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DPG 2022

Strain-induced bandgap transition in III-V semiconductors

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> Tonner.group

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DFT computational details[1]

- VASP 5.4.4
- $6 \times 6 \times 6$ supercell
- Geometry optimization: PBE + DFT-D3; Bandgap: TB09
- ENCUT: 450 eV (optimization), 350 eV (bandgap)
- Convergency criteria (optimization): 10^{-6} eV (electronic energy); 10^{-2} eVÅ^{-1} (force)
- Convergency criteria (bandgap): 10^{-4} eV (electronic energy); 10^{-2} eVÅ^{-1} (force)
- Spin-orbit coupling during bandgap calculation
- GaAsN: 10 sqs for each composition and strain point

[1] P. Rosenow et al., *Phys. Rev. B* **97**, 075201 (2018).

Binary experimental verification *

System	Eqm. E_g (eV)		Isotropic DIT (%)		Transition	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Si	1.19	1.12	–	–	–	–
GaP	2.36	2.26	–	–	–	–
GaAs	1.47	1.42	-1.56	-2.10	$\Gamma \rightarrow$ L	$\Gamma \rightarrow$ X
GaSb	0.64	0.73	-1.00	-0.70	$\Gamma \rightarrow$ L	$\Gamma \rightarrow$ L
InP	1.43	1.34	-4.40	-3.51	$\Gamma \rightarrow$ X	$\Gamma \rightarrow$ X
InAs	0.36	0.35	-7.41	-6.84	$\Gamma \rightarrow$ X	$\Gamma \rightarrow$ X
InSb	0.03	0.17	-5.18	-3.09	$\Gamma \rightarrow$ L	$\Gamma \rightarrow$ X

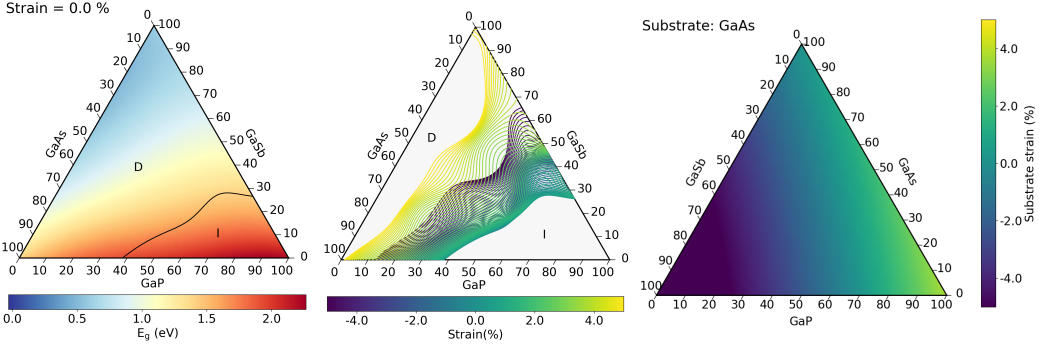
* B. Mondal, R. Tonner-Zech, arXiv:2208.10596 (2022)

Ternary experimental verification

System	Substrate	x (%)	E_g (eV)	exp. E_g (eV)
$GaAs_{1-x}P_x$ [1]	GaAs	20	1.66 (D)	1.66 (D)
		25	1.72 (D)	1.72 (D)
		28	1.74 (D)	1.76 (D)
$GaP_{1-x}Sb_x$ [2]	GaP	14	1.70 (I)	1.61 (I)
	GaAs	14	1.43 (I)	1.61 (I)
		29	1.41 (I)	1.39 (I)
		32	1.39 (D)	1.31 (D)
	GaSb	93	0.61 (D)	0.73 (D)

[1] Strömberg *et al., J. Crys. Growth* **540**, 125623 (2020)
[2] M.J. Jou *et al., App. Phys. Lett.* **52**, 549 (1988)

Quaternary


Strain = 0.0 %
GaAs
GaSb
GaP
D
I
E_g (eV)
Strain(%)
Substrate: GaAs
Substrate strain (%)

Bloch spectral weight

$$|\vec{K}m\rangle = \sum_{i=1}^{N_{\vec{K}}} \underbrace{w(\vec{k}_i, n; \vec{K}, m)}_{\text{contribution of } |\vec{k}_i n\rangle \text{ to SC eigenstate } |\vec{K}m\rangle} |\vec{k}_i n\rangle \Rightarrow \sum_{i=1}^{N_{\vec{K}}} \sum_{n} w(\vec{k}_i, n; \vec{K}, m) |\vec{k}_i n\rangle$$

