MATERIALS PROCESSING WITH LOW PRESSURE PLASMA: PRESENT ISSUES AND POSSIBLE SOLUTIONS

MASAHARU SHIRATANI
Kyushu University,

Agenda

3 crisis on information & possible solutions

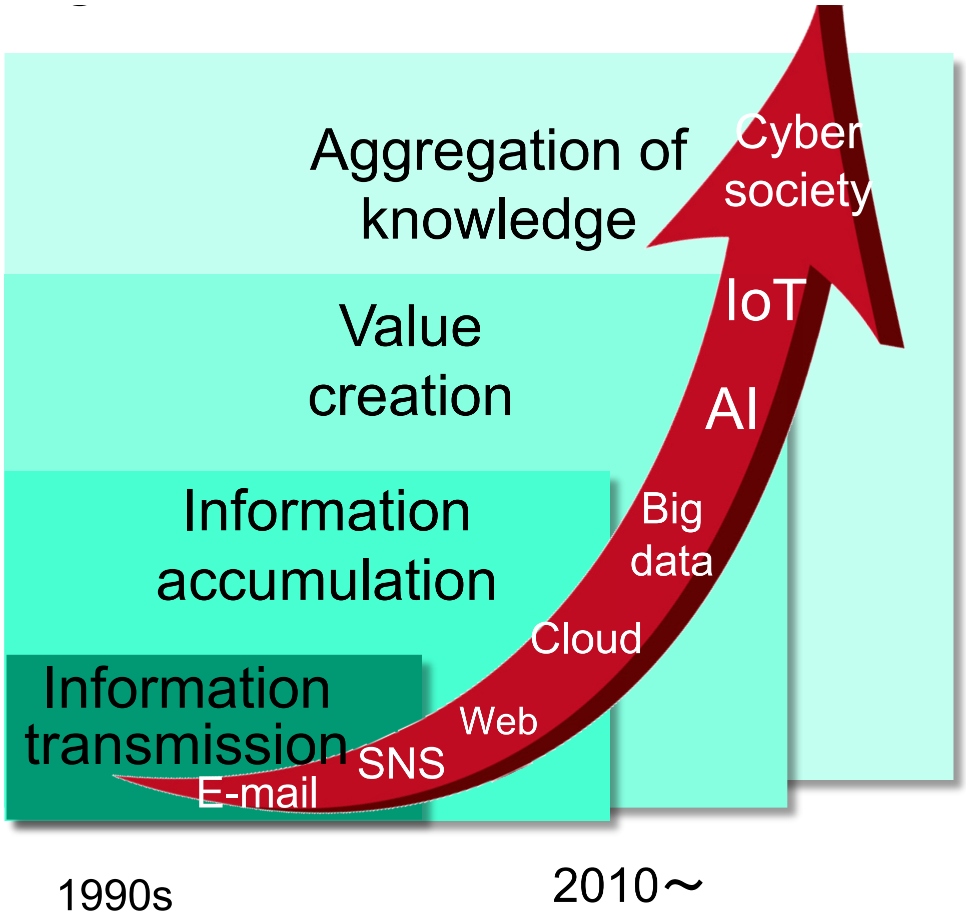
1. Data Storage: 3D memory
   100ºC a-SiNx by PECVD

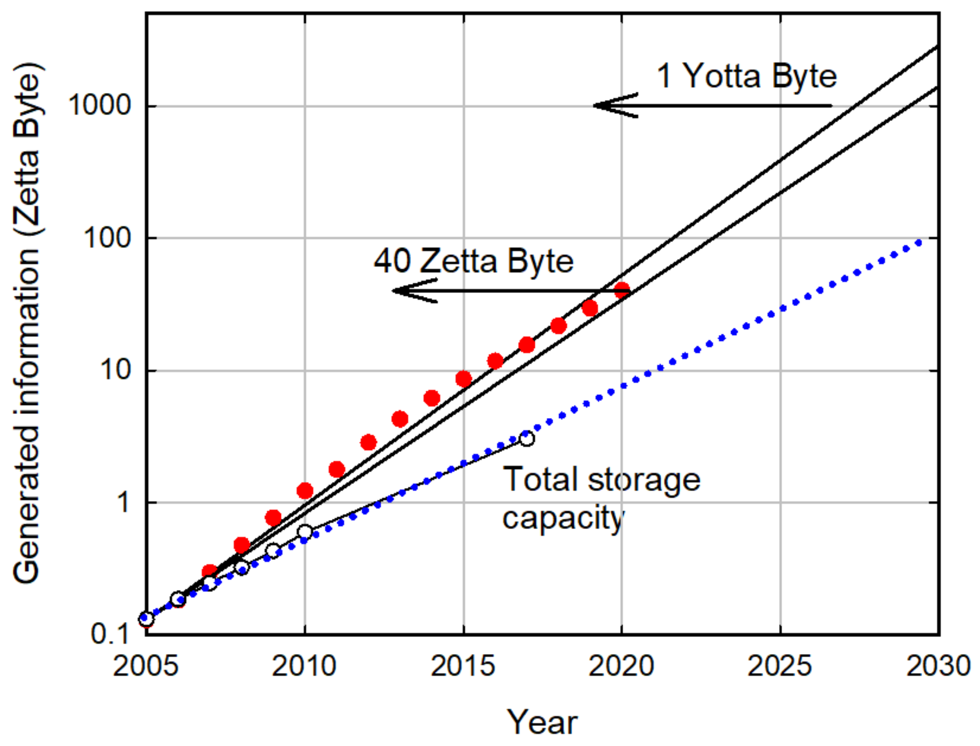
2. Data Transmission: E/O device
3. Data Processing: Quantum Computing
   ZION by Inverse SK mode using sputtering

九州大学 Kyushu University

Yotta=10^{24} Each Person has Tera Byte Info in2030.

3 crises on information:
Data Storage, Transmission, Processing.





IDC Dec 2012, "Digital universe in 2020"

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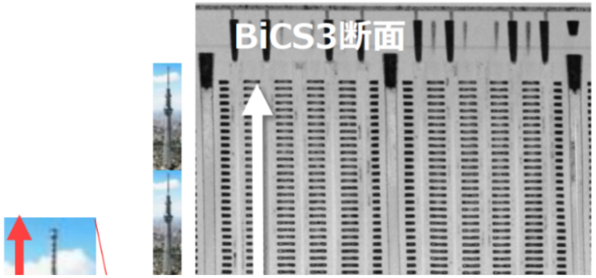
Kyushu University 九州大学

Demands

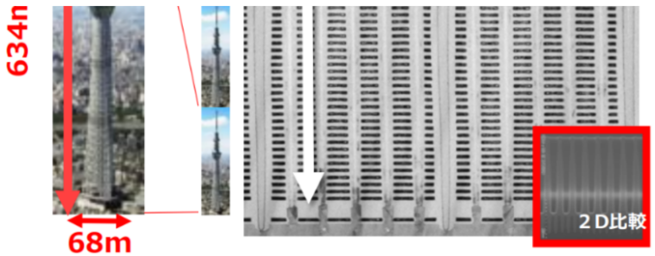
Ultra-high capacity , high speed, low energy consumption

Hard disk to flash memory with 3D & low energy.

96 Memory Layers fabricated by making 1.7 trillion holes of 100 nm dia & 4.5 μm deep.

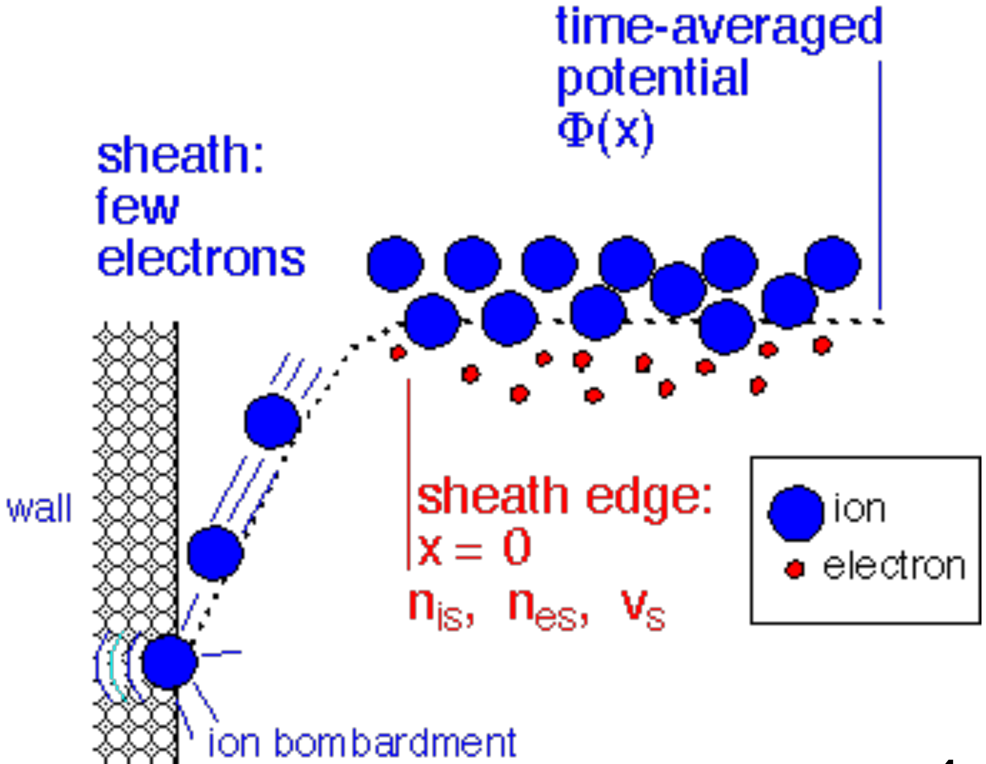


96 Layers =64G Byte



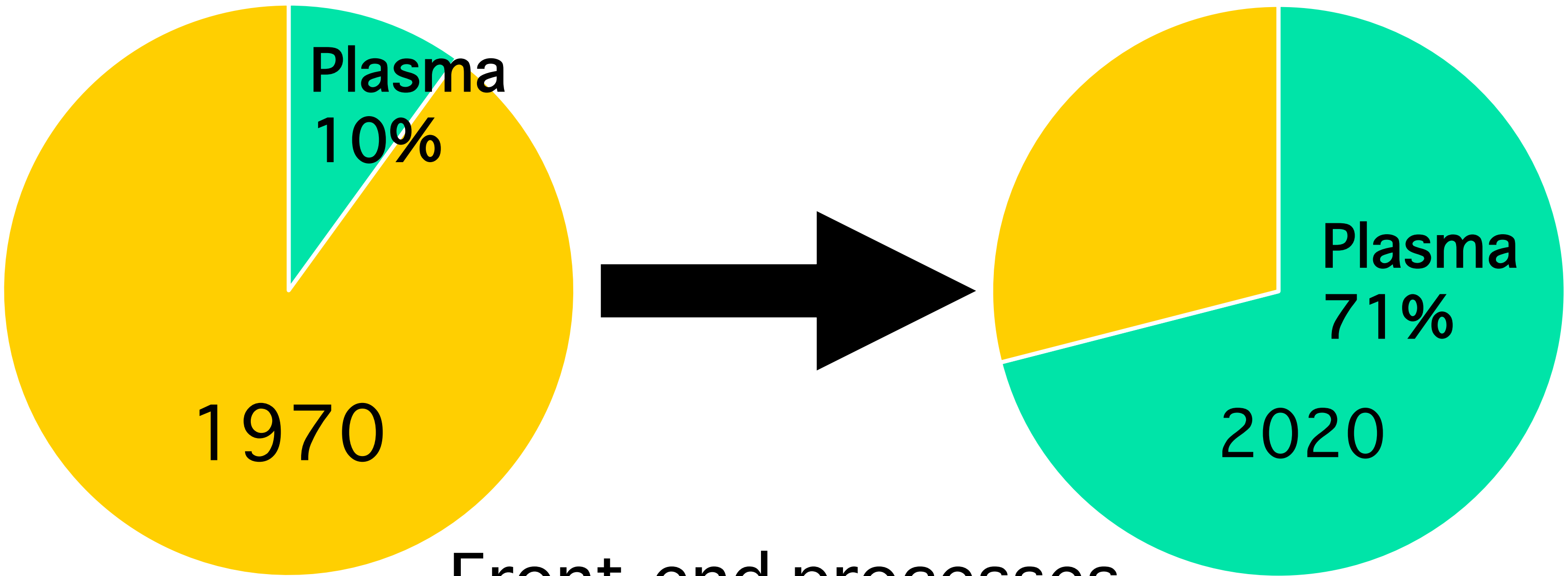
	2次元 (15nm)	3次元 (48層)
記憶素子密度	1	2.3倍
書き換え回数(信頼性)	1	10倍
プログラム速度(性能)	1	2倍
消費電力	1	0.5倍

Ref. TOSHIBA(2016)



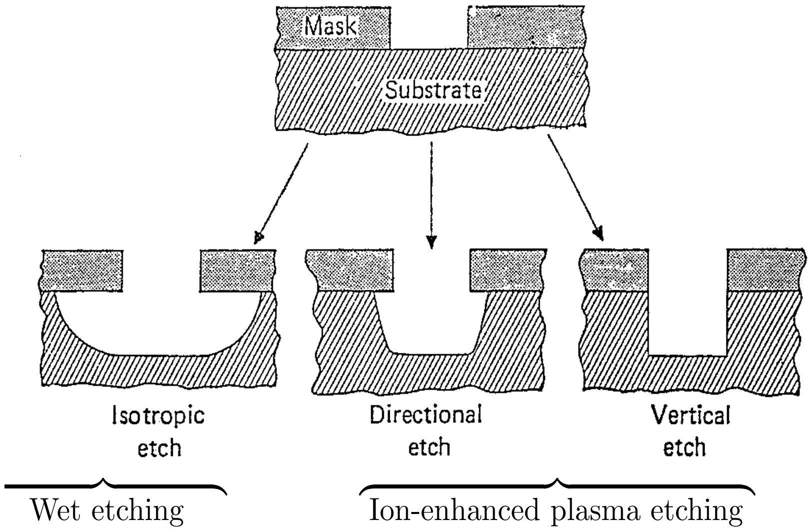
Breakthroughs in Semiconductor Integration

1948 Transistor (Bell Lab.) by J. Bardeen, W. Brattain, W. Shockley
1956 Novel prize in physics
1958 Integrated ciruit (Texas Instr.) by J. Kilby
2000 Novel prize in physics
1974 Plasma etching (reactive ion etching) by N. Hosokawa (Anelva Co.)
1980 Flash memory by F. Masuoka (Toshiba Co,)



Front-end processes

反応性プラズマエッチング(RIE)



ISOTROPIC PLASMA ETCHING

1. Start with inert molecular gas CF_4
2. Make discharge to create reactive species:

$$CF_4 \longrightarrow CF_3 + F$$

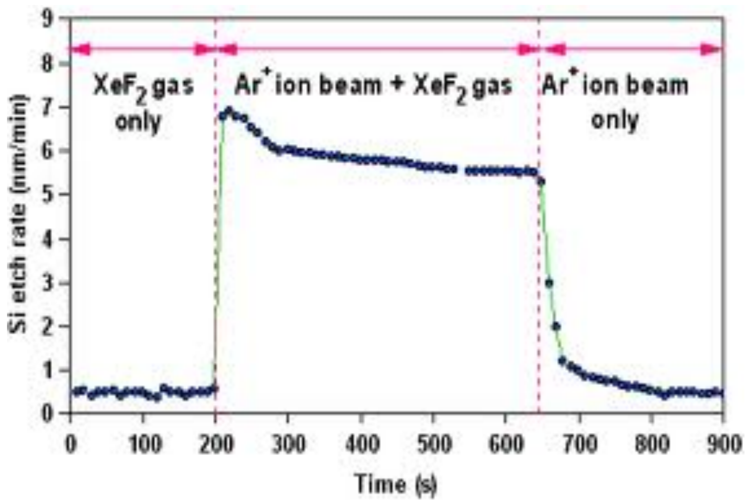
3. Species reacts with material, yielding volatile product:

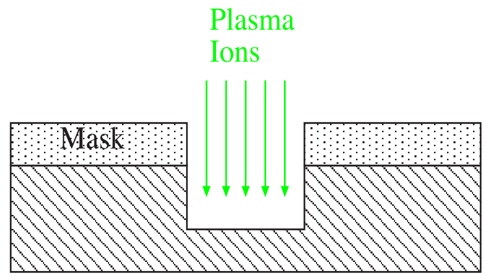
$$Si + 4F \longrightarrow SiF_4 \uparrow$$

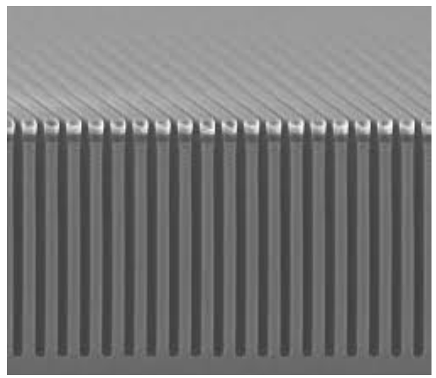
4. Pump away product

ANISOTROPIC PLASMA ETCHING

5. Energetic ions bombard trench bottom, but not sidewalls:
   (a) Increase etching reaction rate at trench bottom
   (b) Clear passivating films from trench bottom





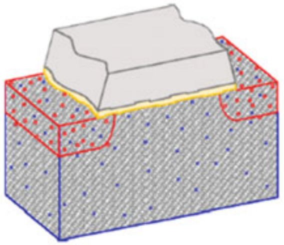


After M. Lieberman

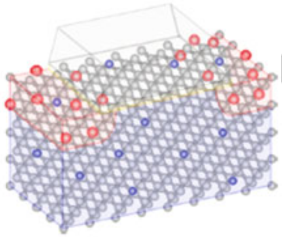
State of the art semiconductor integration

