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Reversible electrochemical modulation of the superconducting transition temperature of $LiTi_2O_4$ ultrathin films by ionic liquid gating

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We demonstrate in situ modulation of the superconducting transition temperature (T_c) of $LiTi_2O_4$ thin films by ionic liquid gating. 15 nm thick $LiTi_2O_4$ thin films grown on $MgAl_2O_4$ substrates with the pristine T_c of 11.5 K was patterned into electric double-layer transistor devices for gating using ionic liquid with or without Li^+ ions. The T_c of the $LiTi_2O_4$ thin film was found to decrease with a negative gate voltage for gating with either pure ionic liquid or Li^+ containing ionic liquid. On the other hand, the recovery of T_c is observed at a positive gate voltage only for gating with the Li^+ containing ionic liquid. The present observation suggests the possibility of reversible electrochemical modulation of superconducting properties by lithiation and delithiation. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4932551]

$LiTi_2O_4$ (LTO) has attracted much attention as it is the only known oxide superconductor with the spinel structure and it has a relatively high bulk superconducting transition temperature (T_c) of 13.7 K.[1] From the bulk studies of Li-rich $Li_{1+x}Ti_{2-x}O_4$ ($0 \leq x \leq 1/3$) solid solution and Li-poor $Li_{1-x}Ti_2O_4$, Li stoichiometry and Ti network disorder in this system are known to influence the superconducting properties.[1–5] LTO is also being explored as an anode material of Li-ion batteries because of its structural stability against electrochemical lithiation and delithiation in electrolyte.[6,7] These features indicate the possibility of modulation of superconducting properties by electrochemical processes in LTO.

Inducing superconductivity in non-superconducting materials and modulation of T_c in superconducting materials by electrostatic modulation of carrier density through ionic liquid (IL) gating have proven to be a powerful tool for studying the doping phase diagram of superconducting systems.[8–15] Recent IL gating experiments on other oxide films have also shown that in addition to electrostatic modulation, reversible oxidation and reduction through induced electrochemical reaction of oxygen ions also play an important role in modifying the properties of thin films.[16] Here, we report on reversible *in situ* modulation of the superconducting T_c of LTO thin films by gating using IL containing Li^+ ions.

We grew LTO films on $MgAl_2O_4$ (100) and (111) substrates by pulsed laser deposition. Previously, epitaxial LTO films with good superconducting properties have been demonstrated on $MgAl_2O_4$ substrates.[17–19] KrF excimer laser pulses (248 nm, 5 Hz) were focused on a $Li_4Ti_5O_{12}$ target at a fluence of 2 J/cm^2. Deposition of thin films was performed in high vacuum ($\sim 10^{-6}$ Torr) at a substrate temperature of 750 °C. Carrier concentration modulation of conducting films through an electric-field induced effect requires the film thickness to be of the order of the Thomas-Fermi screening length ($\sim$0.7 nm for our LTO films).[9] Given that different possible mechanisms might take place in modifying the transport properties of the films under IL gating,[16,20] we have elected to use 15 nm thick LTO, which were the thinnest films we could consistently obtain with good superconducting properties. We have found that it is important to use substrates with atomically flat surfaces to grow such films. In order to obtain flat substrate surfaces, $MgAl_2O_4$ (100) substrates were annealed at 1000 °C for 2 h in air prior to the deposition. X-ray diffraction (XRD) measurements were used to identify the lattice constant and the structural phase. The thickness of thin films was estimated by X-ray reflectometry. Atomic force microscopy (AFM) was used to observe the surface morphology of the substrate. Temperature dependence of resistivity (ρ vs. T) was measured by the four-terminal method with Au/Cr electrode dots deposited by thermal evaporation.

Figure 1(a) shows the typical AFM image of a $MgAl_2O_4$ (100) substrate after annealing it at 1000 °C in air for 2 h. It shows step and terrace structures, and the RMS roughness is 0.16 nm. The 15 nm LTO thin films grown on such smooth substrates showed the (400) peak in the XRD pattern as seen in Figure 1(b), indicating that single phase (100)-oriented films were obtained. The cube-on-cube epitaxial growth of the LTO thin films grown on the $MgAl_2O_4$ (100) substrates was confirmed by a φ-scan of a 180 nm thick LTO thin film.[19] The ρ(T) of the 15 nm LTO thin film (Figure 1(c)) shows metallic behavior at the normal state and a full superconducting transition at $T_{c0} \sim 11.5$ K. This result indicates that high quality LTO ultrathin films were achieved by annealing the (100)-oriented $MgAl_2O_4$ substrate. Similar quality films were also demonstrated on (111)-oriented substrates following the similar annealing procedure.[21]

