2008.3.5-7 JST-DGF Nano Electronics Seminor at Achen

National Institute for Material Science

Landscape of materials design for future nano electronics And high-throughput materials exploration

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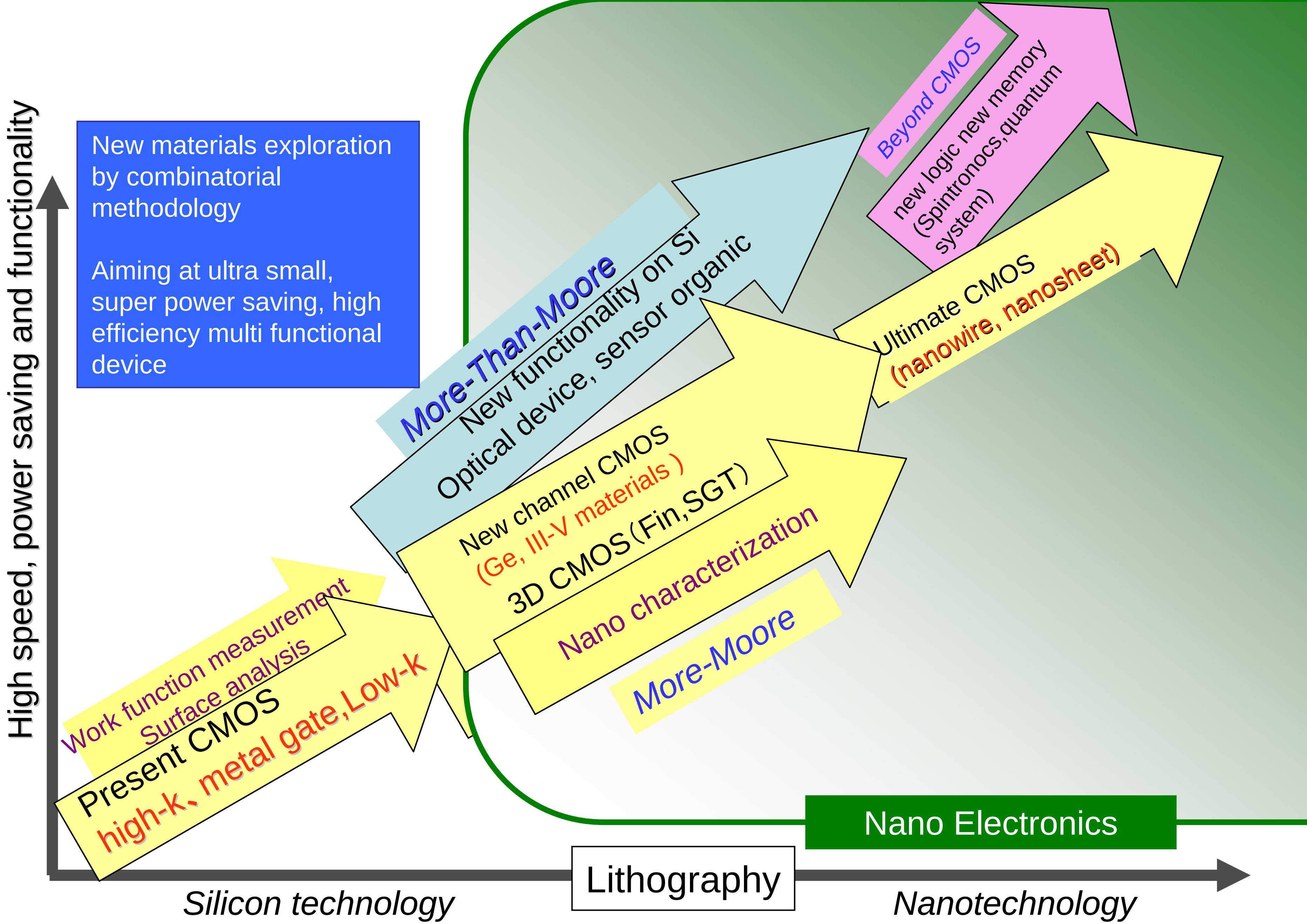
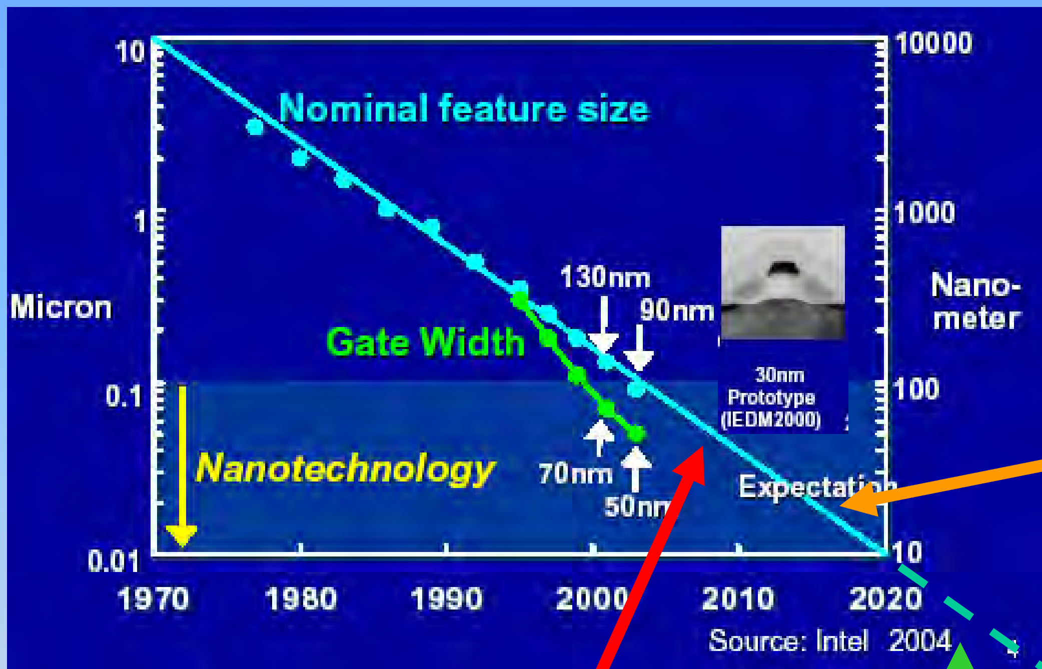


Development of ultra small, super power saving, high efficiency multi function by integration with Si device technology and nano technology

Research Trend in Si nano device

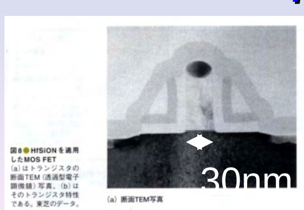
High speed operation、High denisty packing、multi –function device



New Materials
based Si device
(*hp32-22 nm node)*

Materials
Exploration for Nano device
High-k ,metal gate,
Nano wires (Si CNT or others
interconnection ets

Present Si nano device
(hp65nm node is completed)

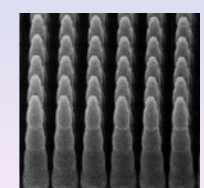


Si,Al, SiO2 have been the major materials

Postscaling generation

- *Mixning technology of top down and bottom up*
- *3D nano structure*
- *Variety of nano interface*

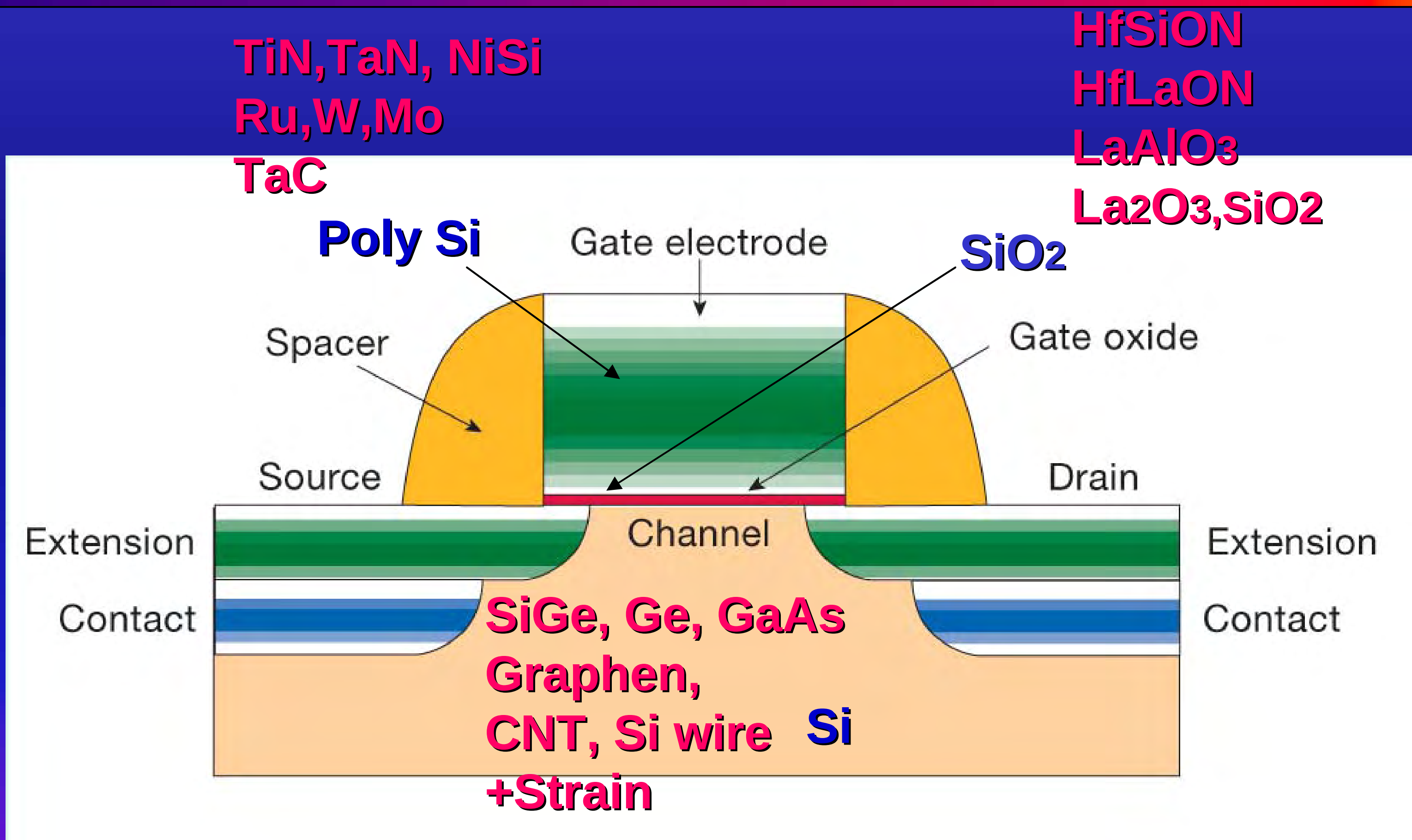
3D nano structures



Prof.Endo Tohoku Univ.

