ANTIREFLECTION COARTING OF
γ-ALUMINA WITH GRADIENT-REFRACTIVE INDEX STRUCTURE

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1. Introduction

Light receiving elements including solar cells generally have laminated structure. Inevitable reflection takes place at the interface where the refractive index changes abruptly. Therefore, in such devices as solar cells, suppression of the optical loss is one of the necessary factors for improving power generation efficiency. In our previous investigation, Ishiguro et al., (2009) found that metallic aluminum film can be changed to transparent boehmite film by hydrothermal (HT-) treatment in ultrapure water. Transmittance of HT-treated film was higher than that of glass substrate itself. One of the reasons was thought to be suppression of reflection due to the gradient-refractive index structure. However, HT-treated film (boehmite film) is poor chemical stability and mechanical strength. In this study, boehmite films were heat-treated in the air in order to stabilize and keep the gradient-refractive index structure at the same time.

2. Experimental

Metallic Al films were prepared on Corning #1737 glass substrate by rf-sputtering method (13.56 MHz, 200 W). HT-treatment was induced at 368 K for 20 min in stirred ultrapure water (resistivity 18.2 MΩ·cm). Then, reformed boehmite films were heat treated for one hour in the air at 573, 673, 773, and 873 K, respectively. Optical properties were measured using an ultraviolet-visible-near infrared spectrometer (UV-3100PC, Shimazu Co.) in a wavelength range of 0.24-2.60 μm. In order to measure both total transmittance (T_{tot}) and total reflectance (R_{tot}), an integrating sphere with a diameter of 60 mm was used. Surface morphologies were observed by using a field-emission scanning electron microscope (FE-SEM) (S-4200, Hitachi High-Technologies Co.). Transmission electron microscopy (TEM) observation was performed by using JEM2000FX (JEOL Ltd.). Quadrupole mass spectrometer (QMS) (BGM101, ULVAC Inc.) was used to detect outgassing from a HT-treated Al film in a vacuum chamber, which was evacuated by a turbo-molecular pump. The temperature of the specimen was increased up to 873 K with a rate of 1.67 K/min. Fourier transform infrared (FT-IR) spectroscopy was also performed by using FT/IR-6200 spectrometer (JASCO Inc.). The specimen was set in an evacuated specimen cell and elevated temperature with a rate of 1.67 K/min.

3. Results and Discussion

3.1. Optical property

Change of optical properties of both T_{tot} and R_{tot} are shown in Fig. 1 and Fig. 2 respectively. The opaque Al film becomes transparent. T_{tot} of as boiled specimen increases and exceeds that of glass substrate. After heat treatment T_{tot} is increased with temperature up to 773 K at around wavelength of 0.50μm, which corresponds to the maximum position of solar spectrum. And then it is decreased at 873 K. On the other hand, T_{tot} decreases with temperature at around 0.65 μm. Because one of the reasons of these wavelength dependences of T_{tot} is thought to be interference of thin film, T_{tot} could be optimized by controlling first Al film thickness. Change in R_{tot} as shown in Fig. 2 compensate the change of T_{tot}. Degradation of optical transparent property due to the heat treatment is not so serious.

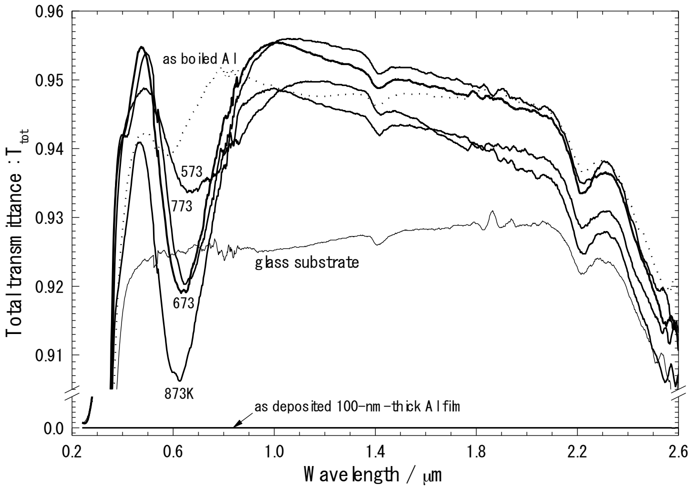

Figure 1: Annealing temperature dependence of total transmittance (T_{tot}) of specimens. Spectra of as prepared Al film, as boiled Al film (boehmite) and glass substrate itself are also shown for comparison.

