materials design

VASP Simulation in Semiconductors Study: From Materials Engineering to Band Alignment

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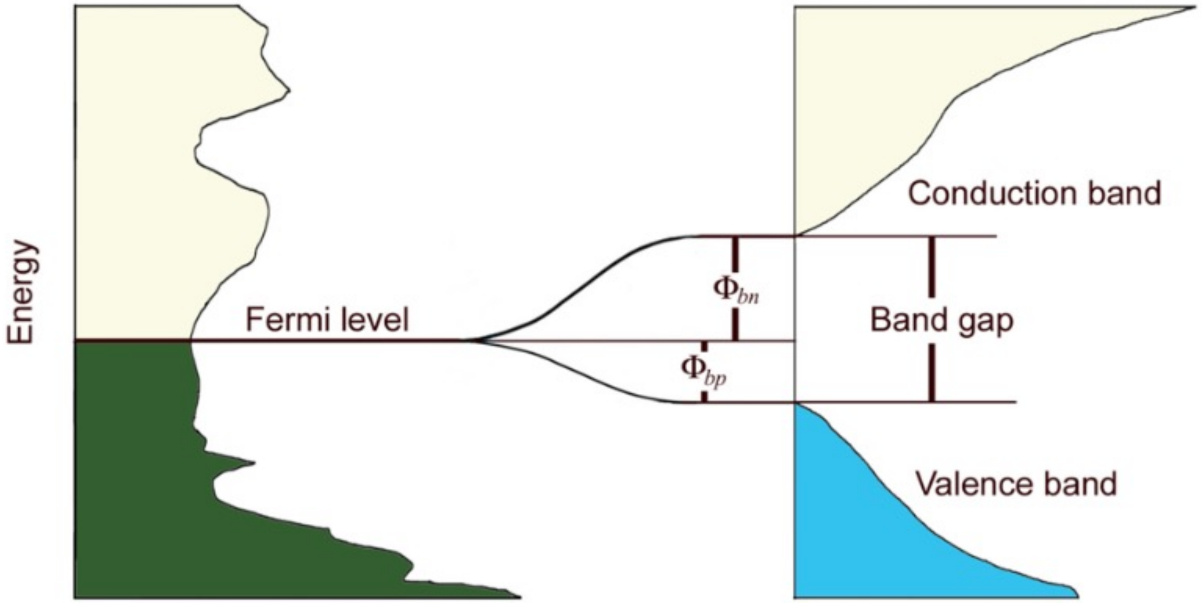
Speaker: Dr. Xiaoli Liu

December 12th -14th, 2023



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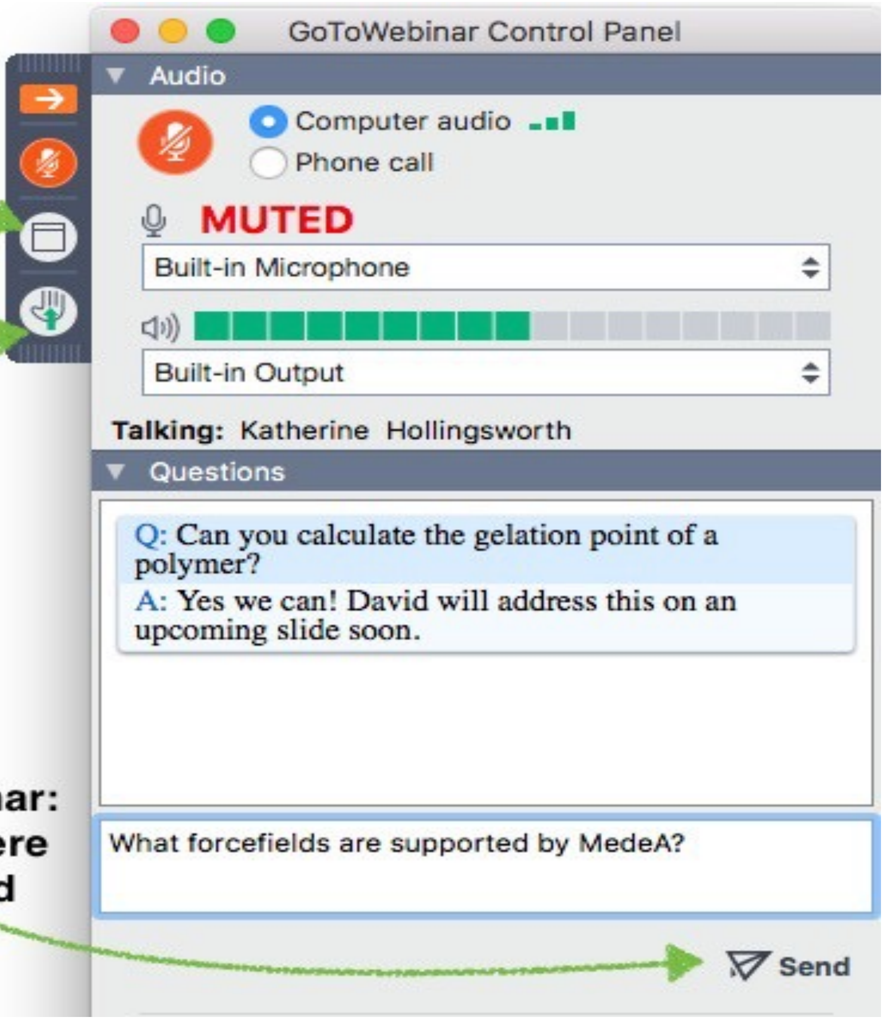

● Computer audio
○ Phone call

MUTED

Built-in Microphone

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Talking: Katherine Hollingsworth

Q: Can you calculate the gelation point of a polymer?
A: Yes we can! David will address this on an upcoming slide soon.

What forcefields are supported by MedeA?

materials design

Webinar Speakers

Katherine Hollingsworth *Presenter: Dr. Xiaoli Liu* *Dr. Shubham Pandey*

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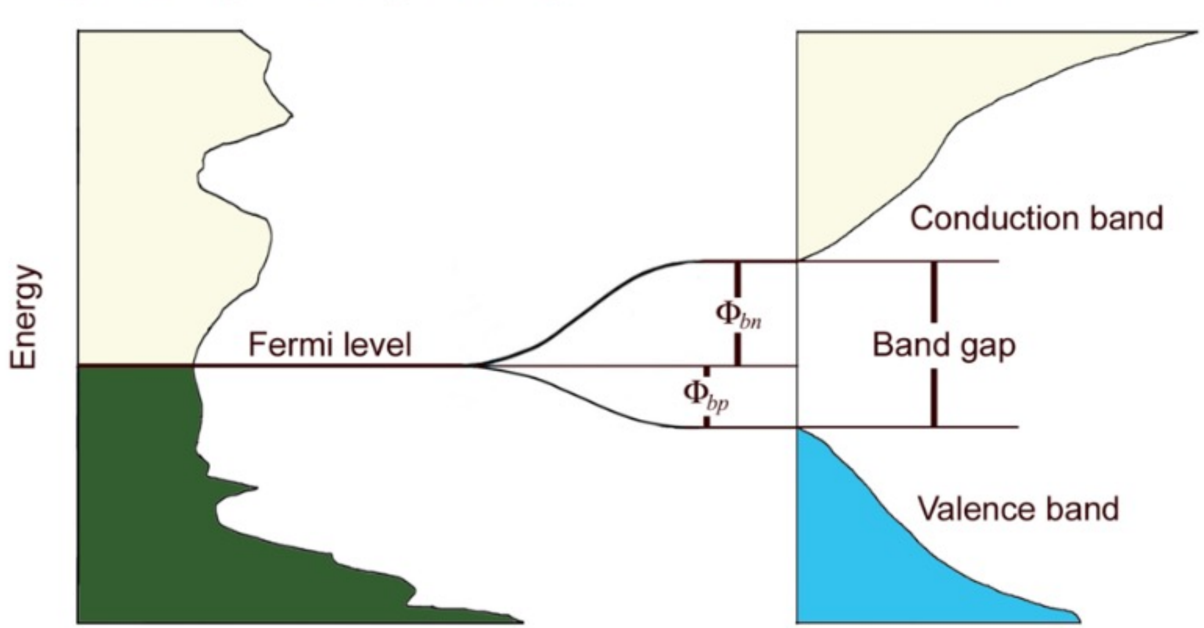


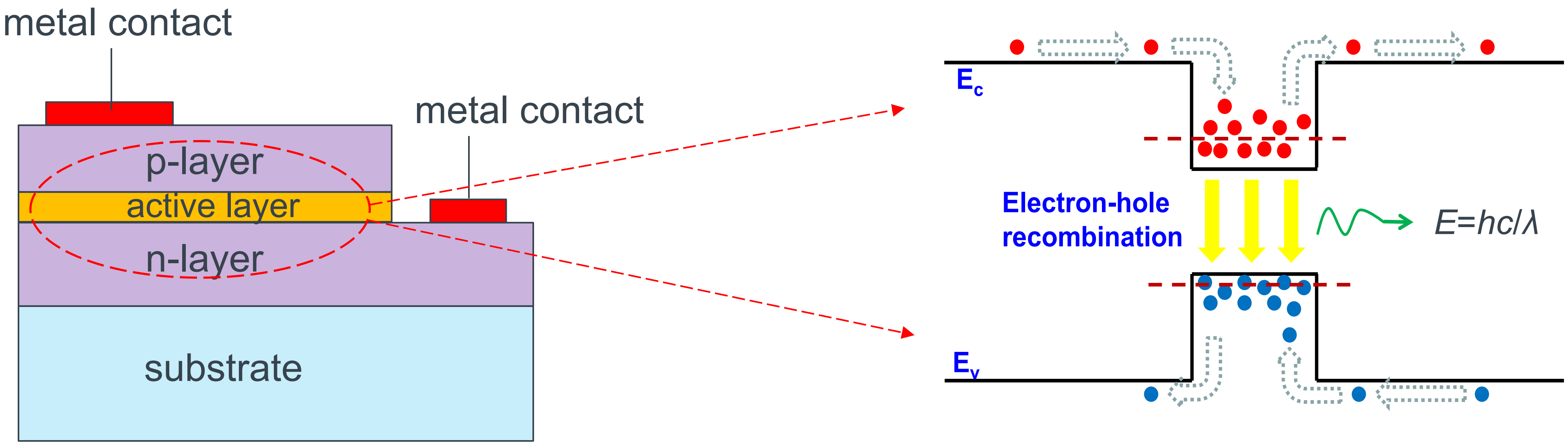
Outline

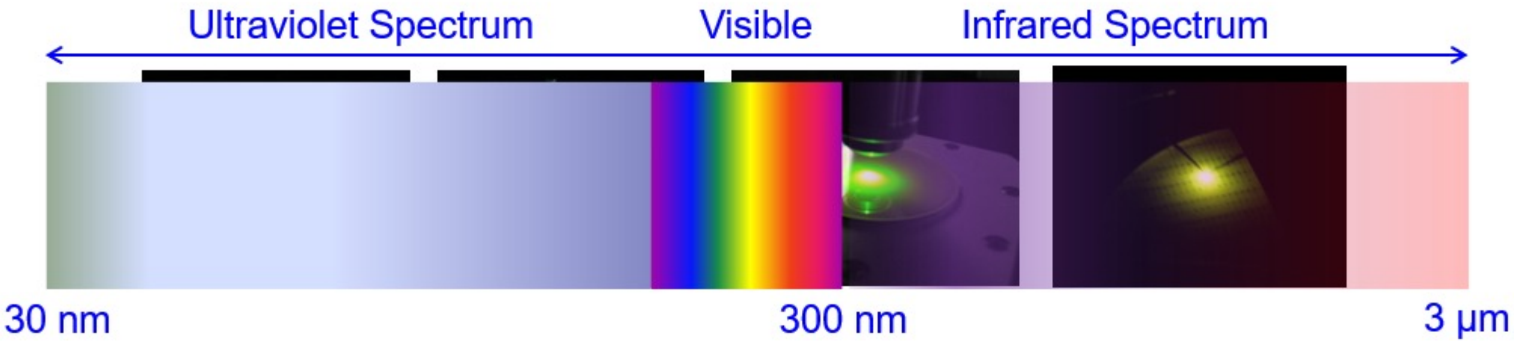
- **The “common” gallium oxide compounds**
  - Why wide bandgap semiconductor?
  - Large bandgap tuning in InGaO

- **Exploring new directions through materials design**
  - Lattice-matching III-Oxide quaternary compound: AlInGaO
  - Large band offset III-Oxide compound: BGaO

- **SBH calculations at a metal-semiconductor interface**
  - $NiSi_2$ /Si interface modeling
  - SBH analysis

Simple device structure





- ➢ **Electron and hole recombine in the well to generate light emission**

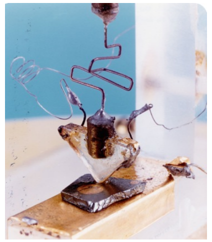
1. **PN junction + heterostructure is fundamental in semiconductor device technologies**
2. **Controlling the carrier transport in materials and structures is critical**
3. **Designing the materials to form junction and heterostructures enable the breakthrough**

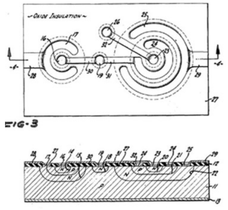
Evolution of semiconductor materials

- **Gen 1**: Si, Ge
- **Gen 2**: GaAs, InP
- **Gen 3**: SiC, GaN

Next-gen: Gallium Oxide?

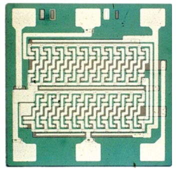
1st Ge transistor
1947

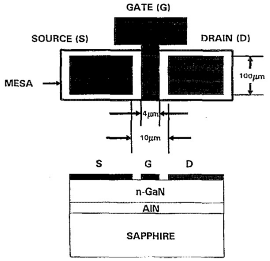




Si based IC
1959

1st commercial
MOS IC
1964

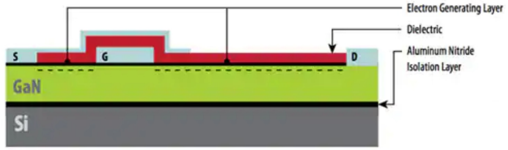




1st GaN transistor
1993

SiC power devices
research started
2000-2002

New method creating
GaN crystal (enhance-
mode trans)
2010



Mass produced SiC
SBDs, MOSFETs
2010

GaN-based driverless
car by Google
2016

High-volt charging
adapter by Tesla
2023

GaN and SiC

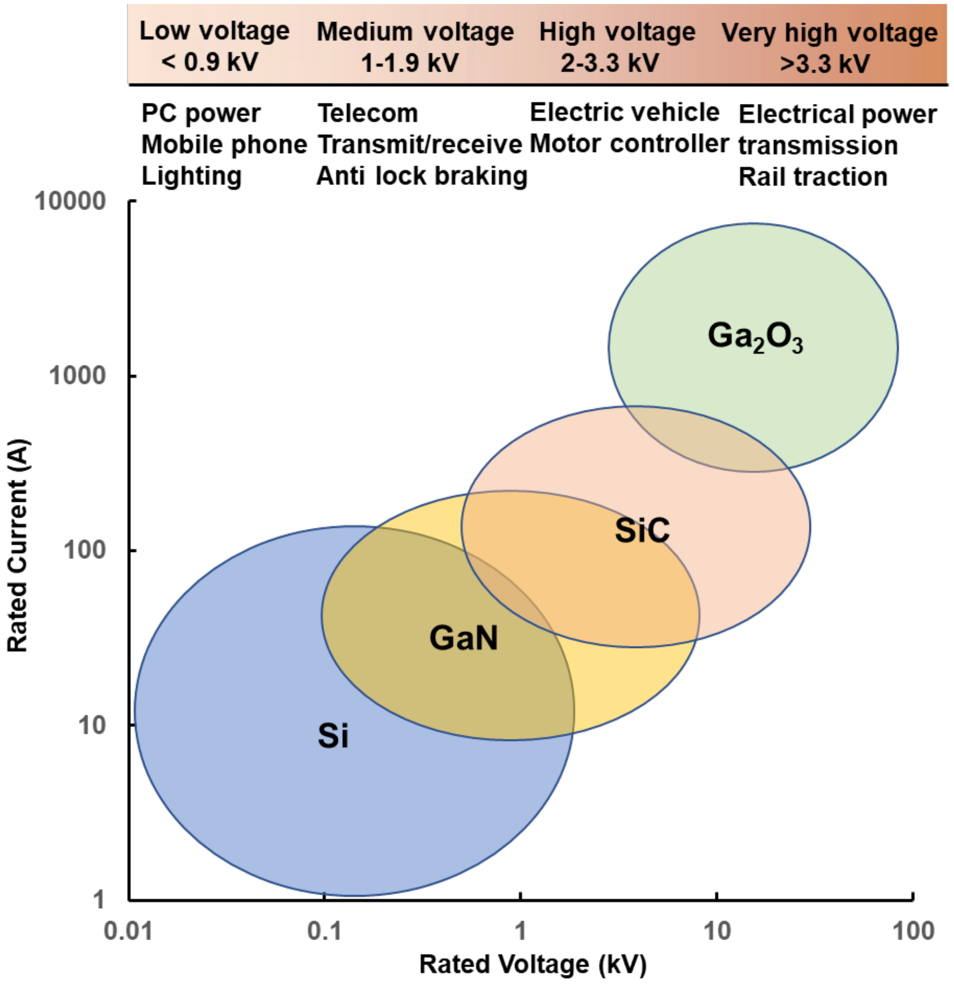
Growth > 15% annually

Size > 10B USD by 2030

How about Gallium Oxide (Ga_2O_3)?