New Materials in Future ULSI

National Institute for Material Science



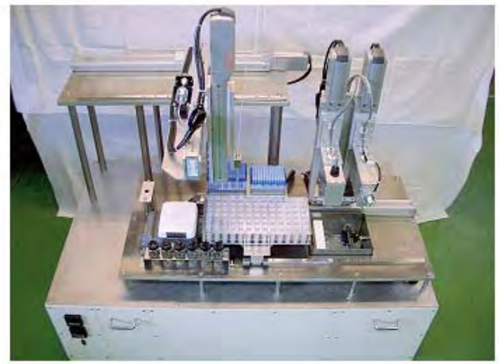
1) Collaboration

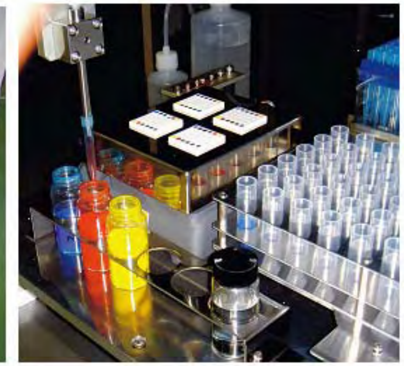
2) HT Experimentation

High-Throughput synthesis：imitation to innovation

Combinatorial Chemistry

Former combi system for inorganic materials

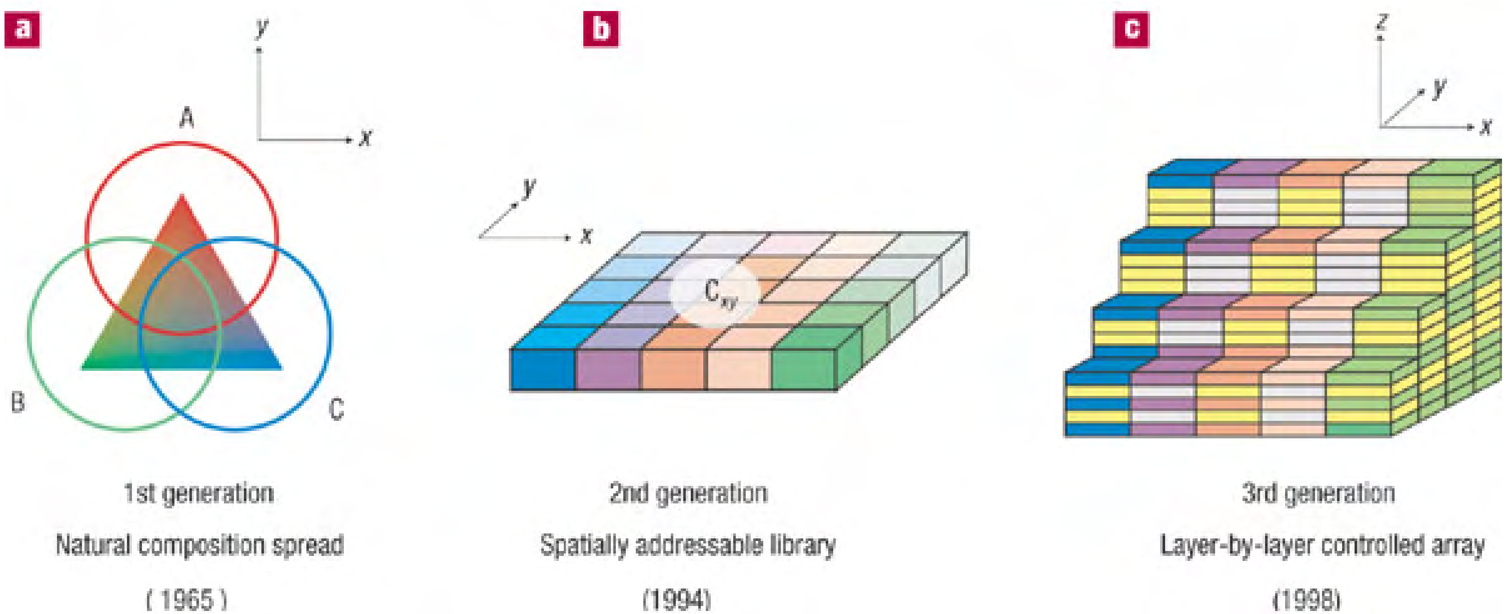




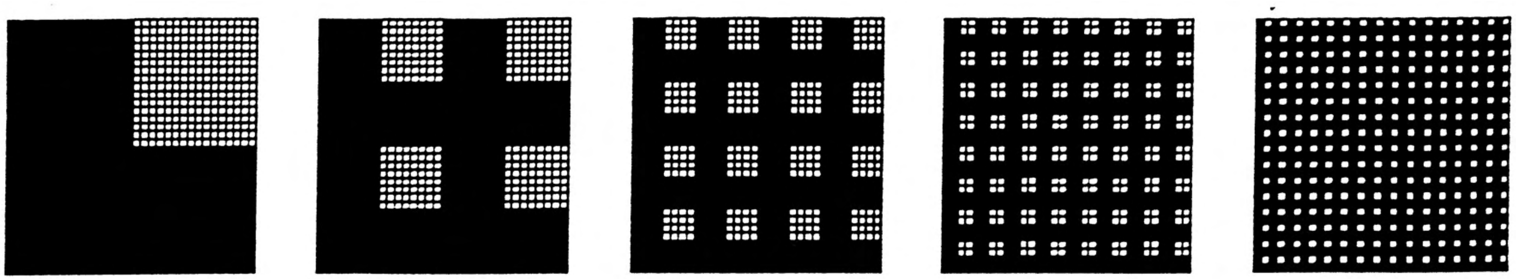
Innovative thin film technology

"*Combinatorial solid-state chemistry of inorganic materials*"

Hideomi Koinuma and Ichiro Takeuchi, Nature Materials 3, 429 - 438 (2004)

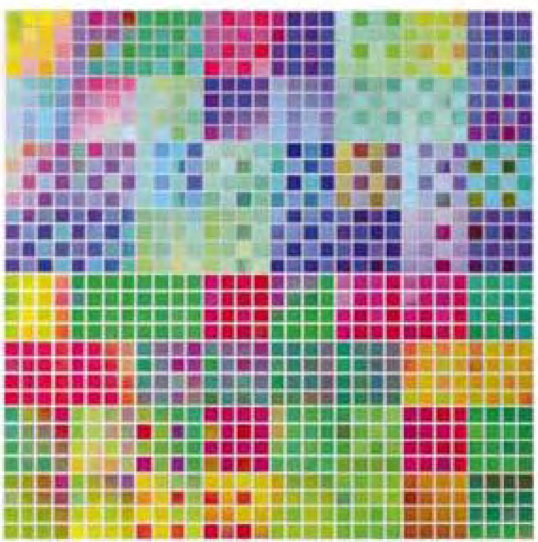


What is combinatorial materials exploration?

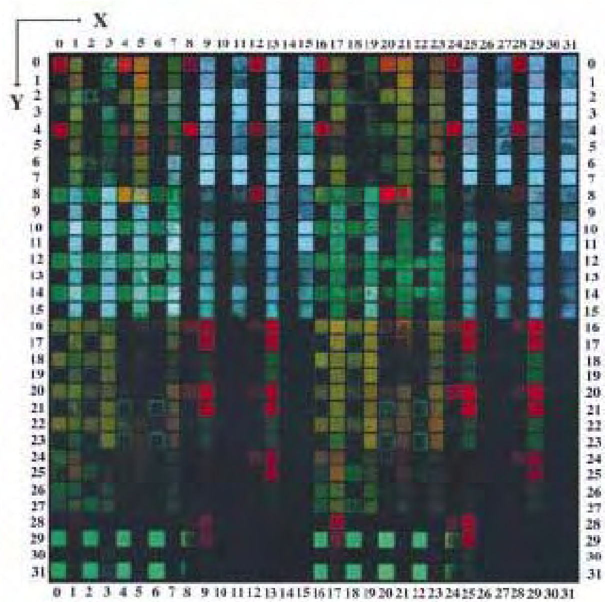


A_i | B_i | C_i | D_i | E_i

2^2 (4) **2^4 (16)** **2^6 (64)** **2^8 (256)** **2^{10} (1024)**



Ambient light



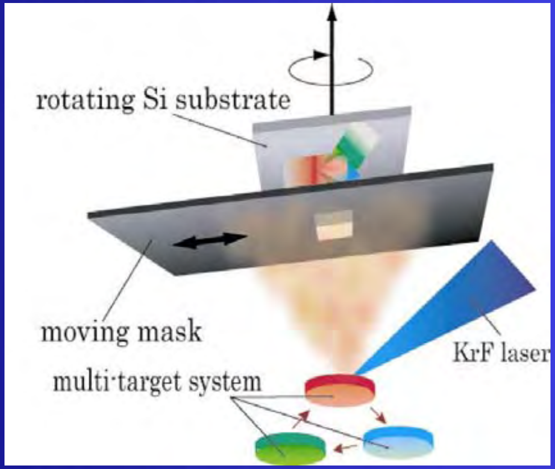
UV irradiation

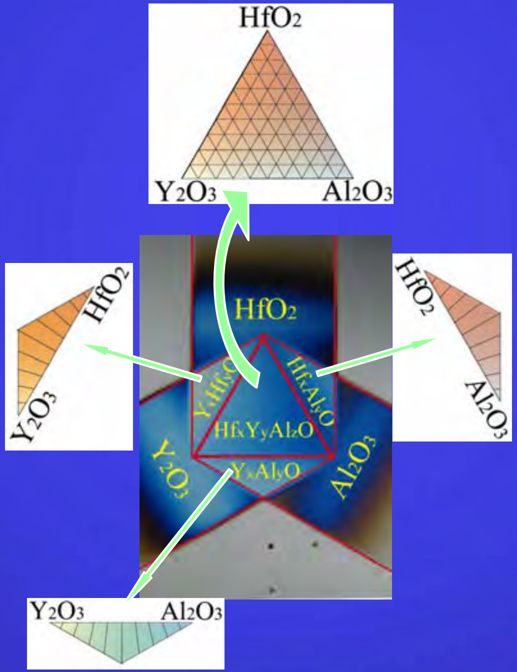
Discovery of new fluorescent materials

Fig. 2. (**A**) Photograph of the as-deposited quaternary library under ambient light. The diversity of colors in the different sites stems from variations in film thicknesses and the optical indices of refraction. (**B**) Luminescent photograph of the processed quaternary library under irradiation from a multiband emission UV lamp at short wavelength (centered around 254 nm).

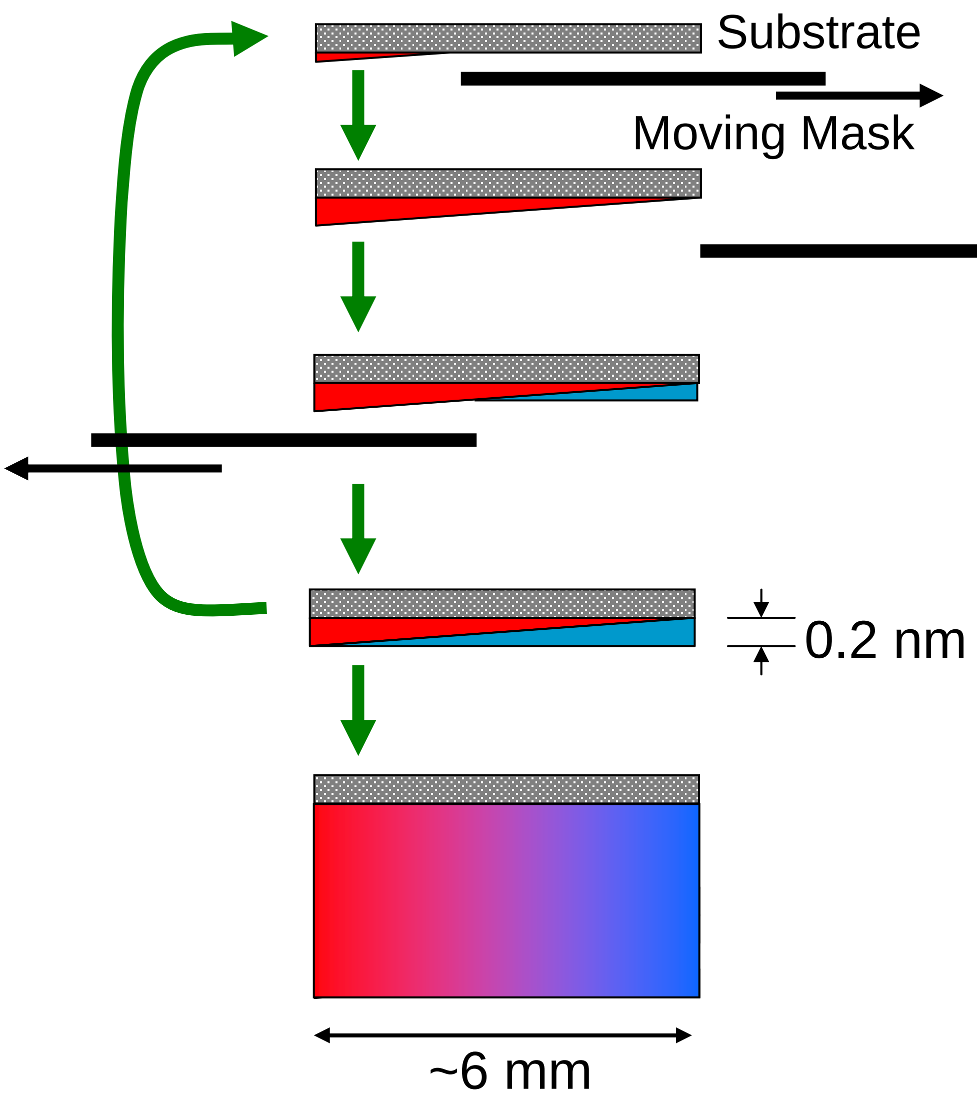
Jingsong Wang et al *Science* 1998 March 13; 279: 1712-1714