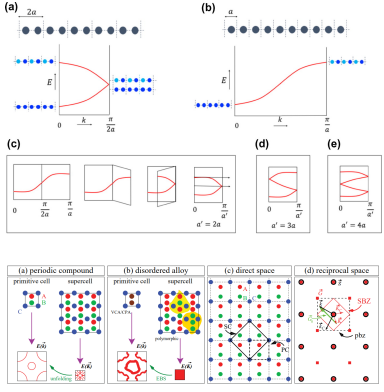
- $w(\vec{k}_i, n; \vec{K}, m) = |\langle \vec{K}m | \vec{k}_i n \rangle|^2$
- Spectral weight: fold2Bloch[2]

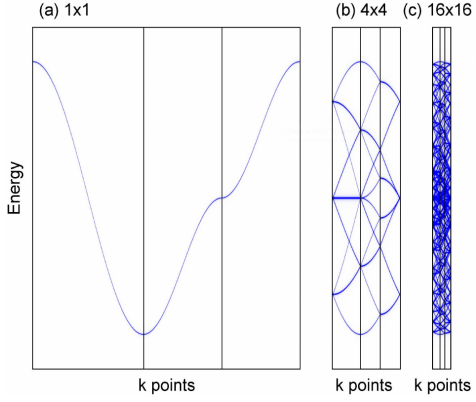
$$P_{\vec{K}m}(\vec{k}_i) = \sum_{n} |\langle \vec{K}m | \vec{k}_i n \rangle|^2 = \sum_{\vec{g}} |C_{\vec{K}m}(\vec{g} + \vec{k}_i - \vec{K})|^2$$

$$\Psi_{\vec{K}m}(\vec{r}) = |\vec{K}m\rangle = \sum_{\vec{G}} C_{\vec{K}m}(\vec{G})\, e^{i(\vec{K}+\vec{G})\cdot\vec{r}}$$

[2] https://github.com/rubel75/fold2Bloch-VASP.

Band (un)folding[1,2,3]

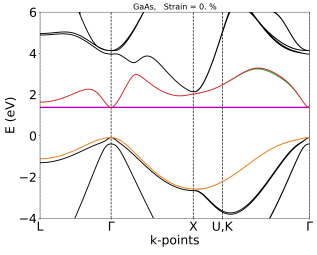


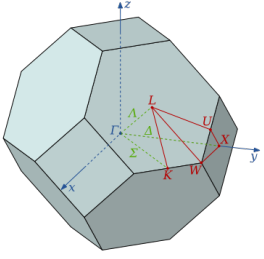


[1] S.-Y. Yang *et al.*, *Adv. Phys.-X* **3**, 1414631 (2018).
[2] W. Ku *et al.*, *Phys. Rev. Lett.* **104**, 216401 (2010).
[3] V. Popescu, A. Zunger, *Phys. Rev. B* **85**, 085201 (2012).

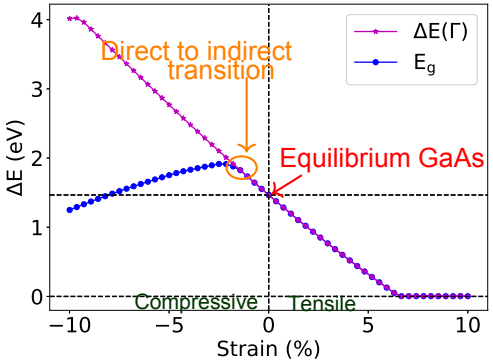
BW $\rightarrow$ CB

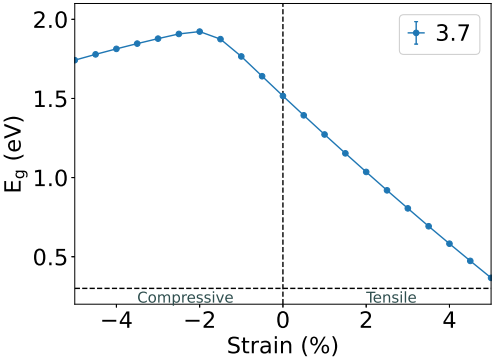
- Γ^f point: [0.0000 0.0000 0.0000]
  - Γ: [0.0 0.0 0.0]
  - L: [0.0 0.0 0.5], [0.0 0.5 0.0], [0.5 0.0 0.0], [0.5 0.5 0.5]
  - X: [0.0 0.5 0.5], [0.5 0.0 0.5], [0.5 0.5 0.0]



