



Sintering effect on crystallite size, hydrogen bond structure and morphology of the silane-derived silicon powders

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ABSTRACT

The effect of sintering treatment on the amorphous silicon powders from monosilane pyrolysis was investigated to enhance polysilicon yield in the FBR-CVD process. The crystallite size, hydrogen bond structure and morphology of the powders were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Diffuse Reflection Fourier Transform Infrared Spectroscopy (DR-FT-IR) and Zeta Potential Analyzer (ZPA). The results showed that the higher sintering temperature and lower pressure were more favorable to the growth of silicon crystallites and the liberation of hydrogen from silicon hydrides. The crystallite size increased significantly with a critical low FWHM when the sintering temperature was at 750 °C, and the hydrogen releasing from polysilanes and OSiH took place remarkably with a relative flat IR spectrum when the vacuum condition was implemented. Moreover, the particle aggregation was strengthened with broad particle size distribution as long sintering duration or high temperature applied, and the fusion occurred as the temperature was high enough but still with good crystallinity.

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1. Introduction

One of the most important issues for polysilicon production by chemical vapor decomposition in fluidized bed reactor (CVD-FBR) is the fine particle formation from silane vapor decomposition, which causes major negative impacts on product yield and purity and is always being a remarkable concern [1].

Many studies have been carried out to explore the detailed mechanism of silane pyrolysis. Thanks to the technology of laser intracavity absorption spectroscopy [2–5], which proves the existence of silylene (SiH_2) in the gaseous products, the formation of SiH_2 and H_2 is believed to be the critical initial step of silane decomposition. Yuuki [6], Guinta [7], Swihart et al. and Swihart and Girshick [8,9] further propose that silane pyrolysis is mostly similar to the polymerization process with bivalent silylenes as active species, which includes the reactions of polysilane growth, hydrogen elimination, silylene isomerization and cyclization, and the heavy silicon hydrides (Si atom ≥ 10) are responsible for the powders. Beyond that, Girshick et al. and Talukdar and Swihart [10,11] also develop an aerosol dynamic model to simulate the process of silane pyrolysis considering nucleation, growth and aggregation of powders. In the experimental aspect, Onischuk et al. [12–14] make a series of characterization studies on silane vapor decomposition, which reveals three types of hydrogen bond structure containing in the silicon hydrides: poly- $(\text{SiH}_2)_n$ ($p\text{-(SiH}_2)_n$), cluster-SiH ($c\text{-SiH}$) and isolated-SiH

(iso-SiH). Odden et al. [15], Sloodman and Parent [16] and Wigger et al. [17] study the impact of operating conditions on silicon powder and find the independence of powder size on operating pressure and the inhibition of hydrogen as diluted gas on the reaction rate. While these results mentioned above provide us a profound understanding on the mechanism of silane thermal decomposition, an effective way is still unable to be figured out for fine suppression due to the complicated flow behavior in a FBR. Therefore, more detailed studies are imperatively required on the property modification of silicon powders for re-utilization.

Sintering is a typical treatment to modify the particle behavior at a sufficient high temperature, and frequently employed in the fields of ceramic powder synthesis, granulation process, semiconductor production and industrial catalyst manufacture [18–20]. Bellanger et al. [21] apply a two-step process (sintering and re-crystallization) to produce silicon wafers with large polysilicon grains; Wolf [22] focuses on improving the efficiency of sintered porous silicon for thin-film solar cells. Zbib et al. [23] anneal the amorphous nanopowders during the FBR-CVD process and find that the crystal transition temperature for these powders is about 650 °C by means of TEM and DSC. These studies give a great inspiration that can help to modify the crystallinity of silicon powders through sintering treatment.

In the present work, we investigated the possibility of sintering treatment on modifying the properties of silicon powders prepared by monosilane pyrolysis in a quartz tube reactor, with a particular focus on the sintering conditions of temperature, duration and pressure. The as-prepared samples and the sintered powders were characterized by X-ray Diffraction (XRD), Scan Electron Microscopy (SEM), Diffuse

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Reflection Fourier Transform Infrared Radiation (DR-FT-IR) and Zeta Potential Analyzer (ZPA) for crystal pattern, morphology, hydrogen bond structure and powder size distribution (PSD), respectively.

2. Experimental section

2.1. Materials and equipment

The silicon powders were obtained by silane thermal decomposition using high purity nitrogen (99.999%) as diluted gas in a horizontal quartz tube reactor (I.D. = 0.02 m, H = 1 m) equipped within high temperature furnace (SK-G06163, Tianjin Zhonghuan Experimental Furnace Co., Ltd.). The detailed schematic of the experimental setup was displayed in Fig. 1, in which flow meters were applied for gas flux control, a thick layer of insulation cotton for temperature maintenance, a vacuum pump at the entrance of furnace for vacuum operation and a GC analyzer for the inlet and out gas compositions. Based on the temperature calibration, the temperature in the middle of the tube reactor, corresponding to the electric heating zone, was basically the same as the set one. Therefore the silicon powders in the middle of the tube reactor were collected as samples for further sintering and characterization.

