Transactions of the Materials Research Society of Japan 32[1] 83-86 (2007)

Electronic and Structural Properties of $La_2Ti_2O_7$ Thin Films Prepared on $SrTiO_3$ Substrates

Mitsuru Wakui, Tohru Higuchi, Makoto Satake, Kou Tanaka, Takeshi Hattori and Takeyo Tsukamoto
Department of Applied Physics, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan,
Fax: 81-3-3260-4772, e-mail: higuchi@rs.kagu.tus.ac.jp

Pyrochlore-type ferroelectric $La_2Ti_2O_7$ thin films were prepared on $SrTiO_3$ (100) substrate by metalorganic deposition. The high-quality $La_2Ti_2O_7$ thin film was obtained using pre-crystallization, which keeps at 660°C for 5 min before final crystallization from 700 to 1100°C. The $La_2Ti_2O_7$ thin film crystallized at 900°C consisted of small surface roughness of 3 nm and small grain size with a diameter of 100 nm against the film thickness of 400 nm. The valence band measured by soft-X-ray emission spectroscopy, which reflects the electronic structure in the bulk state, accords with band calculation of $La_2Ti_2O_7$. The resistivity was approximately 10^9 Ω. These findings are considered to be due to the activation of nuclear creation for growth of thin film with pre-crystallization.

Key words: $La_2Ti_2O_7$ thin film, metalorganic deposition (MOD), interface, pre-crystallization, electronic structure

1. INTRODUCTION

$La_2Ti_2O_7$, which belongs to the point group of $P2_1$ at room temperature, is ferroelectric oxide with a monoclinic structure [1-4]. The lattice constants of *a*-, *b*- and *c*-axes are 13.01 Å, 5.55 Å and 7.81 Å, respectively. The $La_2Ti_2O_7$ crystal has the spontaneous polarization of 5 $\mu C/cm^2$ and dielectric constant of 50. With further research, applications of $La_2Ti_2O_7$ as catalysts, high temperature transducers, and hosts of fluorescence centers have been reported [5,6]. Furthermore, it also shows a low dielectric loss at microwave frequencies. However, $La_2Ti_2O_7$ has a high melting point, which leads to the difficulty in the single crystal growth [7-10].

In recent years, Li *et al.* and co-workers have prepared the $La_2Ti_2O_7$ thin film on $Pt/Ti/SiO_2/Si$ substrate by chemical solution deposition [11]. They used low electric field for annealing of the thin film. This applied low electric field annealing was significant influence on the structure and surface morphologies. Furthermore, the applied low electric field decreases crystallization temperature by 50~100°C. However, the thin film exhibited a random orientation and consisted of large grain with diameter of 300 nm against the film thickness of 400 nm. Therefore, it is necessary to probe a new process for crystallization of $La_2Ti_2O_7$ thin film.

In this study, the $La_2Ti_2O_7$ thin films have prepared on $SrTiO_3$ (100) substrates by metalorganic deposition (MOD) and characterized their structural properties. In order to obtain high quality thin film, a pre-crystallization process was added in normal MOD process. The thin film was prepared using pre-crystallization, which keeps at 660°C before final crystallization. In this paper, we report that the pre-crystallization is effective for crystallization of high-quality $La_2Ti_2O_7$ thin film with small grain and very smooth surface.

2. EXPERIMENTAL

The precursor materials used to prepare the MOD solution were lanthanum nitrate hydrate $La(NO_3)_3 \cdot 6H_2O$ and *n*-tetrabutyl titanate $(C_4H_9O)_4Ti$. $La(NO_3)_3 \cdot 6H_2O$ dissolved into 2-methexythnol and acetic acid. The desired amount of $(C_4H_9O)_4Ti$ was added into the solution with continuous stirring until the homogeneous solution was formed. Finally, the 0.2 mol/l stock solution with viscosity of 6 cps was obtained. Slight amount of acetyl acetone was used to stabilize the precursor solution as the chelated agent. The substrate used $SrTiO_3$ (100) single crystal. The thin films were spin-coated with the mixed solutions at 3000 rpm for 50 s. The spin-coated films were dried at 250°C for 5 min and crystallized at 400°C for 10 min. Then, the $La_2Ti_2O_7$ thin films were sintered at the temperature region of 600 and 1100°C for 10 min in a tube furnace in O_2 for crystallization.

