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CHARACTERIZATION OF POLYCRYSTALLINE SILICON PARTICLES PRODUCED VIA CVD FROM MONOSILANE IN A FLUIDIZED BED REACTOR

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Abstract-Characterization of polycrystalline silicon particles produced in a fluidized bed reactor via CVD from monosilane was carried out. It was observed that part of the hydrogen from monosilane remained in the particles. Most of hydrogen was bonded to silicon and temperatures as high as 1300 K were required to dehydrogenate the silicon particles. Particles were contaminated with metal elements which were diffused from the reactor wall, suggesting that the material used in constructing the fluidized bed reactor wall also needed to be controlled to improve the purity of product.

1.-Introduction

Polycrystalline silicon has conventionally been produced by using the bell-jar type reactor in a batch-wise manner. It takes about two weeks to industrially produce polycrystalline silicon via CVD on a Si substrate from SiHCl_3 , leading to low thermal efficiency. Continuous production of polycrystalline silicon particles via CVD from SiHCl_3 or SiH_4 has been proposed to increase thermal efficiency and to develop a continuous CZ furnace system. Several types of fluidized bed reactors for production of polycrystalline silicon particles via CVD have recently been developed [1-7].

In the present study, poly-Si particles were produced in a laboratory-scale fluidized bed reactor in a step-wise manner and properties of produced poly-Si particles were investigated. In particular, characterization in relation to the amount and chemical state of remaining hydrogen was carried out because hydrogen contained in poly-Si particles creates a splashing problem in a crucible for pulling out a single silicon crystal.

2.-Experimental

Polycrystalline silicon particles were produced in a fluidized bed reactor via CVD from monosilane. The reactor was a 50 mm i.d. tube made of stainless steel. Detailed apparatus and experimental procedure were reported elsewhere [5,7]. CVD experiments to grow particles were carried out at 870 - 700 K. Ten vol% of SiH_4 diluted with hydrogen was supplied into the fluidized bed. The flow rate of feed gas was adjusted to 5 U_{mf} in each run; the actual flow rate was increased with particle growth.

Morphology of produced particles was observed by means of Secondary electron microscopy (SEM). Structural characteristics were measured by X-ray diffraction (XRD) and FT-IR.

Temperature-programmed desorption (TPD) experiments for hydrogen remaining in poly-

Si particles were conducted in the temperature range from 773 to 1373 K at four different heating rates of 2.5, 5.0, 7.5 and 10 K min⁻¹ in a stream of argon. Hydrogen was determined by gas chromatograph with a TCD detector.

Depth distribution of hydrogen was measured by means of secondary ion mass spectrometry (SIMS, Hitachi IMA-2) using Ar⁺ ion. The particles were stuck on a sample holder with adhesive silver paste. Then it was mounted in a UHV chamber which was evacuated to better than 10⁻⁸ torr before ion bombardment. The primary ion beam energy was 10 keV and incident Ar⁺ ion beam flux was 5X10³ A m⁻².

3.-Results and discussion

Poly-Si particles were produced in the fluidized bed via CVD on seed poly-Si particles from SiH₄. Particles were taken out from the reactor after each run of 2.5 - 6 h to remove fine powders by sieving. CVD of silicon on seed particles was repeatedly carried out 9 times. Figure 1 illustrates the growth of poly-Si particles in 9 times of experiments. Seed poly-Si particles having the average particle diameter of 339 μm was grown to 545 μm , namely 3/4 of the product came from CVD by monosilane decomposition. Density of produced poly-Si particles were 2.319(± 0.001)X10³ kg m⁻³, which was slightly less than 2.330X10³ kg m⁻³ of the density of Si metal.

