Computics Approach to Development of the Next-Generation Semiconductor Science

- Importance of energy-saving semiconductor technology in sustainable society
  - Power electronics, Non-volatile memories
  - Necessity of quantum-theory based calculations
- Computics: present capability of calculations based on density-functional theory (DFT)
  - On current massively parallel computer architecture not with accelerators yet
- Mechanism of the flash memory: Nitrogen vacancy (V_N) in Silicon Nitride
  - Floating state distributed in internal space in the host sparse material
  - Multiple charge states which store multi-electrons around V_N

[F. Nanataki, K. Shiraishi & A. Oshiyama: Phys. Rev. B (2022)]

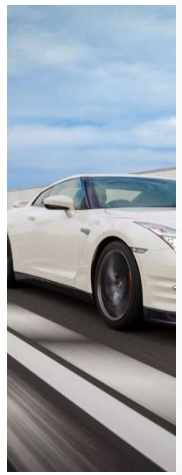
Life and Electron Devices

PCs

Mobile

Networking

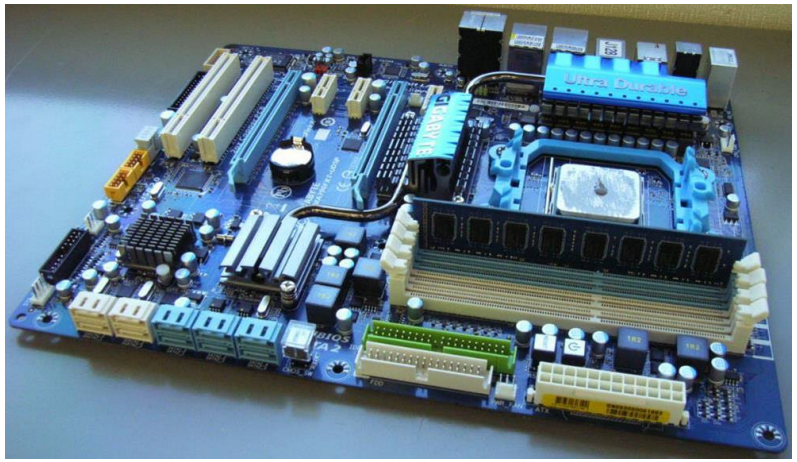
Cloud



Autom

https://weekly.ascii.jp/elem/000/002/629/2629133/

Electron Device

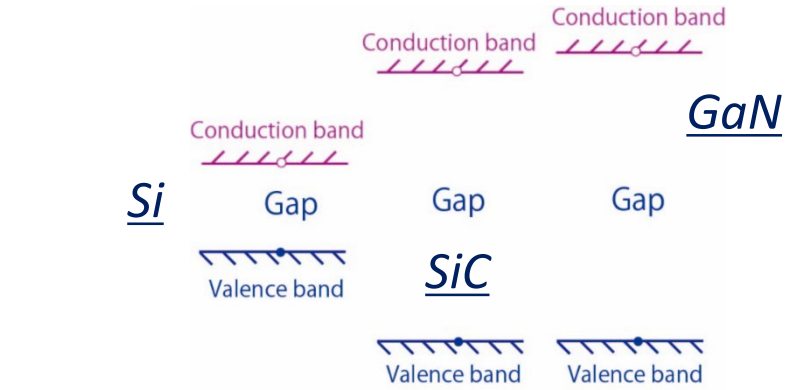


Assembly of CPU, Memory, NAND Flash ….