Key trends: Nano&3D

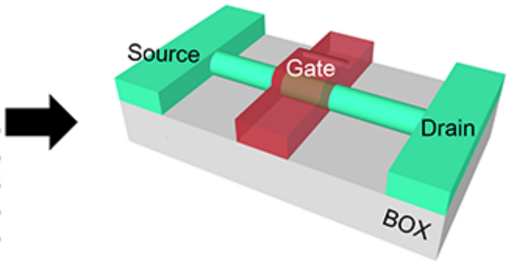
①Miniatualization=Moor’s law



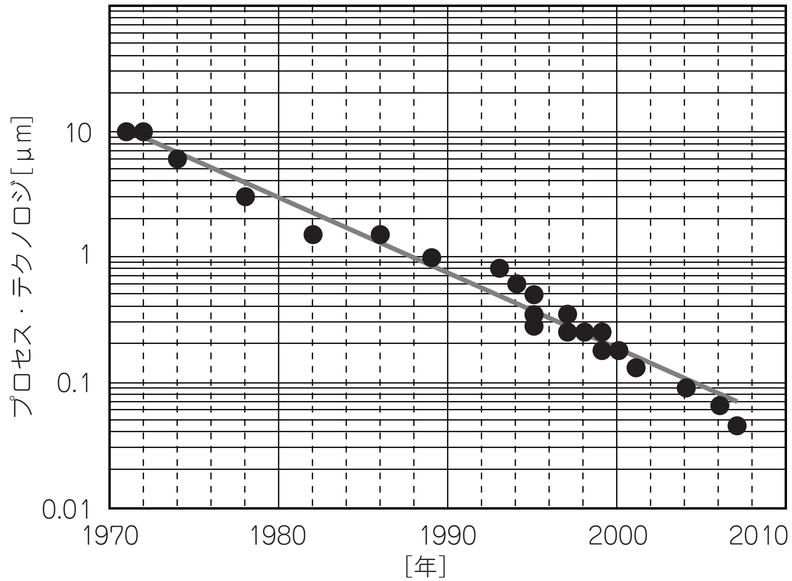
A 22 nm MOSFET
In production 2008



A 4.2 nm MOSFET
In production 2023

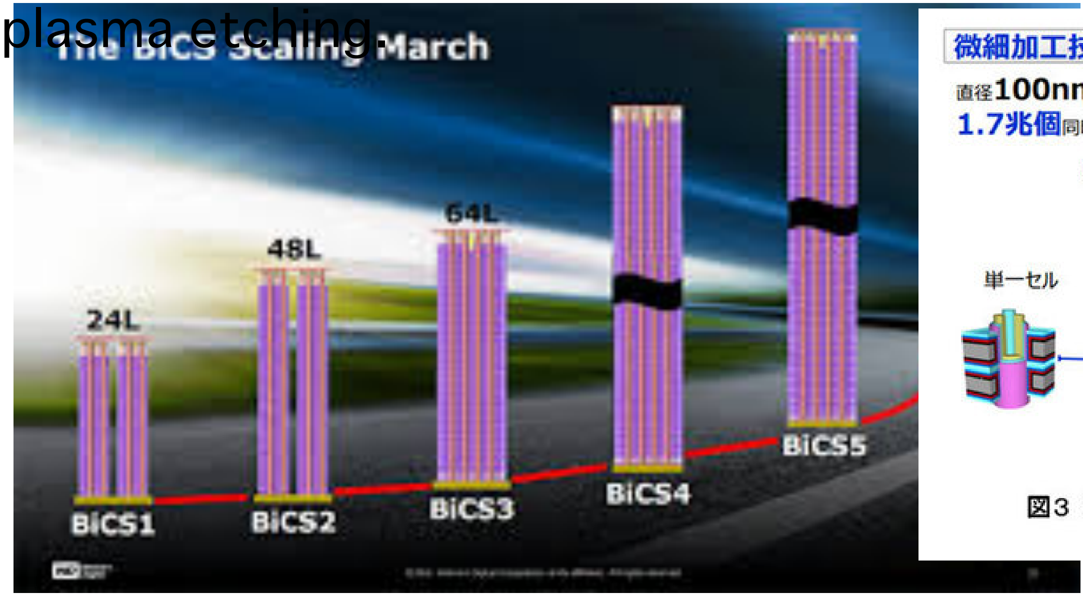


Nanowire-MOSFET



②3D layer stacking: 24➡48➡64➡96 Layers

1.7 trillion holes of 100nm dia.&4.5 μm deep are made simultaneously by plasma etching.



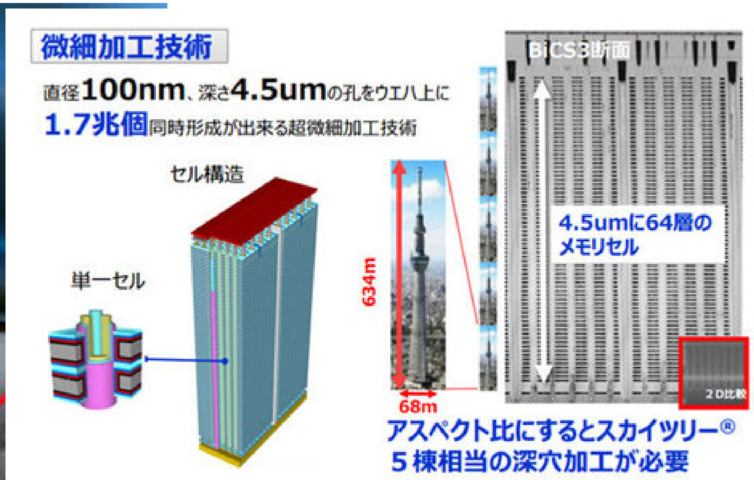
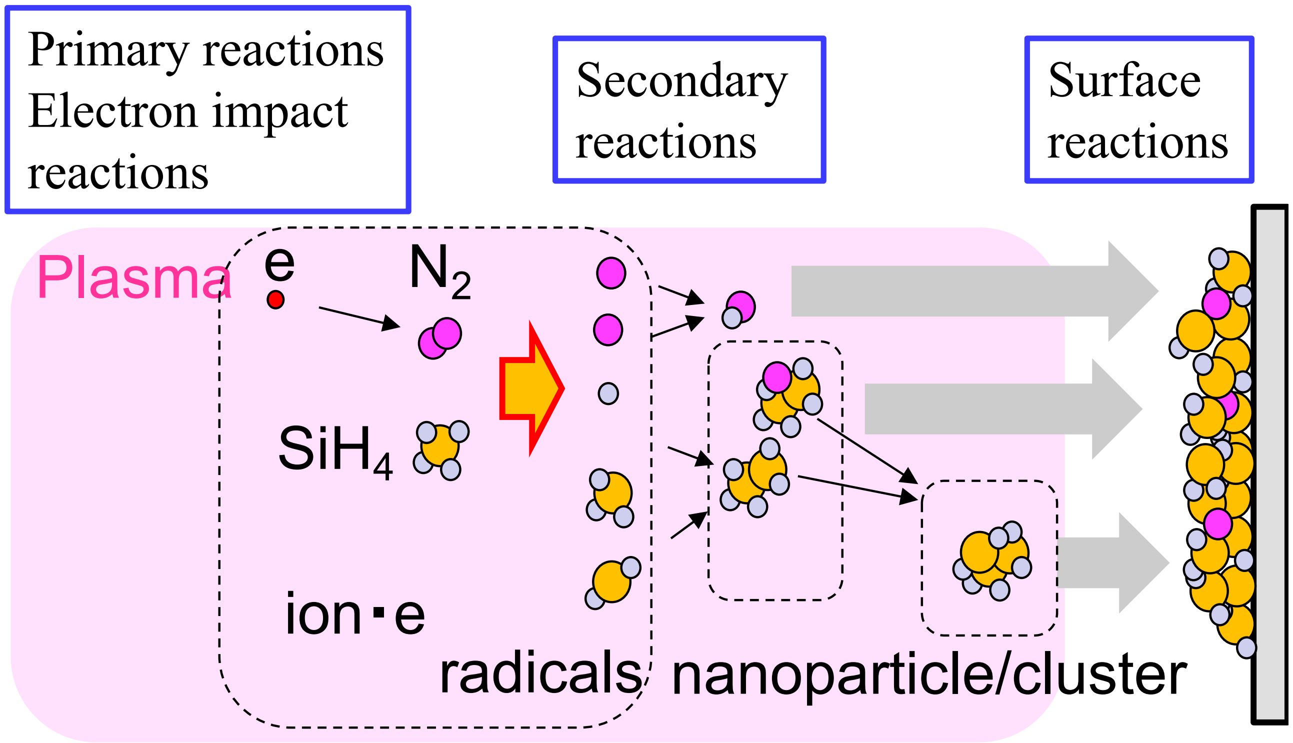


図3　東芝の64層の3次元NANDとメモリセルの断面

出所 https://www.toshiba.co.jp/about/ir/jp/pr/pdf/opr20161207_3.pdf

Elementary processes in plasma CVD

A-SiNx films and SiOx multilayers are employed in 3D flash memory.
Reduction in film stress is one of main issues for increasing stacking layers.



Demand
Lowering
Substrate temperature
300 ºC ➡100 ºC

Motivations
Less device damages
Less thermal expansion
Less film stress
Polymer substrates

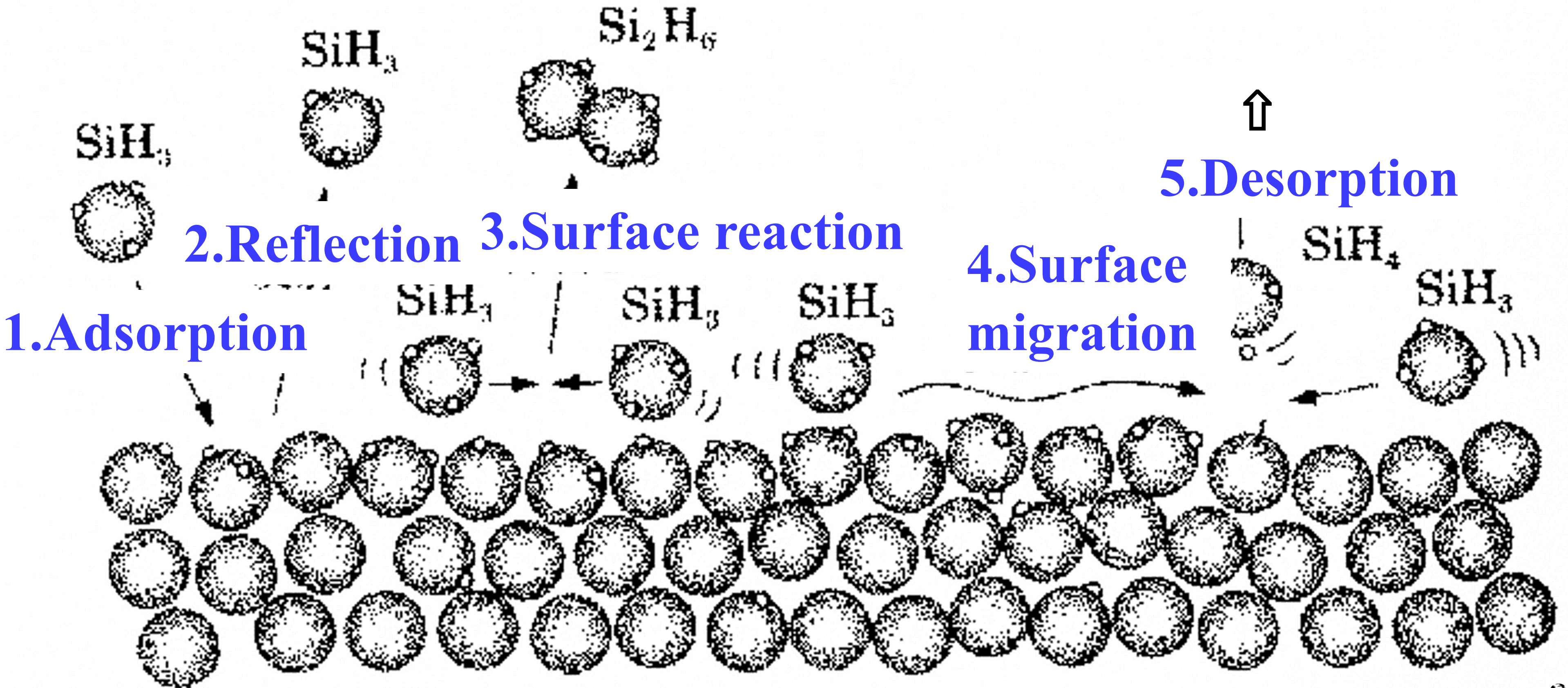
K. Koga, et al., Appl. Phys. Lett., **77** (2000) 196.

5 elementary surface processes

Slower surface process rates at lower temperature.

⇩

Difficulty in nitriding and dehydrogenating films at low temperature.



M. Kondo, Jpn. Inst. Enegry, Vol. 87, No. 3, (2008)

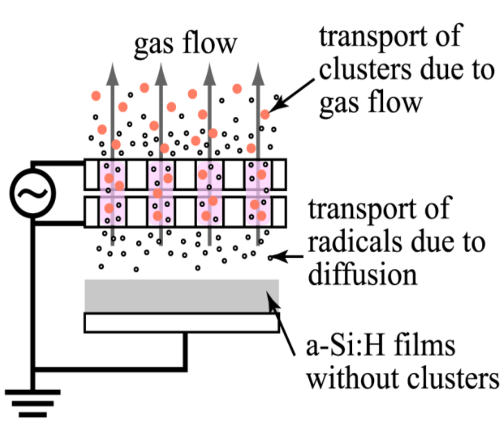
Three experimental methods

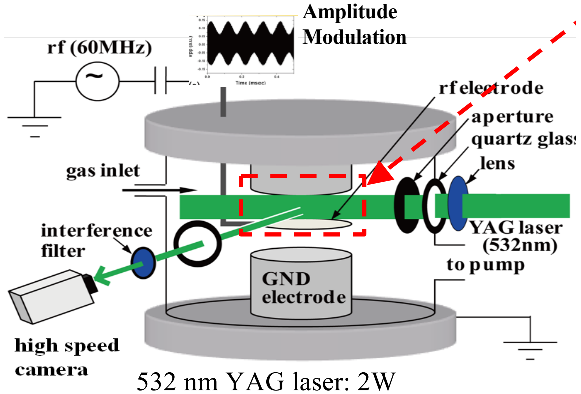
Deposition method

In-situ detection of clusters (>2nm) in plasma

In-situ detection of cluster incorporation into films

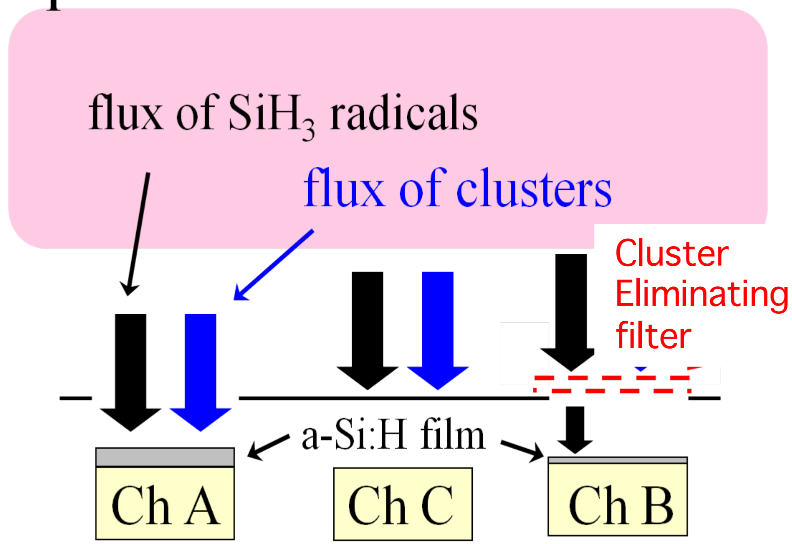
Multi-hollow discharge plasma CVD method



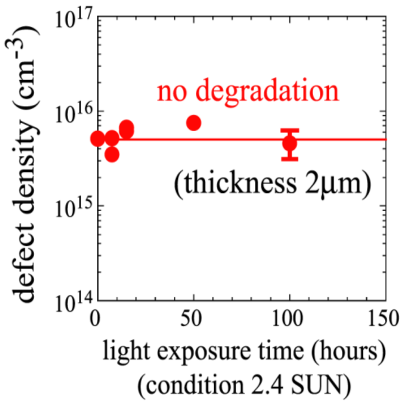


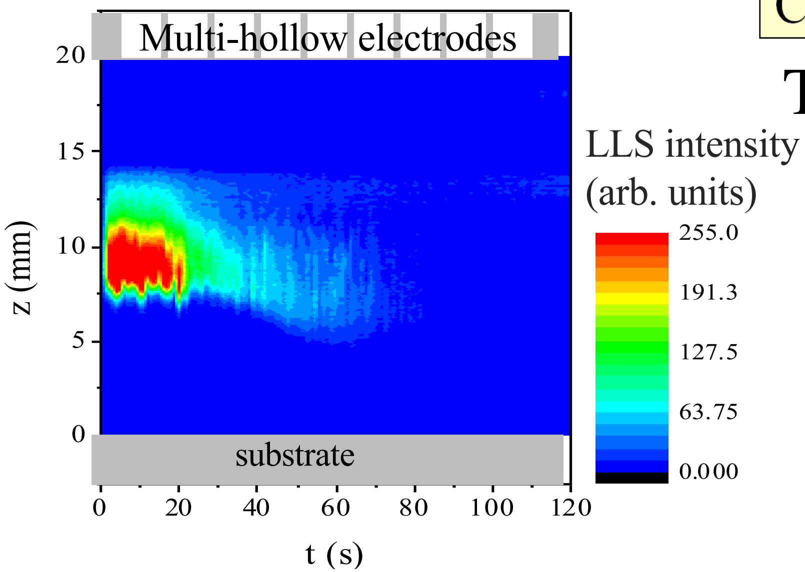
532 nm YAG laser: 2W

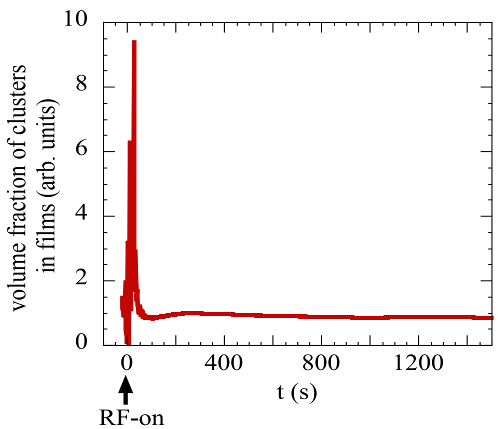
plasma



Three quartz X'tal sensors



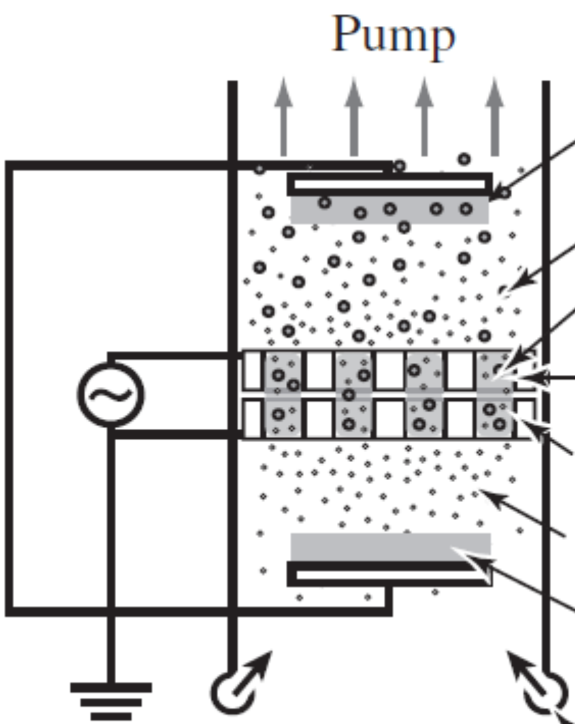




K.Koga, et al. : J. Vac. Sci. Technol. A, **22** (2004) 1536.