The decomposition characteristics of the precursor were investigated by the thermogravimetric and differential thermo analysis (TG-DTA). The structural properties of the $La_2Ti_2O_7$ thin films were characterized by XRD. Surface morphology was observed by AFM. Electrical structure was measured using impedance analyzer. SXES was carried out at the revolver undulator beamline BL-19B at the Photon Factory (PF) of the High Energy Accelerator Organization (KEK), in Tsukuba, Japan. High brightness and high resolution were realized using a varied-line-spacing plane grating monochromator. The SXES spectra were measured by a soft-X-ray emission spectrometer [12-13]. The spectrometer used the Rowland circle geometry that consisted of a grating with

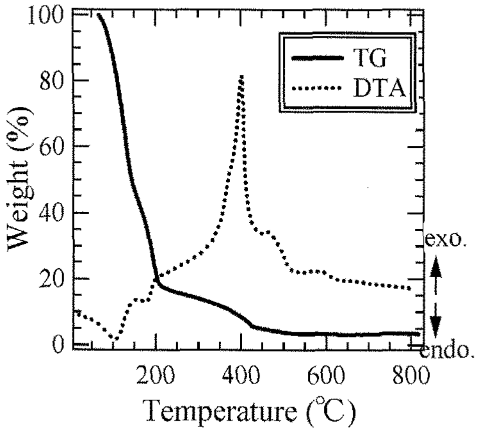

Fig. 1: TG-DTA curves of $La_2Ti_2O_7$ MOD solution heated with a ramp rate 10°C/min in air.

a groove density of 300 lines/mm and a Cs-coated multichannel detector. The total resolution of the SXES spectrometer was approximately 0.4 eV at *hv*=450 eV. The incidence angle of the soft-X-ray was set at approximately 75° against to the surface in order to avoid the surface effect.

3. RESULTS AND DISCUSIONS

Figure 1 shows the TG-DTA curves of the $La_2Ti_2O_7$ MOD solution heated from room temperature to 1200°C with a ramp rate of 10°C/min. It can be seen that the dramatic weight loss below 400°C is due to the severe decomposition and burning of lanthanum nitrate and organic components, which conforms to several large exothermic peaks, especially the sharp one at around 380°C. Between 450°C and 800°C, the weight basically keeps constant.

Figure 2 shows the XRD patterns as a function of crystallization temperature in $La_2Ti_2O_7$ thin film of direct crystallization, which pre-crystallization was not carried out. Two peaks at 22.5 ° and 47 ° are (100) and (200), respectively, of $SrTiO_3$ substrate. The $La_2Ti_2O_7$ thin film is not crystallized at 600°C. Above the crystallization temperature of 700°C, the

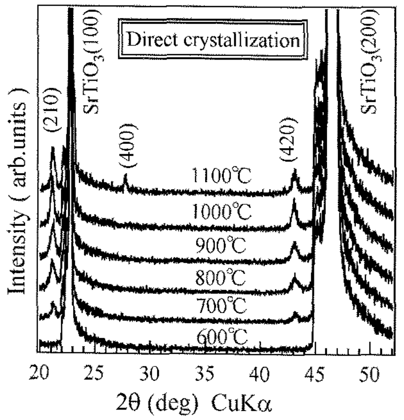

Fig. 2: XRD patterns as a function of crystallization temperature in $La_2Ti_2O_7$ thin films prepared by direct crystallization.

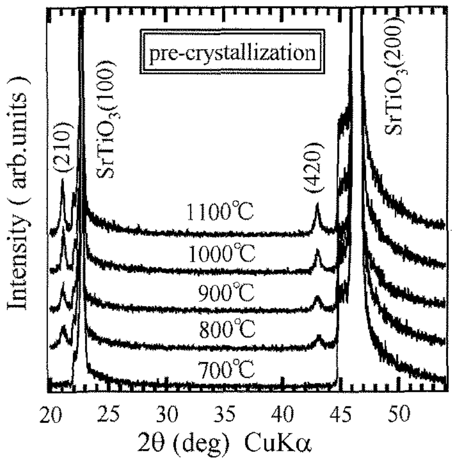

Fig. 3: XRD patterns as a function of crystallization temperature in pre-crystallized $La_2Ti_2O_7$ thin films.

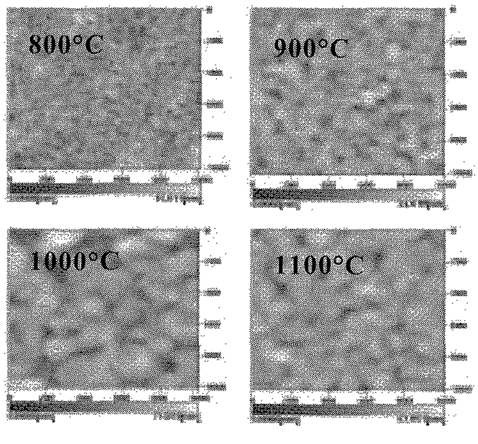

Fig. 4: AFM images as a function of crystallization temperature in pre-crystallized $La_2Ti_2O_7$ thin films.

