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Microstructure Analysis and Properties of Anti-Reflection Thin Films for Spherical Silicon Solar Cells

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ABSTRACT

Structure and properties of anti-reflection thin films of spherical silicon solar cells were investigated and discussed. Conversion efficiencies of spherical Si solar cells coated with F-doped SnO_2 anti-reflection films were improved by annealing. Optical absorption and fluorescence of the solar cells increased after annealing. Lattice constants of F-doped SnO_2 anti-reflection layers, which were investigated by X-ray diffraction, decreased after annealing. A mechanism of atomic diffusion of F in SnO_2 was discussed. The present work indicated a guideline for spherical silicon solar cells with higher efficiencies.

Keywords: Solar Cells; Spherical Silicon; Anti-Reflection Film; FTO; SnO_2

1. Introduction

Solar cells are expected to be clean energy devices instead of fossil fuels. They are clean energy devices which discharge no greenhouse gas. However, reduction of the cost of solar cells is an important issue. Spherical silicon (Si) solar cells [1-3] are the technology that can reduce the consumption of Si compared with conventional crystal Si solar cells [4-6]. Flexible solar cells are also manufactured by silicon spheres with a diameter of ~1 mm with p-n junction [7]. To Improve the efficiencies of the Si solar cells [8], formation of a texture structure on Si surface [9-11], optimization of structures of reflectors [12-14], reduction in resistance and high transmission of anti-reflection films [15-17] are also needed.

The purpose of the present work is to investigate spherical Si solar cells with anti-reflection (AR) SnO_2:F thin films.

2. Experimental

The spherical silicon used in the present experiment was supplied by Clean Venture 21 Co., Ltd. [18,19]. The surface is covered with anti-reflection films of SnO_2:F. The SnO_2:F anti-reflection films were prepared by spraying hydrolyzed SnF_4, and annealed at 650˚C for 4 h to form the SnO_2:F crystal structure [20-23]. **Figure 1** shows a schematic illustration of spherical Si solar cell. Reflectors gather lights to improve conversion efficiency. Optical absorption of the solar cells was measured by photo spectroscopy (Jasco V-670). Fluorescence spectra of the samples were measured by fluorescence spectrophotometer (Hitachi F-4500), and excitation wavelength was 250 nm. The microstructures of SnO_2:F films were investigated by X-ray diffraction (XRD, Philips X'Pert-MPD System). Thermodynamical calculation of reactions of SnO_2 was performed by HSC Chemistry 5.

3. Results and Discussions

Figure 2(a) shows measured optical absorption of spherical Si before and after annealing. The spherical Si absorbs the light in the range of 300 to 1200 nm. The optical absorption of the spherical Si increased after annealing at 650˚C. **Figure 2(b)** shows optical absorption spectra of SnO_2:F, which was an enlarged spectrum of **Figure 2(a)**. Since the absorption range was shifted to lower energy, a structural change would occur after annealing. The refractive index of anti-reflection SnO_2:F films changed from 1.8 to 1.9 after annealing. Refractive indices of the substrate and anti-reflection films would influence reflectance and optical absorption. Since refractive indices are different for wavelengths of light, the effect of the reflectance reduction depends on the wave-

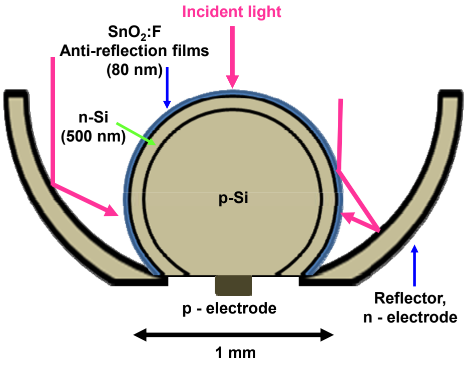

Figure 1. Schematic illustration of spherical Si solar cell.

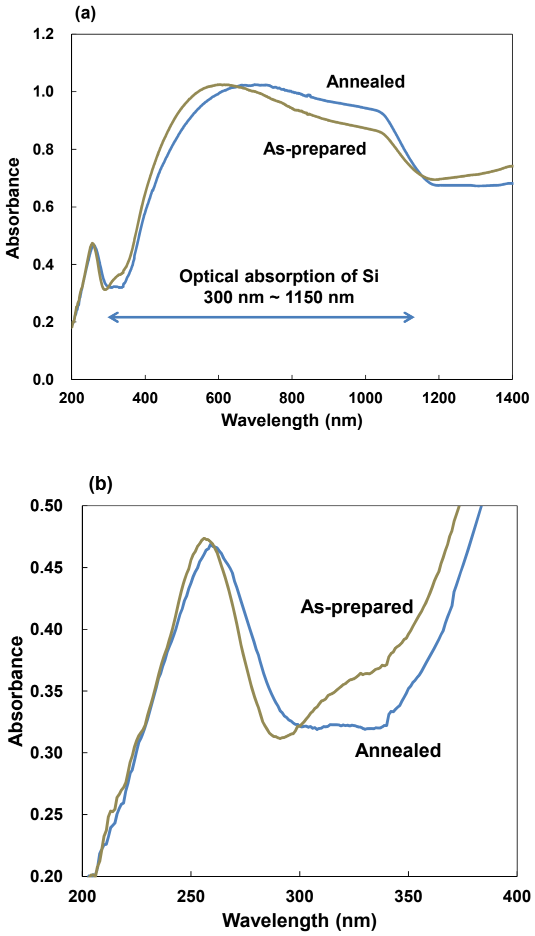

Figure 2. Optical absorption of (a) spherical Si with AR films. (b) Enlarged spectra of (a) for SnO_2:F spectra.

length.

