Tokodai Institute for Element Strategy (TIES)
ESIAC2019 Activity Report

Hideo Hosono
Director/Representative Researcher

December 13, 2019

Outline

1. Background
2. Goals and Approaches
3. Organization
4. Roadmap
5. Technical Topic
6. Achievement
7. Summary

1. Background

Characteristics of Electronic Materials

- Contributions of electronics industry to GDP is as large as those of automotive and chemical ones.
- Almost all elements are used in electronic materials composed of wide variety of matters: dielectrics, semiconductors, superconductors, etc.
- There has so far been a large number of big national projects in Japan.

Style of TIES

- Persistently based on academia.
- Different perspective from those of previous national projects.
- Focus on variety of matters and utilization of abundant elements.

Problems in previous materials researches

matters	Similarity of crystal structure	Similarity of chemical bonding
Semiconductors	Diamond-like structure	Covalent bonding
TCOs	Heavy-metal cation oxides	Ionic bonding
Ferroelectrics	Perovskite structure	s^2 electron configuration Heavy metals

Approaches are deadlocked!

We need exploring studies based on novel viewpoints.

2. Goals & Approaches

1. Breaking the spells over old-fashioned materials design concepts base on past experiences of successes,
2. Exploring electronic material frontiers by non-conventional combination and arrangements of elements,
3. Establishing new design concepts and guidelines for further advancement of materials technologies,
4. Creating and utilizing dreamlike electronic materials composed of abundant and non-toxic elements.

Technical issues

- Stagnant development of semiconductor materials
- Stagnant development of ferroelectric materials
- Demand for better TCO
- Stagnant increase of superconductor T_C

Reason why unresolved

- Impact of previous successes in existing specific materials
- Concentration upon specific elements and crystal structures
- Immature guiding principles

Approaches

- Ubiquitous elements
- Novel anions, H^-, electrides, metalides
- Unique nanostructures
- Unique electronic states Dirac electron systems

Novel materials

- High mobility/highly stable /flexible semiconductors
- Highly efficient inorganic light-emmiting materials
- Heavy metal-free flexible TCOs
- Heavy & toxic elements -free ferroelectrics
- Toxic elements-free high T_C superconductors

3. Organization: strong collaborations among institutes

Tokodai Institute for Element Strategy (TIES)
H. Hosono (Representative)

Tokyo Institute of Technology

MCES

Materials Reseach Center for Element Strategy

Steering Committee

Planning Div.:  H. Kumomi (PM)

Materials Creation Gr.


H. Hosono (GL)


A. Otomo (SGL)

Analysis & Evaluation Gr.


Y. Majima (GL)

Electron Theory Gr.


T. Kamiya (GL)

Overseas Collaborators:
UCL, McGill, etc.

Industrial Collaborators:
Various companies

Tohoku University
University of Tsukuba
Tokyo University of AT
University of Yamanashi
Nagoya University
Kyoto University

National Institute for Materials Science

Materials Creation Gr.


N. Ohashi (GL)

Analysis & Evaluation Gr.


K. Kimoto (GL)

High Energy Accelerator Research Organizatioin

Analysis & Evaluation Gr.


Y. Murakami (GL)

The University of Tokyo

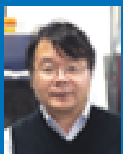
Electron Theory Gr.


S. Tsuneyuki

3. Organization: young P.I.s for 10-years project

Most of the P.I.s are forties at the beginning of the project.