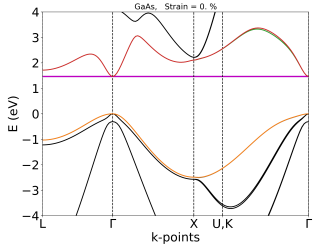


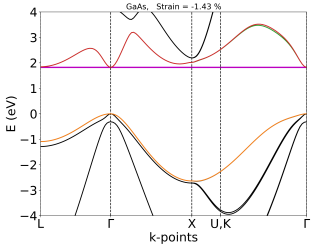
Revisit: GaAs, $GaAs_{0.963}P_{0.037}$ [100] isotropic strain

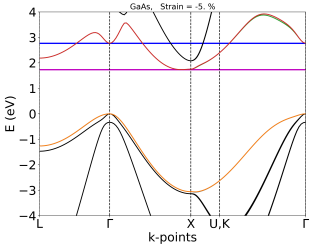




GaAs isotropic strain: BW=(Γ:L:X)

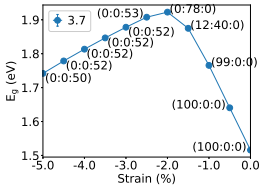


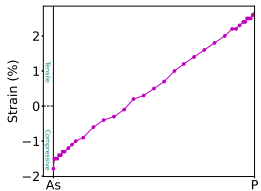


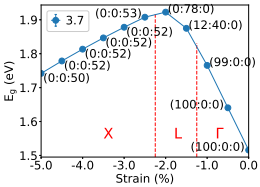


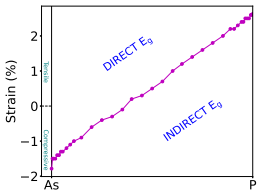
$BW_\Gamma:BW_L:BW_X$ = 100:0:0 $BW_\Gamma:BW_L:BW_X$ = 50:50:0 $BW_\Gamma:BW_L:BW_X$ = 0:0:100

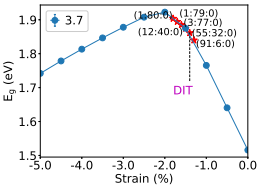
$GaAs_{1-x}P_x$ isotropic strain: BW=(Γ:L:X)

