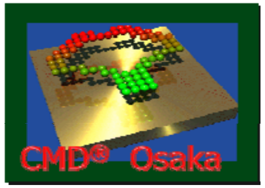
# Present Status and Frontiers of Computational Materials Design




**Hiroshi Katayama-Yoshida**
**Graduate School of Engineering Science, Osaka University, Japan**


## ■Industrial Society to Knowledge-based Society

■「Knowledge-based Fabrication」&「New Business Model」*(Knowledge-based Society)*

■$20^{th}$ C: Mechanism by Quantum Mechanics
■$21^{st}$ C: Design by Quantum Mechanics

$21^{st}$ century's Social Problems

Energy・Environment・Aging Society・Security

- *High-efficiency energy conversion*
- *Next generation nano-electronics*
- *Environment-friendly materials*
- *Life-science-related materials*
- *Security & Safety-related materials*

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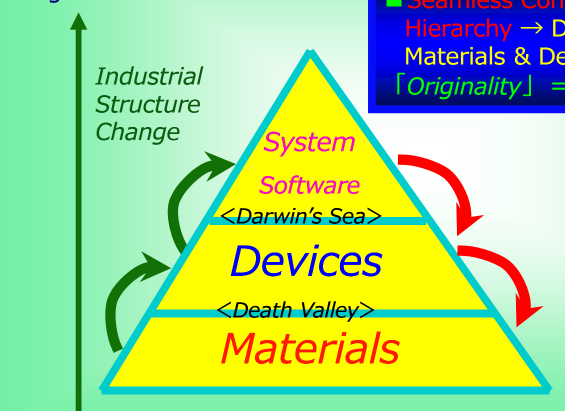
## ■Industrial-Structure Change

*Industrial Society to Knowledge-based Society*




■Seamless Connection in the Hierarchy → Design-based Materials & Device Fabrications
*「Originality」 = 「Profitability」*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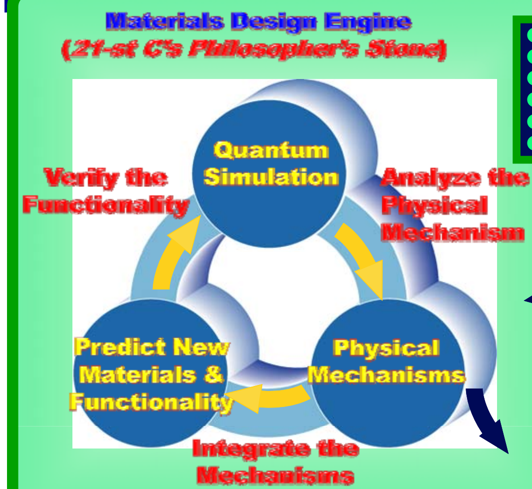
## Computational Nano-Materials Design CMD® OSAKA




- OSAKA-2010-nano
- MACHIKANEYAMA-2010nano
- KANSAI-2010
- T-SPACE
- NANIWA-2010
- HiLAPW-2010
- STATE-senri 2010
- QSGW-2010
- R-SPACE
- PSIC-Machi-2010



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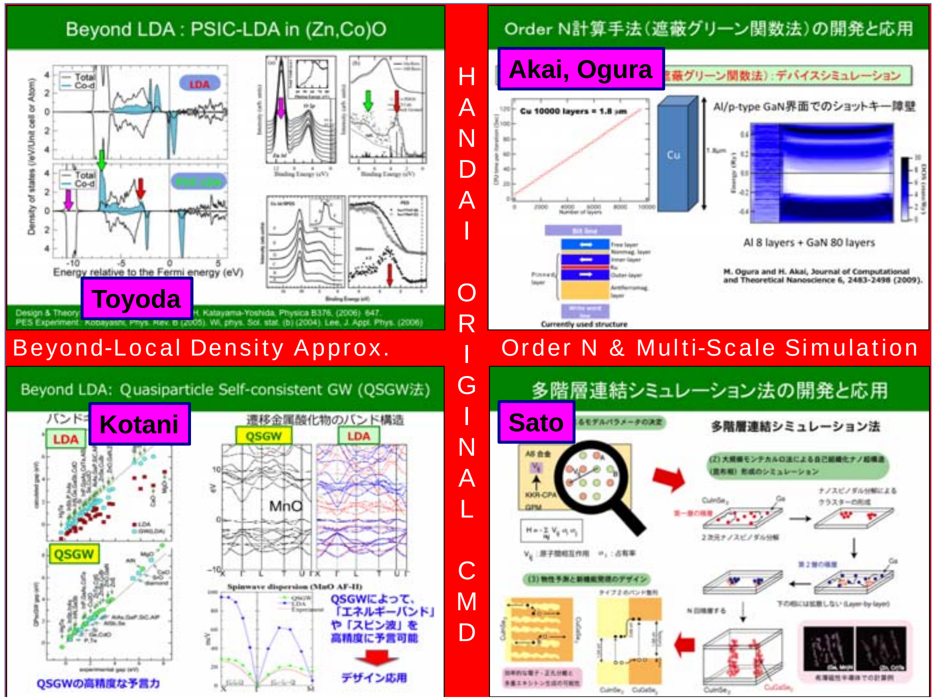
*Quantum Mechanics-based 21-st Century's Alchemy*

## Computational Materials Design (CMD®) Workshop


# Outline

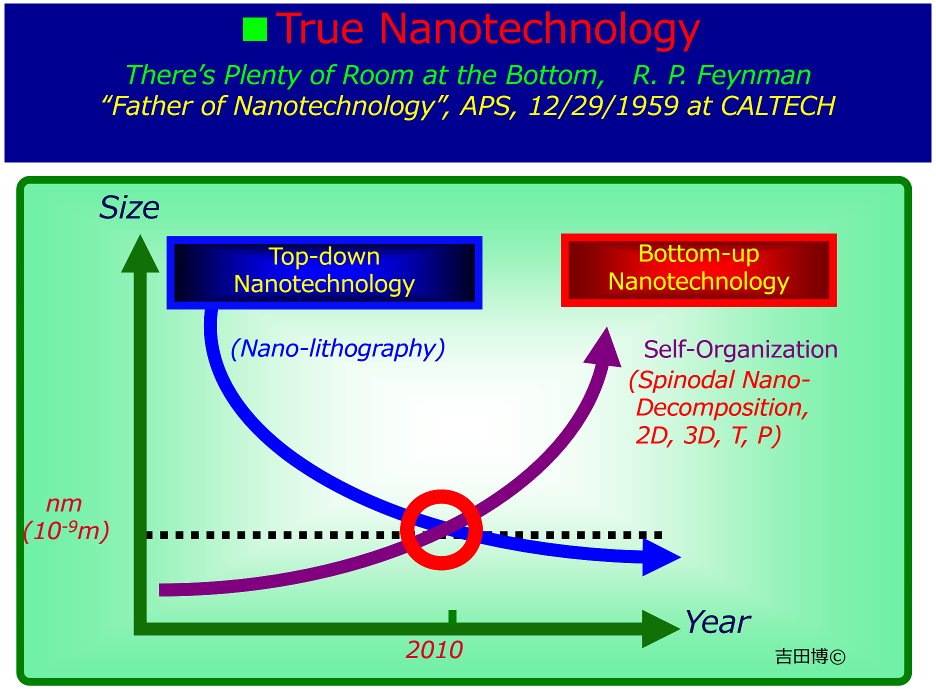
1. Spinodal Nano-technology as a New Class of Bottom-up NT.
   - *Self-Organized & Universal Nano-Fabrication Method*

2. Spintronics Materials Design
   - *New Materials Design, Realization & Tc*

3. Photovoltaic Materials Design by Codoping, Self-Regeneration, and Spinodal Nano-Decomposition for PVSCs.
   - *Electron-Hole Separation & Nano-Superstructurs*



# Spinodal Nanotechnology as a New Class of Bottom-up Nanotechnology


■True Nanotechnology
There's Plenty of Room at the Bottom, R. P. Feynman
"Father of Nanotechnology", APS, 12/29/1959 at CALTECH
Size
Top-down Nanotechnology
Bottom-up Nanotechnology
(Nano-lithography)
Self-Organization
(Spinodal Nano-Decomposition, 2D, 3D, T, P)
nm (10-9m)
Year
2010
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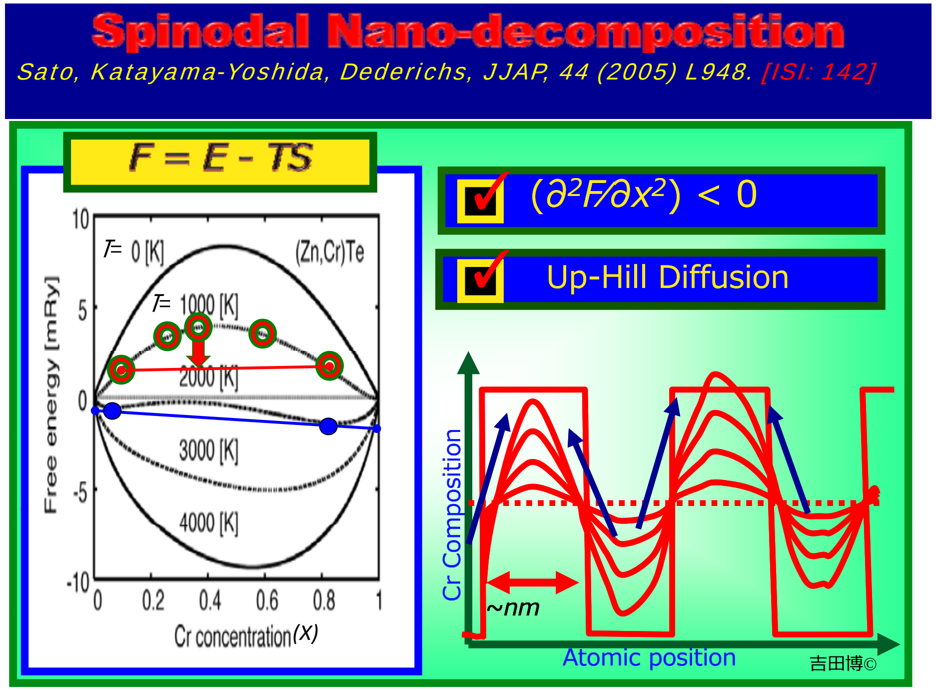
Spinodal Nano-decomposition
Sato, Katayama-Yoshida, Dederichs, JJAP, 44 (2005) L948. [ISI: 142]
F = E - TS
(∂2F/∂x2) < 0
Up-Hill Diffusion
T= 0 [K]
(Zn,Cr)Te
T= 1000 [K]
2000 [K]
3000 [K]
4000 [K]
Free energy [mRy]
Cr concentration (X)
Cr Composition
~nm
Atomic position
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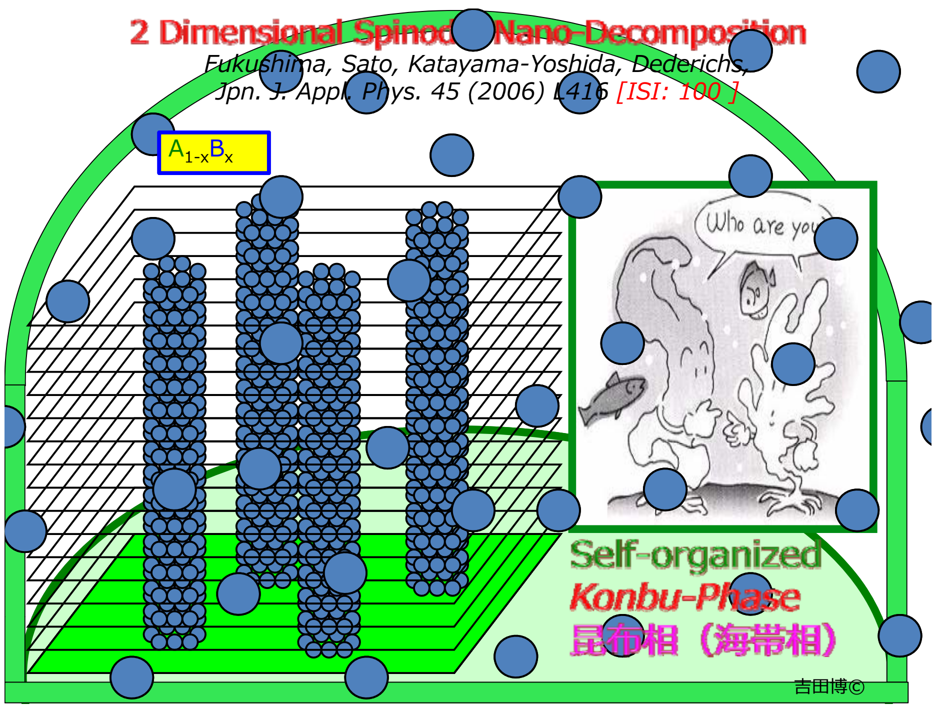
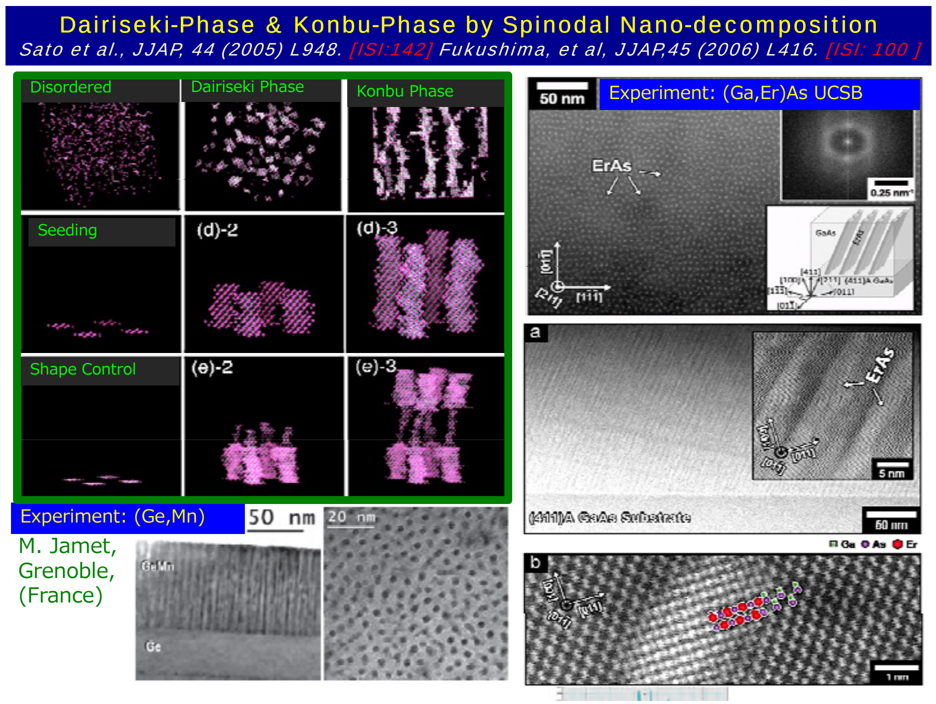