Materials Creation Group


Hosono GL


Funakubo
ferro/dielectrics


Kondo
2D nano sheets


Ohashi
semiconductor dielectrics


Ohtomo SGL
semiconductor superconductor


Hiramatsu
epitaxial films

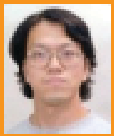

Yamada *
tunable dielectrics

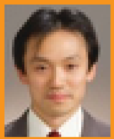

Shimamura
single crystal growth

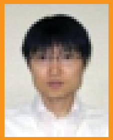

Kanemitsu *
optical property emissive material

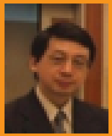

Wakabayashi *
SR X-ray informatics-based

Electronic Theory Group


Kamiya GL
semiconductor


Murakami
DIrac electrons


Oba
semiconductor

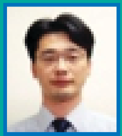

Saito
2D materials

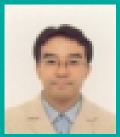
Analysis & Evaluation Group


Murakami
PF X-ray neutron

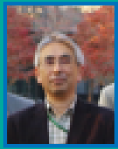

Majima GL
sub-nano devices


Kimoto
HRTEM


Kumigashira
PF X-ray ARPES


Yamaura
PF X-ray neutron


Sakata
SPring-8 X-ray

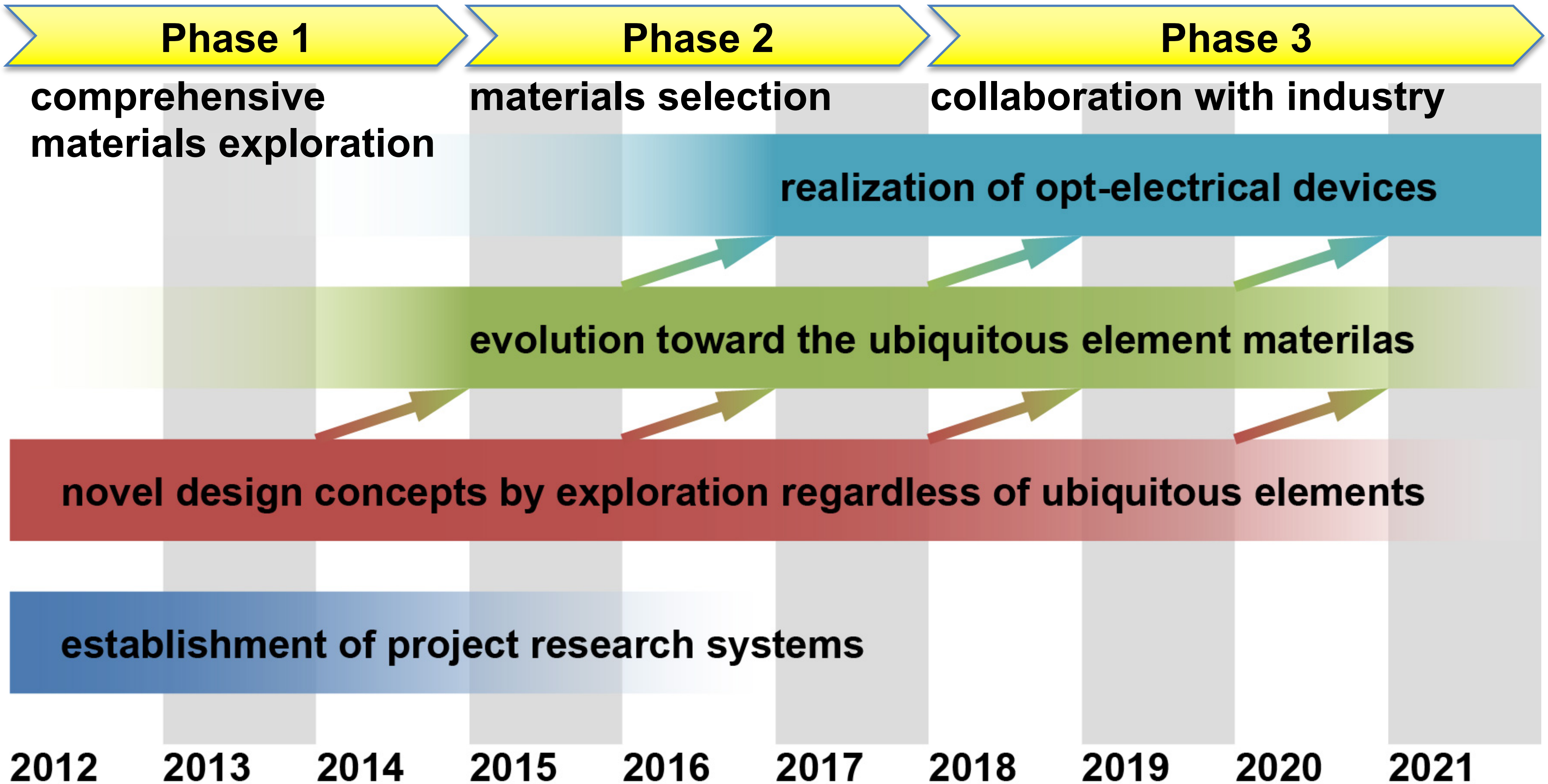

Kadono
J-PARC muon

NIMS members

KEK members

* New attendees in 2019

4. Roadmap


Phase 1
Phase 2
Phase 3
comprehensive materials exploration
materials selection
collaboration with industry
realization of opt-electrical devices
evolution toward the ubiquitous element materilas
novel design concepts by exploration regardless of ubiquitous elements
establishment of project research systems
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021

4. Focus areas after Phase 2

Semiconductors

- Lacked areas in mainstream of Japan
- High mobility/Bipolar/Ultra-wide Eg
- Novel doping methods
- P-type amorphous semiconductors
- Nitrides, Sulfides、Hydrides
- Dirac electron systems

