

Application Of Pyroelectric Crystal And Ionic Liquid To The Production Of Metal Compounds

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Abstract. Zinc fluoride (ZnF_2) was deposited on a silicon substrate by changing temperature of a pyroelectric crystal of LiTaO_3 on which ionic liquid (EMI- Tf_2N) containing zinc ions was dripped at 1 Pa. ZnF_2 was also obtained by bombarding argon ions on EMI- Tf_2N containing zinc ions. From these results, it is concluded that EMI- Tf_2N containing zinc ions on the LiTaO_3 crystal was evaporated on the silicon substrate by changing temperature of the LiTaO_3 crystal in vacuum and that the evaporated EMI- Tf_2N containing metal zinc ions was decomposed to ZnF_2 by the bombardment of electrons accelerated by the electric field between the LiTaO_3 crystal and the silicon substrate.

Keywords: Pyroelectric crystal, Ionic liquid, Metal fluoride, XPS

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INTRODUCTION

When a temperature change under a vacuum condition around 1 Pa is applied to a pyroelectric crystal such as lithium tantalate (LiTaO_3) and lithium niobate (LiNbO_3), an electric field is produced due to uncompensated charge on the surface of the pyroelectric crystal. For example, 50 kV can be obtained by applying a temperature difference of 80 K to a pyroelectric crystal of LiTaO_3 with 3 mm $\times$ 3 mm in x-y plane and 5 mm in z-axis at 1 Pa. Then, small amounts of suspended electrons and ions in the condition are accelerated by the produced electric field. Brownridge first generated X-rays using a pyroelectric crystal of CsNO_3 and gold foil as a target.¹ After that, several researchers have been working on the application of pyroelectric crystals to X-ray generator with high energy,²⁻⁵ electron and ion beams,⁶ ion source for mass spectrometry,⁷ and an electron source for electron probe X-ray microanalyzer.⁸ In the present study, we applied the high voltage produced with the pyroelectric crystal to a production of metal compounds such as fluoride and sulfide. We selected an ionic liquid containing metal ions as a reactant because ionic liquid has low vapor pressure. The produced electric field is expected to be effectively applied to the ionic liquid because ionic liquid has high ionic conductivity.

EXPERIMENTAL

Figure 1 shows a schematic view of the experimental set-up in the present study. +z plane of a single crystal of LiTaO_3 with 3 mm $\times$ 3 mm in x-y plane and 5 mm in z-axis was attached on a Peltier device with silver paste. Ionic liquid, EMI- Tf_2N (1-Ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide) whose structure was shown in Fig. 2, containing 1 mol L^{-1} zinc ion (Zn^{2+}) was dripped on the LiTaO_3 crystal. EMI- Tf_2N containing zinc ions was produced by dissolving $\text{Zn}(\text{Tf}_2\text{N})_2$ into EMI- Tf_2N . $\text{Zn}(\text{Tf}_2\text{N})_2$ was prepared according to the reported literature.⁹ The other face of the Peltier device was attached on a copper rod with silver paste. The copper rod with a hole in the center was connected to a rotary vane pump. The temperature of the LiTaO_3 crystal was controlled by connecting the Peltier device to DC power supply. A silicon substrate was attached on another copper rod with silver paste. The distance between the pyroelectric crystal and substrate was set to 30 mm. The chamber was sealed with detachable vacuum joints (quick release couplings). The two copper rods were grounded in order to keep the electric potential of the substrate the same as +z plane of the LiTaO_3 crystal. The LiTaO_3 crystal was heated at 100 °C for 2 minutes by applying +3 volt DC to the Peltier device. Then, the LiTaO_3 crystal was cooled at 5 °C for 2 minutes by applying -3 volt DC to the Peltier device. This heating and cooling cycle was

Diagram illustrating the experimental setup for the electrochemical deposition of a polymer on a substrate. The setup is a vertical assembly. The components, from top to bottom, are:

- Detachable vacuum joint
- Vacuum flange (Nipple, KF-25)
- Copper rod
- Substrate
- 5 mm gap containing Ionic liquid
- Peltier device
- Copper rod
- Detachable vacuum joint
- Resin
- Battery (3V)
- To RP

A coordinate system is shown at the top left, indicating the y-axis (out of the page), x-axis (to the right), and z-axis (downwards).