The material is Si

However, for energy saving society, *HEAT* is the problem

Wide Bandgap Semiconductors such as GaN or SiC Save Energies



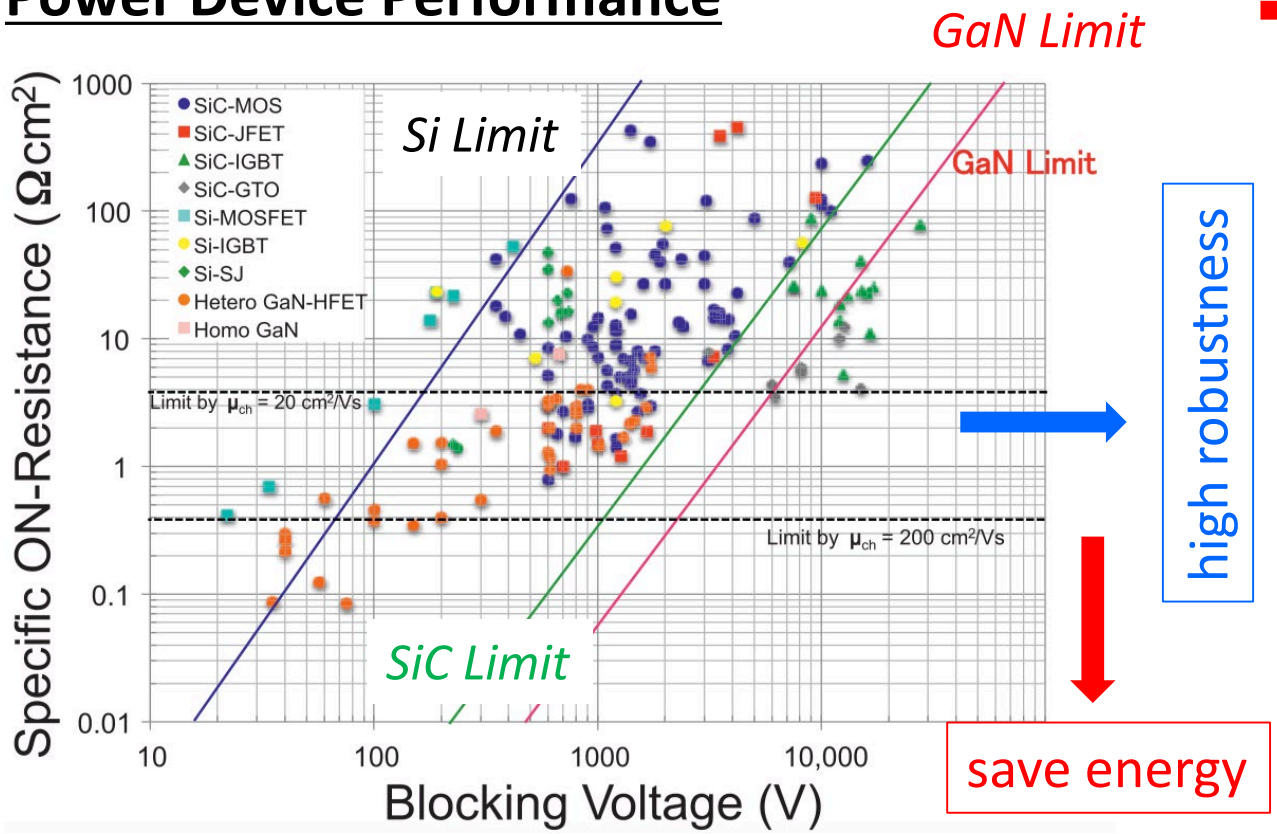

Tokyo Metro


Shinkansen


Automobile

However, the device performance is much lower than expected

Power Device Performance

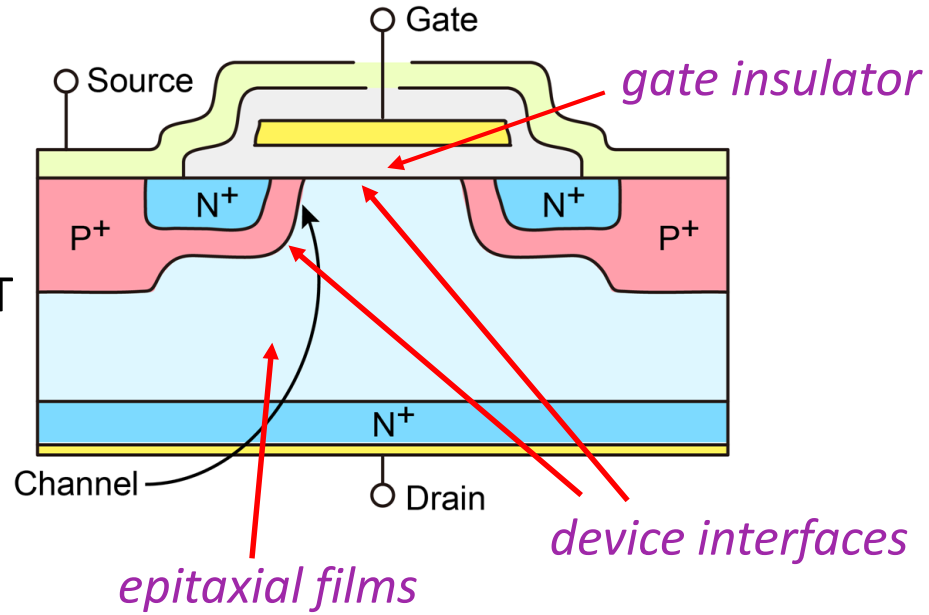


high robustness

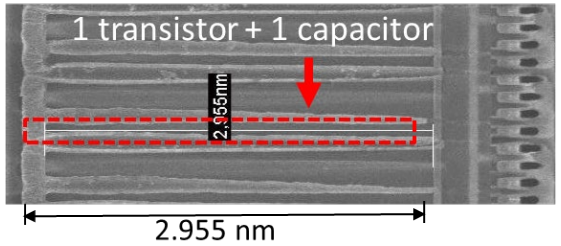
save energy

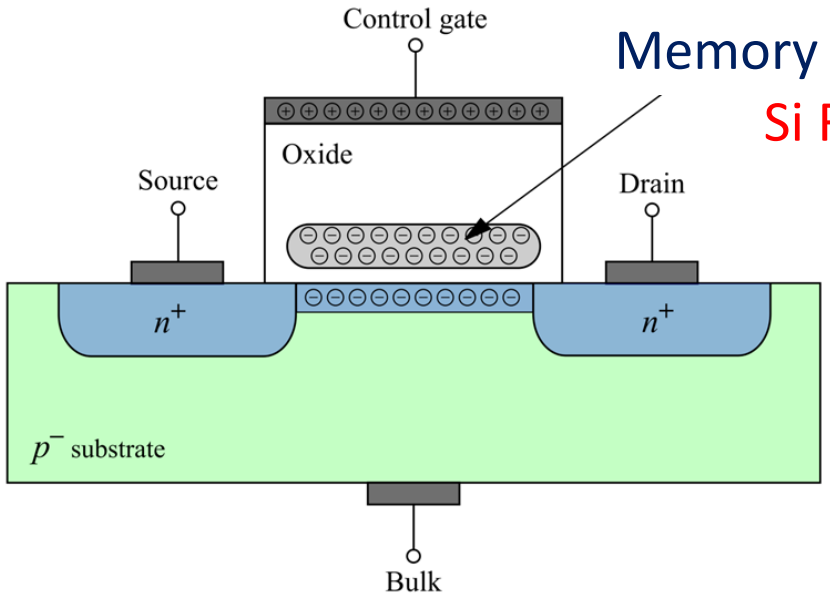
Fabrication Processes should be Optimized

Vertical MOSFET



Non-Volatile Flash Memory





Memory Cell= Charge Storing Space

Si Floating Gate → SiN

- Requirement of Integration
- Multi-Level Cell

What is the memory cell in SiN?
What is the localized electron state there?
Physics is unknown.

NEED: *Accurate Large-Scale Calculations Based on Quantum Theory for 10,000 – 100,000-Atom Systems*