High-k dielectrics/ferroelectrics

- For power electronics at high T
- Stable oxygen deficiencies
- Abundant & nontoxic elements
- Non/low-dimensional perovskytes
- Non-oxide/(oxy)nitrides
- Hydrides

Roles & Functionalities of Hydrogen

- Ever-ignored hydrogens in oxides
- Quantification & state analyses
- Correlation between hydrogens and electronic states
- Hydrogens as functional elements
- Novel hydride materials

Collaboration of theory & synthesis

Rapid screening

- Calculation methods with defects
- Theoretical prediction of synthesis routes
- Materials Informatics

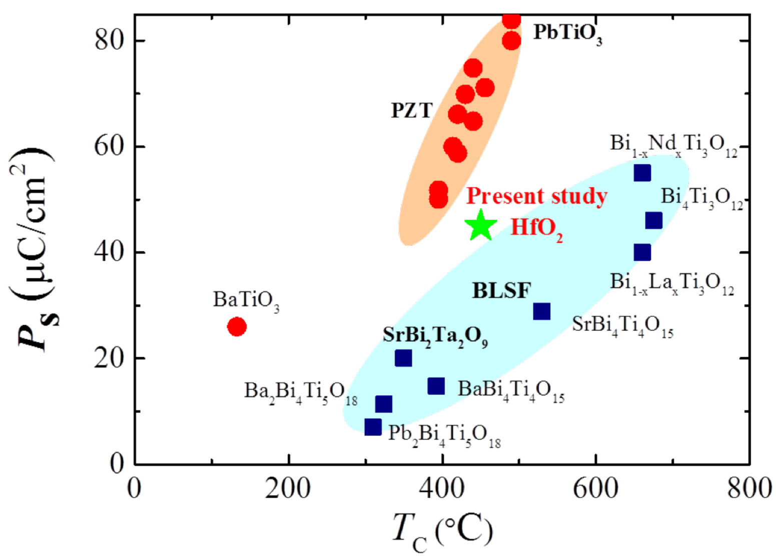
5. Technical Topics

Dielectrics *Sci. Reps.* **6**, 32931 (2018)

Collaboration with industry

Fluorite Ferroelectrics with high T_C & P_S: HfO_2:Y

- Ferroelectric epitaxial thin films of Y-doped HfO_2 was successfully grown and high T_C and P_S were demonstrated.
- In addition to power electronics application, the thin film exhibits highly-stable ferroelectric memory switching with retention cycle over 10^{11}.



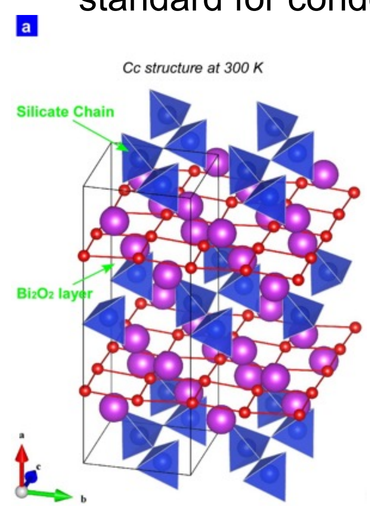
Positioning map of T_C-P_S correlation

Dielectrics *Phys. Rev. Mater.* **2**, 045603 (2017)

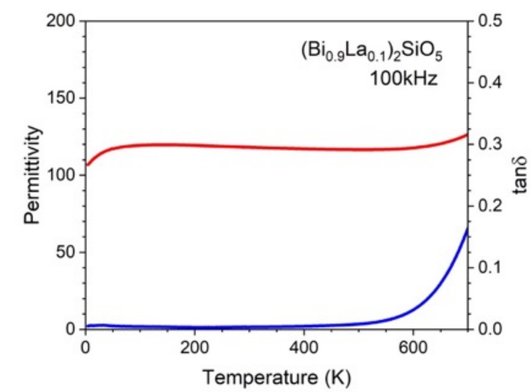
Collaboration with industry

Stable High-*k* Silicate Dielectrics: $(Bi_XLa_{1-X})_2SiO_5$

- The materials creation group discovered silicate ferroelectrics of Bi_2SiO_5 (BSO).
- DFT calculations elucidated the origin of ferroelectricity, implying the BSO can be paraelectric by substitutional La doping into Bi sites.
- $(Bi_XLa_{1-X})_2SiO_5$ shows stable high-*k* for wide temperature range which satisfies an industrial standard for condensers on automobiles.