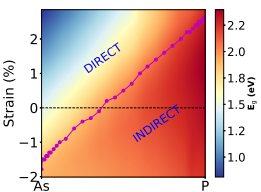




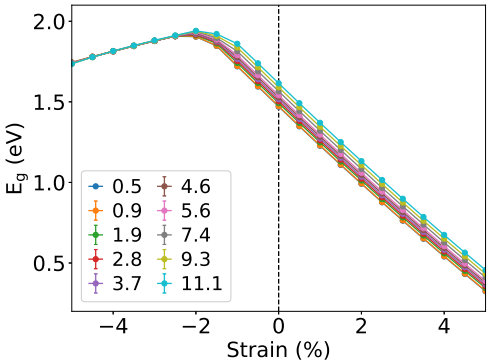


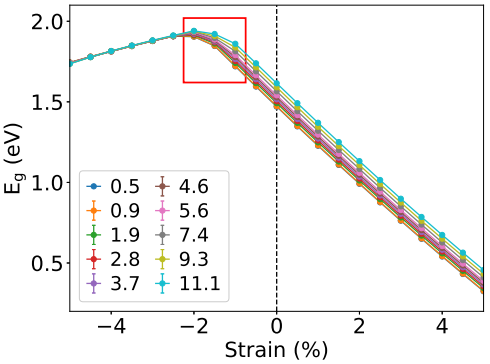




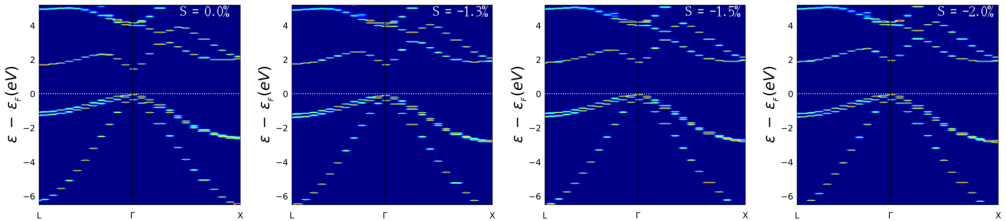


GaAsP isotropic strain: Bandgap variation

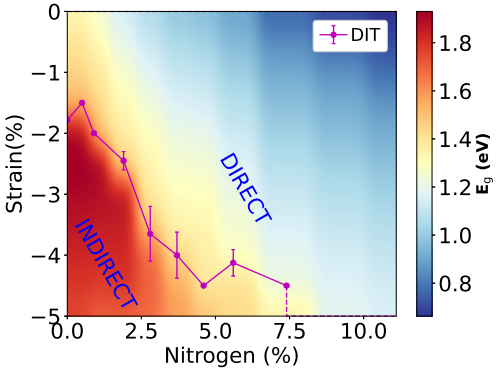




$Ga(As_{0.963}P_{0.037})$ bandstructures, isotropic strain

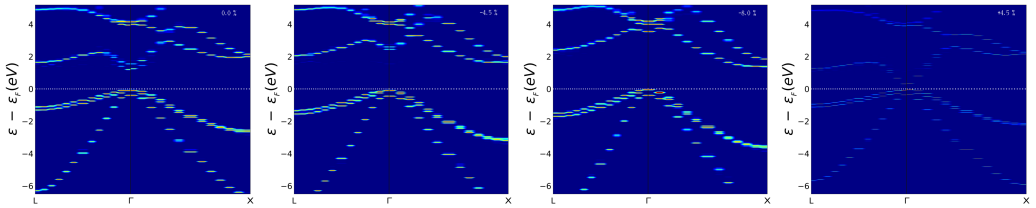


Ga(AsN) isotropic strain bandgap phase diagram

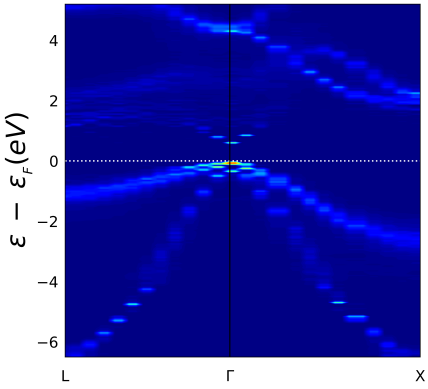


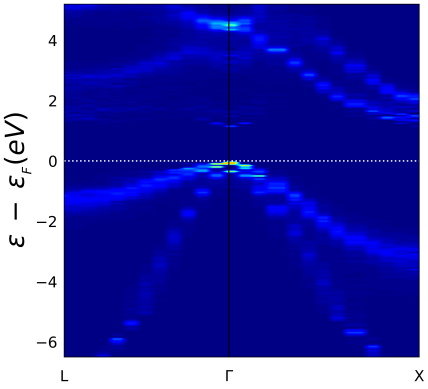
- No transition within ± 5% biaxial strain

GaAsN: 0.5% N bandstructure, isotropic strain

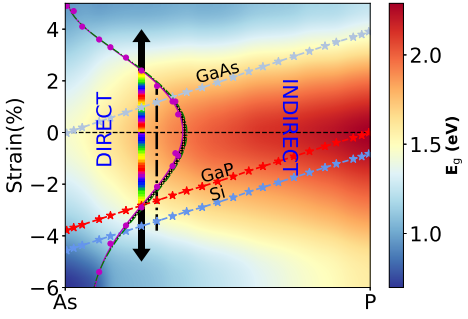


GaAsN: 11.1% N, S0, S-5 bandstructure, isotropic strain

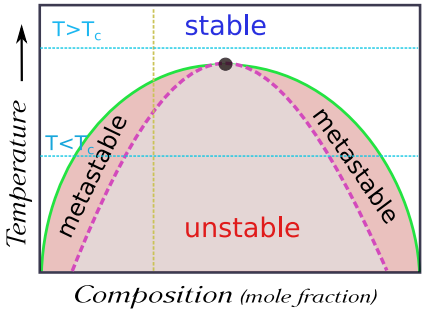




Significance



Bandgap phase diagram



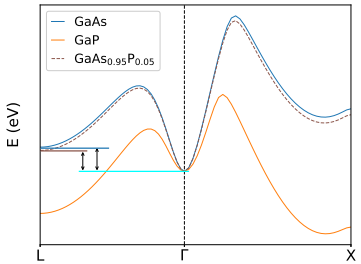
Compositional phase diagram

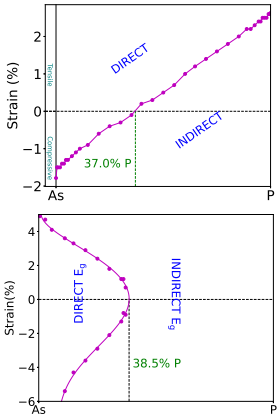
- Bandgap phase diagram: **What do you want to grow?**
- Thermodynamic (+ kinetics) phase diagram: **Can you grow?**