Table: Semiconductor materials comparison

	Si	GaAs	SiC	GaN	Ga_2O_3	Diamond
Band gap E_g (eV)	1.1	1.4	3.2	3.4	4.9	5.5
Breakdown ***V*** field (MV / cm)	0.3	0.4	3.2	3.7	9.2	12.2
Size ratio	1	1/2	1/15	1/17	1/45	1/55
Working Temperature (°C)	300	500	1300	400	1000	>1000
Price (USD / 2")	0.01k	0.15k	0.3K	2K	<<2K	>10K

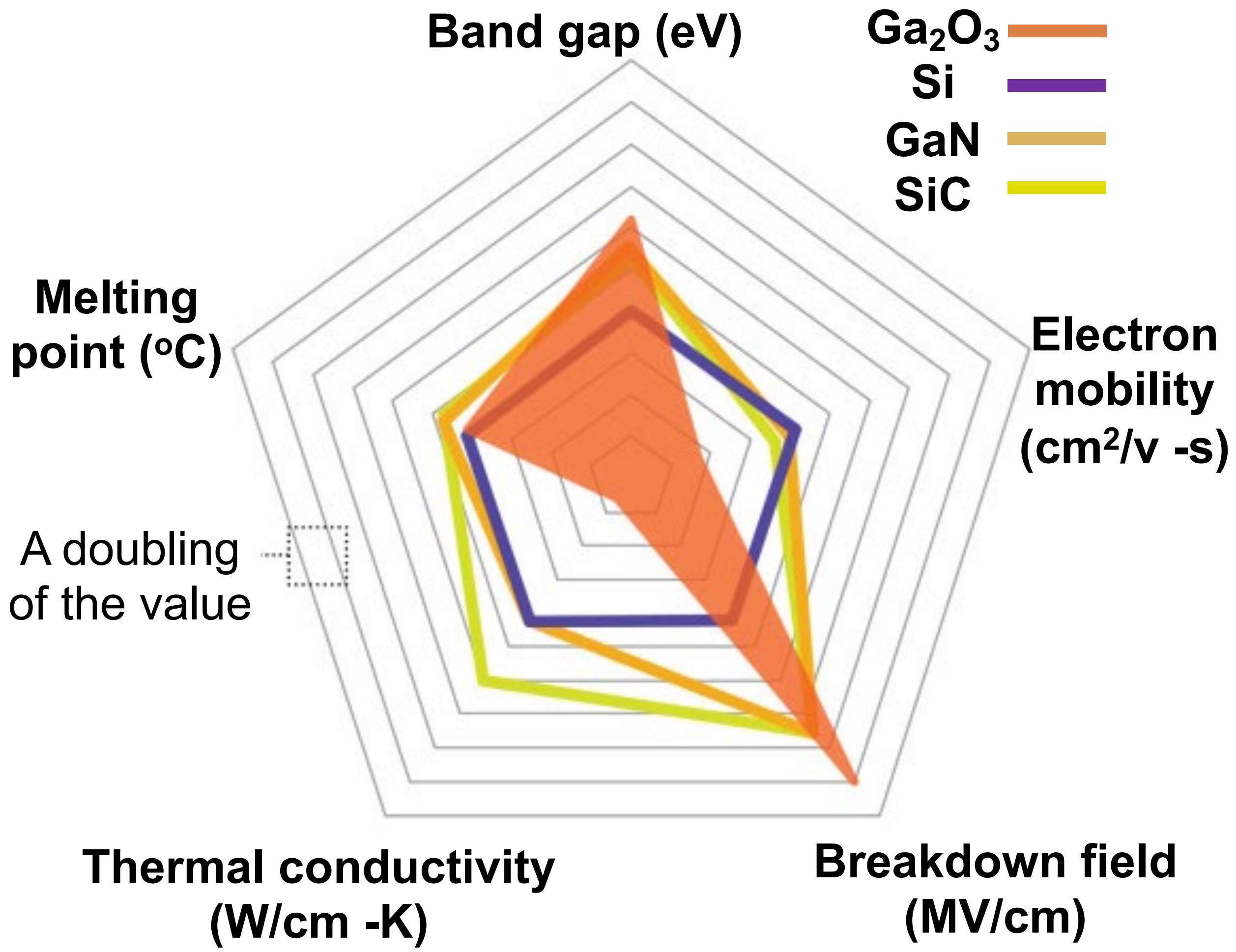


Why wide bandgap material?

$$V \propto E_g^{2.5}$$

1 Ga_2O_3 > 40 Si devices

Ga_2O_3-Advantages and disadvantages



Advantages

- ✓ Large bandgap 4.9 eV
- ✓ High breakdown voltage
- ✓ Low cost (melting growth) large scale growth
- ✓ Low on resistance
- ✓ N-type doping

Challenges

- ✓ Low electron mobility
- ✓ Low thermal conductivity
- ✓ P-type doping

Potential applications

Electronics:

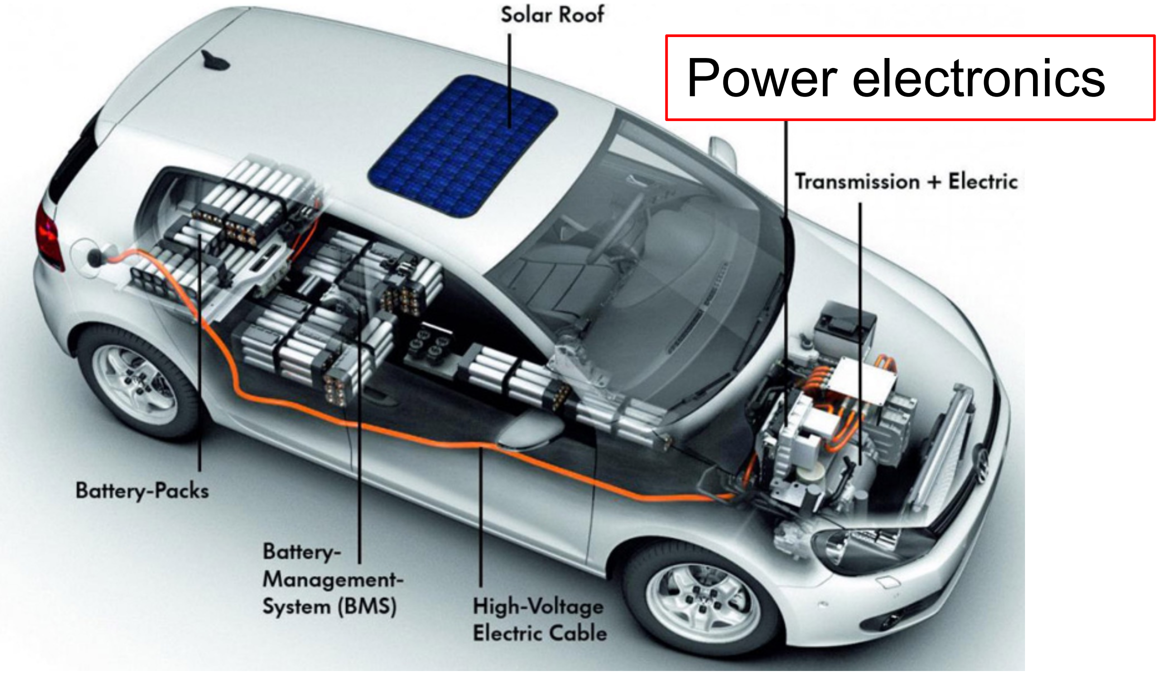
Integrated circuits

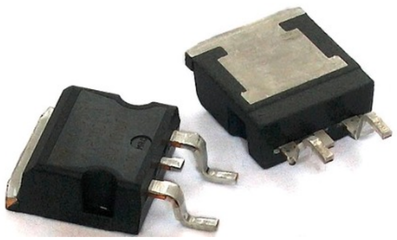
Power electronics

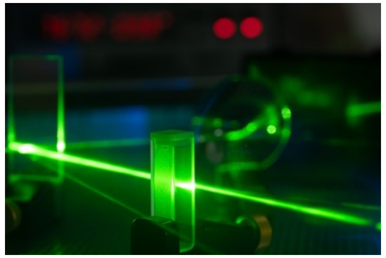
Optoelectronics:

Laser, optical fiber,

LED, photodiodes, solar cells



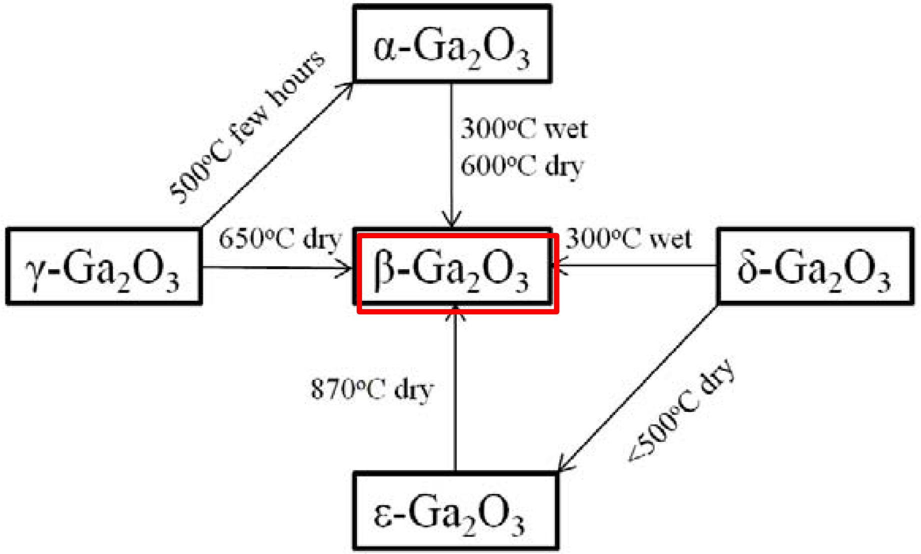




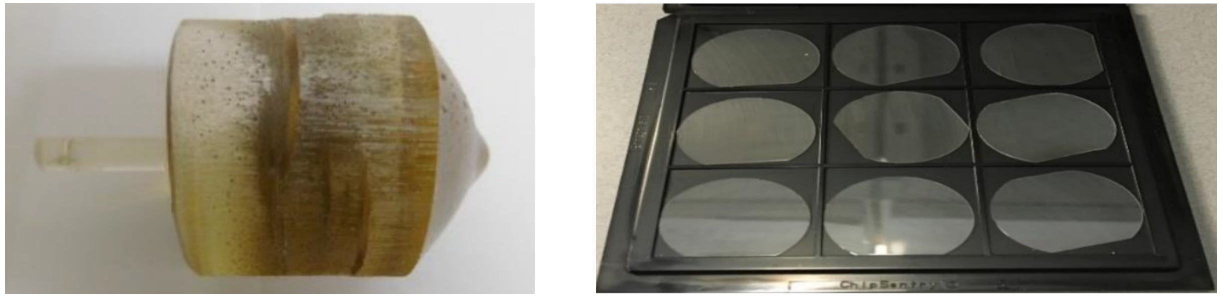
Miniaturization? Low-cost?

Ga_2O_3– Polymorphs

Polymorph	α	β	γ	ε	κ
Space group	$R\bar{3}c$	$C2/m$	$Fd\bar{3}m$	$P6_3mc$	$Pna2_1$
Structure	rhombohedral	monoclinic	cubic	hexagonal	orthorhombic
Lattice parameter	a=4.983 Å c=13.433 Å	a=12.214 Å b=3.037 Å c=5.798 Å β=103.83°	a=8.238 Å	a=2.908 Å c=9.262 Å	a=5.0557 Å b=8.6884 Å c=9.2759 Å



Ref: Rustum Roy, et al., J. Am. Chem. Soc. 1952.



Left: 50 mm Fe-doped <010> β-Ga_2O_3 boule; Right: 25 mm epi-ready β-Ga_2O_3 substrates.

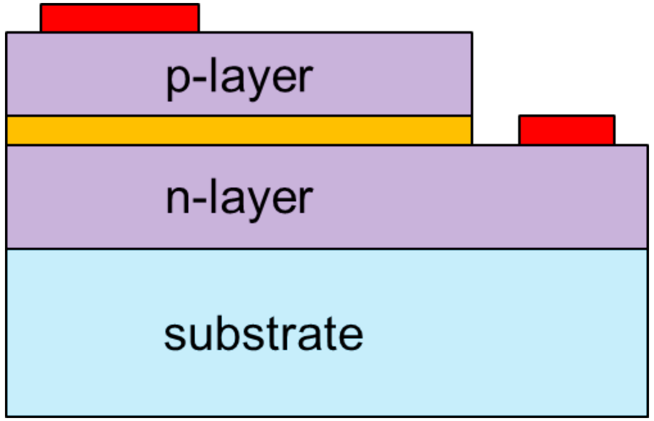
Ref: Blevins, J. D., et al., In CS MANTECH 2018-2018 Int. Conf. Compd. Semicond. Manuf. Technol.,1, 010, 2018.

Our interests: Bandgap tuning in III-Oxide compound

Group III-Oxide Semiconductor

Al_2O_3 $E_g \sim 8.8$ eV [1]
Ga_2O_3 $E_g \sim 4.9$ eV [2]
In_2O_3 $E_g \sim 3$ eV [3]

Huge tuning range



- ✓ Heterostructures are essential in device
- ✓ Require different materials to build the structures
- ✓ No exception to Gallium oxide – III-oxide compound needed!

➢ Ternary and quaternary III-oxide is not actively explored.

Ref: 1. Hartwin Peelaers, et al., Appl. Phys. Lett. 112, 242101, 2018.
2. Hartwin Peelaers, et al., Phys. Status Solidi B 252, 4, 2005
3. P.D. C. King, et al., Physical Review B 79, 205211, 2009.

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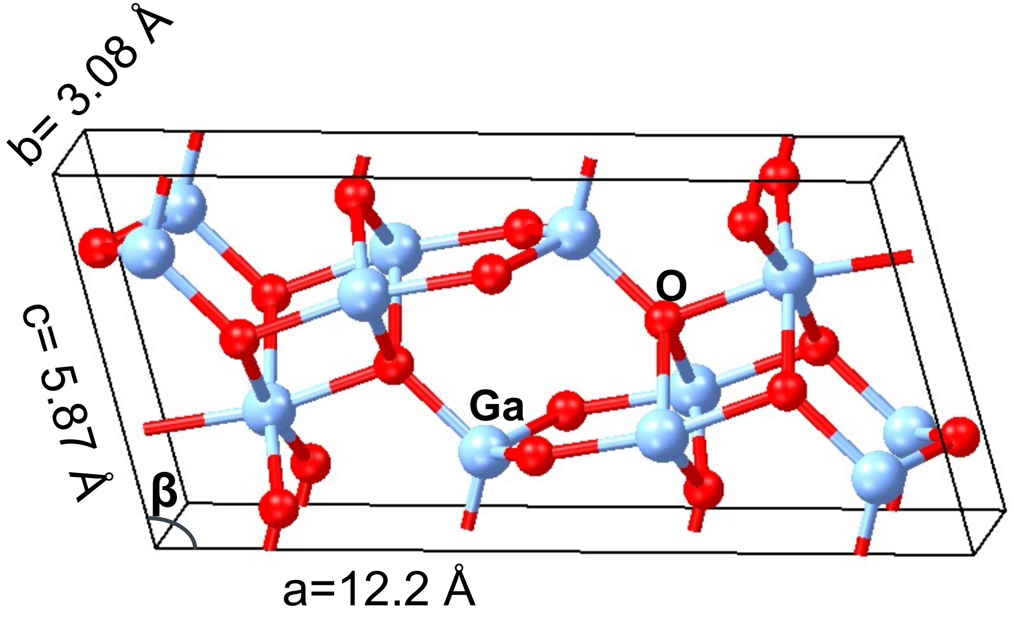
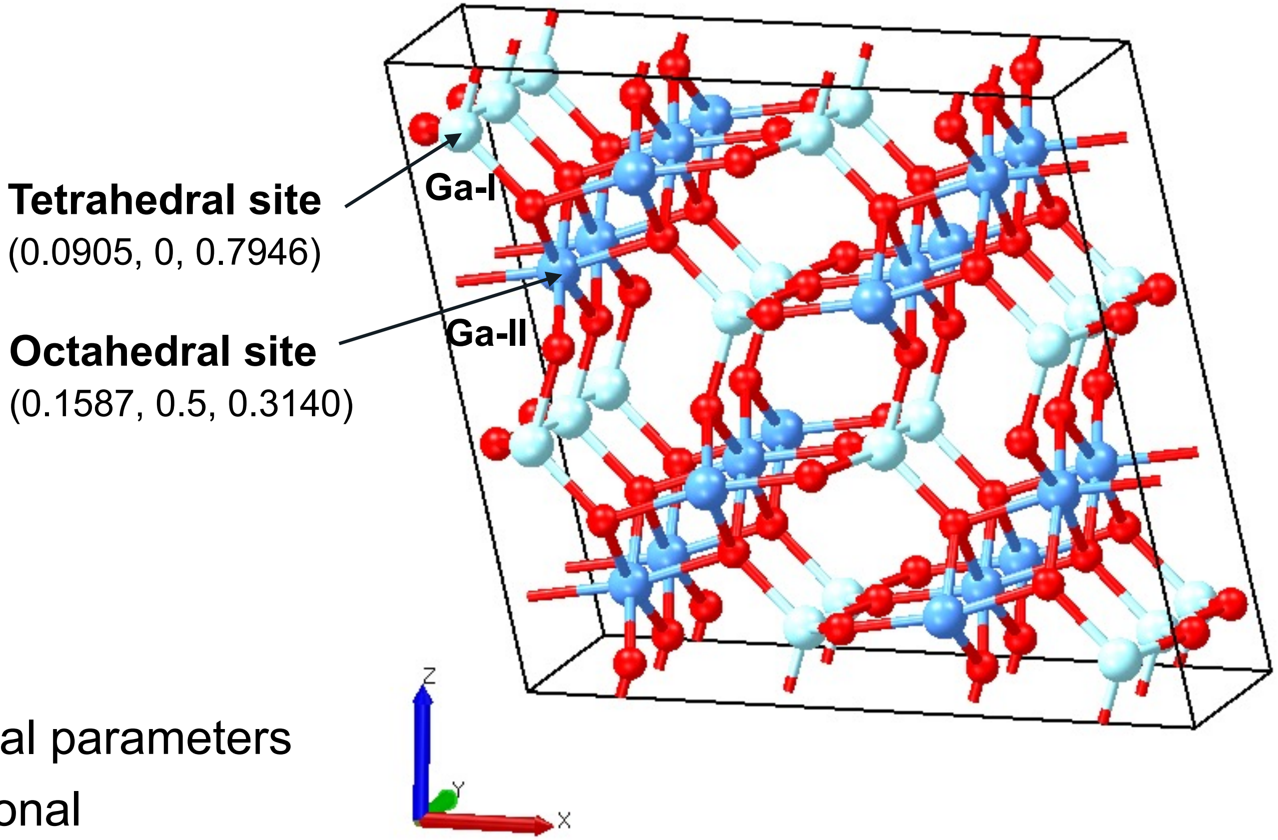
InGaO