Combinatorial automatic ternary and binary Composition spread synthesis system with Moving Mask System





Schematics of binary composition spread film



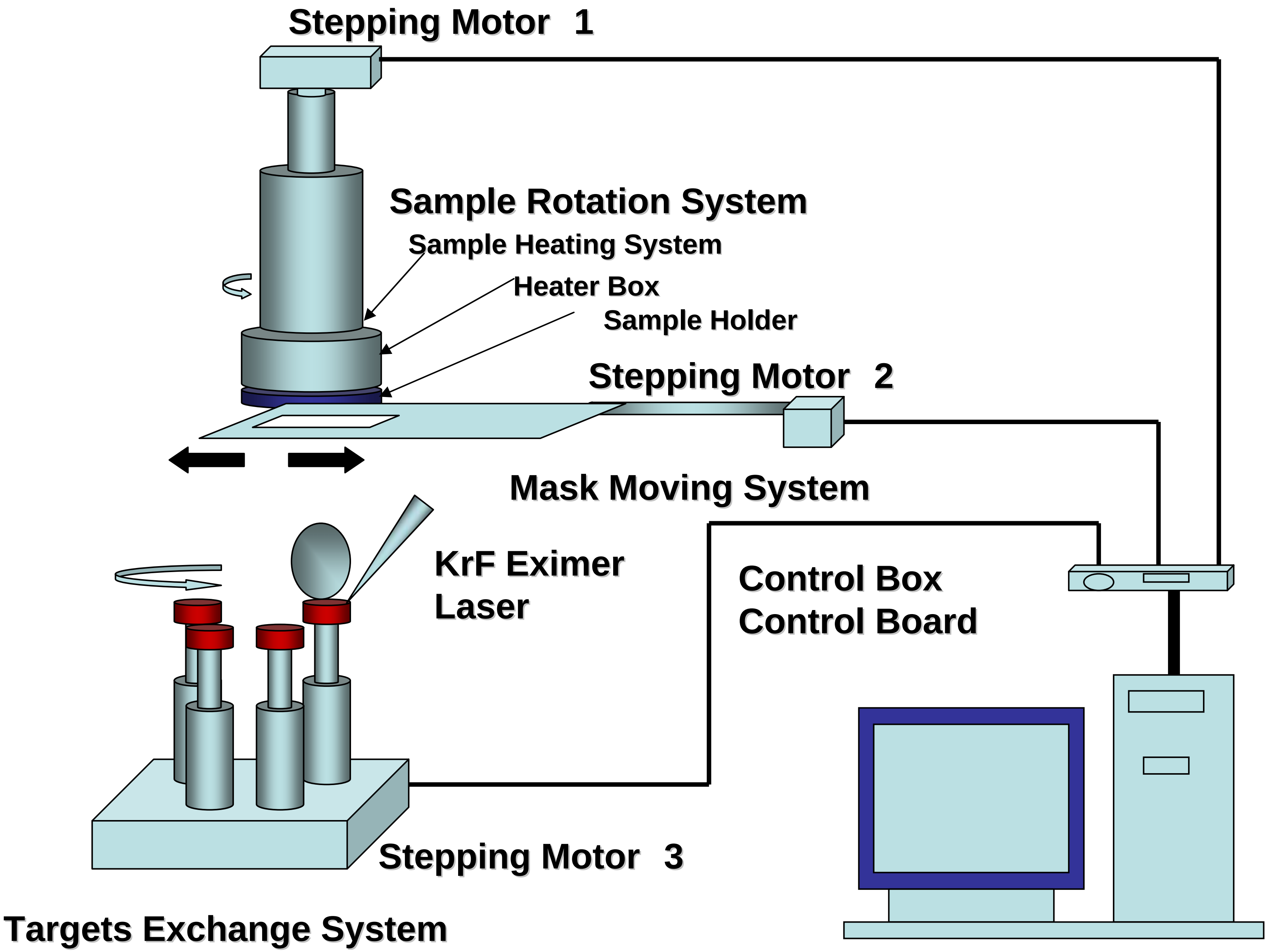
1) Deposition of Material A

2) Deposition of Materials B

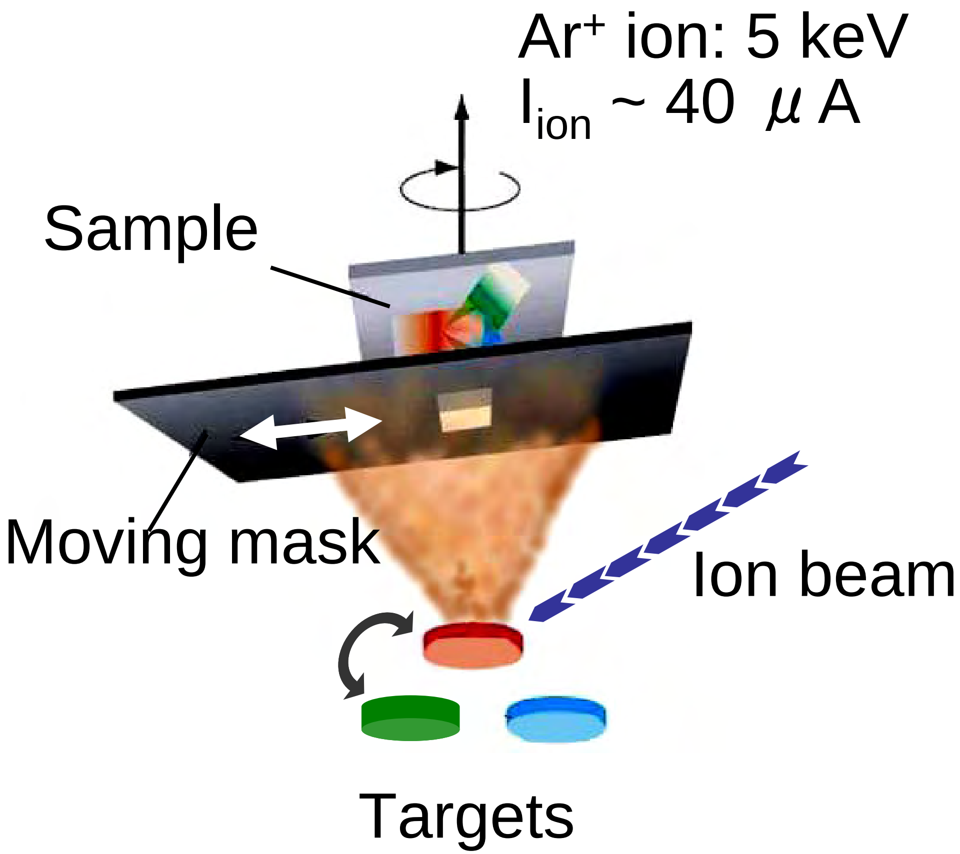
3) Continuous composition spread in 1 atomic layer

4) Complete continuous composition spread film

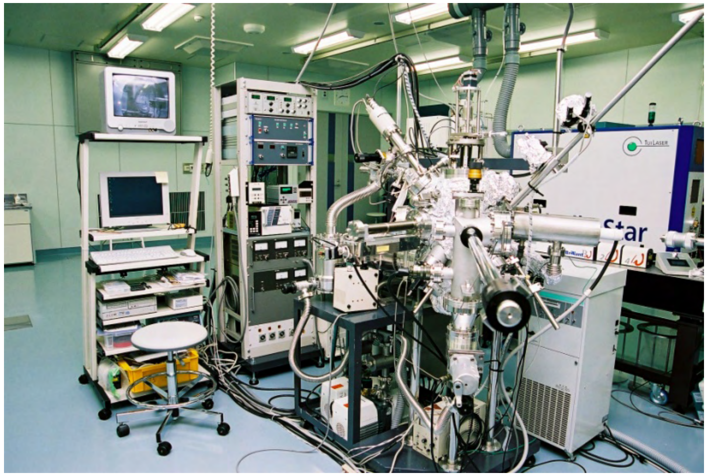
Concept of ternary materials combinatorial synthesis



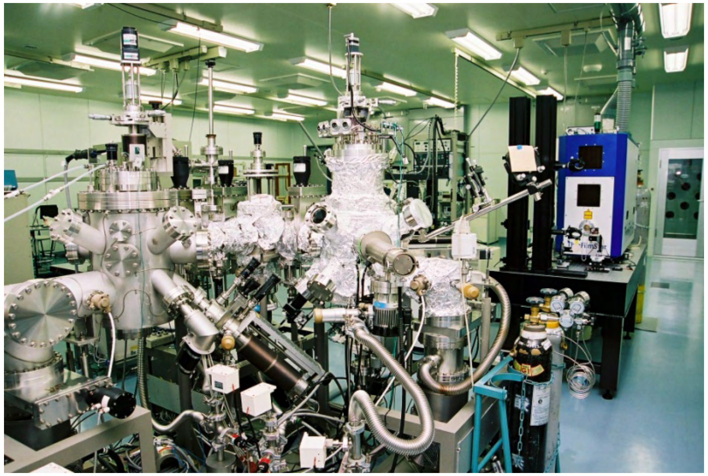
Combinatorial deposition systems (@NIMS)



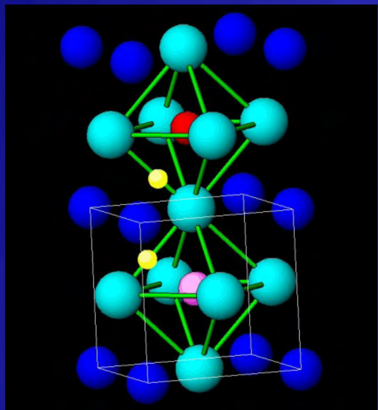
Ion sputtering (metal gate materials)



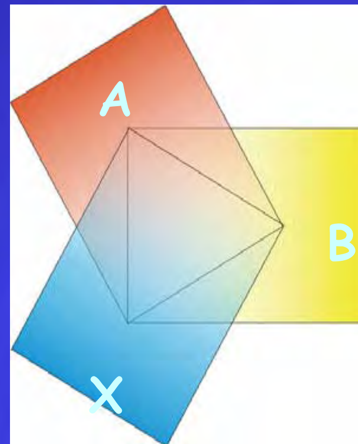
Pulsed laser deposition (oxides, high-k films)



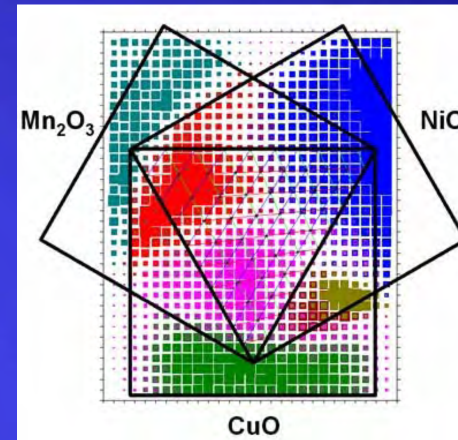
New materials discovery loop



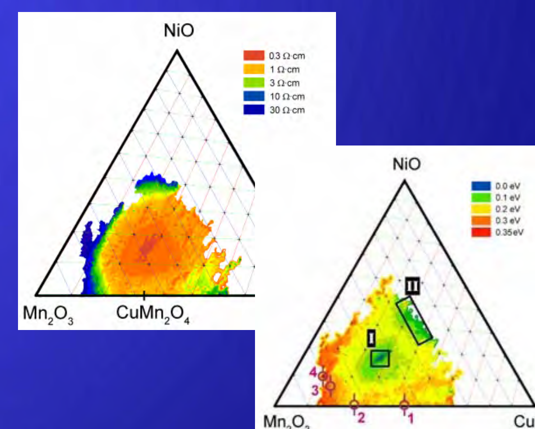
① Predict (Calculation, Data base)



