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Crystal Growth Mechanism of Spherical Silicon Fabricated by Dropping Method

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1. Introduction

In today's photovoltaic industry, crystalline Si solar cells fabricated by Si wafers dominate solar cell market. Si wafers are made of Si ingots through the cutting and polishing processes where some parts of the ingot are wasted. Therefore, that prevents the further cost reduction of crystalline Si solar cells. In order to solve the problem, the electronic devices using a spherical Si, which is made by a method different from the conventional crystal growth method, are investigated [1,2]. We proposed novel fabrication method of spherical Si, i.e. a dropping [3]. Spherical Si sollar cells fabricated from the Si spheres are expected to be low cost cells in comparison with conventional Si solar cells, because Si spheres can be produced directly from molten Si without the cutting and polishing process.

Recently, some organizations investigated other fabrication method of spherical Si [4,5]. The crystal growth of spherical Si in containerless states with electromagnetic and electrostatic levitator was also reported [6]. However the crystal growth mechanism of spherical Si fabricated by dropping method is not investigated. Si spheres of 1 mm in diameter fabricated by this method are seedless crystal growth in rapid cooling condition. Therefore crystal growth model of silicon spheres remain unknown and the productivity of the high quality Si spheres is also problem. In this paper, the relationship between the surface morphology and the grain size is investigated. Moreover, we propose the crystal growth mechanism of spherical Si.

2. Experimental

Si spheres are produced by the dropping method from molten Si. Figure 1 shows the schematic illustration of spherical Si production apparatus. First, pieces of boron doped p-type Si are melted in a quartz crucible with carbon heaters. The small drops of Si are instilled from the nozzle at the bottom of the crucible by Ar gas pressure to alumina sheet in the collection area. The gas in dropping area is Ar gas and dropping distance is about 12.5 m. Therefore, dropping time of Si droplets is approximately 2 sec.. The droplets Si are solidified into spherical shape by surface tension. The surface morphology of spherical Si was observed by scanning electron microscopy (SEM). The crystallinity was investigated by the SEM observation of the spherical Si etched in 5% KOH solution at 70°C for 1 hour. The etching under this condition forms {111} pyramid to Si. In order to clarify the crystal growth mechanism, crystal Si of the various crystal size were observed by SEM.

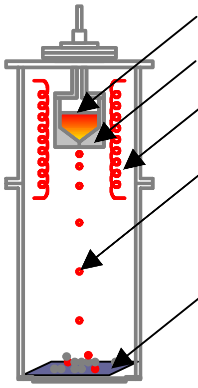

Fig. 1 Schematic image of the dropping method.

3. Result and Discussion

Characterization of silicon spheres

The Si spheres were classified into two categories by a surface morphology. Figure 2 shows the surface morphology of Si spheres of 1 mm in diameter with (a) rough and (b) smooth surface. As shown in Fig. 2 (a), the whole surface of the spherical Si is rough and has many lines. The lines are related to grain boundaries. On the other hand, In Fig. 2 (b), the lines and the rough surface are partly observed, but the most of the surface is smooth. It is expected that the grains grew large.

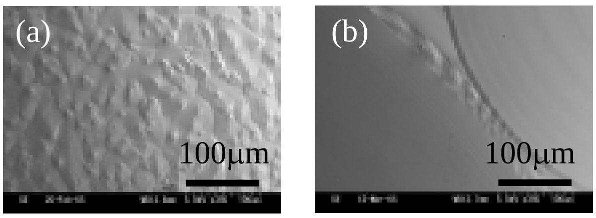

Fig.2 The surface morphology of Si spheres of 1 mm in diameter with (a) rough and (b) smooth surface.

In order to confirm the grain size of Si spheres classified into two categories, the cross section images of the Si spheres etched in KOH solutions were observed by SEM as shown in Fig. 3 (a) with rough surface and (b) with smooth surface. In Fig. 3(a), the {111} pyramids having various directions were observed. Since the {111} pyramid depends on the crystalline orientation of each grain, this observation indicates that the Si sphere is multicrystalline Si. Moreover, it is possible to observe the grain size of the Si sphere. The grain size from the SEM image is 50-100 μm. In Fig. 3 (b), the same direction pyramids were observed at large area on cross section of the Si sphere. The sphere includes over 500 μm grain size. These results indicate the relationship between the surface morphology and the grain size. Moreover, it is confirmed that the smooth surface of Si spheres is desirable to obtain high performance solar cells.

