Effects of heat treatment on fluorine-doped tin oxide anti-reflection films coated on silicon spheres

Yasuhiro SHIRAHATA, Takeo OKU†, Youichi KANAMORI† and Mikio MUROZONO†

Department of Materials Science, The University of Shiga Prefecture, Hikone, Shiga 522-8533, Japan
†Clean Venture 21 Corporation, 38 Ishihara Domo-Ushirocho, Kishoin, Minami-ku, Kyoto 601-8355, Japan

Fluorine-doped tin oxide (SnO\textsubscript{2}:F\textsubscript{y}) anti-reflection films coated on the surface of silicon spheres were investigated to clarify the effects of heat treatment on the microstructure and optical properties of the SnO\textsubscript{2}:F\textsubscript{y} films. The lattice constants, crystallite size, and bandgap of the SnO\textsubscript{2}:F\textsubscript{y} films depended on both heat treatment temperature and time. Fluorescence spectra of the SnO\textsubscript{2}:F\textsubscript{y} films showed a broad luminescence peak associated with point defects in the films. These results were attributed to the dependence of the O and F contents in the SnO\textsubscript{2}:F\textsubscript{y} crystals on heat treatment conditions.

Key-words: Tin oxide, Fluorine, Annealing, Spherical silicon

1. Introduction

Solar cells have attracted attention over the years because photovoltaic devices are major players in energy conversion technology.\textsuperscript{9)} However, the rapid growth of photovoltaic technology and the photovoltaic market will lead to a shortage and price rise of solar cell materials.\textsuperscript{2) Lowering the cost of solar cells is also a crucial issue for further development of photovoltaics. Crystalline silicon (Si) solar cells are currently the most popular type of solar cell, and have been dominating the photovoltaic market.\textsuperscript{3)} Spherical Si is a promising candidate as a material for low-cost solar cells that require less Si than crystalline Si-based ones. Spherical Si solar cells consist of arrays of many tiny Si spheres of \textasciitilde{1} nm in diameter, and a p-n junction. Anticipated advantages of spherical Si solar cells include flexibility and scalability. To date, the performance of spherical Si solar cells has been improved by production of high-quality Si spheres,\textsuperscript{19)–22) formation of textured surface structure,\textsuperscript{23) deactivation of defects by passivation,\textsuperscript{24) optimization of the concentrator module and reflector cup,\textsuperscript{25) and coating with anti-reflection (AR) films.\textsuperscript{12),13),18)–22)}}

The structural, electrical, and optical properties of AR films such as tin oxide (SnO\textsubscript{2}), zinc oxide, and indium tin oxide have been investigated thoroughly. In particular, SnO\textsubscript{2} is attractive for AR films because it has a rutile-type crystal structure with a tetragonal system, and is an n-type semiconductor. SnO\textsubscript{2} films have been prepared by many techniques, such as radio-frequency magnetron sputtering,\textsuperscript{25) chemical vapor deposition,\textsuperscript{26) the sol–gel method,\textsuperscript{27) and spray pyrolysis.\textsuperscript{28,29) The properties of SnO\textsubscript{2} films can be influenced by doping. Among various possible dopants such as antimony\textsuperscript{30) and fluorine (F),\textsuperscript{24,25,28) F is probably the most effective for SnO\textsubscript{2} because such films show very high transparency and good conductivity,\textsuperscript{29) and the ionic radius of F (133 pm) is close to that of O (140 pm).\textsuperscript{29) To develop F-doped SnO\textsubscript{2} films for use as AR films in solar cells, low-cost and damage-free preparation processes are required. Spray pyrolysis is an attractive prospect for this role. In fact, we prepared F-doped SnO\textsubscript{2} (SnO\textsubscript{2}:F\textsubscript{y}) films on Si spheres using a spray-pyrolysis method, which gave uniform quality.\textsuperscript{12,13,20–22) However, there are still few reports on F-doped SnO\textsubscript{2} films coated on Si spheres.

The purpose of the present work is to investigate the effects of heat treatment on SnO\textsubscript{2}:F\textsubscript{y} films coated on Si spheres. The microstructures of SnO\textsubscript{2}:F\textsubscript{y} films fabricated under different heat treatment conditions are examined using X-ray diffraction (XRD) and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS). The optical properties of the SnO\textsubscript{2}:F\textsubscript{y} films are also probed using optical spectroscopies.