Crystal structure



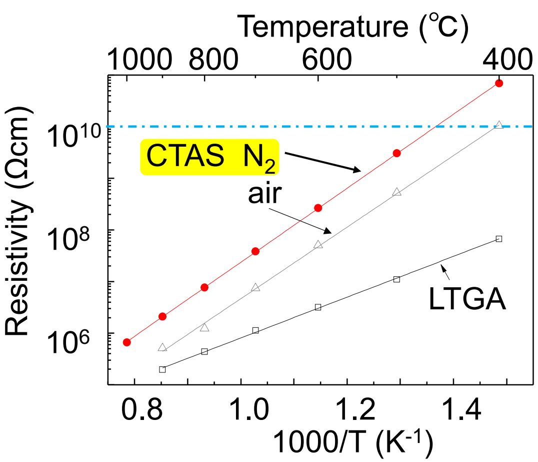
Temperature dependence of dielectric constant and loss

5. Technical Topics

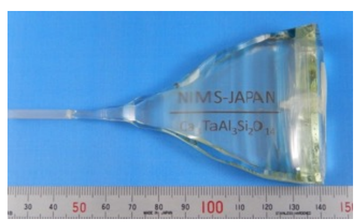
Dielectrics *Cryst. Growth Des.* **16**, 2151 (2016) — Collaboration with industry

Piezoelectrics for Automobiles : CTAS ($Ca_3TaAl_3Si_2O_{14}$)

- The materials creation group succeeded in grow over two-inches wide single crystals of Langasite piezoelectric CTAS ($Ca_3TaAl_3Si_2O_{14}$).
- CTAS satisfies a demand of high-temperature leakage (>10^{10} Ω cm at 400 ℃) for extreme lean-burn conditions in automobile combustion engines.
- Pressure sensor manufacturer fabricated prototype module showing 150% larger sensitivity.



Temperature dependence of resistivity



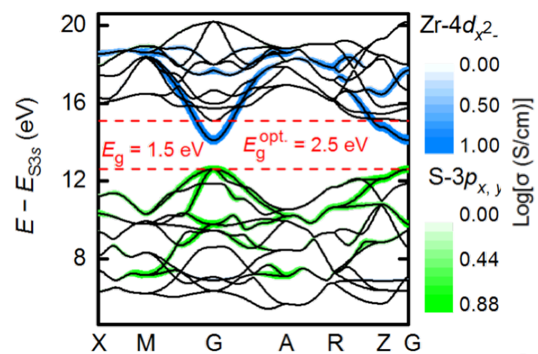
2-inch single crystal

Sensor module

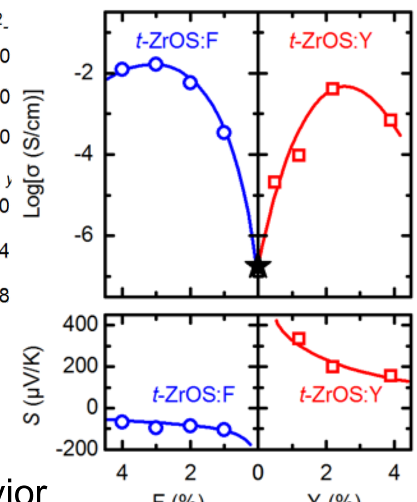
Semiconductor *JACS* **139**, 17175 (2017) — Collaboration with industry

Transparent Bipolar Oxysulfide Semiconductor: ZrOS

- P-type doping is difficult in late/post-transition metal oxides due to oxygen vacancies.
- New design concept was established based on early transition metals with high valence and coordination numbers suppressing anion vacancies.
- Tetragonal ZrOS was theoretically predicted and experimentally demonstrated with wide band gap of 2.5 eV and bipolar dopability.



Band structure



Bipolar doping behavior

5. Technical Topics

Semiconductor

Adv. Mater. **30**, 1706573 (2018)

Collaboration with industry

P-type Amorphous Semiconductor: *a*-Cu-Sn-I

- Among previous amorphous semiconductors, only n-type oxides show high carrier mobility.
- We notice that 5*p* orbitals of iodine are similar to *s* orbitals of heavy metals and could have a large spherical spread around an iodine atom.
- P-type transparent (Eg~3 eV) amorphous semiconductor with 9 $cm^2V^{-1}s^{-1}$ was demonstrated by 140 ℃ solution-processed *a*-Cu-Sn-I thin films to be applied to PV/light-emitting devices or TFTs.