Ternary DIT Assumptions/ Errors/ Limitations

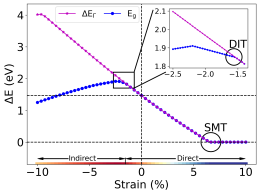
- Statistical error: Finite resolution (in strain and conc.), SQS
- Inherent error: Effective Bloch weight.
- Uncertainty in exact DIT: $BW_G = BW_L$
  - BW_G: BW_L = 40:60 vs 60:40
  - Cutoff criteria for minimum BW %
- k-point error: DIT at other k-point
- BW's directional dependency in L and X point (biaxial strain)
- Energetically closely spaced bands: Average, Near flat bands
- Extremely sparse BWs in bands
- Not generizable to higher(lower) bands other than CB(VB)

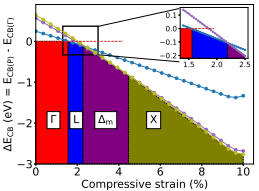
Binary approximation: Ga(AsP)

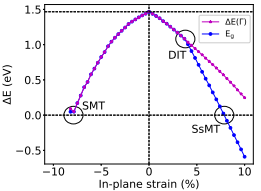


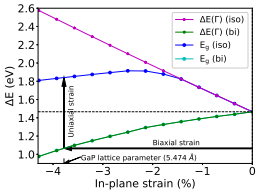


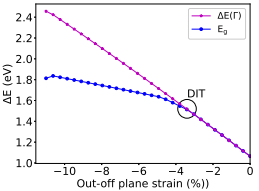
GaAs system summary

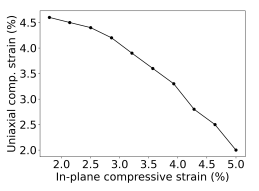












Binary systems

System	Transition	Transition path (iso)	Transition path (bi)
Si	IDT	$\Delta_m \rightarrow$ L $\rightarrow \Gamma$ (t)	$\Delta_m \rightarrow$ K $\rightarrow$ L (c)
GaP	IDT	$\Delta_m \rightarrow$ L $\rightarrow \Gamma$ (t)	$\Delta_m \rightarrow$ L (c)
GaAs	DIT	$\Gamma \rightarrow$ L $\rightarrow \Delta_m \rightarrow$ X (c)	$\Gamma \rightarrow \Delta_m$ (t)
GaSb	DIT	$\Gamma \rightarrow$ L $\rightarrow \Delta_m$ (c)	$\Gamma \rightarrow \Delta_m$ (t)
InP	DIT	$\Gamma \rightarrow$ X (c)	$\Gamma \rightarrow \Delta_m$ (t)
InAs	DIT	$\Gamma \rightarrow$ X (c)	$\times$
InSb	DIT	$\Gamma \rightarrow$ L $\rightarrow \Delta_m$ (c)	$\times$

System	Si	GaSb	GaAs	GaP	InSb	InAs	InP
T1 (%) §	$\sim 15^{@}$	2.85	6.67	$\sim 13^{@}$	0.34	2.10	8.20
T2 (%) ¶	10.31 (t)	1.00 (c)	1.56 (c)	2.63 (t)	5.18 (c)	7.41 (c)	4.40 (c)
T3 (%) □	$\times$	3.71 (t)	3.52 (t)	$\times$	$\times$	$\times$	7.66 (t)

't' and 'c' in brackets indicate to tensile and compressive strain, respectively.

@ Linear extrapolation

§ Semiconductor to metal transition under isotropic tensile strain

¶ Direct to indirect (DIT) or indirect to direct (IDT) transition under isotropic strain.