2. Experimental procedures

Si spheres were fabricated using a powder melting method. The fabrication process of the Si spheres was described in detail in our previous reports.\textsuperscript{12,13,21,30–32) We deposited n-type SnO\textsubscript{2}:F\textsubscript{y} films on the n-type surface of Si spheres by spraying with tin(IV) fluoride solution.\textsuperscript{12,13,21,22,30–32)} The n-type Si was approximately 500 nm thick. The SnO\textsubscript{2}:F\textsubscript{y} films were treated at 650°C for 4 h or at 710°C for 15 min in air atmosphere. After heat treatment, the film thickness of SnO\textsubscript{2}:F\textsubscript{y} was approximately 100 nm. The performance of spherical Si solar cells with the SnO\textsubscript{2}:F\textsubscript{y} films that were as-prepared and treated at 650°C for 4 h were described in our previous reports.\textsuperscript{12,13,21)}

The microstructure of the SnO\textsubscript{2}:F\textsubscript{y} films was investigated using XRD (Bruker, Billerica, MA, USA, D2 PHASER) and SEM (JEOL, Tokyo, Japan, JSM-6010PLUS/LA). The compositions of the SnO\textsubscript{2}:F\textsubscript{y} films were analyzed by SEM/EDS. A ZAF correction procedure was used to quantify the ratio in the EDS analysis. The optical absorption spectra of the SnO\textsubscript{2}:F\textsubscript{y} films were collected by ultraviolet–visible–near infrared spectroscopy (JASCO, Tokyo, Japan, V-770). Three-dimensional fluorescence measurements were performed by fluorescence spectroscopy (Hitachi, Tokyo, Japan, F-4500). All measurements were performed at room temperature.

3. Results and discussion

Figure 1 shows XRD patterns of SnO\textsubscript{2}:F\textsubscript{y} films coated on Si sphere surfaces and then heat treated under different conditions. XRD measurements were carried out 20 times for each sample.
Shirahata et al.: Effects of heat treatment on fluorine-doped tin oxide anti-reflection films coated on silicon spheres

because the present Si spheres were single crystals, and the orientation plane of the Si spheres could not be controlled.12)(13)(21)(22) Hundreds of spherical Si single crystals were randomly placed on the sample holder, and the sample setting was changed for each measurement. The XRD patterns were picked out from the measurement results. Four identifiable diffraction peaks corresponding to SnO2 were observed at 26.6, 33.8, 37.9, and 51.8°, indicating that the SnO2:F films were a rutile-type tetragonal system (space group P42/mnm).33) The lattice constants of the SnO2:F films were estimated, and are summarized in Table 1. The calculated lattice constants suggests generation of point defects. Especially, the c-axis of the SnO2:F films. The variation of the lattice constants with respect to 4 sinθ decreased, interstitial F atoms (Fi) were removed, and/or Vf were filled with substitutional F atoms (F0) in the SnO2:F crystal by heat treatment. Canestra et al. proposed that F atoms prefer to substitute Vf as F0 atoms at low F concentration. In contrast, at high F concentration, F atoms prefer to enter interstitial sites as Fi atoms in the SnO2 crystal to create neutralizing F0-Fi defects,35) where the Fi atoms are sited at (0, 1/2, 1/2) in the SnO2 unit cell.34) The latter possibility is a feasible explanation for the behavior of our present system. Unit cell volumes (V) of the SnO2:F films were calculated from the estimated lattice constants, and are summarized in Table 1. The calculated V decreased after heat treatment because of lattice shrinkage along the a-axis of the SnO2:F crystals. The Williamson–Hall equation was used to estimate the crystallite size (D) and strain (ε) in the SnO2:F films:

![Image](https://example.com/image1.png)

Fig. 1. XRD patterns of SnO2:F films coated on Si spheres and heat treated under different conditions.

| Sample | Lattice constant (a/Å) | c/Å | V/Å³ | D/Å | ε/% |
|--------|-----------------------|-----|------|-----|-----|
| As-prepared | 0.4765 | 0.3192 | 0.0724 | 27 | 0.05 |
| 650°C, 4 h | 0.4745 | 0.3197 | 0.0720 | 47 | 0.13 |
| 710°C, 15 min | 0.4739 | 0.3193 | 0.0717 | 34 | 0.10 |
| Ref. 33 | 0.4737 | 0.3185 | 0.0715 | — | — |

Table 1. Lattice constants, unit cell volumes (V), crystallite sizes (D), and strains (ε) of SnO2:F films coated on Si spheres and heat treated under different conditions.

The composition of SnO2:F films were analyzed; the crystallographic information file of SnO2 crystal was downloaded from Ref. 38.