Figure 3 shows fluorescence spectra of spherical Si before and after annealing. The energy gap of SnO_2 is 3.8 eV, and fluorescence peaks of SnO_2 are observed at ~350 nm. Fluorescence spectra due to impurities in Si might also be contained in the spectra [24]. The fluorescence of SnO_2 increased after annealing. Therefore, the crystallinity would be improved by the annealing.

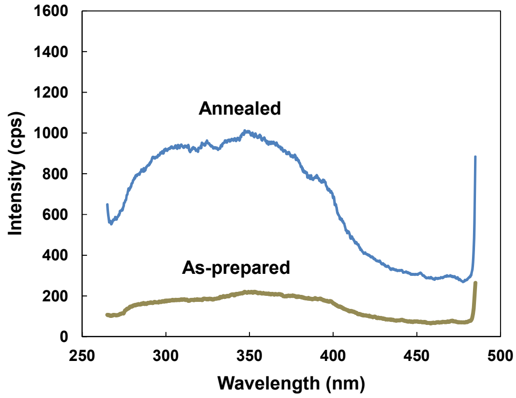

Figure 3. Fluorescence spectra of spherical Si with AR films.

Figure 4 show measured X-ray diffraction patterns of spherical silicon before and after annealing. Miller indices of Si and SnO_2 are indicated in **Figure 4(a)** [25,26]. **Figure 4(b)** shows that the 110 peak of SnO_2 shifted to higher diffraction angle after annealing.

The SnO_2 grain sizes calculated from the XRD measurements are summarized in **Table 1** and **Figure 5**. The grain sizes D were calculated using Scherrer's formula.

$$D = 0.9\lambda / B\cos\theta \tag{1}$$

where λ, B, and θ represent the wavelength of X-ray source, the full width at half maximum, and the Bragg angle, respectively.

Lattice constants of a-axis and c-axis for SnO_2 calculated from the XRD measurements are shown in **Figure 6**. The measured grain sizes and lattice constants of SnO_2 before and after annealing are summarized in **Table 1**.

SnO_2 crystals have high electrical resistance, and doped F and oxygen vacancies are electrical carriers for SnO_2:F [27-30]. To consider the change of the oxygen vacancy by annealing, thermodynamical calculation was carried out as shown in **Figure 7**. Gibbs free energy change (ΔG) for SnO_2 oxidation is negative at 650˚C in the atmosphere, which suggests oxygen vacancies in SnO_2 decrease after annealing, and F atoms would occupy oxygen sites.

If oxygen vacancy decreases, an increase of lattice constants may be expected, but they decreased as indicated in **Table 1**. Therefore, it is considered that reduction of lattice constants occurred since interstitial F atoms were removed or substituted for the oxygen sites. Schematic illustration of structural change of SnO_2:F by annealing is shown in **Figure 8**.

The performances of the present solar cells are summarized in **Table 2**. The performance of the spherical Si solar cells was improved after annealing. If some atoms exist at interstitial sites, electronic resistance increases. Although SnO_2 has no optical absorption on the absorption wavelength of Si, the contained impurities in SnO_2

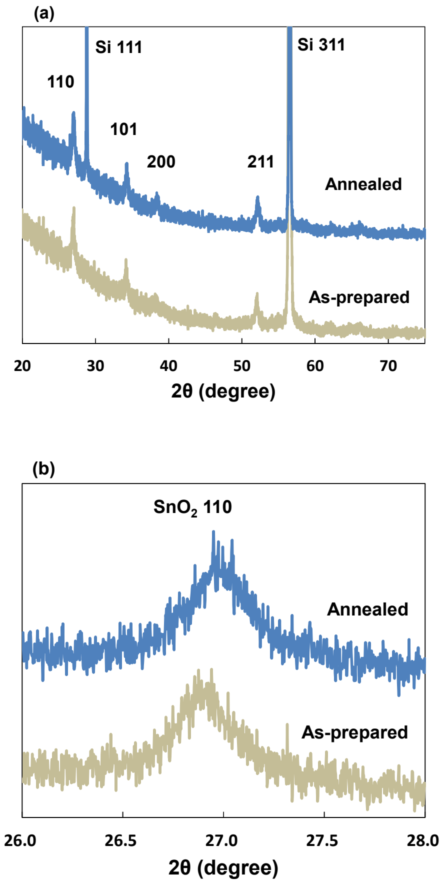

Figure 4. (a) XRD patterns of spherical Si with AR films. (b) Enlarged patterns of (a) for SnO_2:F 110.

