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^{57}Fe conversion electron Mössbauer study on tin oxide films doped with dilute two metal ions

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Abstract
Tin dioxide (SnO_2) films codoped with 1% mole ratio of (Co, Fe) ions, (Cu, Fe) ions, and (Ti, Fe) ions were prepared on SnO_2 (1% Sb) thin film on glass by a spray pyrolysis. Fe species included in these films were characterized by ^{57}Fe conversion electron Mössbauer (CEM) spectra measured at room temperature (RT) and low temperatures (50 K and 16 K). Three paramagnetic Fe^{3+} species were observed in RT CEM spectra of two metal ions codoped SnO_2 films. The broad magnetic sextet was observed in 16 K CEM spectra of (Co, Fe) codoped SnO_2 and (Cu, Fe) codoped SnO_2 films, but not even at low temperature for (Ti, Fe) codoped SnO_2 film. The relationship between isomer shift and quadrupole splitting were shown and compared with the results of ab initio calculations based on the configuration models of metal ions and oxygen defects.

Keywords ^{57}Fe conversion electron Mössbauer spectrometry · Spray pyrolysis · Metal doped tin dioxide thin film · Diluted magnetism

1 Introduction

Tin dioxide (SnO_2) is a transparent semiconductor material for many applications. SnO_2 doped with dilute metal ions have shown an interesting magnetic behavior at room temperature (RT)

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and can apply to spintronic devices in the future. The ferromagnetism of SnO_2 doped with several % iron ions has been studied by Mössbauer spectrometry [1, 2]. It is found that the ferromagnetism of SnO_2 powders codoped with dilute (Co, Fe), (Mn, Fe), (Ni, Fe), and (V, Fe) ions are enhanced, compared with that of single ions doped SnO_2 powders [3–5]. It is also reported by the other group that in SnO_2 doped with Mn and codoped with (Mn, Fe) or (Mn, Co) prepared by a sol-gel method, 2% (Mn, Co) dopants showed the high magnetic properties ($Ms = 0.168$ emu/g), $Hc = 2.896$ Oe, $Mr = 0.09$ emu/g) [6]. In the previous study [7], SnO_2 films codoped with two metal ions (V-Fe, Mn-Fe, and Co-Fe) prepared by spray pyrolysis were characterized by ^{57}Fe CEM spectrometry. In CEM spectra for all samples, any magnetic sextet was not observed even if these SnO_2 films were measured at 20 K. In contrast, broad magnetic components were observed together with paramagnetic doublets in RT Mössbauer spectra of two metals codoped SnO_2 powders prepared by a sol-gel and thermal decomposition method. These results indicate that the magnetic properties of samples are influenced by preparation conditions and methods.

On the other hand, ab initio calculations on supercell models of SnO_2 doped with Fe species have been studied [8]. These results showed that the configuration of substituted iron and oxygen vacancy is important for the magnetic behavior of tin dioxide semiconductor. In order to confirm the previous study and to reconsider the analytical method, SnO_2 films codoped with (Co, Fe), (Cu, Fe), and (Ti, Fe) ions were prepared by spray pyrolysis, and were characterized by ^{57}Fe CEM spectrometry at RT and low temperatures. Mössbauer parameters obtained in this experiment are compared with those of the configuration model of metal ions and oxygen vacancies by ab initio calculations to clarify more doping effect.

2 Experimental

Each 0.01 M metal chloride solution of Fe, Co, Ti and Cu was prepared. Each solution of two different metal ions with 1:1 percentage ratio was added in 0.1 M Sn chloride solution. Just before spray pyrolysis, 20% ethanol was added and mixed in the prepared solution. SnO_2 films codoped with dilute two metal ions were formed on quartz glass heated at higher than 400 °C by spraying the solution. The thickness of the films is less than 100 nm. ^{57}Fe CEM spectra were measured using He-CH_4 gas mixture and H_2 gas-filled counters at RT and low temperatures, respectively [9]. Doppler velocity calibration was carried out with a natural iron foil at RT. The observed spectra were analyzed by Mosswinn program (version 4.0).