$La_2Ti_2O_7$ thin films exhibit (210), (400) and (420) peaks. These intensities increase with increasing the crystallization temperature.

Figure 3 shows the XRD patterns as a function of crystallization temperature in pre-crystallized $La_2Ti_2O_7$ thin film. The pre-crystallization was carried out at 660°C for 5 min in O_2 atmosphere. After the pre-crystallization, the $La_2Ti_2O_7$ thin film was crystallized at the temperature from 700 to 1100°C. The thin film prepared at 700°C is not crystallized. Above the crystallization temperature of 800°C, the thin films exhibit the existences of (210) and (420) peaks. These intensities increase with increasing crystallization temperature. Furthermore, the peak width of pre-crystallized thin film is narrower than that of direct crystallized thin film shown in Fig. 2. This may indicate that the crystallization of $La_2Ti_2O_7$ thin film is improved by pre-crystallization.

Figure 4 shows the AFM images as a function of crystallization temperature in $La_2Ti_2O_7$ thin film of Fig. 3. The thin film prepared at 800°C is a poor crystallization. Above 800°C, the thin films consist of grain with diameter of 100~150 nm, although the grain size depends on the crystallization temperature.

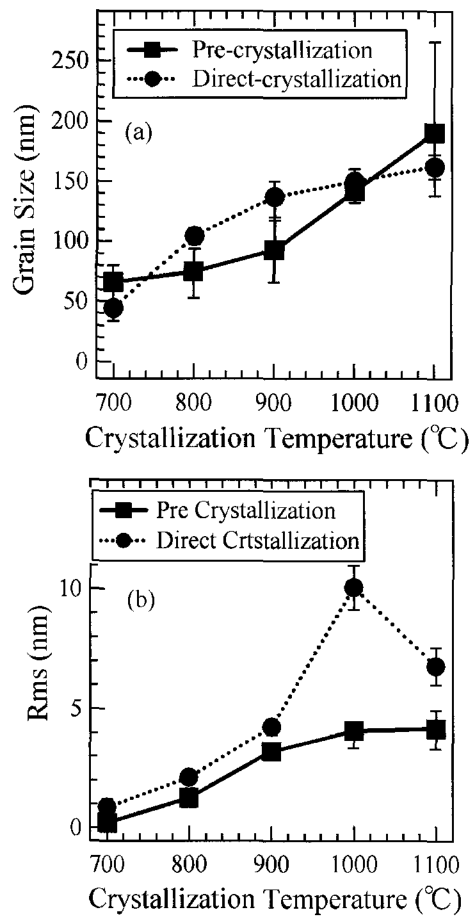

Fig. 5: (a) Grain size and (b) surface roughness as functions of crystallization temperature in pre-crystallized $La_2Ti_2O_7$ thin films. Solid (closed square) and dashed (closed circle) lines are pre-crystallization and direct crystallization, respectively.

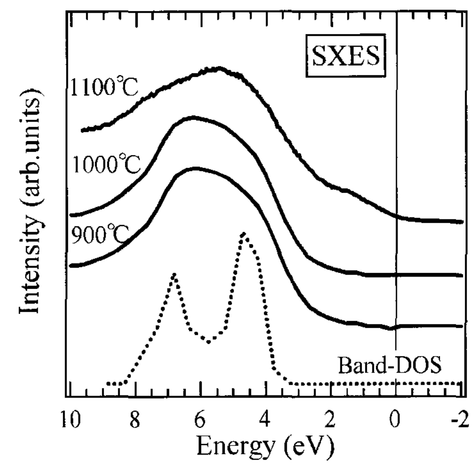

Fig. 6: SXES spectra in the valence band region as a function of crystallization temperature in pre-crystallized $La_2Ti_2O_7$ thin films. As reference, the ban calculation is also shown as dashed line.

Figure 5(a) shows the grain size as a function of crystallization temperature in pre-crystallized $La_2Ti_2O_7$ thin film. As a reference, the grain size of direct crystallized $La_2Ti_2O_7$ thin film is also shown. Although the grain sizes of both crystallized $La_2Ti_2O_7$ thin films increase with increasing crystallization temperature, the grain size of pre-crystallized $La_2Ti_2O_7$ at 900°C is relatively small. This result is clear from Fig. 4. On the other hand, the R_{ms} as a function of crystallization temperature in pre-crystallized $La_2Ti_2O_7$ thin film is shown in Fig. 5(b). The R_{ms} of pre-crystallized $La_2Ti_2O_7$ thin film is lower than that of direct-crystallized $La_2Ti_2O_7$ thin film. The R_{ms} of pre-crystallized $La_2Ti_2O_7$ thin film does not depend on the crystallization temperature above 900°C. From these results, the pre-crystallized $La_2Ti_2O_7$ thin film at 900°C is relatively good film, which consisted of small grain with a diameter of 100 nm and very smooth surface.