Table 1. Grain sizes and lattice constants of SnO_2:F.

Samples	Grain size (nm)	Lattice constant (nm)	
		a-axis	c-axis
As-prepared	41.0	0.4713	0.3182
Annealed	56.4	0.4695	0.3170
SnO_2	–	0.4737	0.3185

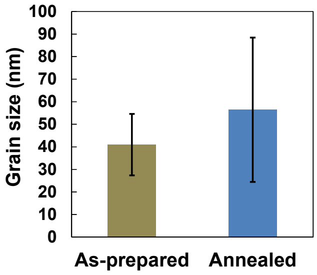

Figure 5. Grain sizes of SnO_2:F.

would be a cause of light dispersion and absorption [31]. Reduction of interstitial atoms caused decreases electronic resistance, and increasing the optical absorption of Si, and improve the conversion efficiency of the solar cells. By F-doping to anti-reflection films, carriers increase and resistance decreases. Simultaneously, transparency decreases since carrier elements absorb light and cause light dispersion. Reduction of the interstitial F atoms also caused increase of the optical absorption of Si. Reduction of the lattice constants would be due to the decrease of F which exists at interstitial sites in SnO_2 cause electronic resistance. The present results indicated that the microstructures and properties of AR films depended on the annealing process, and that optimization of the formation process of AR films are mandatory for further improvement of the performance.

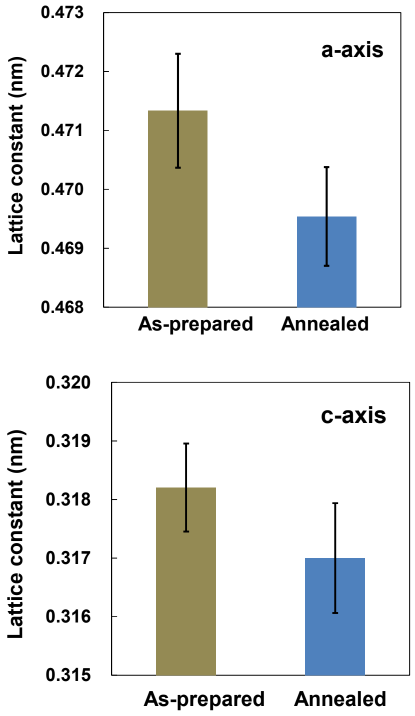

Figure 6. Lattice constants of SnO_2:F.

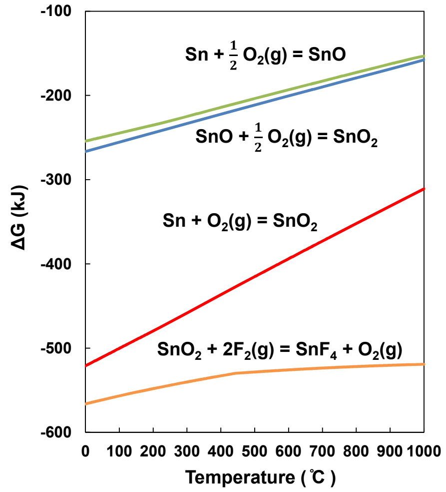

Figure 7. Thermodynamical calculation of SnO_2.

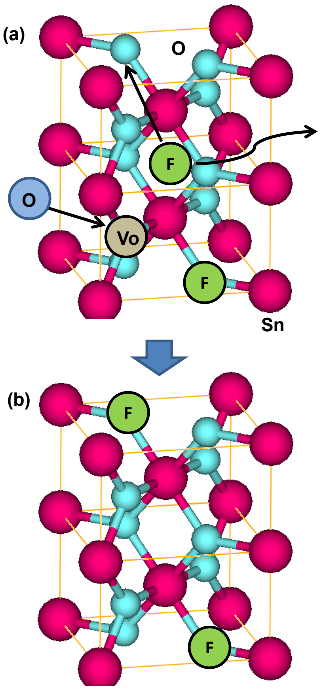

Figure 8. Schematic illustration of atomic transfer (a) during and (b) after annealing.

Table 2. Parameters of spherical silicon solar cells.

Samples	J_{sc} (mA·cm^{-2})	V_{oc} (V)	FF	η (%)	*Rs* (Ω)
As-prepared	24.9	0.511	0.542	6.90	89.0
Annealed	26.3	0.593	0.717	11.2	59.3

4. Conclusion

The efficiency of the spherical Si solar cells with AR F-doped SnO_2 films was improved after annealing at 650˚C for 4 h. After annealing, the optical absorption of spherical Si increased and resistance decreased. Since the lattice constants of SnO_2:F decreased after annealing, the interstitial F atoms would be reduced. The reduction of resistance and the improvement of optical absorption would be due to the reduction of the interstitial F atoms, and it is possible to adjust F doping for the SnO_2 by annealing.

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