3 Results and discussions

(i) CEM spectra.

CEM spectra of SnO_2 films codoped with two metal ions (Co-Fe, Cu-Fe, and Ti-Fe) were measured at RT and low temperatures. Asymmetrical peaks with broad linewidth were observed in all spectra at RT. These spectra obtained were analyzed by three doublets. Isomer shifts (*IS*) of these doublets were between 0.29 mm/s and 0.38 mm/s, which indicate that these doublets were due to paramagnetic Fe^{3+} ions. In descending order of *IS* value, these doublets were named as D1, D2, and D3. These Mössbauer parameters are listed in Table 1.

Table 1 Mössbauer parameters of SnO_2 thin films codoped with Fe ions and the other metal ions

Dopants in SnO_2	Co-Fe RT	Co-Fe 50 K	Co-Fe 16 K	Cu-Fe RT	Cu-Fe 16 K	Ti-Fe RT	Ti-Fe 16 K
D1 (%)	28.6	26.0	13.6	33.7	28.4	29.3	17.9
IS (mm/s)	0.38	0.49	0.49	0.38	0.49	0.37	0.49
QS (mm/s)	0.61	0.68	0.71	0.65	0.68	0.69	0.64
LW (mm/s)	0.29	0.36	0.43	0.31	0.38	0.32	0.31
D2 (%)	42.8	22.0	7.9	46.3	16.0	47.1	43.7
IS (mm/s)	0.37	0.47	0.46	0.35	0.46	0.35	0.47
QS (mm/s)	0.95	1.07	1.25	1.03	1.14	1.12	1.03
LW (mm/s)	0.34	0.40	0.56	0.40	0.38	0.39	0.41
D3 (%)	28.6	12.5		20.0	10.5	23.6	38.4
IS (mm/s)	0.33	0.42		0.29	0.37	0.33	0.45
QS (mm/s)	1.38	1.58		1.54	1.66	1.59	1.52
LW (mm/s)	0.44	0.53		0.44	0.58	0.41	0.52
magnetic comp. (%)		39.5	78.5		45.1		
IS (mm/s)		0.45	0.46		0.43		
QS (mm/s)		−0.09	−0.08		−0.21		
ave. HF (T)		39.9	38.6		40.6		

(ii) Co and Fe codoped tin oxide film.

CEM spectra of tin oxide film codoped with (Co, Fe), measured at RT, 50 K, and 16 K, are shown in Fig. 1. Magnetic sextet with broad peaks was observed in low temperature CEM spectra. The hyperfine field (*HF*) distributions calculated are also given in each CEM spectrum. The intensities of three doublets decreased as temperature decreased. Especially the intensities of doublets D2 and D3 decreased relatively as measuring temperature decreased from 50 K to 16 K, but the intensity of doublet D1 was not so much changed. Furthermore, the intensity of broad sextet became large at 16 K. The *HF* distribution is a little different from 50 K *HF* distribution at glance since low magnetic components were relatively grown at 16 K. In the previous report [7], the (Fe, Co) codoped SnO_2 films were about one half in thickness and twice in doping ratio compared with the films prepared this time, and the previous CEM spectra were decomposed into two components of doublets without discrimination of D2 and D3. Since the ferromagnetic sextet was hardly observed for more than 2% Fe and 2% Co ions codoped tin oxide, it might be reasonable to explain the dilute magnetism by the model such as large polaron formation due to magnetic ions and oxygen defects [10].

(iii) Cu and Fe codoped tin oxide film.