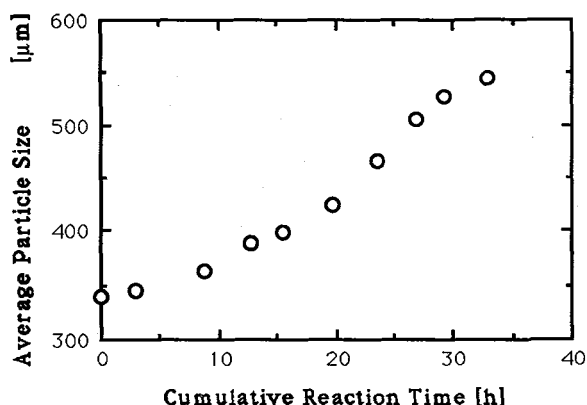
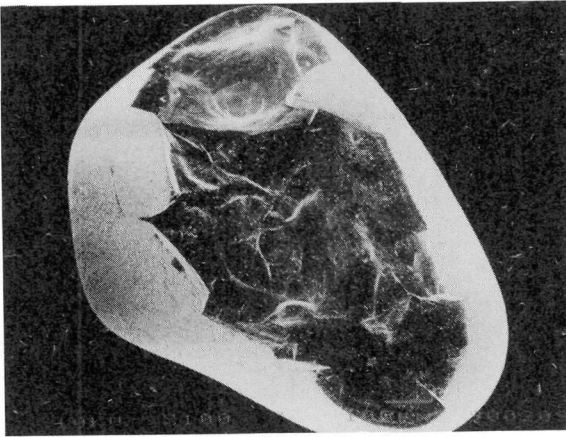


Figure 1 Growth of Polycrystalline Silicon Particles by CVD from Monosilane.

Figure 2(a) shows a typical SEM image for cross section of the produced poly-Si particles. The central part showing in dark contrast was a seed particle and the surrounding part showing in bright contrast was the layer of silicon deposited. Figure 2(b) presents morphology of the boundary between seed particle and deposited silicon. It was apparent that the layer of deposited silicon consisted of assemblages of tiny silicon particles. As typically shown in Figure 2(c), the accumulation of tiny particles was observed on the surface of produced particles as well.

FT-IR spectra for 4 kinds of silicon particles are compared in Figure 3. Stretching vibrations of Si-H bond were observed at around 2000 - 2100 cm⁻¹ for the surface of poly-Si particles produced, whereas no signal indicative of Si-H bond was detected both for seed poly-Si particles and for poly-Si produced in a conventional bell-jar type of reactor. Another FT-IR spectrum was taken for a sample which was obtained by finely crushing produced poly-Si particles in order to observe the chemical structure of the bulk of the

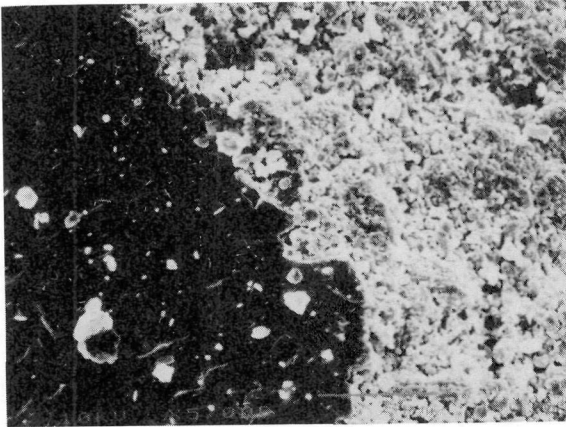
(a)



0.1 mm



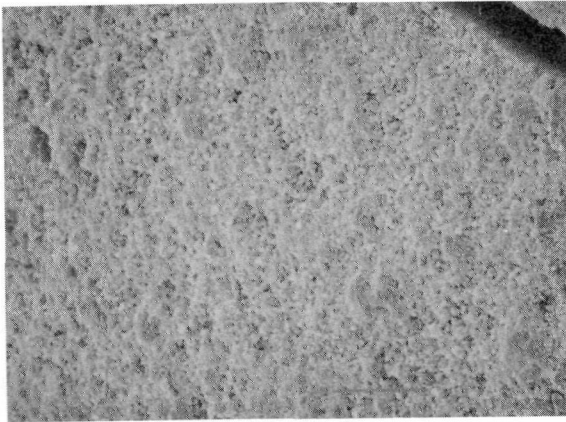
(b)



50 μm



(c)



20 μm



Figure 2 SEM images (a) for cross section of a polycrystalline particle produced, (b) for the boundary between a seed silicon particle and deposited layer and (c) for the surface of a polycrystalline silicon particle produced