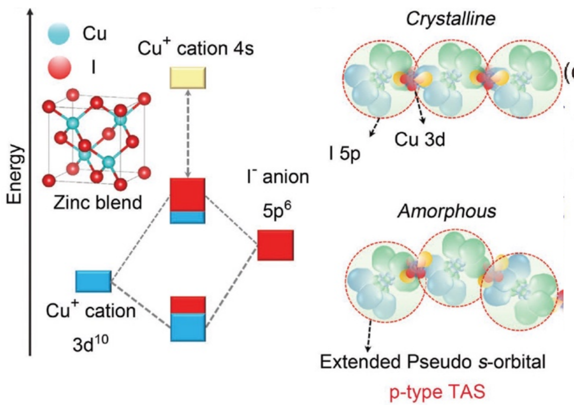
Semiconductor

Adv. Mater. **30**, 1804547 (2018)

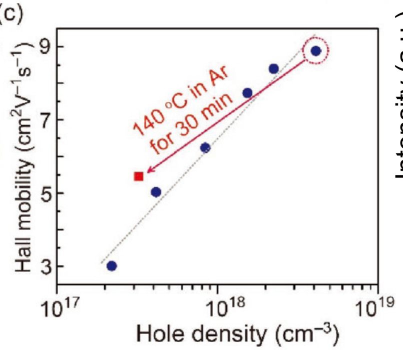
Collaboration with industry

Blue-Light Emitting Lead-Free Inorganic Perovskite: $Cu_3Sn_2I_5$

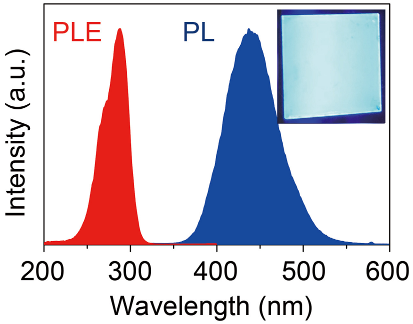
- Halide perovskite semiconductors for inorganic light emitters always contain a toxic element, lead.
- We focused on Cu halides with small binding energy, and found lead-free $Cu_3Sn_2I_5$ having zero-dimensional optically-active sites in the electronic structure.
- Bright blue-light emission with PLQY>90% and LED were demonstrated.



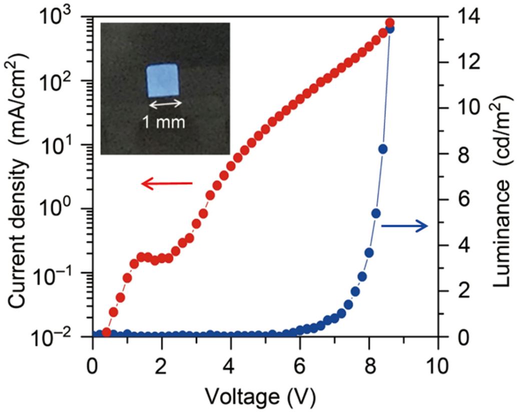
Crystal & band structure



Hall mobility



PL & PLE spectra



I-V / L-V characteristics of LED

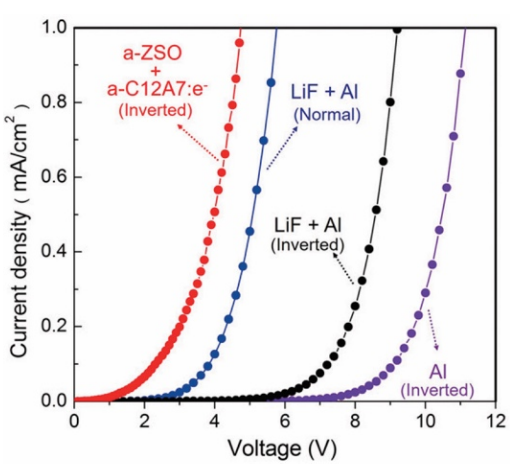
5. Technical Topics

Semiconductor *PNAS* **114**, 233 (2017) Collaboration with industry *Appl. Phys. Rev.* **6**, 031402 (2019) Collaboration with industry

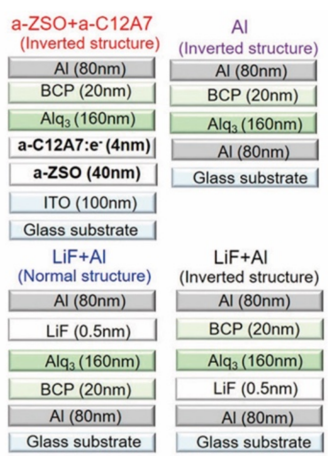
Universally Ohmic with Low Work Function & High Mobility ZSO

Application to OLED

- Electron transport layers (ETL) of current OLED are made of organics with very low mobility (~10^{-3} $cm^2V^{-1}s^{-1}$) which limits yield and efficiency.
- We discovered amorphous Zn-Si-O (ZSO) exhibit high mobility (~1 $cm^2V^{-1}s^{-1}$) and low work function (3.5 eV), and can form excellent ohmic contact.
- OLED devices with ETL of ZSO show better performance than ordinary devices with organic ETL even in the inverted device structure.