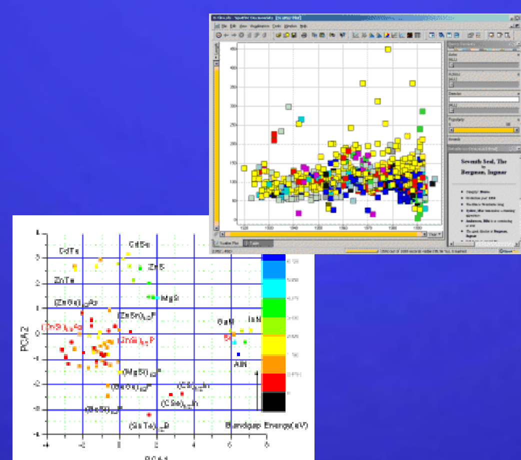
② Experiment design



③ Combi synthesis

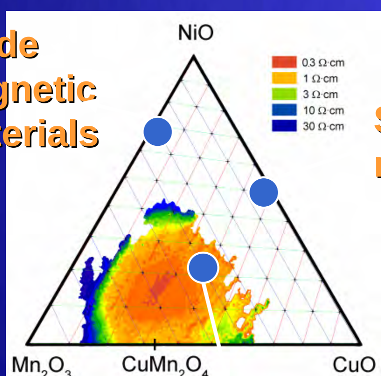


④ High throughput Characterization



④ Date handling in informatics

Oxide Magnetic materials



Sencor materials

Materials for thermometer

⑤ Starting another PJ

Example 1 :Gate oxide

Requirement

1) Higher dielectric constant
2)Amorphous structure

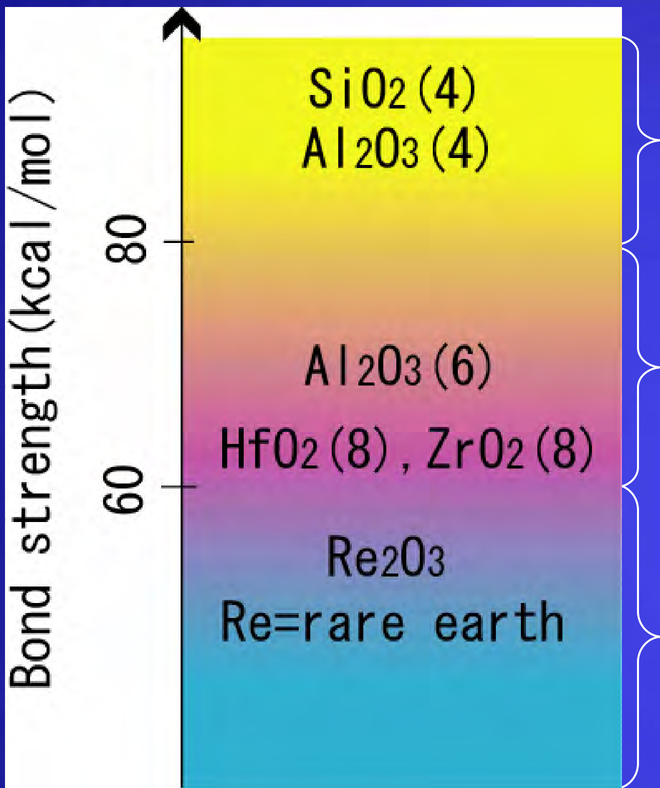
Defect density in Oxide

(1) Ionicity : Y_2O_3< HfO_2、MgO< TiO_2, Al_2O_3 < ZnO<SiO_2

(2) Valency : Y:3+, Hf:4+, Al:3+ Zn :2+, : simple

; Ti 3+, 4+ : mixed

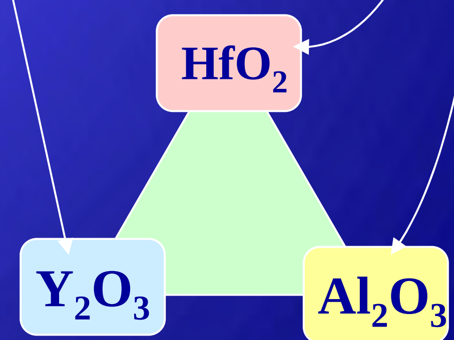
Sun, Zachariasen Glass empirical rule



Network former
(Can be amorphous for itself)

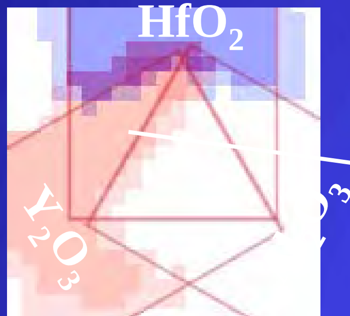
Intermediate oxide
(Can be amorphous with
Network forming oxide and modifier)

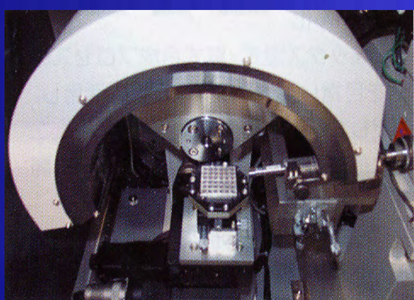
Additional oxide
(can be amorphous
with network forming oxide)



Ternary alloying is inevitable for HfO_2 to be amorphous

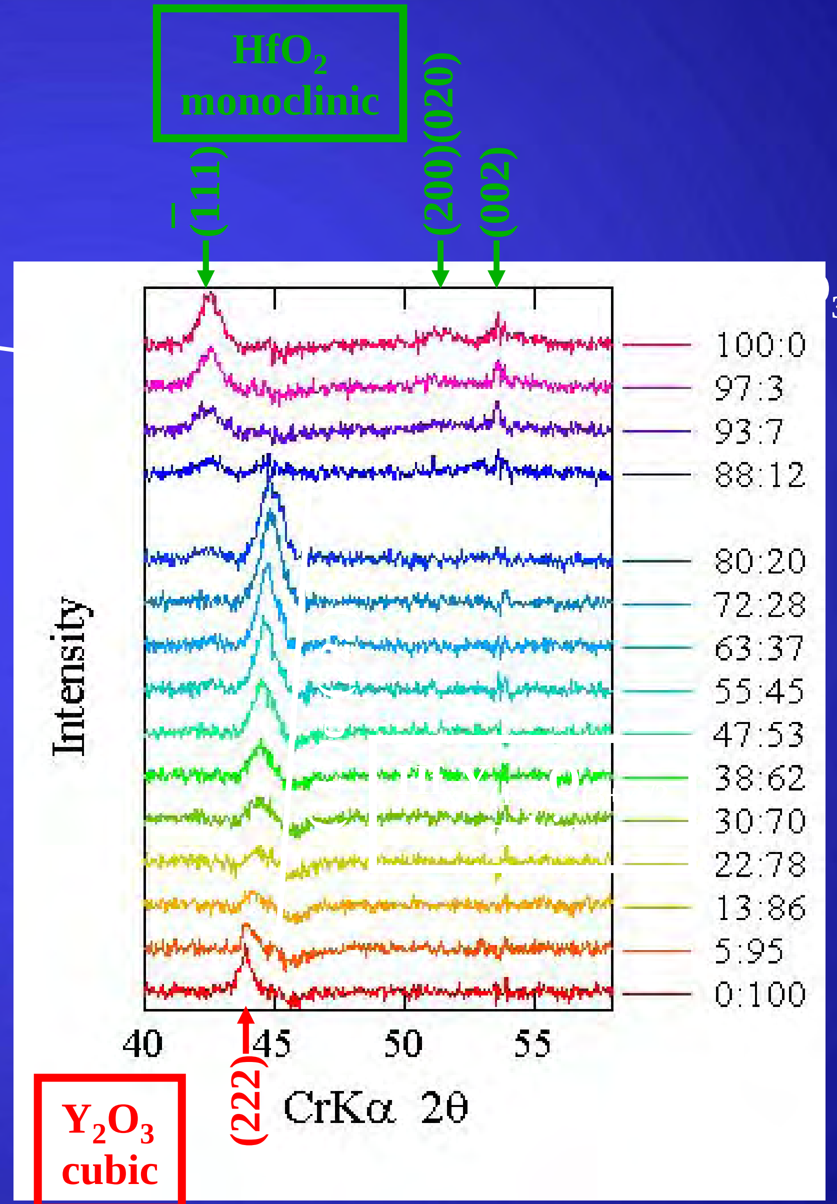
Combinatorial X-ray Diffraction System



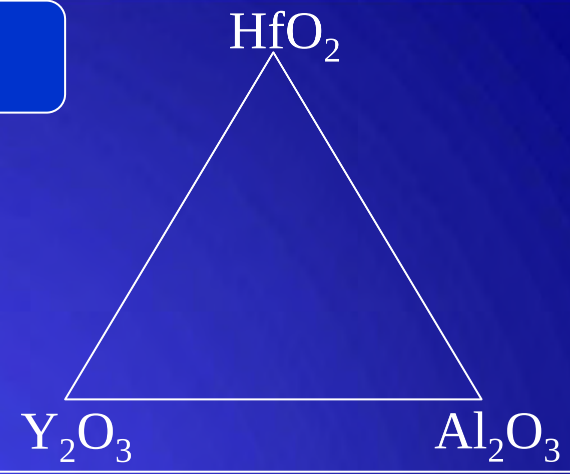


(Developed by Dr.Watanabe Dr.Fujimoto , AML-NIMS)

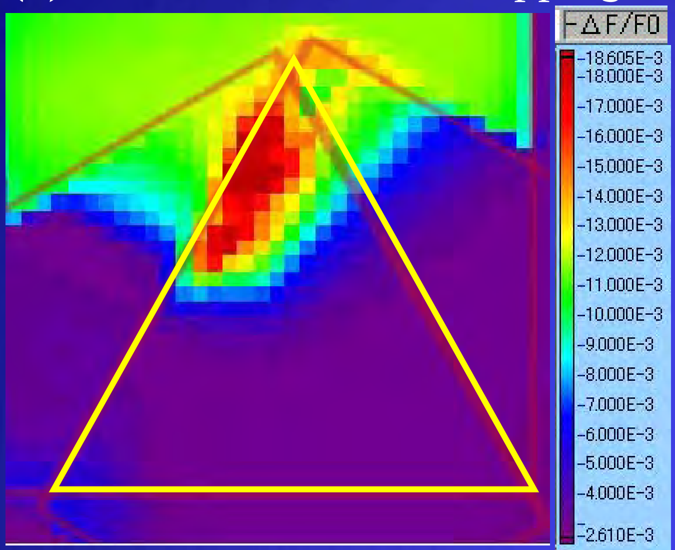
CombiXRD (Bruker: D8 Discovery System)



