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Production of Crystalline Si Nano-particles Using VHF Discharges and Their Properties

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We have developed a method for producing crystalline Si nano-particles using VHF discharges. The size of Si nano-particles can be controlled by a discharge duration or by a gas residence time in the discharge region. Using the method, we have succeeded in producing particles having a mean size of 2.0 nm and 100 % crystallinity. The crystalline Si nano-particles have an initial defect density of 4×10^{17} cm^{-3} and show little light-induced degradation, while amorphous particles have an initial value of 6×10^{17} cm^{-3} and the density increases by more than one order of magnitude after light soaking. The hydrogen content C_H of crystalline Si nano-particles is below the minimum detection limit of 0.01 at. %.

Key words: nano-particle, Si, solar cell, crystallinity

1. INTRODUCTION

The indirect and narrow band gap of crystalline Si (c-Si) is the major drawback to apply c-Si to the opto-electric devices such as solar cells. To overcome this drawback by utilizing the quantum size effect in a quantum dot, we have deposited "crystalline Si nano-particle films". Nano-particles of about 2 nm in size produced using pulse discharges have a band gap of 1.7 eV. For a solar cell of films composed of such crystalline Si nano-particles, the theoretical conversion efficiency is the highest and the optical absorption coefficient increases since the interband transition takes place without assistance of phonons due to quantum size effects. Deposition of such films demands the following three requirements; (1) production of a large amount of particles below 3.8 nm in size and of 100 % crystallinity, (2) their high transport efficiency to depositing film surface, and (3) their high sticking probability to the surface.

Based on our previous results concerning their formation in SiH_4 high frequency (HF) discharges [1-7], we have developed a method of controlling their size using a periodical HF discharge (referred to as a pulsed discharge). For this method, the size of Si nano-particles is controlled by the discharge duration, and their structure is done by the H_2/SiH_4 ratio, discharge power density, and excitation frequency. Particles of 100 % crystallinity are produced for a H_2/SiH_4 ratio of 20, a power density of 0.6-0.8 W/cm^2, and an excitation frequency of 60 MHz [8]. Recently, we have succeeded in producing Si nano-particles of 1.6 nm in size and 100 % crystallinity by applying the method. Moreover, their size can be controlled by a gas residence time in the discharging region. We also evaluate the stability of the nano-particles against light soaking using ESR. In this paper, we report on these experimental results.

2. EXPERIMENTAL SETUP

Experiments were carried out using a reactor for producing Si nano-particles as shown in Fig. 1. Stainless-steel-mesh powered and grounded electrodes of 80 mm in diameter were placed at a separation of 20 mm. The electrodes were placed in a stainless-steel vessel of 95 mm in inner diameter and 400 mm in length. Moreover, multi-hollow electrodes were employed to increase the transport efficiency of particles. For this configuration, powered and grounded electrodes of 70 mm in diameter, which have 32 holes of 5 mm in diameter, were placed 2 mm apart. Gases of SiH_4 and H_2 were fed from the bottom

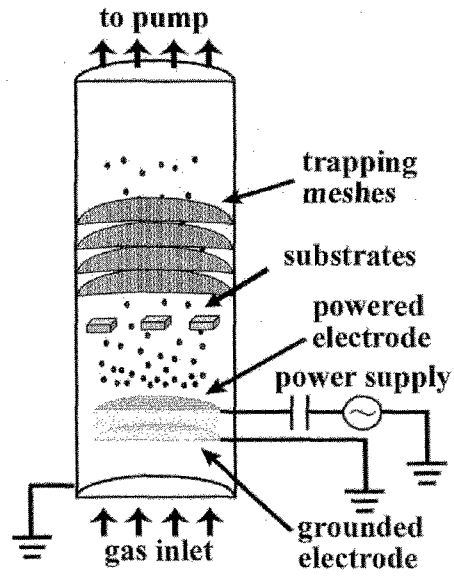

Fig. 1. Experimental setup for producing crystalline Si nano-particles.

of the reactor at flow rates of 0.5-10 sccm and 18-398 sccm respectively, so as to form a one-dimensional gas flow. Under such flow conditions, the pressure in the reactor was 13.3-266 Pa. The excitation frequency and supplied power were 60 MHz and 35-46 W (0.70-0.84 W/cm^2), respectively.