Equations in Density-Functional Theory (DFT)

Hohenberg, Kohn: PR 136, B864 (1964)

- Total Energy of a material: $E[n] = \int v_{\mathrm{nucl}}(r) n(r) dr + T[n] + \frac{1}{2} \iint \frac{n(r) n(r')}{|r - r'|} dr dr' + E_{XC}[n]$

  is a functional of the electron density, *universal functional*

$$n(r) = N \int |\Psi(r, r_2, r_3, r_4, \cdots r_N)|^2 \, dr_2 dr_3 \cdots dr_N$$

- Euler equation: $\frac{\delta E[n]}{\delta n} = \mu$

Kohn, Sham: PR 140, A1133 (1965)

Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}(\mathbf{r}; n(\mathbf{r})) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

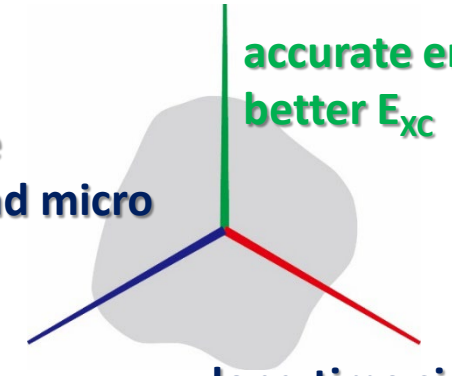
$$v_{\mathrm{eff}}(\mathbf{r}) = v_{\mathrm{nucl}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})}$$

Car, Parrinello: PRL 55, 2472 (1985)