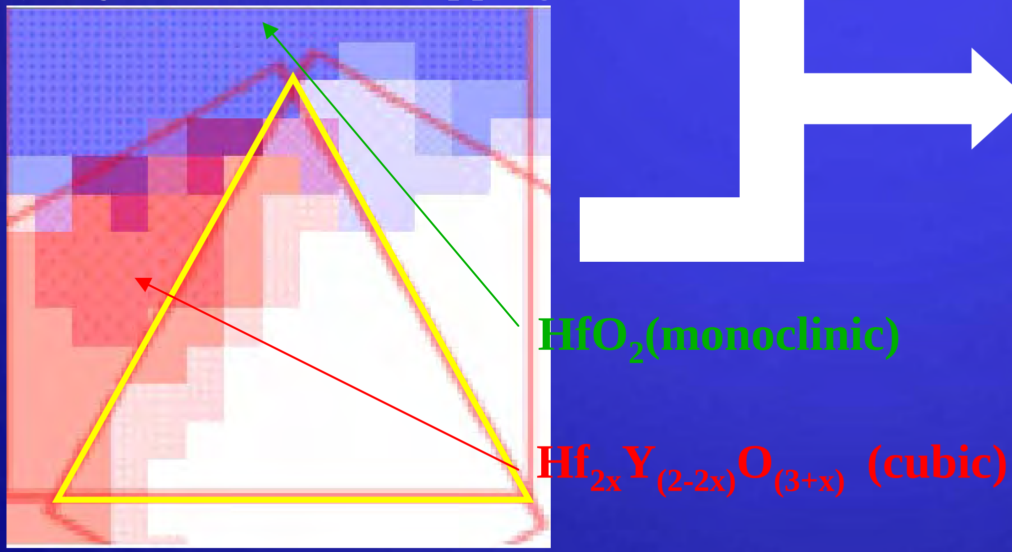
HfO_2-Y_2O_3-Al_2O_3 system



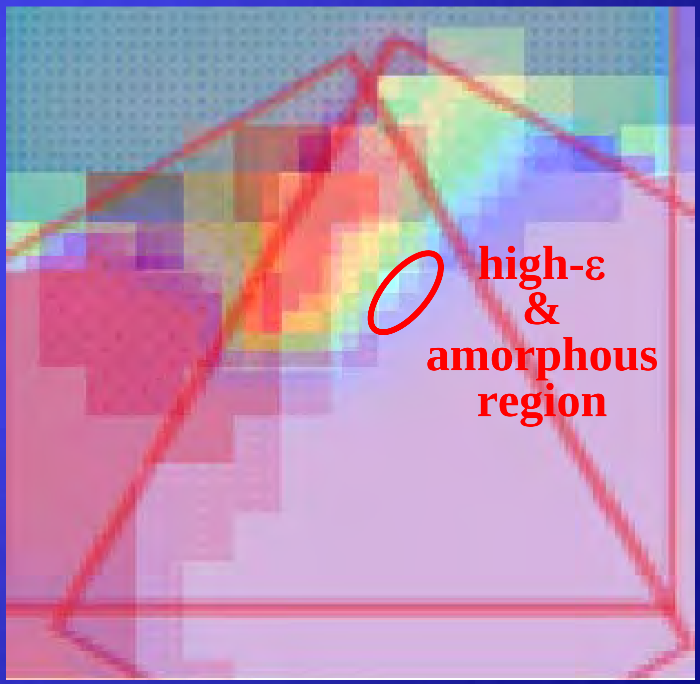
(1) Dielectric constant mapping



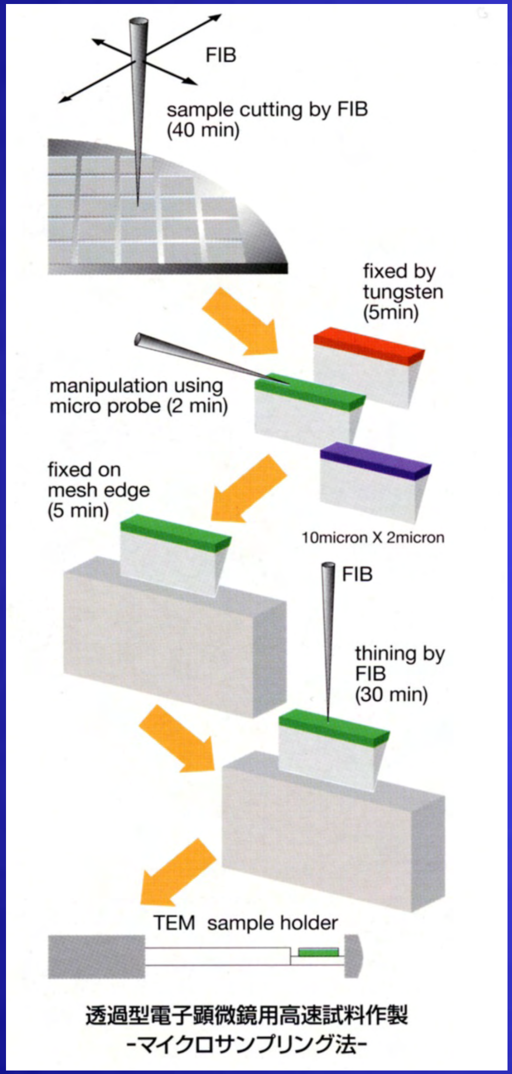
(2) Crystal structure mapping



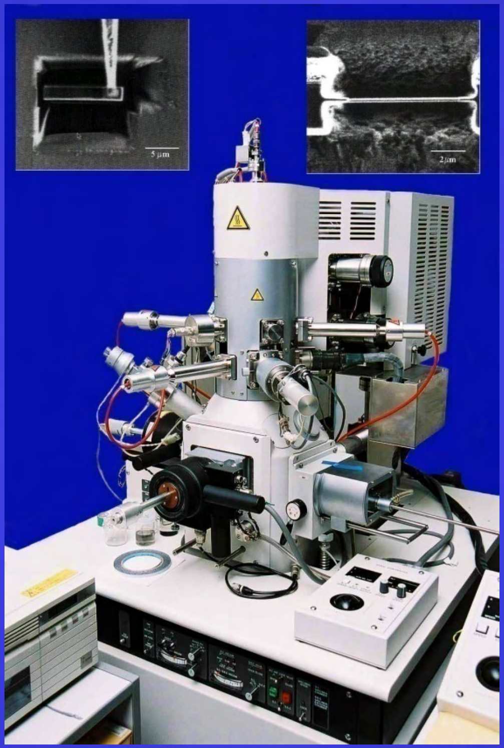
T_{sub} = 300℃, laser power = 3J/cm^2,
P_{O2} = 1e^{-6}Torr, post-annealed at 700℃



Micro Structure Characterization for Combinatorial Samples



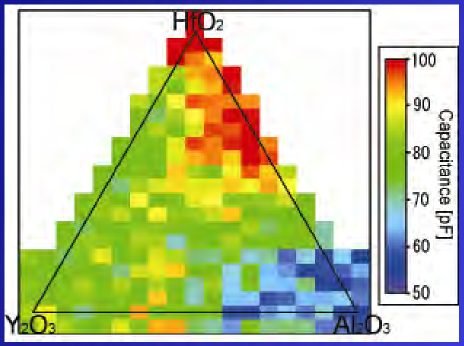
Micro Sampling Method



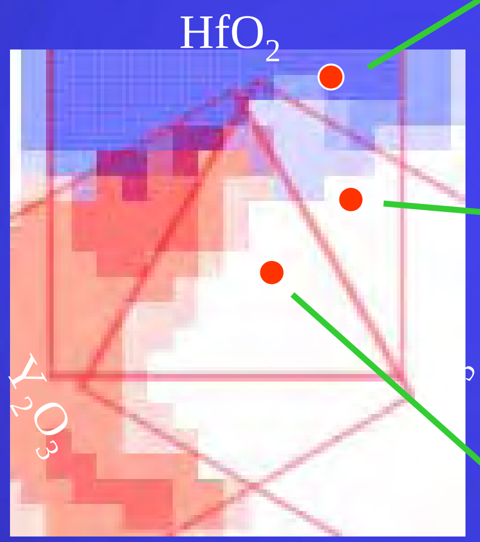
Hitachi FB-2000
+Micro sampling Unit

JEOL 4000EX (NIMS)
H-9000NAR (T.I.T)

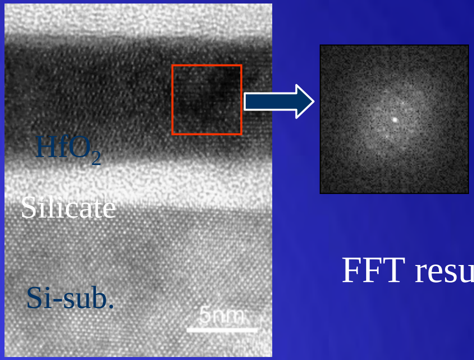
Characterizations of the combinatorial specimens



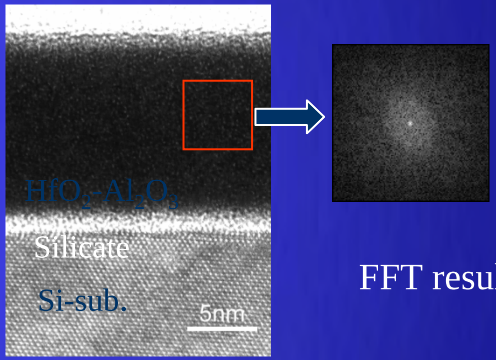
Dielectric Mapping by C-V, I-V



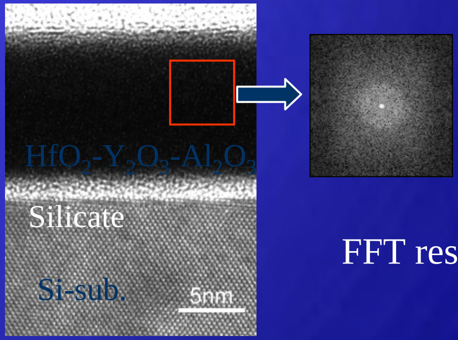
Structure mapping by Combinatorial XRD



FFT result



FFT result



FFT result

Interface structure mapping by TEM

Example 2 : Metal Gate

Requirement

1) Work function tuning
2)Interface control
3) Amorphous structure

Challenge of metal gate issues in *hp*32-22nm node

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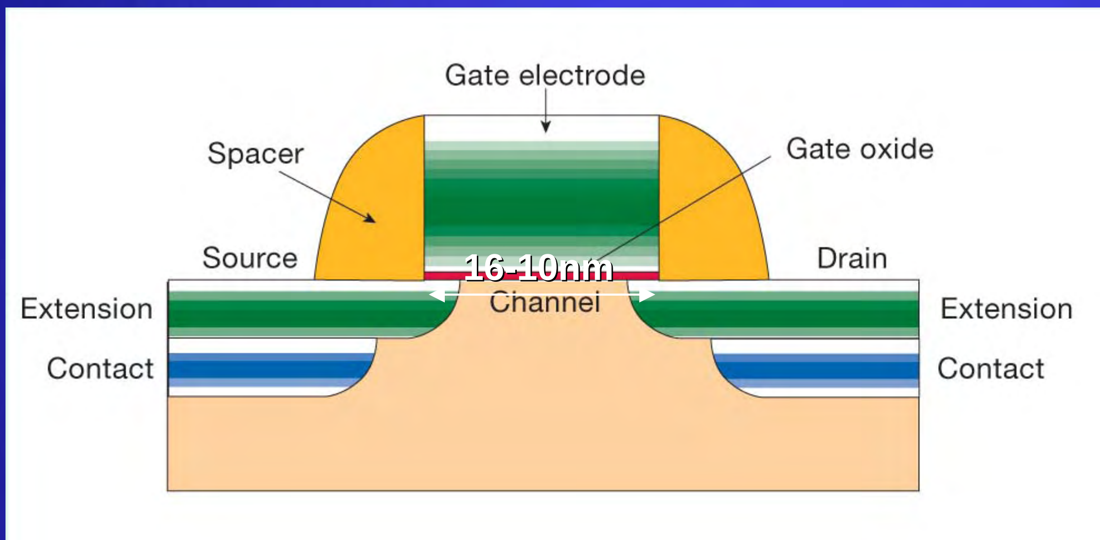
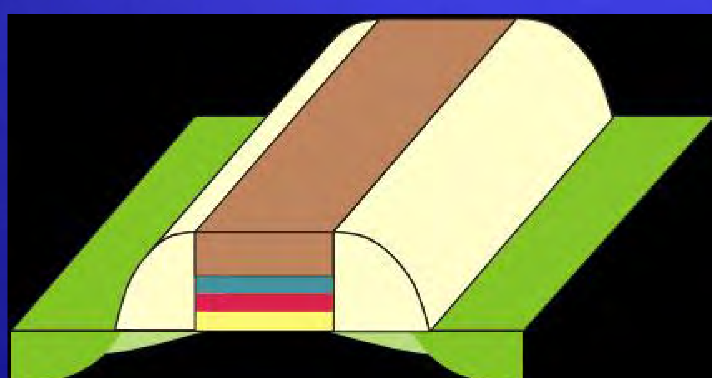
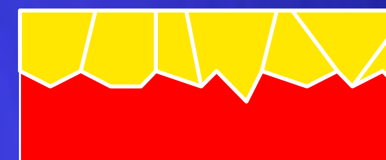