20-atom β-Ga_2O_3 unit cell



α= γ=90°
β=103.8°

β-Ga_2O_3 80-atom 1×2×2 supercell

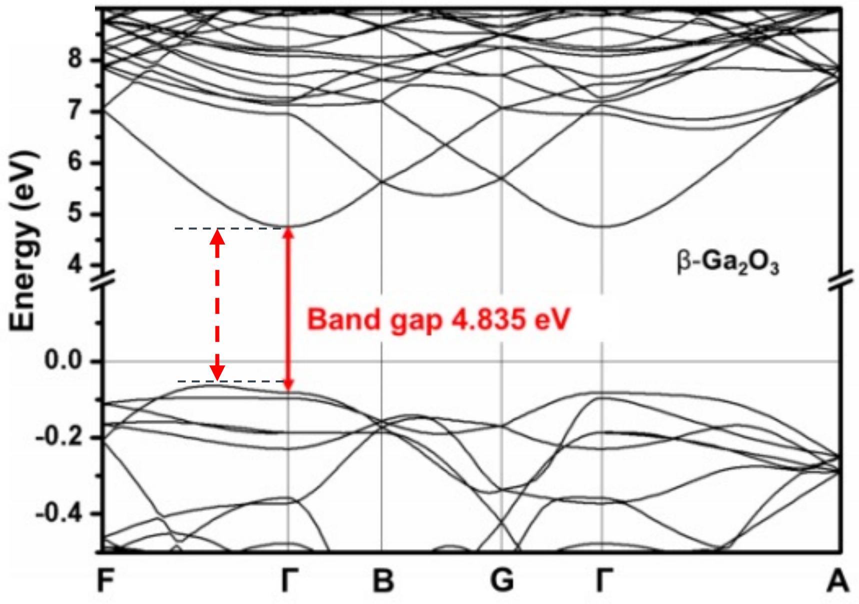

Tetrahedral site
(0.0905, 0, 0.7946)

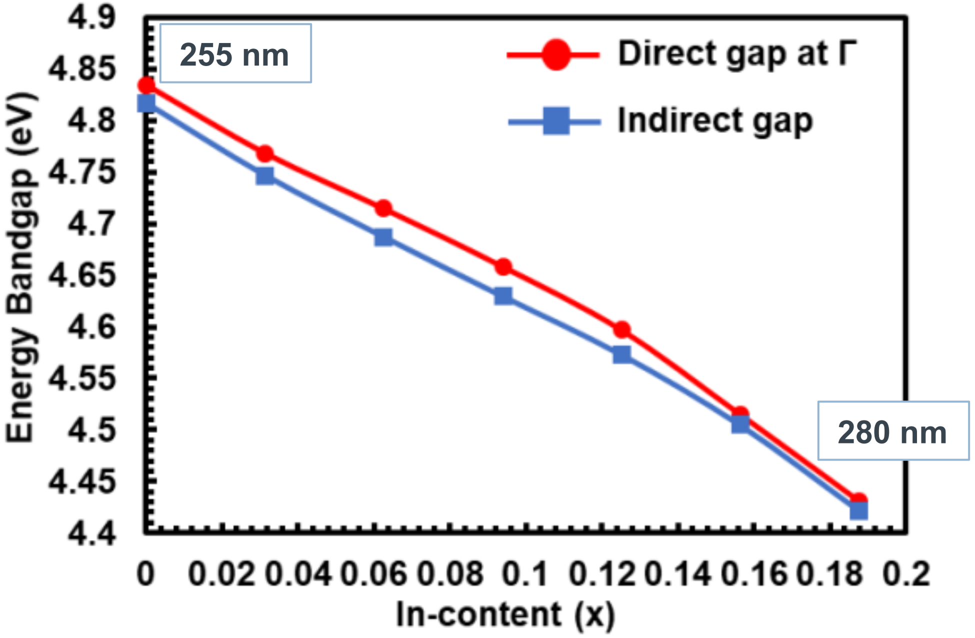
Octahedral site
(0.1587, 0.5, 0.3140)

VASP computational parameters

- GGA-PBE functional
- 400 eV plane-wave cutoff
- **k**-point spacing 0.2 $Å^{-1}$

InGaO: Band properties





- ➢ Results agree considerably with published literature[2]
- ➢ Indirect energy gap property in β-$(In_xGa_{1-x})_2O_3$ alloys
- ➢ Band gap energy reduction as In-content increases
  - ✓ Almost-linear reduction: difference of 0.4 eV
  - ✓ Wavelength from 255 nm to 280 nm → Deep UV

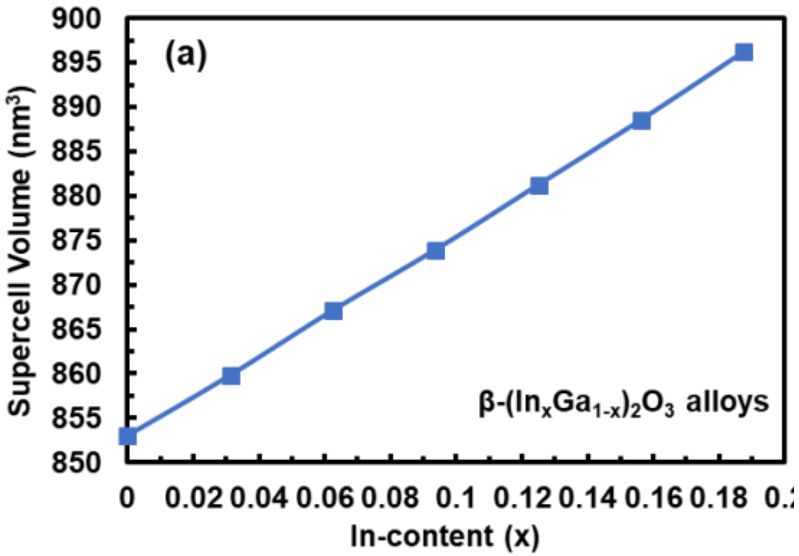
Bandgap energies corrected using scissor operator approach:

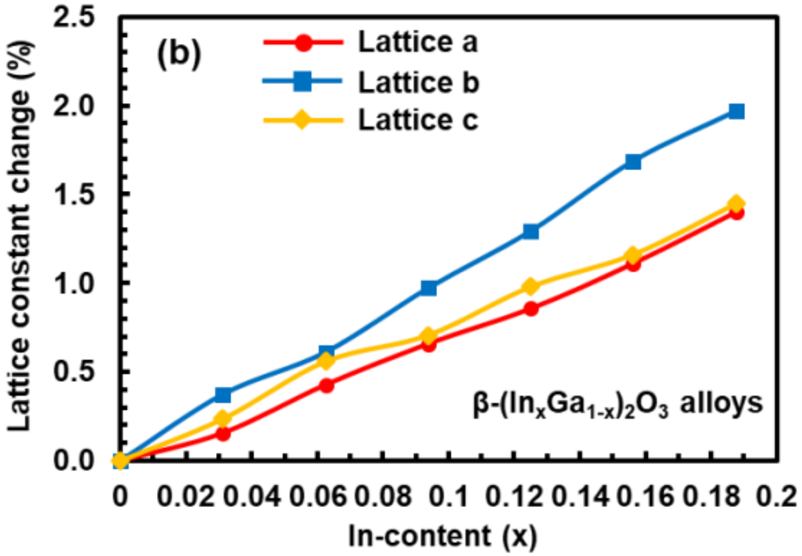
$$E_g=E_o+9.1/[(x\varepsilon_{In2O3}+(1-x)\varepsilon_{Ga2O3}]$$

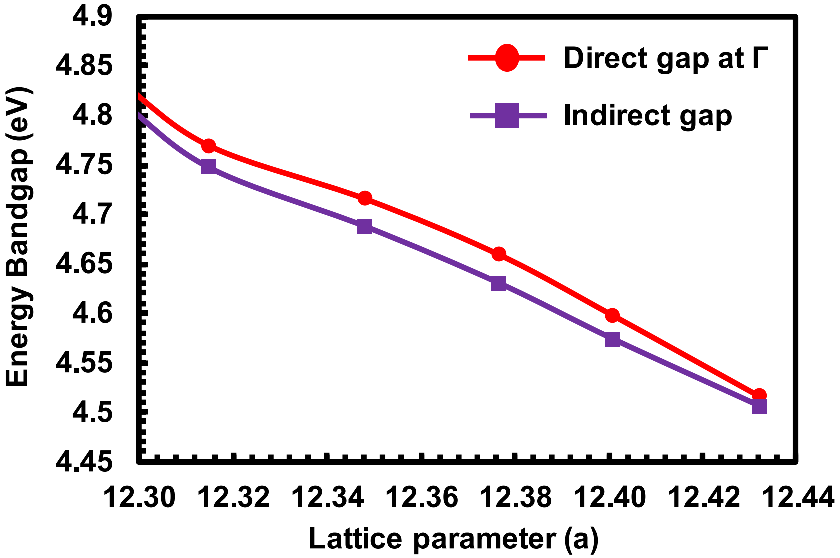
Ref: Fiorentini et al., Physical Review B 51.23, 17196, 1995

1. X. L. Liu, and C. K. Tan, AIP Advances, 9(3), 035318, 2019
2. M B Maccioni et al., J. Phys.: Conf. Ser. 566 012016, 2014

InGaO: Lattice constants

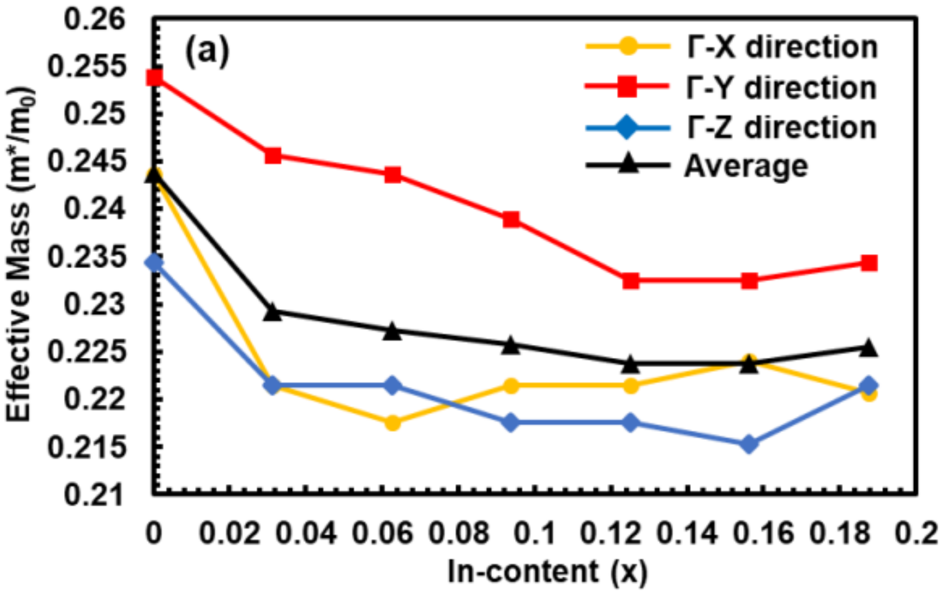


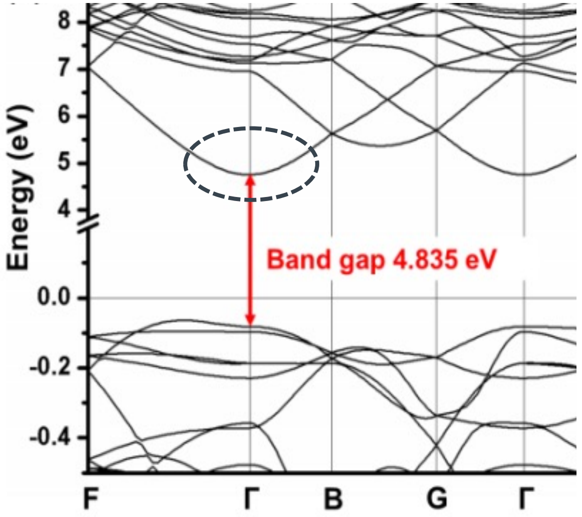




- ➢ Volume increases as In-content increases
- ➢ The lattice a, b and c increase expectedly
- ➢ Difference between direct-indirect band gap reduces as the In-content / lattice parameter increases

InGaO: Electron effective mass





$$E_{th} \approx \frac{(1+2u)}{(1+u)} E_g$$

$$u = \frac{m_c^*}{m_v^*}$$

m_c^* : electron effective mass
m_v^* : hole effective mass

- Y direction: Effective mass decreases
- X and Z direction: Effective mass fluctuates

Impact ionization in photodiode:

- **2 e^- and 1 h^+**
- **Carrier increase-amplified signal**
- **High applied voltage is necessary**
- **Lower E_{th} implies higher sensitivity**

MedeA -Electronics

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  - Lattice-matching III-Oxide quaternary compound: AlInGaO
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- ☐ **SBH calculations at a metal-semiconductor interface**
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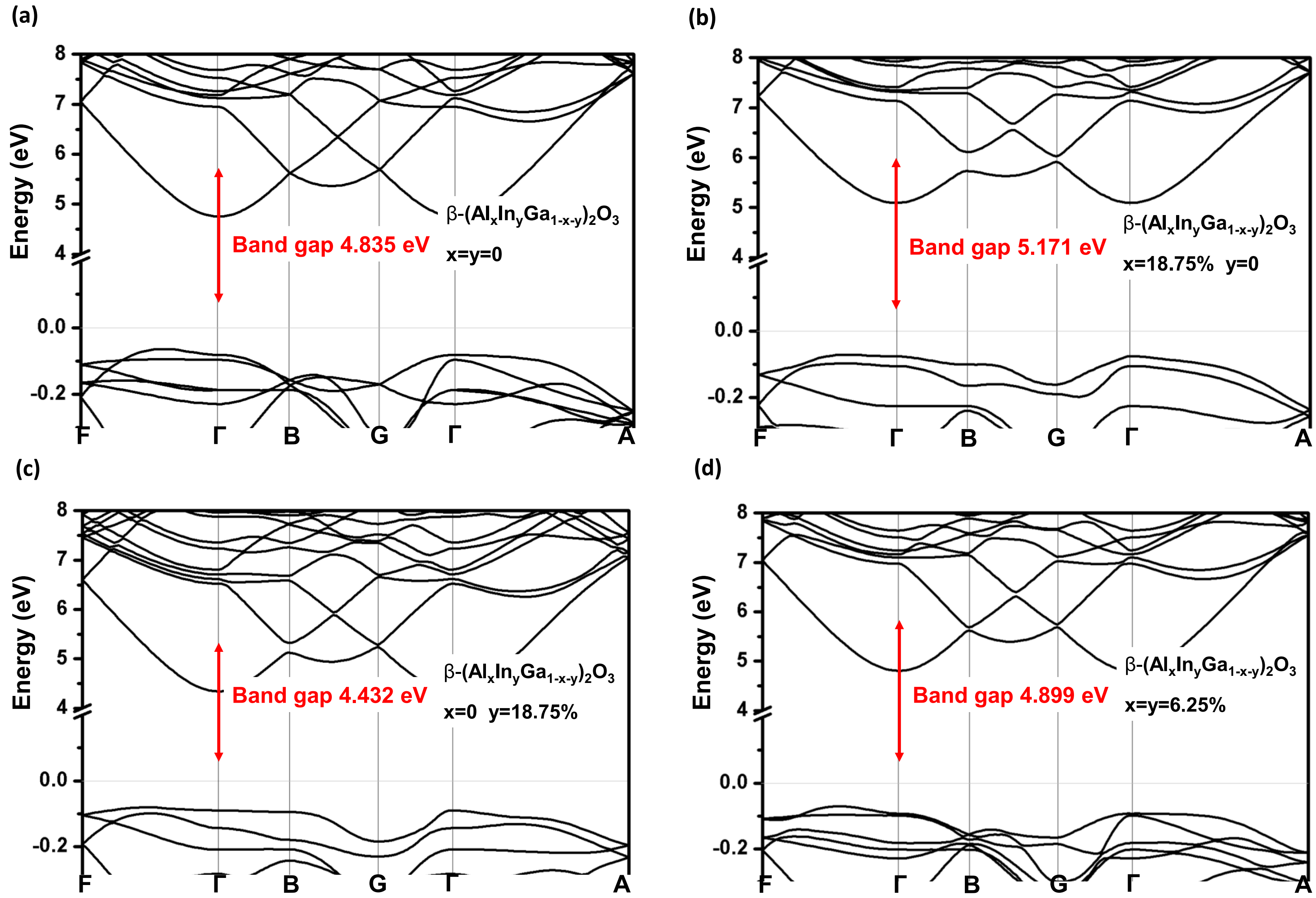
  - SBH analysis

How about AlInGaO?

- Ternary alloy (AlGaO, InGaO) — recently explored and studied
- Quaternary alloy (AlInGaO) ? Lattice matching?

