Microstructure analysis of spherical silicon solar cells coated with anti-reflection films

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Abstract. Microstructures of spherical silicon solar cells were investigated by transmission electron microscopy and X-ray diffraction. Optical absorption and photoluminescence of the solar cells were also measured by UV-visible and fluorescence spectroscopy. F-doped SnO₂ anti-reflection coating layers were investigated by XRD, and the nanostructures and grain sizes were determined. The present work indicated a guideline for spherical silicon solar cells with higher efficiencies.

1. Introduction
Solar cells are expected to be clean energy devices instead of fossil fuels in the view point of no emission of greenhouse gas. However, production cost of silicon solar cells is high, and the cost reduction of the silicon solar cells is one of the most important issues. From the view point of the cost reduction, spherical silicon solar cells are a promising technology [1-3]. Silicon spheres with a diameter of ~1.0 mm are used as p-n junction solar cells, and consumption of silicon is lower and more flexible compared to the conventional silicon solar cells. However, the conversion efficiency of the spherical silicon solar cells should be improved further compared to the crystalline silicon solar cells.

To improve the conversion efficiency, various properties are mandatory as follows; high quality silicon balls, optical confinement structures, inactivation of defects by passivation, low resistances of conductive anti-reflection coating, and effective reflecting mirror structure. The purpose of the present work is to investigate microstructures of spherical silicon with F-doped SnO₂ for anti-reflection coating layers. Combination of microstructure analysis and optical property characterization of the spherical silicon with anti-reflection films will give us a guide line for improvement of the efficiency.

2. Experimental
The spherical silicon used in this experiment was supplied by Clean Venture 21 Co., Ltd [4,5], and the surface of the spherical silicon was coated by SnO₂ as anti-reflective coating (ARC) with a film thickness of ~100 nm [6]. The microstructure of SnO₂:F film was investigated by X-ray diffraction (XRD, Philips X’Pert-MPD System). Optical absorption of the solar cells was also measured by UV-
visible spectroscopy (Hitachi U-4100). Photoluminescence measurements were performed using (Jasco FP-6600) at room temperature employing a Xenon lump.

3. Result and discussion

X-ray diffraction pattern of spherical silicon coated by SnO$_2$:F is shown in Fig. 1(a). Diffraction peaks corresponding to SnO$_2$ crystal are observed [7-10]. The SnO$_2$:F were found to be a cassiterite type with a tetragonal rutile structure as shown in Fig. 1(b), and lattice parameters were $a = 0.4681$ nm and $c = 0.3156$ nm in the present work, whereas the reported values of SnO$_2$ lattice parameters are $a = 0.4737$ nm and $c = 0.3185$ nm [11], as summarized in Table 1. The differences of lattice parameters of SnO$_2$:F are 1.2 % and 0.9 % for $a$ and $c$-axes, respectively. The difference between the present values and reported values would be due to the fluorine ions (F$^-$) and crystal distortion. In the SnO$_2$:F, oxygen ions (O$^{2-}$) were estimated to be substituted by the fluorine ions (F$^-$) as following reasons [4]: similar ionic size (F$^-$: 0.136 nm, O$^{2-}$: 0.140 nm), the energy of the Sn-F bond (~26.75 D$_0$/kJmol$^{-1}$) is comparable to that of the Sn-O bond (~31.05 D$_0$/kJmol$^{-1}$), and Coulomb forces that bind the lattice together are reduced, since the charge on the F$^-$ is only half of the charge on the O$^{2-}$. Here, D$_0$ is the unit of bond-dissociation energy. The particle size of the SnO$_2$:F was estimated using Scherrer’s formula: $D = 0.9/\beta \cos \theta$, where $\lambda$, $\beta$, and $\theta$ represent the wavelength of X-ray source, the full width at half maximum, and the Bragg angle, respectively. The crystallite size of SnO$_2$:F was determined to be 57.5 nm. Since the grain boundaries would disturb the light incidence and carrier transport by scattering the light and electronic carrier, single crystal or crystals with larger grain size would be desirable. Although it seems to be difficult to deposit thin films with a single crystal on the spherical Si surface, further improvement would be expected by optimizing deposition and annealing conditions.

