Spring 5-2-2011

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MANUFACTURE OF GRANULAR POLYSILICON FROM TRICHLOROSILANE IN AN INTERNALLY CIRCULATING FLUIDIZED BED REACTOR

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ABSTRACT

A lab scale internally circulating fluidized bed (ICFB) with a centrally located draft tube was designed to make polysilicon from trichlorosilane. Experimental results and evaluations showed that particle circulation could carry enough heat for reaction and effectively decrease wall deposition. Well grown granular polysilicon was obtained in a stable fluidization state and particle circulation rate.

INTRODUCTION

Solar grade silicon is in ever-increasing demand due to the rapid development of the photovoltaic (PV) industry (1). One challenge the PV industry is currently facing is the development of cheap solar grade silicon feedstock (2). The traditional method for producing high purity polysilicon is the Siemens process that uses the decomposition of trichlorosilane ($SiHCl_3$ or TCS) on a high purity silicon rod in a bell-jar reactor. However, the cost of polysilicon made by this method (30-45 $\cdot kg^{-1}$) is too high for the PV industry (3,4). Therefore, several manufacturers have developed other new production technologies for solar grade polysilicon (5), which could be divided into two categories. The metallurgical routes produce solar grade silicon directly from metallurgical grade silicon by a purification process. The chemical routes are based on different reactor types such as a tubular reactor and fluidized bed reactor for the decomposition of a silicon-containing gas.

The technology that makes polysilicon by decomposing a silicon-containing gas in a fluidized bed reactor is considered to be the most attractive alternative to the conventional bell-jar process (6). This technology produces polysilicon in the form of silicon granules instead of the traditional silicon rods (7). The purity level of the granular materials produced is slightly lower than that produced with the Siemens process, but it meets the requirement of the PV industry. The feasibility and operating costs have been estimated in a pilot scale reactor by Wacker-Chemie, who showed that the energy consumption of polysilicon from the fluidized bed process

can be decreased to below half that of the Siemens process. The low energy consumption advantage would be more pronounced in large scale reactors.

The chemical vapor deposition (CVD) reaction of polysilicon from $SiHCl_3$ is a highly endothermic reaction and is sensitive to operating temperature. In a traditional fluidized bed reactor, deposition on the inner reactor wall is significant. This phenomenon will limit the life time of the reactor and cause problems due to the different thermal expansion coefficients of silicon and quartz. One effective way to limit wall deposition is the design of a novel reactor with an appropriate heating method. This is the most important issue in future demonstration of making polysilicon in a fluidized bed reactor.

In this work, a type of internally circulating fluidized bed (ICFB) with a novel gas distributor was developed for producing high purity polycrystalline silicon. The ICFB consisted of a downcomer with low gas velocity and a riser with high gas velocity. The separate aeration of gas for the riser and downcomer provides a more flexible operation.

EXPERIMENTAL

In order to determine optimized reaction conditions such as temperature, molar ratio of H_2 to $SiHCl_3$ and superficial gas velocity, a lab scale bubbling fluidized bed reactor (I.D.=0.025 m, H=0.6 m) was designed for producing granular polysilicon from $SiHCl_3$. The schematic diagram of the experimental apparatus is given in Figure 1. The fluidized bed reactor was made of quartz and heated by a resistance furnace outside the reactor. Liquid $SiHCl_3$ was vaporized and mixed with H_2 in a specially designed heated mixer, and the gas mixture was fed into the reactor through a gas distributor at the bottom of the reactor. The fluidized bed had an expanded head of 0.08 m I.D. to reduce particle entrainment. The gas distributor was placed below the heated zone to avoid plugging that would occur if there was silicon deposition on it. At the beginning of the experiment, the fluidized bed reactor was loaded with silicon particles. The incipient fluidization velocity, U_{mf}, was calculated with the following empirical correlation (8):

