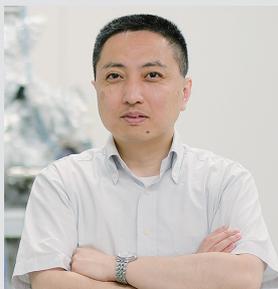


Exploration of Novel Electronic/Ionic Physical Properties Using Inorganic Thin Films

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Education

2006 B.S. The University of Tokyo
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Professional Employment

2011 Research Associate, Tohoku University
2012 JSPS Reserach Fellowship (PD)
2013 Visiting Researcher, University of California (2013.8–2014.2)
2015 Assistant Professor, Tohoku University
2016 Contract Lecturer, Tokyo Institute of Technology
2017 JST-PRESTO full-time Research Fellowship
2018 Assistant Professor, Tokyo Institute of Technology
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2020 Associate Professor, Tokyo Institute of Technology
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Awards

2011 NF-Foundation R&D Encouragement Award
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Keywords

Inorganic Solid-State Chemistry, Surface-Interface Science, Solid-State Electrochemistry

Interface control is a critical issue in both electronic and electrochemical devices. Using thin-film technologies, our group constructs well-defined model interfaces and explore novel electronic and ionic properties.

For electronic devices, we focus on the synthesis and characterization of metastable metal hydrides. Non-equilibrium film growth processes and epitaxial growth techniques enable the realization of functionalities unattainable in bulk materials. By controlling the charge states of hydrogen in solids, we aim to achieve high-transition-temperature superconductivity and develop multifunctional switching devices driven by external fields such as light, heat, and electric fields.

For ionic devices, we are working to improve the performance of fluoride-ion secondary batteries toward high-capacity energy storage. Batteries consist of a cathode, electrolyte, and anode, and operate through the migration of carrier ions between electrodes across the electrolyte. In this process, the electrode–electrolyte interface, where dissimilar materials come into contact, often represents the bottleneck for ion transport. By fabricating model interfaces within thin-film battery and conducting quantitative evaluations, we establish

strategies for controlling carrier-ion transport at interfaces.

In addition, to accelerate materials research we are working on the digital transformation (DX) of materials research, including laboratory automation. Conventionally, materials were carefully synthesized and optimized one by one to evaluate their electronic and ionic properties. In this context, we are introducing robots and AI technologies. The use of robots allows experiments to be conducted in extreme environments, such as inert gas atmospheres or X-ray irradiation conditions, where humans cannot enter. Our goal is to advance the automation of experiments and promote the coexistence of humans and robots in materials research.

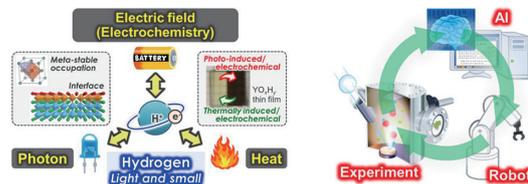


Figure 1. (left): Multiple-field-induced functions of hydride-related materials. (right): Conceptual illustration of experiments combining artificial intelligence (AI) and robots.

Selected Publications

- Y. Komatsu, R. Shimizu *et al.*, “Repeatable Photoinduced Insulator-to-Metal Transition in Yttrium Oxyhydride Epitaxial Thin Films,” *Chem. Mater.* **34**, 3616 (2022).
- K. Nishio, R. Shimizu *et al.*, “Immense Reduction in Interfacial Resistance between Sulfide Electrolyte and Positive Electrode,” *ACS Appl. Mater. Interfaces* **14**, 34620 (2022).
- M. Haruta, R. Shimizu *et al.*, “Negligible “Negative Space-Charge

Layer Effects” at Oxide-Electrolyte/Electrode Interfaces of Thin-Film Batteries,” *Nano Lett.* **15**, 1498 (2015).

- R. Shimizu *et al.*, “Autonomous Materials Synthesis by Machine Learning and Robotics,” *APL Mater.* **8**, 111110 (2020).
- S. Kobayashi, R. Shimizu *et al.*, “Autonomous Exploration of an Unexpected Electrode Material for Lithium Batteries,” *ACS Mater. Lett.* **5**, 10 (2023).

1. Hydrogen Charge-State Control of Multi-Anion Hydrides

The charge state of hydrogen in solids depends on the electronegativity of its bonding partner and can exist as a proton (positively charged), atomic hydrogen (electrically neutral), or a hydride (negatively charged). In this study, we achieved control over protonic and hydridic states in thin-film materials with multi anions with oxygen and nitrogen.

In the calcium–nitrogen–hydrogen system ($\text{Ca}_x\text{N}_y\text{H}_z$), protonic CaNH (imide) and hydridic Ca_2NH (nitride hydride) are known. However, no synthesis of these compounds in thin-film form had previously been reported, and no guidelines for their fabrication were available. Using reactive magnetron sputtering, we achieved the selective epitaxial growth of both CaNH and Ca_2NH thin films.

