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State analysis of fluorine-doped SnO_2 (FTO) by ^{57}Fe Mössbauer spectroscopy

Kiyoshi Nomura[1,2] · Maho Sasaki[2] · Rintarou Saito[2] · Yuya Koike[2] · Shiro Kubuki[1] · Akio Nakanishi[3]

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Abstract
Fe doped FTO powders were prepared by a chemical precipitation method. Mössbauer spectra of FTO with several concentrations of Fe dopants were decomposed into two doublets (D1 and D2). A doublet with a small electric field gradient (D1) is assigned to Fe^{3+} in a small distorted site of the rutile structure, and another doublet (D2) to Fe^{3+} in a large distorted site due to F^- ion and oxygen defect. Furthermore, with increase of the annealing temperature the isomer shifts tended to decrease. It suggests that Fe^{3+} bonds are more covalently bonded than ionic at the higher annealing temperatures. The surface layer of grains were also characterized by ^{57}Fe CEMS. The defect structures of Fe doped FTO were estimated using the oxygen defect models of tin oxide [Mudarra Navarro et al., J. Phys. Chem. C, **119**, 5596 (2015)].

Keywords Fe doped FTO · Fe doped SnO_2 · Dilute magnetism · Mössbauer spectroscopy · CEMS

1 Introduction

There are many papers of fluorine-doped tin oxide (FTO) films, prepared by sol-gel process and splay pyrolysis. FTO with a wide band gap (Eg) is used as more stable transparent electrode in solar cells than SnO_2 with Eg = 3.62 eV at room temperature [1]. To improve the properties of FTO, many preparation studies have been reported recently. For example, the electrical and optical properties of FTO films have been studied as a function of the F/Sn ratio. The optical Eg of FTO thin films is in a

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✉ Kiyoshi Nomura
dqf10204@nifty.com

[1] Radioisotope Center, Tokyo Metropolitan University, Minami Osawa, Hatiouji, Tokyo 192-0364, Japan

[2] Applied Chemistry, Meiji University, Higashi-Mita, Kawasaki, Kanagawa 214-8571, Japan

[3] Physics, Shiga University of Medical Science, Tsukinowa, Otsu, Shiga 520-2192, Japan

3.70–4.07 eV range. The optimal FTO films revealed a maximum value of around 8.05×10^{-3} (Ω^{-1}) at $\lambda = 400$ nm [2]. Mutual effect of F dopant and oxygen vacancies on structural and luminescence characteristics of FTO nanoparticles also has been studied [3].

Spintronics materials that control electron spin in addition to electric charge by doping magnetic ions to an oxide semiconductor with a wide band gap are fascinating. Influence of Fe and Fe + F doping on the properties of sprayed SnO_2 thin films was studied [4]. The tetragonal rutile structure of SnO_2 is unaltered with Fe and Fe + F doping, and the formation of Sn–O bond is confirmed by FTIR analysis. We have studied the crystal structure, chemical state and magnetic properties of tin oxides doped with Fe [5], and present here the results of FTO doped with Fe, prepared by a chemical method. Especially the effects of F-doping and Fe contents of FTO microstructure were studied using conventional Mössbauer spectrometry and conversion electron Mössbauer spectrometry (CEMS) [6].

2 Experimental

FTO samples with different doping amounts ($Sn_{1-x}Fe_xO_{2-y}F_{2y}$): x = 0.01 to 0.04, y = 0.10 and 0.20) were prepared by mixing 0.1 M NH_3F, 0.2 M $SnCl_4$, 0.01 M $FeCl_3$ and 0.01 M ^{57} Fe solutions with nominal mole ratios, and by heating, drying, grinding and calcinating at several temperatures. Each FTO contained 1% ^{57}Fe. The obtained samples were analyzed by X-ray diffraction (XRD), vibration sample magnetometer (VSM), and ^{57}Fe Mössbauer spectroscopy for estimating the crystalline distortion, magnetic properties, and chemical states, respectively. Doppler velocity was calibrated by using α-Fe foil. Conversion electron Mössbauer (CEM) spectra of the surface layer on powder samples fixed on conductive carbon film were measured at room temperature (RT) and 16 K, using a gas filled proportional counter and cryostat.

