired deposition surface. Unreacted silicon containing gas in the exhaust as well as undesired depositions and fines formation will cause a reduction in the yield.

An alternative to the Siemens reactor is the fluidized bed reactor (FBR). In a FBR, the reactor vessel is filled with silicon particles Fig. 1. A fluidizing gas like hydrogen or helium is injected

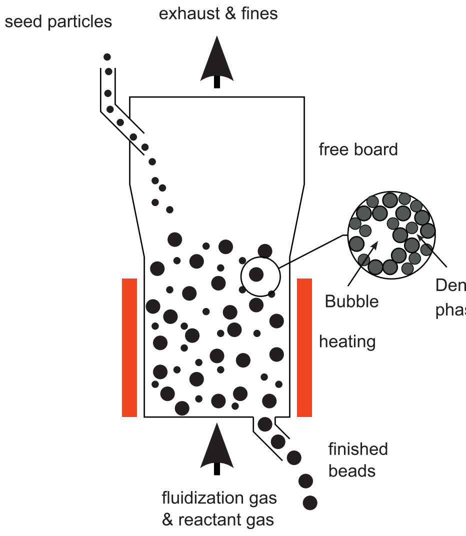

Fig. 1. The fluidized bed reactor.