Upstream films vs downstream films

Conditions	
Pressure	0.5 Torr
SiH_4	1-10 sccm
N_2	10-500 sccm
Frequency	60 MHz
Power	20 W
$T_{substrate}$	55, 100 °C
T_e	~ 4 eV
n_e	2×10^9 cm^{-3}

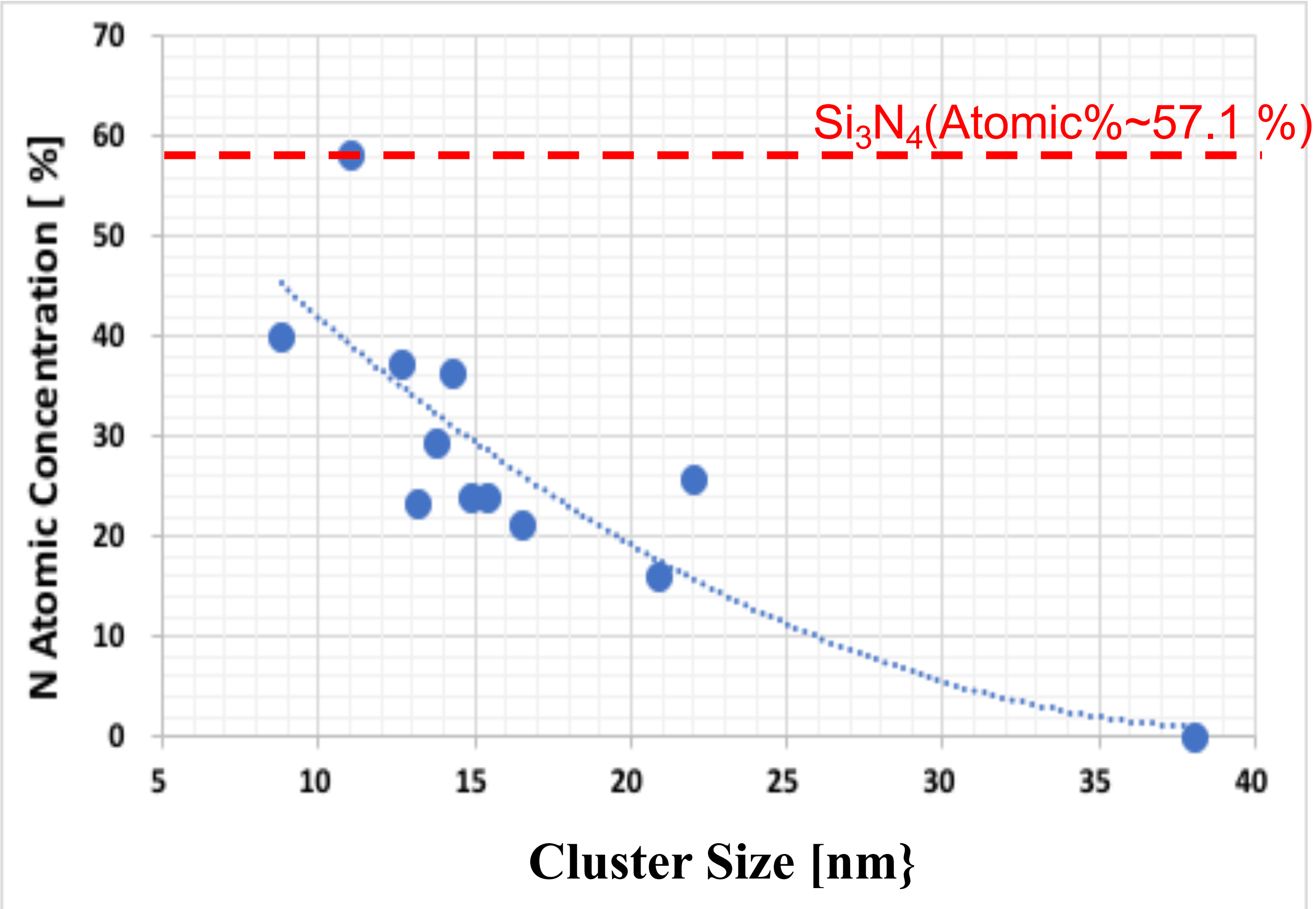


Downstream
SiNx films with clusters

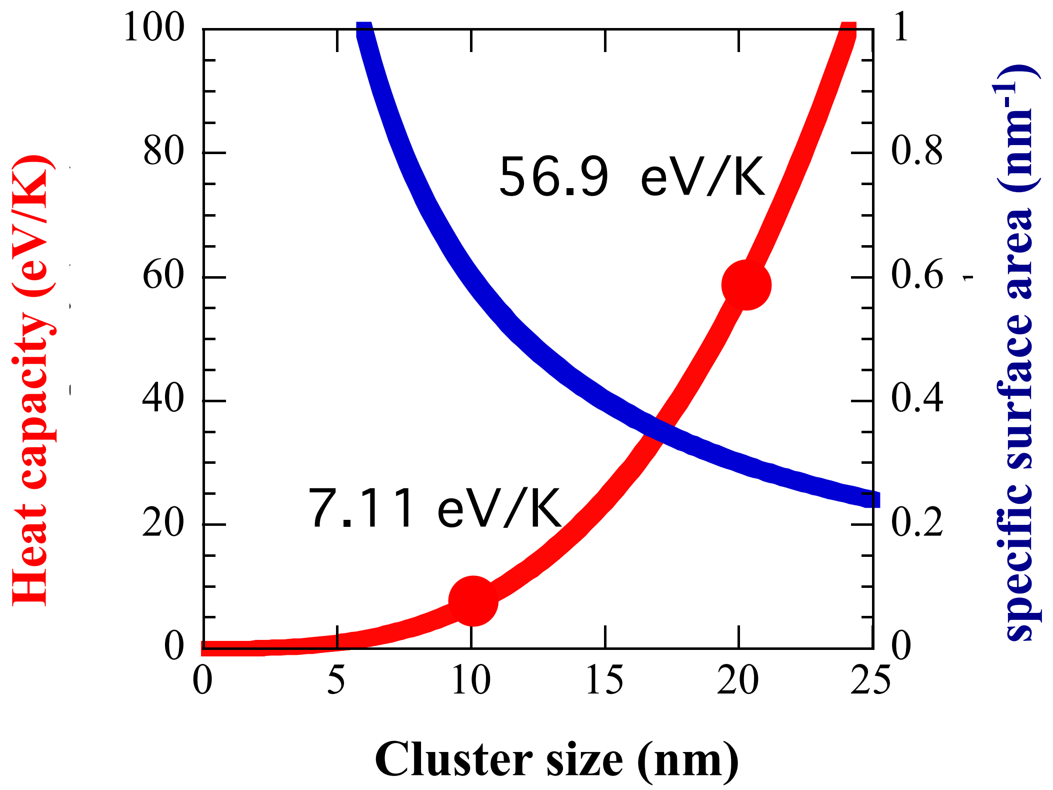
Upstream
SiNx films without clusters: Conventional plasma CVD films

N concentraton in SiNx clusters

N concentration in SiNx clusters is analyzed by EDS with TEM.
Smaller clusters contain higher N concentration.

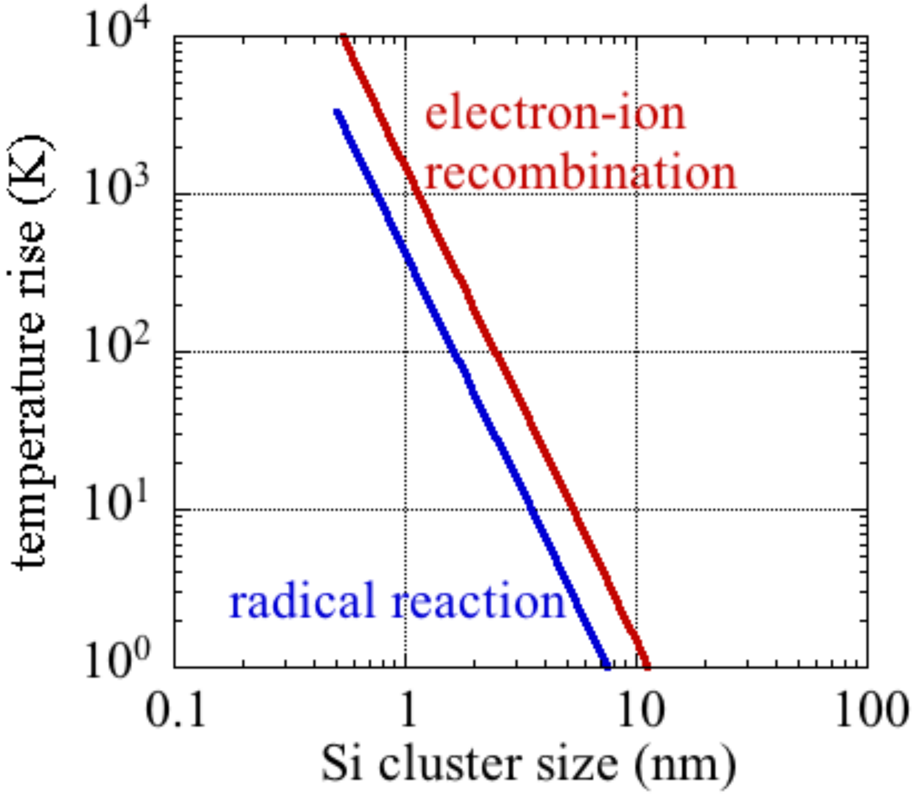


- Smaller clusters have smaller heat capacity.
- Smaller clusters have larger surface to volume ratio (specific surface area).

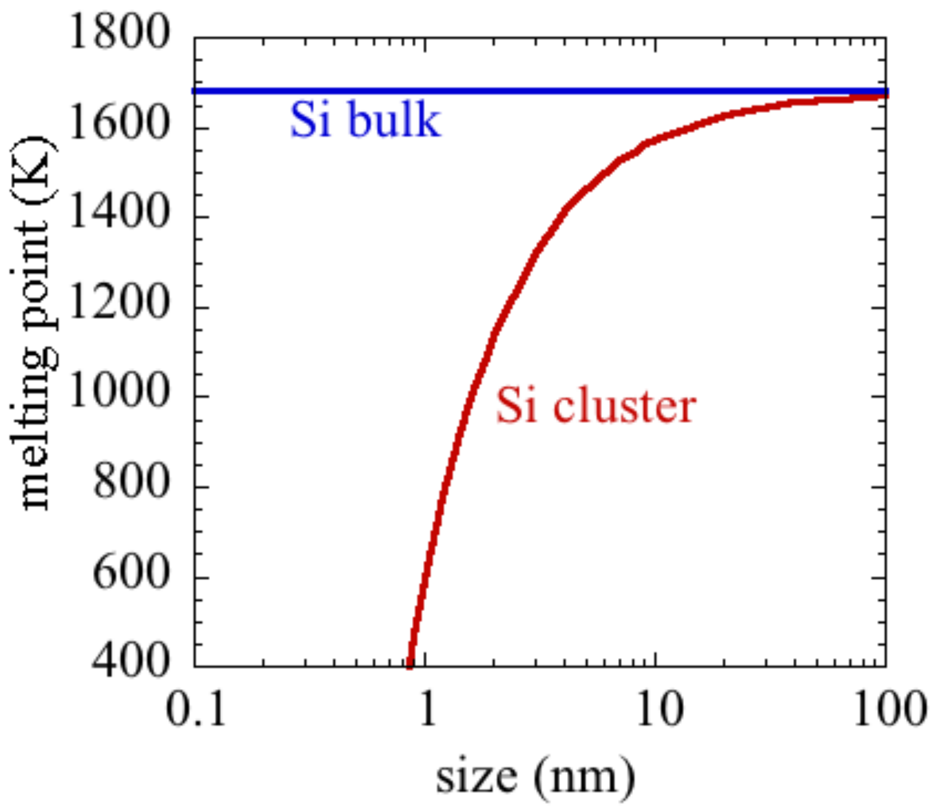


Smaller clusters have higher reactivity

Smaller clusters have smaller heat capacity.

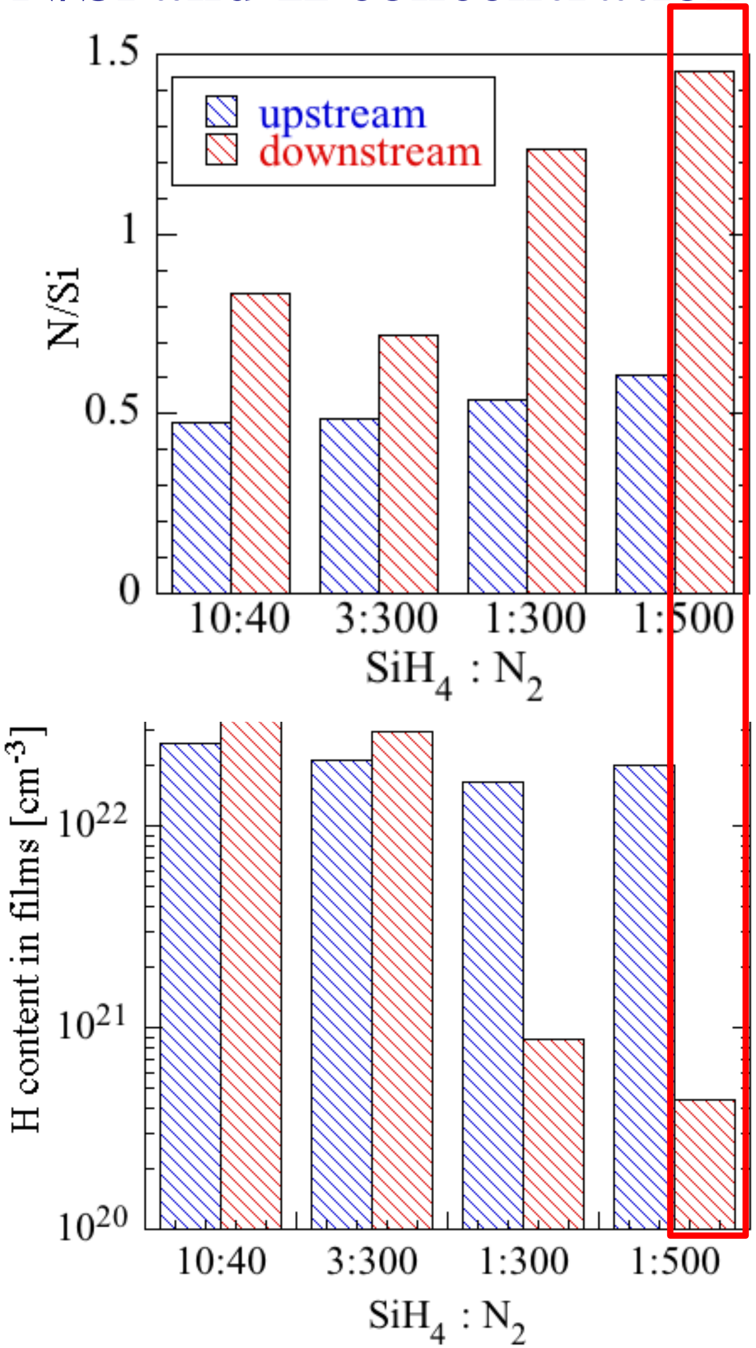


Smaller clusters have larger surface to volume ratio.