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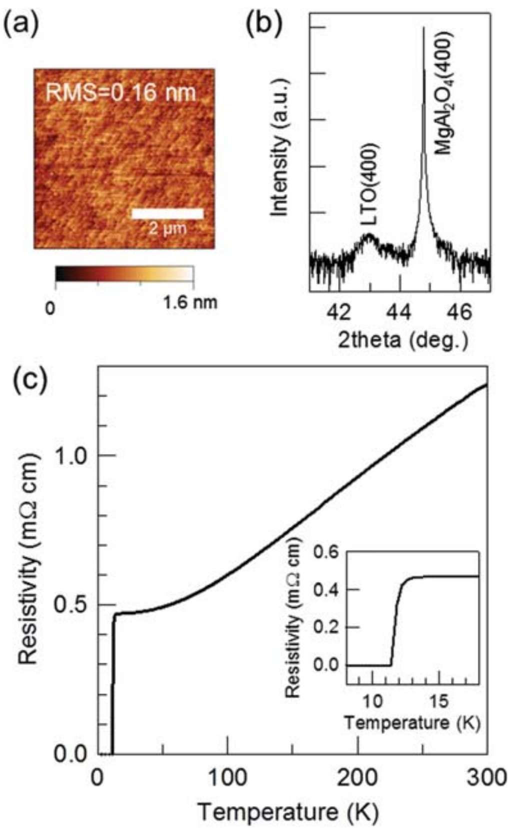

FIG. 1. (a) AFM image of a $MgAl_2O_4$ (100) substrate after annealed in air for 2 h at 1000 °C. (b) XRD pattern and (c) ρ-T curve of a 15 nm $LiTi_2O_4$ thin film grown on the annealed $MgAl_2O_4$ (100) substrate. The inset shows the magnified curve around the critical temperature.

Figures 2(a) and 2(b) show the optical view and a schematic illustration of the electrolyte gating device. Photolithography and ion milling were used to make a channel ($0.5 \times 0.7\,mm^2$) and a gate electrode ($5 \times 5\,mm^2$). Both the gate electrode and the channel area were covered by the electrolyte with a glass plate, which determines the contact area of the electrolyte. *N*,*N*-Diethyl-*N*-methyl-*N*–(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide ([DEME][TFSA]) and the mixture of [DEME][TFSA] with 0.33 mol/kg of lithium bis(trifluoromethanesulfonyl)amide ([Li][TFSA]) were used as electrolytes. Gate voltage (V_G) was applied at 230 K for 20 min and kept throughout the ρ-T curve measurements.

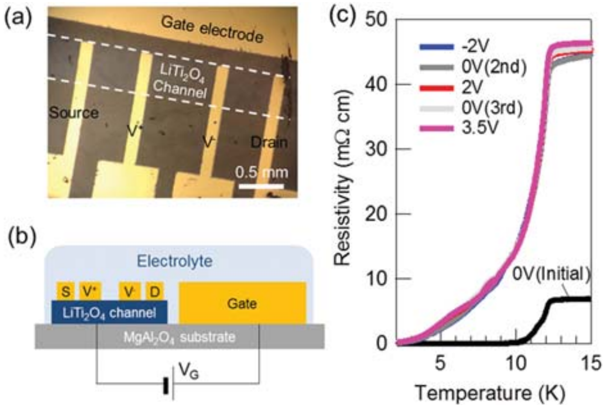

FIG. 2. (a) Optical microscope image and (b) a schematic cross-sectional illustration of the channel and the gate electrode. (c) Gate voltage dependence of ρ-T curve using [DEME][TFSA] as the gate electrolyte. The gate voltages were applied in the order of 0 V (Initial) → −2 V → 0 V (2nd) → +2 V → 0 V (3rd) → 3.5 V at 230 K.

Figure 2(c) shows ρ-T curves of the [DEME][TFSA] gated LTO thin films at different gate voltages. When $V_G = -2\,V$ was applied after the initial ρ-T measurement at $V_G = 0\,V$ (denoted as 0 V (Initial)), the normal state resistivity increased by about a factor of 6. The full transition was not observed down to 2 K, yet the onset of the transition temperature remained unchanged. The subsequent ρ-T curve at $V_G = 0\,V$ did not recover the initial 0 V state. Afterward, when we applied a positive V_G at +2 and +3.5 V following the initial measurement, the ρ-T curves below the superconducting onset were not changed, while the normal state resistivity at 200 K did decrease by ∼6% compared to the state with $V_G = -2\,V$. Such an irreversible process indicates an electrochemical effect at work instead of electrostatic doping. While the effect of oxygen ions cannot be definitively ruled out, we believe it is predominantly the delithiation of Li^+ ions from LTO thin film at the negative gate voltage, which are dissolved in the [DEME][TFSA] but not recovered at the positive gate voltage, due to the limited concentration of Li^+ ions in the electrolyte and the film.