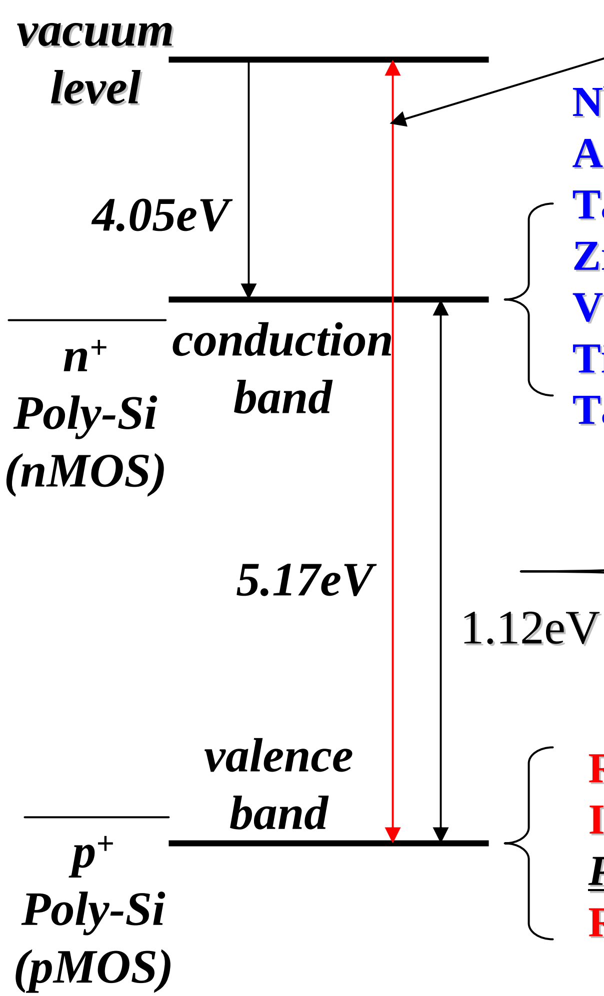
Poly metal gate



1) interface roughness
2) Work function fractuation
3) Edge roughness

Metal glass gate

Work functions of various metals



Work Functions

Nb:3.99-4.3
Al:4.06-4.2
Ta:4.12-4.25
Zr:3.9-4.05
V:4.12-4.3
Ti:3.95-4.33
TaN:3.9-4.25

For nMOS

Co:4.41-5.0
W:4.1-5.2
Mo:4.3-4.6
Os:4.7-4.83
Cr:4.5-4.6
Ru:4.60-4.71
Rh:4.60-4.71
Au:4.52-4.77
Pd:4.8-5.22
Ni:4.5-5.3
WN_x, TIN_x silicides:4.2-5.0

Threshold voltage ±0.5V larger than poly-Si!

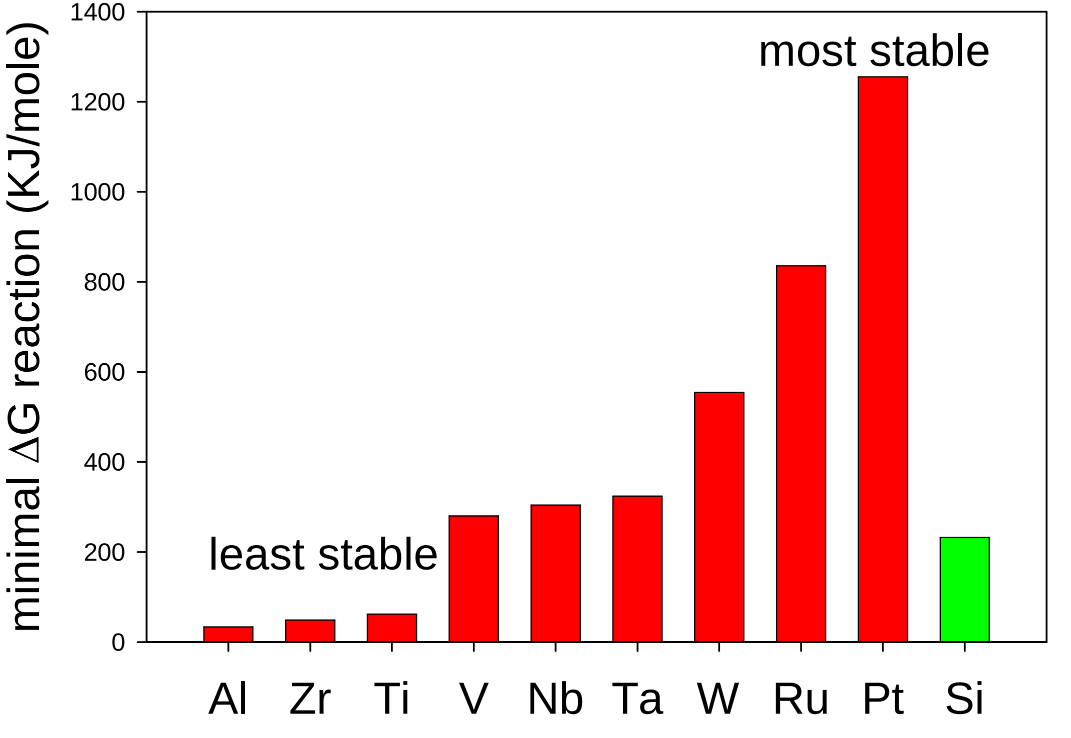
Re:4.72-5.0
Ir:4.72-5.0
Pt:5.32-5.5
RuO_2:4.9-5.2

For pMOS

(from Dr.Takagi Data)

Thermal reaction with HfO_2

Metal	Minimal Gibbs free energy of reaction (KJ/mole)
Al	33.42739
Zr	48.556
Ti	61.724
V	279.854
Nb	304.396
Ta	323.8836
W	554.42
Ru	835.599
Pt	1255.189
Si	231.836

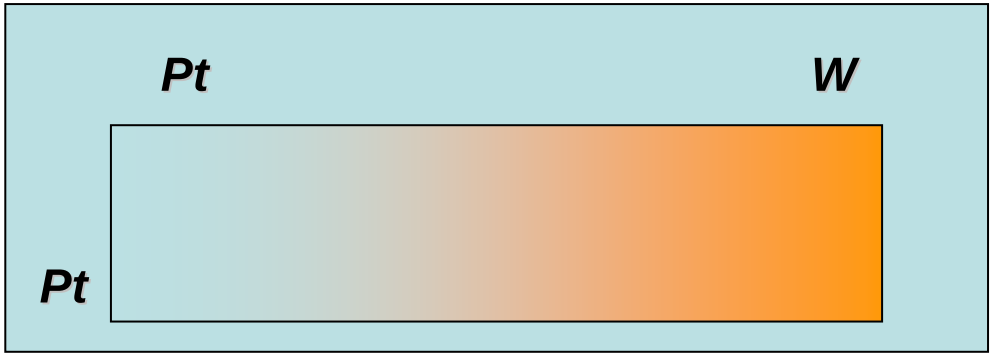


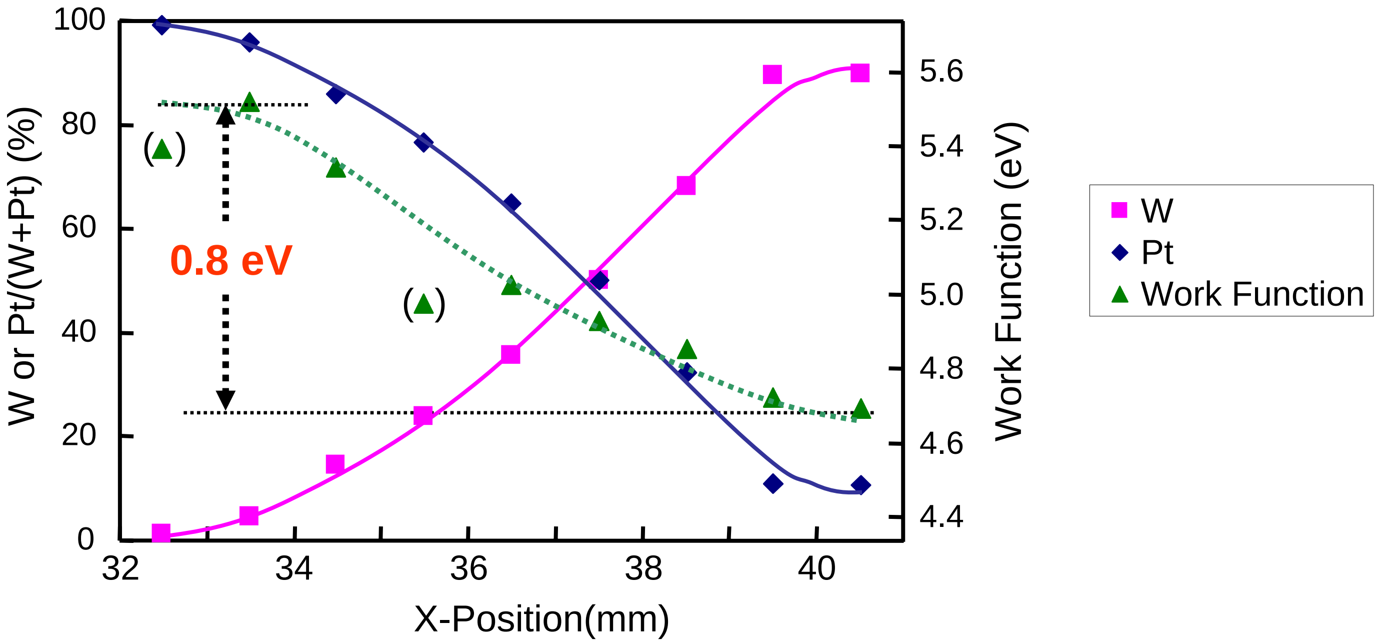
Work Function variation
with compostion spread film of Pt-W

High-k Net 次世代ゲート絶縁膜 研究ネットワーク

NIMS

Thickness
:10 nm





Experimental

Pt-W alloy/p-Si

XPS

XRD

Composition
Work function
Crystal structure

HfO_2/SiO_2/p-Si, **La_2O_3**/p-Si

HfO_2: MOCVD
La_2O_3: E-beam evaporation

Deposition of Pt-W composition spread films with contact mask for capacitor electrodes