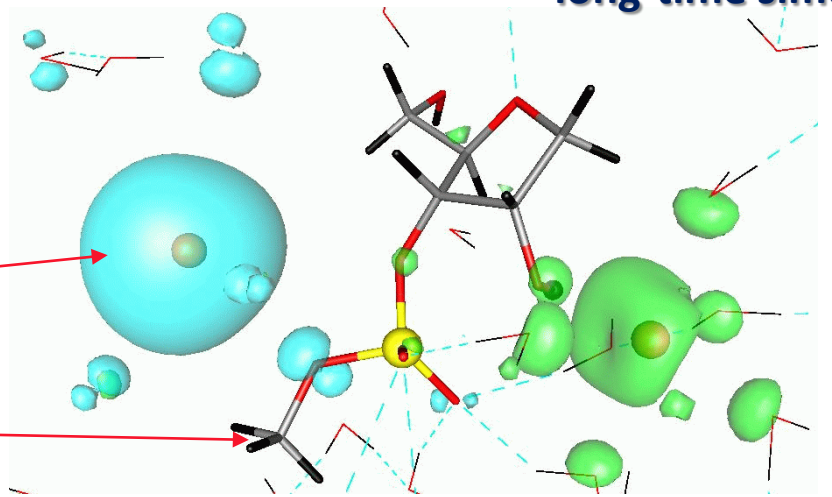
Car-Parrinello Molecular Dynamics equation

$$\mu \ddot{\varphi}_i = -\delta E / \delta \varphi_i^* + \sum_j \Lambda_{ij} \varphi_j$$

$$M_I \ddot{\mathbf{R}}_I = -\partial E_{DFT} / \partial \mathbf{R}_I$$



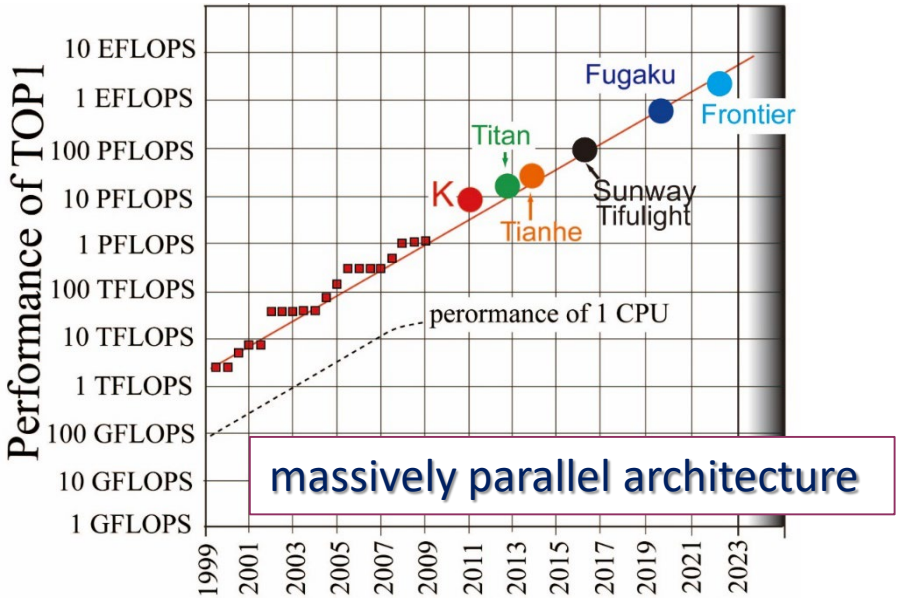
long-time simulation



Need Cross-Disciplinary Approach (Computics) between Physics/Chemistry and Computer Science & Technology

http://computics-material.jp/index.html

Theoretical Performance of TOP1 Supercomputer



Computics:

Collaboration between Physics/Chemistry & Computer Science

methodology and algorithms suitable to current architecture

Our real-space scheme: RSDFT code

https://github.com/j-iwata/RSDFT

All the quantities such as n(r), v(r) etc computed at each real-space mesh points, leading to that Fourier Transform is essentially unnecessary.

Currently,

- ✓ 100,000-atom DFT calculations for Si-Nanowire FET (2011 Gordon-Bell Prize)
- ✓ 10,000-atom DFT calculations with semilocal approximations (LDA/GGA) to E_{XC} feasible
- ✓ 1,000-5,000-atom calculations with hybrid approximation also feasible
- ✓ CPMD simulations for 1000 – 3000 atom systems up to nano seconds feasible