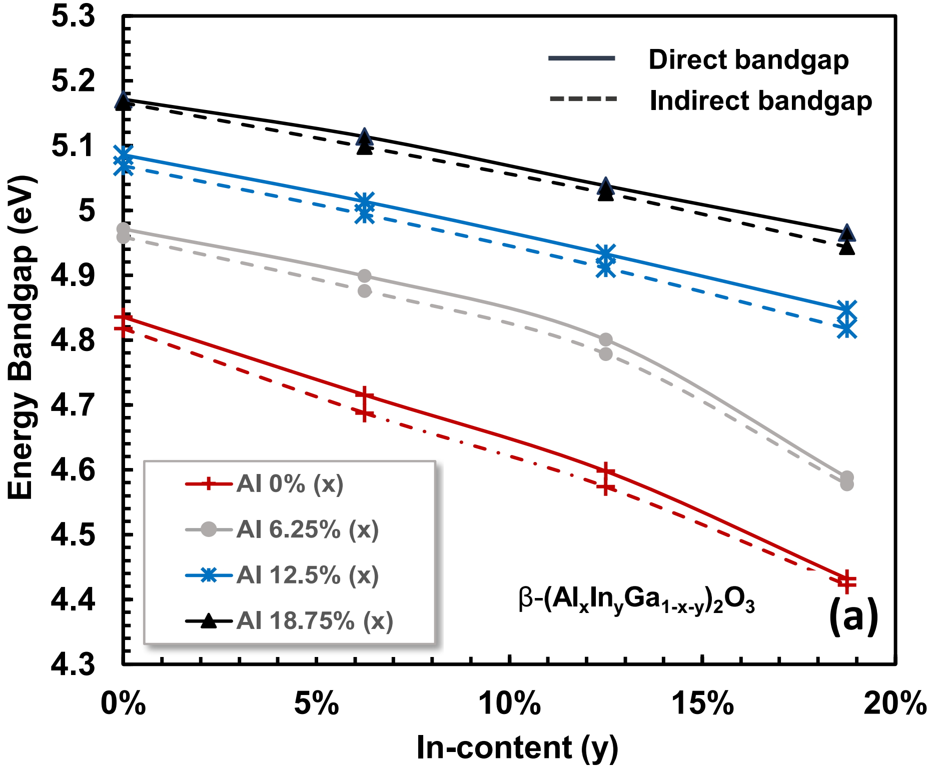
GaInAsP / InP	(0.74 -1.35 eV) for diode laser, infrared
GaInAsP / GaAs	(1.42-1.9 eV) for solar cell
AlGaInP / GaAs	for solar cell
AlGaInN	for blue and near UV LED active region
AlInGaO / Ga_2O_3	Yet to be studied

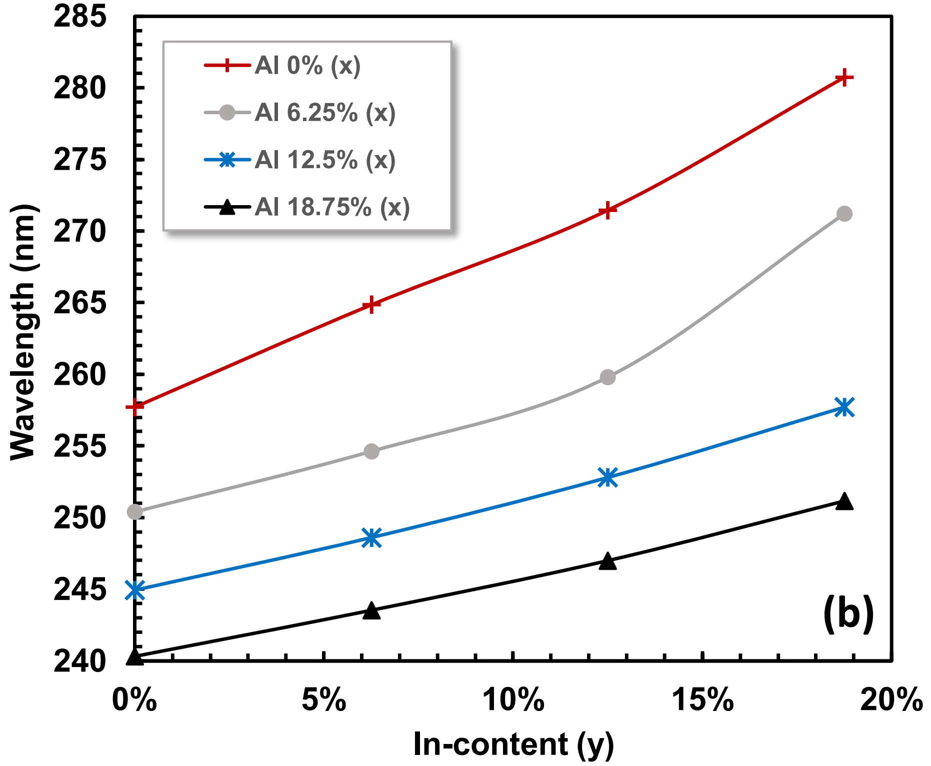
AlInGaO-Band structures



Al: 0%~18.75%
In: 0%~18.75%

AlInGaO-Bandgap energy

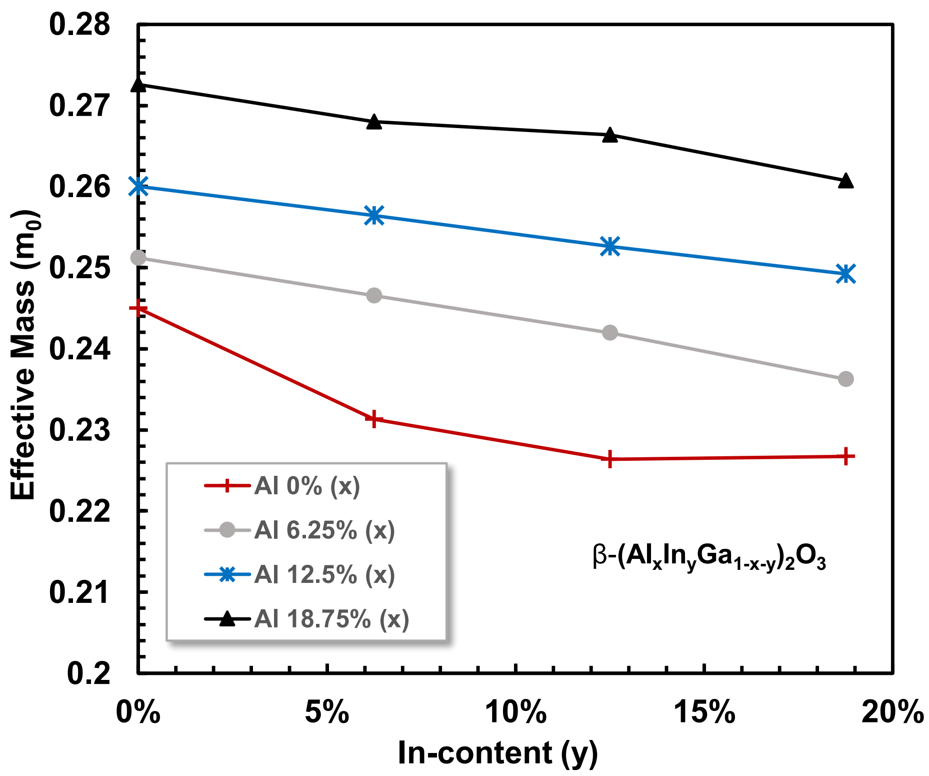


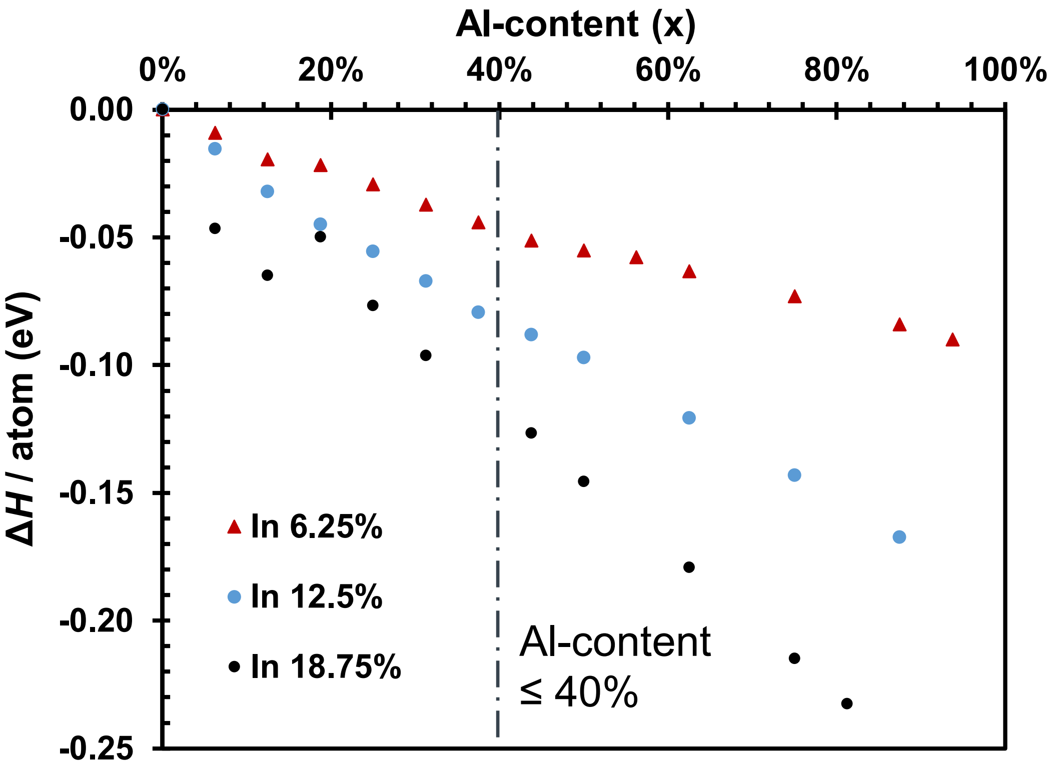


- ➢ Band gaps energy corrected by scissor operator: $E_g = E_o + 9.1/[(x\mathcal{E}_{Al2O3} + y\mathcal{E}_{In2O3} + (1-x-y)\mathcal{E}_{Ga2O3}]^2$
- ➢ Band gap energy reduction as Al-content decreases and In-content increases
  - ✓ Almost-linear reduction
  - ✓ Difference between direct and indirect bandgap < 0.03 eV
    - ➢ Covering wavelength from 240 nm to 280 nm → Deep UV region

AlInGaO-Effective mass and *ΔH*

m_c^* in Γ-Y (0, 0.5, 0) direction





- Electron effective mass decreases with In-content increasing, and increases with Al-content increasing

- AlInGaO could be stable refer to InGaO
- At the same In-content, higher Al-content shows lower formation energy

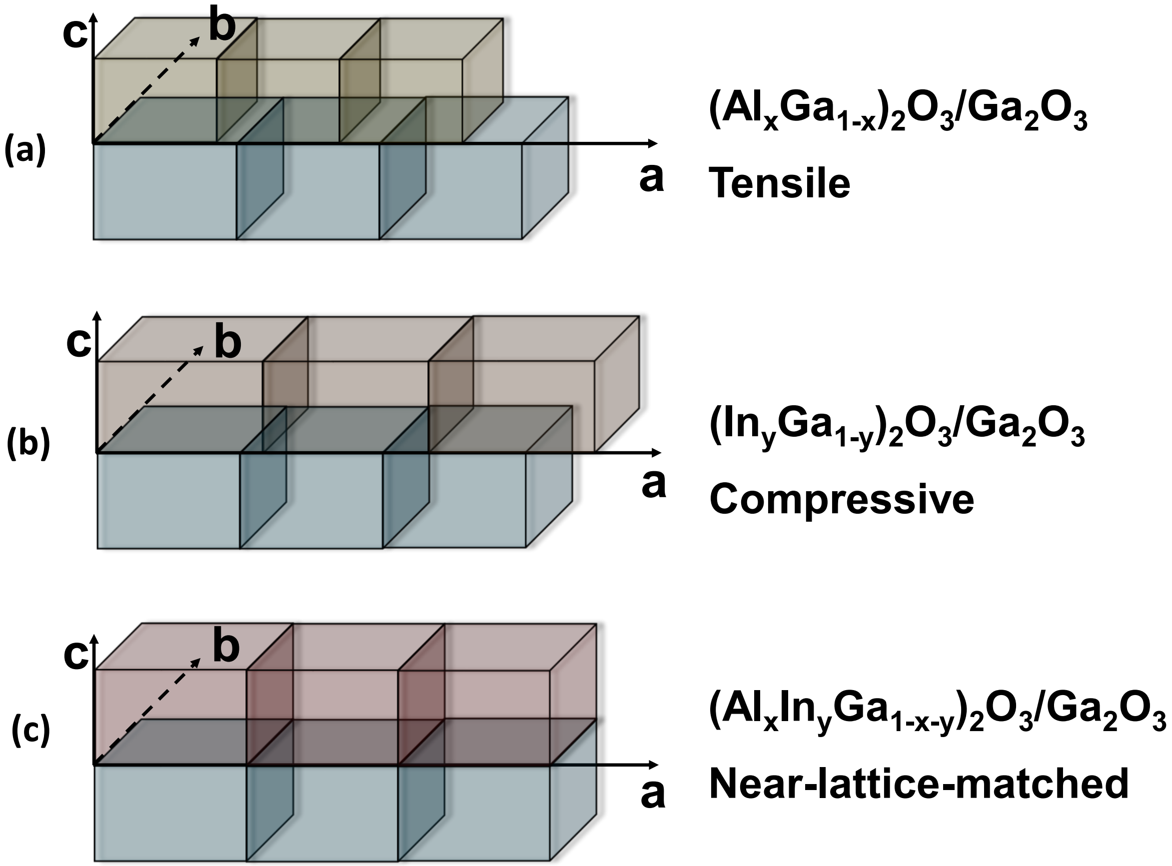
Could it be lattice-matched?

Lattice mismatching issue:

- Interface defects
- Misfit dislocation
- Strain

Examples:

- InGaN / GaN
- InGaAs / GaAs
- InGaAsP / InP
- GeSi / Si

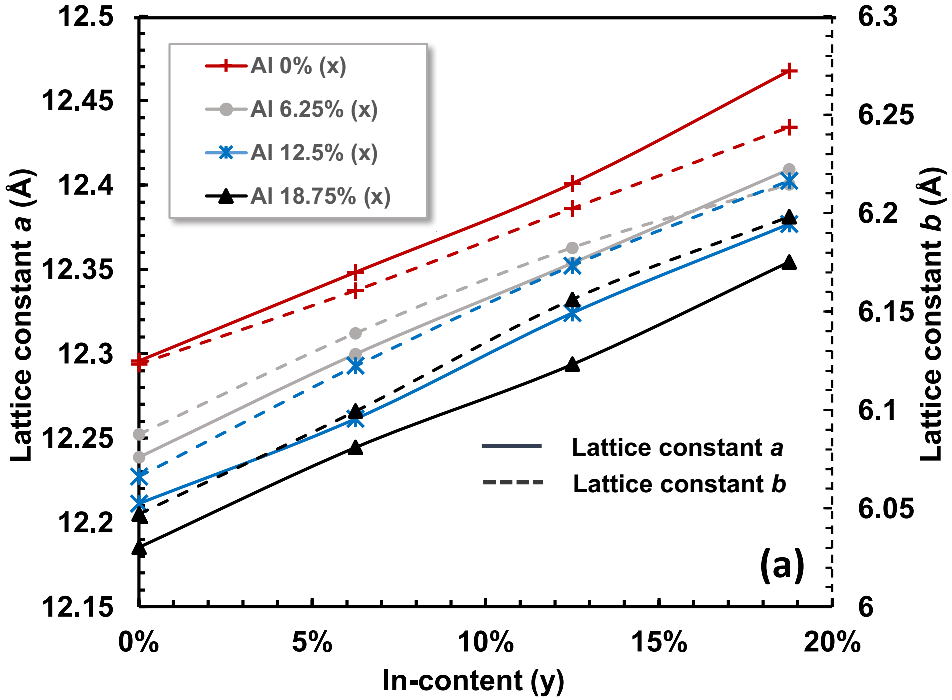


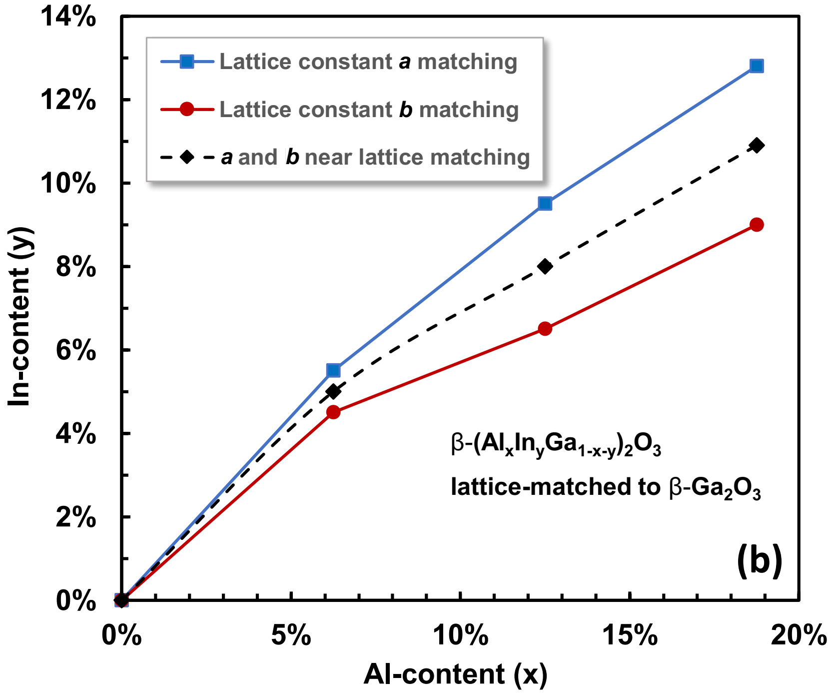
$(Al_xGa_{1-x})_2O_3/Ga_2O_3$
Tensile

$(In_yGa_{1-y})_2O_3/Ga_2O_3$
Compressive

$(Al_xIn_yGa_{1-x-y})_2O_3/Ga_2O_3$
Near-lattice-matched (Expectation)

AlInGaO structural properties





- Volume decreases as Al-content increases, and increases as In-content increases
- Lattice a, b, c changing tendency is the same with volume
- Lattice matching can be achieved at a certain direction at one time

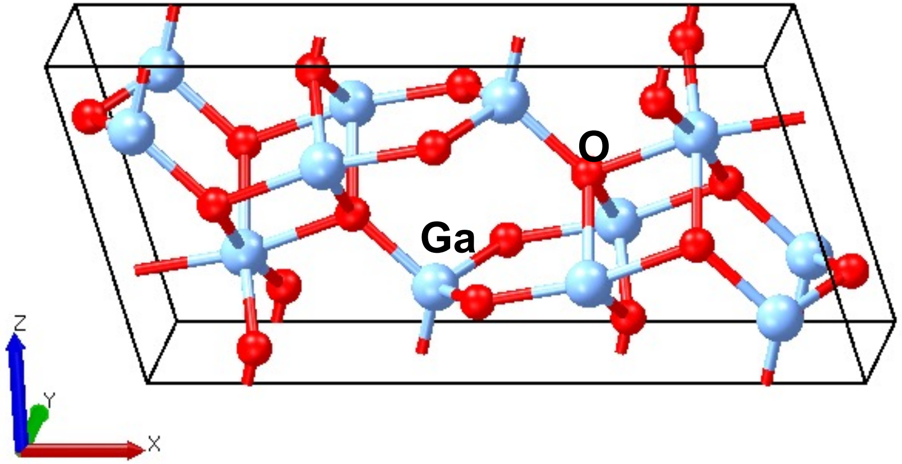
Ref: X. L. Liu, and C. K. Tan, *Semiconductor Science and Technology*, *35*(2), 025023, 2020.