$$U_{mf} = \frac{d_e^2(\rho_p - \rho)g}{1650\mu}$$

The cold flow experiments were first carried out in an ICFB reactor (I.D.=0.12 m, H=0.80 m) made of Plexiglas to determine the appropriate superficial gas velocity in the real CVD reaction. A Schematic of the ICFB is shown in Figure 2. The draft tube (I.D.=0.07 m, H=0.25 m) with 24 orifices of 0.01 m in diameter was fixed in the bottom of the reactor. For gas supply to the reactor, two separate tubular gas

distributors were used: one was in the annular downcomer with 12 orifices, and the other was in the central riser with 24 orifices. All the orifices were 2 mm in diameter. An expanded section (I.D.=0.25 m, H=0.4 m) was installed in the top of the reactor to reduce particle entrainment. The bed was loaded with silicon beads (d_p=300 μm, ρ_p=2.71 kg·m^{-3}, U_{mf}=0.051 m·s^{-1}) at the beginning of the experiment.

The real CVD reactor for making polysilicon from $SiHCl_3$ on granular silicon is the same in structure as the cold flow reactor. It was made of quartz and heated by a resistance furnace outside the reactor.
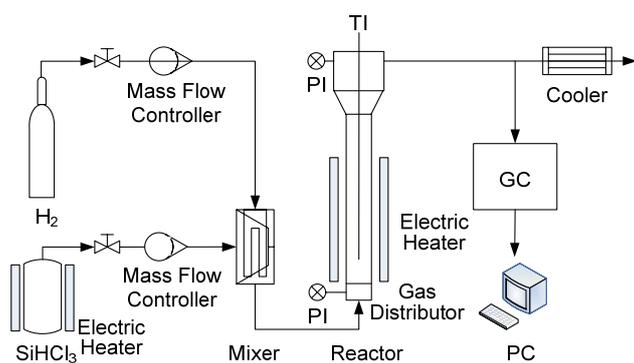

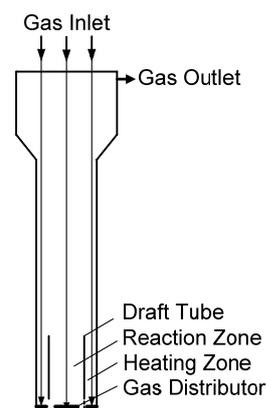Figure 1. Schematic of experimental apparatus

Figure 2. Schematic of cold flow ICFB

The product gas contained $SiHCl_3$, $SiCl_4$, SiH_2Cl_2 and HCl. The molar fractions of these species were determined by GC analysis using an empirical molar calibration ratio. The main reactions were

$$SiHCl_3 + H_2 \rightarrow Si + 3HCl \tag{1}$$

$$4SiHCl_3 \rightarrow Si + 3SiCl_4 + 2H_2 \tag{2}$$

$$SiHCl_3 + H_2 \rightarrow SiH_2Cl_2 + HCl \tag{3}$$

The conversion of $SiHCl_3$ (*X*), the yield of silicon (*Y*) and the selectivity to silicon (*S*, which was defined as the molar ratio of the produced silicon to the converted $SiHCl_3$) calculated from the molar fractions of silicon-containing products and HCl. The microstructure of the polysilicon deposited on the surface of seed particles was investigated by scanning electron microscopy (SEM, JEOL-7410). The particle size distribution of the silicon particles was obtained using Image-Pro Plus software by analysis of high-resolution digital photos of the silicon particles.

RESULT AND DISCUSSION

The CVD in Bubbling Fluidized Bed Reactor

The preparation of polysilicon from $SiHCl_3$ was studied in a bubbling fluidized bed reactor under a wide range of reaction conditions in previous research with small size silicon particles (d_p=300 μm). The effects of temperature (T), molar ratio of H_2 to $SiHCl_3$, superficial gas velocity (U_g) and particle seed loading were investigated. The temperature and molar ratio of H_2 to $SiHCl_3$ have notable effects on the reaction. The conversion was more sensitive to temperature below 900 ^oC. The optimized operating conditions were determined to be 950~1050^oC for temperature, 4:1~6:1 for the molar ratio of H_2 to $SiHCl_3$, and 2.5~4.5 for fluidization number (U_g/U_{mf}). The deposition reaction occurred by heterogeneous deposition to produce polysilicon, and this avoided the generation of fines which would occur in silane pyrolysis by homogeneous deposition ([9]).

