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NONSTOICHIOMETRY OF EPITAXIAL $FeTiO_{3+\delta}$ FILMS

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ABSTRACT

Epitaxial thin films of (001)-oriented $FeTiO_{3+\delta}$ were prepared on α-Al_2O_3(001) single crystalline substrates by helicon plasma sputtering technique. The $FeTiO_{3+\delta}$ films had large oxygen nonstoichiometry, which seriously depended on both substrate temperature and oxygen pressure during the sputtering deposition. The valence states of Fe ions in $FeTiO_{3+\delta}$ changed monotonically from Fe^{2+} to Fe^{3+} with decreasing the substrate temperature from 900 to 400°C or with increasing the oxygen pressure from 0.9 to 1.8×10^{-6} Pa. The change of Fe valence states from Fe^{2+} to Fe^{3+} induced the magnetic phase transition only for the films prepared at 900°C. The films containing Fe^{2+} were paramagnetic while those with Fe^{3+} were antiferromagnetic at room temperature. The oxygen nonstoichiometry of the $FeTiO_{3+\delta}$ films was probably produced by cation vacancies and disarrangement of Fe^{3+} and Ti^{4+} ions, which randomly occupied both interstitial and substitutional sites of the $FeTiO_3$ related structure.

INTRODUCTION

Solid solutions of α-Fe_2O_3-$FeTiO_3$ (hematite-ilmenite) series are known to have interesting magnetic and electric properties [1,2]. Though the end members of this series are antiferromagnetic insulators, the intermediate compositions between them are half-metallic ferrimagnets. The compositions are nominally expressed as $Fe^{3+}_{2-2x}Fe^{2+}_xTi^{4+}_xO_3$, where x is the mole fraction of ilmenite. The crystal structure of them has rhombohedral symmetry and is considered as a slightly distorted hcp O^{2-} framework with cations lying in two thirds of octahedral interstices in ordered way. We have recently succeeded in preparing well-crystallized epitaxial $Fe_{2-x}Ti_xO_3$ films by activated reactive evaporation [3,4]. The films of intermediate composites had large ferrimagnetic moments and their resistivity dropped to $10^{-1}\Omega$cm at room temperature. However the Fe^{2+} content of the films was rather small as compared with stoichiometric $Fe_{2-x}Ti_xO_3$. The Ti-rich films we previously prepared seemed to have large oxygen nonstoichiometry about δ=0.3 in $Fe_{2-x}Ti_xO_{3+\delta}$.

Prior to preparing the stoichiometric solid-solution films of $Fe_{2-x}Ti_xO_3$, we tried to confirm preparation conditions of stoichiometric $FeTiO_3$ films. According to a literature on bulk crystal growth of $FeTiO_3$ [5], very low oxygen pressure of about 10^{-12} Pa is required to prevent the oxidization of Fe^{2+}. In the present study helicon plasma sputtering (magnetron sputtering assisted by inductively coupled RF plasma) technique was applied to prepare stoichiometric $FeTiO_3$. The helicon plasma sputtering system we used had very high vacuum and low contaminations. The base pressure was less than 10^{-7} Pa. The structural and magnetic properties of epitaxial $FeTiO_{3+\delta}$ films were reported as a function of the preparation conditions, *i.e.* stoichiometry of the films. The carefully controlled heating temperature and oxygen pressure should be essential to prepare stoichiometric films.

EXPERIMENT

$FeTiO_{3+\delta}$ films were prepared on α-Al_2O_3(001) single-crystalline substrates. Fig.1

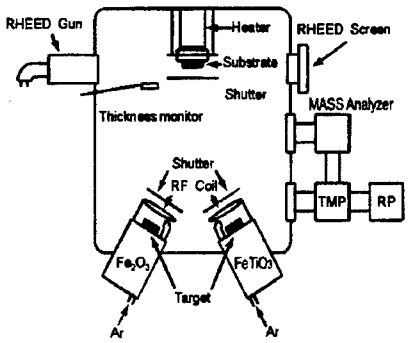

Figure 1. Schematic drawing of the helicon plasma sputtering system we used.