Figure 6 shows the O 1*s* SXES spectra as a function of crystallization temperature in pre-crystallized $La_2Ti_2O_7$ thin film. As a reference, the DOS by band calculation is also shown as dashed line. The SXES spectra reflect the electronic structure of the bulk state [14], because the mean free path of a soft-X-ray is very long compared with that of an electron. The clear selection rule of SXES is caused mainly within the same atomic species, because the core hole is strongly localized. For this reason, the O 1*s* SXES spectra reflect the O 2*p* PDOS. The obtained O 2*p* PDOS corresponds to the band structure in the valence band region, since the valence band of $La_2Ti_2O_7$ is mainly composed of O 2*p*. The bottom axis is relative energy from Fermi level (E_F=0 eV).

The $La_2Ti_2O_7$ thin film prepared at 1100°C has the DOS in the band gap energy region. This indicates the metallic state of the thin film with high crystallization temperature. On the other hand, the valence bands of $La_2Ti_2O_7$ thin films prepared at 900 and 1000°C are in agreement with the band calculation. Furthermore, there is no structure in the band gap region of thin films prepared at 900 and 1000°C. In particular, the electrical resistivity of thin film prepared at 900°C is approximately ~10^9 Ω, which corresponds to the bulk crystal [11].

4. CONCLUSIONS

We have prepared the $La_2Ti_2O_7$ thin films on $SrTiO_3$ (100) substrate by metalorganic deposition. The high-quality $La_2Ti_2O_7$ thin film was obtained using pre-crystallization, which keeps at 660°C for 5 min before crystallization from 700 to 1100°C. The pre-crystallized $La_2Ti_2O_7$ thin film crystallized at 900°C consisted of small surface roughness of 3 nm and small grain size with a diameter of 100 nm against film thickness of 400 nm. The valence band estimated from SXES spectrum accords with band calculation of $La_2Ti_2O_7$. The resistivity was approximately 10^9 Ω. These findings are considered to be due to the optimization of nuclear creation for growth of thin film with pre-crystallization.

ACKNOWLEDGEMENTS

We would like to Professor S. Shin of University of Tokyo for his useful discussion.

REFERENCES

[1] W. R. Cock Jr. and H. Jaffe: Phys. Rev. B **88** (1952) 1426.
[2] R. S. Roth: J. Res, Natl. Bur. Stand. **56** (1956) 17.
[3] S. Nanamatsu, M. Kimura, K. Doi, S. Matsushita and N. Yamada: Ferroelectrics **8** (1974) 511.
[4] M. Kimura, S. Nanamatsu, T. Kawamura and S. Matsushita: Jpn. J. Appl. Phys. **13** (1974) 147.
[5] R. A. McCuley, F. A. Hummel: J. Lumin. **6** (1973) 105.
[6] R. A. McCuley: J. Appl. Phys. **51** (1980) 290.
[7] L. G. Shcherbakova, L. G. Mamsurova and G. E. Sukhanova: Russ. Chem. Rev. **48** (1979) 288.
[8] J. Takahashi and T. Ohtsuka: J. Am. Ceram. Soc. **72** (1989) 426.
[9] U. Balachandran and N.G. Eror: J. Mater. Res. **4** (1989) 1525.
[10] E.B. Panasenko and R.G. Beyunora: Russ. J. Chem. **29** (1984) 1430.
[11] A-D. Li, Y-J. Wang, S. Huang, J-B. Cheng, D. Wu and N-B. Ming: J. Cryst. Growth **268** (2004) 198.
[12] Y. Harada, T. Kinugasa, R. Eguchi, M. Matsubara, A. Kotani, M. Watanabe, A. Yagishita and S. Shin: Phys. Rev. B **61** (2000) 12854.
[13] T. Higuchi, T. Tsukamoto, M. Watanabe, M. M. Grush, T. A. Callcott, R. C. Perera, D. L. Ederer, Y. Tokura, Y. Harada, Y. Tezuka and S. Shin: Phys. Rev. B **60** (1999) 7711.
[14] T. Higuchi, Y. Moriuchi, Y. Noguchi, M. Miyayama, S. Shin and T. Tsukamoto: Jpn. J. Appl. Phys. **42** (2003) 6226.

(Received December 19, 2006;Accepted January 11, 2007)