Findings in AlInGaO

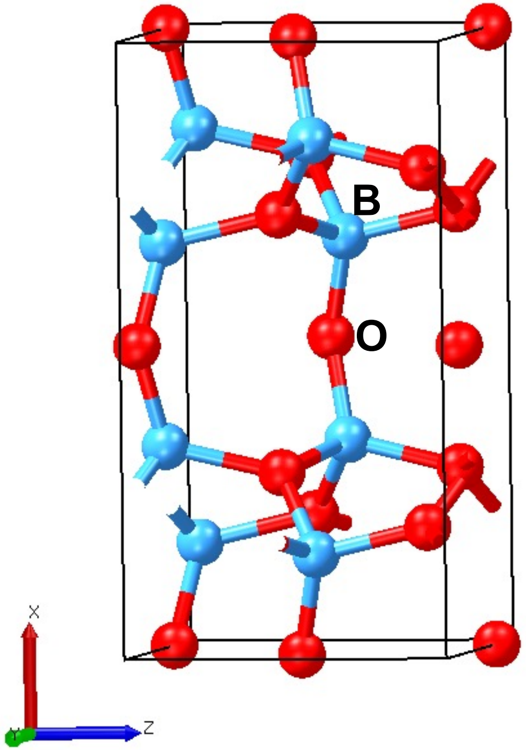
- Investigated the effect of Al/In content on the electronic and structural properties of β-Ga_2O_3 using the DFT calculations.
- Bandgap is adjusted from 4.43 eV to 5.17 eV by changing Al/In-content from 0% ~ 18.75% in the alloys but it remains indirect band gap property.
- Near lattice-matched condition is possible for $(Al_xIn_yGa_{1-x-y})_2O_3$ / Ga_2O_3.

The beginning adventure of B-incorporated Ga_2O_3…

monoclinic Ga_2O_3

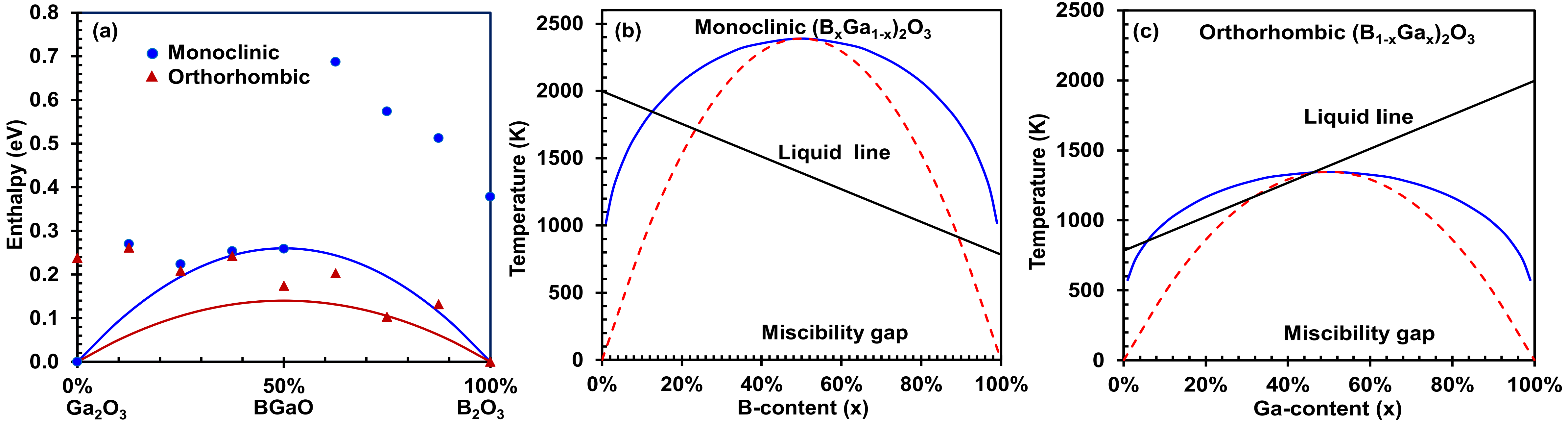


orthorhombic B_2O_3



B incorporation cause the crystal structural change, will BGaO growth be feasible?

BGaO-Formation energy



$$\Delta H[(B_xGa_{1-x})_2O_3] = E[(B_xGa_{1-x})_2O_3] - (1-x)E[Ga_2O_3] - xE[B_2O_3],$$

$$\Delta H[(B_xGa_{1-x})_2O_3] = 4x(1-x)\Delta H_0\,,$$

$$T = \Delta H_0/k_b * (8x-4)/(\log(x) - \log(1-x))$$

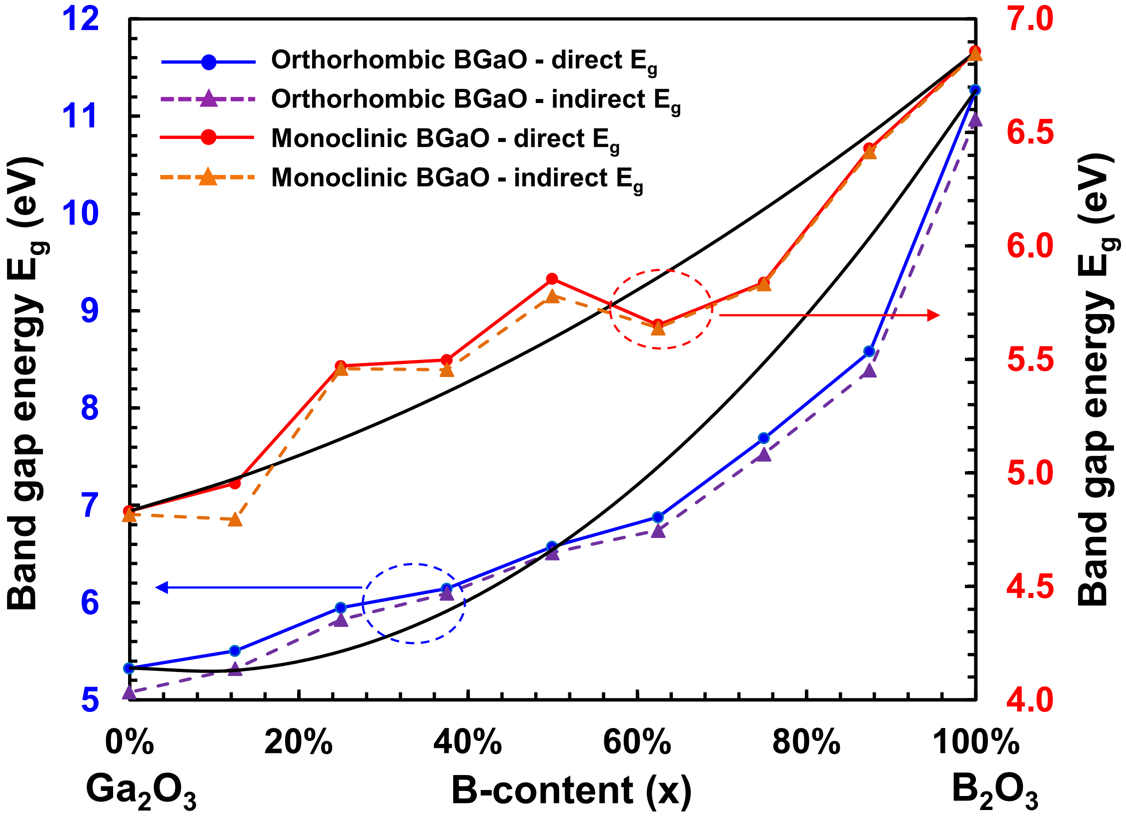
MedeA -UNCLE

(UNiversal CLuster Expansion)

- B-content required for single-crystal or metastable solid phase of monoclinic (orthorhombic) BGaO alloys is estimated to be < 17% (< 35%).

Ref: X. Liu, etc., and C.K. Tan, Applied Physics Letters, 117(1), 012104, 2020

BGaO-Bandgap energy



Band gap increases:
4.83 eV ~6.86 eV (monoclinic)
5.32 eV ~11.27 eV (orthorhombic)

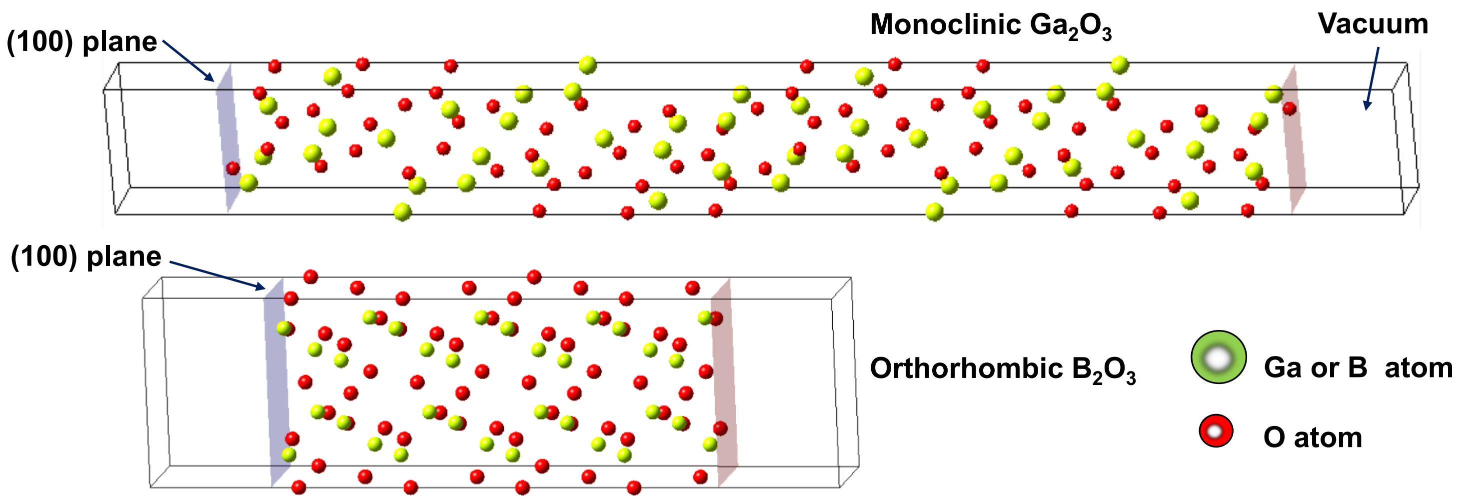
- ➢ Maximum increase of bandgap energy:

  2.03 eV (monoclinic) BGaO alloys;

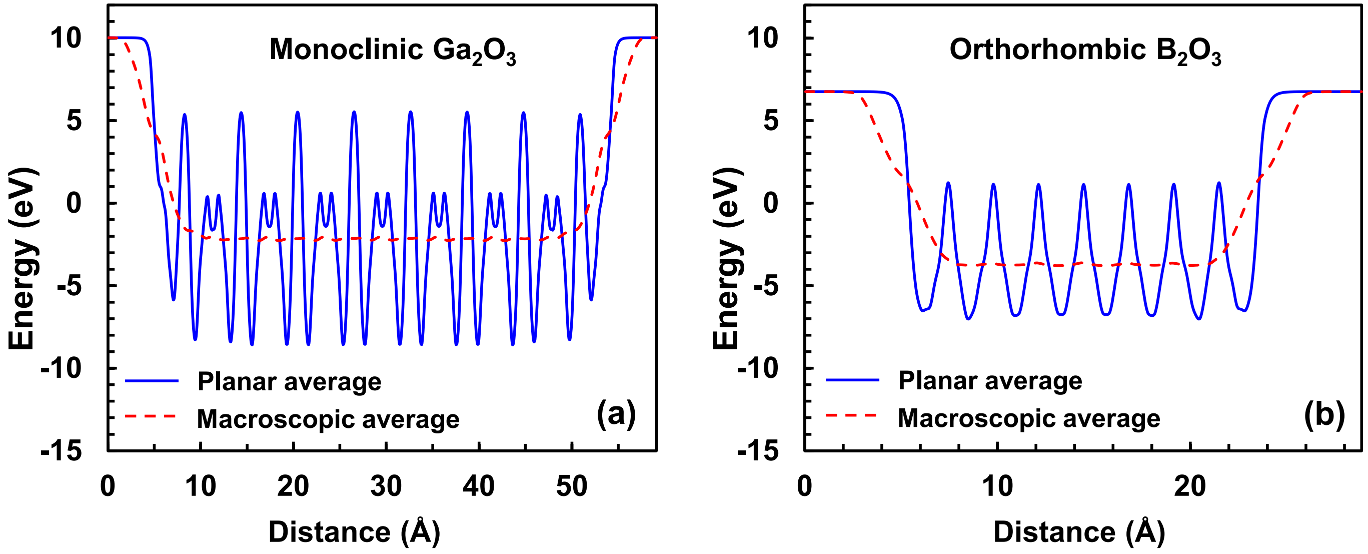
  5.95 eV (orthorhombic) BGaO alloys

Ref: X. Liu, C. Sammarco, G. Zeng, D. Guo, W. Tang, and C.K. Tan, *Applied Physics Letters*, 117(1), 012104, 2020

BGaO-Surface calculation

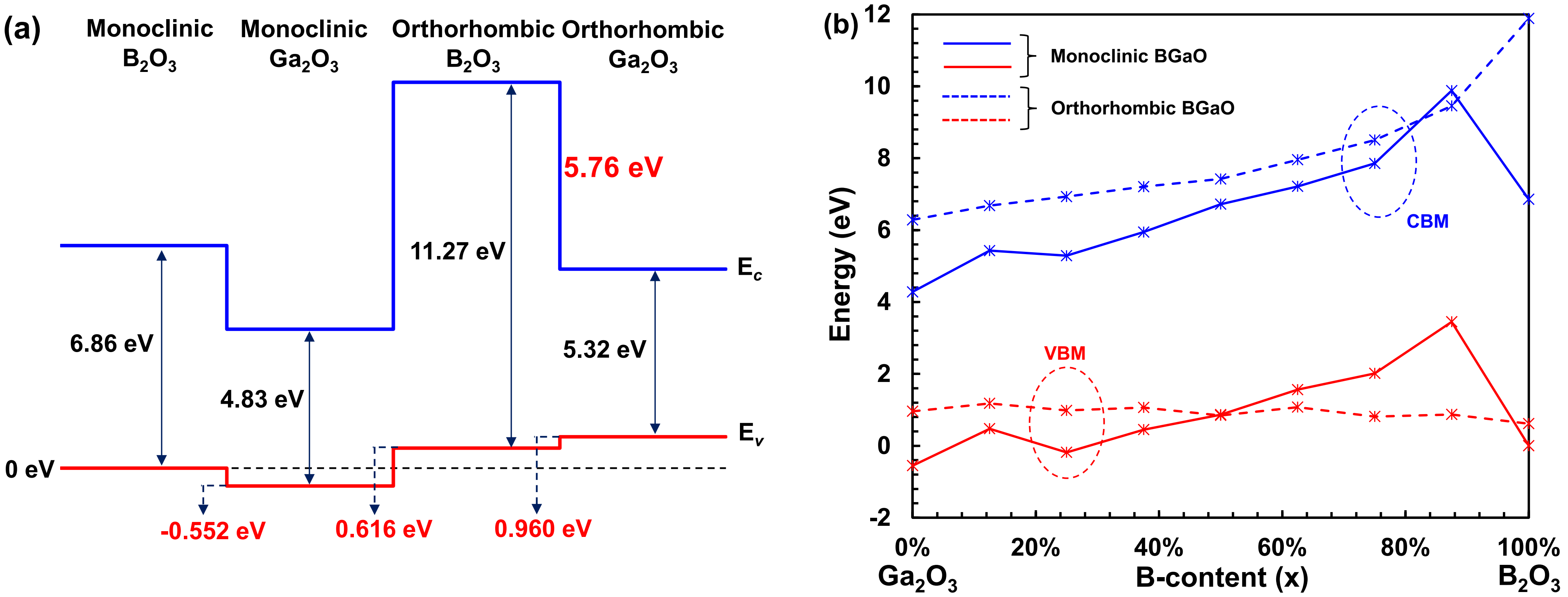


The 80-atom model of Ga_2O_3 and B_2O_3 with (100) crystal plane as surface.



Surface potential of Ga_2O_3 and B_2O_3

BGaO-Band offsets



- ➢ Major changes in conduction band and minor changes in valence band indicates possibility of using BGaO as an electron blocking layer.