![Image](https://example.com/image2.png)

Fig. 2. (a) SEM image of a Si sphere coated with a SnO2:F film heat treated at 710°C for 15 min. Schematic illustration of the unit cells of (b) as-prepared and (c) heat-treated SnO2:F films. The crystallographic information file of SnO2 crystal was downloaded from Ref. 38.

Table 2. Measured compositions of SnO2:F films.

| Sample | Composition/at% |
|--------|-----------------|
| Sn     | O    | F    |
| As-prepared | 22 ± 4.6 | 59 ± 2.6 | 20 ± 2.1 |
| 650°C, 4 h | 21 ± 3.8 | 71 ± 5.7 | 7.5 ± 1.4 |
| 710°C, 15 min | 21 ± 7.1 | 67 ± 2.8 | 12 ± 1.2 |

wavelength (0.154184 nm), respectively. In the present study, the K of 0.94 was introduced into Eq. (1) because the XRD patterns were fitted by a Gaussian function.37) Then, βfi was determined as follows:

\[ \beta_{fi} = \sqrt{\beta^2 - \beta_i^2}, \]

(2)

where β and βi are the estimated FWHM from the Gaussian function and instrument coefficient, respectively. Using Eq. (1), D and ε derived from F doping and the shape of the Si spheres were simultaneously estimated. The term βfi cosθ was plotted with respect to 4 sinθ, and the slope and y-intersect of the fitted line represent ε and D, respectively. The averaged D and ε values for each film are listed in Table 1. Heat treatment caused both D and ε to increase. The increase of ε is associated with decreased numbers of Vf and Fi atoms, and/or an increased number of F0 atoms in the SnO2:F films. Furthermore, the D were consistent with the SnO2:F observed by transmission electron microscopy.12)
composition that resulted in decreased numbers of F\textsubscript{i} atoms and V\textsubscript{O}, and an increased number of F\textsubscript{O} atoms in the SnO\textsubscript{2}:F\textsubscript{y} crystals, as illustrated in Figs. 2(b) and 2(c). Figure 3(b) presents Tauc plots of the SnO\textsubscript{2}:F\textsubscript{y} films, which were determined from

\[(h\nu)^n = A(h\nu - E_g)\]  

(3)

Here, \(h\), \(\nu\), \(\alpha\), \(A\), \(E_g\), and \(n\) are the Planck constant, light frequency, absorption coefficient, proportional constant, energy gap, and power index, which depends on the nature of the transition, respectively. In the present study, \(n = 2/3\) was used for the SnO\textsubscript{2}:F\textsubscript{y} films because SnO\textsubscript{2} is a direct forbidden transition semiconductor.\textsuperscript{39} \(E_g\) values were obtained by extrapolating the linear region of the Tauc plots to meet \((h\nu)^n = 0\), and were 3.37, 3.75, and 3.70 eV for the as-prepared film, that treated at 650°C for 4 h, and the film treated at 710°C for 15 min, respectively. \(E_g\) of the as-prepared SnO\textsubscript{2}:F\textsubscript{y} film was close to that in our previous report.\textsuperscript{11} \(E_g\) of the treated SnO\textsubscript{2}:F\textsubscript{y} films depended on heat treatment conditions. The difference of \(E_g\) is associated with the O and F contents of the films.

Figure 4 show three-dimensional fluorescence intensity maps of the SnO\textsubscript{2}:F\textsubscript{y} films. The purple-colored radial lines are derived from the excitation light. In the as-prepared SnO\textsubscript{2}:F\textsubscript{y} films [Fig. 4(a)], weak luminescence intensities were seen in the emission wavelength range from 350 to 400 nm and the excitation wavelength range from 240 to 250 nm. Compared with that of the as-prepared film, the luminescence intensities of the treated SnO\textsubscript{2}:F\textsubscript{y} films [Figs. 4(b) and 4(c)] increased in the emission wavelength range from 330 to 400 nm and the emission wavelength range from 240 to 255 nm. These increases were attributed to improvement of the crystallinity of the SnO\textsubscript{2}:F\textsubscript{y} films and composition variation of O and F atoms in the heat-treated films.