2 Dimensional Spinodal Nano-Decomposition
Fukushima, Sato, Katayama-Yoshida, Dederichs,
Jpn. J. Appl. Phys. 45 (2006) L416 [ISI: 100 ]
A1-xBx
Who are you
Self-organized
Konbu-Phase
昆布相（海帯相）
吉田博©


Dairiseki-Phase & Konbu-Phase by Spinodal Nano-decomposition
Sato et al., JJAP, 44 (2005) L948. [ISI:142] Fukushima, et al, JJAP,45 (2006) L416. [ISI: 100 ]
Disordered
Dairiseki Phase
Konbu Phase
Seeding
(d)-2
(d)-3
Shape Control
(e)-2
(e)-3
Experiment: (Ga,Er)As UCSB
50 nm
ErAs
Experiment: (Ge,Mn)
M. Jamet, Grenoble, (France)
50 nm
20 nm

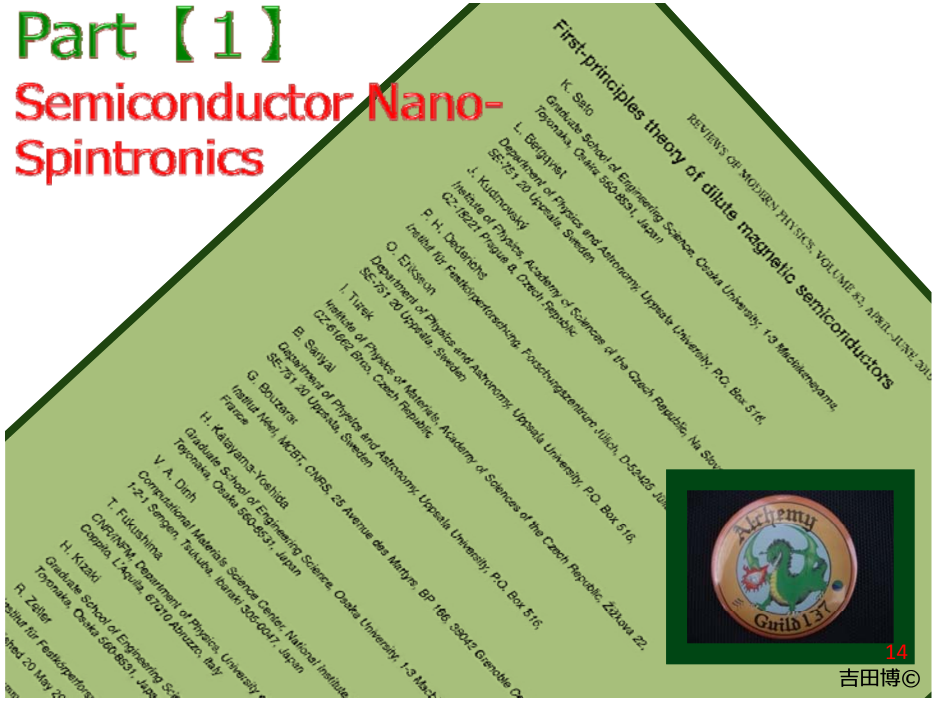
## A New Class of Bottom-up Nanotechnology

### Spinodal Nanotechnology

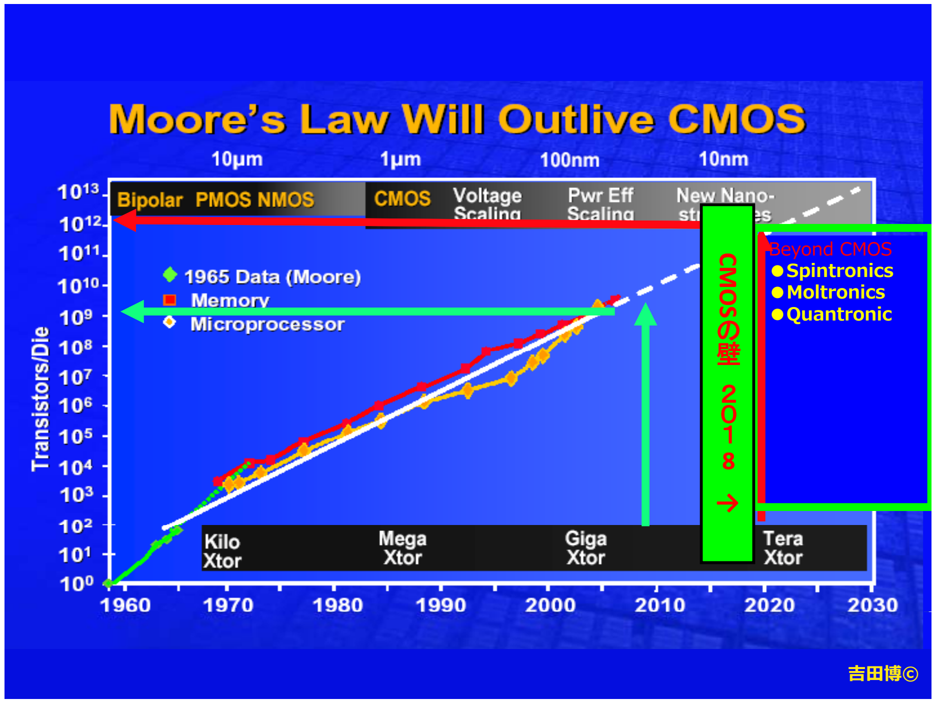
- ☑ Semiconductor Nano-Spintronics
- ☐ Semiconductor Nano-Spincaloritronics
- ☐ Spinodal Thermoelectric-Power Materials
- ☐ High-efficient Nano-Spinodal LED & LASER
- ☐ Nano catalyst for Automotive Gas-Emission
- ☑ Nano-Spinodal Photovoltaic Solar Cells
- ☐ Hydrogen Photosynthesis Nano catalyst
- ☐ Semiconductor-DMS Hydrogen Storage
- ☐ High-$T_c$ Nano-Superconductors
- ☐ Nano catalyst for Fuel Cells
- ☐ Multi-ferroic Nano composites
- ☐ Spinodal Nano-Quantronics
- ☐ Spinodal Nano-Moltronics
- ☐ Spinodal Nano-Water-Splitting
- ☐ Spinodal Nano-Artificial Photosynthesis

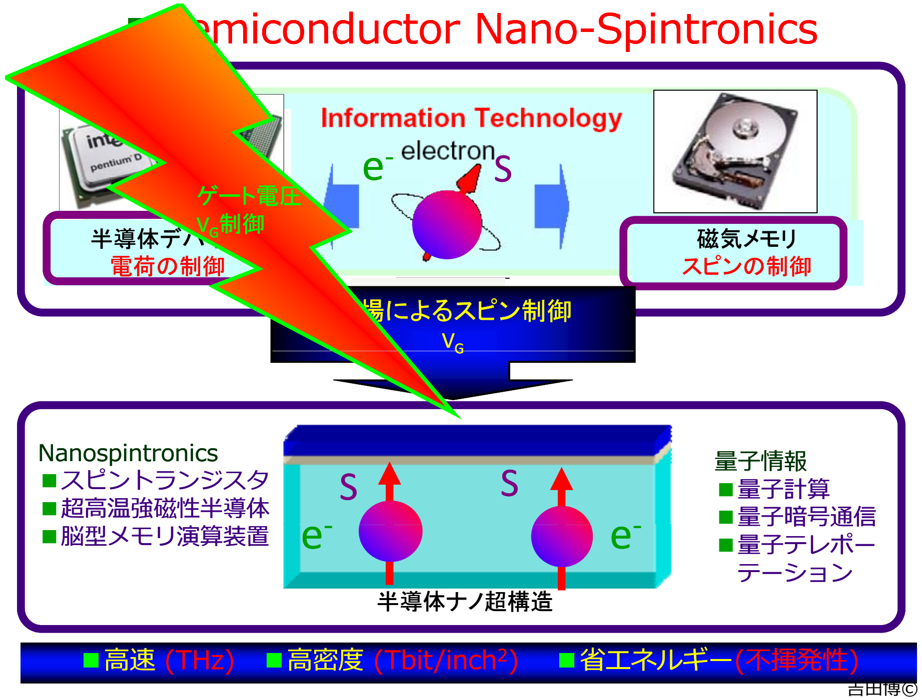


## Part【1】 Semiconductor Nano-Spintronics





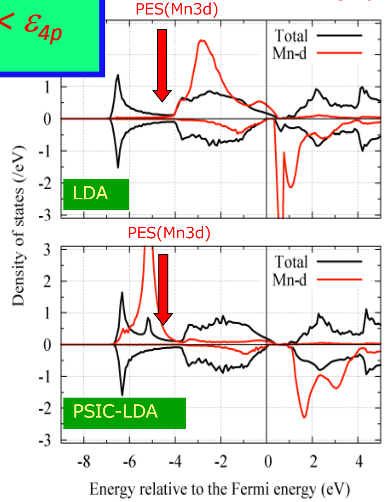
## LDA vs. PSIC-LDA : Akai-KKR-CPA (Ga,Mn)As

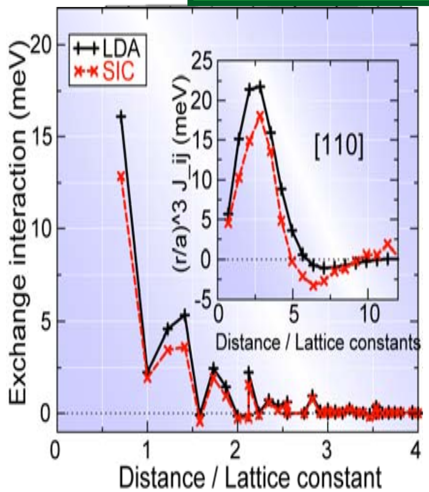
*Zener's p-d exchange mechanism*

$H = -\sum_{i \neq j} J_{ij} S_i \cdot S_j$

$\varepsilon_{3d} < \varepsilon_{4p}$

Mn 5%




- *M.Toyoda et al., Physica B, 376 (2006) 647. (ISI: 87)*
- *K. Sato et al., Rev. Mod. Phys. 82 (2010) 1633. (ISI: 196)*