In this work, larger diameter granular silicon (d_p=742 μm) was used to make polysilicon, the molar ratio of H_2 to $SiHCl_3$ was 5 and the fluidization number was 4.5. Well grown polysilicon product was obtained in the optimized operating conditions. The influence of different temperatures (Figure 3) is the same as was found with the deposition reaction with smaller size silicon particles (d_p=300 μm). The average particle was about 912 μm after CVD reaction. The total reaction time was about 8 h. The growth rate was evaluated to be 10 μm/h, which was consistent with previous experience.
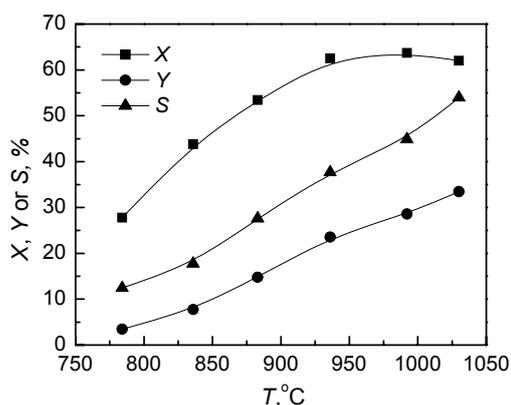

Figure 3. Conversion of $SiHCl_3$ (X), yield (Y), and selectivity (S) of Si (molar ratio of H_2 to $SiHCl_3$ is 5)
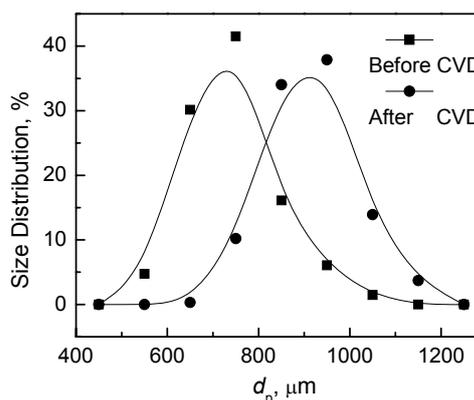
Figure 4. Particle size distribution of silicon before and after CVD reaction ($d_{p, seed}$ =742 μm, $d_{p, product}$ =912 μm)

Figure 5 shows the digital photos of the granular silicon before and after the CVD reaction. It shows that compared with the seed silicon particles, the surface of silicon

granules become bright after the CVD reaction. The cross-sectional microstructure of the silicon particle after reaction is shown in Figure 6. It shows the clear interface between the deposited polysilicon and seed silicon particle after the CVD reaction. The growth thickness was about 80μm, which was consistent with the average diameter change analyzed by particle diameter size statistics.
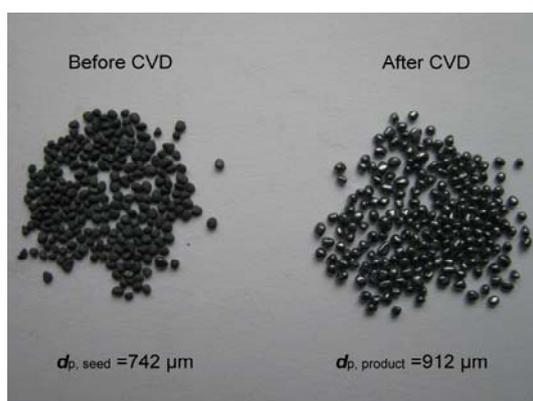
**Figure 5.** Digital photos of granular silicon before and after CVD
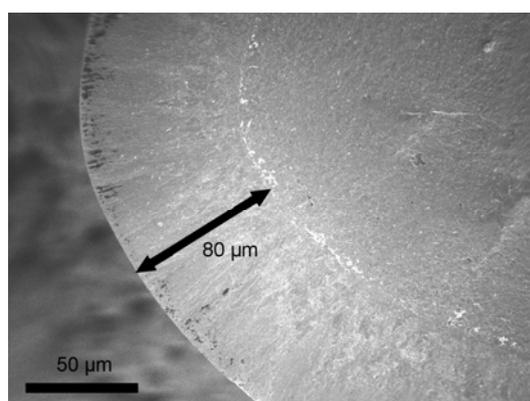
Figure 6. Cross-sectional microstructure of granular silicon after CVD