The size of Si nano-particles was controlled by changing the power-on duration T_{on} of the pulsed discharge. In-situ measurements of size and density of Si nano-particles were carried out by a double-pulse discharge method, in which their size was deduced from their diffusion rate after turning off the discharge and their density was done from an electron attachment rate to them in the after-glow phase [1]. Their size, number density, shape and structure were also obtained by an ex-situ method using a high resolution transmission electron microscope (HRTEM, JEOL: JEM-2010) [9]. Defect density and a hydrogen content C_H of Si nano-particles were obtained by electron spin resonance (ESR) and Fourier-transform infrared (FTIR) spectroscopy, respectively. For this purpose, Si nano-particles were collected with 2-4 stainless-steel-meshes of 70 or 92 mm in diameter placed at a position 80-140 mm downstream from the powered electrode, as well as with Si (111) and quarts substrates of 4 × 10 mm^2 placed at a position 70 mm downstream from the powered electrode.

3. RESULTS AND DISCUSSION

First, we have tried producing Si nano-particles suitable for "crystalline Si nano-particle films" for a gas flow rate ratio R= $SiH_4/(SiH_4+H_2)$= 0.5, 1 and 10 %. Figures 2 (a) and (b) show typical HRTEM images of Si nano-particles obtained for R= 10 and 0.5 % respectively. The diffraction patterns of these particles show that nano-particles for R= 10 % have amorphous structure and ones for R= 0.5 % have crystalline structure (not show here). Their size distributions are shown in Fig. 3. Particles of 2.0 nm in mean size and 100 % crystallinity suitable for depositing "crystalline Si nano-particle films" are successfully produced for R= 0.5 %. As these particles have been produced with CW discharges using multi-hollow electrodes, the results indicate that their size can be controlled by the gas residence time in the discharge region. The discharges realize a high production rate several times as high as pulsed discharges.

Second, we have measured C_H of Si nano-particles using FTIR. Figures 4 (a) and (b) show the infrared absorption spectra of Si nano-particles. While amorphous Si nano-particles have large absorption as 2090 cm^{-1} (Si-H_2 stretching mode), 2000 cm^{-1} (Si-H_2 stretching mode), 880 cm^{-1} (Si-H_2 bending mode) and 630 cm^{-1} (Si-H_x: x= 1-3 wagging mode), crystalline Si nano-particles have little of them. Whereas C_H of amorphous particles measured at 2000-2090 cm^{-1} is 1-10 at. %, the one of crystalline nano-particle is below the minimum detection limit of 0.01 at. %. To evaluate contribution of surface modes in these absorptions at 2000 and 2090 cm^{-1}, dependence of a ratio of Si-H_2 bond density to Si-H one (C_{SiH2}/C_{SiH}) on a ratio of absorption intensity at 880 cm^{-1} to one at 630 cm^{-1} (Abs_{880}/Abs_{630}), which are bulk modes. The results are shown in Fig. 5. Since these two ratios are proportional to each other, the absorption around 2000

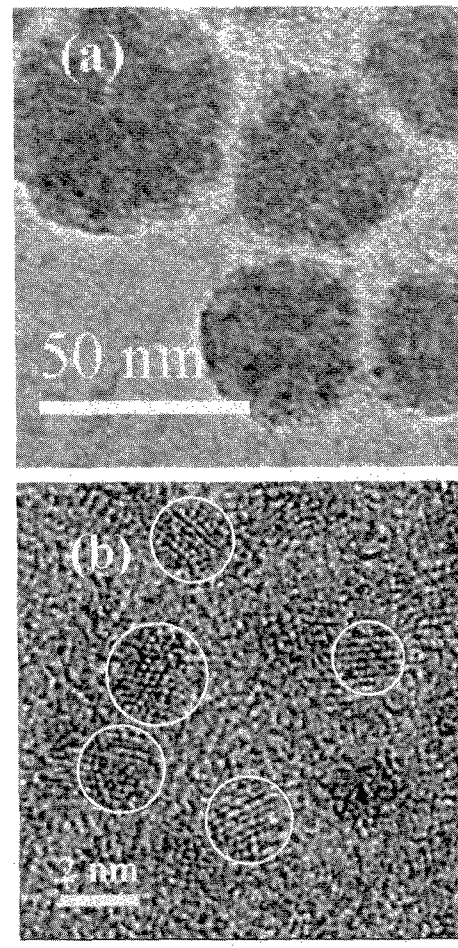

Fig. 2. HRTEM images of (a) amorphous and (b) crystalline Si nano-particles. Experimental conditions: excitation frequency 60 MHz, supplied power density 0.70 W/cm^2, (a) SiH_4 2.0 sccm, H_2 18 sccm, total pressure 13.3 Pa, (b) SiH_4 2.0 sccm, H_2 398 sccm, total pressure 266 Pa.