To analyze the results of fluorescence measurements, fluorescence spectra of the SnO\textsubscript{2}:F\textsubscript{y} films at an excitation wavelength of 250 nm are presented in Figs. 5(a)–5(c). A characteristic peak was observed in the range of 330–420 nm for all films. Heat treatment affected both fluorescence intensity and peak sharpness. To identify the origin of the fluorescence peaks, the spectra were fitted by the Voigt function, which is the convolution of Lorentzian and Gaussian forms; the decomposed Voigt functions are included in the figures. Peak 1 at 310 nm was attributed to the near-band-edge emission originating from the recombination of electrons and holes in the conduction and valence bands of the SnO\textsubscript{2}:F\textsubscript{y} films.\textsuperscript{40} Peak 2 at 349–354 nm was ascribed to electron transitions mediated by defect levels. The defect levels would be derived from V\textsubscript{O} and luminescent centers formed by interstitial Sn (Sn\textsubscript{i}) atoms or dangling bonds in the films.\textsuperscript{41} Peak 3 was attributed to donor-to-acceptor emission. The donor level was formed by V\textsubscript{O} or F\textsubscript{O}, and the acceptor level was formed by F\textsubscript{i}, because V\textsubscript{O} commonly introduces intrinsic donor-type defects into oxide-based semiconductors, and F\textsubscript{O} and F\textsubscript{i} are considered to
act as a donor and acceptor in the SnO$_2$:F$_x$ films, respectively. The XRD measurements indicated the presence of F$_0$ and F$_1$ in the films. Peak 4 originated from charged VO or luminescent centers in the films. Slight shifts of peak 2 and 3 were also seen, which would be caused by Sn$_x$ and VO$_y$.

Because the defect formation energies of Sn$_x$ and VO$_y$ are negative, Sn$_x$ and VO$_y$ are probably dominant in the defect structure of SnO$_2$, which explains the natural nonstoichiometry of SnO$_2$. For qualitative comparison, integrated intensities of the four Voigt functions were plotted as a function of desorbed F content (ΔF), which was calculated by subtracting the F content of the heat-treated SnO$_2$:F$_x$ films from that of the as-prepared SnO$_2$:F$_x$ film; the results are shown in Fig. 5(d). The integrated intensities of peak 1 and 4 increased and decreased with increasing ΔF, respectively. The variations of the integrated intensities of peak 1 and 4 indicate the improved crystallinity of the SnO$_2$:F$_x$ films and decreased content of point defects, respectively, upon heat treatment, leading to the observed variations of lattice constants, D, and E$_g$.

Lattice constants, V, D, and E$_g$ were plotted as a function of ΔF, as depicted in Fig. 6. With increasing ΔF, the a-axis lattice constant decreased, suggesting that excess F atoms were removed from the SnO$_2$:F$_x$ crystal, and/or filled vacant O sites in the crystal, which caused the lattice shrinkage along the a-axis. Likewise, D and E$_g$ increased with decreasing ΔF. In our previous report, the transmittance of as-prepared SnO$_2$:F$_x$ films decreased in the range of 250–600 nm following heat treatment. Thus, the microstructure and optical properties of SnO$_2$:F$_x$ films strongly depend on F content. Furthermore, O content is also important. It is considered that the increases of D and E$_g$ are correlated with O content in the SnO$_2$:F$_x$ films because the integrated intensities of peak 1 and 4 shown in Fig. 5(d) were associated with the crystallinity of the SnO$_2$:F$_x$ films and decreased content of VO$_y$ in the films, respectively.

Controlling the microstructures and optical properties of AR films coated on the surface of Si spheres by using suitable starting materials, dopants, concentrations, and heat treatment conditions is of great interest. In the present work, the effects of heat treatment on SnO$_2$:F$_x$ films were investigated from the viewpoints of treatment conditions and ΔF. However, further investigation of microstructure, electrical, optical, and photovoltaic properties and interfacial conditions at Si/SnO$_2$:F$_x$ and SnO$_2$:F$_x$/metal electrode interfaces are required to shed light on the full effects of heat treatment of SnO$_2$:F$_x$ films, and to achieve conversion efficiencies higher than reported previously.

4. Summary

The effects of heat treatment on the microstructure and optical properties of SnO$_2$:F$_x$ films coated on the surface of Si spheres were investigated. The lattice constants, D, and E$_g$ varied according to heat treatment conditions. Fluorescence spectra of the SnO$_2$:F$_x$ films showed a broad luminescence. The enhancement of luminescence intensity was associated with defects in the films, indicating that the microstructure and optical properties of the films strongly depended on the O and F contents in the SnO$_2$:F$_x$ crystals. These findings can be used to improve spherical Si solar cells.

Acknowledgments This work was partly supported by the Super Cluster Program of the Japan Science and Technology Agency (JST), and JSPS KAKENHI Grant Number 25420760.