Cold Flow Experiments in ICFB

A big problem in the manufacture of granular polysilicon from $SiHCl_3$ in a fluidized bed reactor is the deposition of silicon on the inner reactor wall. The ICFB reactor has a centrally located draft tube to form separate heating and reaction zones in the fluidized bed reactor. In this work, the interior of the draft tube was used as the reaction zone and the exterior was the heating zone. The difference in superficial gas velocity was the driving force for particle internal circulation between the heating zone and reaction zone. In the ICFB, another important issue was to guarantee the quantity of heat carried by the high temperature granular silicon for the CVD reaction. One aim of the cold flow experiments was to estimate whether the particle solid circulation rate was enough to supply heat for the reaction zone, the other was to investigate whether the gas bypassing between the two zones was small enough to reduce the wall deposition of silicon in the heating zone.

The same optimized operating conditions (T=1000 ^{o}C, H_2:$SiHCl_3$=5:1, fluidization number=4.5) in the reaction zone were used to estimate the minimum solid circulation rate in the ICFB. The conversion of $SiHCl_3$ (X) at 1000 ^{o}C was about 63% and the selectivity to Si (S) was about 45%. According to the optimized operating conditions, the inlet amount of $SiHCl_3$ was 0.008 mol·s^{-1}. In consideration of the reaction selectivity, the needed reaction heat was about 40.16 kJ·mol^{-1} $SiHCl_3$. The sensible heat of feed H_2 and $SiHCl_3$ from 25 ^{o}C to 1000 ^{o}C was about 192.35 kJ·mol^{-1}

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SiHCl$_3$. So the total heat needed was 1.74 kJ·s^{-1}. The heat capacity of silicon granules at 1000 $^{\circ}$C was 27.52 kJ·mol^{-1}·K^{-1}. Assuming that the temperature difference between the heating zone and reaction zone was 25 $^{\circ}$C, the needed minimum solid circulation rate was 0.071 kg·s^{-1}. Taking into account the cross-sectional area of the heating zone, the needed minimum solid circulation rate per unit area, $G_{s,min}$, was about 10 kg·m^{-2}·s^{-1}. The cold flow experiments show that when U_D/U_{mf}>1.8 and U_R/U_{mf}>4.5, the solid circulation rate per unit area G_s (Figure 7) could satisfy the heat demand. Heat supply could also be increased with a larger heating zone or a larger temperature difference between the two zones. For example, if the temperature difference between the heating zone and reaction zone was 50 $^{\circ}$C, $G_{s,min}$ was about 5 kg·m^{-2}·s^{-1}.
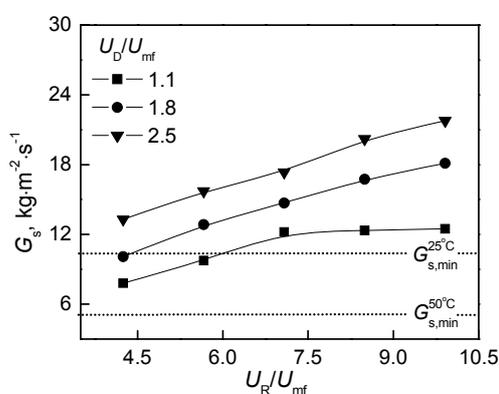
Figure 7. Effect of superficial gas velocity in downcomer (U_D) and riser (U_R) on solid circulation flux (G_S)
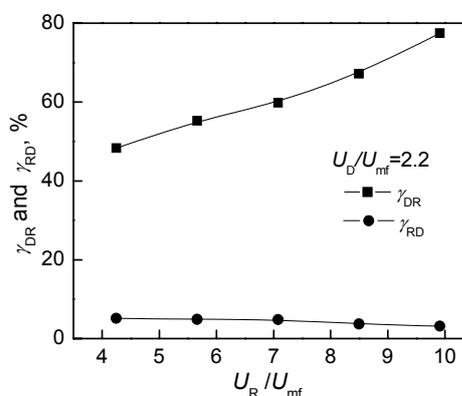
Figure 8. Effect of superficial gas velocity in riser (U_R) on gas bypassing fraction γ_{RD} and γ_{DR}