Forming gas annealing and/or oxidizing gas annealing

FGA (H_2/N_2, 5% H_2): 300-450ºC
OGA (O_2/N_2, 0.1% O_2): 250-350ºC

CV measurements

Electric properties

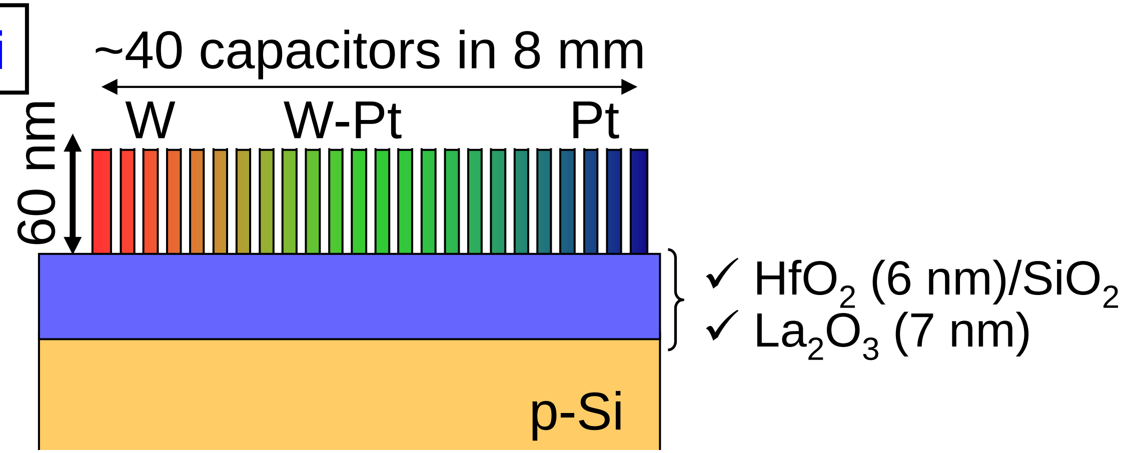
XTEM

Stacking structure

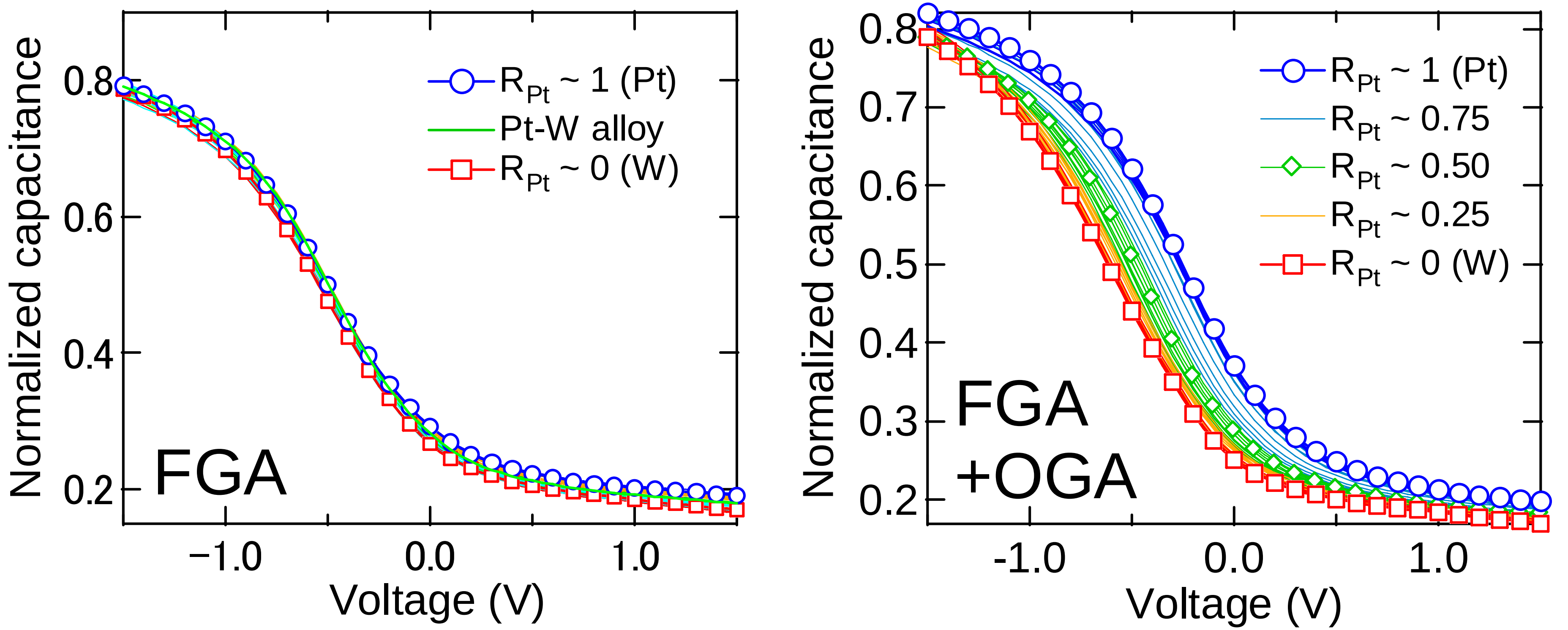
Pt-W (6nm)/HfO_2/SiO_2/p-Si

HXPES (6keV, SPring-8)

Composition
Depth profile



Comparison of CV curves from HfO_2 films under different annealing conditions

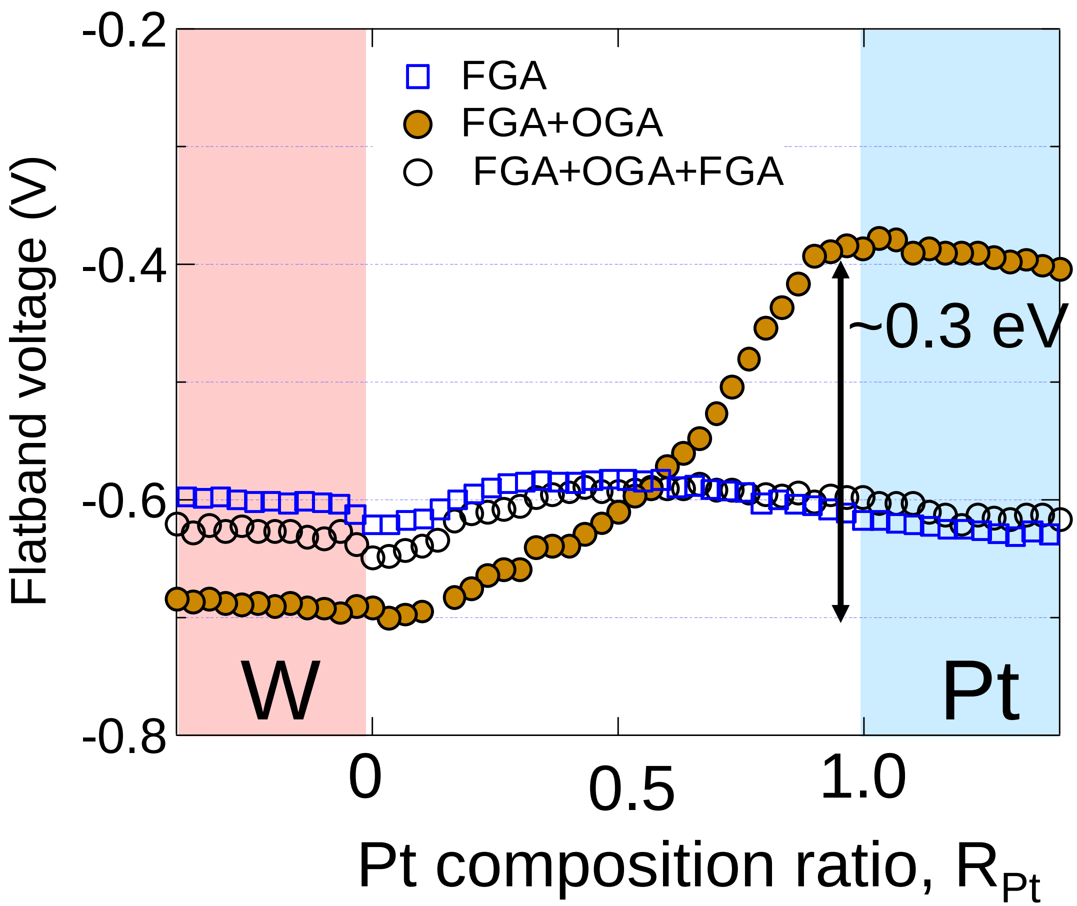


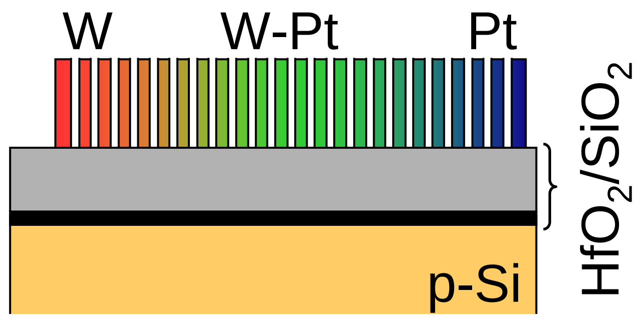
$\Delta V_{fb} < 0.1$ V

$\Delta V_{fb} = 0.3$ V

- Relative dielectric constant: $\varepsilon = 18.0$.

Changes in flatband voltage

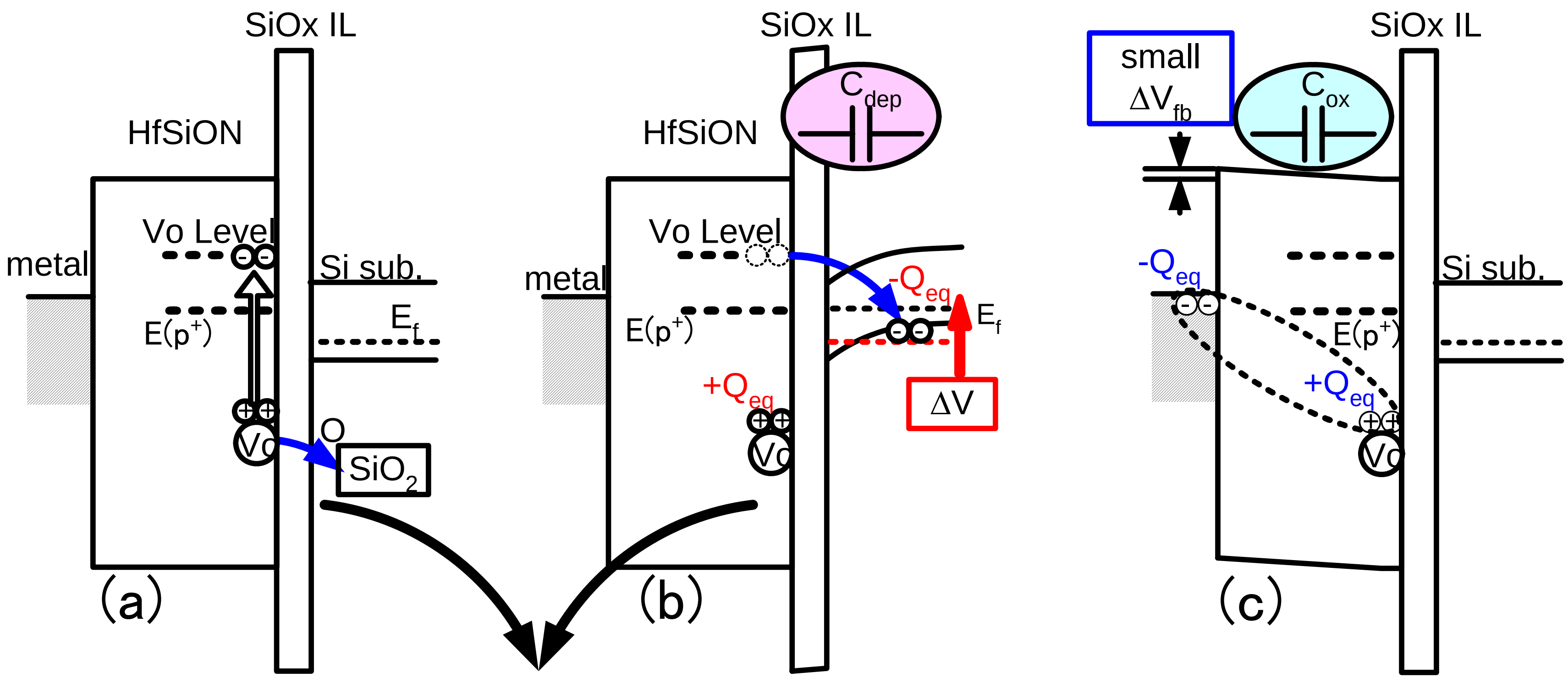




FGA: 450ºC, 30 min
OGA: 300ºC, 30 min

- The higher WF is, the larger the V_{fb} value after OGA becomes.
- The shift can be reversed by an additional second FGA.
- This observed phenomena is general and mainly depends on work function.