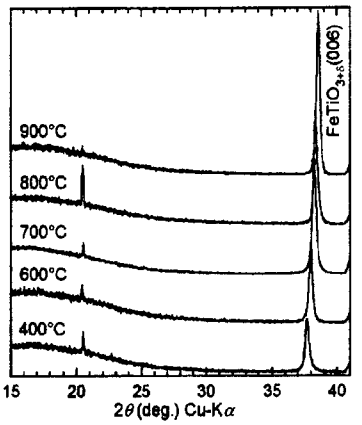

Figure 2. XRD patterns of $FeTiO_{3+\delta}$ films prepared on α-Al_2O_3(001) substrates at different substrate temperatures.

shows a schematic drawing of the helicon plasma sputtering system we used. Two targets for helicon cathodes were made of sintered α-Fe_2O_3 and $FeTiO_3$, respectively. In the present study only the $FeTiO_3$ target was operated. The base pressure of the system was 10^{-7} Pa, and the oxygen partial pressure during the sputtering deposition was measured *in situ* by a mass analyzer unit. Before the sputtering deposition an α-Al_2O_3(001) substrate was annealed in vacuum at about 900°C for 1 hour in order to obtain a clean and well-ordered surface. $FeTiO_{3+\delta}$ films with the thickness of 100 nm were deposited on the substrates at various substrate temperatures ranging from 400 to 900°C. The deposited films were characterized by conventional θ-2θ x-ray diffraction (XRD) measurement, XRD pole figure measurement and conversion electron Mössbauer spectroscopy (CEMS). Chemical formula of prepared $FeTiO_{3+\delta}$ films analyzed by energy dispersive X-ray spectroscopy (EDS) was $Fe_{1.23}Ti_{0.77}O_{3+\delta}$

RESULTS AND DISCUSSION

Substrate Temperature

Fig.2 shows XRD patterns of the sample films prepared at various substrate temperatures between 400 and 900°C. All sample films showed only one intense diffraction line just beside a strong α-Al_2O_3(006) line at 2θ=41.68°. It is well-known that $FeTiO_3$ has the same hcp O^{2-} framework as α-Al_2O_3, so the films could epitaxially formed on the substrates. Assuming the same lattice parameters as those of bulk $FeTiO_3$ crystals [6], the $FeTiO_3$(006) diffraction line should appear at 2θ=38.29° which was very consistent with the observed 2θ values for the sample films shown in Fig.2. Therefore the observed lines were indexed as $FeTiO_{3+\delta}$ (006). However the 2θ values of $FeTiO_{3+\delta}$(006) depended considerably on the substrate temperature when the films were prepared. With decreasing the substrate temperature the 2θ value decreased gradually than that of the bulk $FeTiO_3$ crystals. Moreover the line intensity was decreased in addition to the line broadening. The calculated grain size by using a Scherrer's equation was typically 325 Å at

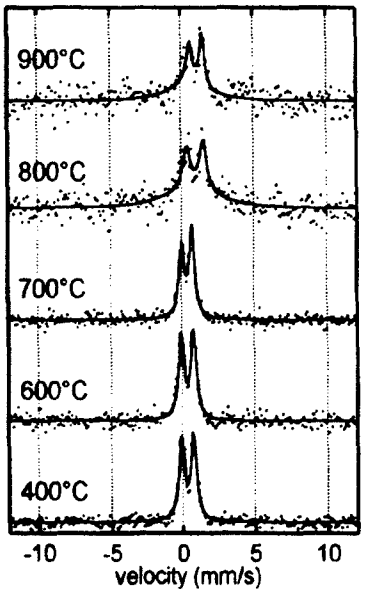

Table I. Fitted parameters for CEMS spectra shown in Fig. 3.