To elucidate the selective growth processes, we monitored plasma emission of atomic Ca (422 nm) during the sputtering process. This result revealed that the growth pathway is governed by the relative reaction probabilities of Ca with hydrogen and nitrogen: Under high hydrogen partial pressure, hydrogen reacts preferentially with Ca to form CaH_x , which subsequently converts into CaNH , whereas under low hydrogen partial pressure, hydrogenation and nitrogenation occur simultaneously in a single step to yield Ca_2NH .

Furthermore, by further reducing the hydrogen partial pressure, we successfully synthesized epitaxial thin films of the layered electride Ca_2N . These findings open up new opportunities for controlling physical properties and exploring novel functionalities across proton, hydride, and electride.

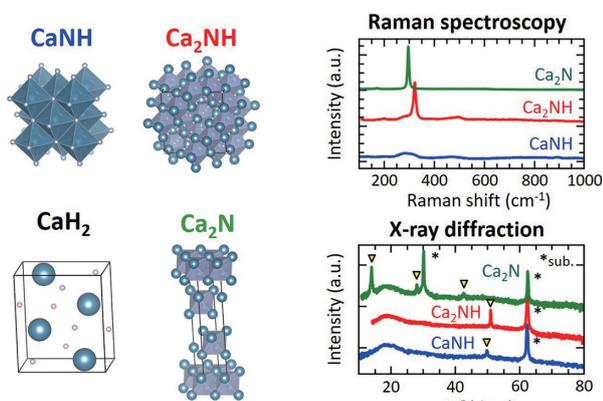


Figure 2. Selective growth of $\text{CaNH}/\text{Ca}_2\text{NH}/\text{Ca}_2\text{N}$ epitaxial thin films.

2. Electrode/Electrolyte Interface Control of Fluoride Ion Batteries

To realize thin-film fluoride batteries, we fabricated and evaluated liquid-electrolyte cells using BiF_3 thin films as a cathode. When the BiF_3 thin-film electrode surface was directly immersed in the liquid electrolyte, the initial discharge capac-

ity exceeded the theoretical value ($\sim 302 \text{ mAh g}^{-1}$), suggesting the occurrence of side reactions. Furthermore, the capacity retention decreased drastically upon cycling.

To address this issue, we applied interfacial control techniques established in Li-ion batteries²⁾ and introduced a chemically stable LaF_3 solid electrolyte buffer layer onto the BiF_3 electrode surface. As a result, side reactions were effectively suppressed, and the decline in capacity retention during cycling was suppressed. Future studies will focus on evaluations under non-exposure conditions by transferring the cells through vacuum and Ar atmospheres, thereby eliminating the influence of ambient moisture.

This study is collaboration with Dr. Taketoshi Minato of Instrument Center.

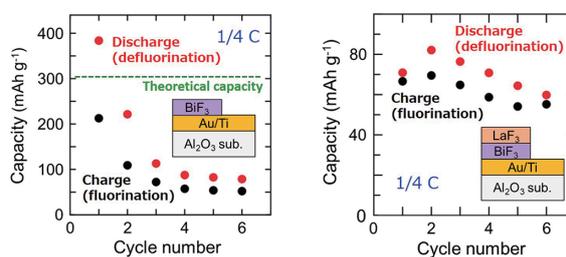


Figure 3. Cycle dependence of charge/discharge capacity. (Left) BiF_3 thin-film electrode in direct contact with liquid electrolyte; (Right) BiF_3 thin-film electrode covered with a LaF_3 solid-electrolyte buffer layer.

3. Format Standardization for Laboratory Automation

In advancing laboratory automation, the standardization of both hardware and software is essential. We have constructed a fully automated and autonomous system for inorganic thin-film synthesis and characterization. In recent years, we have also promoted the standardization of data format generated by automated measurement systems. Here, by employing the MaiML (Measurement, Analysis, Instrument Markup Language) framework—newly standardized as a JIS specification by the Japan Analytical Instruments Manufacturers' Association (JAIMA)—we established a scheme for data sharing on the cloud and successfully applied it to the optimization of synthesis conditions.³⁾

At present, through collaborative research, we are extending such autonomous materials exploration systems to a variety of fields, including spintronics materials and hydrogen storage materials.

References

- 1) S. Chon, R. Shimizu *et al.*, *J. Phys. Chem. Lett.* **13**, 10169 (2022).
- 2) S. Kobayashi, R. Shimizu *et al.*, *J. Phys. Chem. C* **127**, 4684 (2023).
- 3) K. Nishio, R. Shimizu *et al.*, *Digit. Discov.* **4**, 1734 (2025).