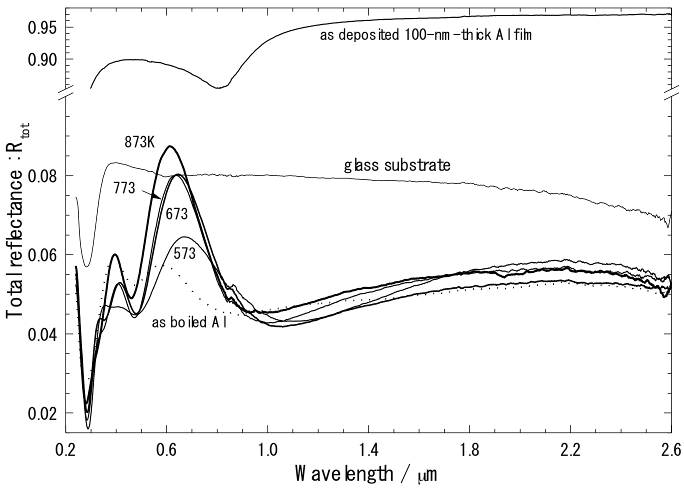

Figure 2: Annealing temperature dependence of total reflectance (R_{tot}) of specimens. Spectra of as prepared Al film, as boiled Al film (boehmite) and glass substrate itself are also shown for comparison.

3.2. Crystal structure and surface morphology

Figure 3 shows annealing temperature variation in electron diffraction pattern and corresponding bright field image. As boiled specimen (Fig. 3(a)) and annealed specimen at 573 K (Fig. 3(b)) are boehmite (orthorhombic, a_0=0.36936 nm, b_0=1.2214 nm, c_0=0.28679 nm) (Christoph, et al. (1979).). Diffraction rings change into rather spotty. This means crystal grain growth of boehmite takes place by annealing at 573 K. The specimens annealed at equal to or higher than 673 K (Figs. 3(c), (d), and (e)) are γ- alumina (cubic spinel structure, a_0=0.790 nm) (Zhou and Snyder (1991).). When the boehmite (Fig. 3(b)) transforms to γ- alumina (Fig. 3(c)), distribution of boehmite rings becomes broad and continuous. This means the crystal refinement takes place during reforming. And then, crystal grain growth of γ-alumina takes place again with increasing temperature. Fiber-like contrast with a width about 5 nm can be seen in all of the bright field images.

Figure 4 shows annealing temperature variation in FE-SEM image of surface morphology. As deposited metallic Al film shows relatively-smooth surface (Fig. 4(a)). After boiling in water, characteristic surface morphology like a surface of desert rose, i.e., intersecting fine plates each other appears (Fig. 4(b)). This characteristic structure is thought to be the gradient-refractive index structure (Ishiguro et al. 2002, 2005, 2006; Hori et al. 2010; Qiu et al. 2010). The width of fine plate is comparable order to the fiber-like contrast in bright field images in Fig. 3. This surface morphology does not change drastically by annealing. This is one of the reasons of less degradation in the optical property as mentioned in Figs. 1 and 2.