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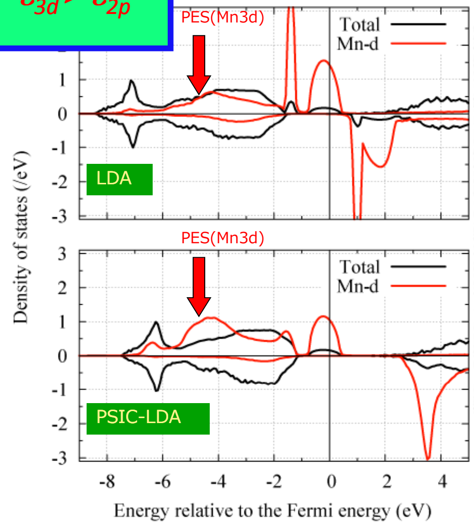
## LDA vs. PSIC-LDA : Akai-KKR-CPA (Ga,Mn)N

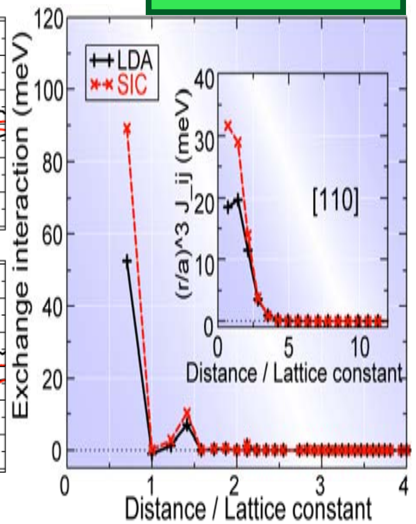
*Zener's double exchange mechanism*

$H = -\sum_{i \neq j} J_{ij} S_i \cdot S_j$

$\varepsilon_{3d} > \varepsilon_{2p}$

Mn 5%




- *M.Toyoda et al., Physica B, 376 (2006) 647.(ISI:87)*
- *K.Sato et al., RMP, 2010 (ISI:196)*

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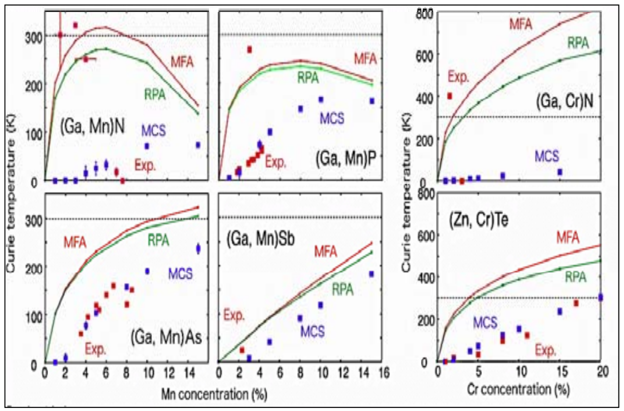
## Semiconductor Nano-Spintronics : Materials Design & $T_c$

Design & Realization of Semiconductor Spintronics




Design-based Realization

(Zn,Co)O
(Ga,Mn)N
(ZnCr)Te
Mg(O,N)
$(Mg,V_{Mg})O$
Ca(O,C)
Ba(O,N)
$(Zn,V_{Zn})O$
Zn(O,N)
………

- *K. Sato, et al., Semiconductor Science and Technology, 17, (2002) 367. (ISI: 518)*
- *K. Sato, et al. Jpn. J. of Appl. Phys., 39, (2000) L555. (ISI: 478)*
- *K. Sato, et al. Jpn. J. of Appl. Phys., 40, (2001) L334. (ISI: 284)*
- *K. Sato et al., Rev. Mod. Phys. 82 (2010) 1633. (ISI: 196)*

# Spinidal Nano-decomposition in Semiconductor Spintronics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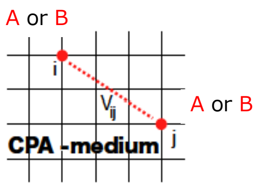
## Effective Chemical Pair Interaction by KKR-CPA & Multiscale Simulation of Spinodal Nano-Decomposition

■ *K. Sato, et al., Rev. Mod. Phys. 82 (2010) 1633. [ISI:196]*




$$H = -\sum_{i>j} V_{ij}\,\sigma_i\,\sigma_j$$

$V_{ij}$ : **Effective** B-B **pair interaction in CPA-medium**

$$V_{ij} = V_{ij}^{AA} + V_{ij}^{BB} - 2V_{ij}^{AB}$$

$\sigma_i$ :B **occupation at i-site**

$$V_{ij} = \frac{-2}{\pi}\,\mathrm{Im}\int^{\varepsilon_F} d\varepsilon\,\mathrm{Tr}\,[\,\Delta_i(\varepsilon)\tau_{ij}(\varepsilon)\,\Delta_j(\varepsilon)\,\tau_{ji}(\varepsilon)]$$

$$\begin{cases}\Delta_i(\varepsilon) = X_A^i(\varepsilon) - X_B^i(\varepsilon) \\ \tau_{ij}(\varepsilon) = \sum_{\vec{k}} [\,t^{-1}(\varepsilon) - g(\vec{k},\varepsilon)\,]^{-1}\exp\{\,i\vec{k}\bullet(\vec{R}_i - \vec{R}_j)\}\end{cases}$$

X: single site scattering-matrix  $\vec{R}$ : lattice vector

τ: scattering path operator  g: KKR structure constant

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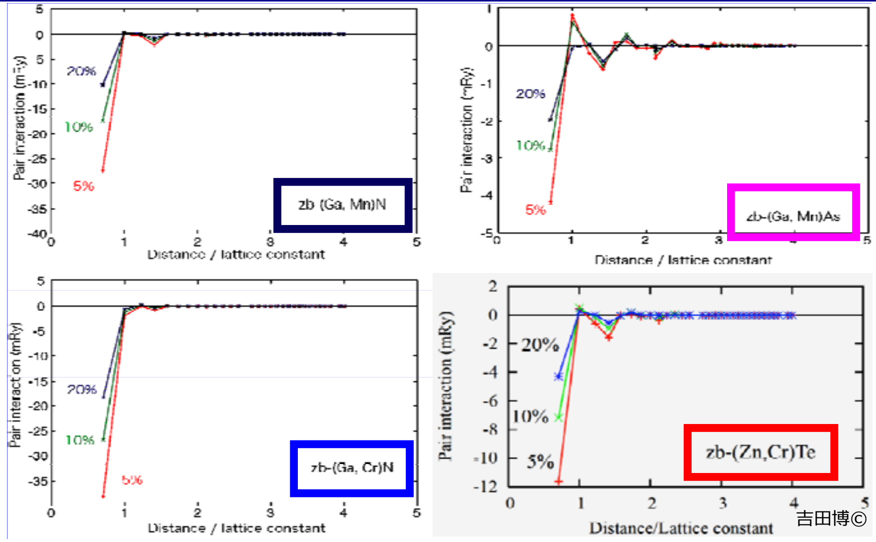
## Spinodal Nano-decomposition

$$H = -\sum_{i>j} V_{ij}\,\sigma_i \cdot \sigma_j \qquad V_{ij} = V_{ij}^{MnMn} + V_{ij}^{GaGa} - 2V_{ij}^{MnGa}$$

■ *Sato, Katayama-Yoshida, Dederichs., Jpn. J. Appl. Phys. 44 (2005) L948. [ISI: 142]*

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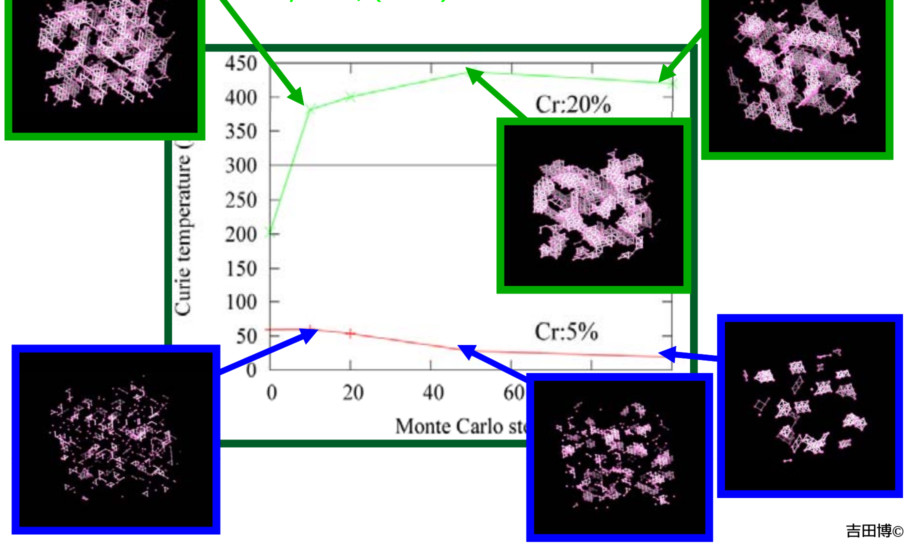
## $T_c$ vs. 3D Spinodal Nano-decomposition in (Zn,Cr)Te

■ K. Sato *et. al:* Jpn. J. Appl. Phys. 44, (2005). L948.

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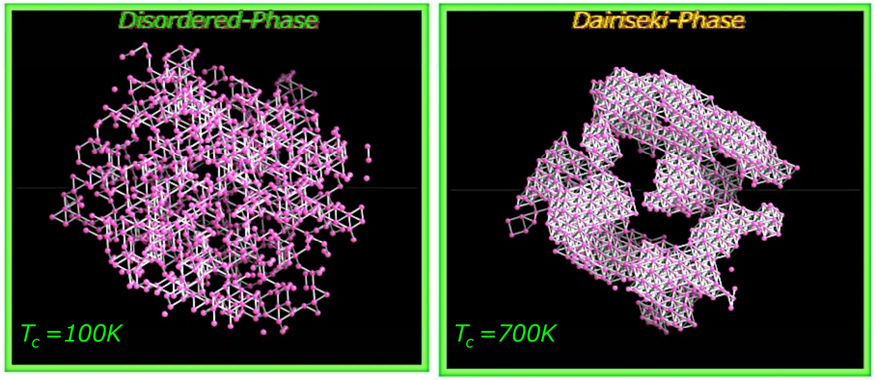
## 3D Spinodal Nano-Decomposition in (Ga,Cr)N ; Cr30%




■ Random configuration

■ *3D Spinodal Nano-Decomposition*

■ *$T_c$ enhances dramatically by 3D Spinodal Nano-decomposition above the percolation limit.*

■ *K. Sato, H. Katayama-Yoshida, P.H. Dederichs, Jpn. J. Appl. Phys. 44 (2005) L948. [ISI: 142]*

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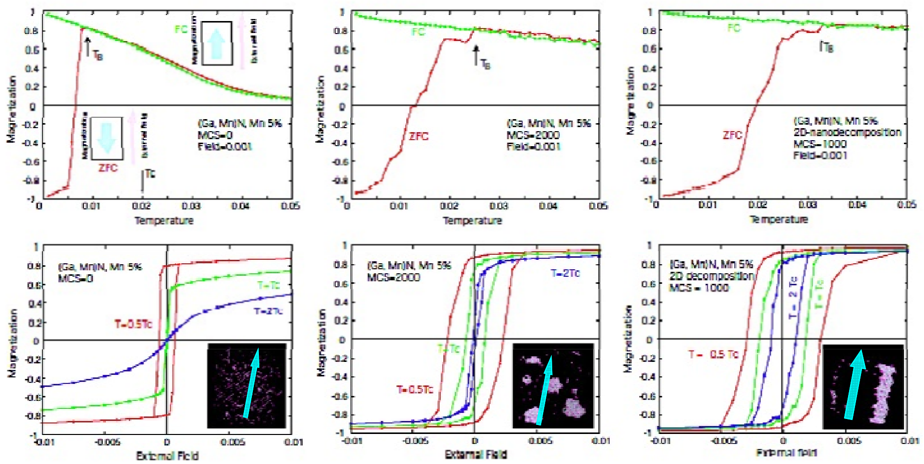
## $T_B$ of (Ga,Mn)N in Spinodal Nano-Decomposition