To test this conjecture, we introduced [Li][TFSA] in the [DEME][TFSA] electrolyte. Figures 3(a) and 3(b) show ρ-T curves of LTO thin films in the mixture of [Li][TFSA] and [DEME][TFSA] at different V_G's. In this experiment, after the initial state 0 V, we applied the voltages in the following order: −1 V → 0 V → +2 V → −2 V → 0 V → + 2 V → 0 V → +3.5 V → 0 V. We have chosen this particular sequence to confirm that the gating mechanism is repeatable and that it is due to the electrochemical delithiation/lithiation process rather than an electrostatic one. If it were due to an electrostatic process, repeated zero gate voltage measurements following positive and negative V_G would result in the curve identical to the initial measurement at 0 V. We see that this is not the case. In the first part of the sequence (shown in Fig. 3(a)), we applied negative voltages (−1 V and −2 V) which reduced the T_c and increased resistivity. In between the negative voltages, we also checked the 0 V state, as well as one positive voltage (+2 V). Then, in the second half of the sequence, we applied positive voltages (shown in Fig. 3(b)), which resulted in recovery of T_c with a 0 V state in between.

Figure 3(c) summarizes the V_G dependence of the resistivity at 15 K (ρ_{15K}) and the T_c. While the T_c tends to decrease and ρ_{15K} tends to increase for negative V_G (and the subsequent zero V_G measurement), the T_c was found to recover and ρ_{15K} decreased for the positive V_G and the subsequent zero V_G measurement. Since we applied the gate voltages during the warming-up process to 230 K, the ρ-T curves of the $V_G = 0\,V$ after negative or positive V_G reflect the additional effect of V_G at above the melting temperature of the electrolyte. These behaviors can be understood as a result of delithiation and lithiation of the LTO thin film due to the electrochemical effect instead of the electrostatic effect. We would like to note that when the experiment was carried out with $V_G = 0\,V$, no difference was discerned between the cooling and heating curves even at above the melting temperature of the ionic liquid. This fact also indicates that just having the LTO film in contact with the ionic

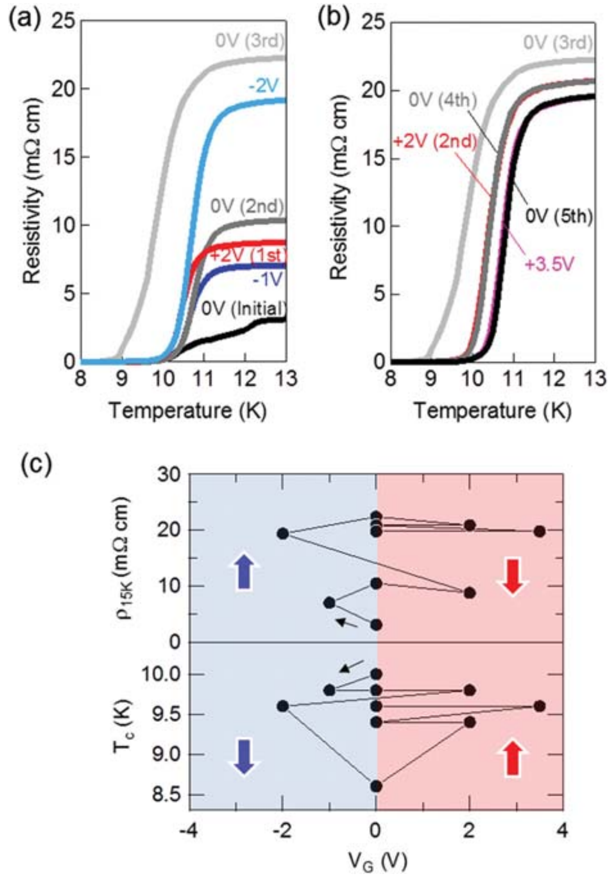

FIG. 3. Gate voltage dependence of ρ-T curve using [DEME][TFSA] containing [Li][TFSA] as the gate electrolyte. The gate voltages were applied in the order of (a) 0 V (initial) → −1 V → 0 V (2nd) → +2 V (1st) → −2 V → 0 V (3rd), (b) → +2 V (2nd) → 0 V (4th) → +3.5 V → 0 V (5th) at 230 K. (c) Summary of the gate voltage dependence of resistivity at 15 K and critical temperature.

liquid (with no finite gate voltage) does not lead to any changes.

