

# X-ray photoelectron spectroscopic and secondary ion mass spectroscopic examinations of metallic-lithium-activated donor doping process on $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$ surface at room temperature

Kai-Yun Yang and Kuan-Zong Fung

Department of Materials Science and Engineering, National Cheng Kung University, No. 1, Ta-Hsueh Road, Tainan 70101, Taiwan

Moo-Chin Wang<sup>a)</sup>

Faculty of Fragrance and Cosmetics, Kaohsiung Medical University, 100 Shi-Chuan 1st Road, Kaohsiung 807, Taiwan

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The donor doping process at the interface between the cation-deficient  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  and lithium was elucidated by x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). XPS revealed a chemical shift ( $\sim 1.48$  eV) from the main peak of  $\text{Ti}^{4+} 2p_{3/2}$  toward the low energy side, due to the conversion of 12%  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ . The SIMS analysis indicates that a local electric field was responsible for the insertion of oxidized  $^6\text{Li}^+$  isotope ions. The doping with  $\text{Ti}^{3+}$  donors, accompanying the insertion of  $\text{Li}^+$  ions into cation vacancies of  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$ , yields the *n*-type semiconducting characteristics at room temperature. © 2006 American Institute of Physics. [DOI: 10.1063/1.2337787]

Perovskite-type  $(\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x})\text{TiO}_3$  (LLT) (where  $\square$  represents a  $\text{La}^{3+}/\text{Li}^+$ -site vacancy;  $0.04 \leq x \leq 0.17$ ) oxides have become attractive candidate solid electrolytes for use in all-solid-state lithium batteries because of their high ionic conductivity (i.e.,  $10^{-3}$ – $10^{-4}$  S/cm) and low electronic conductivity ( $< 10^{-8}$  S/cm) as reported by Belous *et al.*<sup>1</sup> However, Inaguma *et al.*<sup>2</sup> found that their use as electrolytes was unfavorable because LLT are not stable in direct contact with metallic lithium anodes at room temperature (RT), perhaps because  $\text{Ti}^{4+}$  ions are converted to  $\text{Ti}^{3+}$  ions when  $\text{Li}^+$  ions are inserted into vacant sites, increasing electronic conductivity.

Most studies in this field have focused on the electrochemical stability/instability of LLT when an electrochemical method is used to intercalate  $\text{Li}^+$  ions into LLT.<sup>3–5</sup> The suggested conversion of  $\text{Ti}^{4+}$  electronic structure to a lower valence of +3 in the chemical interfacial instability between LLT and metallic lithium is believed to be the same as that in electrochemical instability. This conversion has been rationalized by the classical sense or understood based on evidence of raised electronic conductivity<sup>2</sup> and other indirect support of the lattice's self-potential, the site potential, and the lattice energy calculation.<sup>5</sup> However, actual scientific evidence of the chemical instability between LLT and metallic lithium is lacking.

This work identifies the mechanism of interfacial instability between cation-deficient  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  and metallic lithium at RT using x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS), and clarifies a metallic-lithium-activated donor doping process on the  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  surface. The results provide a better understanding than the classical sense in this area, and support an

improved approach for enhancing the semiconductivity of oxides.

The 11%  $\text{La}^{3+}/\text{Li}^+$ -site vacant  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  ( $x=0.11$  in LLT) powder was prepared by a solid state reaction method. The stoichiometric powders of  $\text{La}_2\text{O}_3$  (99.99% purity),  $\text{Li}_2\text{CO}_3$  (99.4% purity), and  $\text{TiO}_2$  (>99% purity) were calcined at 1200 °C for 12 h in air. The samples were sintered at 1250 °C for 8 h. Prior to reaction with metallic lithium, the surfaces of the samples were polished with 0.3  $\mu\text{m}$  diamond pastes. Then, the lithium foil was pressed onto the polished surface of the sample and held for 24 h in argon at RT.

XPS characterization was conducted using an ESCALAB 250 spectrometer with an Al target. The energy resolution reached up to 20 meV. Moreover, the binding energy scale was calibrated by a C 1s peak at 285.00 eV. Atomic analysis was performed by using an IMS-4f mass spectrometer to give the elemental depth profiles by  $\text{O}_2^+$  ion bombardment.