2.2. General procedure

The preparation procedure was generally described as follows. Before each experiment, due to the flammability of silane, a vacuum leak test was carefully carried out for the whole system followed by the blowing of the system with high purity nitrogen for oxygen replacement. Then the tube reactor was heated to a set value with the flow of nitrogen in a programmed way. When the temperature became steady, the flow rate of nitrogen was adjusted to a desired value and silane was gradually introduced. The silane reaction was carried out for 30 min with enough amount of powders for characterization and the exhausted gas passed through a lye seal vessel. When finished, the system was naturally cooled to the room temperature by nitrogen and the products were obtained and preserved in a drying oven. As for sintering, the obtained samples were put in a corundum crucible, placed in the middle of the furnace and sintered under nitrogen atmosphere or vacuum condition after getting rid of oxygen. The sintering treatment continued 30 min for all the cases unless specified otherwise and a vacuum condition of about 20 Torr, which may promote the densification of composites [24,25], was also applied.

2.3. Characterization

The crystal structure of the as-prepared and sintered powders was determined by XRD measurement (D8 Advance, Bruker Co., Germany)

using Cu-K α radiation ($\lambda = 0.15404$ nm) at the scan rate of 4°/min in the 2θ range of 20° to 60°. Hydrogen bond structures on the powder surface were analyzed by DR-FT-IR spectrometry (PerkinElmer Inc., Shanghai) in the absorption range of 500–4000 cm^{-1} . The morphology of the powders treated by gold sputter coating was observed with SEM (Nova NanoSEM 450, FEI). PSD was obtained by ZPA (NANO-ZS90, Malvern Instruments Ltd., UK) after several measurements on average.

3. Results and discussions

3.1. Characterization on sample powders

The silicon powders, obtained by silane pyrolysis at different temperatures as shown in Table 1 are characterized as follows. The crystal structures of the powders as XRD analysis are shown in Fig. 2. It is found that the basic diffraction peaks at $2\theta = 28^\circ, 47^\circ$ and 56° , corresponding to the reflections from the lattice planes (111), (220) and (311) of typical polycrystalline silicon [26,27], can be distinguished as the operation temperature reaches 700 °C. Besides, the silicon powders are all amorphous dominated without obvious characteristic peaks.

The DR-FT-IR analyses of the bond structures on the powder surface are shown in Fig. 3 in which several absorption bands due to the vibration signatures of Si–H and Si–O are observed: 600 cm^{-1} (①), 900 cm^{-1} (②), 1000–1200 cm^{-1} (③), 1900–2000 cm^{-1} (④), 2100 cm^{-1} (⑤), 2200–2300 cm^{-1} (⑥), 2900–3000 cm^{-1} (⑦) and 1400–1500 cm^{-1} (⑧). Combining with the previous studies by Wigger [17] and Onischuk [13,14] as summarized in Table 2, it can be concluded that bands ③ and ⑥ are corresponding to the vibrations of SiOSi and OSiH due to inevitable air exposure during operation; the peak at position ① is attributed to the vibration of p-(SiH₂)_n, the intensity of which decreases with raising temperature due to hydrogen releasing with low activation energy; the peak at position ② is attributed to Si–H vibrations, which is probably formed from the hydrogen-released p-(SiH₂)_n and becomes obvious as the temperature over 650 °C; the peak at position ④ is attributed to the vibration of c-SiH, the intensity of which also greatly weakens with the increase in temperature; the peak at position ⑤ is attributed to the vibrations of p-(SiH₂)_n and iso-SiH the latter of which dominates as the temperature over 650 °C; and bands ⑦ and ⑧ are probably attributed to the ring structure of silicon hydrides or the other impurity disturbances, which exist strongly at low temperature (600 °C). The above analyses on the Si–H bond structures at positions ①, ④ and ⑤ are in accord with those of Onischuk's [13,14], and the one at position ② which appears at relative high temperature (700 °C) agrees with those of Wigger's [17].

The amorphous silicon powders obtained at 650 °C were applied as samples for further sintering which can be regarded as fines formed in granular polysilicon production [28,29]. A further morphology

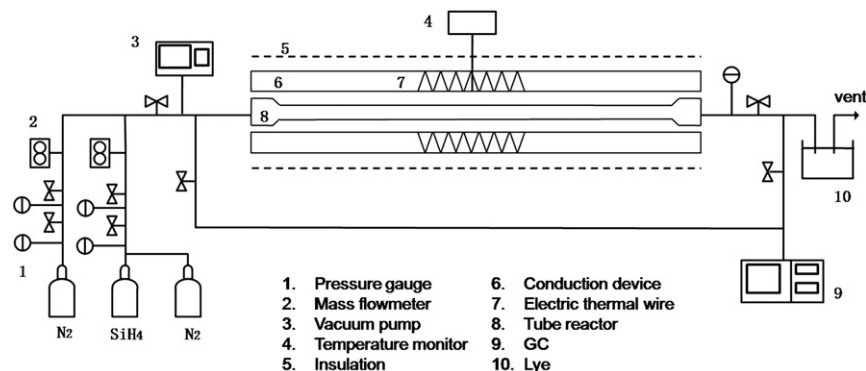


Fig. 1. Schematic diagram of experimental setup.

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