Although delithiation from $LiTi_2O_4$ places the compound out of the range of the homogeneous stoichiometry in the $Li_{1+x}Ti_{2-x}O_4$ system,[1] we have observed the recovery of T_c, suggesting that the presence of extended structural stability in this system. In a previous systematic study of single crystal $Li_{1-x}Ti_2O_4$, the T_c was reported to vary in the range from 11.2 to 13.6 K for Li content from 1 to 0.89.[3,4] In those studies, disorder in the Ti network was found to play a dominant role in determining the T_c in delithiation for Li content of 0.86 and less, resulting in complete suppression of T_c. Therefore, the observed modulation of T_c in the present work might also be attributed to the change of the Ti network disorder by lithiation and delithiation.

In summary, we demonstrated modulation of the T_c of high-quality 15 nm LTO ultrathin films on $MgAl_2O_4$ (100) by the electrolyte gating technique using a Li^+ ion containing IL. The behavior of the ρ(T) with different gate voltages indicates that the electrochemical process, i.e., lithiation and delithiation of the LTO thin film, dominates the modulation. While further study is needed to understand the detailed electrochemical mechanism of the modulation, the present work implies the possibility of reversible *in situ* modulation of superconducting properties via an electrochemical route in a gating configuration.

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[1] D. C. Johnston, J. Low Temp. Phys. **25**, 145 (1976).
[2] M. R. Harrison, P. P. Edwards, and J. B. Goodenough, J. Solid State Chem. **54**, 136 (1984).
[3] E. Moshopoulou, P. Bordet, A. Sulpice, and J. J. Capponi, Phys. C Supercond. **235–240**, 747 (1994).
[4] E. G. Moshopoulou, J. Am. Ceram. Soc. **82**, 3317 (1999).
[5] X. G. Qiu, C. Z. Bi, J. Y. Ma, X. Fang, M. Kamran, and B. R. Zhao, Phys. C Supercond. **460–462**, 540 (2007).
[6] J. Yang, J. Zhao, Y. Chen, and Y. Li, Ionics **16**, 425 (2010).
[7] W. Ra, M. Nakayama, Y. Uchimoto, and M. Wakihara, J. Phys. Chem. B **109**, 1130 (2005).
[8] K. Ueno, S. Nakamura, H. Shimotani, A. Ohtomo, N. Kimura, T. Nojima, H. Aoki, Y. Iwasa, and M. Kawasaki, Nat. Mater. **7**, 855 (2008).
[9] J. T. Ye, S. Inoue, K. Kobayashi, Y. Kasahara, H. T. Yuan, H. Shimotani, and Y. Iwasa, Nat. Mater. **9**, 125 (2010).
[10] J. T. Ye, Y. J. Zhang, R. Akashi, M. S. Bahramy, R. Arita, and Y. Iwasa, Science **338**, 1193 (2012).
[11] A. T. Bollinger, G. Dubuis, J. Yoon, D. Pavuna, J. Misewich, and I. Božović, Nature **472**, 458 (2011).
[12] J. Garcia-Barriocanal, A. Kobrinskii, X. Leng, J. Kinney, B. Yang, S. Snyder, and A. M. Goldman, Phys. Rev. B **87**, 024509 (2013).
[13] X. Leng, J. Garcia-Barriocanal, S. Bose, Y. Lee, and A. M. Goldman, Phys. Rev. Lett. **107**, 027001 (2011).
[14] K. Ueno, H. Shimotani, H. Yuan, J. Ye, M. Kawasaki, and Y. Iwasa, J. Phys. Soc. Jpn. **83**, 032001 (2014).
[15] K. Jin, W. Hu, B. Zhu, D. Kim, J. Yuan, T. Xiang, M. S. Fuhrer, I. Takeuchi, and R. L. Greene, e-print arXiv:1506.05727.
[16] J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant, and S. S. P. Parkin, Science **339**, 1402 (2013).
[17] R. V. Chopdekar, F. J. Wong, Y. Takamura, E. Arenholz, and Y. Suzuki, Phys. C Supercond. **469**, 1885 (2009).
[18] A. Kumatani, T. Ohsawa, R. Shimizu, Y. Takagi, S. Shiraki, and T. Hitosugi, Appl. Phys. Lett. **101**, 123103 (2012).
[19] K. Jin, G. He, X. Zhang, S. Maruyama, S. Yasui, R. Suchoski, J. Shin, Y. Jiang, H. S. Yu, J. Yuan, L. Shan, F. V. Kusmartsev, R. L. Greene, and I. Takeuchi, Nat. Commun. **6**, 7183 (2015).
[20] M. Nakano, K. Shibuya, D. Okuyama, T. Hatano, S. Ono, M. Kawasaki, Y. Iwasa, and Y. Tokura, Nature **487**, 459 (2012).
[21] See supplementary material at http://dx.doi.org/10.1063/1.4932551 for the effect of surface roughness of the $MgAl_2O_4$ (111) substrate on crystallinity and transport properties of $LiTi_2O_4$ films. Also included is the thickness dependence of the lattice parameter of $LiTi_2O_4$ (111) thin films.