Crystal evaluation of spherical silicon produced by dropping method and their solar cell performance

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Abstract

The characterization of silicon spheres 1 mm in diameter, which were produced by a dropping method and solar cell performance using spheres are reported. Scanning electron microscopy observations of the Si spheres after Dash etching and X-ray pole figures indicate that the spherical Si has many defects and crystal grains. Systematic study of the crystal growth temperature and the atmosphere in the dropping area yields improvements in the crystallinity as well as a decrease in the concentrations of oxygen and carbon. Moreover, the spherical Si solar cell performance improved because these impurities are the prime factor for recombination centers.

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1. Introduction

Bulk Si solar cells currently used for PV power generation are made from Si ingots, which are cut into wafers for the fabrication of conventional solar cells. A portion of the ingot is lost during the cutting and polishing process. Therefore, cost reduction for crystalline Si solar cells is very difficult. Spherical solar cells fabricated from Si spheres are expected to be lower cost cells compared to conventional Si solar cells, since Si spheres can be produced directly from molten Si without cutting and polishing. Moreover, in order to
reduce the quantity of Si used, we proposed a module structure to set a micro-concentrator around spherical Si solar cells.

Texas Instruments (TI) researchers have reported the results of their research work on spherical Si solar cells [1–3]. A large number of Si spheres are required to form large area solar cells since the size of the Si spheres produced by their method is smaller than 1 mm in diameter. We have developed a dropping method to fulfill this requirement and have succeeded in extremely high-speed production of Si spheres of about 1 mm in diameter [4]. This paper describes the crystallinity of and impurity concentrations in spherical Si, as well as improvements in solar cell efficiency.

2. Experimental

Fig. 1 shows the schematic illustration of the spherical Si production apparatus. First, pieces of boron-doped p-type Si are melted in a quartz crucible with carbon heaters. Small drops of Si are instilled from the nozzle at the bottom of the crucible by inert gas pressure.

![Schematic illustration of the apparatus for the dropping method used to form spherical Si.](image-url)
The free-fall tower height is approximately 7m. The Si droplets are solidified into a spherical shape by surface tension. To fabricate spherical Si solar cells, first, an n-type layer is formed by vapor phase deposition using phosphorus. The typical deposition temperature is about 900°C for approximately 50 min. Next, a part of the spherical Si is cut to expose the p-layer. The p-electrode is formed by the application of an aluminum–silver paste to the p-layer followed by drying (20 min at 200°C) and firing (10 min at 700°C). Details of the process are given elsewhere [5].

Two improvements were proposed to clarify the effect of the temperature gradient and the atmosphere in the dropping area of the apparatus. First, the crystal growth temperature just under the nozzle was raised by using heaters. The function to heat in the spherical Si production apparatus has only the heater, and the temperature is about 1450°C. The heater length can be changed from 20 to 40 cm. The change in the heater length influences the temperature just under the nozzle since the crucible length is 10 cm. The Si spheres are expected to be cooled slowly by using the longer heater. Second, the atmosphere in the dropping area is changed to Ar gas from air. Table 1 shows a summary of the fabrication conditions.

The surface morphology of the spherical Si was observed by scanning electron microscopy (SEM). The crystallinity was investigated by SEM observations of the spherical Si etched in a Dash etch solution for 1 h [6]. X-ray pole figures were obtained using an X-ray diffraction (XRD) system (PANanalytical X’pert MRD) operated at 45 kV and 40 mA using Cu Kα (λ = 1.5405 Å) radiation. The impurity concentration in the spherical Si was analyzed by secondary-ion mass spectroscopy (SIMS). Solar cell performance was characterized by J–V measurements under an incident power of 100 mW/cm² AM 1.5 illumination at 25°C. The external quantum efficiency (EQE) was also measured.

3. Results and discussion

3.1. Crystal quality and solar cell performance

Figs. 2(a)–(c) show SEM micrographs of the spherical Si grown using the conditions shown in Table 1, A–C, respectively. As shown in Fig. 2(a), the whole surface of the spherical Si was rough and had many lines. The lines are related to grain boundaries. On the other hand, In Figs. 2(b) and (c), the lines and rough surface are partly observed; however, most of the surface is smooth. It is likely that the grains grew larger in these samples.

In order to confirm the number of crystal grains in the Si spheres classified into two categories, X-ray pole figures were measured. The X-ray pole figure measurement analyzes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heater length (cm)</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20</td>
<td>Air</td>
</tr>
<tr>
<td>B</td>
<td>40</td>
<td>Air</td>
</tr>
<tr>
<td>C</td>
<td>40</td>
<td>Ar</td>
</tr>
</tbody>
</table>
the crystal grains of the Si spheres. A Si sphere was placed on a sample holder, and X-ray pole figure measurement was carried out by rotating the sample holder, thereby fixing the incident and detection X-ray angles. The \{1 1 1\} X-ray pole figure results are shown in Figs. 3(a)–(c) corresponding to Si spheres grown using the conditions shown in Table 1, A–C, respectively. As can be seen in Fig. 3(a), approximately 50 poles appeared. On the other hand, approximately 10 poles appeared in Figs. 3(b) and (c). These results indicate that the spherical Si corresponding to Fig. 3(a) consists of many grains, since the number of poles in the pole figure is proportional to the number of crystalline grains.