Curve 1 in Fig. 1(a) is the La 3d core spectrum of the  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  sample before it reacted with lithium. Spin-orbital splittings of La  $3d_{5/2}$  and La  $3d_{3/2}$  are observed at binding energies of 834.97 and 851.24 eV, respectively, caused by  $\text{La}^{3+}$ .<sup>6</sup> The satellite lines at high binding energy are separated from the main peaks of the  $3d_{5/2}$  and  $3d_{3/2}$  levels by 4.42 and 4.45 eV, respectively. These results are due to monopole excitation caused by a sudden change in the screening of the valence electrons upon the removal of a core electron.<sup>7,8</sup> Curve 2 in Fig. 1(a) is the La 3d core level spectrum of the  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  sample after a reaction with lithium. These binding energies of  $\text{La}^{3+} 3d_{5/2}$  and  $\text{La}^{3+} 3d_{3/2}$  electrons are similar to those obtained prior to the reaction [curve 1 in Fig. 1(a)], because the electronic structure of the  $\text{La}^{3+}$  ions at the local  $\text{La}^{3+}/\text{Li}^+$  sites is unchanged by the reaction with highly active metallic lithium, so the La 3d

<sup>a)</sup>Author to whom correspondence should be addressed; FAX: (886)62502734; electronic mail: mcwang@kmu.edu.tw

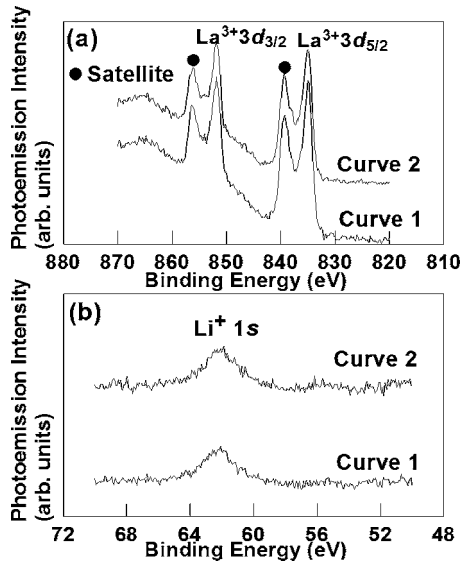


FIG. 1. XPS spectra of the (a) La 3d and (b) Li 1s core levels. Curve 1: before reaction; curve 2: after reaction for 24 h.

core levels are not significantly chemically shifted.

Figure 1(b) presents the XPS spectra of the Li 1s core level for the  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  sample before (curve 1) and after (curve 2) its reaction with lithium. The binding energies of the Li 1s before and after the reaction are equal (61.69 eV) to those in the monovalent chemical state, indicating that the state of the  $\text{Li}^+$  ion does not change at the  $\text{La}^{3+}/\text{Li}^+$  site, and that no  $\text{Li}^0$  atoms are present in the structure.

Figure 2(a) displays the XPS spectra of the Ti 2p core levels before (curve 1) and after (curve 2) the reaction of the  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  sample with metallic lithium. Curve 1 has a narrow  $\text{Ti}^{4+} 2p_{3/2}$  peak at a binding energy of 458.57 eV with a full width at half maximum (FWHM) of 1.18 eV. A small shoulder is present approximately 5.73 eV above the energy of the main peak, which corresponds to the  $\text{Ti}^{4+} 2p_{1/2}$ .

Curve 2 in Fig. 2(a) shows that, after the reaction with lithium, the binding energies of the  $\text{Ti}^{4+} 2p_{3/2}$  and  $\text{Ti}^{4+} 2p_{1/2}$  are the same as those in curve 1; additionally, two small shoulders are present on the low-binding-energy sides of the respective  $\text{Ti}^{4+} 2p_{3/2}$  and  $\text{Ti}^{4+} 2p_{1/2}$  peaks: they are separated from the main peak by approximately 1.48 and 1.45 eV, respectively, which is ascribed to the presence of  $\text{Ti}^{3+} 2p_{3/2}$  and  $\text{Ti}^{3+} 2p_{1/2}$  electrons. The chemical shift of 1.48 or 1.45 eV is caused by a significant valence electron transition from tetravalent  $\text{Ti}^{4+}$  to trivalent  $\text{Ti}^{3+}$  ions at the interface when the  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  sample directly reacts with the lithium.

Rao and Sarma<sup>9</sup> reported that the binding energy of  $\text{Ti}^{3+} 2p_{3/2}$  is lower than that of the main peak by approximately 1 eV in the Ti 2p XPS spectra of  $\text{Ti}_4\text{O}_7$  and  $\text{Ti}_3\text{O}_5$ . Moreover, the binding energy shift of 1.4 eV from the main peak to the low-binding-energy side is characteristic of  $\text{Ti}^{3+}$  defects, as reported by Guillemot *et al.*<sup>10</sup> Larger shifts of 3.1 and 4.0 eV are typically associated with  $\text{Ti}^{2+}$  and  $\text{Ti}^0$  states,<sup>11</sup> respectively, but they are not observed in Fig. 2(a). Accordingly, trivalent defects can be determined to be the only contributors to Ti 2p peak broadening; metallic lithium activates