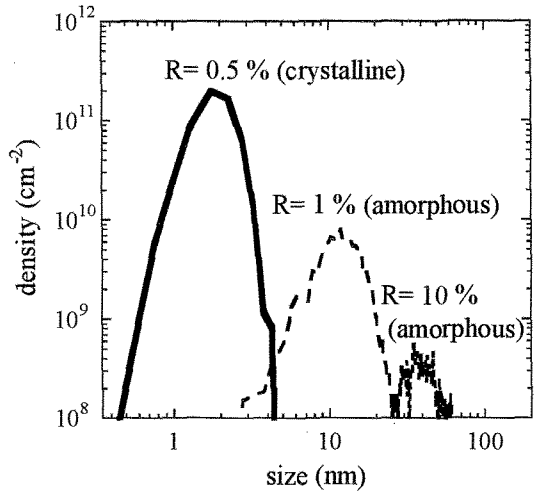

Fig. 3. Size distribution of Si nano-particles. Experimental conditions: excitation frequency 60 MHz, supplied power density 0.70 W/cm^2; R= 0.5 %, SiH_4 2.0 sccm, H_2 398 sccm, total pressure 266 Pa; R= 1 %, SiH_4 2.0 sccm, H_2 198 sccm, total pressure 133 Pa; R= 10 %, SiH_4 2.0 sccm, H_2 18 sccm, total pressure 13.3 Pa.

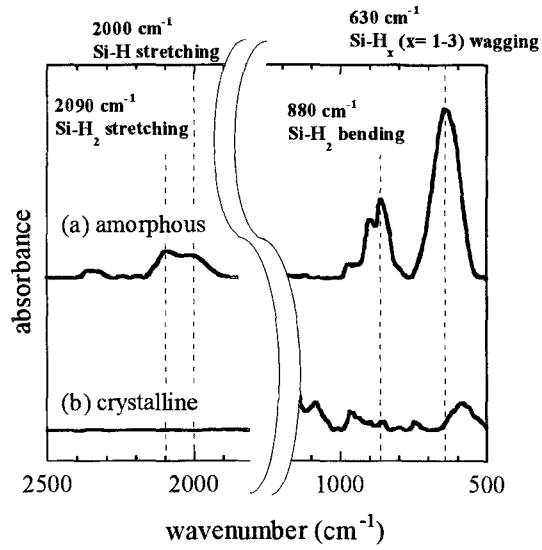

Fig. 4. FTIR spectra of (a) amorphous and (b) crystalline Si nano-particles. Experimental conditions: excitation frequency 60 MHz, supplied power density 0.70 W/cm^2, (a) SiH_4 2.0 sccm, H_2 18 sccm, total pressure 13.3 Pa, (b) SiH_4 2.0 sccm, H_2 398 sccm, total pressure 266 Pa.

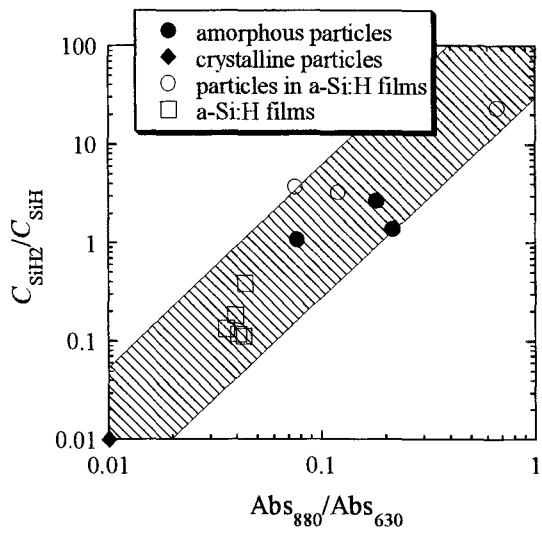

Fig. 5. Dependence of C_{SiH2}/C_{SiH} on Abs_{880}/Abs_{630}. Experimental conditions: excitation frequency 60 MHz, supplied power density 0.035-0.70 W/cm^2, SiH_4 2.0-30 sccm, H_2 18-398 sccm, total pressure 9.3-266 Pa.

cm^{-1} of nano-particles is mainly bulk mode.