EMI⁺



Tf₂N⁻

the thickness of ionic liquid on both the LiTaO_3 crystal

Figure 3 shows XPS spectra around Zn 2p, F 1s, O 1s, N 1s, C 1s, and S 2p of the silicon substrate after changing temperature of the LiTaO₃ crystal on which EMI-Tf₂N containing metal zinc ions was dripped with an XPS spectrum of EMI-Tf₂N containing zinc ions. Zn 2p_{1/2} and 2p_{3/2} peaks were detected on the silicon substrate. Although the intensity ratio of C 1s peaks at 285.5 and 286.9 eV changed, F 1s (688.7 eV), O 1s (532.5 eV), N 1s (399.9 and 402.4 eV), C 1s (285.5, 286.9, and 293.4 eV), and S 2p (169.4 eV) peaks related to EMI-Tf₂N were detected on the silicon substrate after changing temperature of the LiTaO₃ crystal on which EMI-Tf₂N containing metal zinc ions was dripped. The position of N 1s, C 1s, and S 2p peaks related to EMI-Tf₂N were coincident with reported values.¹⁰⁻¹³ This result indicates that ions such as Zn²⁺, EMI⁺, and Tf₂N⁻ were field-emitted from EMI-Tf₂N containing zinc ions or that EMI-Tf₂N containing zinc ions was evaporated on the silicon substrate. F 1s peak of 684.7 eV was additionally detected on the silicon substrate after applying electric field to EMI-Tf₂N containing zinc ions as shown in Fig. 3 (b). The additional F 1s peak of 684.7 eV was closed to F 1s peak of zinc fluoride (ZnF₂). Other additional peaks were not detected after changing temperature of the LiTaO₃ crystal on which EMI-Tf₂N containing metal zinc ions was dripped. When argon ions accelerated with the voltage of 300 V were bombarded on EMI-Tf₂N containing zinc ions, F 1s peak was also detected at 685.1 eV which was closed to F 1s peak of ZnF₂, but F 1s peak related to Tf₂N⁻ was not detected as shown in Fig. 4. On the other hand, when argon ions were bombarded on EMI-Tf₂N without zinc ions, the F 1s peak related to Tf₂N⁻ was detected, but F 1s peak closed to ZnF₂ peak was not detected. These results suggest that EMI-Tf₂N containing zinc ions was decomposed to ZnF₂ by bombarding argon ions on EMI-Tf₂N containing zinc ions. In addition, vapor pressure of EMI-Tf₂N is calculated to be 1.2×10^{-5} Pa at 100 °C in contrast to 2.8×10^{-10} Pa at 25 °C.¹⁴⁻¹⁶ Therefore, by changing temperature of the LiTaO₃ crystal on which EMI-Tf₂N containing zinc ions was dripped, EMI-Tf₂N containing zinc ions on the LiTaO₃ crystal was evaporated on the silicon substrate and then the evaporated EMI-Tf₂N containing zinc ions was decomposed to ZnF₂ by the bombardment of suspended electrons accelerated by the electric field between the LiTaO₃ crystal and the silicon substrate. However, reproducibility of the detection of the F 1s peak related to ZnF₂ was not confirmed using the LiTaO₃ crystal. This poor reproducibility is related to the thickness of ionic liquid on both the LiTaO₃ crystal

and substrate. A static dielectric constant of EMI-Tf₂N ($\epsilon_r = 15.2$)¹⁷ was lower than that of LiTaO₃ ($\epsilon_r \sim 40$).¹⁸⁻²² Thus, energies of electrons bombarded on the substrate decrease with increasing the thickness of EMI-Tf₂N containing zinc ions on the LiTaO₃ crystal and/or substrate because electric field between the LiTaO₃ crystal and substrate decrease. Therefore, EMI-Tf₂N containing zinc ions is not decomposed to ZnF₂ if the amount of EMI-Tf₂N containing zinc ions on LiTaO₃ crystal and/or substrate is large.