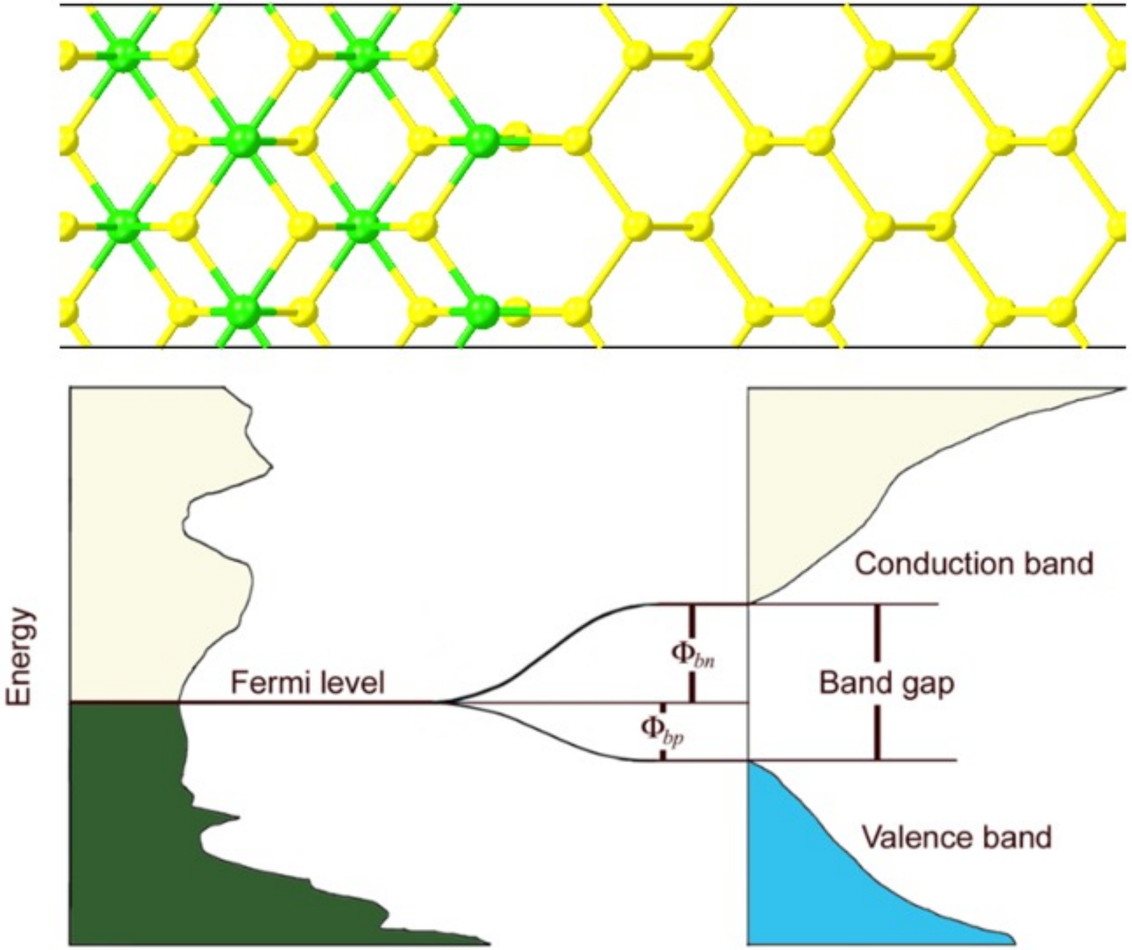
Ref: X. Liu, C. Sammarco, G. Zeng, D. Guo, W. Tang, and C.K. Tan, *Applied Physics Letters*, 117(1), 012104, 2020

Findings in BGaO

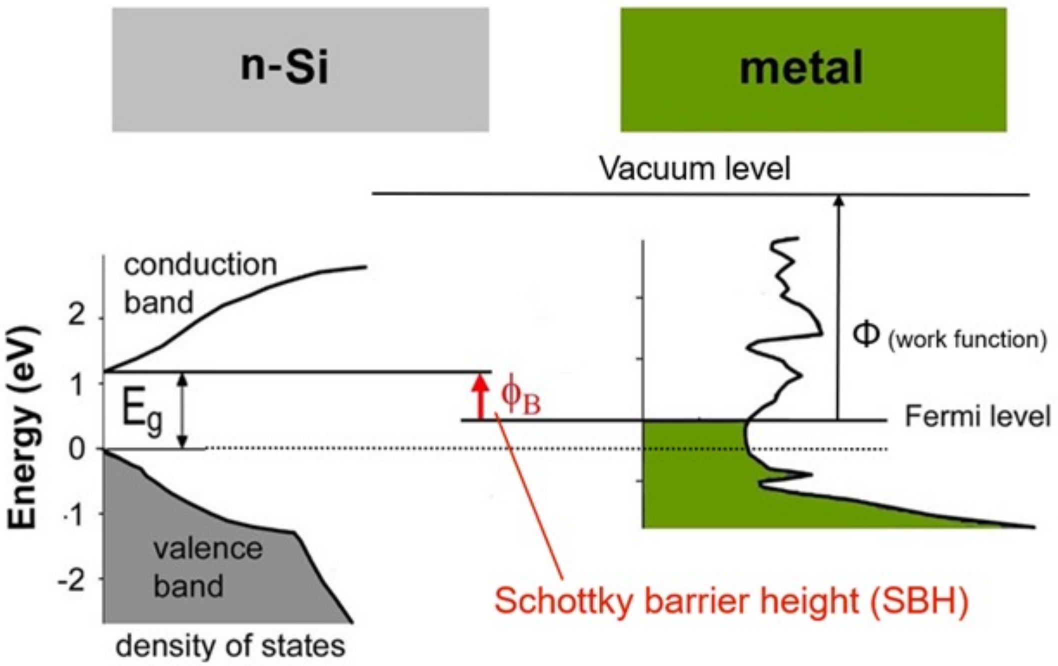
- Raising B-content leads to a maximum increase of bandgap energy of 2.03 eV in monoclinic-based BGaO and 5.95 eV in orthorhombic-based BGaO, respectively.
- Maximum B-content in monoclinic and orthorhombic BGaO estimated to be 17% and 35%, respectively.
- The Ga_2O_3 / B_2O_3 interface in <100> direction exhibits ***large CB offset and “large” VB offset***.
- Possibility of BGaO functioning as an electron blocking layer.

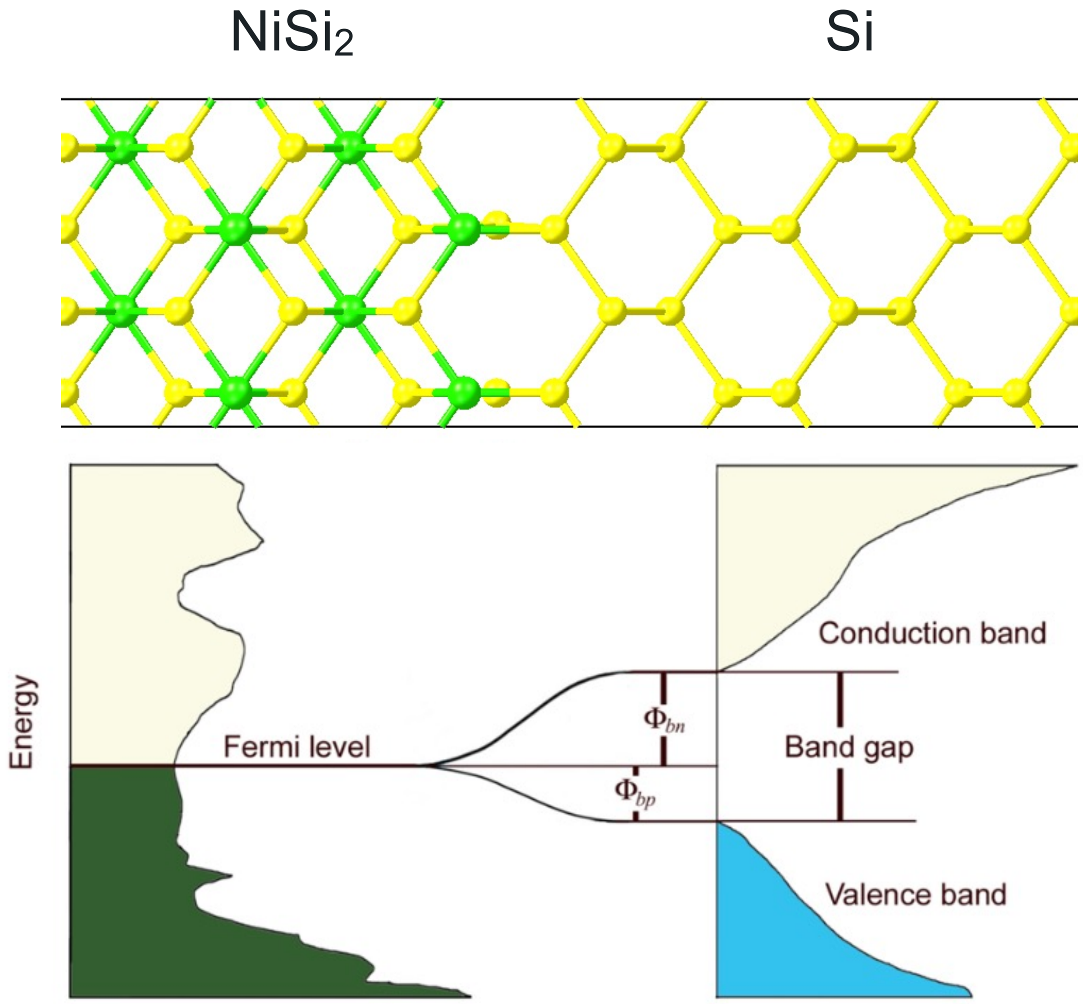
Schottky barrier height

Band alignment at $NiSi_2$/Si interface

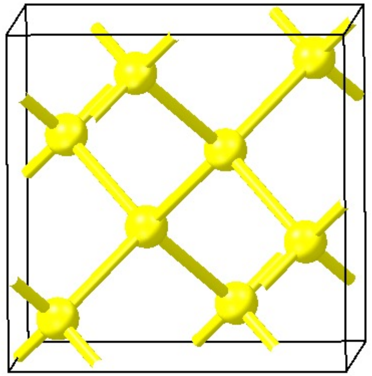


SBH at a metal-semiconductor interface

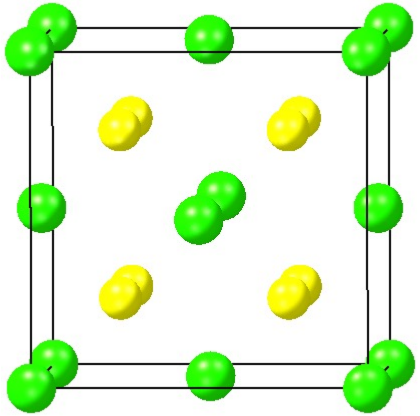




Modeling of bulk and interface structures

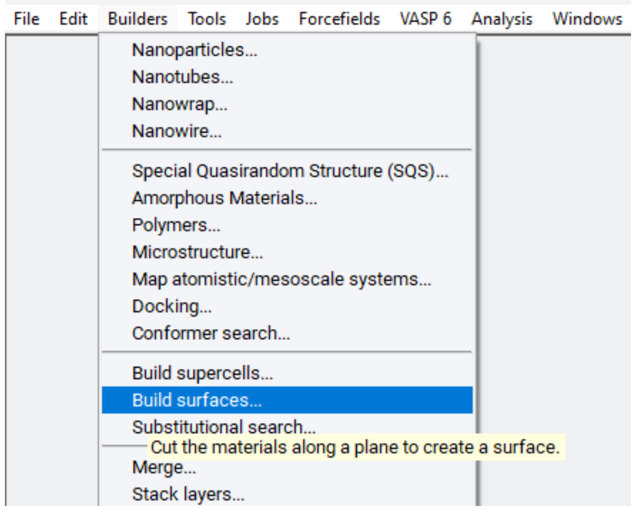


Si (Fd-3m)

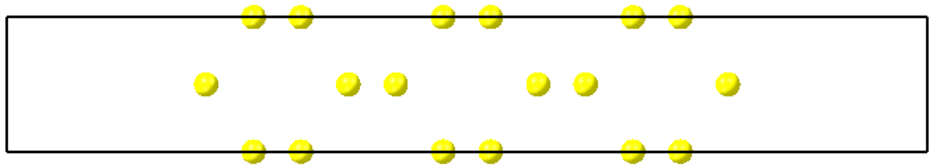


$NiSi_2$ (Fm-3m)

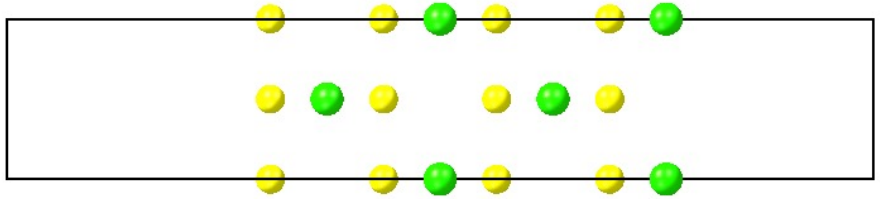
Surface Builder



Cut the materials along a plane to create a surface.

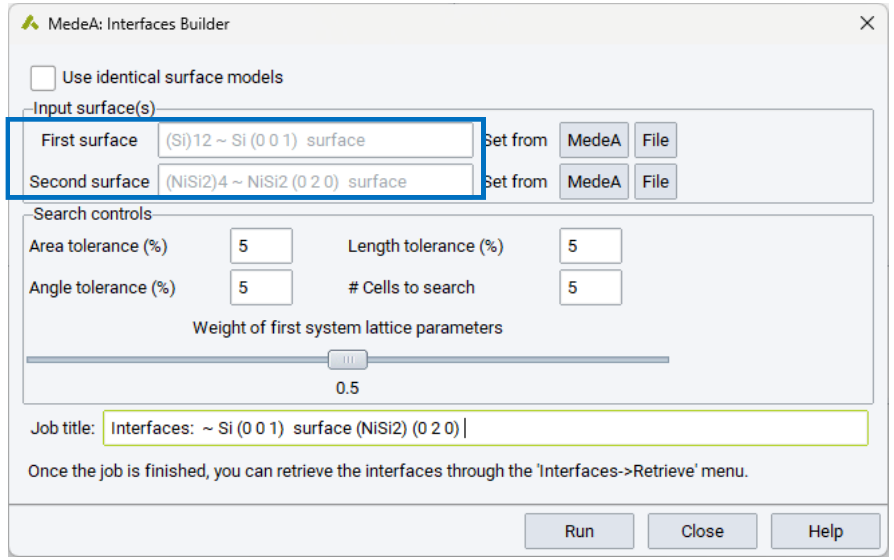


Si (001) slab



$NiSi_2$ (020) slab

Interface Builder



☐ Use identical surface models

Input surface(s)

First surface: (Si)12 ~ Si (0 0 1) surface

Second surface: (NiSi2)4 ~ NiSi2 (0 2 0) surface

Search controls

Area tolerance (%): 5

Length tolerance (%): 5

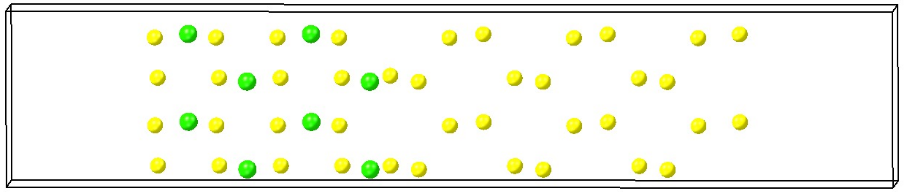
Angle tolerance (%): 5

Cells to search: 5

Weight of first system lattice parameters: 0.5

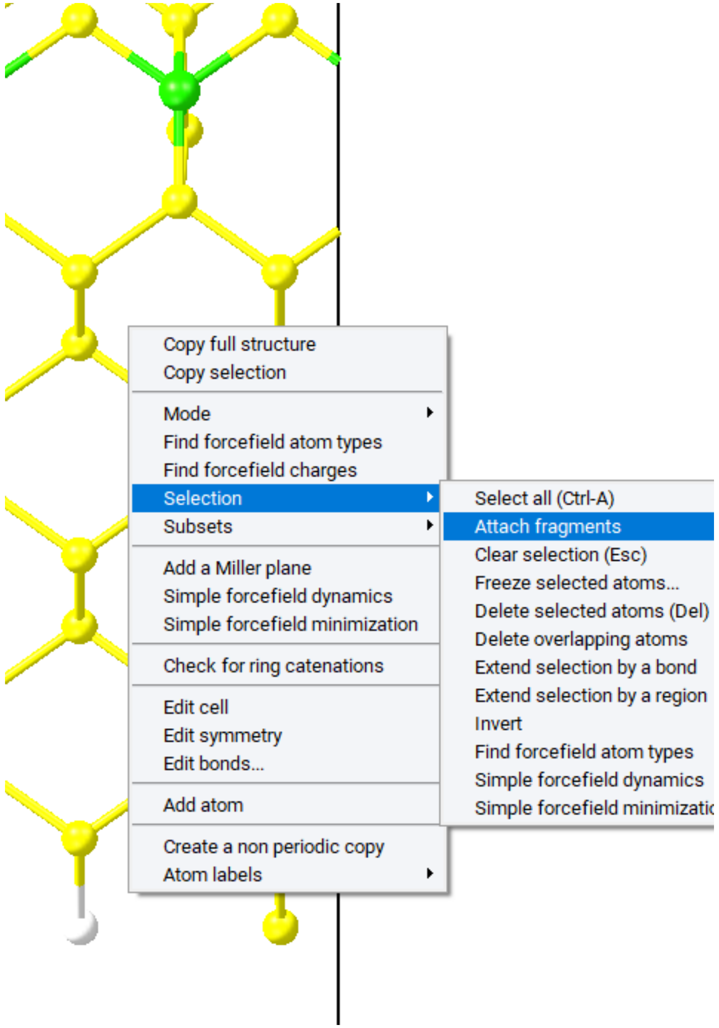
Job title: Interfaces: ~ Si (0 0 1) surface (NiSi2) (0 2 0)

Once the job is finished, you can retrieve the interfaces through the 'Interfaces->Retrieve' menu.