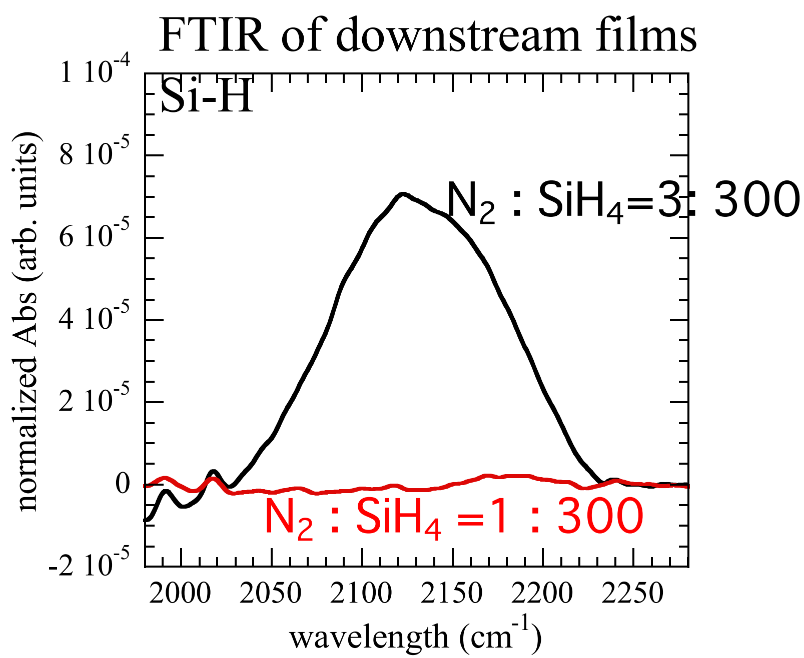
Upstream films vs downstream films
N/Si and H concentration

T=100°C



Downstream films with clusters
- **High N/Si > 1.3**
- **Low H concentration < 5x10^20 cm^-3 detection limit**

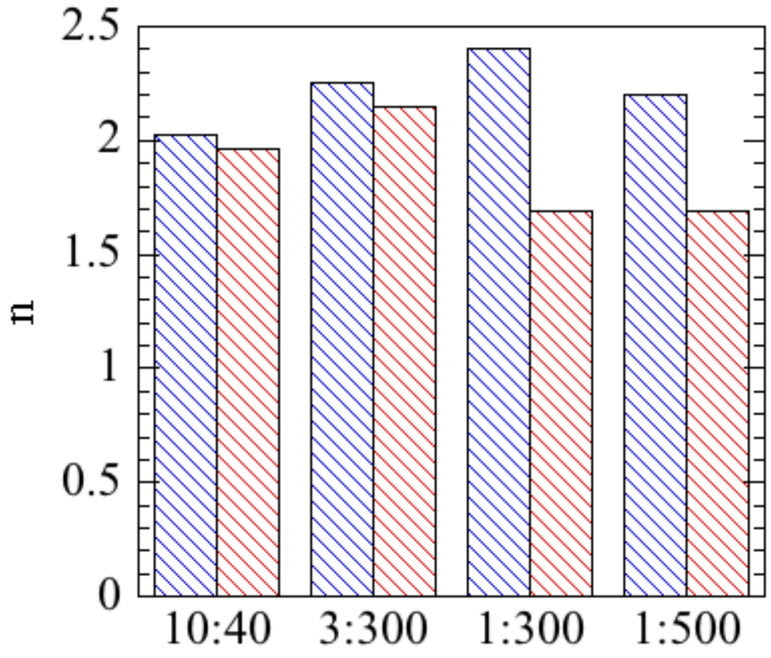
Upstream films without clusters
- **Low N/Si = 0.5**
- **High H concentration > 1x10^22 cm^-3**

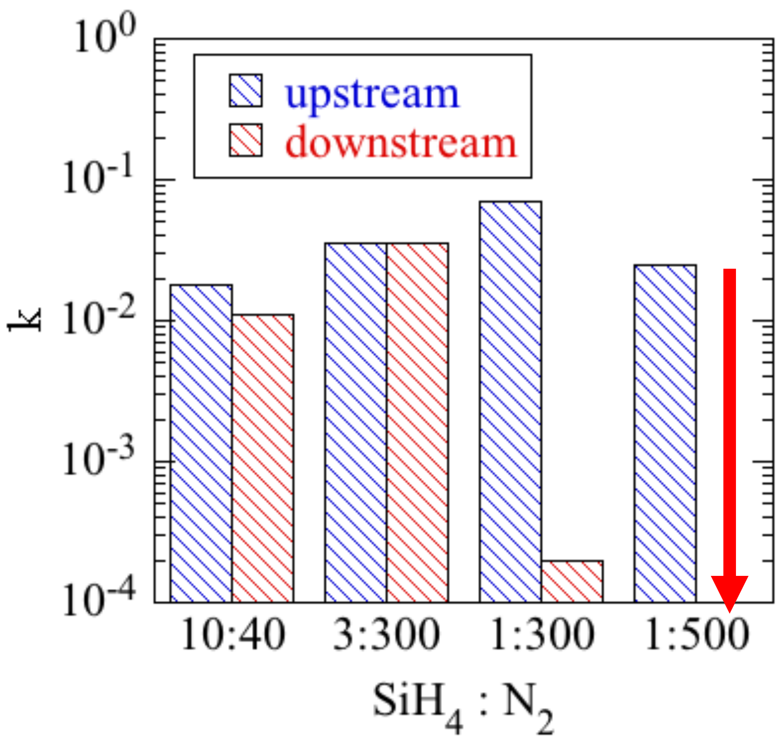


Upstream films vs downstream films

complex refractive index n-ik @ 500 nm

T=100°C





Downstream films with clusters

- **n = 1.6 — 2.1**
- **k = 10^{-4} — $3x10^{-2}$**
- **k < 10^{-4} Transparent**

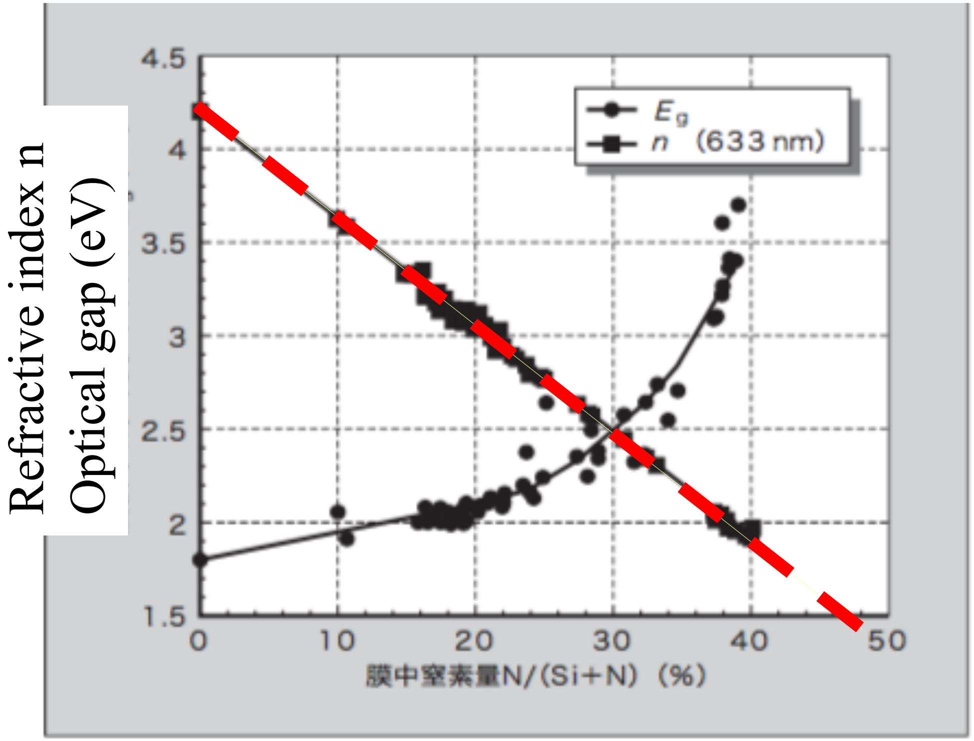
Upstream films without clusters

- **n = 2.0 — 2.4**
- **k = $3x10^{-2}$ — $5x10^{-2}$ Optical loss**

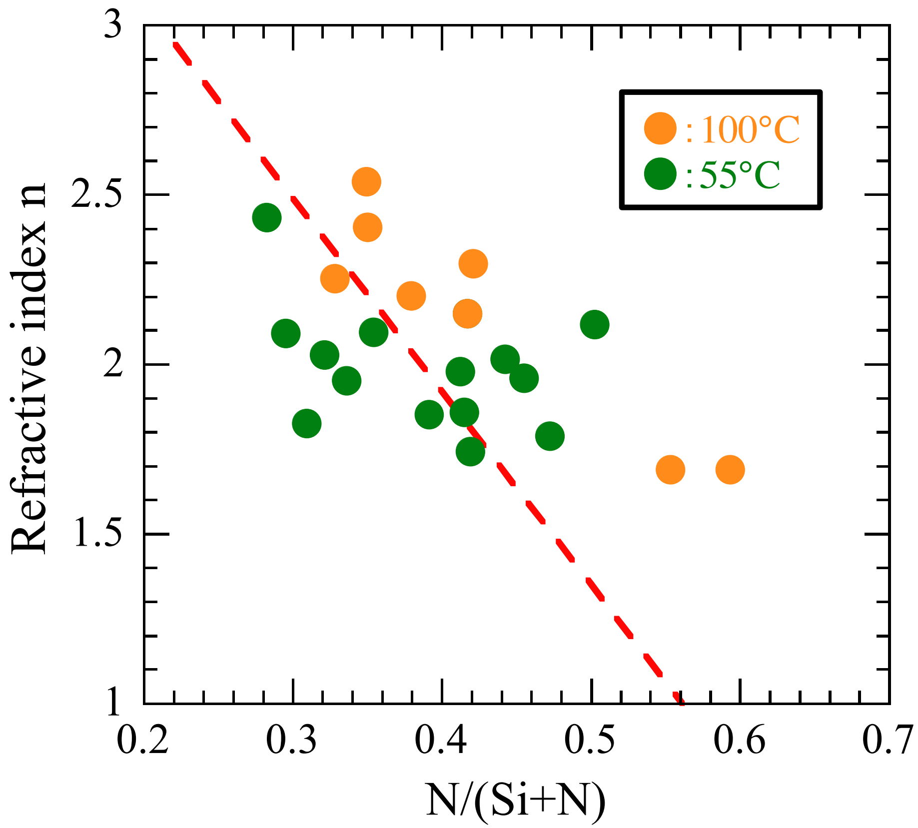
N/(Si+N) and refractive index n of amorphous SiNx films

A-SiNx films with clusters show another trend of refractive index.
➡Cluster inclusion is a tuning knob for optical properties of films.

Conventional a-SiNx films



a-SiNx films in this study



Ref) Narita, et al.、Fuji Jiho, Vol.78,No.4(2005).

Conclusion: part 1

Demand for a-SiNx films

Lowering
Substrate temperature
300 ºC ➡100 ºC

Motivations

Less device damages
Less thermal expansion
Less film stress
Polymer substrates

Surface reactions are hard to take place at low substrate temperature.

A-SiNx films of N/Si > 1.3 and low H content are obtained at 100 ºC by containing SiNy clusters into the films.

Cluster inclusion is a tuning knob for optical properties of films.

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Trends of Si semiconductors: the periodic table

1980: 12 elements
Now: 71 elements
Out of 118 elements

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	*1	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	*2	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

*1	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
*2	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

12 elements 1980
71 elements Now
Out of 118 elements

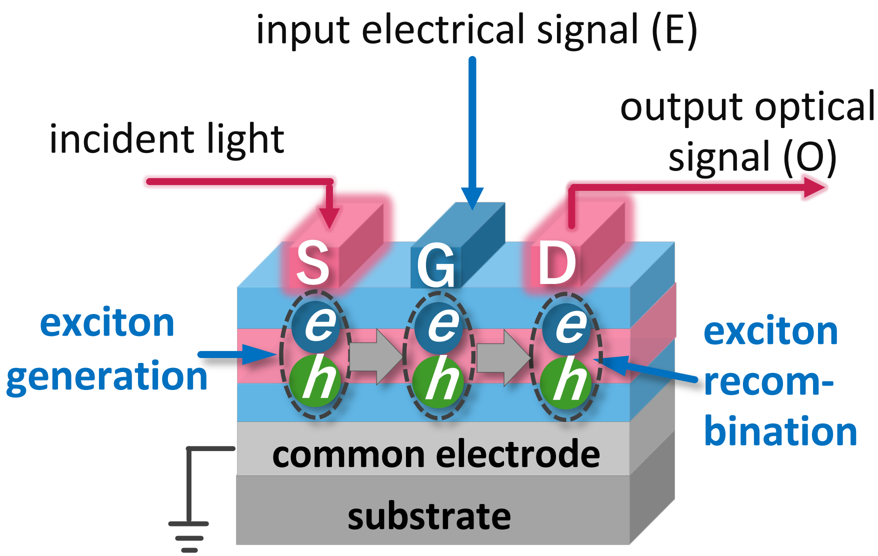
E/O & O/E are bottlenecks of data transmission.

Why ZnO?

- wide band gap: 3.37 eV (direct)
- abundance of reserves
- **large exciton binding energy (60 meV)**

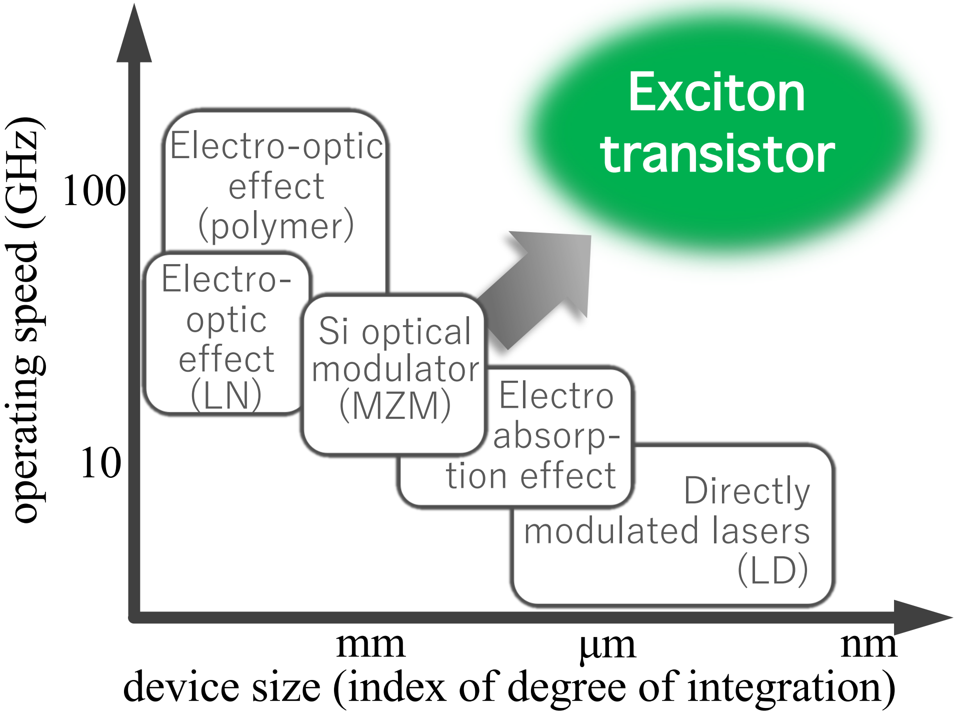
→ ***promising for excitonic devices***

exciton transistor



Grosso et al., *Nature Photonics* 2009

operating speed & size of E/O

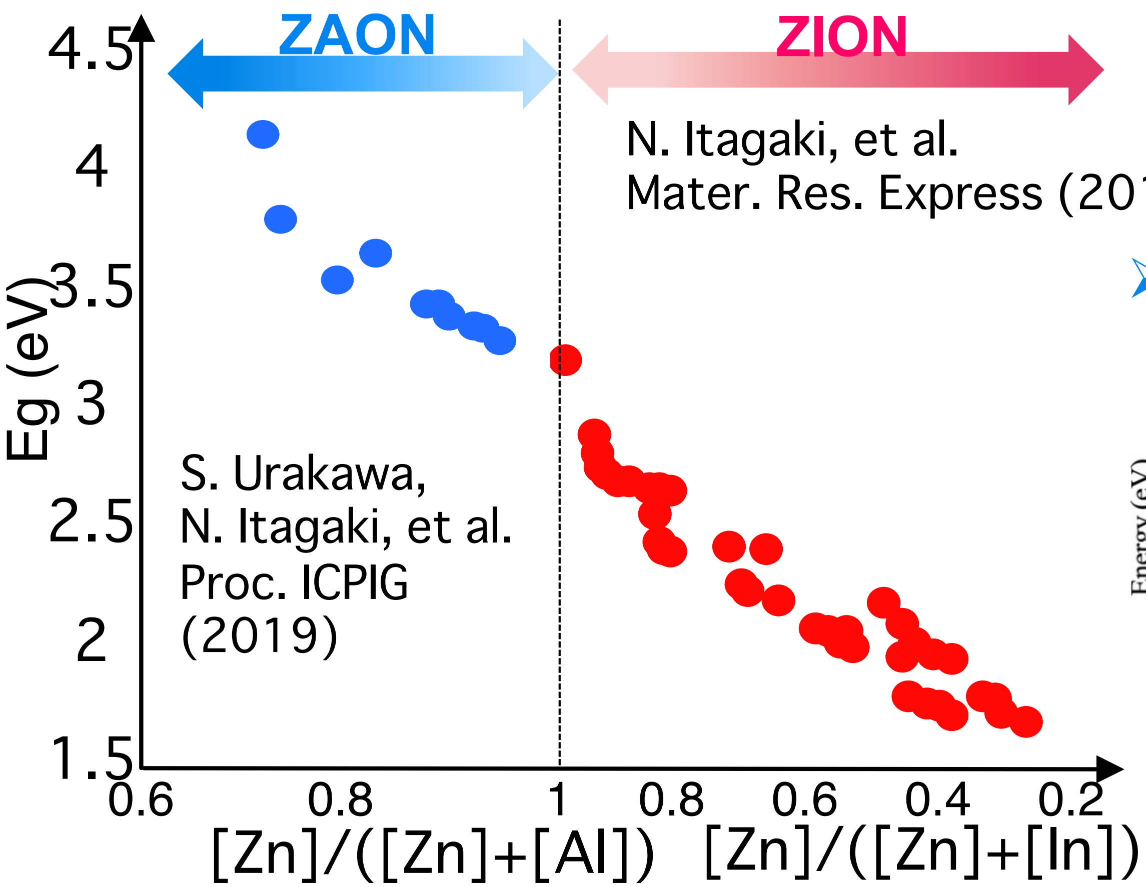


Exciton transistors may enable "on-chip" optical interconnect

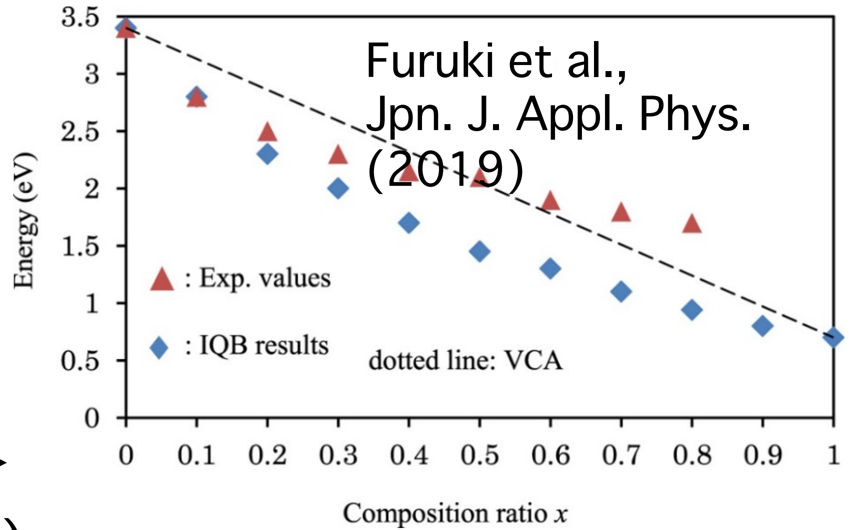
ZION and ZAON

$(ZnO)_x(InN)_{1-x}$ "ZION"

$(ZnO)_x(AlN)_{1-x}$ "ZAON"