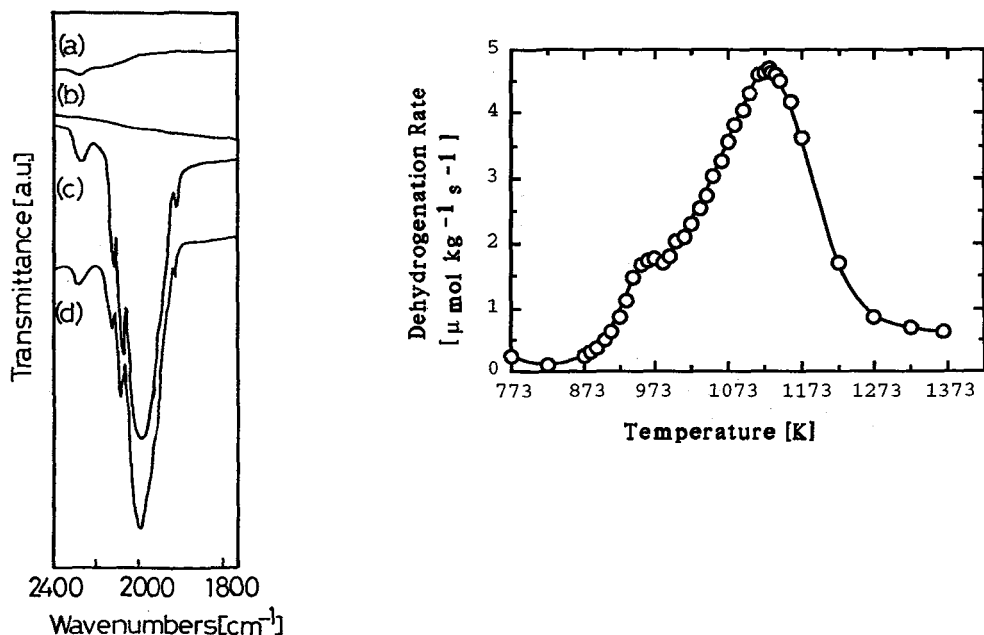


Figure 3 FT-IR spectra for (a) poly-Si produced in a bell-jar type of reactor, (b) seed poly-Si particles, (c) poly-Si particles produced in a fluidized bed and (d) sample obtained by crushing poly-Si particles shown in (c).

Figure 4 TPD spectrum for hydrogen remaining in poly-Si particles. The particles were heated at a rate of 2.5 K min^{-1} .

particles. The spectrum obtained was similar to that for produced particles themselves.

As mentioned above, hydrogen remaining in poly-Si particles causes a splashing problem which means irregularities in convection in a CZ crucible to produce silicon single crystals. Thus, dehydrogenation of poly-Si particles produced in this study are believed to be required. TPD experiments were expected to gather information on chemical nature and kinetics of dehydrogenation. Figure 4 shows the TPD spectrum for poly-Si produced in this study. Hydrogen was solely observed as the desorbed species and no compound containing silicon such as SiH_4 and SiH_2 was detected. The dehydrogenation was appreciable at 873 K and the maximum rate of dehydrogenation was observed at approximately 1128 K. Desorption peak had a small shoulder at 973 K. A TPD experiment for seed poly-Si particles was conducted. Since desorption of hydrogen from seed particles was not appreciable, we conclude that hydrogen observed in Figure 4 was due to dehydrogenation of deposits on seed particles. The amount of remaining hydrogen in poly-Si particles was calculated by graphical integration of the rates of hydrogen desorption observed in the TPD spectra and determined as $2.63 \times 10^{-2} \text{ mol kg}^{-1}$.

SIMS measurements were carried out to study depth distribution of hydrogen in the layer of silicon deposited. Three kinds of poly-Si samples were used for the measurements: (1) Fresh poly-Si particles produced in the present study, (2) poly-Si particles heated up to 973 K at a heating rate of 10 K min^{-1} in flowing argon and kept at that temperature for 0.5 h and (3) poly-Si heated in flowing argon up to 1373 K at a heating rate of 10 K min^{-1} . Figure 5 shows the depth distribution of hydrogen measured by SIMS. In these experiments, the samples were sputtered in a depth of $3 \mu\text{m}$. The concentration of hydrogen in the bulk of deposited silicon layer decreased with increasing temperature for

dehydrogenation as shown in Figure 5. This result strongly indicated that dehydrogenation occurred not only from the surface but also from the bulk. Alternatively, hydrogen remaining in the deposited silicon diffuses toward the surface at above 770 K and leaves the surface. The depth distribution suggested that the concentration of hydrogen increased with depth. Such a distribution probably gave driving force for hydrogen to diffuse from the bulk of deposited layer of silicon to the surface. The observed I_H/I_{Si} ratio did not approach zero owing to the contribution of hydrogen and water remaining in the UHV chamber to the signal intensity of 1H . Accordingly, the experimental result that the I_H/I_{Si} ratio observed for the sample dehydrogenated at 1373 K was about 0.03 does not indicate such a conclusion that complete dehydrogenation of poly-Si particles is impossible.