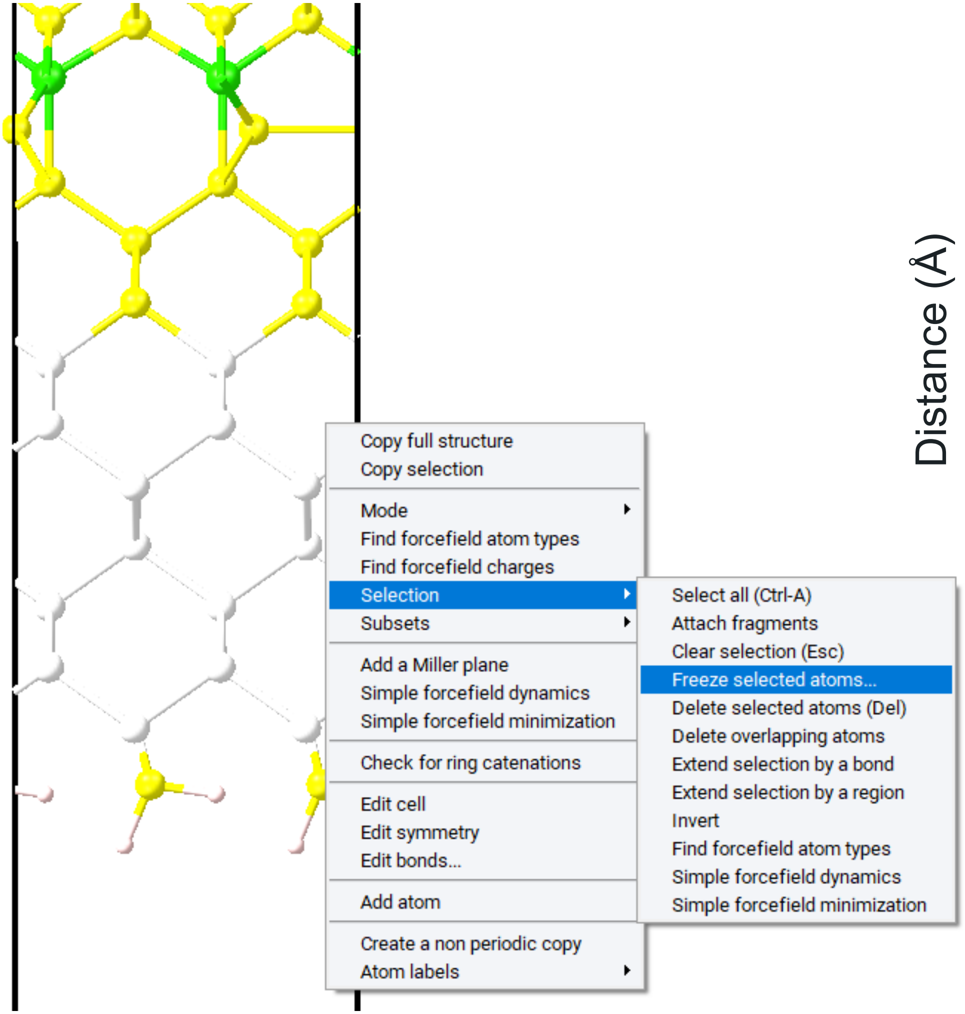


$NiSi_2$ /Si Interface

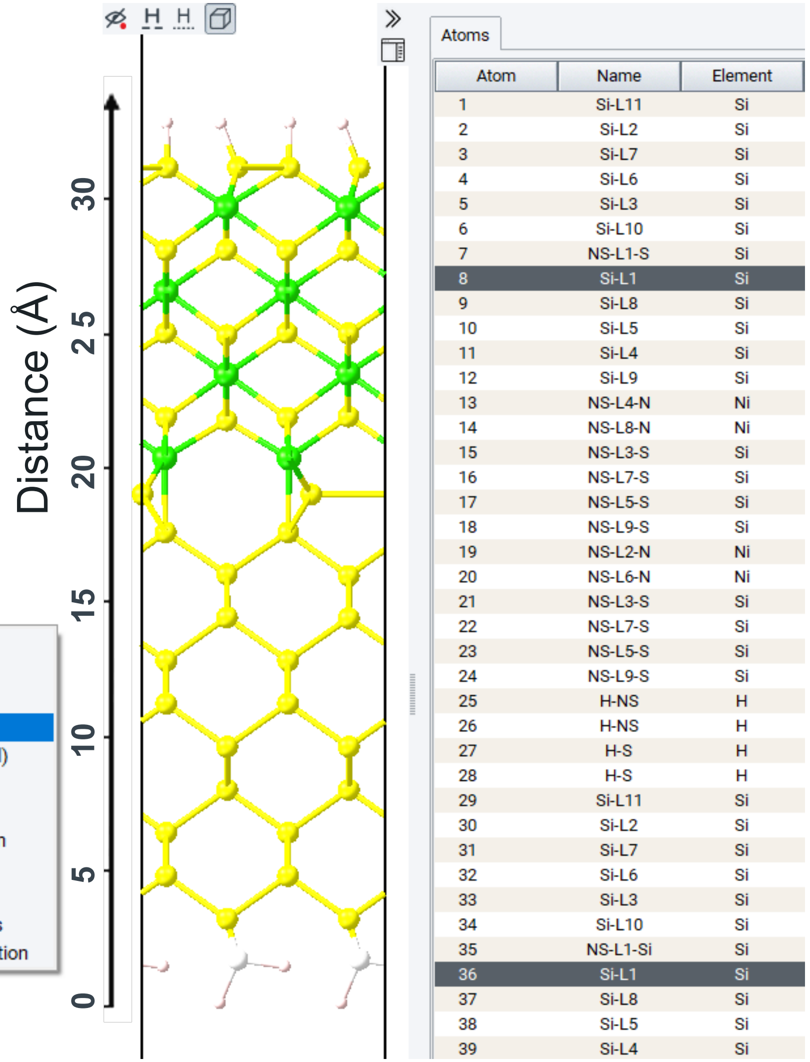
Tailoring the interface model



Passivate the dangling surface Si bonds by H atoms



Freeze selected Si layers



Atom	Name	Element
1	Si-L11	Si
2	Si-L2	Si
3	Si-L7	Si
4	Si-L6	Si
5	Si-L3	Si
6	Si-L10	Si
7	NS-L1-S	Si
8	Si-L1	Si
9	Si-L8	Si
10	Si-L5	Si
11	Si-L4	Si
12	Si-L9	Si
13	NS-L4-N	Ni
14	NS-L8-N	Ni
15	NS-L3-S	Si
16	NS-L7-S	Si
17	NS-L5-S	Si
18	NS-L9-S	Si
19	NS-L2-N	Ni
20	NS-L6-N	Ni
21	NS-L3-S	Si
22	NS-L7-S	Si
23	NS-L5-S	Si
24	NS-L9-S	Si
25	H-NS	H
26	H-NS	H
27	H-S	H
28	H-S	H
29	Si-L11	Si
30	Si-L2	Si
31	Si-L7	Si
32	Si-L6	Si
33	Si-L3	Si
34	Si-L10	Si
35	NS-L1-Si	Si
36	Si-L1	Si
37	Si-L8	Si
38	Si-L5	Si
39	Si-L4	Si

Rename atoms by layers

Properties of bulk Si and NiSi$_2$

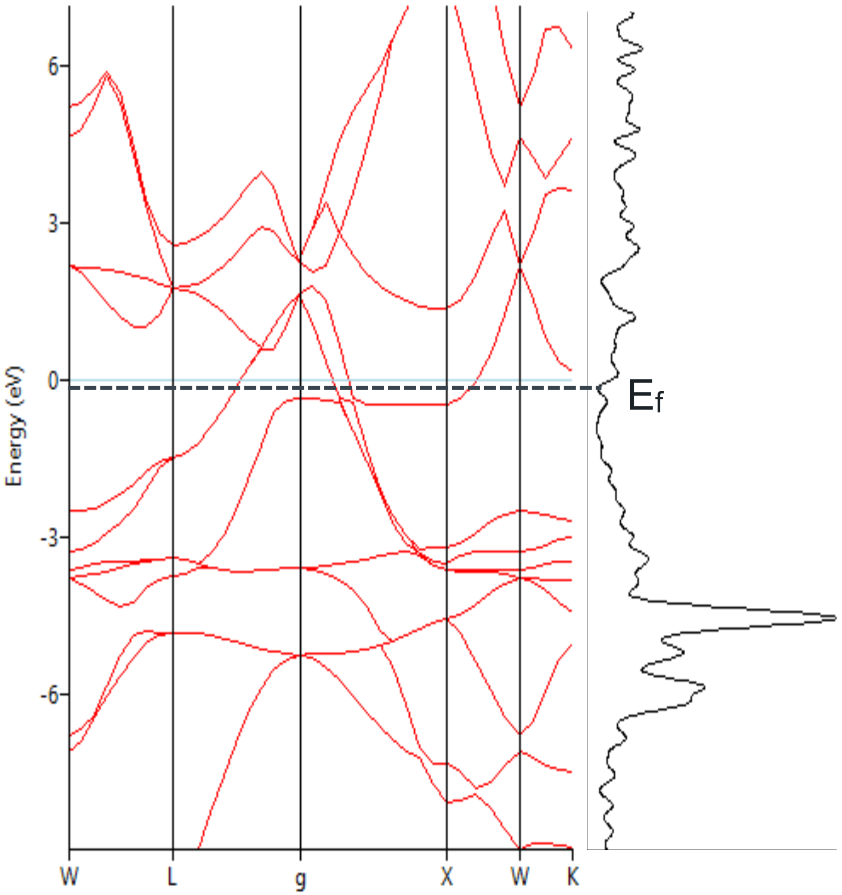
- Optimize the bulk structures
    - Type of Calculation:

      Structure Optimization
    - SCF tab: use odd size grids
    - Type of smearing:

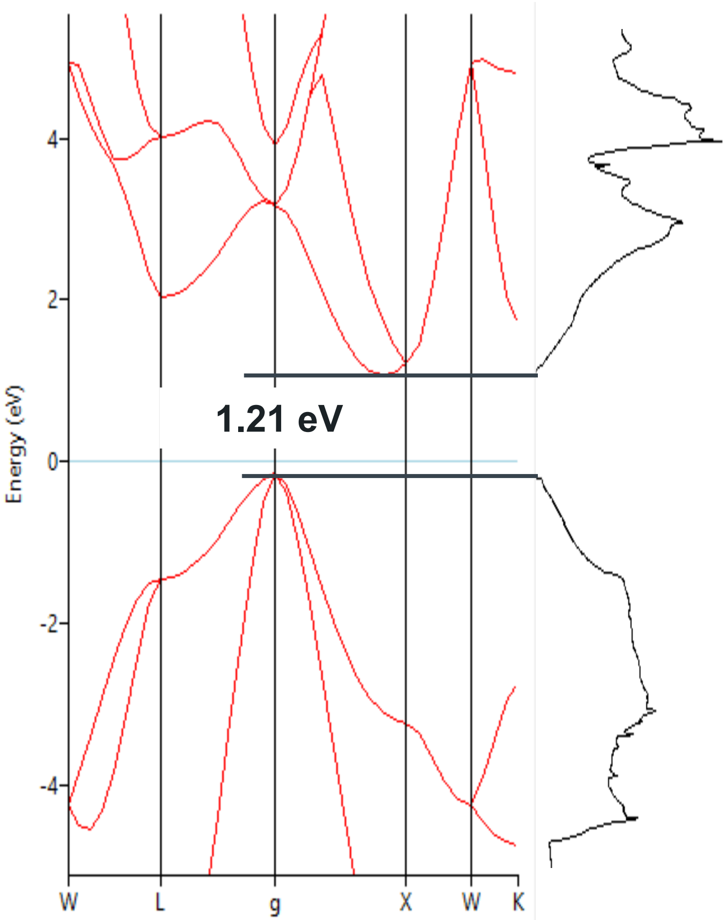
      Tetrahedron with Bloechl corrections
- Calculate the band structures

  >>***Analysis***>>***Band Structure*** and select `Bandstructure` from the relevant job
- Calculate the density of states

  >>***Analysis***>>***Density of States***



Band structures and density of states of bulk NiSi$_2$



Band structures and density of states of bulk Si

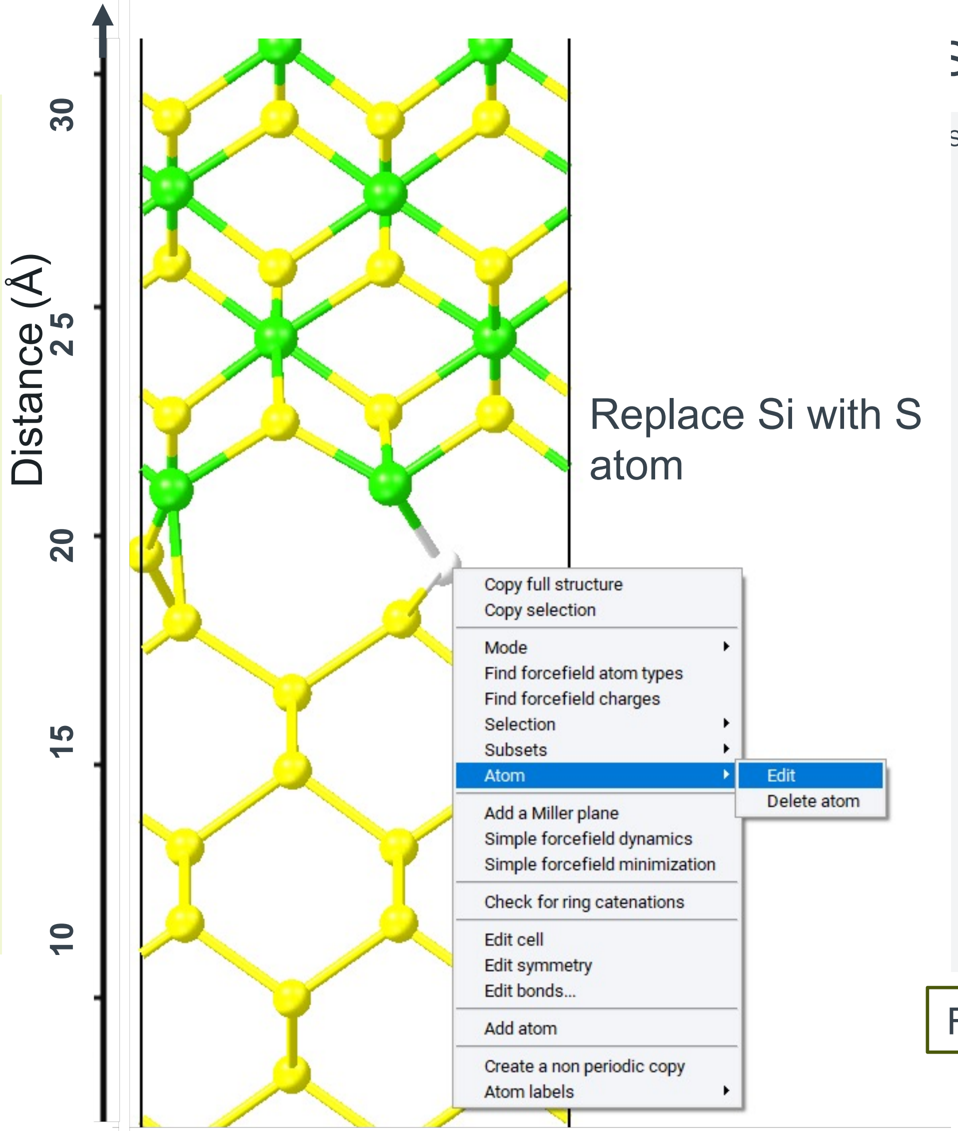
Core level energy at the interface and S doping

Si(001)/NiSi$_2$(001)

```
Si 2p core states(OUTCAR.out)

   1-  2p    -86.1957
   2-  2p    -86.0178
   3-  2p    -86.1035
   4-  2p    -86.0920
   5-  2p    -86.1229
   6-  2p    -86.2403
   7-  2p    -86.2953
   8-  2p    -85.9694
   9-  2p    -86.1028
  10-  2p    -86.1012
  11-  2p    -86.1153
  12-  2p    -86.1900
  13-  2p    -86.5553
  14-  2p    -87.0270
  15-  2p    -86.9806
  16-  2p    -86.4228
  17-  2p    -86.8519
  18-  2p    -87.0151
  19-  2p    -86.9729
  20-  2p    -86.4313
  21-  2p    -86.1915
  22-  2p    -86.0140
  23-  2p    -86.1043
  …
```

Fermi energy = 4.189 eV



Replace Si with S atom

Si(001)/S/NiSi$_2$(001)

```
Si 2p core states(OUTCAR.out)

   1-  2p    -86.3843
   2-  2p    -86.0383
   3-  2p    -86.1672
   4-  2p    -86.1307
   5-  2p    -86.1430
   6-  2p    -86.4432
   7-  2p    -86.8634
   8-  2p    -85.9924
   9-  2p    -86.1902
  10-  2p    -86.1348
  11-  2p    -86.1415
  12-  2p    -86.3514
  13-  2p    -86.5541
  14-  2p    -86.9446
  15-  2p    -86.8928
  16-  2p    -86.3427
  17-  2p    -86.7991
  18-  2p    -86.9295
  19-  2p    -86.8896
  20-  2p    -86.3522
  21-  2p    -86.9522
  22-  2p    -86.0326
  23-  2p    -86.1514
  …
```

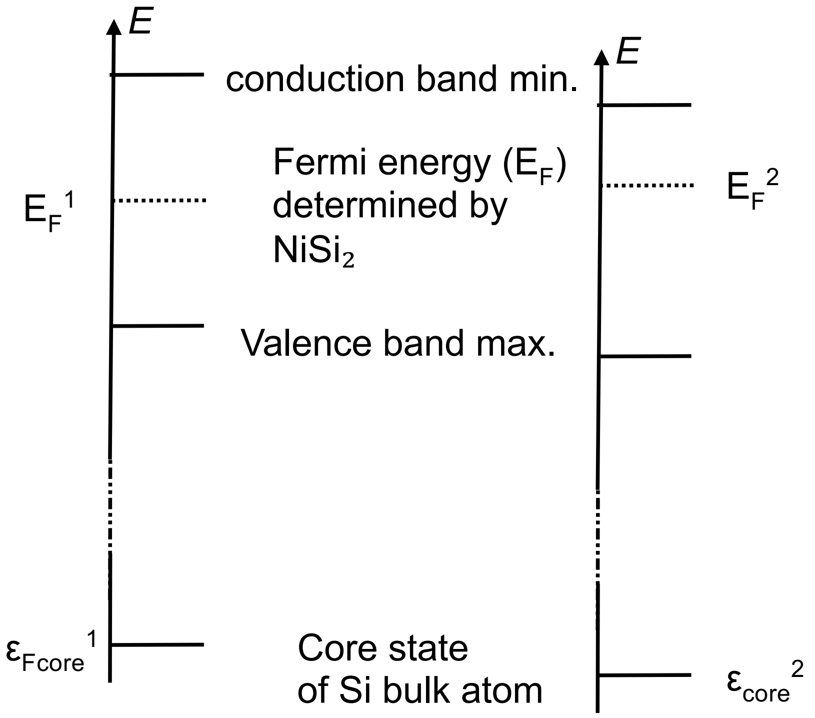
Fermi energy = 4.257 eV

VASP calculations

- GGA-PBE
- ICORELEVEL=1

Schottky barrier height shift - effect of S dopant on $NiSi_2$/Si interface

Variations of the Schottky-Barrier Height (ΔSHB) can be derived from energy shifts of the core states (core level shifts) of bulk Si atoms



E

conduction band min.