CEM spectra of tin oxide film codoped with (Cu, Fe) measured at RT and 16 K are shown in Fig. 2. The intensities of doublets D1, D2, and D3 decreased relatively as measuring temperature decreasing from RT to 16 K, and a weak sextet with broad tailing peaks was observed in the 16 K CEM spectrum, in which the *HF* distribution calculated was similar to the *HF* distribution in 50 K CEM spectrum of tin oxide film codoped with (Co, Fe). It is found that the Mössbauer parameters of high spin Fe^{3+} ions are a little affected by the Cu metal ion, which exits normally as Cu^{2+}.

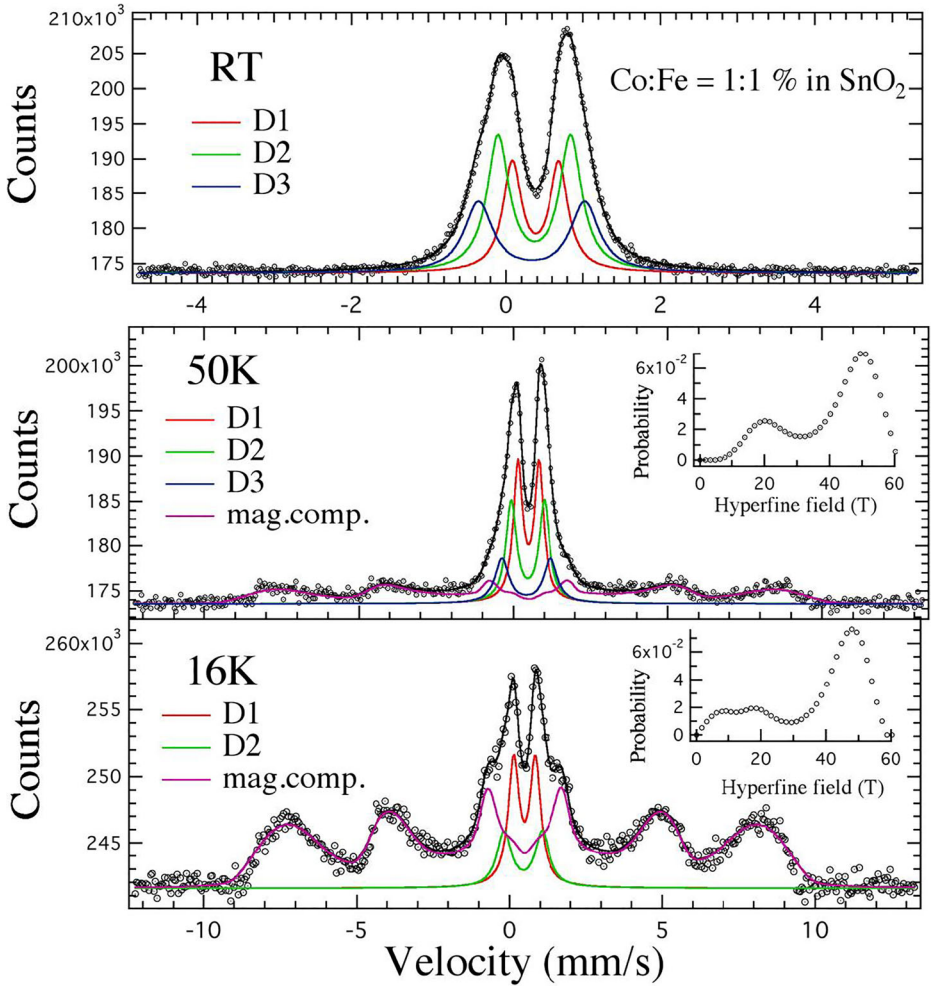

Fig. 1 CEM spectra of Co and Fe codoped SnO_2 thin film measured at RT, 50 K and 16 K. Corresponding probability distributions of the hyperfine field are also shown

(iv) Ti and Fe codoped tin oxide film.