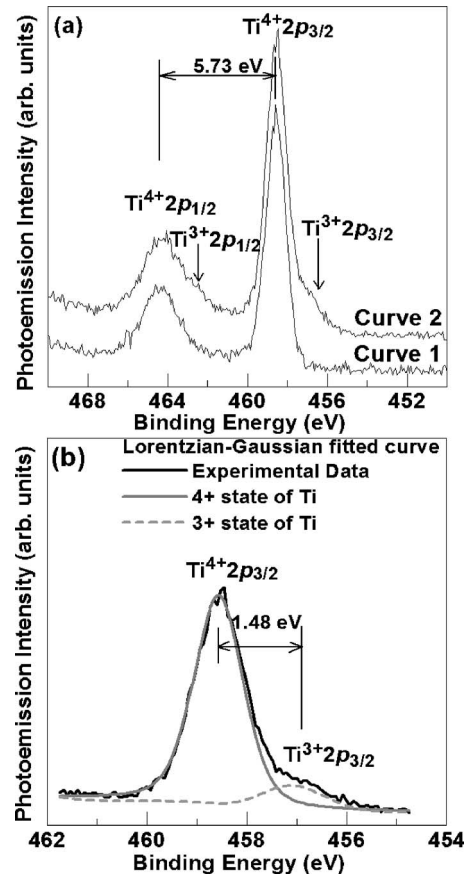


FIG. 2. (a) XPS spectra of the Ti 2p core level and (b) Gaussian-Lorentzian curve fitting of the  $\text{Ti}^{4+} 2p_{3/2}$  and  $\text{Ti}^{3+} 2p_{3/2}$  core levels.

$\text{Ti}^{3+}$  donor doping on the  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  surface at room temperature.

The concentration of the trivalent  $\text{Ti}^{3+}$  ions at Ti sites was determined from the results of Gaussian-Lorentzian curve fitting of the  $\text{Ti}^{4+} 2p_{3/2}$  peak, as presented in Fig. 2(b). The integral intensity of the  $\text{Ti}^{3+} 2p_{3/2}$  peak at 457.09 eV to that of the  $\text{Ti}^{4+} 2p_{3/2}$  at 458.57 eV yields a concentration of trivalent  $\text{Ti}^{3+}$  of approximately 12%. We suggest that the  $\text{La}^{3+}/\text{Li}^+$ -site vacancies limit the number of  $\text{Ti}^{3+}$  donors, and the doped  $\text{La}_{0.56}\text{Li}_{0.33}(\text{Ti}^{4+})\text{O}_3$  becomes the *n*-type semiconductor,  $\text{La}_{0.56}\text{Li}_x(\text{Ti}^{3+})_{0.12}(\text{Ti}^{4+})_{0.88}\text{O}_3$ . The increase in the electronic conductivity to  $10^{-2}$  S/cm reported by Inaguma *et al.*<sup>2</sup> supports this latter suggestion.

When 12%  $\text{Ti}^{4+}$  ions are converted to  $\text{Ti}^{3+}$  ions in the  $\text{La}^{3+}/\text{Li}^+$ -site vacant material, the charge is balanced via two possible routes: (i) the generation of positively charged oxygen vacancies or (ii) the insertion of  $\text{Li}^+$  ions into  $\text{La}^{3+}/\text{Li}^+$ -site vacancies.

After a tracer isotope of  $^6\text{Li}$  metal was placed in contact with  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  for 24 h, SIMS was used to measure the ion distribution of  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  as a function of depth. Figure 3(a) depicts the depth profiles of  $\text{La}^{3+}$ ,  $^6\text{Li}^+$ ,  $^7\text{Li}^+$ , and  $\text{Ti}^{4+}$  ions. The intensities of  $^7\text{Li}^+$ ,  $\text{La}^{3+}$ , and  $\text{Ti}^{4+}$  remain almost constant, whereas the  $^6\text{Li}^+$  count declines with distance from the interface; this phenomenon is caused by the insertion and diffusion of  $\text{Li}^+$  ions, and demonstrates that charge was balanced through the insertion of  $\text{Li}^+$  ions into  $\text{La}^{3+}/\text{Li}^+$ -site vacancies.