*K. Sato, T. Fukushima, H. Katayama-Yoshida, Jpn. J. Appl. Phys., 46, (2007) L687.* *[ISI: 41]*

Disdorded Phase | Dairiseki-phase(3D) | Konbu-phase(2D)




High Blocking Temperature ($T_B$) by Magneto Crystal Anisotropy

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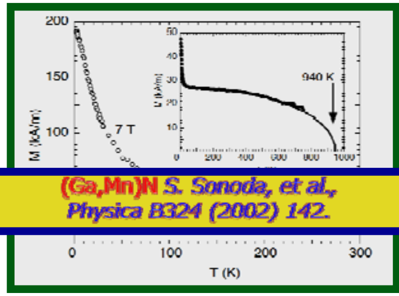
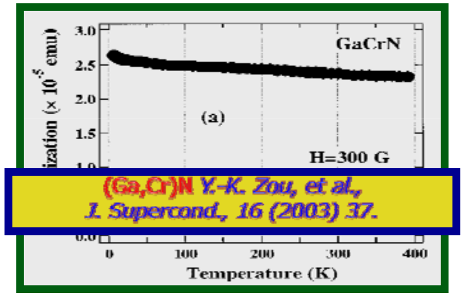
## Konbu-Phase with High-$T_B$ is Ubiquitous

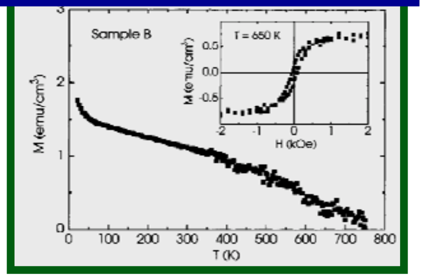



(Ga,Mn)N S. Sonoda, et al., Physica B324 (2002) 142.




(Ga,Cr)N Y.-K. Zou, et al., J. Supercond., 16 (2003) 37.

(Ga,Mn)N S. Dhar et al., APL 82 (2003) 2077.




(Ga,Cr)N N. Newman et al., ($T_B$) $T_c$=1,050K (Arizona)

**Basic Patent (EU, USA, Japan)**

- EP-1219731B1,
- USP-0112278A1,
- EP-1367151A1
- JP2001-059195, 0593030

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## Codoping for High-$T_c$ DMS

Self-compensation is *"Mother Nature's Codoping"*.

We propose a new class of *"Alchemist's Codoping"*.

- *Yamamoto, Katayama-Yoshida, JJAP, 38 (1999) L166.* *[ISI: 340]*
- *Sato, Katayama-Yoshida, Dederichs, JJAP. 44 (2005) L948.* *[ISI: 142]*

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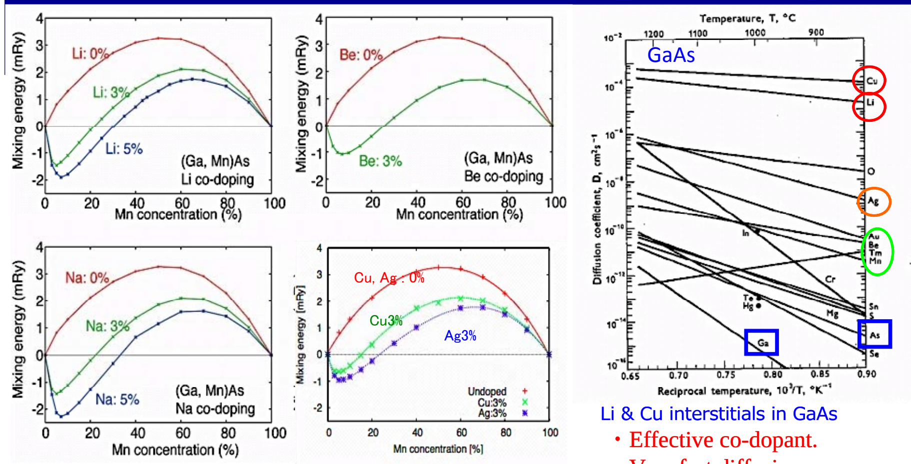
## Codoping with interstitial impurities in GaMnAs




$$\Delta E = E[Ga_{1-c}Mn_cAs + Li_y] - c \times E[MnAs + Li_y] - (1-c) \times E[GaAs + Li_y]$$

Li & Cu interstitials in GaAs

- Effective co-dopant.
- Very fast diffusion.
- Anneal out after crystal growth to recover the ferromagnetism.

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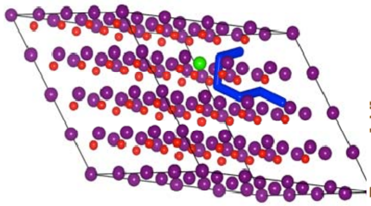
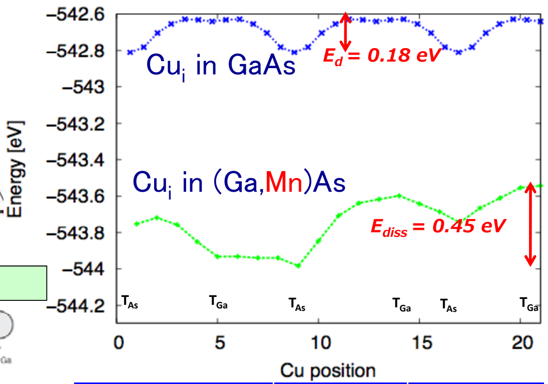
- *L. Bergqvist et al., Phys. Rev. B83 (2011) 165201.* $Mn_s + Li_i$
- *H. Fujii, K. Sato et al., APEX 4 (2011) 043003.* $Mn_s + Cu_i$

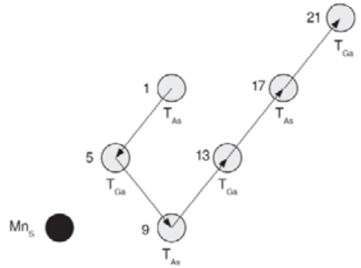
# Diffusion & Dissociation energy

■ ***$Cu_i$ in Mn-doped p-type GaAs ; H. Fujii et al., (2011).***



diffusion and dissociation path



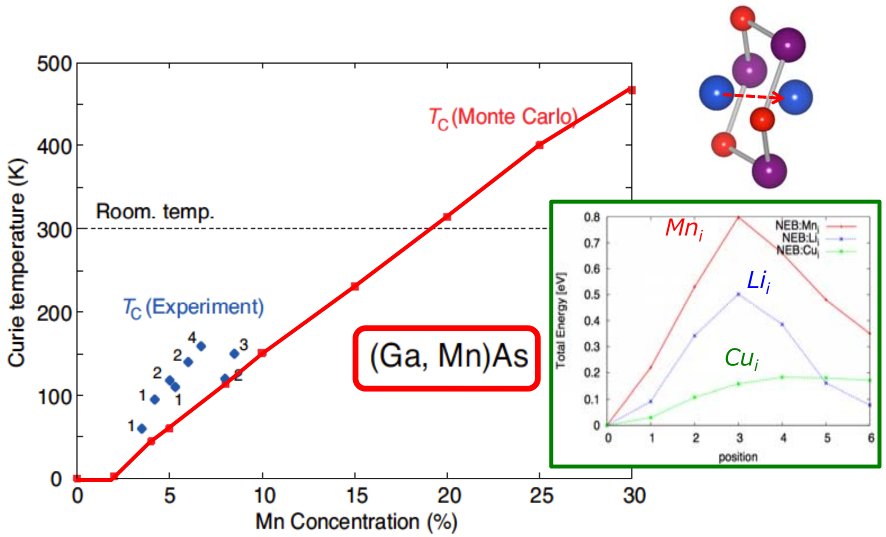

| (Ga,Mn)As | $E_d$ [eV] | $E_{diss}$ [eV] |
|---|---|---|
| $Mn_i^{2+}$ | 0.8 | 1.2 [1] |
| $Li_i^{+}$ | 0.5 | 0.73 [1] |
| $Cu_i^{+}$ | 0.18 | 0.45 |


[1] L. Bergqvist, K. Sato et. al.,: PRB 83, 165201 (2011).


# Alchemist's Codoping Method :

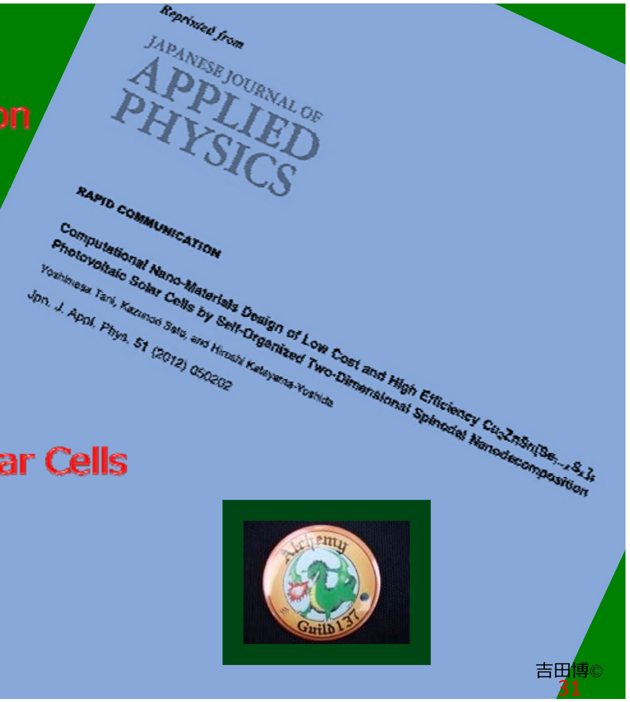
■ *L. Bergqvist et al. PRB 83 (2011) 165201.* $Mn_s + Li_i$

■ *H. Fujii et al., APEX 4 (2011) 043003.* $Mn_s + Cu_i$




# Part [2]

Self-Regeneration
&
Spinodal Nano-Decomposition
for
Low-Cost
&
High-Efficiency
Photovoltaic Solar Cells


Reprinted from
JAPANESE JOURNAL OF APPLIED PHYSICS

RAPID COMMUNICATION

Computational Nano-Materials Design of Low Cost and High Efficiency Cu-ZnSn(Se1-xSx)4 Photovoltaic Solar Cells by Self-Organized Two-Dimensional Spinodal Nanodecomposition

Yoshimasa Tani, Kazunori Sato, and Hiroshi Katayama-Yoshida

Jpn. J. Appl. Phys. 51 (2012) 050202

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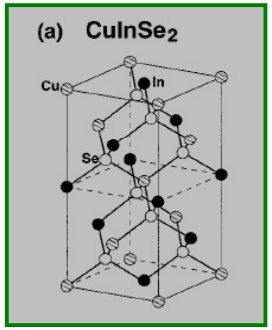
# Diamond Mutation

## Family Tree of Diamond Mutation

C, Si, Ge

**IV**

- GaAs, LiZnAs → **III-V, (I,II)-V**
  - ZnGeAs$_2$ → **(II,IV)-V$_2$**
    - LiGaGe$_2$As$_4$ → **(I,III,IV$_2$)-V$_4$** →
- ZnSe → **II-VI**
  - CuInSe$_2$ → **(I,III)-VI$_2$**
    - Cu$_2$ZnSnSe$_4$ → **(I$_2$,II-IV)-VI$_4$** →
- CuCl → **I-VII**




■ *H. Katayama-Yoshida, T. Yamamoto, US-Patent US6153895,* 特願平8-14091、特開平09-213978, 特願平9-308765、特開平11-145500, 特願平9-239839、特開平11-87750

# Photovoltaics Materials Design by Codoping and Self-Regeneration

**Self-Regeneration*
**Artificial Doping of Acceptor and Donor*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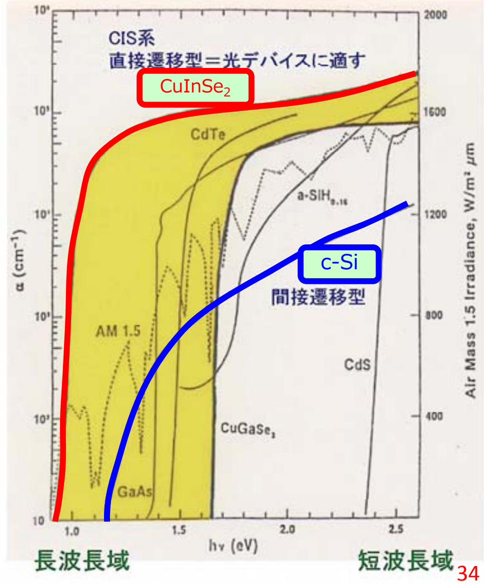
# Chalcopyrite $CuInSe_2$ (CIS)