CEM spectra of tin oxide film codoped with (Ti, Fe), measured at RT and 16 K, are shown in Fig. 3. Magnetic sextet was not observed in the 16 K spectrum. As chemical state of titanium ions is the same as that of tin although the ionic radii of Ti^{4+} (ionic radius(IR): 0.061 nm) is a little smaller than that of Sn^{4+} (IR: 0.069 nm), it is expected that the substitution of Sn^{4+} ion with Ti^{4+} does not influence charge neutralization in tin dioxide matrix structure. In this case, the doped Fe^{3+} ion only affected the micro-environmental site. As results, it is considered that the density of produced oxygen vacancies in (Ti, Fe) ions codoped SnO_2 is smaller than that in (Co, Fe) ions codoped SnO_2 or that in (Cu, Fe) ions codoped SnO_2. Since the oxygen vacancies play an important role in the ferromagnetism of tin dioxide semiconductors

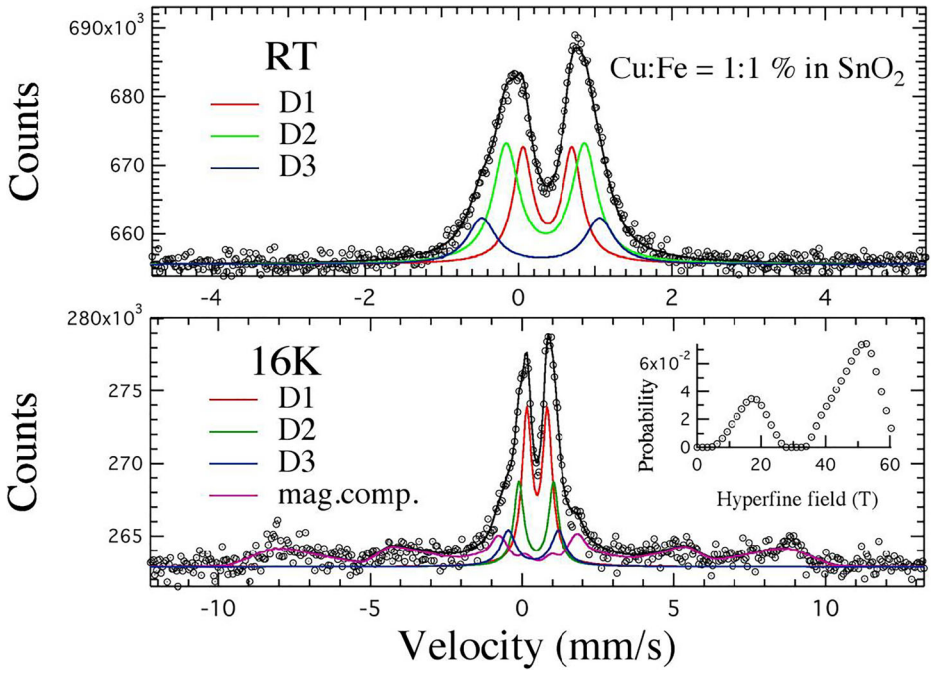

Fig. 2 CEM spectra of Cu and Fe codoped SnO_2 thin film measured at RT and 16 K. Corresponding probability distribution of the hyperfine field is also shown