Finally, we have examined the stability of Si nano-particles against light soaking by measuring their defect density using ESR. ESR spectra of Si nano-particles are shown in Figs. 6 (1) and (2). The samples for this measurement were prepared (1) by depositing them in a-Si:H films on a quartz substrate (2) by collecting particles from the trapping meshes and inner wall. The sample (1) has a signal of a-center at g= 2.005 due to dangling bonds and E'-center at g= 2.000 due to lack of oxygen atoms in Si-O_2, while sample (2) has a signal of a-center. Regarding the a-center, we have examined

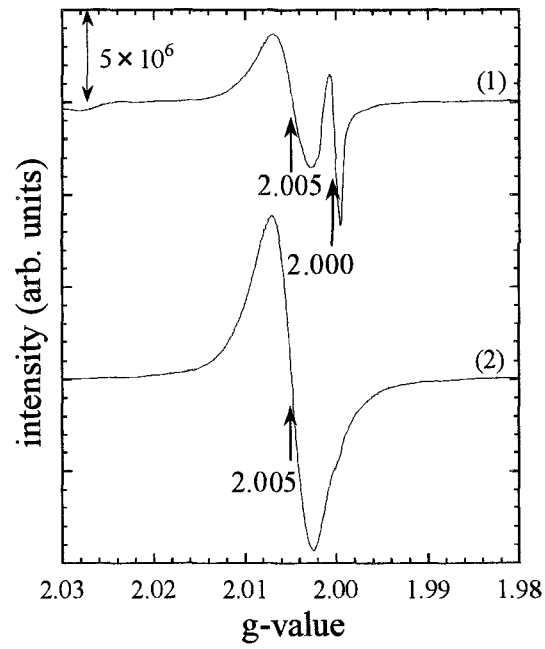

Fig. 6. ESR spectra of (1) crystalline Si nano-particles in a-Si:H films (2) Si nano-particles. Experimental conditions: excitation frequency 60 MHz, supplied power density 0.92 W/cm^2, T_{on}= 15 s and power-off duration T_{off}= 1 s, SiH_4 8.0 sccm, H_2 200 sccm, total pressure 160 Pa.

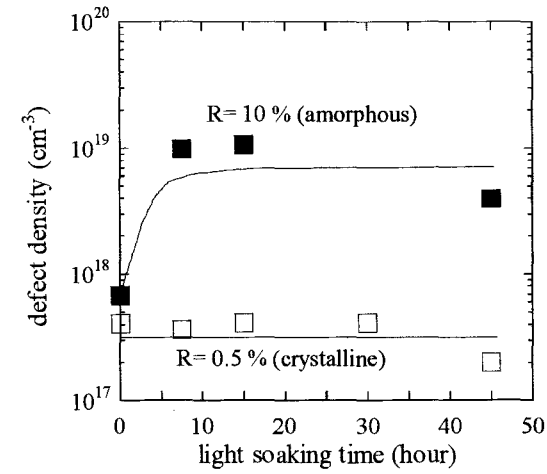

Fig. 7. Dependence of defect density of Si nano-particles on light soaking time (2.4 SUN, 60 °C). Experimental conditions: excitation frequency 60 MHz, supplied power density 0.70 W/cm^2, (a) SiH_4 2.0 sccm, H_2 18 sccm, total pressure 13.3 Pa, (b) SiH_4 2.0 sccm, H_2 398 sccm, total pressure 266 Pa.

dependence of defect density of Si nano-particles on light soaking time. The result is shown in Fig. 7. Amorphous particles for R= 10 % have an initial defect density of 6×10^{17} cm^{-3} and the density increases by more than one order of magnitude after the light soaking. In constant, crystalline particles for R= 0.5 % have an initial defect density of 4×10^{17} cm^{-3} and show little degradation. Since C_H value of crystalline nano-particles is below the minimum detection limit of 0.01 at. %, the defect density of crystalline nano-particles may be reduced using an appropriate H-termination.

4. CONCLUSIONS

Size-controlled formation of crystalline Si nano-particles has been demonstrated by using the VHF discharges. The following conclusions are obtained in this study,

1) Production of particles of 2.0 nm and 100 % crystallinity has been successfully demonstrated.
2) C_H value of crystalline Si nano-particle is below the minimum detection limit of 0.01 at. %
3) Crystalline Si nano-particles have a density of 4×10^{17} cm^{-3} and show little light-induced degradation.

5. ACKNOWLEDGEMENTS

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