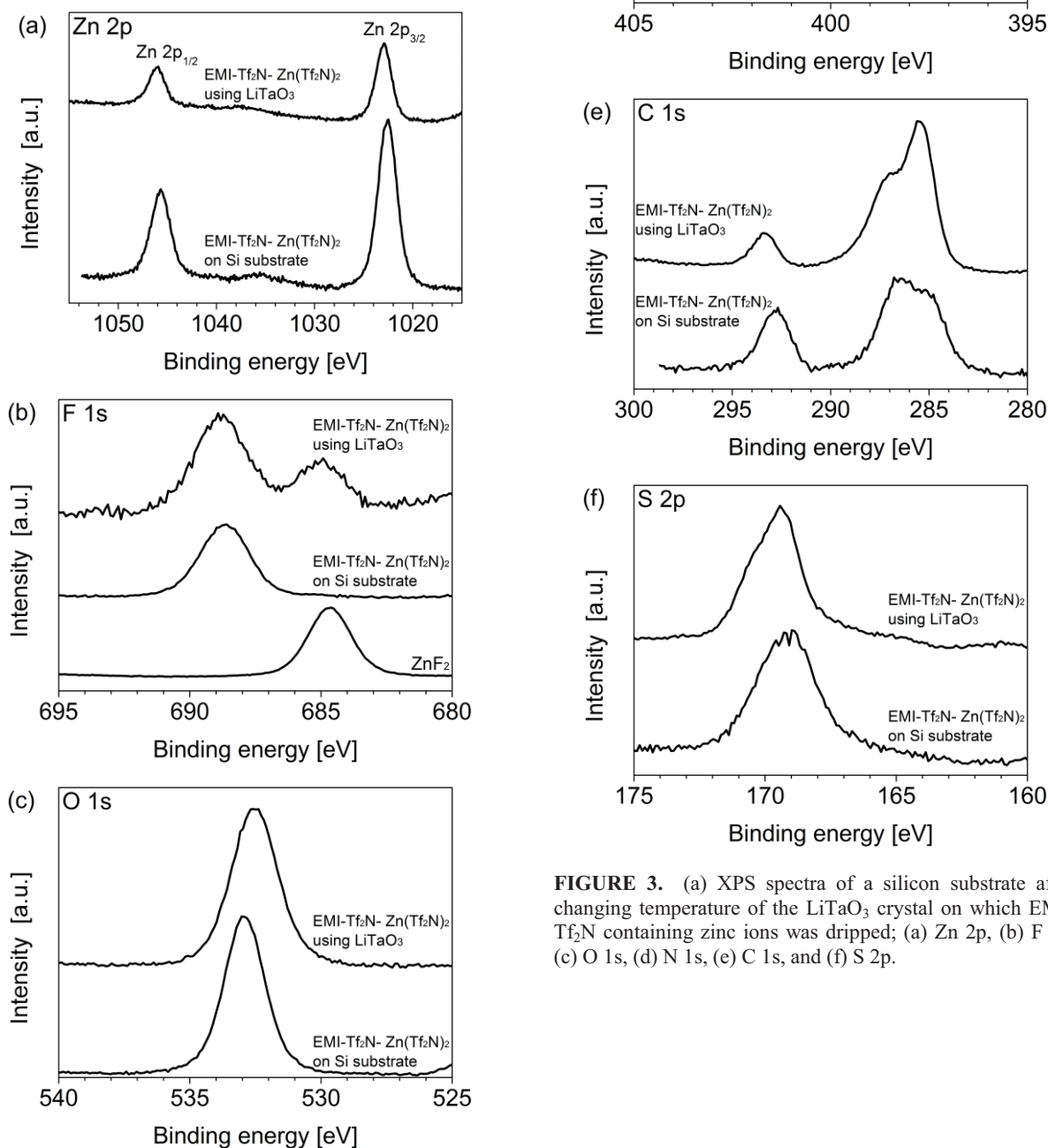


FIGURE 3. (a) XPS spectra of a silicon substrate after changing temperature of the LiTaO₃ crystal on which EMI-Tf₂N containing zinc ions was dripped; (a) Zn 2p, (b) F 1s, (c) O 1s, (d) N 1s, (e) C 1s, and (f) S 2p.

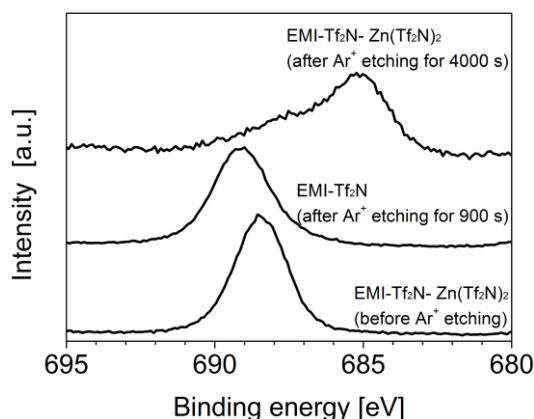


FIGURE 4. XPS F 1s spectra of EMI-Tf₂N containing zinc ions and EMI-Tf₂N after bombarding argon ions accelerated with the voltage of 300 V with an XPS spectrum of EMI-Tf₂N containing zinc ions before bombarding argon ions.

CONCLUSIONS

We obtained thin ZnF₂ film by changing temperature of a pyroelectric crystal of LiTaO₃ on which an ionic liquid (EMI-Tf₂N) containing zinc ions was dripped at 1 Pa. EMI-Tf₂N containing zinc ions was evaporated on a silicon substrate and then the evaporated EMI-Tf₂N containing zinc ions was decomposed to ZnF₂ by the bombardment of electrons accelerated by the electric field between the LiTaO₃ crystal and the substrate. The thickness of EMI-Tf₂N containing zinc ions layer on LiTaO₃ crystal and substrate is an important factor for forming the ZnF₂ film. When the amount of EMI-Tf₂N containing zinc ions on LiTaO₃ crystal and substrate is large, ZnF₂ film is not formed. Electrons bombarded on the substrate do not have enough energy to decompose EMI-Tf₂N containing zinc ions to ZnF₂ because a static dielectric constant of EMI-Tf₂N is lower than that of LiTaO₃ crystal.

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