Substrate temperature (°C)	Isomer shifts (mm/s)	Quadropole splitting (mm/s)
900	1.13	0.98
800	1.03	1.14
700	0.37	0.73
600	0.37	0.87
400	0.35	0.85

Figure 3. Room temperature CEMS spectra of $FeTiO_{3+\delta}$ films prepared at different substrate temperatures.

900°C and 260 Å at 400°C, respectively.

Room temperature CEMS spectra of sample films prepared at various substrate temperatures are shown in Fig.3. All sample films were paramagnetic. Assuming the analyzed chemical formula of $Fe_{1.23}Ti_{0.77}O_3$, the Néel temperature of stoichiometric films should be about –25°C [1], *i.e.* below the room temperature. The magnetic properties seemed to be consistent with those of bulk crystals. But the valence states of Fe ions evaluated from the Mössbauer isomer shifts showed considerable changes depending on the substrate temperature. The films prepared at higher substrate temperature consisted of Fe^{2+} ions, while those at lower substrate temperature consisted of Fe^{3+} ions. The isomer shifts of sample films gradually increased with increasing the substrate temperature. The quadropole splitting also reflected the valence states of Fe ions. Fe^{2+} ions, which had a remnant orbital angular momentum in crystal fields, normally gave larger quadupole splitting than Fe^{3+} ions.

Oxygen Pressure

The 2θ values of $FeTiO_{3+\delta}$(006) seriously depended on the oxygen pressure during the sputtering deposition. Fig.4 shows the 2θ values for sample films prepared at the substrate temperature of 900°C as a function of the oxygen pressure. With increasing the oxygen pressure the 2θ value increased from literature values for stoichiometric $Fe^{2+}TiO_3$ [6] to α-$Fe^{3+}{}_2O_3$ [7]. There were small possibilities that the $FeTiO_{3+\delta}$ films decomposed into two phases like α-Fe_2O_3 and TiO_2, because the diffraction lines of $FeTiO_{3+\delta}$(006) maintained sharp profiles and no diffraction lines due to the secondary phases appeared when oxygen pressure was increased.

Room temperature CEMS spectra of sample films prepared at various oxygen pressures are shown in Fig.5. The spectrum with a paramagnetic doublet at lower oxygen pressure

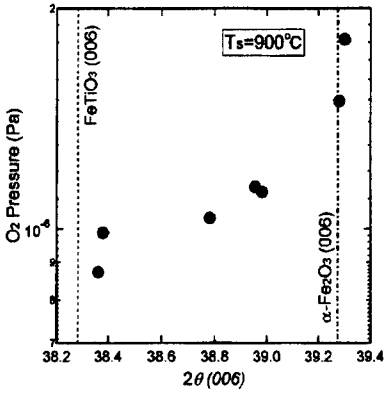

Figure 4. 2θ values for $FeTiO_{3+\delta}$ films prepared at 900°C as a function of the oxygen pressure during the sputtering deposition.

changed to magnetically split sextet patterns at higher oxygen pressure. The Néel temperature of sample films increased gradually above room temperature. Moreover the valence states of Fe ions evaluated from the Mössbauer isomer shifts changed from Fe^{2+} to Fe^{3+} with increasing the oxygen pressure. Fe^{3+} (S=5/2) ions had a larger spin magnetic moment than Fe^{2+} (S=2) ions. Therefore the formation of Fe^{3+} ions from Fe^{2+} ions raised the Néel temperature of the films.

The increased oxygen pressure and the decreased substrate temperature seemed to produce same effects on the iron valence states of the $FeTiO_{3+\delta}$ films. However the 2θ values of $FeTiO_{3+\delta}$(006) gave the contrary results depending on the respective preparation conditions. The oxidized films owing to the increased oxygen pressure showed the increased the 2θ values, while the films prepared at the decreased substrate temperature had the decreased 2θ values. This contradictory was probably due to the inferior crystallinity of the $FeTiO_{3+\delta}$ films prepared at lower

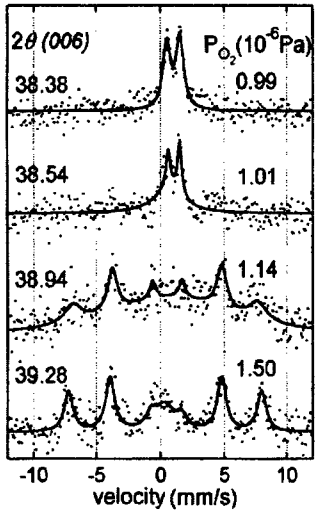

Table II. Fitted parameters for CEMS spectra shown in Fig. 5.