- First principles calculation



$(ZnO)_x(InN)_{1-x}$ Novel Materials

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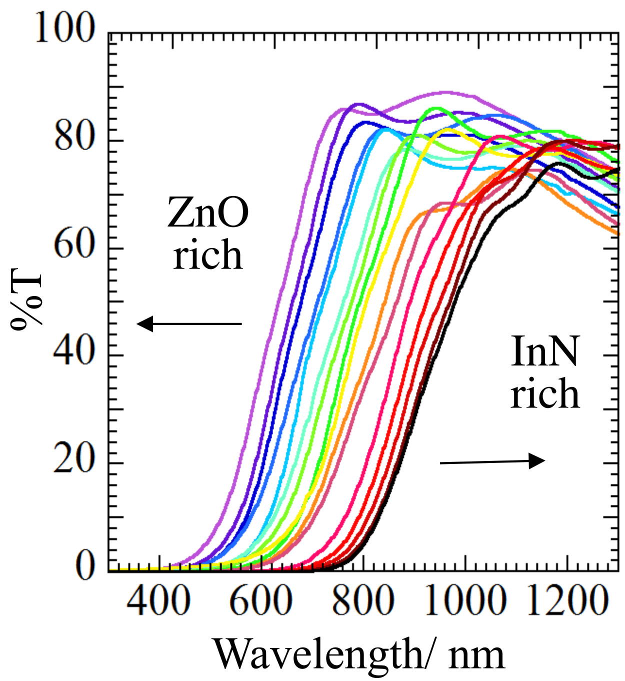
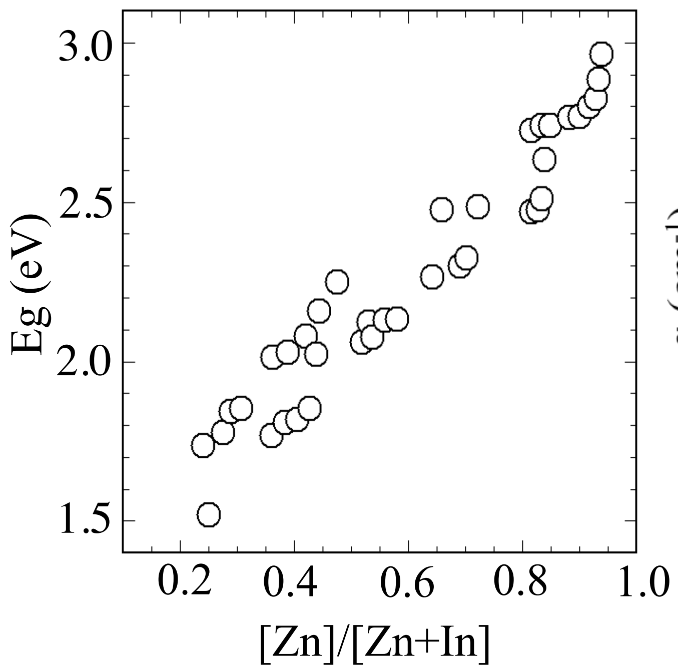
- Band gap is tuned in a wide range (1.5 eV -3.0 eV)
- Optical absorption coefficient is high of 10^5 cm^{-1}

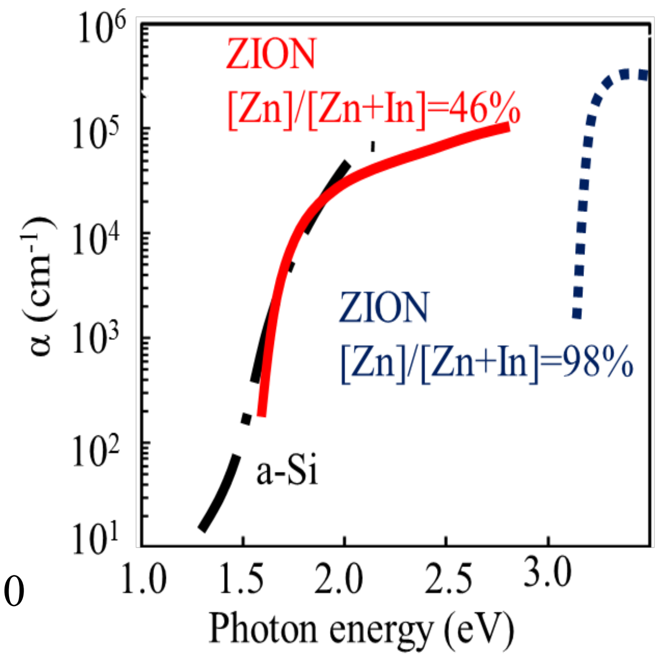
Optical Transmission



Bandgap



Absorption coef.



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$(ZnO)_x(InN)_{1-x}$ Devices

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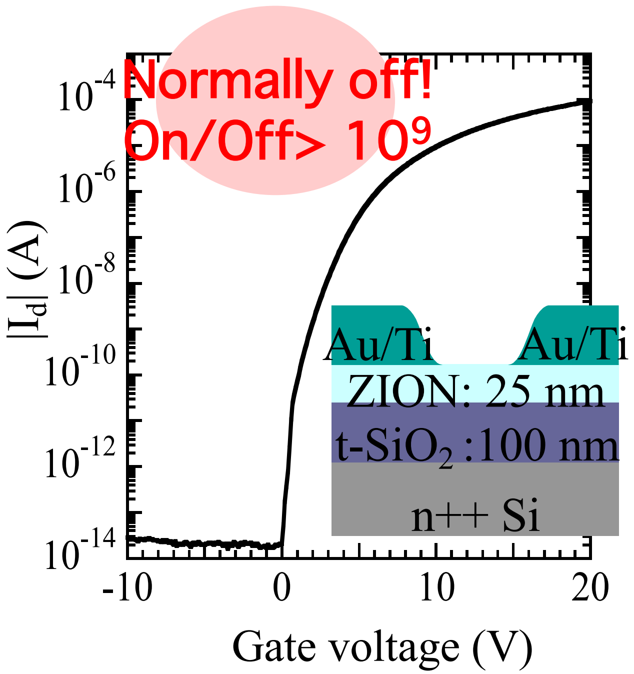
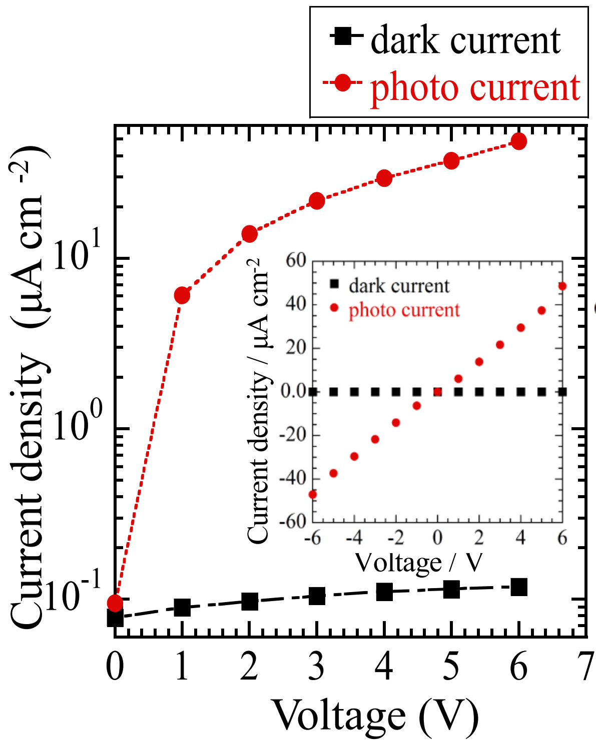
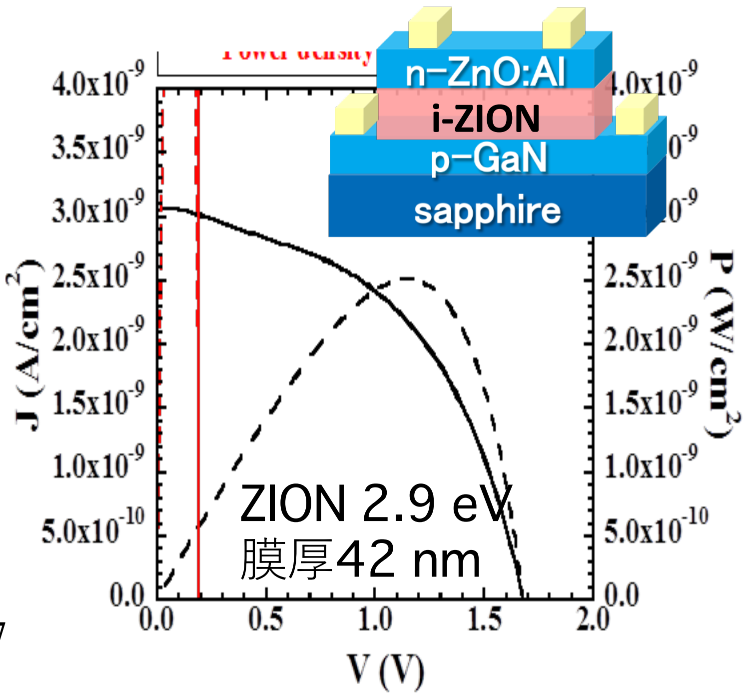
FET



Photo/dark current



Photovoltaic



Conductivity can be controlled by *voltage, light, and so on…*

Generalized Structure Zone Diagram:

3 factors=Temperature, Kinetic Energy, Film Thickness

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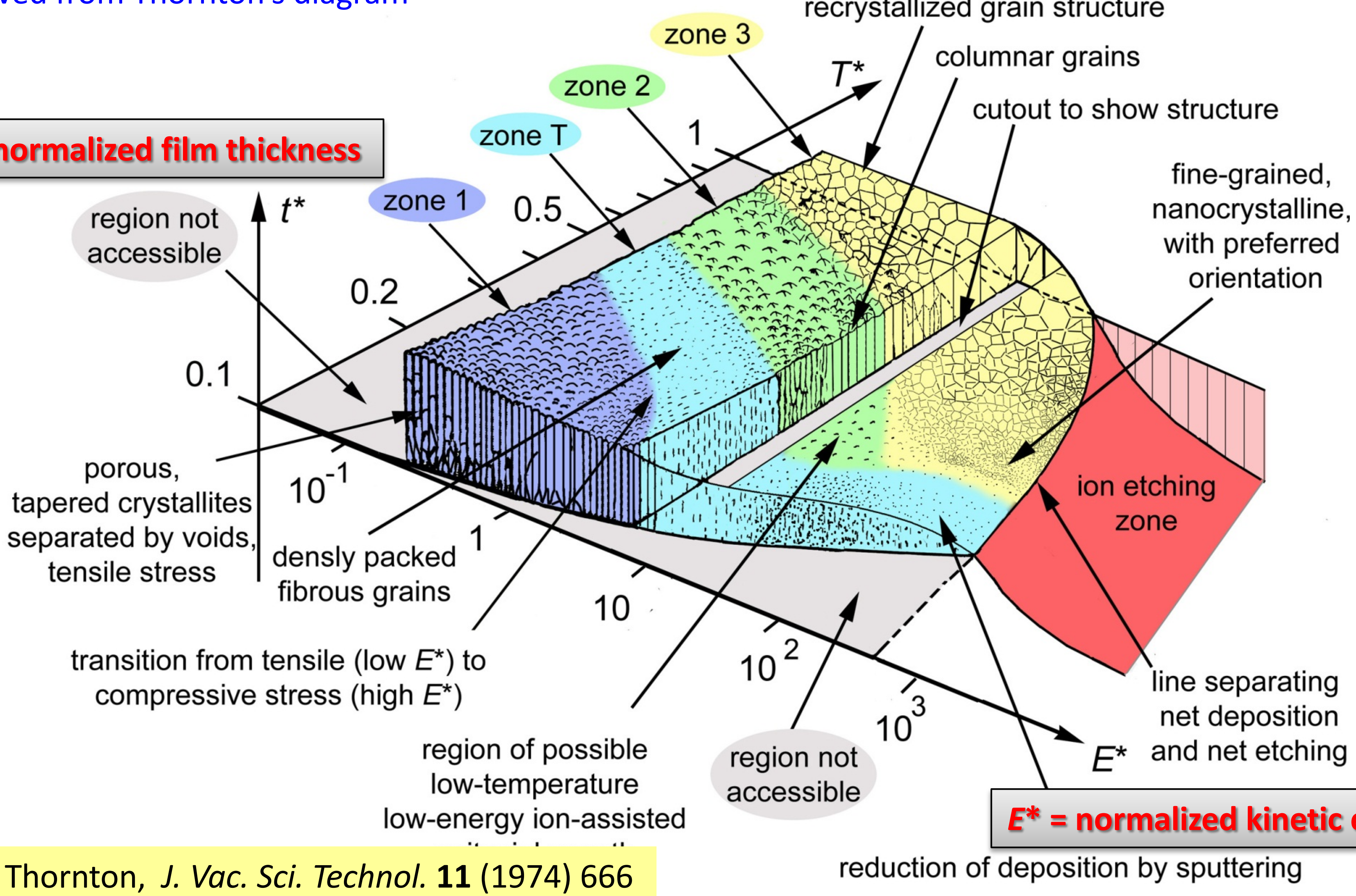
T^* = T/Tm normalized temperature and potential energy

derived from Thornton's diagram

t^* = normalized film thickness



E^* = normalized kinetic energy

J. A. Thornton, *J. Vac. Sci. Technol.* **11** (1974) 666

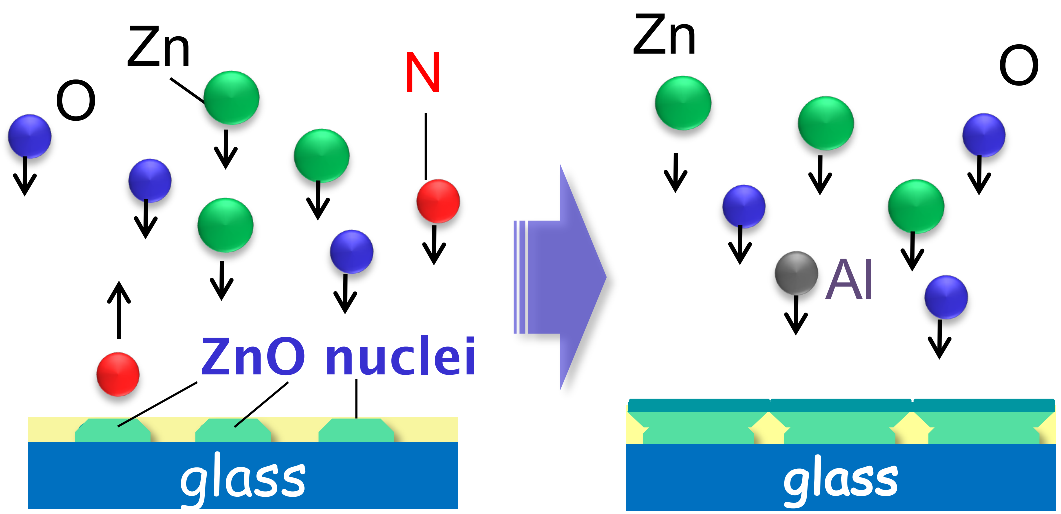
A. Anders, Thin Solid Films **518** (2010) 4087

Novel factor= impurity

High quality ZnO based TCO
on Nitrogen Mediated Crystallization (NMC) buffer

Google Scholar
zinc oxide 185 millions
The lowest resistivity of very thin ZnO: Al