1）光吸収係数
：半導体の中で最大
＿$\alpha = 1 \times 10^5 cm^{-1}$程度

2）直接遷移型半導体
：光デバイスに適す
結晶Si：間接遷移型半導体

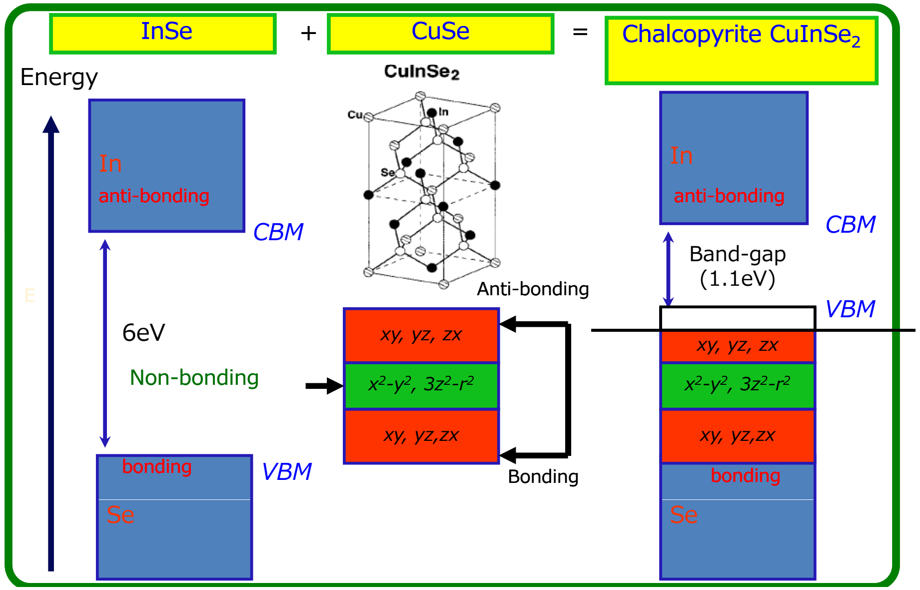
⇒ 原理的には、
厚さ1μm以下の薄膜で、
高効率太陽電池が作れる。





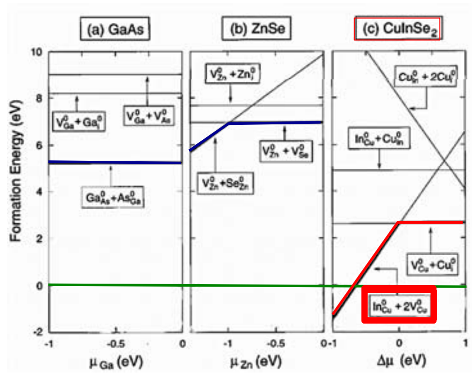

# Electronic structure: $CuInS_2(Se_2)$

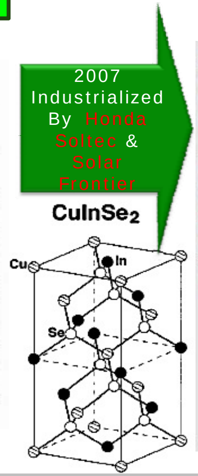
■*Yamamoto, Katayama-Yoshida、JJAP (1995).* *[ISI: 340]*




# Self-Regenerated Low-Cost & High-Efficiency PVSCs : $[2V_{Cu}^{-} + In_{Cu}^{2+}]$

Mother Nature's Codoping




■*Zhang, Wei, Zunger, Katayama-Yoshida, Phys. Rev. B57 (1998) 9642.* (*ISI: 586*)
■*Yamamoto, Katayama-Yoshida, JJAP, 36(1997) L180.* (*ISI: 76*)
■*Yamamoto, Katayama-Yoshida, JJAP, 38 (1999) L166.* (*ISI: 340*)
■*Yamamoto, Katayama-Yoshida, PHYSICA B, 302 (2001) 115.* (*ISI:111*)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## Self-Regeneration in $CuInSe_2$ [General Rule]

### $n$ x [$CuInSe_2$] + $m$ x[$2V_{Cu}^{-} + In_{Cu}^{2+}$] = $Cu_{n-3}In_{n+1}Se_{2n}$ ($m$ =1)

| | | | | |
|---|---|---|---|---|
| (n = 3) | $Cu_3In_3Se_6$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | | $In_2Se_3$ |
| (n = 4) | $Cu_4In_4Se_8$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | | $CuIn_5Se_8$ |
| (n = 5) | $Cu_5In_5Se_{10}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | | $CuIn_3Se_5$ |
| (n = 6) | $Cu_6In_6Se_{12}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | | $Cu_3In_7Se_{12}$ |
| (n = 7) | $Cu_7In_7Se_{14}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | $Cu_4In_8Se_{14}$ | ⇨ | $Cu_2In_4Se_7$ |
| (n = 8) | $Cu_8In_8Se_{16}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | | $Cu_5In_9Se_{16}$ |
| (n = 9) | $Cu_9In_9Se_{18}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | $Cu_6In_{10}Se_{18}$ | ⇨ | $Cu_3In_5Se_9$ |
| (n = 10) | $Cu_{10}In_{10}Se_{20}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | | $Cu_7In_{11}Se_{20}$ |
| (n = 11) | $Cu_{11}In_{11}Se_{22}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | $Cu_8In_{12}Se_{22}$ | ⇨ | $Cu_4In_6Se_{11}$ |
| (n = 12) | $Cu_{12}In_{12}Se_{24}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | | $Cu_9In_{13}Se_{24}$ |
| (n = 13) | $Cu_{13}In_{13}Se_{26}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | $Cu_{10}In_{14}Se_{26}$ | ⇨ | $Cu_5In_7Se_{13}$ |
| (n = 14) | $Cu_{14}In_{14}Se_{28}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | ⇨ | $Cu_{11}In_{15}Se_{28}$ |
| (n = 15) | $Cu_{15}In_{15}Se_{30}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | $Cu_{12}In_{16}Se_{28}$ | ⇨ | $Cu_3In_4Se_7$ |
| (n = 16) | $Cu_{16}In_{16}Se_{32}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | ⇨ | $Cu_{13}In_{17}Se_{32}$ |
| (n = 17) | $Cu_{17}In_{17}Se_{34}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | $Cu_{14}In_{18}Se_{34}$ | ⇨ | $Cu_7In_9Se_{17}$ |
| (n = 18) | $Cu_{18}In_{18}Se_{36}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | ⇨ | $Cu_{15}In_{19}Se_{36}$ |
| (n = 19) | $Cu_{19}In_{19}Se_{38}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | ⇨ | $Cu_{16}In_{20}Se_{38}$ |
| (n = 20) | $Cu_{20}In_{20}Se_{40}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | ⇨ | $Cu_{17}In_{21}Se_{40}$ |
| (n = 21) | $Cu_{21}In_{21}Se_{42}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | $Cu_{18}In_{22}Se_{42}$ | ⇨ | $Cu_9In_{11}Se_{21}$ |
| (n = 22) | $Cu_{22}In_{22}Se_{44}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | ⇨ | $Cu_{19}In_{23}Se_{44}$ |
| (n = 23) | $Cu_{23}In_{23}Se_{46}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | $Cu_{20}In_{24}Se_{46}$ | ⇨ | $Cu_{10}In_{12}Se_{23}$ |
| (n = 24) | $Cu_{24}In_{24}Se_{48}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | ⇨ | $Cu_{21}In_{25}Se_{48}$ |
| (n = 25) | $Cu_{25}In_{25}Se_{50}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | $Cu_{22}In_{26}Se_{50}$ | ⇨ | $Cu_{11}In_{13}Se_{25}$ |
| (n = 26) | $Cu_{26}In_{26}Se_{52}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | | ⇨ | $Cu_{23}In_{27}Se_{52}$ |
| (n = 27) | $Cu_{27}In_{27}Se_{54}$ + ($2V_{Cu}^{-} + In_{Cu}^{2+}$) = | $Cu_{24}In_{28}Se_{54}$ | ⇨ | $Cu_{12}In_{14}Se_{27}$ |

..............................................................................

Red Color : *Experimentally observed up to 2013.*

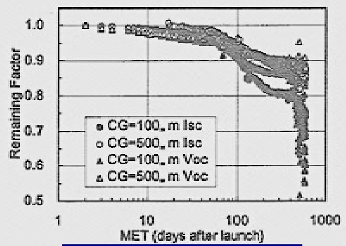


## Self-Regeneration & Spinodal Nano-Decomposition

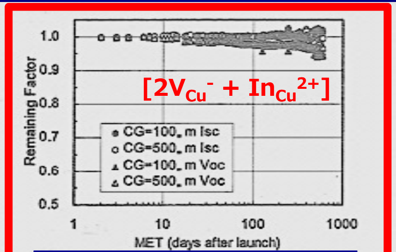
| Stoichiometric Compounds | [Rule 1] : Self-Regeneration Mechanism | Self-Regenerated Compounds | [Rule 2] : Spinodal Nano-Decomposition |
|---|---|---|---|
| $CuIn[S,Se]_2$ **(CIS)** | [$2V_{Cu}^{-} + In_{Cu}^{2+}$] | $Cu_{1-3\alpha}In_{1+\alpha}[S,Se]_2$ | [$Cu,V_{Cu}$] [S,Se] [Se,O] |
| $Cu[In,Ga][S,Se]_2$ **(CIGS)** | [$2V_{Cu}^{-} + In_{Cu}^{2+}$] | $Cu_{1-3\alpha}[In_{1+\alpha-x}Ga_x][S,Se]_2$ | [$Cu,V_{Cu}$] [In,Ga] [S,Se] [Se,O] |
| $Cu_2ZnSn[S,Se]_4$ **(CZTS)** | [$V_{Cu}^{-} + Zn_{Cu}^{+}$] | $Cu_{2-2\alpha}Zn_{1+\alpha}Sn[S,Se]_4$ | [$Cu,V_{Cu}$] [S,Se] [Se,O] |



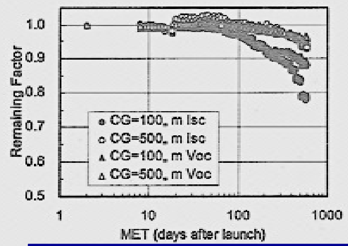
## Experimental Verification of Self-Regeneration from the Radiation Damage Tested by JAXA's Satellite "TUBASA" : Cu[In,Ga]$Se_2$