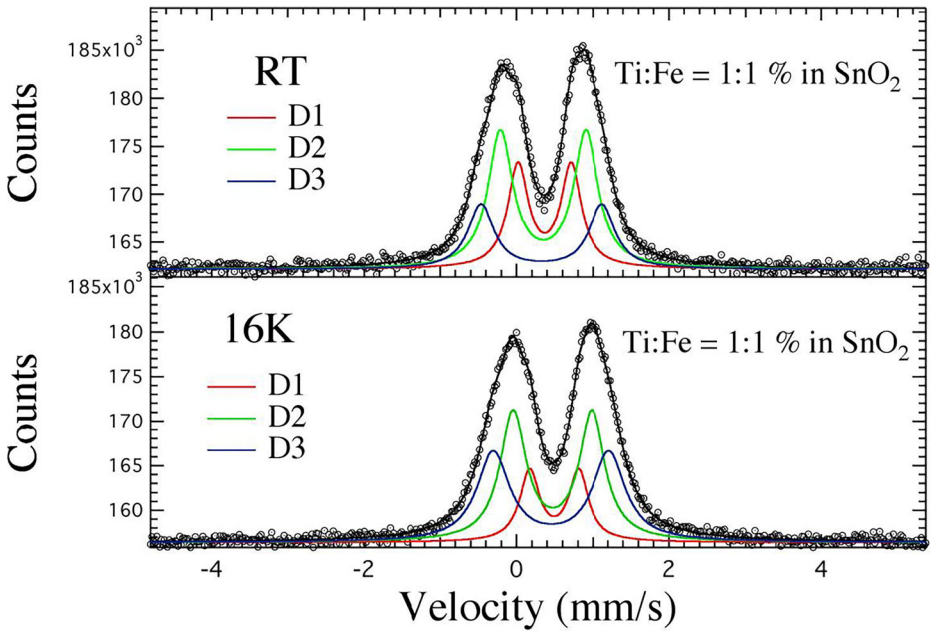

Fig. 3 CEM spectra of Ti and Fe codoped SnO_2 thin film measured at RT and 16 K

[10], it is considered that no magnetic sextet appeared in (Ti, Fe) ions codoped SnO_2 film even if non-magnetic Ti^{4+} ions were located surrounding Fe^{3+}.

(v) Comparison with ab initio calculations.

The plot graphs of the quadrupole splitting (*QS*) as a function of *IS* obtained at RT are shown in Fig. 4. The relationship between *IS* and *QS* are grouped in three classes, which are corresponding to D1, D2, and D3. Ab initio calculations of SnO_2 codoped with Fe ions and oxygen vacancies have been studied [1, 8]. Configurations of oxygen vacancy, Fe atom and metal ion (Cu, Co or Ti) are shown in Fig. 5. The configuration models are described as follows: the model of "Fe-VO1" means one oxygen vacancy nearest Fe atom. "Fe-2VO1-" shows two oxygen vacancies nearest Fe atom. The detail configuration was described in the reference [8].

Comparing with the calculation results of the configuration models, the configuration of Fe^{3+} (D1) and oxygen vacancy is close to that of Fe-2VO1-(Co, Cu, Ti) (conf.A). The configuration of Fe^{3+} (D2) is close to that of Fe-VO1. The configuration of Fe^{3+} (D3) is close to that of Fe-VO1-(Co, Cu, Ti) (conf.B) and/or Fe-2VO1-(Co, Cu, Ti) (conf.C). But further ab initio study would be necessary to understand the magnetic properties of two metals codoped tin dioxide semiconductor.

4 Conclusion

RT CEM spectra of Fe ions and other metal ions codoped tin oxide films prepared by a spray pyrolysis consist of three kinds of Fe^{3+} states with different *IS* and *QS* values. It is considered from the *IS* and *QS* values that the configurations of Fe ions and oxygen vacancies correspond to models of Fe-2VO1-(Co, Cu, Ti) (conf.A), Fe-VO1, Fe-2VO1-(Co, Cu, Ti) (conf.C) and/or