NMC buffer | **ZnO:Al on NMC buffer**

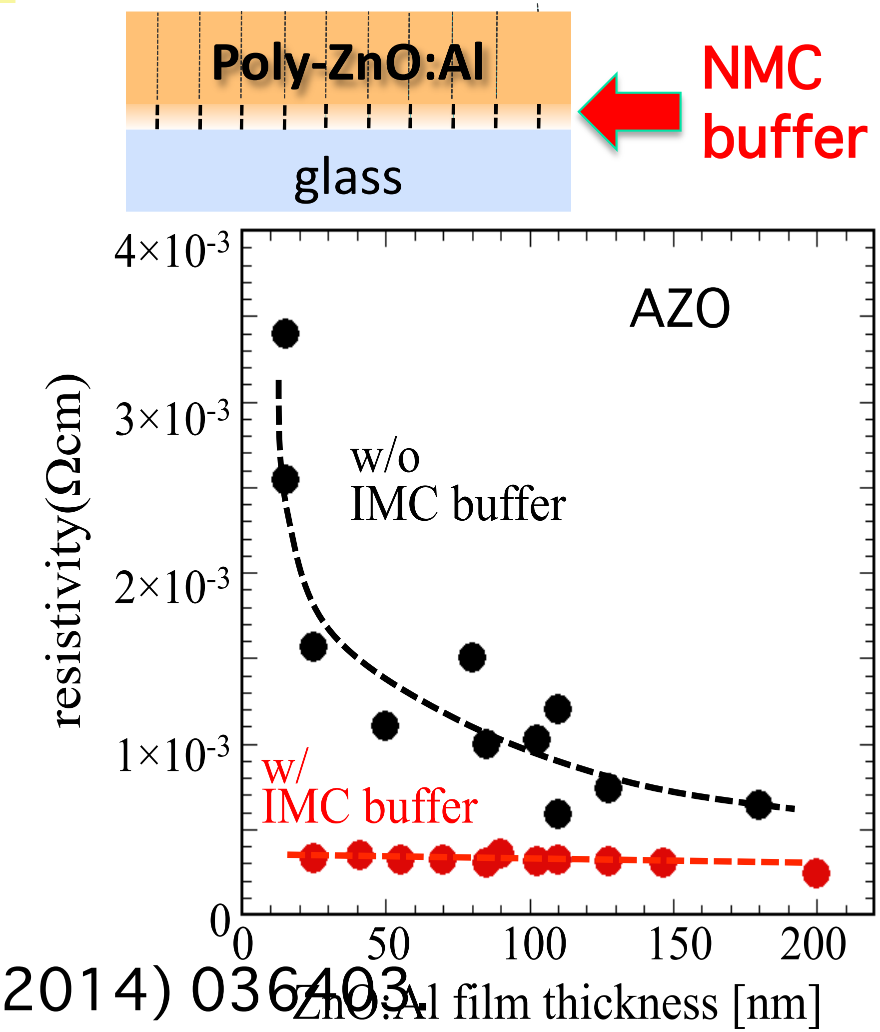


nucleation control by nitrogen addition

ZnO:Al film deposition on NMC seed layers

- **Crystallinity**
- **Morphology**

- **Crystallinity**
- **Electrical properties**
- **Transparency**

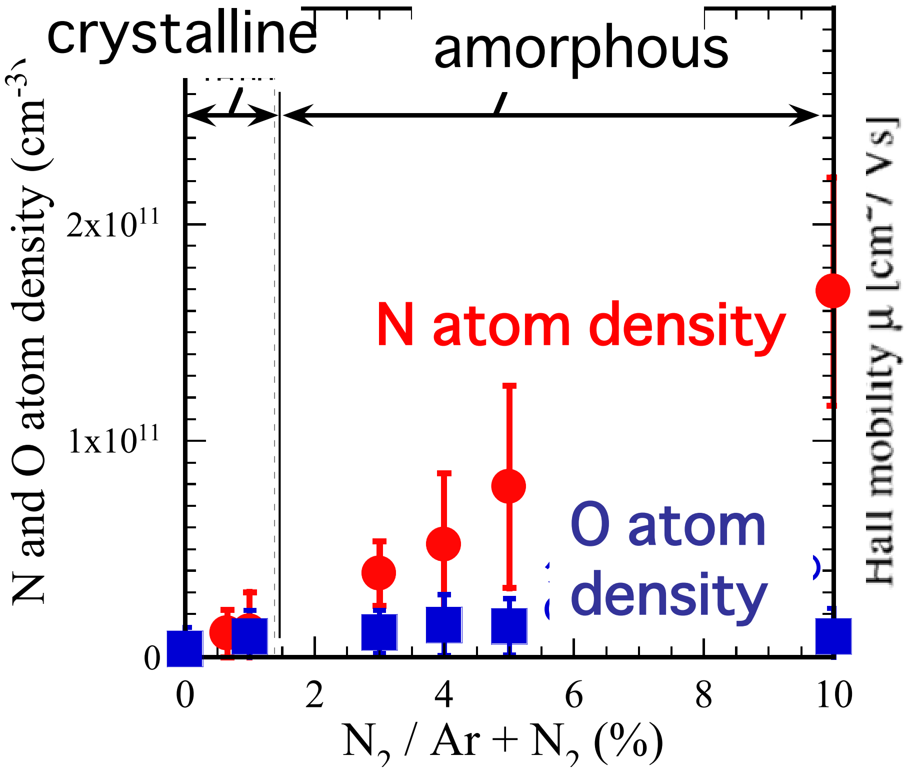


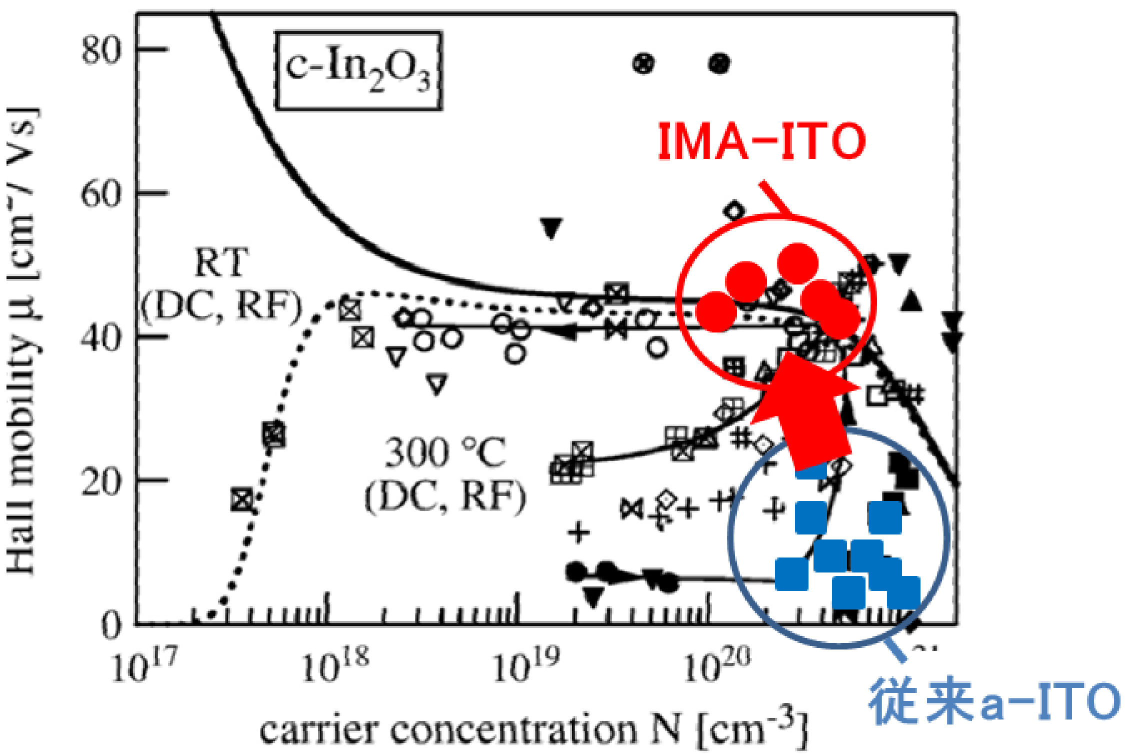
I. Suhariadi, et al., Mater. Res. Express 1 (2014) 036403.

Novel factor= impurity

High mobility amorphous ITO is realized by Impurity Mediated Amorphization (IMA).

1. Amorphous without any crystals,
2. Amorphous up to 300C,
3. High mobility of 55 cm^2/Vs,
4. Smooth surface < 0.3nm RMS roughness.





Work with Prof. Hori, Nagoya Univ., Japan.

How to control nucleation&growth of ZnO crystal ?

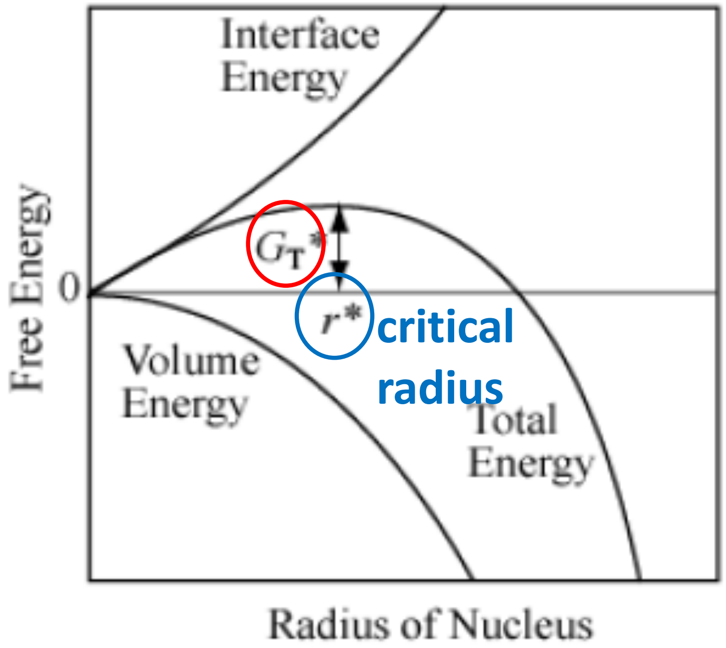
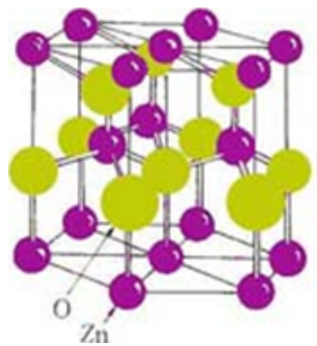
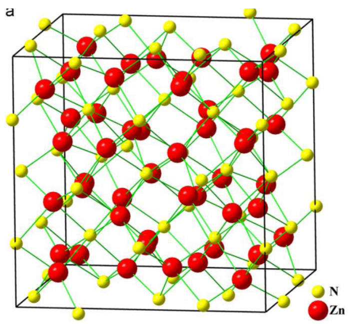


Illustration of the most simple nucleation theory



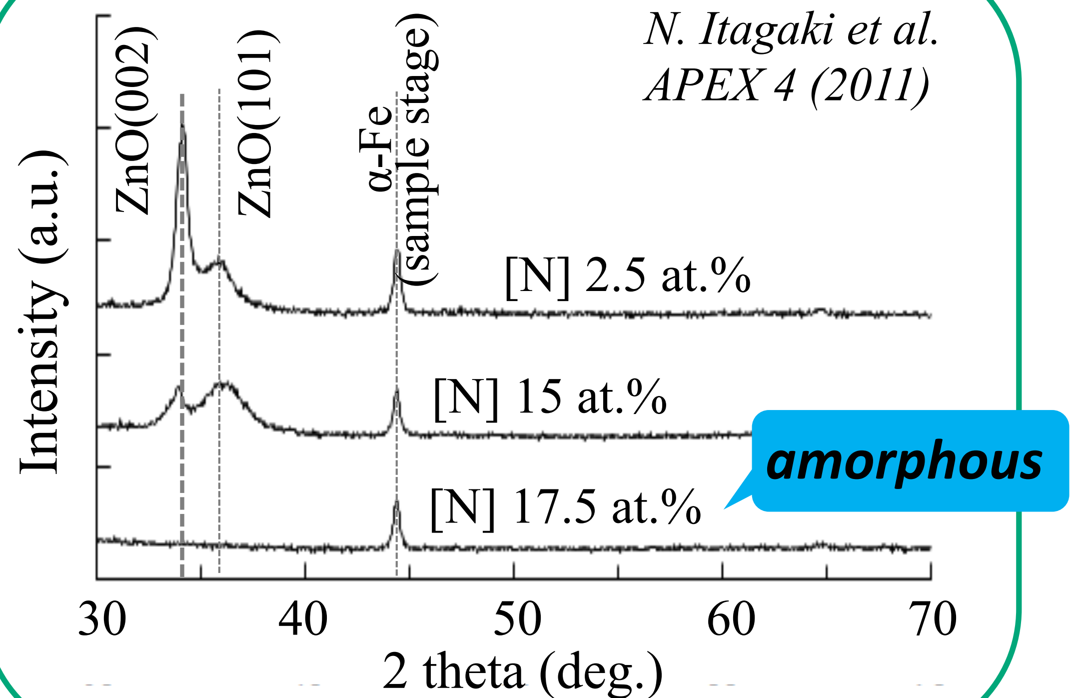


How to reduce nucleation rate ?

- ~~Lower film growth temperature~~
- **Interfere nuclei growth before they reach critical radius**

Impurity adsorption to nuclei ***Nitrogen***

XRD patterns

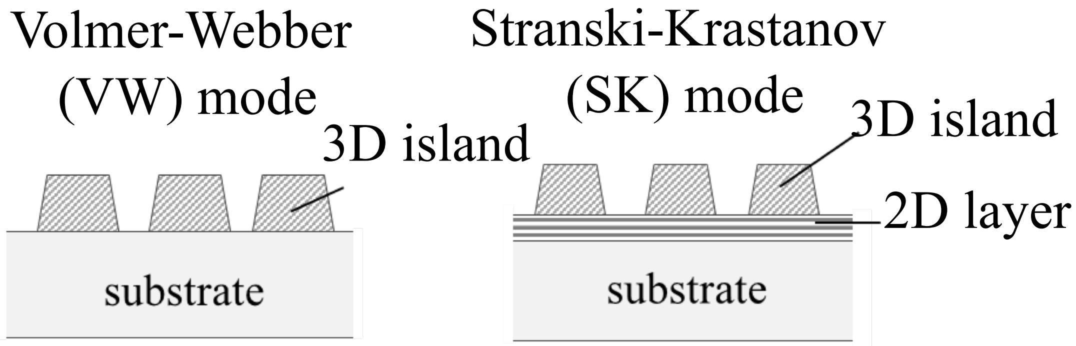


I. Suhariadi, et al., Mater. Res. Express 1 (2014) 036403.

Inverse SK mode=A novel and useful film growth mode

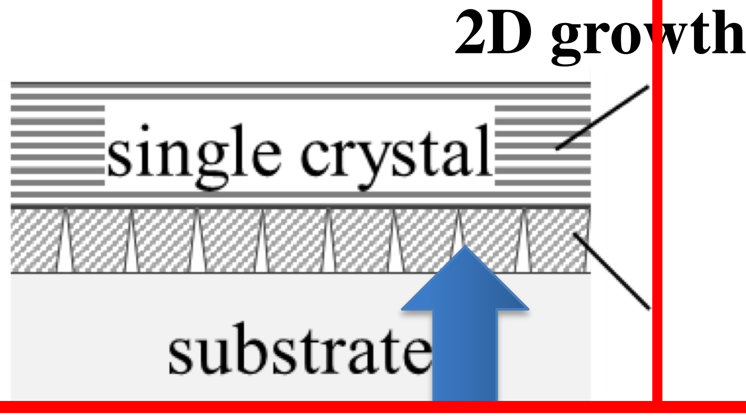
Hetero-epitaxy on lattice mismatched substrate

Two common growth modes



New growth mode

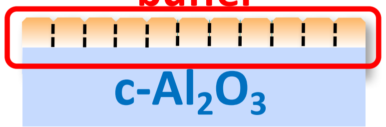
"Inverse SK mode"



3 requirements
#1. in&out of plane aligned grains,
#2. atomically flat surface,
#3. nm grains reduce strains.

Impurity reduces surface energy of nuclei.
Nano crystallites realize stress control.

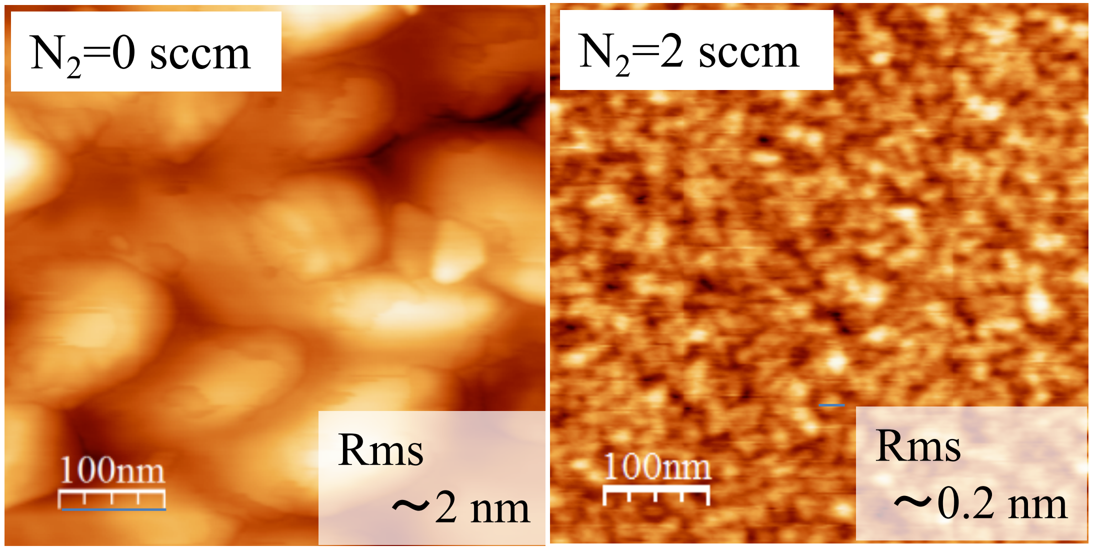
Morphology of buffer layer

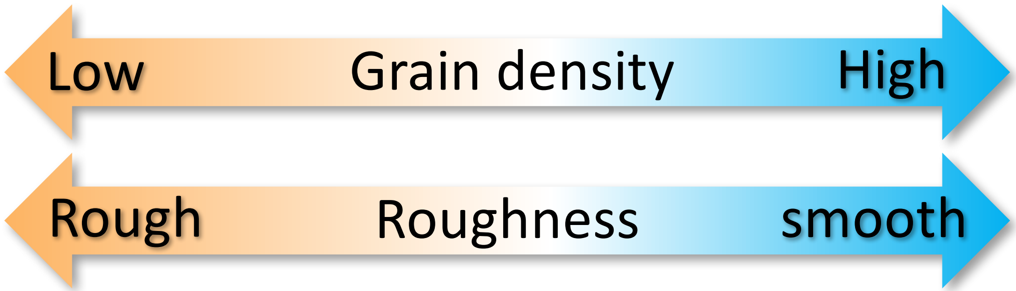


IMC method provides high nuclei density & very smooth surface

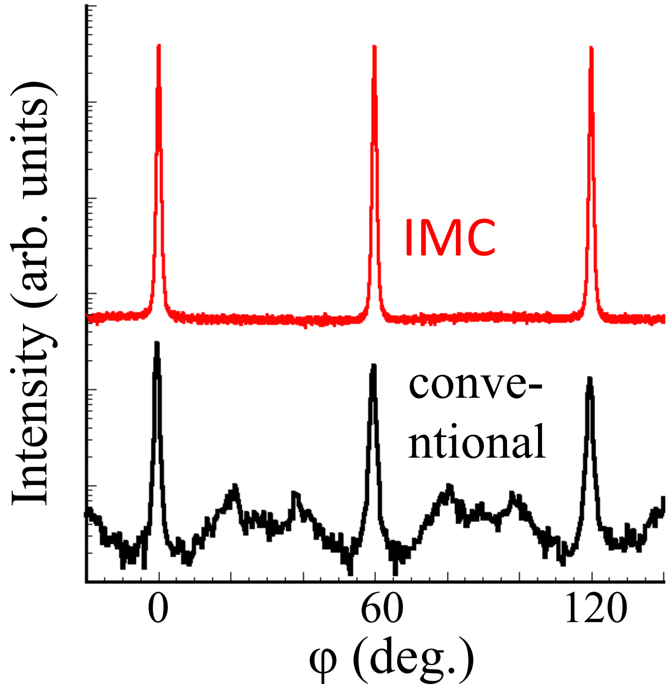
- AFM images of **buffer layers**

conventional IMC





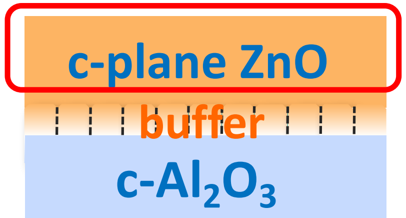
- XRD ϕ scan of (101) plane



In-plane alignment
([10-10]//[11-20])

3 requirements
#1. in&out of plane aligned grains,
#2. atomically flat surface,
#3. nm grains reduce strains.