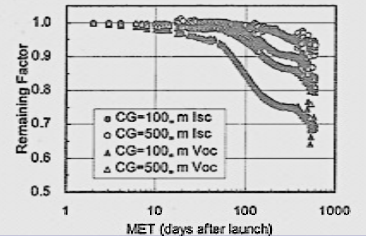

Bulk Poly Si-PVSC




Large Scale $CuInGaSe_2$-PVSC




InGaP/GaAs Tandem PVSC

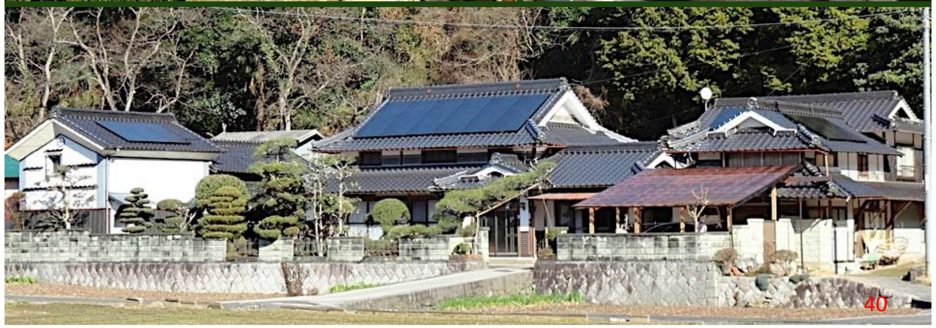



Si Single Crystalline Space-Use PVSC



## My Parent's Country House, Okayama, Japan

Buy : 9 Yen/kW・h
Sell : 42 Yen/kW・h

# Spinodal Nanotechnology as a New Class of Bottom-up Nanotechnology to Increase the PVSC Efficiency Dramatically


吉田博©

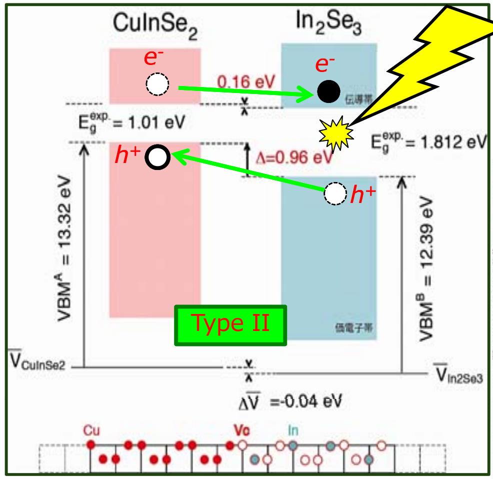
# CIS : $CuInSe_2$ $[Cu,V_{Cu}]$

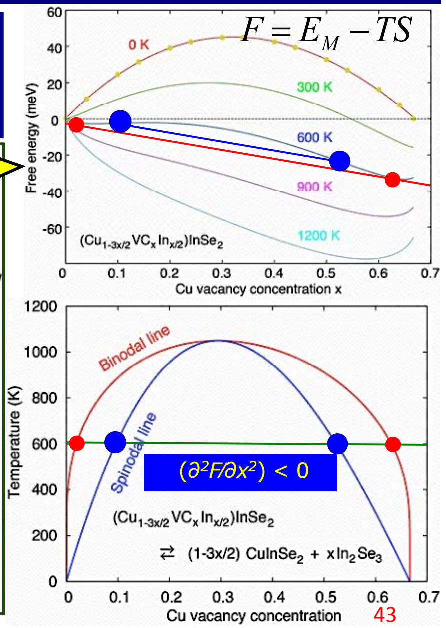
We Can Increase the Energy Conversion Efficiency Dramatically, By Controlling the Spinodal Nano-Decomposition.




## Spinodal Nano-Decomposition & Self-Regeneration by Mother Nature's Codoping $[2V_{Cu} + In_{Cu}]$ in $CuInSe_2$

$$E_M = E[Cu_{1-\frac{3}{2}x}Vc_xIn_{\frac{x}{2}}InSe_2] - (1-\frac{3x}{2})E[CuInSe_2] - \frac{3x}{2}E[In_2Se_3]$$






# CIGS : $Cu[In,Ga]Se_2$

We Can Increase the Energy Conversion Efficiency Dramatically, By Controlling the Spinodal Nano-Decomposition.

# Mixing Energy & Spinodal Nano-Decomposition : CIGS & CZTSSe

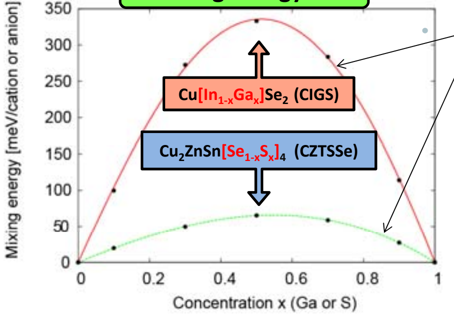
**Mixing energy : ΔE**

**ΔE [CIGS]** = $E[Cu(In_{1-x}Ga_x)Se_2]$ − $(1-x)\,E[CuInSe_2] + x\,E[CuGaSe_2]$

**ΔE [CZTSSe]** = $E[Cu_2ZnSn(Se_{1-x}S_x)_4]$ − $(1-x)\,E[Cu_2ZnSnS_4] + x\,E[Cu_2ZnSnSe_4]$

Mixed States — Phase Separated States

**Mixing energy ΔE**




**Positive and Convex upward ΔE**

**Spinodal Nano-decomposition.**

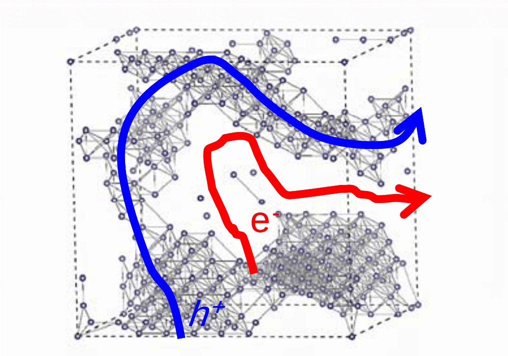
- *$CuIn_{1-x}Ga_xSe_2$ → $(1-x)\ CuInSe_2$ + $x\ CuGaSe_2$*
- *$Cu_2ZnSn(S_{1-x}Se_x)_4$ → $(1-x)\ Cu_2ZnSnS_4 + x\ Cu_2ZnSnSe_4$*



# 20% Efficiency $Cu[In_{1-x}Ga_x]Se_2$ : $X_{Ga} = 0.3$ Spinodal Nano-Decomposition (*Dairiseki-Phase*)

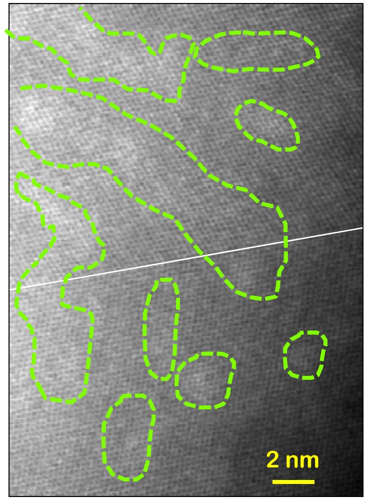
- *Tani, Sato, Katayama-Yoshida*

Multi-scale Simulation of 3D Spinodal Nano-Decomposition $Cu[In_{1-x}Ga_x]Se_2$ : $X_{Ga} = 0.15$




3D Crystal Growth
*Dairiseki-Phase*

- *Y. Yan, M.M. Al-Jassim. NREL.*



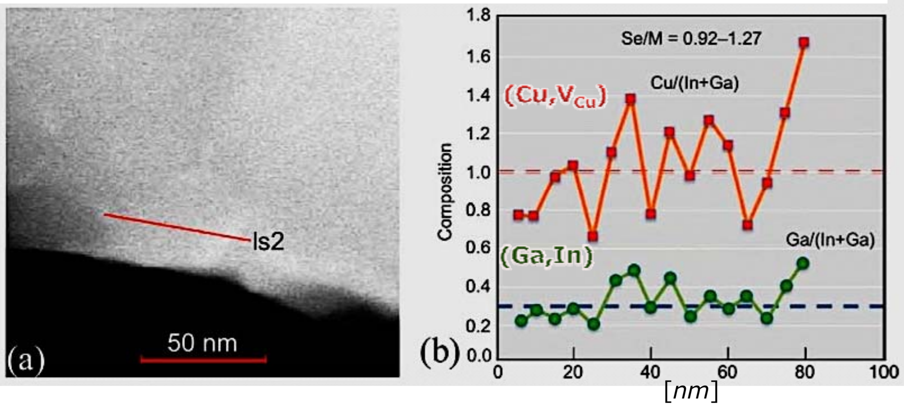

**Z-contrast STEM (EDX) Image** 吉田博©



# 20% PC Efficiency $Cu[In_{1-x}Ga_x]Se_2$ : $X_{Ga} = 0.3$ Nanodomains (*Dairiseki-Phase*)

Nanoscale Spinodal Wave Length : 10~20 *nm*

- *Y. Yan, M.M. Al-Jassim & R. Noufi, NREL.*



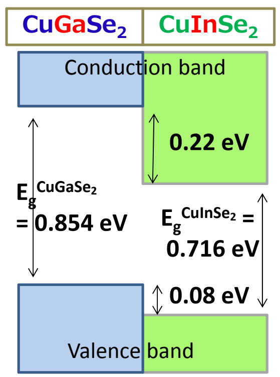

Z-contrast STEM (EDX) Image : Self-Regeneration by **$[2V_{Cu}^- + In_{Cu}^{2+}]$**

$0.65 \leqq [Cu/(In+Ga)] \leqq 1.7$
$0.20 \leqq [Ga/(In+Ga)] \leqq 0.55$
$0.82 \leqq [In/Ga] \leqq 4$

吉田博©



# Band Alignment between $CuInSe_2$ & $CuGaSe_2$




**Type II**

***Valence band offset : $\Delta E_v$***

$$\Delta E_v = \Delta E_{VBM}^{CIS} - \Delta E_{VBM}^{CGS} + \Delta E_{C,C'}$$

$$\Delta E_{VBM}^{CIS\ or\ CGS} = E_{VBM}^{CuInSe_2\ or\ CuGaSe_2} - E_{Cu\text{-}1s}^{CuInSe_2\ or\ CuGaSe_2}$$

$$\Delta E_{C,C'} = E_{Cu\text{-}1s}^{CuInSe_2} - E_{Cu\text{-}1s}^{CuGaSe_2}$$

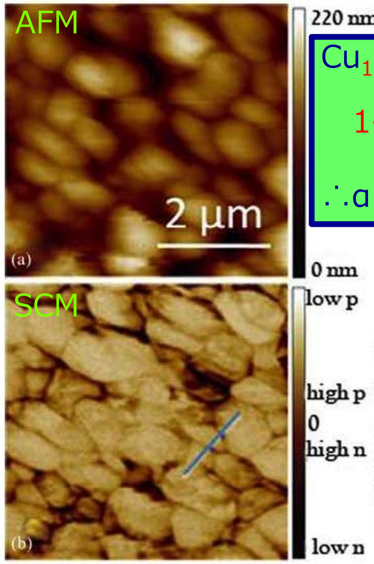
$$\Delta E_v = -0.08\ [eV] < 0$$

$$E_g^{CuInSe_2} < E_g^{CuGaSe_2}$$

**Type Ⅱ Band Alignment**

***Effective Electron & Hole separation***

## AFM Topography & SCM Data of $CuIn_{0.68}Ga_{0.32}Se_2$

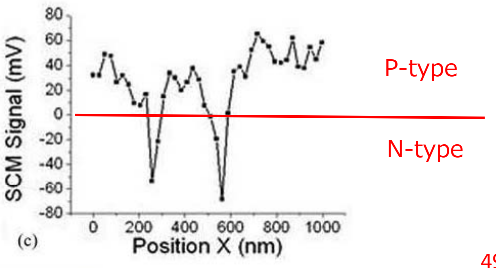



$Cu_{1-3\alpha}In_{1-X+\alpha}Ga_XSe_2$ : $[2V_{Cu}+In_{Cu}]$

$1-3\alpha \geqq 0$ , $1-X+\alpha \geqq 1$

$\therefore \alpha \leqq 1/3$, $\therefore X \leqq 1/3$

David Cahen (Weizmann Institute)





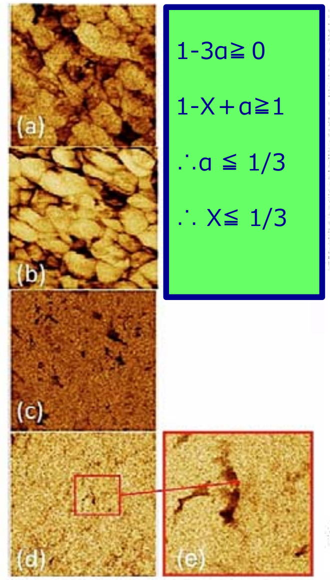

## SCM Data of $Cu_{1-3\alpha}In_{1-X+\alpha}Ga_XSe_2$ : $[2V_{Cu} + In_{Cu}]$ *p*-, *n*-type Inversion Area Ratio & Efficiency