One interface affects another interface

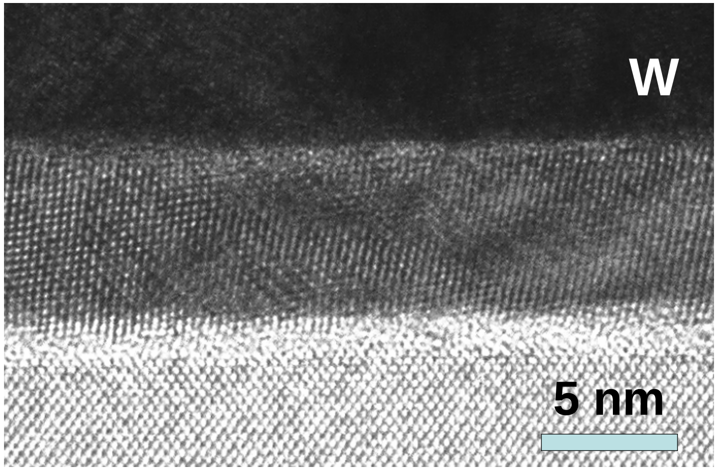


(HfO_2) +1/2Si-> Vo^{2+} +2e$^-$ +(HfO_2)+1/2SiO_2 ΔG_{total}

Flat-band Condition

Cross-section TEM (HfO_2, after FGA)

W/HfO_2/SiO_2/Si

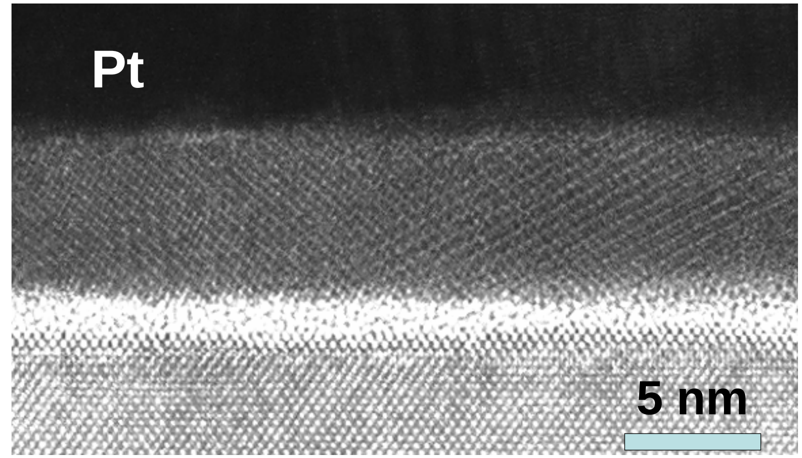


HfO_2

SiO_2

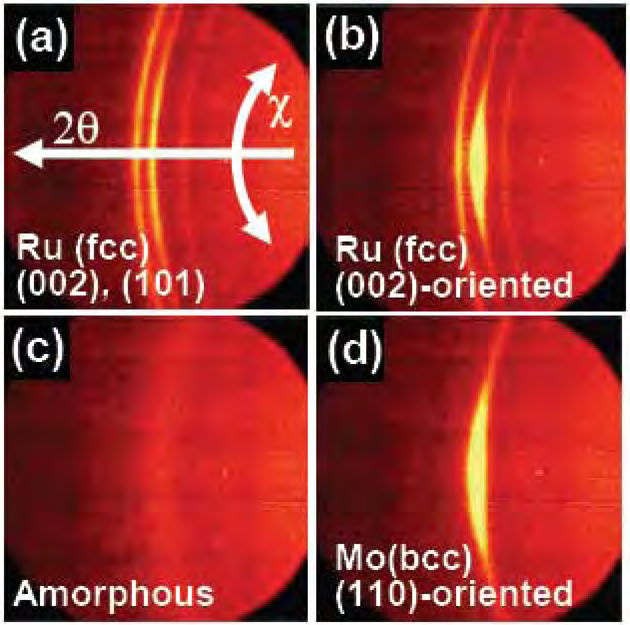
Si

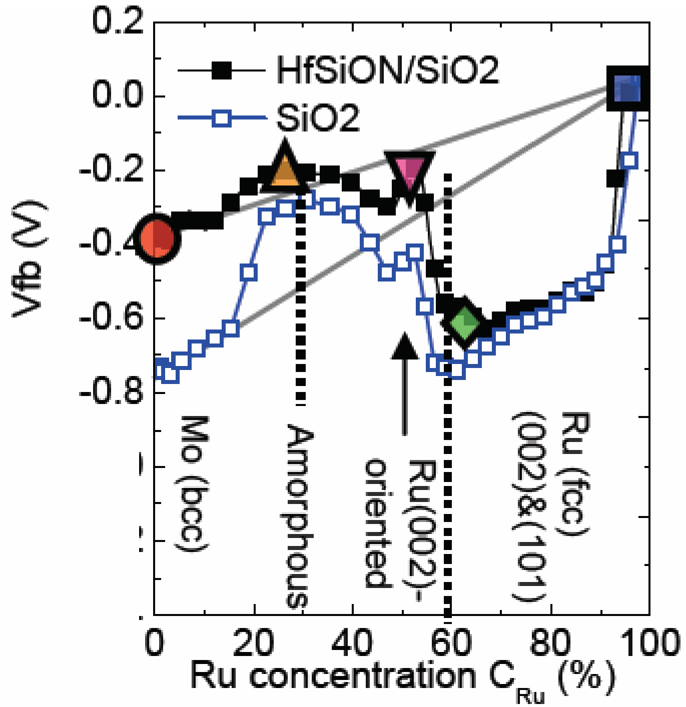
Pt/HfO_2/SiO_2/Si



(1) 6-nm-thick HfO_2 + 1-nm-thick interfacial SiO_2 layer
(2) Crystallized
(3) Grain size > film thickness
(4) Bright portion (reaction layer?) at the metal/high-k interface.

Amorphous and phase separation

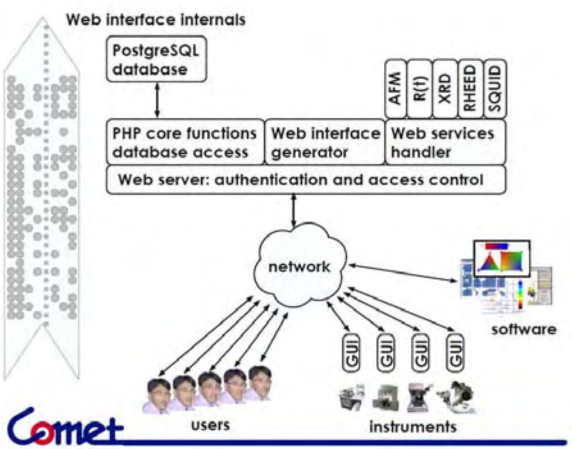




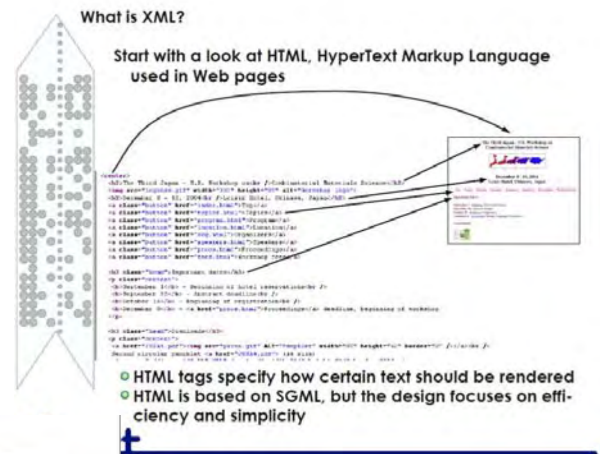
From K.Ohmori et at from IEDM 2007

Archtecture of the materials informatiocs

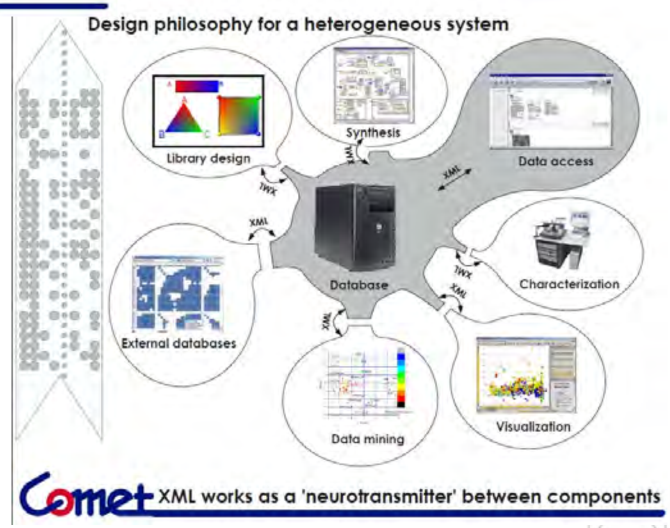
National Institute for Material Science



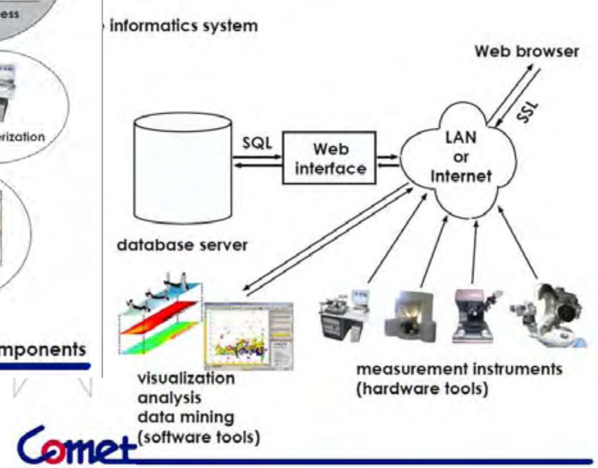
1）Group servors



3） data sharing on website by XML data



2）experiment design、conditions、results、
measurement data are categorized
by “MatLab”

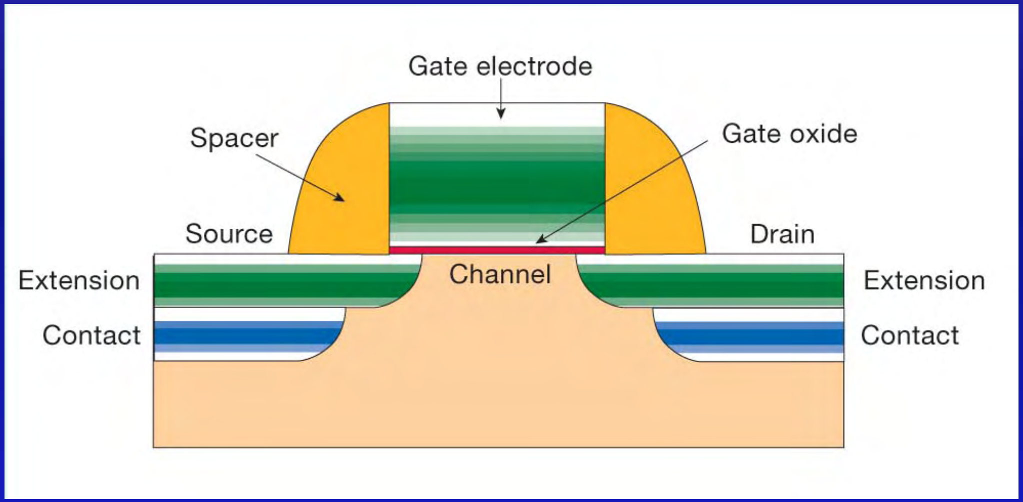


4）domestic and international data sharing on web bases

reference from other date

Basic structure in Nano Electronics

National Institute for Material Science



1) Meta/Oxide Interface

Nano CMOS
Spintronics (MIM)
Ohmic contact (GaN ,ZnO)

2) Oxide/ Semiconductor Interface

Nano CMOS
Hetero Epitaxy on Si

3) Metal /Oxide/ Semiconductor nano scale Interface

Fermi level Pining
Solar Cells

Hints from Photo catalysis

Informatics Network with NIMS

Max Plank Institute （Stuttgart ）

Thin film ternary phase diagram

Reseacher exchange

Material informatics

National Institute of Standards and Technology

...working with industry to develop and apply technology, measurements and standards

NIST

Reseacher exchange

UNIVERSITY OF MARYLAND

University of Maryland

Ferroelectric

Magnetic

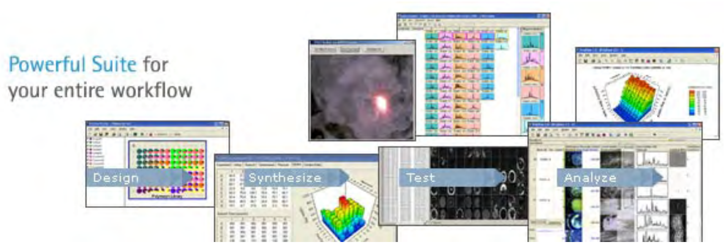
Univ. of North Carolina

NIMS
Tokyo Inst. of Tech
Tohoku University
Univ. of Tokyo

Thermoelectric oxides

Professor And student

Univ. of Washington



Material Informatics and its standardisation

High throughput nano materials exploration in nano electronics

1）Accelerating the nano materials exploration.

2）Systematic materials data can be used
for other research.

3）Materials informatics which is shared
with researchers or community can provide
a lot of seeds for future innovation.