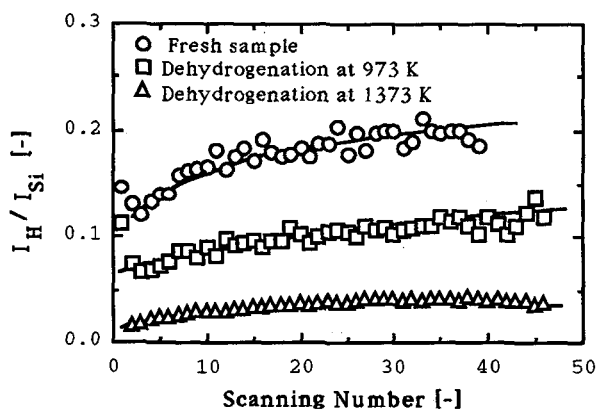


Figure 5 Depth Distribution of Hydrogen in Polycrystalline Silicon. The ordinate represents relative signal intensity of 1H normalized by signal intensity of ^{28}Si and the abscissa represents depth.

It is well known that a series of TPD experiments using different heating rates gives kinetic information. By assuming that hydrogen desorption is first order, that surface sites bound to hydrogen are uniform and that readsorption of hydrogen desorbed is negligible, the following equation to express kinetics for desorption of chemical species from solid surface has been proposed /8/.

$$(kd)_M = \frac{\beta E_d}{RT_M^2} \quad (1)$$

where $(kd)_M$ represents rate constant of hydrogen desorption at a temperature at which a maximum rate of desorption was observed in a TPD spectrum, T_M , temperature at which a maximum rate of hydrogen desorption was observed and β , heating rate.

$$(kd)_M = A \exp\left(-\frac{E_d}{RT}\right) \quad (2)$$

Thus,

$$2\log T_M - \log \beta = \frac{E_d}{2.303R T_M} + \log\left(\frac{E_d}{AR}\right) \quad (3)$$

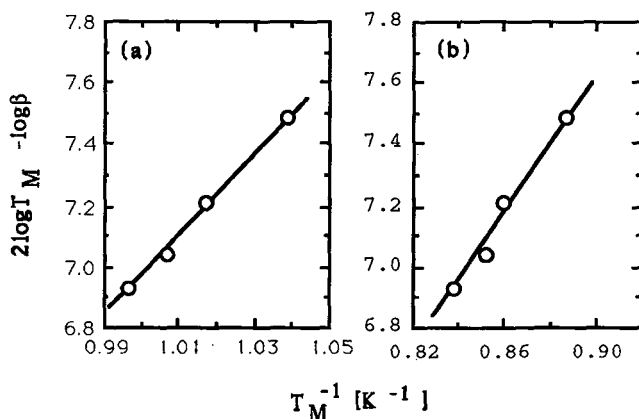


Figure 6 T_M^{-1} vs $(2\log T_M - \log \beta)$ plots (a) for shoulder peak and (b) for main peak appeared in TPD spectra.

Equation (3) suggests that the temperature at which a maximum rate of hydrogen desorption is observed in a TPD spectrum is only a function of heating rate. An apparent activation energy of hydrogen desorption can be determined by TPD experiments with varying heating rate. TPD spectra were taken at different heating rates of 2.5, 5, 7.5 and 10 K min^{-1} .

As a shoulder peak appeared as shown in Figure 2, a couple of T_M , a lower temperature at which a maximum of the shoulder peak appeared and a higher temperature at which a maximum of a main desorption peak, were obtained from a TPD spectra. According to equation (3), $2\log T_M - \log \beta$ was plotted against the reciprocal of T_M as shown in Figure 6. Apparent activation energies were separately determined from the slopes illustrated in Figures 6(a) and (b). The energies were 265 and 226 kJ mol^{-1} for the shoulder peak and for the main peak, respectively.