X=0.0

X=0.32

X=0.5

X=0.75



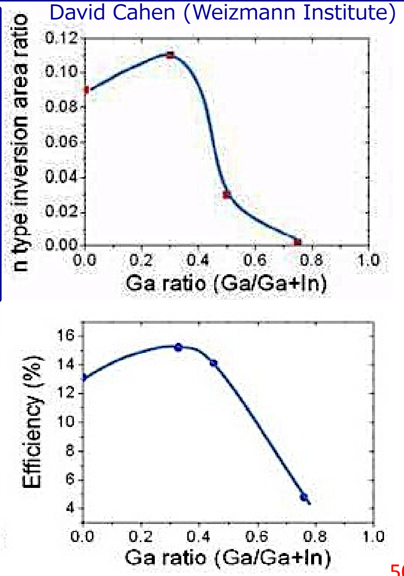

$1-3\alpha \geqq 0$

$1-X+\alpha \geqq 1$

$\therefore \alpha \leqq 1/3$

$\therefore X \leqq 1/3$

David Cahen (Weizmann Institute)






## Cu(In,Ga)(Se,O)$_2$ : Grain Boundaries

STEM/EELS image

*Yanafa Yan et al. NREL*

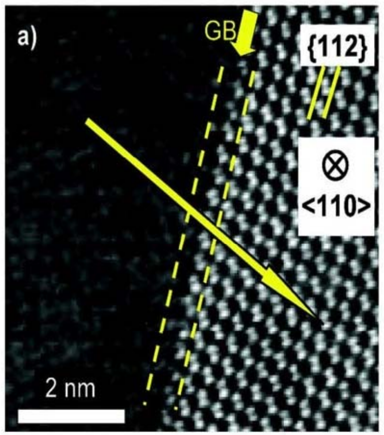
- Spinodal Nano-Decomposition of (Cu, $V_{Cu}$) , (Se, O), (In, Ga) in $Cu(In,Ga)Se_2$.
  - Anti-Correlation of Cu/In & Se/O.
  - Self-Regeneration by [ 2 $V_{Cu}^-$ + $In_{Cu}^{2+}$ ]

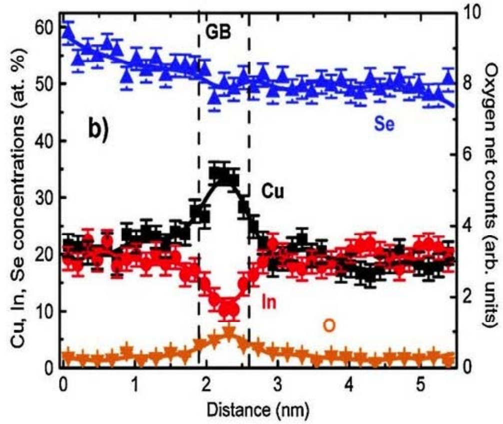


## Cu(In,Ga)[Se,O]$_2$ : Grain boundaries

STEM/EELS image

Element profile



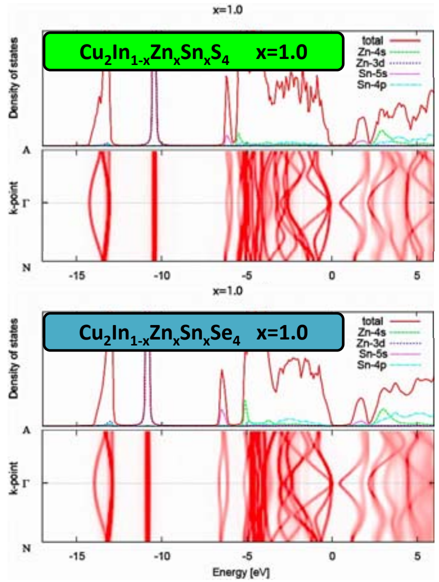

- Spinodal Nano-Decomposition of (Cu, $V_{Cu}$) , (Se, O), (In, Ga) in $Cu(In,Ga)Se_2$.
  - Anti-Correlation of Cu/In & Se/O.
  - Self-Regeneration by [ 2 $V_{Cu}^-$ + $In_{Cu}^{2+}$ ]

# CZTSSe : $Cu_2ZnSn[S,Se]_4$

We Can Increase the Energy Conversion Efficiency Dramatically, By Controlling the Spinodal Nano-Decomposition.




# Substitution of $2In^{3+}$ by $Zn^{2+}$ & $Sn^{4+}$ : Akai-KKR-CPA & PSIC-LDA by Codoping




$2\ In^{3+} \rightarrow Zn^{2+} + Sn^{4+}$

In All of the Substitution,

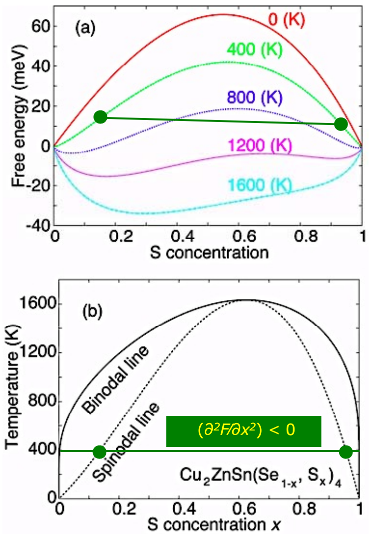
(1) Direct band gap
(2) No impurity states in the band gap
(3) Fano Anti-Resonance

Good for High-efficiency Photovoltaic Solar Cells.

吉田博©



# Spinodal Nano-Decomposition in $Cu_2ZnSn[Se,S]_4$




- Alloying Se and S
- Free energy $F$

$$F = E_M - TS$$

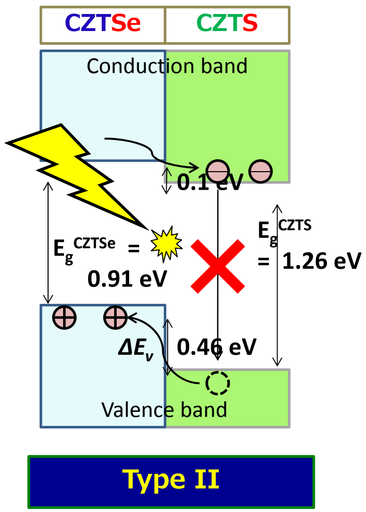
$$E_M = E[Cu_2ZnSn(Se_{1-x}, S_x)_4] - (1-x)E[Cu_2ZnSnSe_4] - xE[Cu_2ZnSnS_4]$$

$$S = -k_B\left[(1-x)\log(1-x) + x\log x\right]$$

- Upward Convexity in $F$ ⇒ Spinodal Nano-Decomposition



# Valence band offset between $Cu_2ZnSnS_4$ and $Cu_2ZnSnSe_4$




***Valence band offset : $\Delta E_v$***

$$\Delta E_v = \Delta E_{VBM}^{CZTSe} - \Delta E_{VBM}^{CZTS}$$

$$\left( \Delta E_{VBM} = E_{VBM} - E_{Cu\text{-}1s} \right)$$

Type Ⅱ band alignment

*Effective Electron & Hole Separation*

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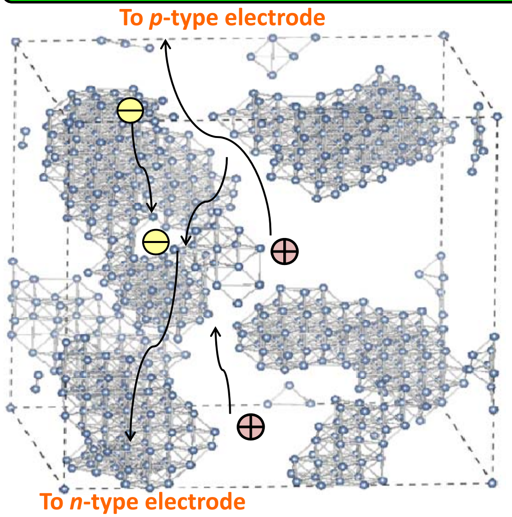
# Monte Carlo Simulation of 3D Spinodal Nano-Decomposition in $Cu_2ZnSn[S,Se]_4$

**Dairiseki-Phase : $Cu_2ZnSn[Se_{1-x}S_x]_4$ $X_S = 0.15$**

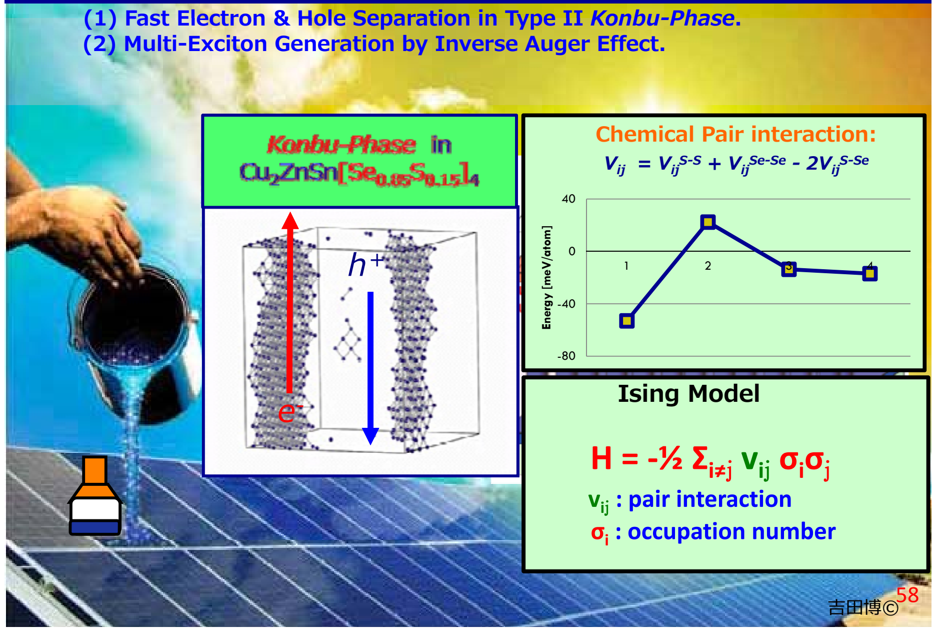



## Calculation details

- Concentration $X_S = 0.15$
- Temperature = 300 K
- 250 MCS / atom
- $H = -\frac{1}{2} \Sigma_{i \neq j} v_{ij} \sigma_i \sigma_j$
  - $v_{ij}$ : pair interaction
  - $\sigma_i$ : occupation number

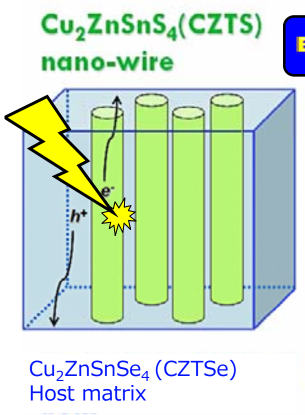
$$V_{ij} = V_{ij}^{S-S} + V_{ij}^{Se-Se} - 2V_{ij}^{S-Se}$$

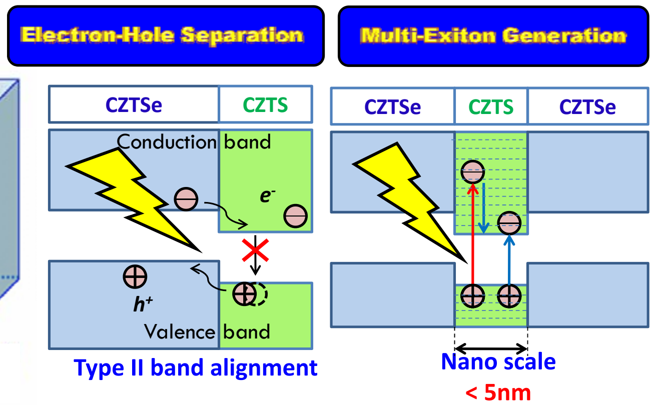
# Self-organized 2D-Spinodal Nano-decmposition & Self-regenerated High-efficiency & Low-cost PVSCs






# High-Efficiency by 2D-Spinodal Nano-Decomposition : *Konbu-Phase*

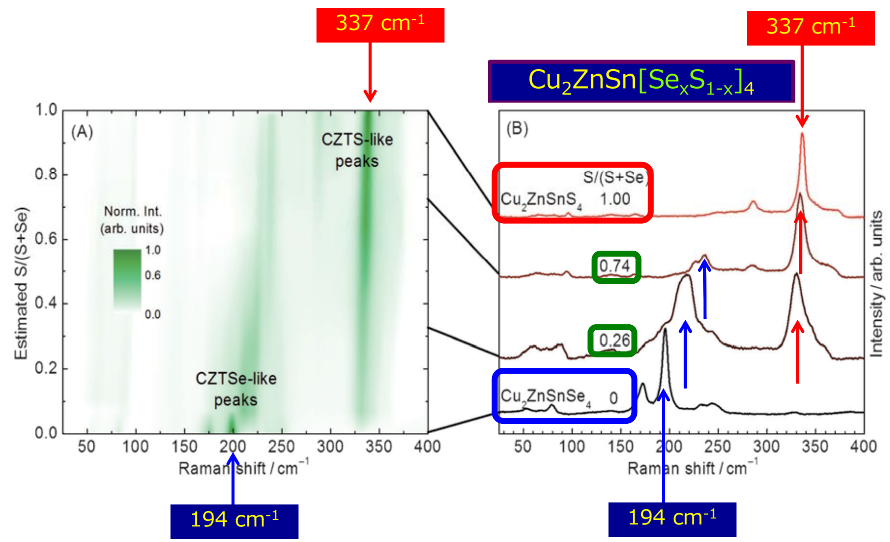



- Efficient Electron-Hole Separation in Type II Band Alignment of [$Cu_2ZnSnS_4$ & $Cu_2ZnSnSe_4$], [$CuInSe_2$ & $CuGaSe_2$ ].
- Generation of Multi-exiton by Inverse Auger effect.