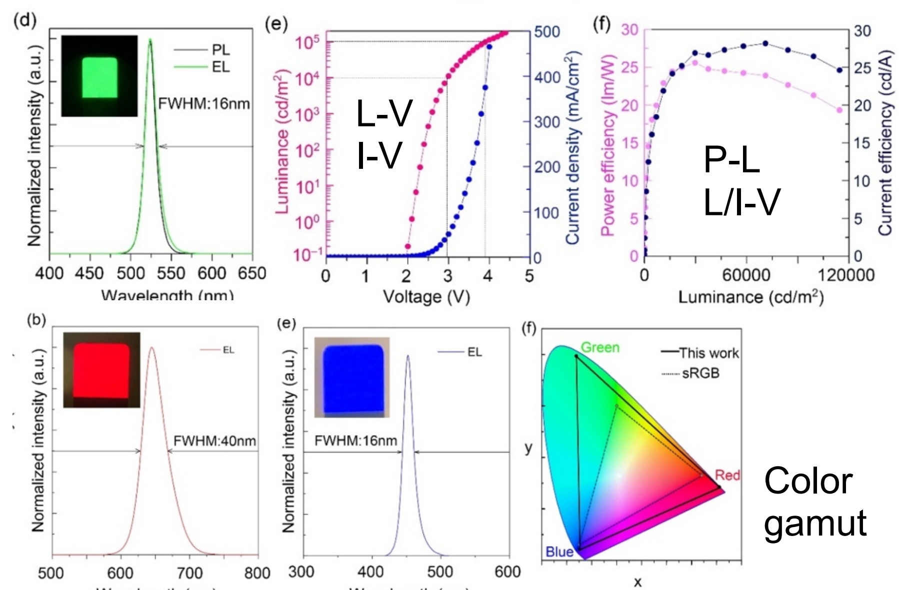
I-V characteristics



Layer structures

Application to PeLED

- Inorganic halide perovskite LED (PeLED) is also suffered from ETL issues to be solved by ZSO.
- Green PeLED exhibit ultimate performance of V_{TH} (2.9 V), efficiency (33 lm·W^{-1}) and brightness (~5×10^5 cd·m^{-2}), and spectrum (FWHM~15 nm) which solve the green-gap in GaN-based LEDs.
- Red and blue PeLEDs are also demonstrated and satisfy wide color gamut for BT2020.