Figs. 4(a)–(c) show SEM micrographs of the cross-section of the spherical Si after Dash etching for 1 h, corresponding to the Si spheres grown using the conditions shown in Table 1, A–C, respectively. The Dash etch is generally used to reveal dislocations in Si, and...
causes etch pits on any surface independent of the Si crystallographic orientation [6]. As seen in Fig. 4(a), the spherical Si has many crystal defects. In contrast, it can be seen in Figs. 4(b) and (c) that the surface is smooth and the density of defects decreased drastically. These results indicate that the moderate cooling rate of melting Si due to the presence of the heater just under the nozzle assists crystal growth with large grain sizes, and the crystallinity improved.

Solar cell performance using the Si spheres grown by the three conditions was measured. Solar cell performance was measured by placing a Si sphere between a metal plate and an electrode thereby forming a cell. The solar cell area is defined as the projection area in this study. The $J-V$ characteristics are shown in Figs. 5(a)–(c) corresponding to the Si spheres grown using the Table 1, A–C conditions, respectively. The performance of the spherical Si solar cell was significantly improved from (a) to (c) and the results are summarized in Table 2. The short circuit current density ($J_{sc}$) and the open circuit voltage ($V_{oc}$) of the
spherical Si solar cells increased after improvements in the spherical Si production, and the conversion efficiency was thereby improved. The crystallinity of the spherical Si solar cell fabricated using condition (a) was found to be very poor, since the whole cross-section of the Si sphere was etched by Dash etching. On the other hand, the cross-sections of spherical Si solar cells fabricated using conditions (b) and (c) were not partly etched by the Dash etching, as can be seen in Figs. 4(b) and (c). The low-efficiency cell has many etch pits compared to the high-efficiency cell.

3.2. EQE and SIMS measurements

The crystallinity of the spherical Si fabricated using conditions (b) and (c) is similar, as shown in Fig. 2. However, the solar cell performance of (b) and (c) is different. In order to
investigate the electrically active defects in the spherical Si solar cells, the EQE was measured. Figs. 6(a) and (b) show the EQE data for the solar cells based on the spheres grown by the B and C conditions, respectively. The EQE was measured for these solar cells with and without white light bias. The carriers generated by white light bias fill up recombination centers. Therefore, the minority carriers current increases and the quantum efficiency increases. The increase in the quantum efficiency with white light bias shown in Fig. 6(b) indicates the existence of recombination centers in the spherical Si. As shown in Fig. 6(c), the correspondence between quantum efficiency with and without white light bias indicates a decrease in recombination centers.

SIMS samples were prepared from spheres grown by the B and C conditions. Fig. 7 shows the oxygen and carbon depth profiles investigated by SIMS. It is seen that the oxygen and carbon concentrations decreased in spherical Si fabricated in Ar gas. From these results, a decrease in recombination centers can be attributed to a decrease in the oxygen and carbon concentrations in the Si spheres. Therefore, these impurities are the prime factor for the recombination centers. These results reveal that the Si sphere should be grown using the C condition.

Fig. 5. (a)–(c) The $J$–$V$ characteristics of spherical Si solar cells corresponding to the Si spheres grown by Table 1, A–C conditions, respectively.

Table 2
Characteristics of the spherical Si solar cells

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Effi. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>8.83</td>
<td>0.330</td>
<td>0.630</td>
<td>1.83</td>
</tr>
<tr>
<td>(b)</td>
<td>14.0</td>
<td>0.394</td>
<td>0.584</td>
<td>3.22</td>
</tr>
<tr>
<td>(c)</td>
<td>21.5</td>
<td>0.492</td>
<td>0.711</td>
<td>7.52</td>
</tr>
</tbody>
</table>
4. Conclusions

We have investigated the crystallinity, oxygen and carbon concentrations, as well as solar cell performance of spherical Si produced by a dropping method wherein the spherical Si was fabricated by the free fall of molten Si from a nozzle at the bottom of a crucible. Raising the temperature immediately under the nozzle by using heaters is effective in improving the crystallinity of the spherical Si, and changing the atmosphere to Ar gas from air in the dropping area is effective for decreasing oxygen and carbon concentrations.
in the spherical Si. The spherical Si solar cell performance improved because these impurities are the prime factors for recombination centers.

Acknowledgments

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References