# Spinodal Nano-decomposition : *Raman Scattering [~100 nm]*




*A. Fairbrotheret al., Chem. Phys. Chem., 14, (2013) 1836.*

# Atom Probe Tomography [Cu,$V_{Cu}$] : $Cu_2ZnSnSe_4$

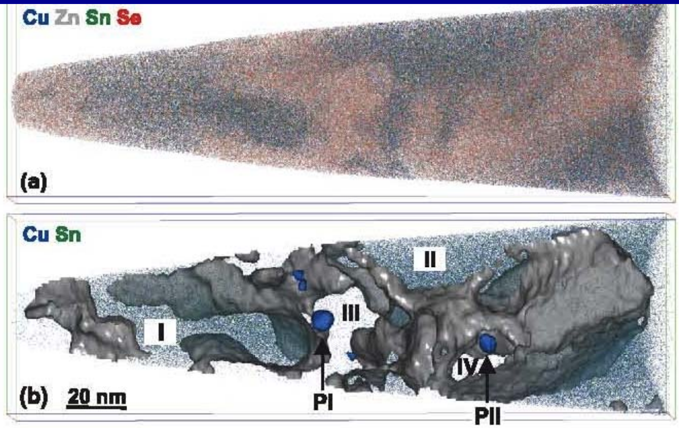
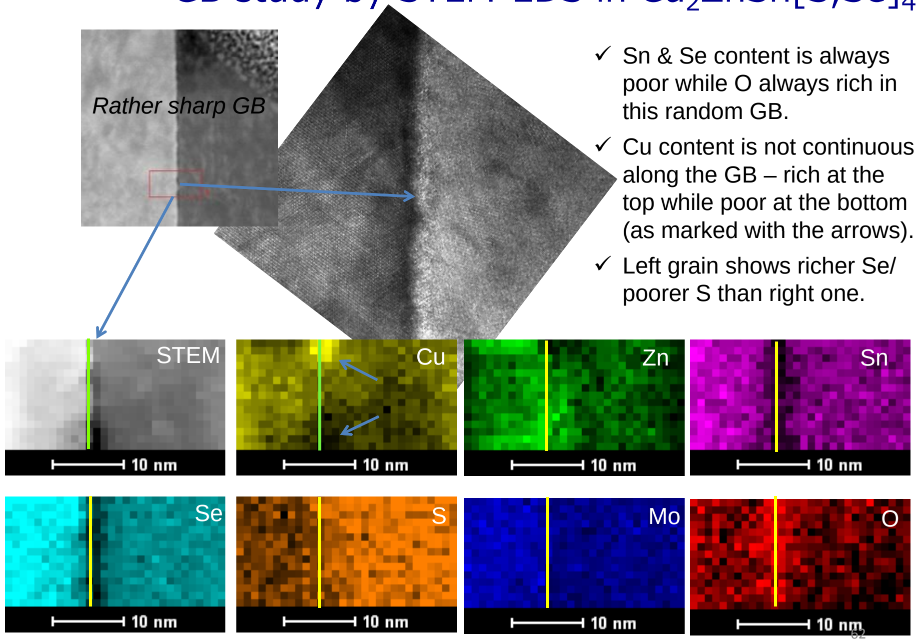



FIG. 2. (a) Three-dimensional elemental map of Cu (blue), Zn (grey), Sn (dark green), and Se (red); (b) only Cu and Sn displayed as well as iso-concentration surface of 32.5 at. % Zn (grey) and 7.0 at. % Cu (blue). Volume size for (a) and (b) is $62 \times 66 \times 219\,nm^3$.

*T. Schwarz et al., Appl. Phys. Lett. 102, 042101 (2013).*

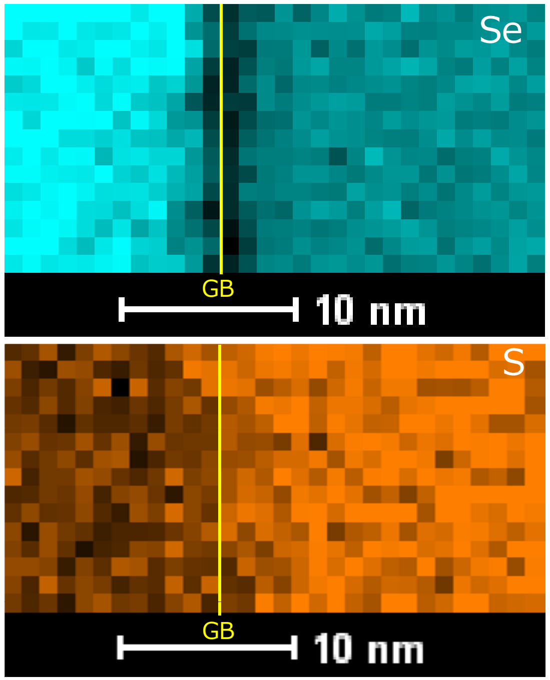


# GB study by STEM-EDS in $Cu_2ZnSn[S,Se]_4$




- ✓ Sn & Se content is always poor while O always rich in this random GB.
- ✓ Cu content is not continuous along the GB – rich at the top while poor at the bottom (as marked with the arrows).
- ✓ Left grain shows richer Se/ poorer S than right one.

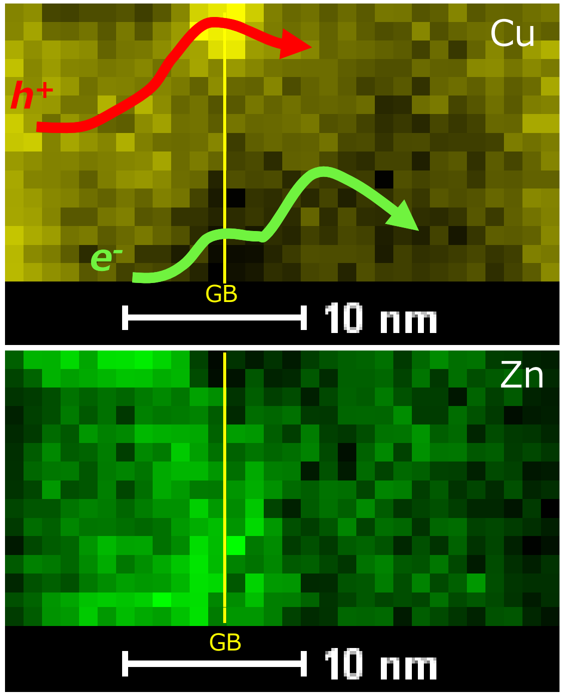





Spinodal Nano-Decomposition in $Cu_2ZnSn(S,Se)_4$

Anti-Correlation of S/Se

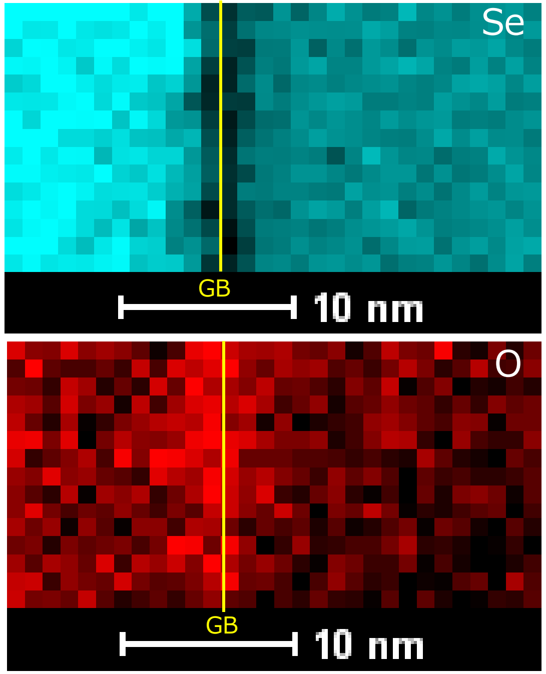
- Se-rich & S-poor.
- S-rich & Se-poor.




Spinodal Nano-Decomposition in $Cu_2ZnSn(S,Se)_4$ at the Grain Boundary

- Anti-Correlation of Cu/Zn
- Anti-Correlation of Cu & $V_{Cu}^-$

Self-Regeneration by [$V_{Cu}^-$ + $Zn_{Cu}^+$ ]




Spinodal Nano-Decomposition in $Cu_2ZnSn(S,Se)_4$ at the Grain Boundary

- Anti-Correlation of Se/O.
- Strong Ionicity of O at GB.

## Printing, Painting, Plating Methods in $Cu_2ZnSn(S,Se)_4$ PVSCs

- IBM
  12.6%
  Spin Coating.
- Osaka Univ.
  9% (Without RC)
  Electrochemical Plating.
- TIT, TOPPAN
  6%
  Painting.

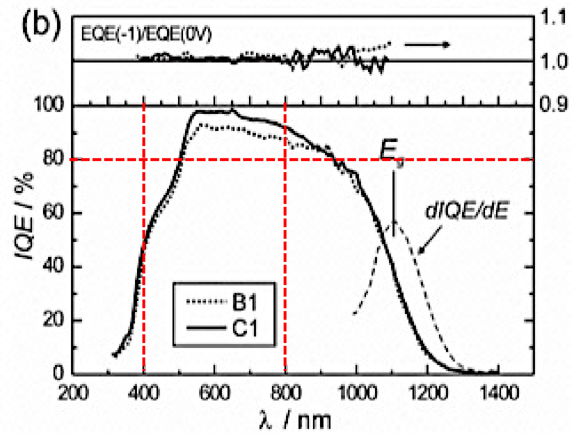



**Figure 2.** (a) J–V characteristics for the 11.1% champion cell C1. (b) Internal quantum efficiency (IQE) and the external quantum efficiency (EQE) bias ratio EQE(−1V)/EQE(0V) (top panel) of the champion cell and of the previous generation cell B1.



## $Cu_2ZnSn(S,Se)_4$ PVSCs 12.6%


13/11/2013 Nikkei

レアメタル不要の太陽電池
最高の変換効率
昭シェル子会社

昭和シェル石油子会社のソーラーフロンティア（東京・港）は10日、レアメタル（希少金属）を使わない次世代型太陽電池「CZTS太陽電池」のエネルギー変換効率が12・6%となり、同型で世界最高になったと発表した。米IBMなどと共同研究チームを組んでおり、従来の世界記録は同チームが昨年8月に達成した11・1%だった。太陽電池の製造コストの低減につながるとみており、実用化を目指す。

CZTS太陽電池は原料に銅、亜鉛、スズ、硫黄、セレンを使用する。ソーラー社が生産する銅、インジウム、セレンを原料とした「CIS太陽電池」に似ているが、希少金属のインジウムを使わず、安価な材料で製造できる。

ソーラー社は2010年にIBMとCZTS太陽電池の共同研究を始めた。IBMが持つ基礎技術に、太陽電池の光を吸収する層を2～3マイクロメートルの薄さで成形するソーラー社の技術を組み合わせて性能を引き上げた。

# SUMMARY

1. Spinodal Nano-technology as a New Class of Bottom-up NT.
   - *Self-Organized & Universal Nano-Fabrication Method*
2. Spintronics Materials Design
   - *New Materials Design, Realization & Tc*
3. Photovoltaic Materials Design by Codoping, Self-Regeneration, and Spinodal Nano-Decomposition for PVSCs.
   - *Electron-Hole Separation & Nano-Superstructurs*