![Figure 1](image1.png)

**Figure 1.** (a) XRD pattern of SnO$_2$ doped with F. (b) Atomic structure model of SnO$_2$.

| Table 1 Lattice parameters of SnO$_2$:F and SnO$_2$. |
|-----------------|-----------------|-----------------|
|                | SnO$_2$         | SnO$_2$:F       | Difference (%) |
| $a$ (nm)        | 0.4737          | 0.4681          | -1.182         |
| $c$ (nm)        | 0.3185          | 0.3156          | -0.911         |
Figure 2 shows measured optical absorption of the spherical silicon with and without ARC. Spherical silicon with ARC shows higher absorption than that of without ARC in the range from 400 nm to 1100 nm, especially around ~600 nm, which indicates the effectiveness of the ARC.

Figure 3 shows photoluminescence (PL) spectrum of spherical silicon with ARC and without ARC. The PL emission of the spherical silicon without ARC is higher than that of spherical silicon with ARC in all range from 400 nm to 900 nm. PL emission observed around 3.3 eV would be due to the impurities contained in silicon, which might contribute formation of exitons that increase efficiency. The spherical silicon coated with SnO$_2$ shows the decrease of the PL emission, which indicated the confinement of light by the ARC. On the other hand, intensity of the PL emission from the spherical silicon without ARC is higher compared to that of spherical silicon with ARC, which also indicated the effectiveness of ARC.

Figure 2. Optical absorption of spherical silicon with ARC and without ARC.

Figure 3. Photoluminescence spectra of spherical silicon with ARC and without ARC.
The solar cell with ARC provided power convergent efficiency ($\eta$) of 11.5 $\%$, a fill factor (FF) of 0.697, $J_{sc}$ of 28.1 mA/cm$^2$, $V_{oc}$ of 0.584 V. About 20 $\%$ increase of efficiency was observed by introducing the ARC. Schematic structure and energy level diagram of spherical silicon solar cell is shown in Figure 4(a) and 4(b), respectively. The spherical Si solar cell with a reflector cup is completed by mounting of the spherical Si on a reflector cup consisting of an Ag-electroplated Al substrate. Electronic carriers of electrons and holes are separated at the p-n junction by light irradiation. Separated holes could be transferred from the valence band of p-Si to FTO of antireflective coating, and separated electrons could be transferred from the conduction band of n-Si to the Al electrode. As shown in Fig. 4(a), charge separation is strongly dependent of incident angle of light. To improve the efficiency, microstructure control of antireflective coating by annealing and deposition conditions would be important. In addition, there would be energy barrier at the semiconductor/metal interfaces as indicated by band bending in Fig. 4(b) [12], which results in contact resistance. Heavy doping or control of interfacial microstructure by annealing would reduce the contact resistance.

Figure 4. (a) Schematic structure and (b) energy level diagram of spherical silicon solar cell.

Figure 5. Mechanism of anti-reflection in the present spherical silicon with ARC.
Figure 5 shows a mechanism of ARC. The principle of the ARC is based on the phase changes. Destructive interference between the two reflected lights occurs, cancelling both lights before they exit the surface. The transmission properties of the ARC are dependent on the wavelength of light, the substrate’s index of refraction, the index of refraction of the coating, the thickness of the coating, and the angle of the incident light. Therefore, the best ARC condition should be investigated further to reduce the reflected light. According to the previous report [13], the best condition of the thickness of the coating and the index of refraction of the coating are 83 nm and 2.0 respectively.

It should be pointed out that the optimization of the thickness of ARC, and the analysis of the impurities contained in spherical silicon are considered to be important factors for higher efficiencies of the spherical silicon solar cell, which should be investigated further.

4. Conclusions

Microstructures of the spherical silicon solar cells with anti-reflection films were investigated by using XRD, which indicated lattice parameters of $a = 0.4681$ nm and $c = 0.3156$ nm, and crystalline sizes of $\text{SnO}_2$:F was determined to be 57.5 nm. Spherical silicon with ARC showed higher optical absorption compared to that of spherical silicon without ARC. Fluorescence measurement indicated that the impurities would be contained at the center of spherical silicon, and the incident and luminescent light is confined by the ARC. The optimization of the thickness of ARC, and the analysis of the impurities contained in spherical silicon are required to improve the efficiency of the spherical silicon solar cells.

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