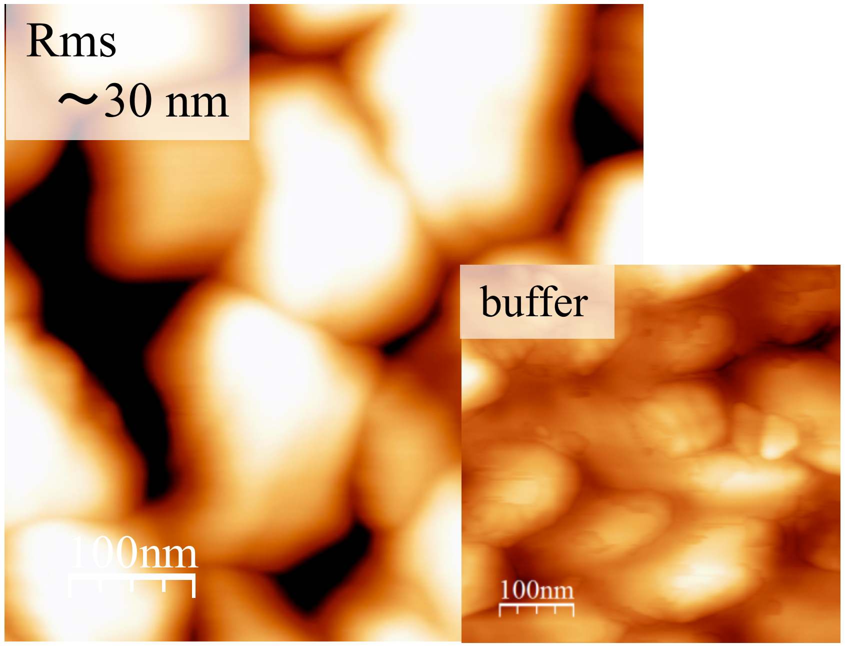
Morphology of ZnO on buffer layer



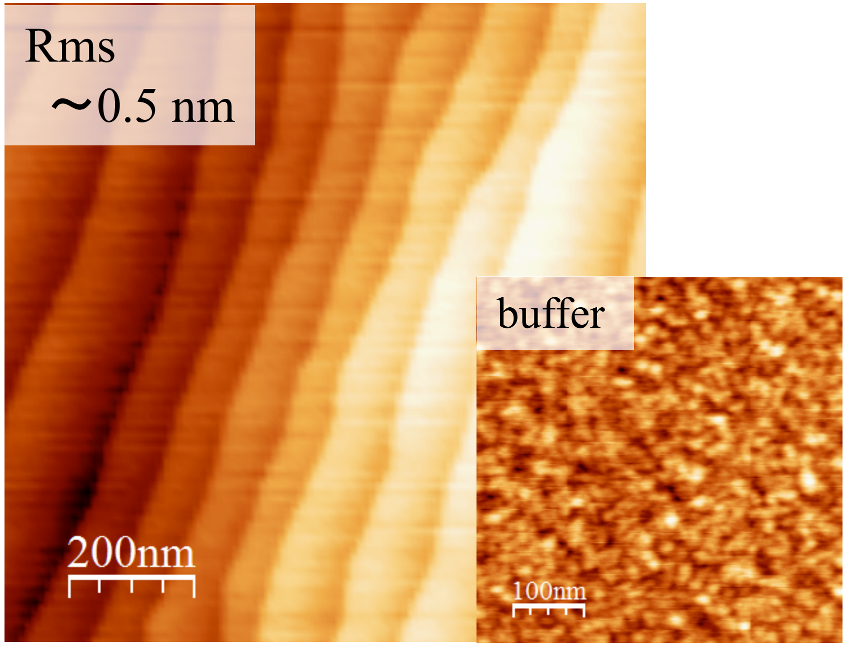
Atomically-flat ZnO films with 0.26-nm-high steps are fabricated on c-Al_2O_3 by sputtering

- AFM images of **ZnO** on buffer layers

ZnO on conventional buffer



ZnO on IMC buffer



IMC method

High nuclei density, Smooth surface
Low strain & interface energy

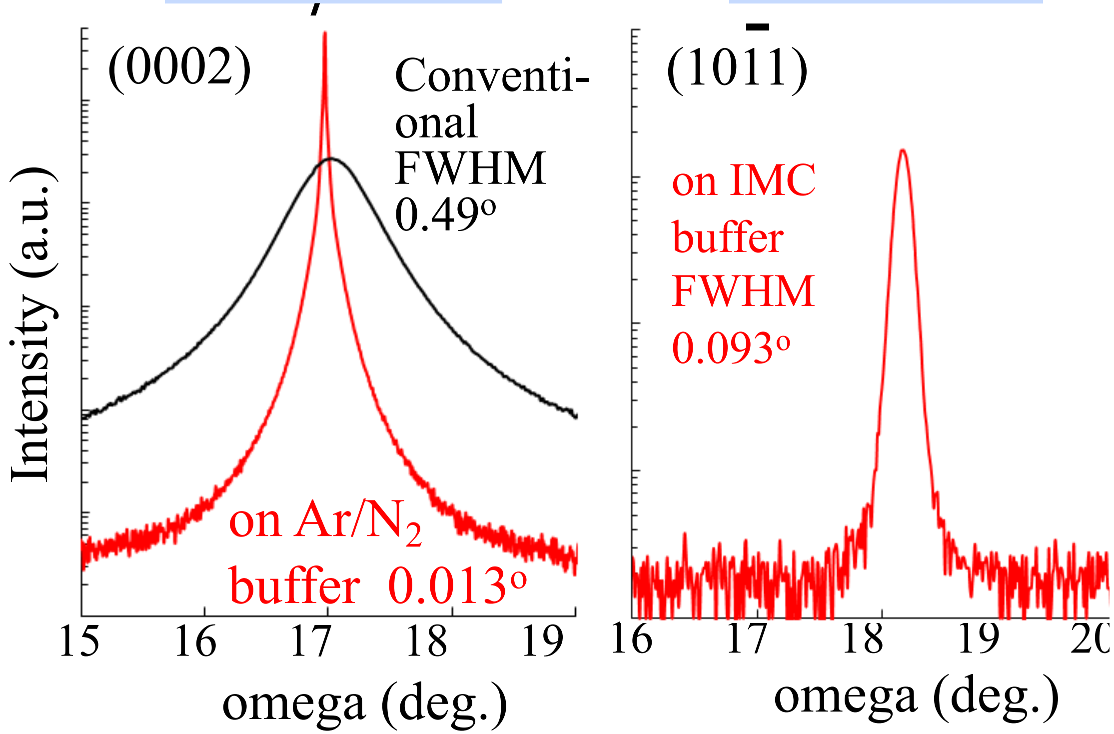
Lateral growth enhanced

Growth of single crystalline ZnO on lattice mismatched substrate -Crystallinity of ZnO on buffer layer

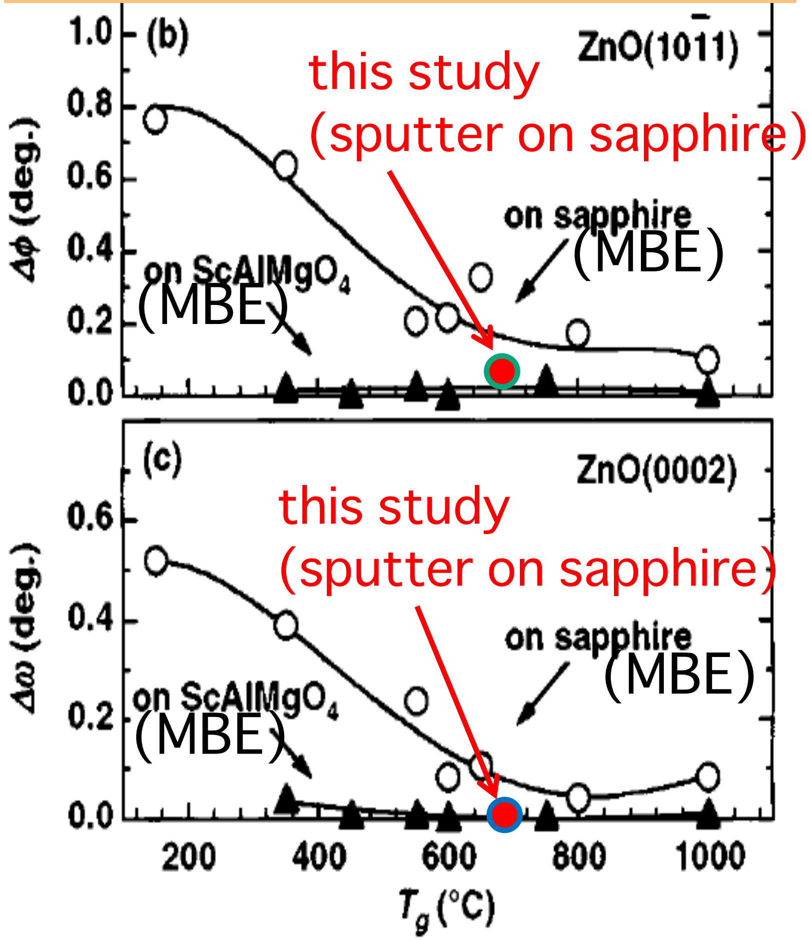
MBE&SCAM-grade epitaxial ZnO films has been fabricated by IMC method.

- XRD results / Rocking curves

out of | *in plane*



Comparison with MBE&SCAM



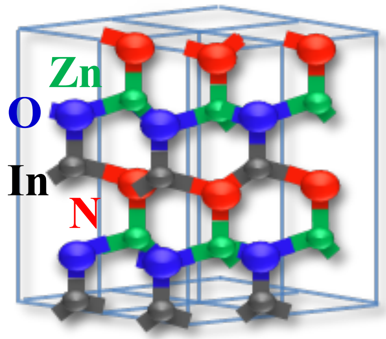
Ohtomo, *et al*., Appl. Phys. Lett., 75 (1999) 25

Properties of ZION

ZION $(ZnO)_x(InN)_{1-x}$ *~ a pseudo-binary alloy of ZnO and InN~*[3, 4]

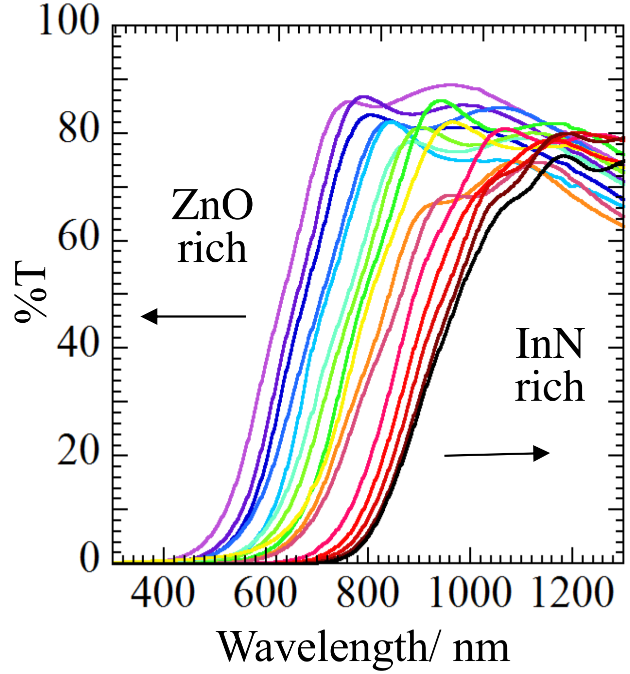
- direct tunable bandgap (0.7-3.4 eV)
- high absorption coefficient ~ 10^5 cm^{-1}
- high piezoelectric field (0.89 MV/cm)

ZION is a promising material for absorption layers of solar cells.

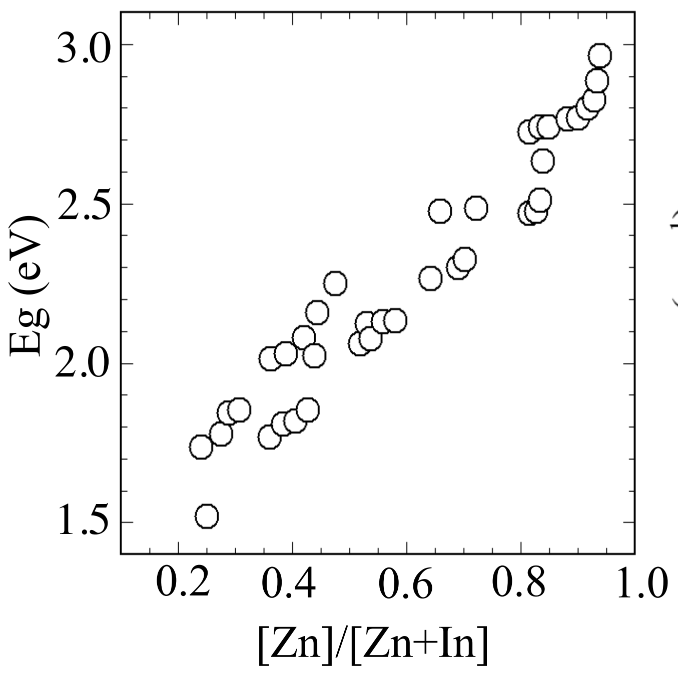


Wurtzite structure

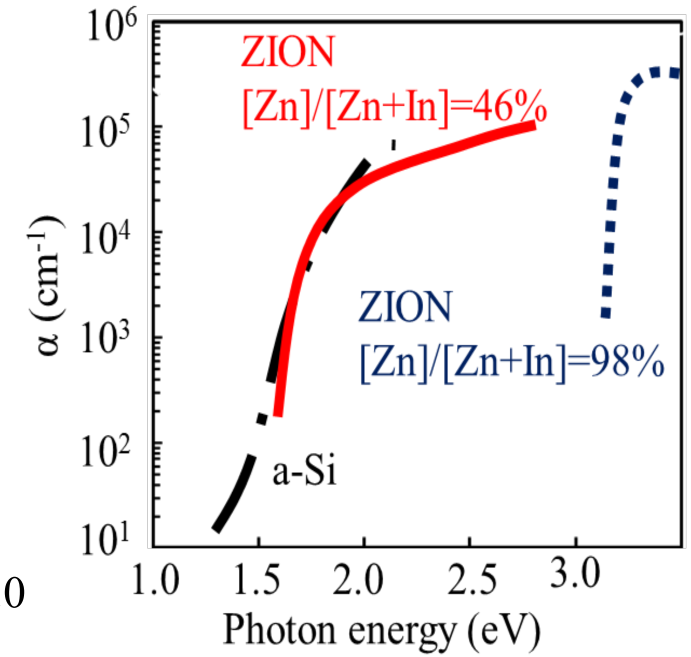
Transmittance



Band gap



Absorption coefficient

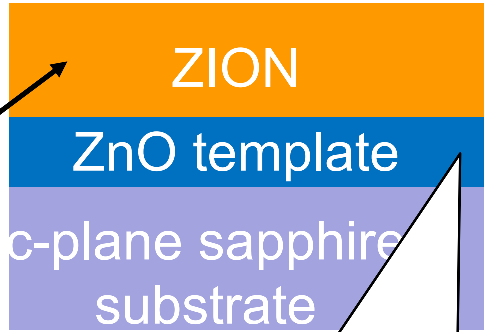


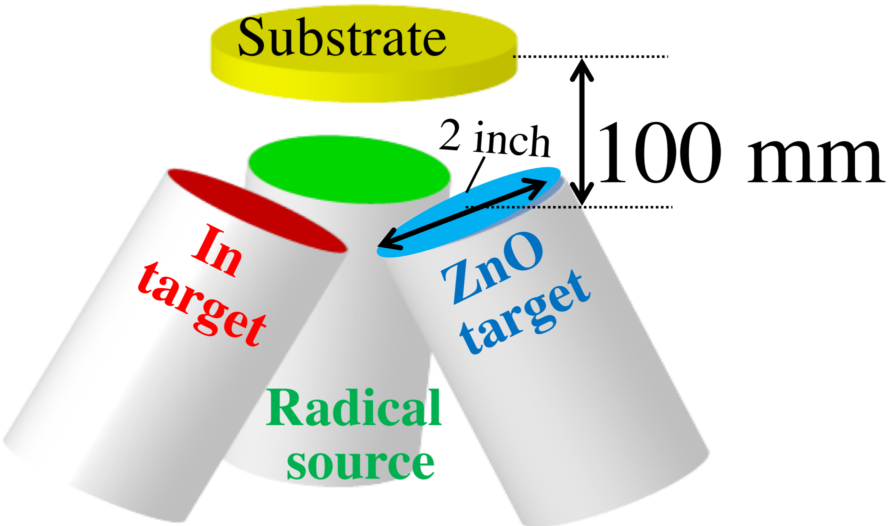
3) N. Itagaki, et al., Mater. Res. Express **1** (2014) 036405.
4) K. Matsushima, et al., Jpn. J. Appl. Phys. 52, 11NM06 (2013)

Fabrication of single crystal ZION films

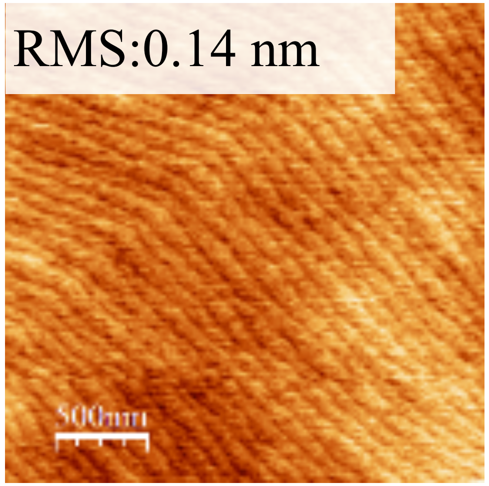
RF magnetron sputtering

- Gasses: Ar, N_2, O_2
- P_{gas} : 0.3 Pa
- T_{sub}: RT-450℃
- Targets: ZnO, In
- Substrate: ZnO template[5]
- Radical Source: ECR plasma





Single crystal ZnO on c-plane sapphire



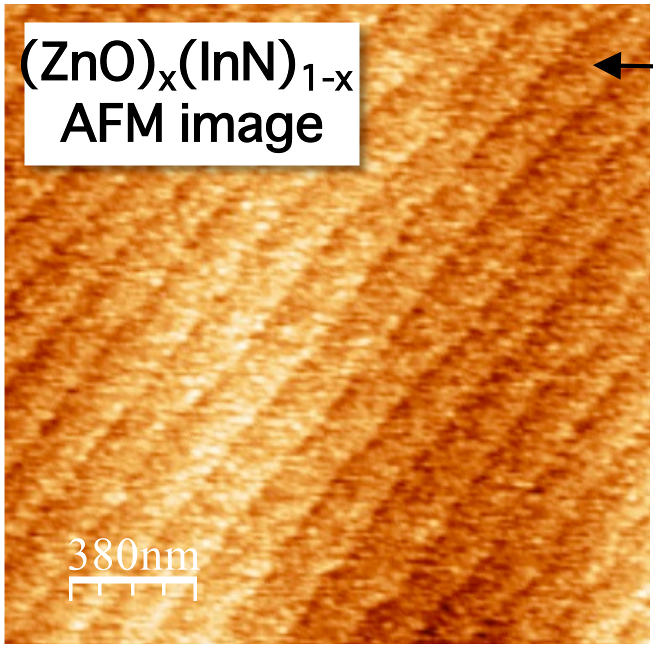
K. Kuwahara, et al., Thin Solid Films **520** (2012) 4674–4677.