3 Results and consideration

3.1 XRD results

XRD patterns of all Fe doped FTO samples after annealed at more than 400 °C showed a rutile structure containing no precipitated iron oxide and iron fluoride compound FeF_3 as shown in Fig. 1 left hand although sharp peaks of FeF_3 and SnO_2 were reorganized before annealing. No significant difference among FTO with different F contents was recongnized as shown in Fig. l right hand.

3.2 VSM results

As shown in Fig. 2, VSM showed weak ferromagnetism for strained samples of 1% Fe doped and 4% Fe doped FTO. Saturation magnetization of 1% Fe doped FTO annealed at 500 °C was a little larger than 4% Fe doped FTO at 400 °C although 4% Fe doped FTO contained paramagnetic and ferromagnetic components. 4% Fe doped STO annealed at higher than 500 °C showed only paramagnetic behavior. When F doping amounts increased like 1% Fe FTO with Sn: F = 10: 2 and 10: 4, the magnetic property showed very weak ferromagnetic behavior with diamagnetic component. Pure SnO_2 and fluorine doped SnO_2 are originally diamagnetic oxides. By doping only 1% Fe into FTO, the weak ferromagnetic behavior was observed. The absence of coercivity may indicate that the magnetization process is dominated

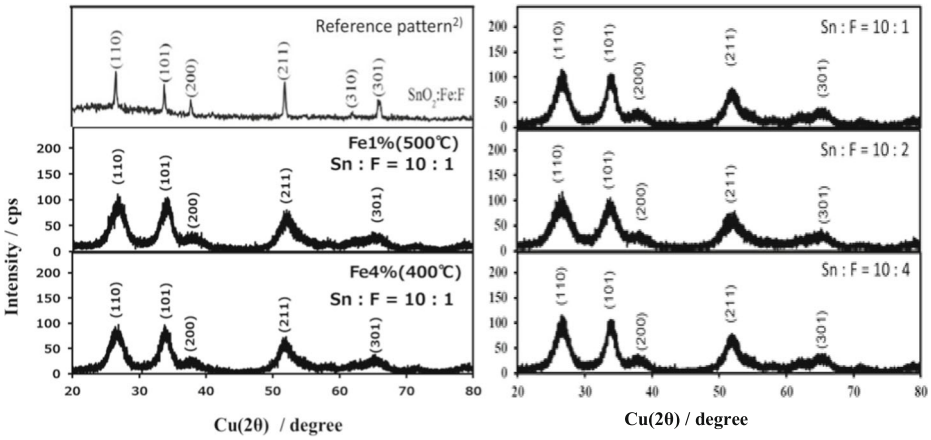

Fig. 1 (left hand) XRD patterns of FTO doped with 4% Fe and 1% Fe annealed at 400 °C and 500 °C, respectively, and (right hand) XRD of 1% Fe doped FTO with the mole ratios of Sn:F = 10:1, 10:2 and 10:4, annealed at 400 °C for 2 h.

by magnetic dipole interactions, not by magnetocrystalline anisotropy [7]. With increase of Fe doping amounts for FTO with Sn: F = 10: 1, the magnetic property showed only paramagnetic behavior. Thus, the VSM behavior of low Fe doped FTO showed dilute magnetism.

3.3 Mössbauer results

Mössbauer spectra of Fe doped FTO were decomposed into two doublets of paramagnetic Fe^{3+} species as shown in Fig. 3. The doublet (D1) with a high isomer shift (IS) and a small quadrupole splitting (QS) is due to Fe^{3+} at the small strain site, and the other doublet (D2) with a low IS and a high QS to Fe^{3+} for the large strain site.