E_F^1

Fermi energy (E_F) determined by $NiSi_2$

E_F^2

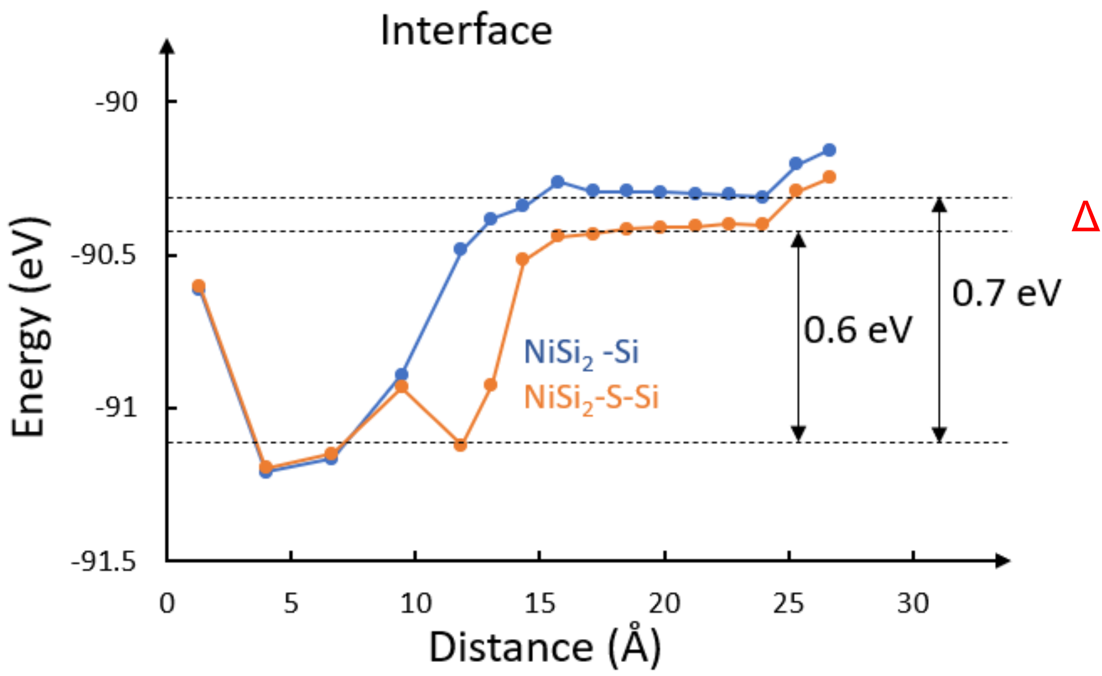
Valence band max.

ε_{Fcore}^1

Core state of Si bulk atom

ε_{core}^2

$$\Delta SBH = \varepsilon_{core}^1 - E_F^1 - (\varepsilon_{core}^2 - E_F^2)$$



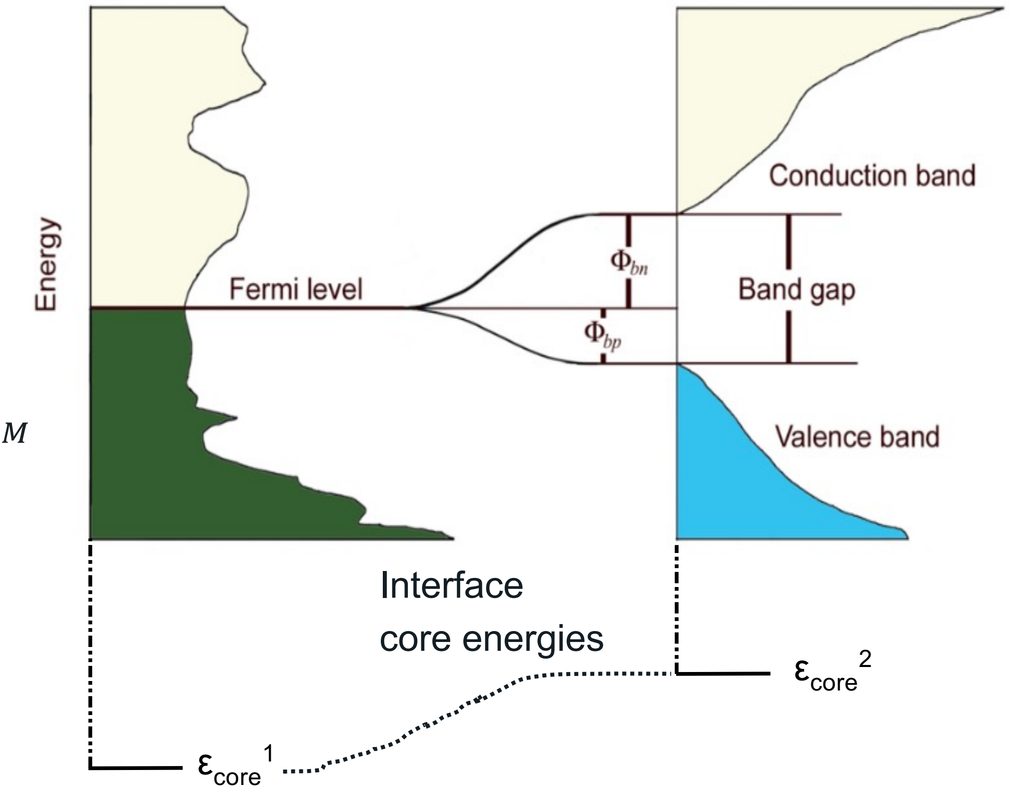
ΔSBH~ 0.1 eV

Q. T. Zhao, etc.,S. “Tuning of NiSi/Si Schotty barrier heights by sulfur segregation during Ni silicidation”, *Appl. Phys. Lett.* 86, 062108 (2005)

How To directly calculate the Schottky barrier

- Bulk semiconductor
  - Perform an accurate band-gap calculation,
    i.e., hybrid functional calculations
  - Add to Input tab:
    `ICORELEVEL=1`
  - Calculate the energy difference between the core level energy $\epsilon_{core}(bulk\ semiconductor)$ and the conduction band minimum E_{CBM}
- Interface
  - Calculate the core level energies $\epsilon_{core}(interface)$ and Fermi energy $E_F(interface)$ of the interface.
  - Identify the $\epsilon^{SC}_{core}\ (interface)$ of atoms in the “bulk” semiconductor region of the interface
- Schottky Barrier $\Delta\ E_{SB}$

$$\Delta\ E_{SB} = E_{CBM} - \epsilon_{core}(bulk\ semiconductor) - [E_F(interface) - \epsilon^{sc}_{core}\ (interface)]$$



Section 2 - summary

- Interface model
- Create and optimize the interface.
- Calculate the core level energies $\epsilon_{core}(interface)$ and Fermi energy $E_F(interface)$ of the interface. (Add to Input tab: ICORELEVEL=1)
- The Schottky barrier at the interface of Si and $NiSi_2$ compares favorably with the experimental data. Additionally, doping with sulfur is found to reduce the barrier by approximately 0.1 eV.
- Atomistic simulations with MedeA have high predictive power in understanding and controlling the contact resistance in electronic devices.

Highlighted *MedeA* Modules

***MedeA* Environment:** with high productivity integrated tools, property prediction using application-specific property modules in conjunction with state-of-the-art simulation engines, reproducible workflows as graphical flowcharts for multi-stage protocols

***MedeA* JobServer & TaskServer:** central unit to manage, monitor, and archive your calculations efficiently and consistently. highly flexible workflow maximizes productivity, on systems with heterogeneous hardware, and different operating systems.

***MedeA* VASP:** Comprehensive access to the VASP code via a graphical user interface (GUI) to set up, run and analyze multi-step VASP calculations

***MedeA* Interface Builder:** Fully Automated search for possible coherent interfaces. Straightforward model construction for subsequent calculation

Related *MedeA* Tutorials/Application Notes

An Introduction to *MedeA* VASP:

Learn how to set up and run *VASP* calculations with *MedeA*

Surface Reconstruction of Si (001):

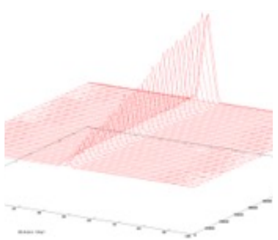
Learn how to set up a *VASP* calculation for the surface reconstruction of Si (001) surface

Calculating the Schottky Barrier Height of a Metal-Semiconductor Interface:

Learn how to calculate the Schottky barrier height at a metal-semiconductor interface with VASP

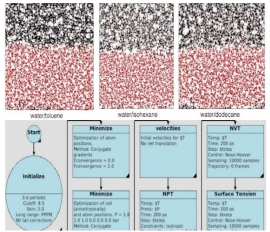
Application note: Prediction of Schottky Barrier in Electronic Devices:

Learn the calculation and modification of the SBH for a NiSi/Si contact



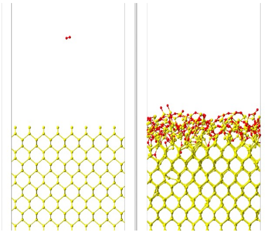
MT, Deformation

Mechanical, Thermal
Plastic deformation



Transport

Diffusion, Viscosity, Thermal conductivity, Surface Tension



Deposition,

Growth, Oxidation, and Etching

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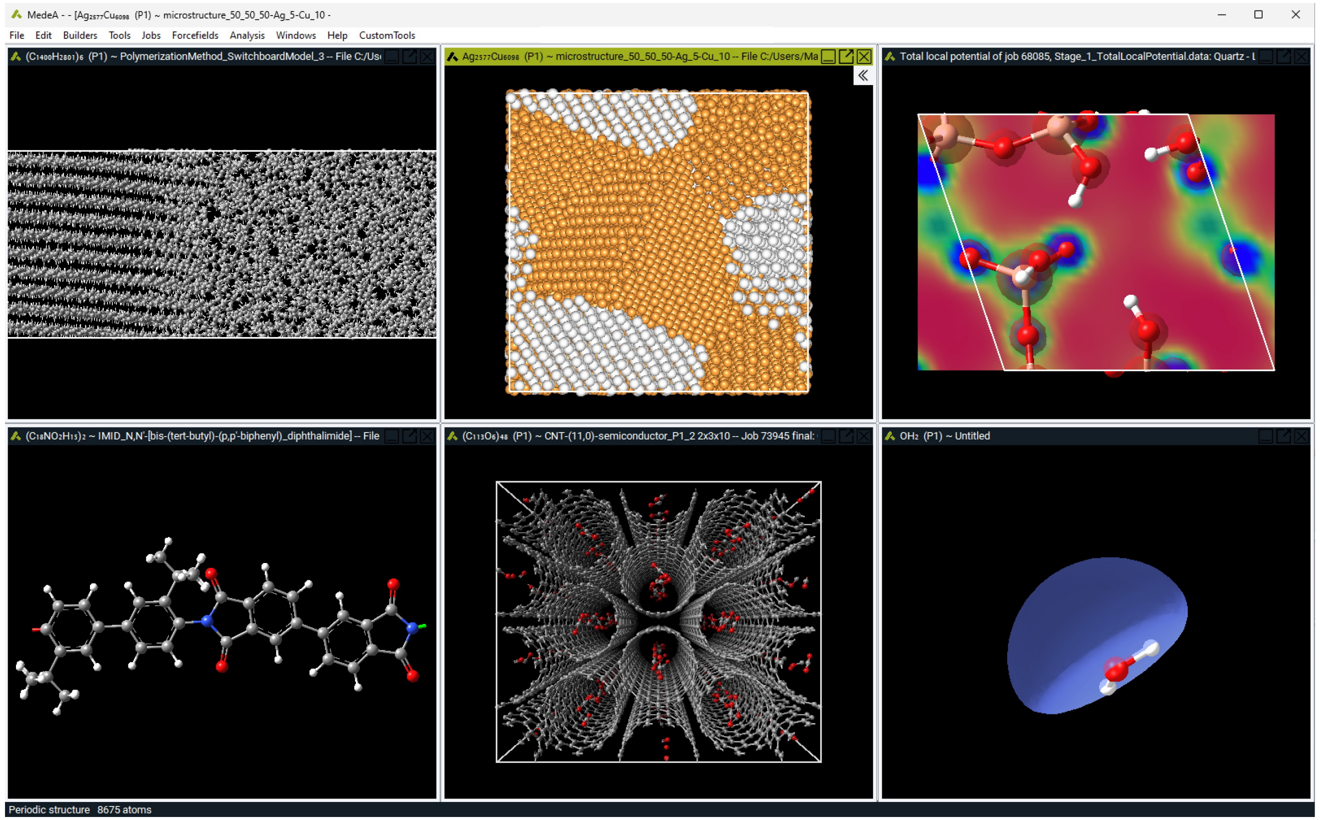
The MedeA 3.8 release features a wide range of enhancements: from machine learning and materials informatics to microstructure construction tools and the latest innovations in density functional theory.

- VASP 6.4.2
- VASP's machine-learning force field (MLFF)
- *MedeA Polymer Expert* (developed in collaboration with Dr Jozef Bicerano, the author of the well-known P3C polymer property method.)
- And more…



www.materialsdesign.com/news
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Question and Answer Session

Dr. Xiaoli Liu

Materials Design

Dr. Shubham Pandey

Materials Design

Questions about Materials Design Webinars

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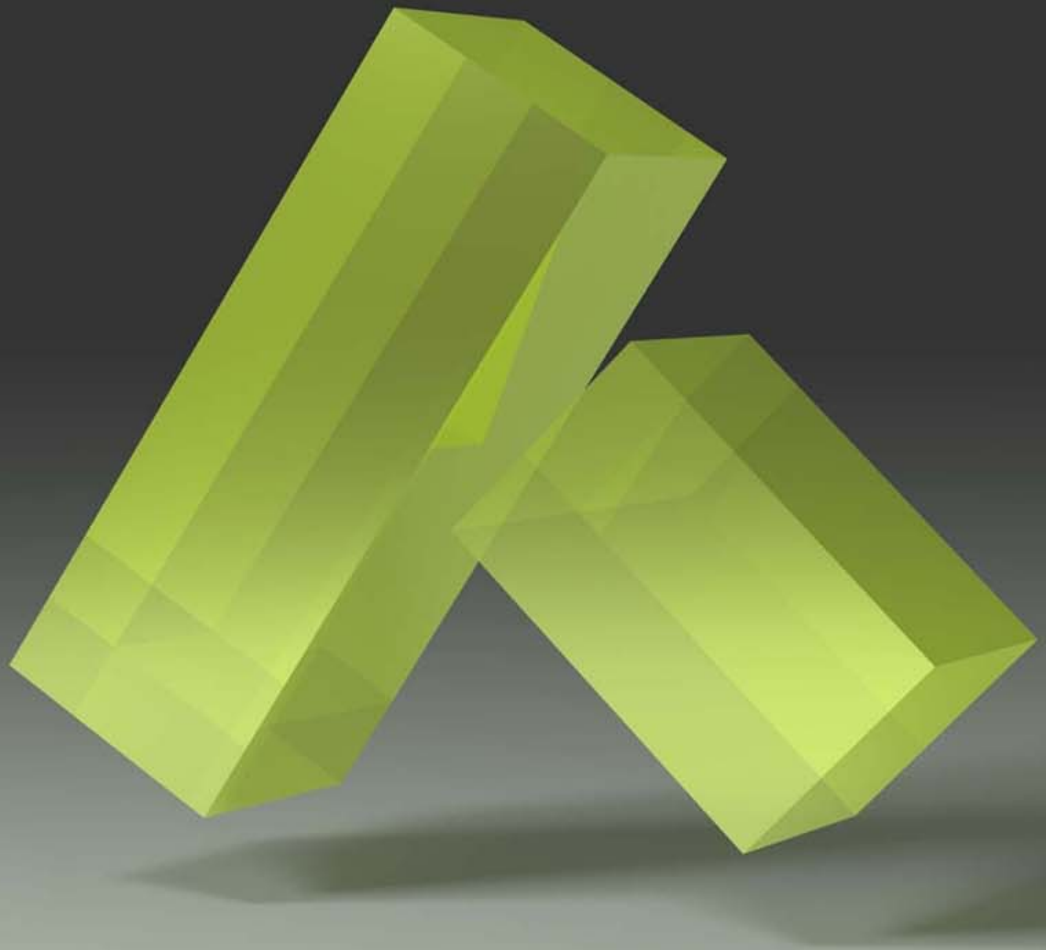

MedeA

Innovation by Simulation