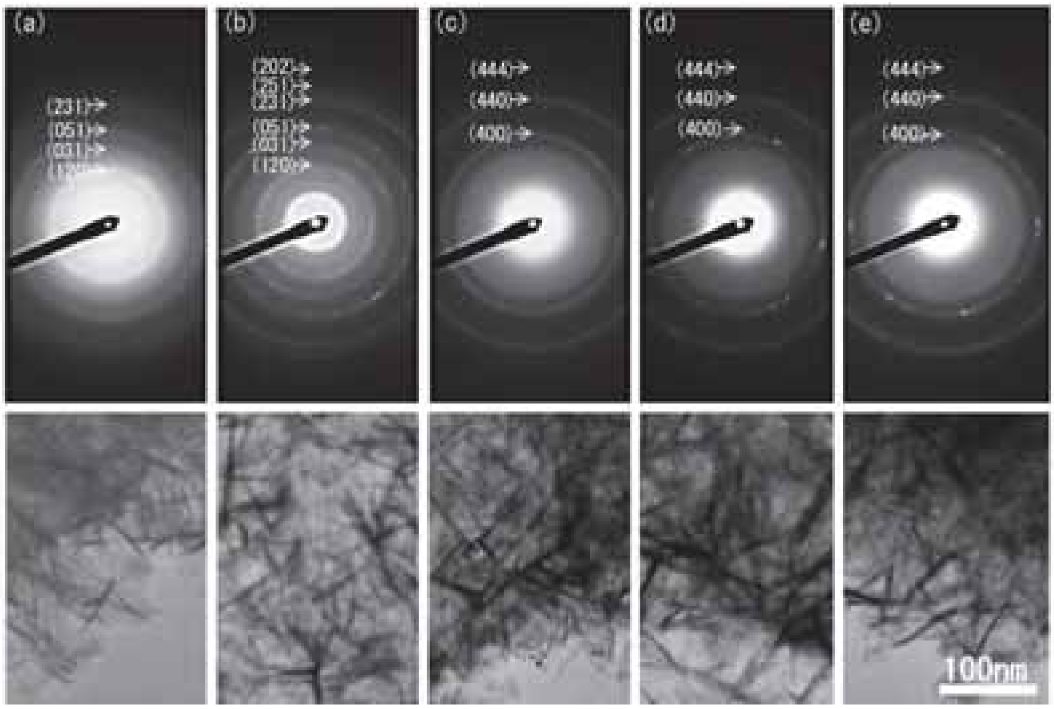

Figure 3: Annealing temperature dependence of selected area diffraction pattern and corresponding bright field image.
(a) as boiled Al film, annealed at (b) 573K, (c) 673K, (d) 773K, and (e) 873K

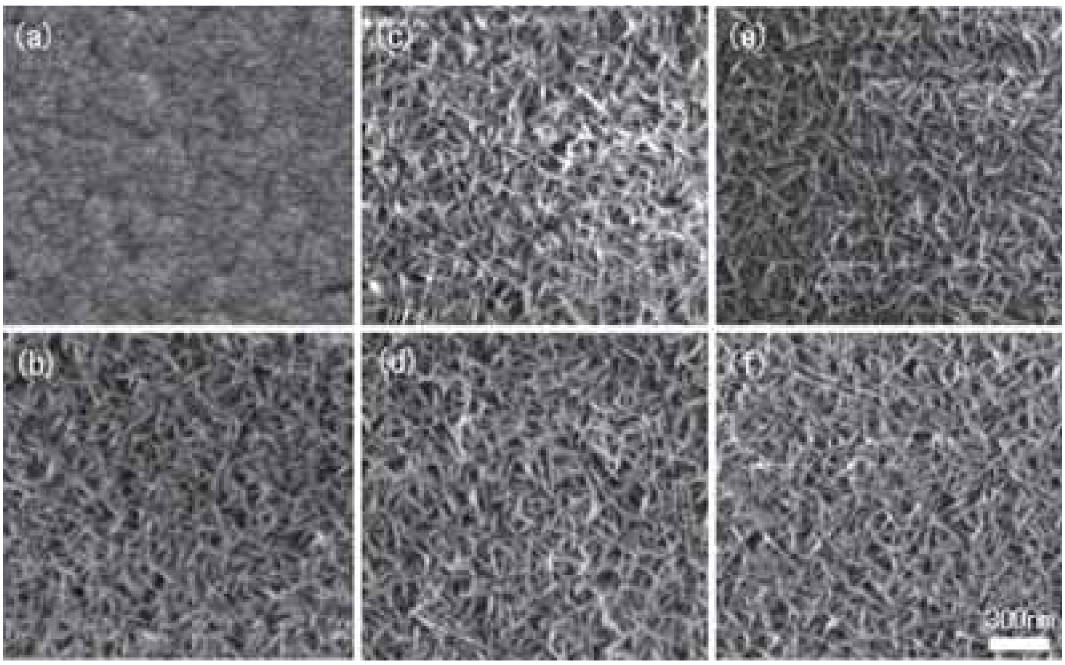

Figure 4: Annealing temperature dependence of surface FE-SEM image.
(a) as deposited Al film, (b) as boiled Al film, annealed at (c) 573K, (d) 673K, (e) 773K, and (f) 873K

3.3. Dehydration process

In order to clarify the dehydration process, heating temperature dependence of partial gas pressure emitted from the HT-treated Al film was detected continuously as shown in Fig. 5. Because of cracking in QMS, several mass numbers relating to the water molecule are detected. Almost all of partial pressures rise up at around 430 K. This is thought to be a critical temperature from which dehydration from boehmite begins strongly. At a temperature of 573 K, which is corresponding TEM observation of Fig. 3(b), outgassing still continues. At 673 K, outgassing of water has gotten over a peak at around 500-550 K. Then the film structure changes to γ-alumina structure (Fig. 3(c)). After that partial pressure turns to increase gradually via plateau. In this stage, γ-alumina grain growth takes place (Figs. 3(c)-(e)).