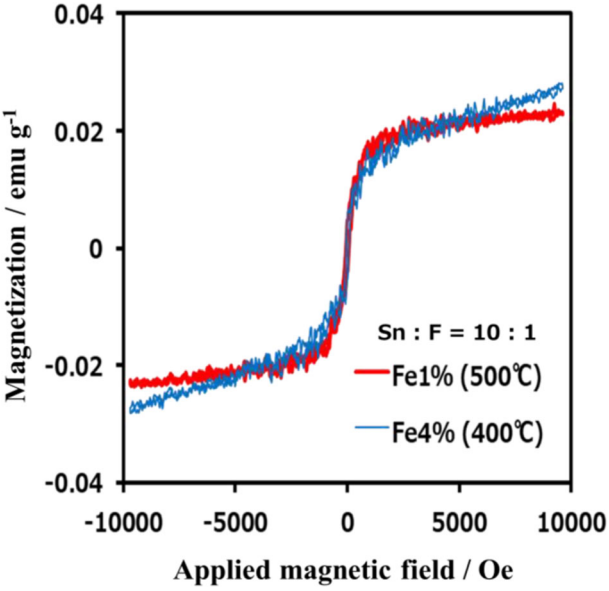

Fig. 2 Magnetization of FTO powders: a) 1% Fe doped FTO annealed at 500 °C and 4% Fe doped FTO annealed at 400 °C

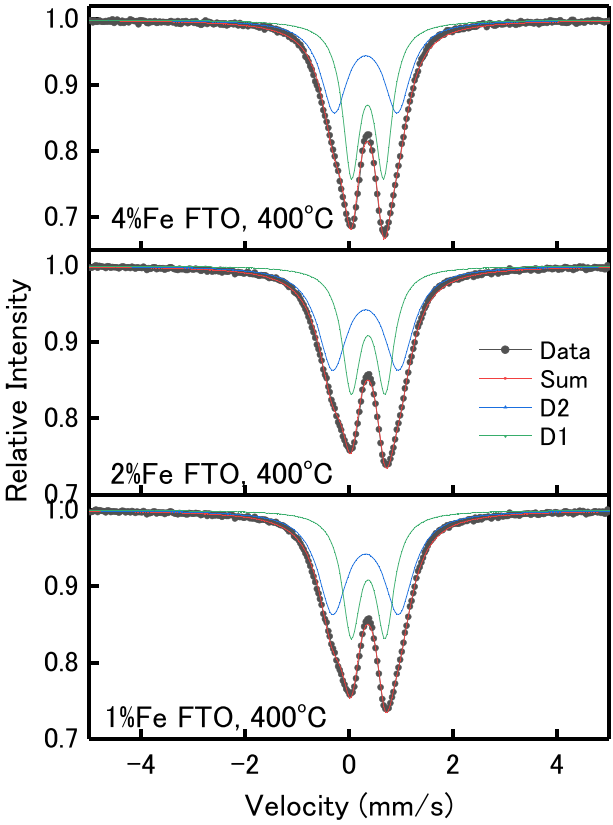

Fig. 3 Mössbauer spectra of 1% Fe doped, 2% Fe doped and 4% Fe doped FTO (Sn: F = 10: 1) powders

With increase of doping Fe amounts for FTO annealed at 400 °C, the QS and area intensity of doublet D2 became small. The Mössbauer results are almost similar to the trend of VSM results. The broad doublet D2 appeared for Fe doped FTO although the Fe doping rate was small. These may be caused by magnetic dipole interactions of dilute Fe ions though the electron around oxygen defects, that is the formation of large polaron [8].

Figures 4 and 5 show the annealing temperature dependency on the Mössbauer spectra. Especially the doublet D2 became the broader lines, larger QS, and stronger area intensity with increase of annealing temperatures. The IS and QS values decreased and increased slightly with the annealing temperature, respectively. This is because as the IS value decreases, the binding force contributes more to the covalent bond than the ionic bond.