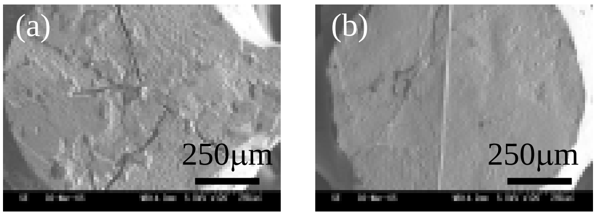

Fig. 3 The cross section images of the Si spheres with (a) rough and (b) smooth surface after 1hour KOH etching.

Crystal growth mechanism

To fabricate Si sphere consisted of large grains, we need to study the crystal growth mechanism of the Si sphere. In-situ observation is effective analysis for crystal growth mechanism, however it is difficult to adapt to the dropping method. In order to investigate the growth of Si spheres, Si crystals on the alumina sheet in the collection area were observed. Some Si crystals, which are not spherical shapes stick to the alumina sheet. These crystals are larger than Si spheres of 1 mm in diameter. The diameter of the Si droplet is expected to be over 1 mm because the Si sample size is related to the size of Si droplet, which influences the ease with solidification. The molten Si sticks to the alumina sheet because the large Si droplet takes longer time to solidify than small one. Thus the Si samples of 4 mm, 2 mm and 1 mm in diameter correspond to the initial, moderate and final stage of crystal growth, respectively. The large Si crystals are important samples to investigate the crystal growth mechanism of the Si sphere.

Figure 4 (a) shows the SEM image of the Si crystal of approximately 4 mm in diameter. The Si crystal stick to the alumina sheet. It is confirmed that the disk state Si crystal including dendrite grow. XRD pole figure measurement and KOH etching of the disk state Si crystal showed that the disk was (111) plane. The results indicate that the initial stage of the crystal growth of the Si sphere is formed the disk of (111) plane of Si crystal.

Figure 4 (b) shows the SEM image of the Si crystal of approximately 2 mm in diameter stick to the alumina sheet. This crystal has some planar Si crystals at the contour of sphere and a cavity. The cavity is generated by flowing out of the partly molten Si to the alumina sheet before the crystallization. It is clear that the grains at the contour of the Si sphere grew large crystal and the surface is smooth at the contour of the Si sphere.

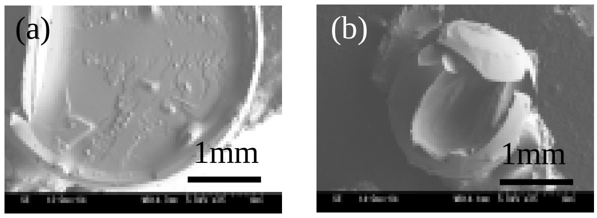

Fig. 4 SEM observation of the Si crystal of approximately (a) 4 mm and (b) 2 mm in diameter.

According to these SEM observations of the Si crystals, we propose the crystal growth mechanism of spheres which consists of large grains. First, the disk of (111) plane Si crystal is grown in the droplet Si. Second, some disks of (111) plane Si crystals grow to the contour of the Si sphere. Finally, the inside the Si droplet is crystallized. Growing the disk of (111) plane is similar to the result of the crystal growth of the Si droplet in containerless states with electromagnetic levitators [6]. Therefore, in case of Si spheres of 1 mm in diameter fabricated by the seedless crystal growth in rapid cooling condition, the disk of (111) plane Si crystal is needed to obtain the Si sphere consisted of large grains.

4. Conclusions

We investigated the classification and the crystal growth mechanism of spherical Si fabricated by the dropping method. The Si spheres were classified into two categories by the surface morphology relating to the grain size. Moreover, we revealed that the smooth surface of Si spheres is desirable to obtain high performance solar cells. In order to investigate the crystal growth mechanism of the spheres, Si samples with various crystal sizes were observed. We proposed the crystal growth mechanism of the Si sphere which consists of large grains. The result suggests that the initial stage of crystal growth of Si sphere with large grains is formed by the disk of (111) plane.

Acknowledgements

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