The purpose of designing the ICFB reactor was to restrict wall deposition of polysilicon during CVD reaction and prevent detrimental destruction of the reactor. In the ICFB reactor, the circulating solid particles were transported upwards in the reaction zone and moved downwards in the heating zone, providing heat transfer between the two zones. At the same time, gas bypassed between the heating zone and reaction zone occurred and should be investigated. In the cold flow experiments, the amount of reaction gas SiHCl$_3$ and the H$_2$ bypassing from the reaction zone to heating zone (γ_{RD}) was slight, while the amount of H$_2$ bypassing from the heating zone to reaction zone (γ_{DR}) was more notable. For example, when the fluidization number of the two zones (U_D/U_{mf} and U_R/U_{mf}) was 2.2 and 7.0, the gas bypassing fraction γ_{DR} was 60% and γ_{RD} was 4% respectively. According to the molar ratio of H$_2$ to SiHCl$_3$ (5) and a ratio of the reaction zone area and heating zone area (1:2), the molar ratio of H$_2$ to SiHCl$_3$ after gas bypassing was 7 and 40. So the molar fraction of SiHCl$_3$ in heating zone was less than one-fifth of the molar fraction in the reaction zone. According to the kinetics of CVD in the SiHCl$_3$-H$_2$ system (10,11), the reaction

is one-order reaction to the concentration of SiHCl$_3$, so the deposition rate in the heating zone is less than one-fifth of the reaction zone.

The CVD Reaction in ICFB

On the basis of the optimized operating conditions in the conventional fluidized bed reactor and cold flow experimental results, tests to manufacture granular polysilicon from SiHCl$_3$ were carried out in an ICFB reactor of 0.12 m I.D.. Well grown polysilicon product was obtained with a stable operation and depressed wall deposition.

CONCLUSIONS

1. Well grown granular polysilicon product was obtained with optimized operating conditions in a bubbling fluidized bed reactor of 0.025 m I.D.. Compared with the seed silicon particles, the silicon granules surface became bright and showed a clear interface between the fresh polysilicon and the seed silicon particle after the CVD reaction. The growth rate on the silicon particle surface was about 10 µm/h.
2. The effect of superficial gas velocity was investigated in cold flow experiments in an ICFB reactor. When U_D/U_{mf}>1.8 and U_R/U_{mf}>4.5, the solid circulation flux G_s (10 kg·m^{-2}·s^{-1}) could satisfy the heat supply needed. The heat transferred could be increased with a larger heating zone or a larger temperature difference between the heating zone and reaction zone. Analysis of the gas bypassing showed that the ICFB reactor could effectively decreased the wall deposition.
3. Well grown polysilicon product was also obtained in an ICFB reactor of 0.12 m I.D. with stable operation and depressed wall deposition at the optimized operating conditions.

ACKNOWLEDGMENT

NOTATION

d_e equivalent diameter, m
d_p diameter of particles, µm
g gravitational acceleration, m·s^{-2}
G_s solid circulation rate, kg·m^{-2}·s^{-1}
H   height of reactor, m
S selectivity to silicon, %
T temperature, ^{o}C

U_D superficial gas velocity in downcomer, m·s^{-1}
U_g superficial gas velocity, m·s^{-1}
U_{mf} incipient fluidization velocity, m·s^{-1}
U_R superficial gas velocity in riser, m·s^{-1}
X conversion of SiHCl$_3$, %
Y yield of silicon, %
γ_{DR} gas bypassing fraction from the downcomer to the riser
γ_{RD} gas bypassing fraction from the riser to the downcomer
μ viscosity, Pa·s
ρ density of gas, kg·m^{-3}
ρ_p density of particles, kg·m^{-3}

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