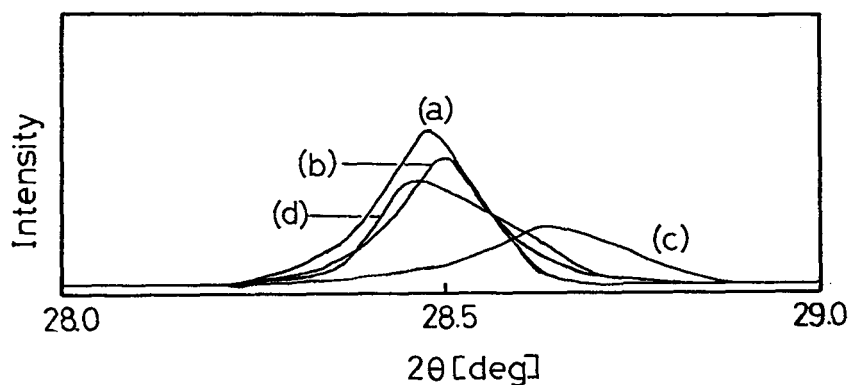


Figure 7 XRD patterns for silicon samples. (a) Standard silicon, (b) poly-Si particles dehydrogenated at 1073 K, (c) non-dehydrogenated poly-Si particles produced in the fluidized bed and (d) seed poly-Si particles.

From the results of FT-IR, TPD and SIMS measurements, we conclude that when CVD of silicon from SiH_4 on poly-Si particles is performed in the fluidized bed hydrogen remains in the layer of poly-Si deposited on seed silicon in the form of Si-H bond. However, it is possible to desorb by heating in an inert atmosphere up to at least 1373 K. TPD results apparently suggested that two kinds of hydrogen remained in poly-Si particles. The apparent activation energies obtained for these two kinds of hydrogen desorption were comparable to the binding energy of Si-H (299 kJ mol^{-1}). We thus infer that desorption of hydrogen involves dissociation of Si-H bond on the surface. The appearance of a small desorption peak giving a larger activation energy at a lower temperature may correspond to desorption of hydrogen existing in the vicinity of surface. Structural change with dehydrogenation was monitored by XRD measurements as shown in Figure 7. Si(111) reflection peak obtained from poly-Si particles produced in the present study was shifted to a higher angle than that for the standard silicon sample, indicating that the average distance between Si atoms in poly-Si particles was smaller than that in the standard silicon sample. This result agreed with the conclusion that the deposited silicon contained a considerable amount of Si-H bond. On heating poly-Si particles produced, the Si(111) reflection peak was shifted toward the position at which the reflection peak for the standard sample appeared, corresponding to the progress of dehydrogenation.

Table 1 Monitoring of the contamination from the reactor wall made of stainless steel

Sample	Normalized signal intensity of ^{52}Cr
Poly-Si particles	0.003
Reactor wall side of silicon deposits	0.40
Bed side of silicon deposits	0.01

Signal intensity of ^{52}Cr was normalized by intensity of total ion.

Finally, contamination of poly-Si particles from the reactor wall made of stainless steel was studied by means of SIMS. The deposits observed on the reactor wall in the form of a film after reaction were analysed together with poly-Si particles. The typical results are listed in Table 1. Signal of ^{52}Cr was adopted as a representative to reveal the level of contamination from stainless steel. Comparison of the results between reactor wall side and bed side of the thin silicon deposit-like film suggests that elements contained in stainless steel diffused toward the bed through the deposit-like thin film in the course of CVD. Poly-Si particles produced were contaminated with these elements to some extent. We believe that the reactor wall should be constructed with material which contains no metallic elements other than Si, for, example, Si itself and SiC.

Conclusions

Polycrystalline silicon particles produced in a fluidized bed reactor via CVD through monosilane pyrolysis contained hydrogen forming Si-H bonds. Such hydrogen remaining in the bulk of silicon particles was desorbed on heating in an inert atmosphere up to 1370 K. Dehydrogenation of polycrystalline silicon particles is essentially required to utilize the present type of fluidized bed reactor for production of a single silicon crystal in a continuous CZ furnace system. The material used to construct the reactor wall is important to prevent products from being contaminated.

Acknowledgement

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Symbols

- A : Exponential factor [-]
Ed : Activation energy for hydrogen desorption [J mol^{-1}]
kd : Rate constant for hydrogen desorption [-]
R : Gas constant [$\text{J mol}^{-1} \text{K}^{-1}$]
T : Temperature [K]
 U_{mf} : Minimum fluidizing velocity [m s^{-1}]
 β : Heating rate [K min^{-1}]

Subscript

- M : Peak top of a TPD spectrum

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