5. Technical Topics (6)

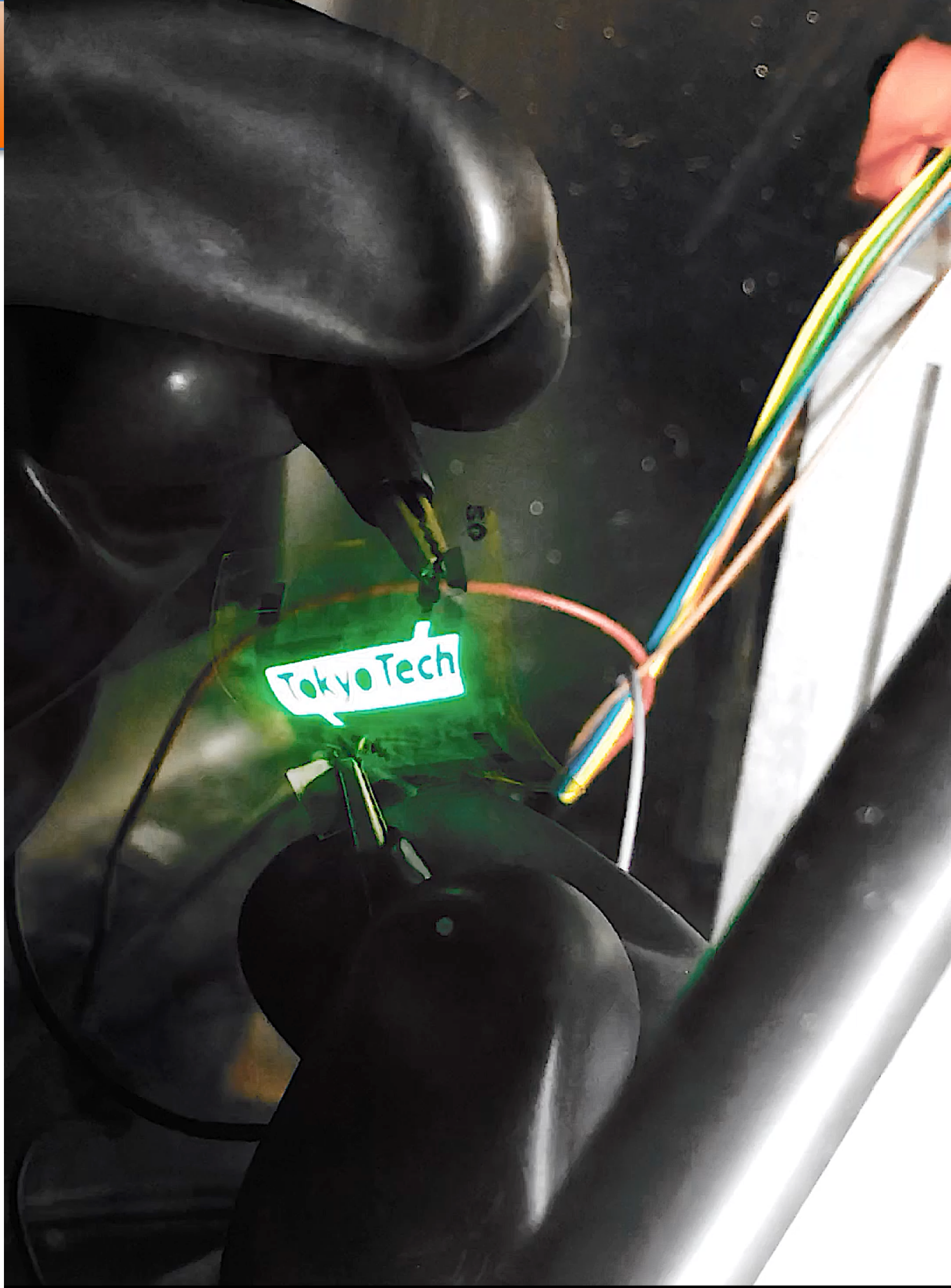
Semiconductor

Appl. Phys. Rev. **6**, 031402 (2019)

Collaboration with industry

Ultra Bright Flexible PeLED

- Green PeLED exhibit ultimate performance of V_{TH} (2.9 V), efficiency (33 lm·W^{-1}) and brightness (~5×10^5 cd·m^{-2}), and spectrum (FWHM~15 nm) which solve the green-gap in GaN-based LEDs.
- Red and blue PeLEDs are also demonstrated and satisfy wide color gamut for BT2020.
- Readily applicable to flexible devices on plastic substrates due to room-temperature sputter deposition of ZSO and low-temperature printable solution process of halide perovskite!



Materials Research Center for Element Strategy, Tokyo Tech

5. Technical Topics

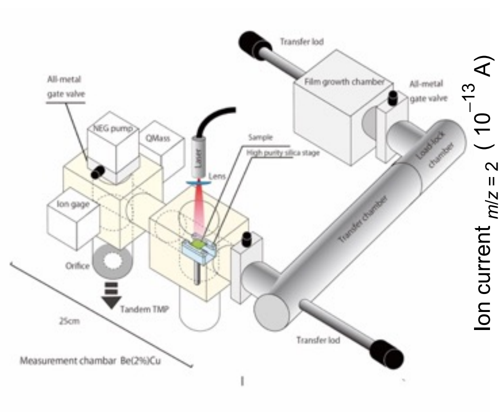
Hydrogen

Rev. Sci. Instrum. **88**, 053103 (2017)

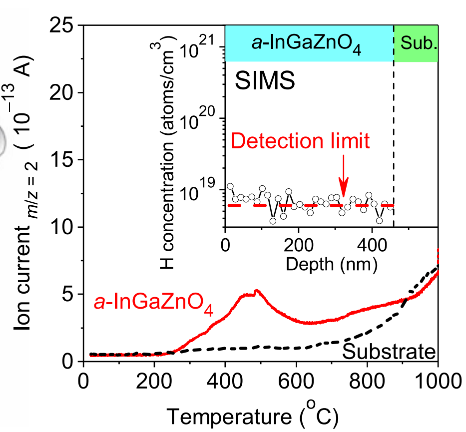
Collaboration with industry

High-Sensitivity Thermal Desorption Spectroscopy

- Ordinary mass spectroscopy like SIMS cannot measure low hydrogen density <~10^{18} cm^{-3}.
- For low hydrogen density limit, we developed an original method and apparatus based on TDS thoroughly suppressing residual hydrogen.
- High sensitivity (~10^{16} cm^{-3}) measurement was demonstrated in *a*-IGZO thin films.
- The apparatus will be commercialized by some companies soon.