Figure 6 shows change of FT-IR spectrum of specimen with increasing temperature. Although the cell holding specimen is continuously evacuating, all spectra show characteristic absorptions at around 1300-2000 cm^{-1} and 3500-4000 cm^{-1}. These are due to water vapor generated by dehydration of the specimen. In the spectrum at 283 K, three absorption peaks at around 3374, 3099, and 1072 cm^{-1} are identified to be Al-O-H asymmetric stretching, symmetric stretching, and symmetric bending respectively (Herzberg 1945; and Priya 1997). Strength of these peaks become weakened with temperature and then disappears at 673 K. This change is consistent with the change of partial pressure relating to water molecule.

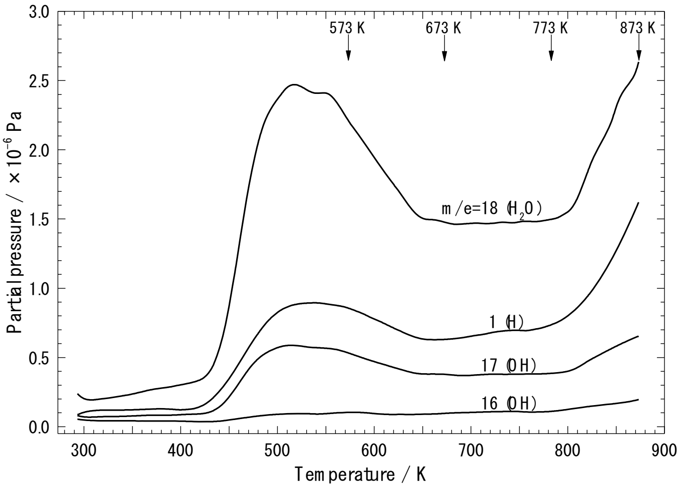

Figure 5: Heating temperature dependence of partial gas pressure emitted from the HT-treated Al film.

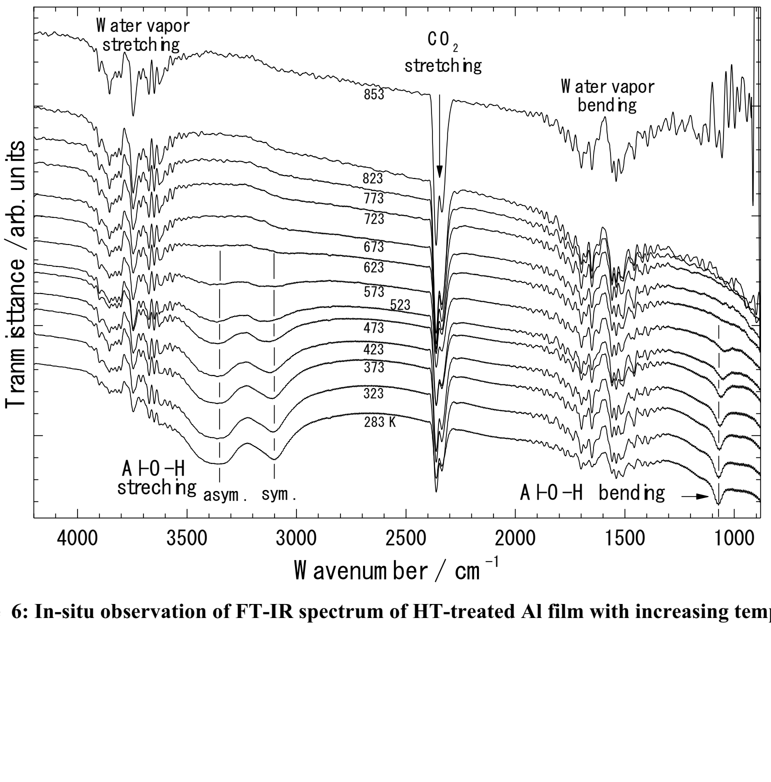

Figure 6: In-situ observation of FT-IR spectrum of HT-treated Al film with increasing temperature.

In conclusion, boehmite films could be transformed into γ-alumina having better stability than boehmite (HT-treated Al film) by heat treatment in the air. In addition, surface roughness or the gradient-refractive index structure remained after heat treatment. The γ-alumina film on a substrate showed the same level of transmittance of boehmite film on the glass substrate. Therefore it can be mentioned that the heat treated boehmite films are useful for anti-reflective coating. Additionally it would be mentioned that in-situ QMS method and in-situ FT-IR method were useful method to clarify the dehydration process continuously.

4. References

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Acknowledgments

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