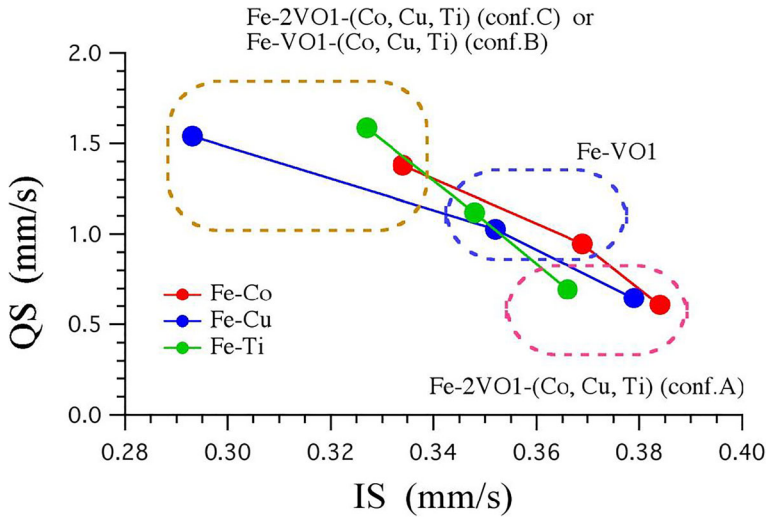

Fig. 4 Relationship between isomer shift (*IS*) and quadrupole splitting (*QS*) at RT. Configurations A, B, and C referred to Fig. 5 [8]

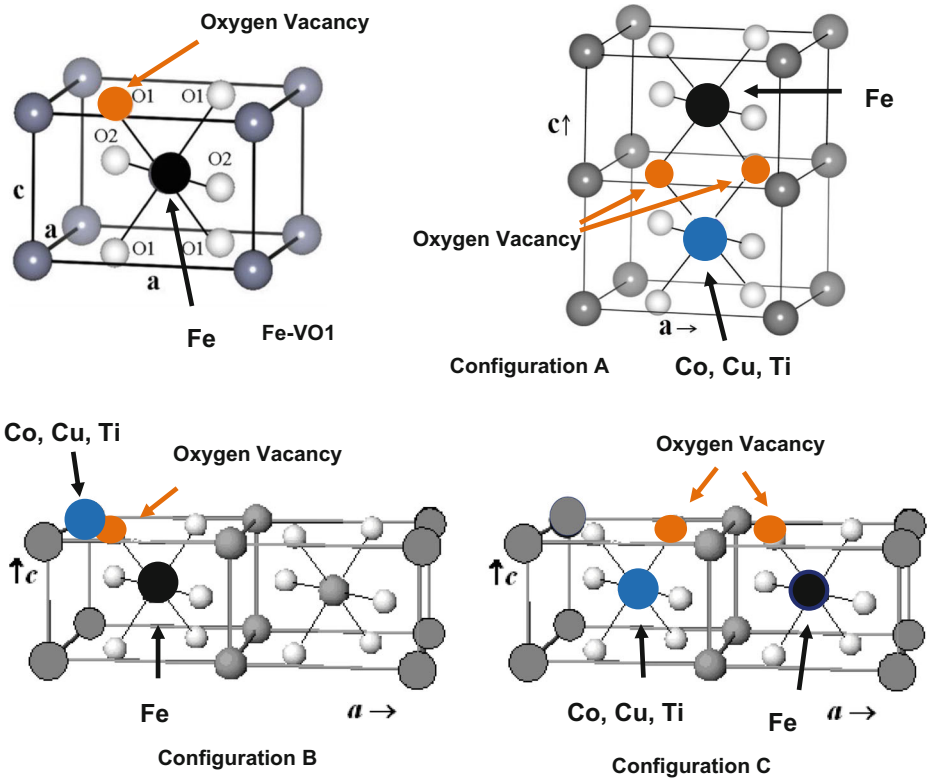

Fig. 5 Configurations of oxygen vacancy and Fe & (Co, Cu or Ti) (from revised figures of ref. [1, 8])

Fe-VO1-(Co, Cu, Ti) (conf.B). At low temperatures, broad magnetic peaks were observed for (Co, Fe) doped SnO_2 and (Cu, Fe) doped SnO_2 films, but not for (Ti, Fe) doped SnO_2 even at low temperature of 16 K. Thus, it is confirmed that the hyperfine parameters (*IS* and *QS*) of Fe ions doped in SnO_2 are affected by the other metal ions (different *d* orbitals) with different valence states, which may be located near oxygen vacancy and Fe substituted sites of tin oxide matrix.

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