2θ value (deg.)	Isomer shifts (mm/s)	Quadropole splitting (mm/s)	Hyperfine field (kOe)
38.38	1.02	1.01	-
38.54	0.82	0.88	-
38.94	0.50	-	449.9
39.28	0.40	-	470.5

Figure 5. Room temperature CEMS spectra of $FeTiO_{3+\delta}$ films prepared at different oxygen pressures.

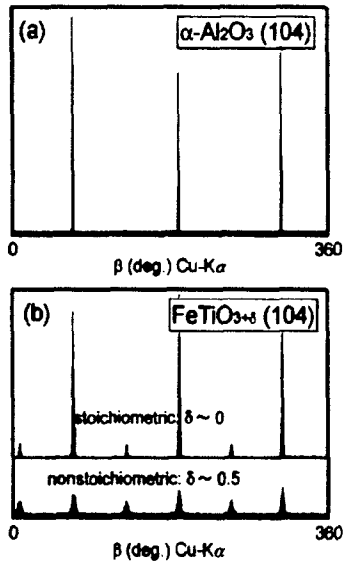

Figure 6. β-scan profiles for (104) pole figures of (a) an α-Al_2O_3 substrate and (b) stoichiometric and nonstoichiometric $FeTiO_{3+\delta}$ films.

substrate temperature. The films prepared at lower substrate temperature earned small crystallization energy and loosened the lattice structures. The inferior crystallinity of sample films maintained the paramagnetic properties though the films contained Fe^{3+} ions with larger spin magnetic moment.

Crystal Structure

It was very interesting to know the crystal structure of nonstoichiometric $FeTiO_{3+\delta}$. In oxidation studies of $FeTiO_3$ bulk crystals, nonstoichiometric $FeTiO_{3+\delta}$ easily decomposed into stable phases of Fe_2TiO_5 and TiO_2, or $Fe_2Ti_3O_9$ and Fe_2O_3 [8]. As far as we know, the nonstoichiometric $FeTiO_{3+\delta}$ was not observed in a bulk form. An epitaxial relationship between the α-Al_2O_3 substrate and the $FeTiO_{3+\delta}$ film was obtained by XRD pole figures. Fig.6 shows the β-scan profiles of (104) diffraction lines for the α-Al_2O_3 substrate, the stoichiometric $Fe^{2+}TiO_3$ film, and the nonstoichiometric $Fe^{3+}TiO_{3+\delta}$ film. According to the crystal symmetries of corundum and ilmenite structures, the (104) poles should have three-hold symmetry and appeared in every 120° for β-scan. The β-scan profiles clearly suggested that the stoichiometric $FeTiO_3$ film had nearly the same in-plane symmetry as that for the corundum or ilmenite structure. However the (104) poles for the nonstoichiometric $FeTiO_{3+\delta}$ film had six-hold symmetry because the diffraction lines appeared in every 60°. The change of in-plane symmetry for nonstoichiometric $FeTiO_{3+\delta}$ suggested the redistribution of cation occupancies in octahedral interstices of hcp oxygen layers. $Fe^{3+}$and Ti^{4+} ions randomly occupied both interstitial and substitution sites in the ilmenite-related structure. And cation vacancies were introduced into the structure to maintain the charge neutrality. The disordered cation occupancies we proposed here were already reported in Sn-, Ti-, and Mg-substituted α-Fe_2O_3 [9].

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