References
1. M. A. Green, K. Emery, Y. Hishikawa, W. Warta and D. Dunlop, Prog. Photovolt. Res. Appl., 24, 3–11 (2016).
2. Z. Liu, A. Masuda, T. Nagai, T. Miyazaki, M. Takano, M. Takano, H. Yoshigahara, K. Sakai, K. Asai and M. Kondo, Sol. Energy Mater. Sol. Cells, 91, 1805–1810 (2007).
3. C. Candelise, M. Winskel and R. J. K. Gross, Renew. Sust. Energ. Rev., 26, 96–107 (2013).
4. W. R. Mckee, IEEE Trans. Components, Hybrid, Manuf. Technol., 5, 336–341 (1983).
5. T. Maruyama and H. Minami, Sol. Energy Mater. Sol. Cells, 79, 113–124 (2003).
6. K. Nagashio, H. Ando, K. Kuribayashi and I. Jimbo, Jpn. J. Appl. Phys., 45, L623–L626 (2006).
7. T. Nagai, Z. Liu, A. Masuda and M. Kondo, J. Appl. Phys., 101, 103530 (2007).
8. Z. Liu, T. Nagai, A. Masuda, M. Kondo, K. Sakai and K. Asai, J. Appl. Phys., 101, 093505 (2007).
9. T. Minemoto and H. Takakura, Jpn. J. Appl. Phys., 46, 4016–4020 (2007).
10) C. Okamoto, T. Minemoto, M. Murozono, H. Takakura and Y. Hamakawa, *Jpn. J. Appl. Phys.*, 44, 7805–7808 (2005).
11) S. Omae, T. Minemoto, M. Murozono, H. Takakura and Y. Hamakawa, *Jpn. J. Appl. Phys.*, 45, 3577–3580 (2006).
12) T. Oku, M. Kanayama, Y. Ono, T. Akiyama, Y. Kanamori and M. Murozono, *Jpn. J. Appl. Phys.*, 53, 0SFJ03 (2014).
13) Y. Shirahata, B. Zhang, T. Oku, Y. Kanamori and M. Murozono, *Mater. Trans.*, 57, 1082–1087 (2016).
14) S. Hayashi, T. Minemoto, H. Takakura and Y. Hamakawa, *Rare Met.*, 25, 115–120 (2006).
15) C. Okamoto, T. Minemoto, M. Murozono, H. Takakura and Y. Hamakawa, *Jpn. J. Appl. Phys.*, 44, 7372–7376 (2005).
16) T. Ikuta, T. Minemoto, H. Takakura and Y. Hamakawa, *Jpn. J. Appl. Phys.*, 45, 3938–3942 (2006).
17) T. Mizuta, T. Ikuta, T. Minemoto, H. Takakura, Y. Hamakawa and T. Numai, *Sol. Energy Mater. Sol. Cells*, 90, 46–56 (2006).
18) T. Minemoto, M. Murozono, Y. Yamaguchi, H. Takakura and Y. Hamakawa, *Sol. Energy Mater. Sol. Cells*, 90, 2995–3000 (2006).
19) T. Minemoto, T. Mizuta, H. Takakura and Y. Hamakawa, *Sol. Energy Mater. Sol. Cells*, 91, 191–194 (2007).
20) Y. Ono, T. Oku, T. Akiyama, Y. Kanamori, Y. Ohnishi, Y. Ohtani and M. Murozono, *J. Phys.: Conf. Ser.*, 352, 012023 (2012).
21) T. Oku, M. Kanayama, T. Akiyama, Y. Kanamori and M. Murozono, *Phys. Status Solidi., C Curr. Top. Solid State Phys.*, 10, 1840–1843 (2013).
22) Y. Shirahata, T. Oku, Y. Kanamori and M. Murozono, *AIP Conf. Proc.*, 1709, 020021 (2016).
23) I. H. Kim, J. H. Ho, D. Kim, K. S. Lee, T. S. Lee, J.-h. Jeong, B. Cheong, Y.-J. Baik and W. M. Kim, *Thin Solid Films*, 515, 2475–2480 (2006).
24) T.-H. Fang and W.-J. Chang, *Appl. Surf. Sci.*, 220, 175–180 (2003).
25) C.-H. Han, S.-D. Han, J. Gwak and S. P. Khatkar, *Mater. Lett.*, 61, 1701–1703 (2007).
26) F. C. Marques, *IEEE Trans. Electron Dev.*, 45, 1619–1622 (1998).