Single crystalline ZION for the first time

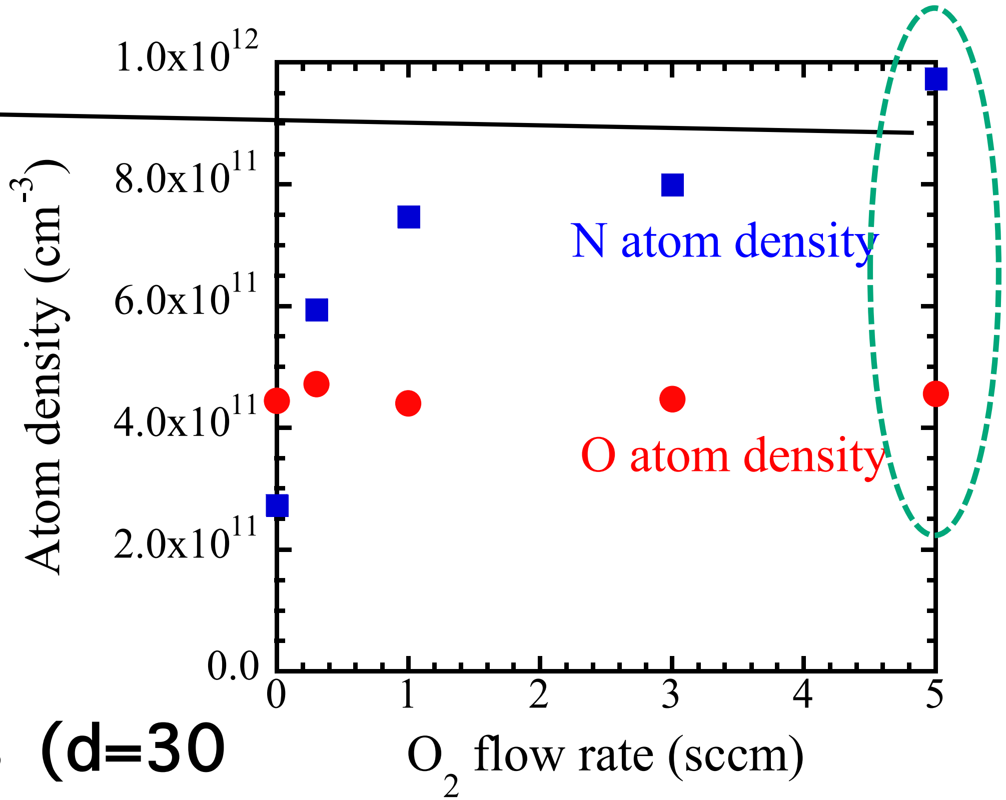
九州大学
Kyushu University

Single crystalline $(ZnO)_x(InN)_{1-x}$ films have been fabricated by using SC-ZnO grown in "inverse SK mode"

$(ZnO)_x(InN)_{1-x}$ on SC-ZnO grown in "inverse SK



N and O density in plasma



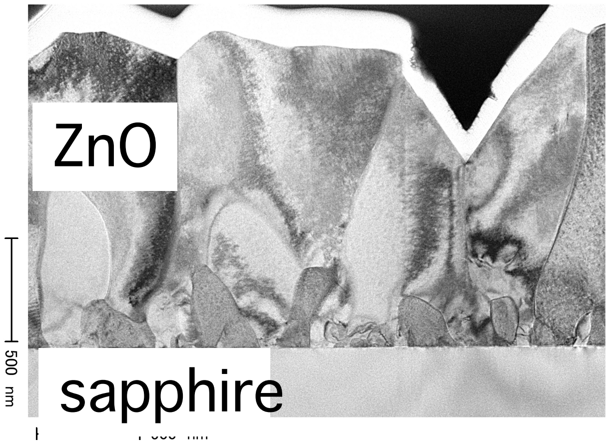
mobility@RT ~110 cm^2/Vs (d=30 nm)

K. Mathusima, et al., IEEE Trans. Plasma Sci. (in press)

Cross sectional TEM

Conventional

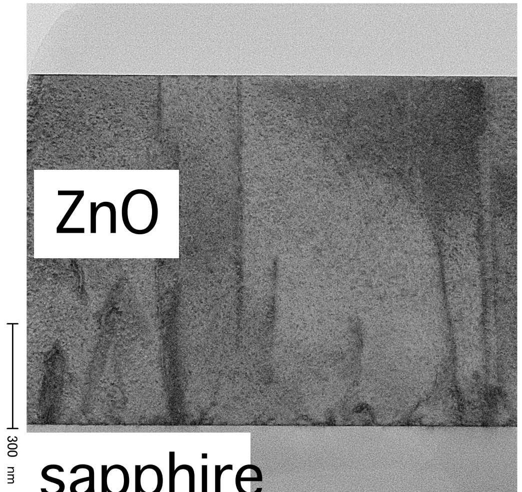
1 μm ZnO/c-plane sapphire



Dislocation density
10^{10} cm $^{-2}$

Inverse-SK

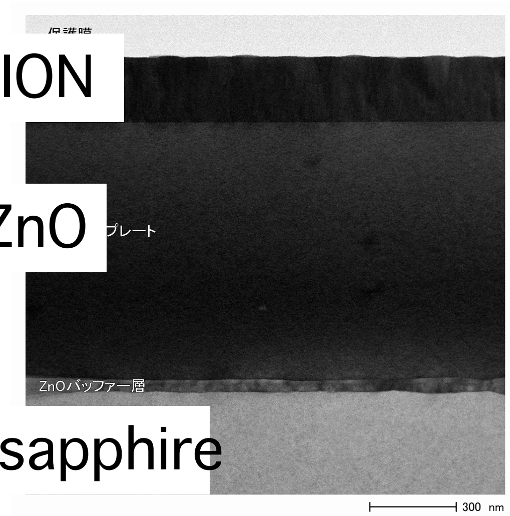
1 μm ZnO/c-plane sapphire



Dislocation density
10^{8} cm $^{-2}$

100 nm ZION
on Inverse-SK

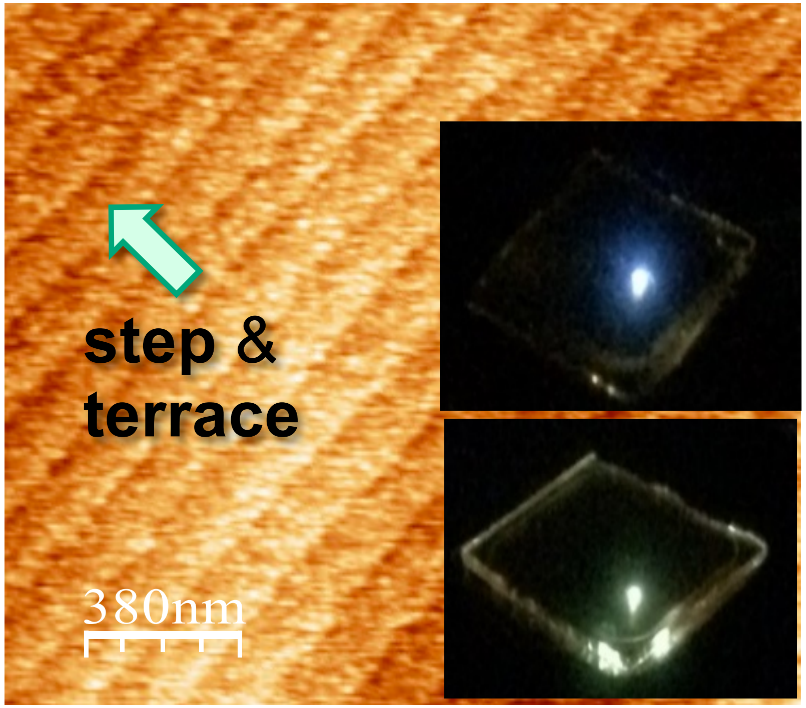
1 μm ZnO/c-plane sapph



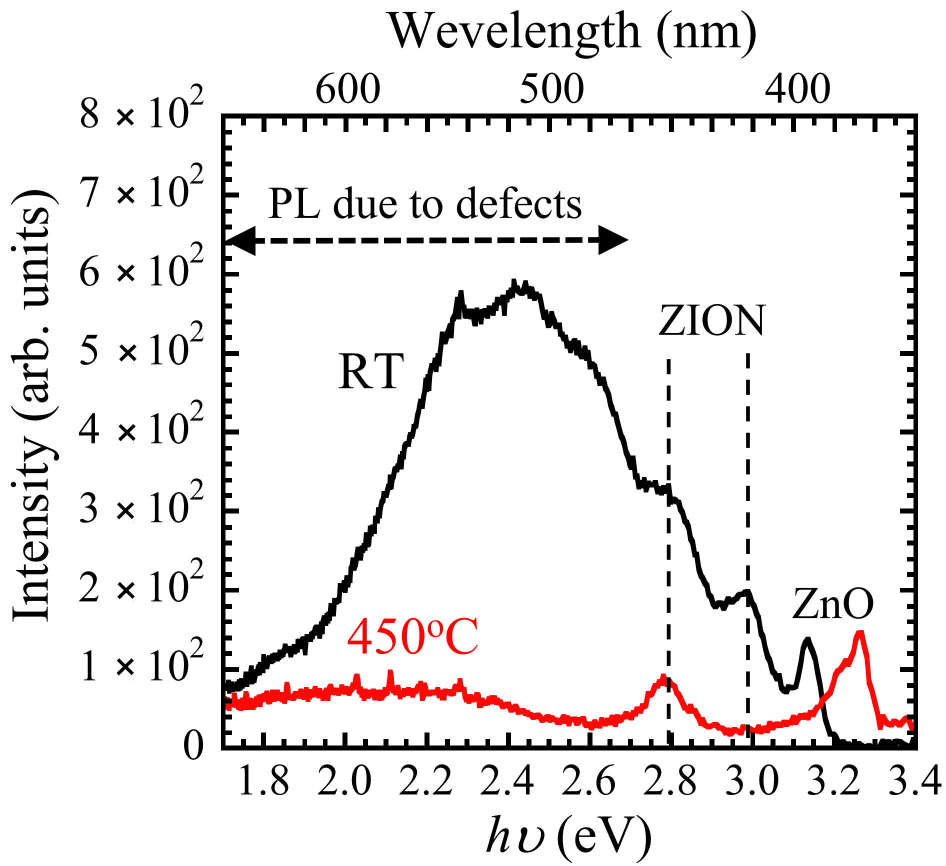
Photoluminescence(PL) of ZION films

Single crystalline ZION films show strong blue and green emission at room-temperature.

AFM



$(ZnO)_{0.92}(InN)_{0.08}$ $(ZnO)_{0.82}(InN)_{0.18}$

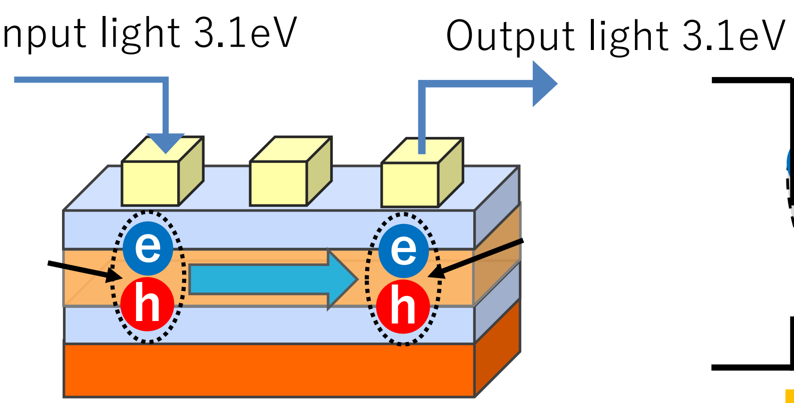


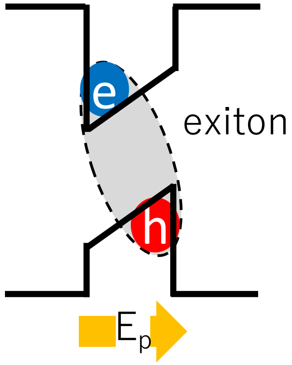
HeCd 325nm (3.8eV) 10mW

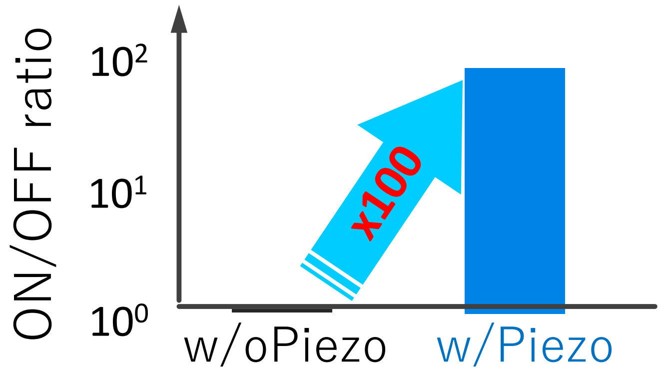
N. Miyahara, et al., Materials Science Forum 941(2018) 2099-2103.
K. Mathusima, et al., MRS Advances 2 (2017), 277-282.

Exotic combination of mechanical & optical properties realize optical transistor.

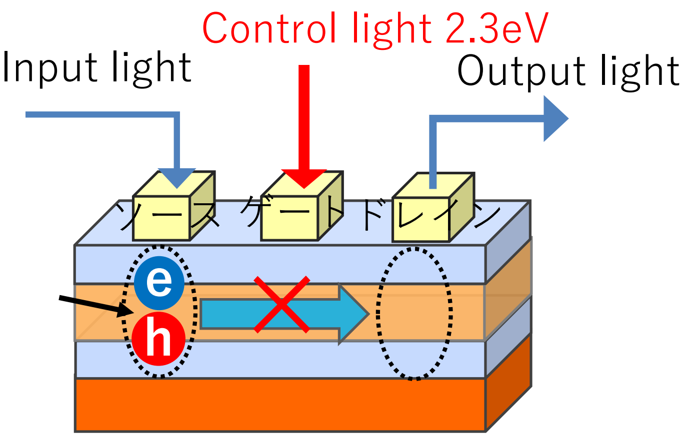
Piezo field separates wavefunctions, prolongs exiton lifetime, realizing optical transistor.

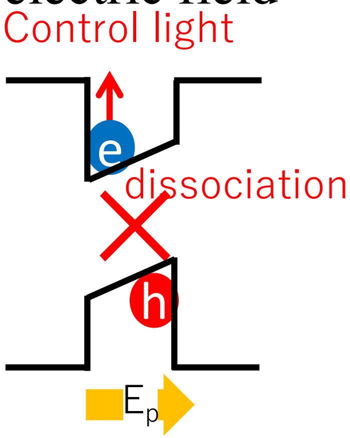






ZION/ZnO quantum well with piezo electric field





K. Matsushima, et al., Thin Solid Films, Vol.587, pp.106-111, (201

Data processing crisis

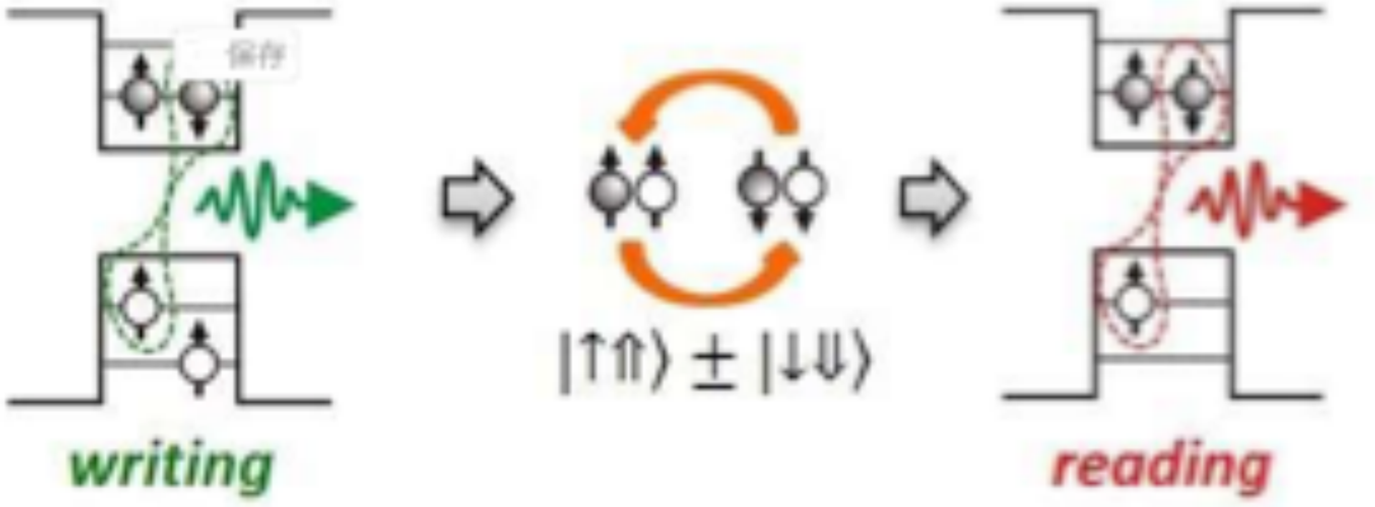
九州大学 Kyushu University

Quantum computing is a kind of parallel data processing, which reduces drastic processing time and energy.
Exciton can be employed as qubit: dark & bright exciton.

A single qubit can be forced into a *superposition* of the two states denoted by the addition of the state vectors:

$$|\psi> = \alpha \ |0> + \alpha \ |1>$$

Where α and α are complex numbers and $|\alpha| + |\alpha| = 1$



Tobias Heindel et al. APL Photonics (2017). DOI: 10.1063/1.5004147
Maria Maragkou, Nature Materials volume 14, page 260 (2015)

Conclusions

Trends:
3D stacking is promoting integration of flash memory (sold state disk, SSD).
Novel materials are needed for novel E/O devices andquantum computing devices.

1. Homogeneous nucleation in PECVD plasma

- High N & low H a-SiNx is realized at 100 ºC.
- Cluster inclusion is a tuning knob for film properties.

2. Heterogeneous nucleation in sputter deposition

- Inverse SK mode leads hetero-epitaxy.
- Impurity is a tuning knob for film growth.
- ZION and ZAON are new opto-electric materials.