Schematic of system



H_2 desorption spectrum from *a*-IGZO thin films

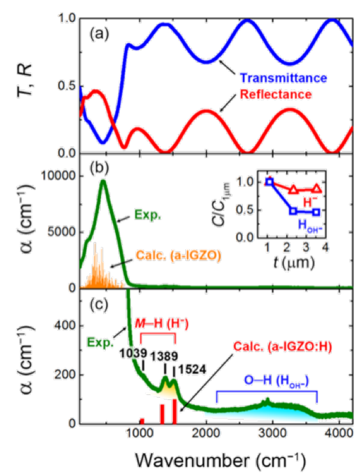
Hydrogen

Appl. Phys. Lett. **110**, 232105 (2017)

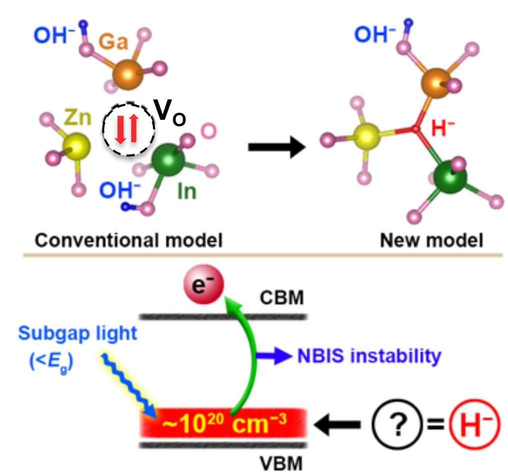
Collaboration with industry

Hydride Anions (H^-) in a-IGZO and the TFT Instability

- Oxide semiconductors like *a*-IGZO usually contain high-density hydrogen (~10^{20} cm^{-3}), but their states, roles, and functionalities have not been elucidated.
- We precisely analyzed the bonding states of H in a-IGZO thin films by FTIR, and identified hydrogen-related peaks in the IR spectra by DFT calculations.
- It is found that 1/3 of H in the film are H^- at oxygen vacancy sites, which form deep sub-gap states and origin of the TFT instability under illumination.



H IR spectra



Local and band structure

6. Achievement: Development of Core Research Center

New building exclusive to MCES
with dedicated collaboration floor (2015-)

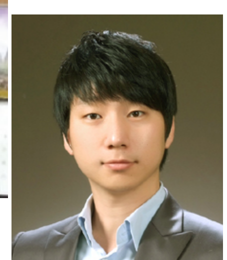
Discussion at monthly meetings
of all researchers

Employment of full-time professors
by MCES (2013-)

T. Tada
Assoc. Prof.
↓
Prof.
Kyushu Univ.

S. Matsuishi
Assoc. Prof.

M. Kitano
Assoc. Prof.



J. Kim
Assist. Prof.

Head-hunt of Prof. F. Oba
from Kyoto Univ. (2015-)

Prof. F. Oba
（Frontier Lab. &
MCES）

Participation utilizing
Tokyo Tech MSL
Collaborative Research Project

Prof. S. Wada
(Yamanashi
Univ. 2013–)

Prof. H. Taniguchi
(Nagoya Univ.
2014–)

6. Achievement: Development of Core Research Center

Camp meeting to summarize the 2nd phase
and discuss the final goal & beyond (2017/10/28-29)

Reinforcement of research portfolio
by incorporation of young researchers
completing JST Element Strategy project

Prof. T. Kondo
(Tsukuba Univ. 2016-)

Prof. A. Yamamoto
(TUAT 2016–)

Tokyo Tech declared "New Element Strategy"
as the top priority research areas
upon selection
as Designated National University (2018-)

Focus Areas

New Element Strategy
toward sustainable society
efficiently utilizing limited resources

Comprehensive Energy Science
toward rich society
based on sustainable energies

Device & System in Digital Society
toward infrastructures of future society
merging hardwares & softwares

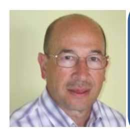
Organized as Focus Research Centers

Basic Structure of Focus Areas

International expansion
using JSPS Core-to-Core Program
to form international research institute (2018-)

Defects Modeling Institute

Surface Analysis Institute



Univ. College London (UK)
Prof. A. Shluger

MacGill Univ.(Canada)
Prof. P. Grutter

TIES (Tokyo Tech)
MCES
Prof. H. Hosono

Materials Creation Institute

7. Summary: Final Goal & Beyond

Development of Electronic Materials Institute in all Tokyo Tech from MCES

Transfer of technical achievements to industry

- Semiconductor Materials for Flat-Panel Displays
- High-k Dielectrics for Power Electronics

Successive Evolution of Challenging Materials Research based on novel ideas

Technology Transfer of Promising Achievements to Industry

Publication of Summaries of TIES's Concept, Approaches, Design Principles, and Achievements

Evolutional Development to Post Element Strategy (New Element Strategy)