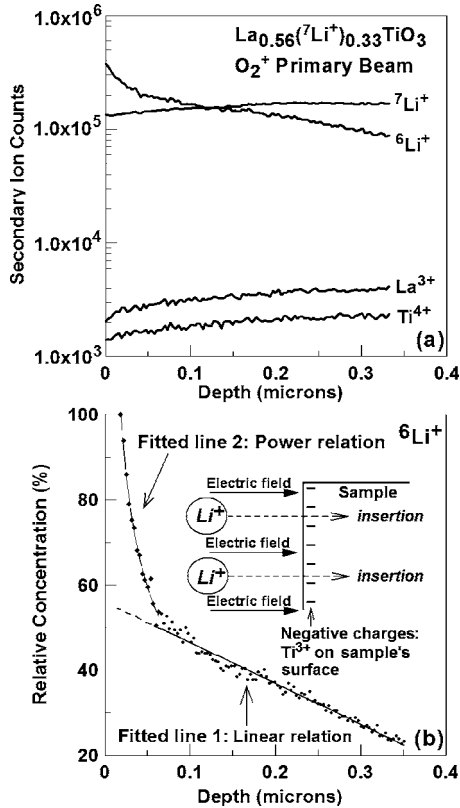
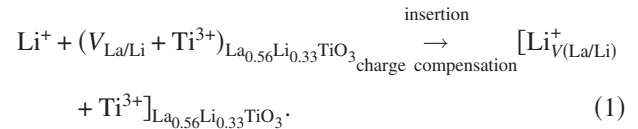


FIG. 3. (a) Depth profiles of  $\text{La}^{3+}$ ,  ${}^7\text{Li}^+$ ,  ${}^6\text{Li}^+$ , and  $\text{Ti}^{4+}$  ions in  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  as measured by SIMS. (b)  ${}^6\text{Li}^+$  distribution behavior: diffusion (fitted line 1) and insertion (fitted line 2).

If only diffusion occurred over a long period at the interface between the reacting materials, then a plot of the diffused ion concentration against depth would be linear. Fitted line 1 in Fig. 3(b) reveals the pure diffusion of  ${}^6\text{Li}^+$  ions into  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$ ; however, fitted line 2 reveals another distribution mode of the  ${}^6\text{Li}^+$  ions with an abnormally high concentration near the contact surface, indicating a driving force that induces the insertion of  $\text{Li}^+$  ions. When the surface  $\text{Ti}^{4+}$  ions are converted to  $\text{Ti}^{3+}$  ions, the surface negative charges ( $\text{Ti}^{3+}$ : electron at  $\text{Ti}^{4+}$  site) set up an electric field until the surface charges are balanced, as shown in Fig. 3(b). Through the  ${}^6\text{Li}^+$  tracing, fitted line 2 shows that the depth affected by the electric field is ca.  $0.25\ \mu\text{m}$ ; thus, the effect of the electric field is localized near the  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$ /metallic lithium interface. The local electric field drives the insertion of the oxidized  ${}^6\text{Li}^+$  ions from the contact surface into the crystal. The distribution of highly concentrated  ${}^6\text{Li}^+$  also indicates that the insertion rate exceeds the subsequent diffusion rate so the  $\text{Li}^+$  ions accumulated in the near-surface layer. Charge compensation involves the insertion of  $\text{Li}^+$  ions into  $\text{La}^{3+}/\text{Li}^+$ -site vacancies

( $V_{\text{La/Li}}$ ), which is described as the charge balance mechanism,



Based on Eq. (1), the defective ( $\text{La}_{0.56}\text{Li}_{0.33}\square_{0.11}$ ) $\text{TiO}_3$  provides only 11% of these  $\text{La}^{3+}/\text{Li}^+$ -site vacancies for the local-electric-field-induced insertion of  $\text{Li}^+$  and so 11% of the tetravalent  $\text{Ti}^{4+}$  ions are available for conversion to trivalent  $\text{Ti}^{3+}$  ions on the contact surface. The XPS results indicate that the number of trivalent  $\text{Ti}^{3+}$  donors (12%) is approximately the number of  $\text{La}^{3+}/\text{Li}^+$ -site vacancies (11%); also, the cation vacancies limit the number of  $\text{Ti}^{3+}$  dopants, further indicating that the variable  $(1/3-2x)$  vacancies of  $(\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x})\text{TiO}_3$  oxides control the doping amount of  $\text{Ti}^{3+}$  donors.

In summary, the interfacial reaction between  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  and metallic lithium was identified by XPS and SIMS, respectively, as the metallic-lithium-activated doping conversion from  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  donors and the subsequent local-electric-field-induced insertion of  $\text{Li}^+$  ions into the  $\text{La}^{3+}/\text{Li}^+$ -site vacancies of  $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$  to compensate for the Ti-site electrons; thus, the metallic-lithium-activated donor doping process *semiconductorized* the oxide to an *n*-type semiconductor, and the number of vacancies limited the doping amount of donors. Based on the above, the amount of doped  $\text{Ti}^{3+}$  donors can be controlled by changing the number of vacancies of the  $(\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x})\text{TiO}_3$  oxides.

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