As compared with the configuration of oxygen defects in a supercell of SnO_2, the configuration of oxygen defect and Fe (D1) is similar to Fe-2Vo_1-Fe (conf.A) and the configuration of oxygen defect and Fe (D2) is closed to Fe-Vo_2, Fe-2Vo_1-Fe (conf. C) and Fe-Vo-Fe (conf. B) by *ab initio* calculations [5, 9]. F^- may substitute O^{2-} and generate Fo^+ and one extra e^-. Subsequently, e^- can combine with Vo^+ or Vo^{++} to generate Vo^0 or Vo^+ to ensure charge balance [3]. Fe^{3+} substitutes Sn^{4+} to generate Fe_{Sn}^- and one hole p+, which can combine with extra F^-. It is considered from the above results that the electron configuration around Fe^{3+} in D2 is much more deformed in local structure by influence of fluorine than Fe^{3+} in D1.

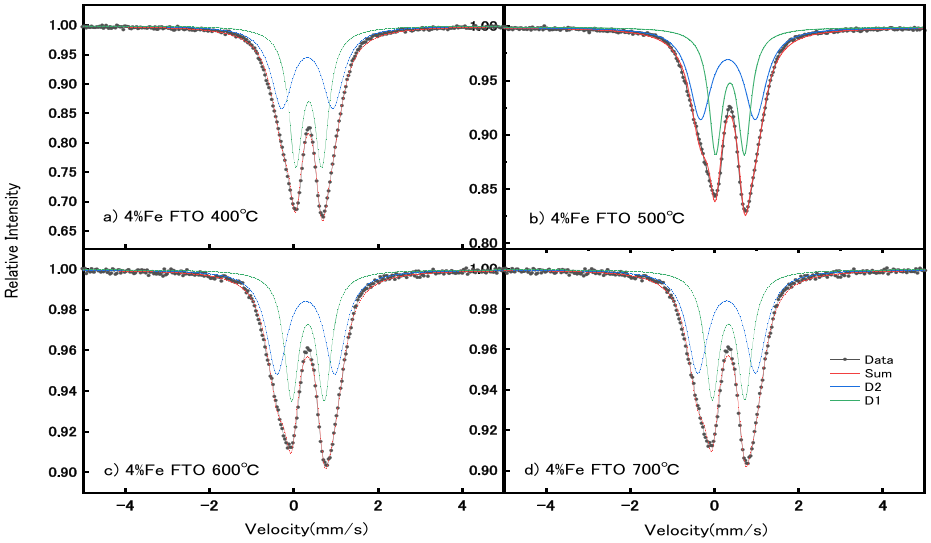

Fig. 4 Mössbauer spectra of 4% Fe doped FTO annealed at various temperatures

The grain surface of FTO doped with Fe is also largely influenced by the local configuration. The deformed surface microstructure can be characterized by conversion electron Mössbauer spectrometry (CEMS). As shown in Fig. 6, it was found that RT CEM spectra of the grain surface of FTO are clearly different from the TMS spectra. it is considered that Fe^{3+} substituted at Sn site (D1) have coordinated loosely with O^{2-} and less oxygen defects, and Fe^{3+} at Sn site (D2) have relatively strong binding with F^{-} ions and more oxygen defects. The intensity of D2 component decreased on the grain surface for 4% Fe doped FTO at 400 °C, but increased on the surface layer for 1% Fe doped FTO annealed at 500 °C. It suggests that iron-fluorine and -oxygen bonds are formed strongly by annealing at high temperature. The Fe species on the surface layer do not bind so strongly with oxygen atoms at room temperature. However, since the Lamb factor *f* increased with cooling to 16 K, a strong bond between Fe^{3+} and oxygen atom are considered to be formed. 16 K CEM spectra are similar to RT TMS spectra in the area intensity ratio of two doublet components. In RT CEMS of 4% Fe doped