□ DIT or IDT transition under bi-axial strain

Machine Learning (ML)

$$\text{System } \underbrace{(\text{composition, strain})}_{\text{features}} \xrightarrow[\text{Supervised ML}]{\text{DFT}} \underbrace{\text{Bandgap } (E_g), \text{ Nature}}_{\text{labels/predictions}}$$

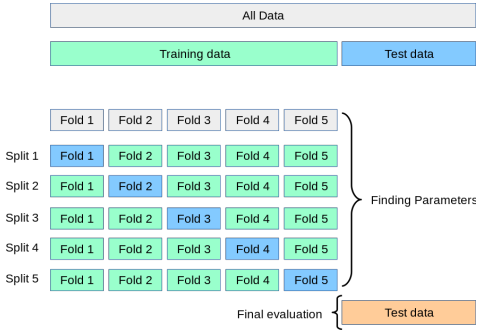
- Informations $\xrightarrow[\text{cross-validation, metric, evaluation}]{\text{training, testing}}$ Learning $\rightarrow$ Prediction
- Hyperparameters tuning (e.g. Grid search cross validation)
- Ga(AsPSb) $\Leftrightarrow$ GaAsP, GaPSb, GaAsSb
  - Biaxial strain

ML models

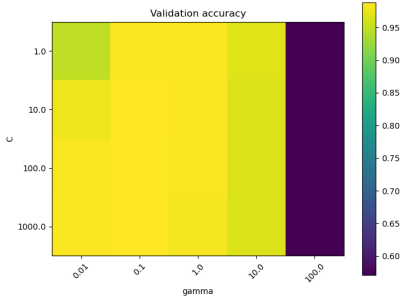
- Support Vector Machine (SVM)**,††
- Kernel function: Radial Basis Function (rbf)
- Bandgap nature: Support Vector Classification (SVC), Binary
- Bandgap: Support Vector Regression (SVR)
- Hyperparameters tuning: Grid search cross validation
  - Regularization parameter (C): squared l2 penalty, Regularization $\propto \frac{1}{C}$
  - Kernel coefficient (γ)
  - C: [1,10,100,1000]; γ: [0.01,0.1,1,10,100]
- Bandgap SVR: [100, 0.1]; Nature SVC: [100, 1]

Z. Zhu *et al.*, *Chinese Physics B* **29, 046101 (2020).
††Y. Huang *et al.*, *J. Mater. Chem. C* **7**, 3238–3245 (2019).

Hyperparameters tuning

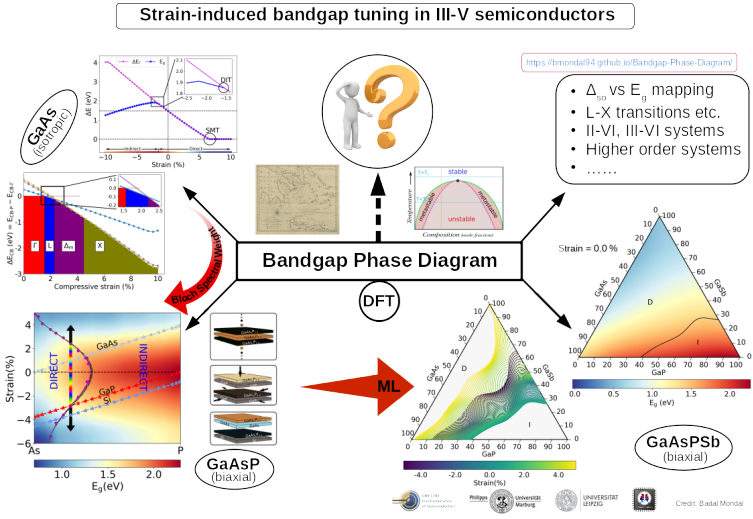


Cross validation‡‡



Grid search (GaAsPSb SVR)

‡‡ https://scikit-learn.org/stable/modules/cross_validation.html.


Strain-induced bandgap tuning in III-V semiconductors
https://bmondal94.github.io/Bandgap-Phase-Diagram/
• Δ_{so} vs E_g mapping
• L-X transitions etc.
• II-VI, III-VI systems
• Higher order systems
• ……
GaAs (isotropic)
DFT
SMT
Strain (%)
Bandgap Phase Diagram
DFT
Pikus-Bir Spectral Weight
ML
stable
unstable
Strain = 0.0 %
GaAs
GaP
GaSb
D
I
E_g (eV)
Strain(%)
DIRECT
INDIRECT
GaAsP (biaxial)
GaAsPSb (biaxial)
Credit: Badal Mondal