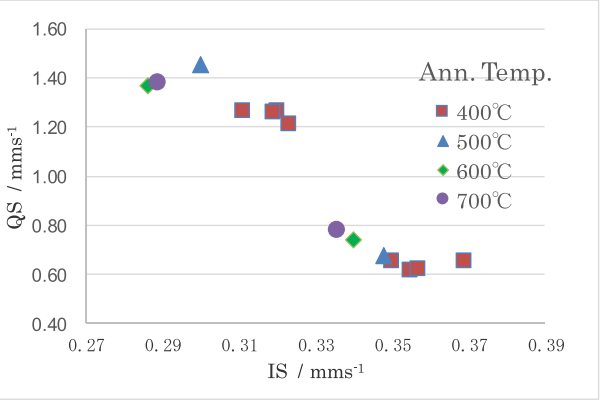

Fig. 5 Relationship between IS and QS for Fe doped FTO annealed at various temperatures

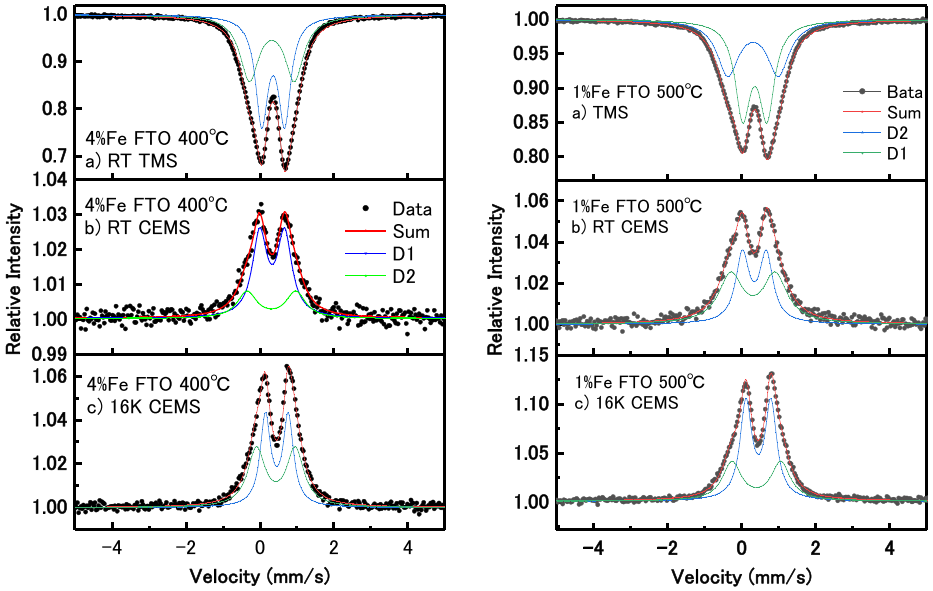

Fig. 6 Transmission and conversion Mössbauer spectra (TMS and CEMS) of 4% Fe doped FTO annealed at 400 °C and 1% Fe doped FTO annealed at 500 °C, respectively

FTO annealed at 400 °C, the linewidth of D1 is a little wider than that of 16 K CEMS. It is also thought to be due to the fluctuation of the contact surface where Fe bond is loosened.

4 Conclusion

The local structure of FTO was clarified by application of ^{57}Fe Mössbauer spectroscopy. Mössbauer spectrum was decomposed into two doublets of Fe^{3+} species. A doublet with a small QS (D1) is assigned to Fe^{3+} at a small strain site in FTO, and a doublet with a large QS (D2) is assigned to Fe^{3+} at a large strain site due to F-ion bonds and oxygen defects. It can be seen that the IS value tends to decrease with increase of the annealing temperature. This result suggests that the Fe^{3+} bond is more covalently bonded than the ionic bond. The particle surface of the FTO powder was more clearly characterized by comparing CEM spectra at room and low temperatures. The defect structures of Fe-doped FTO were estimated using the oxygen defect models of Fe doped tin oxide [9] although the *ab initio* calculation of Fe-doped FTO may be required in more detail. A CEMS technique would be useful for application to powder particles as well as thin film.

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