A Recent Example: Epitaxial Growth of Power Semiconductor GaN

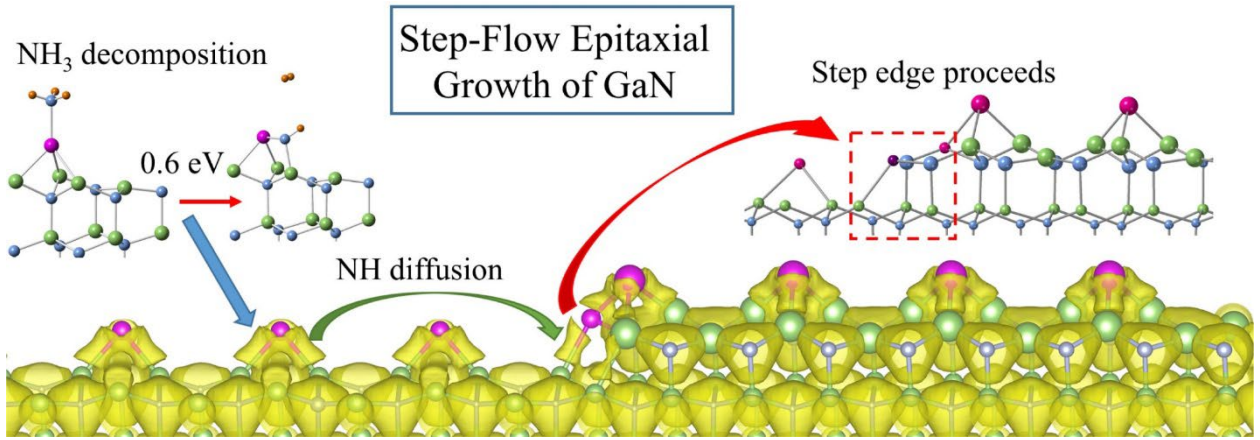
Bui, Boero, Shiraishi, Oshiyama: J. Phys. Chem C (2017); J. Cryst Growth (2019); JJAP (2020); Appl Surf Sci. (2021, 2022)

DFT calculations has revealed:

Gas Source NH_3 decomposed on the growth surface

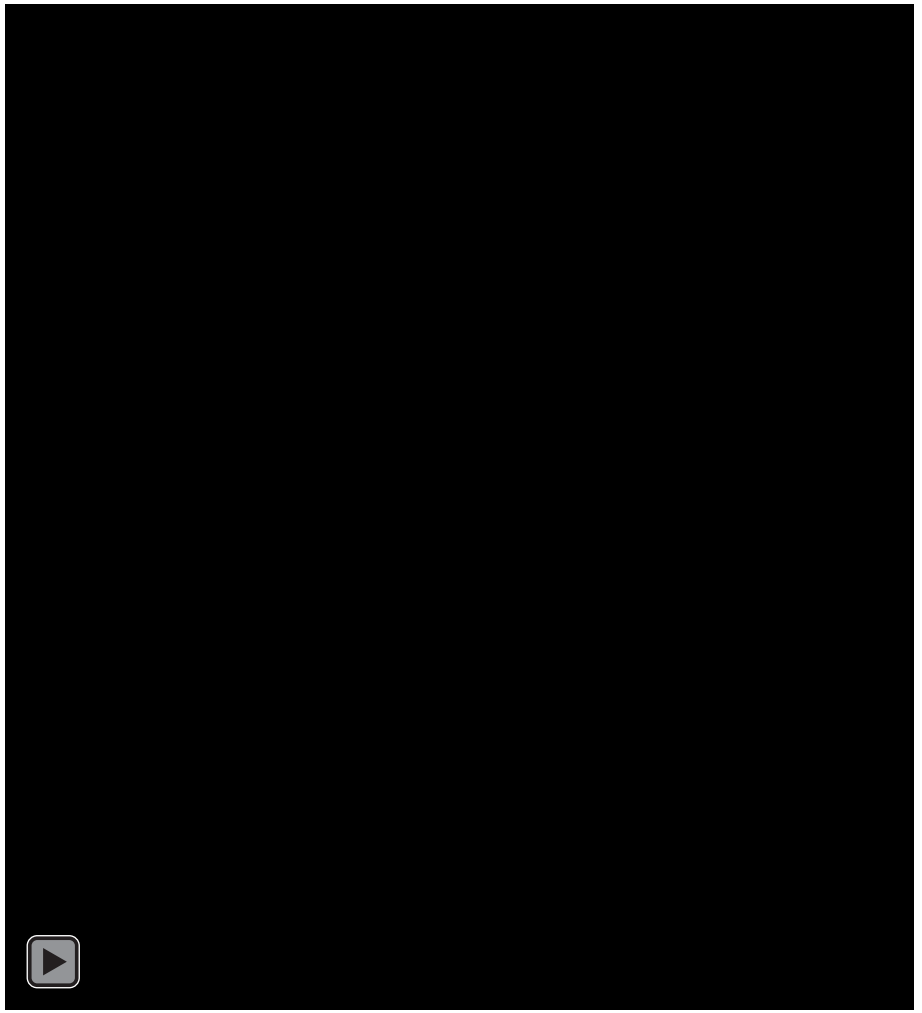
→ Resulting NH diffusing to the surface step-edges

→ NHs at the edge incorporated to the GaN film



However, real growth surface seems to be a *liquid* at growth temperature 1300 K.

Car-Parrinello Molecular Dynamics



Ga adatom

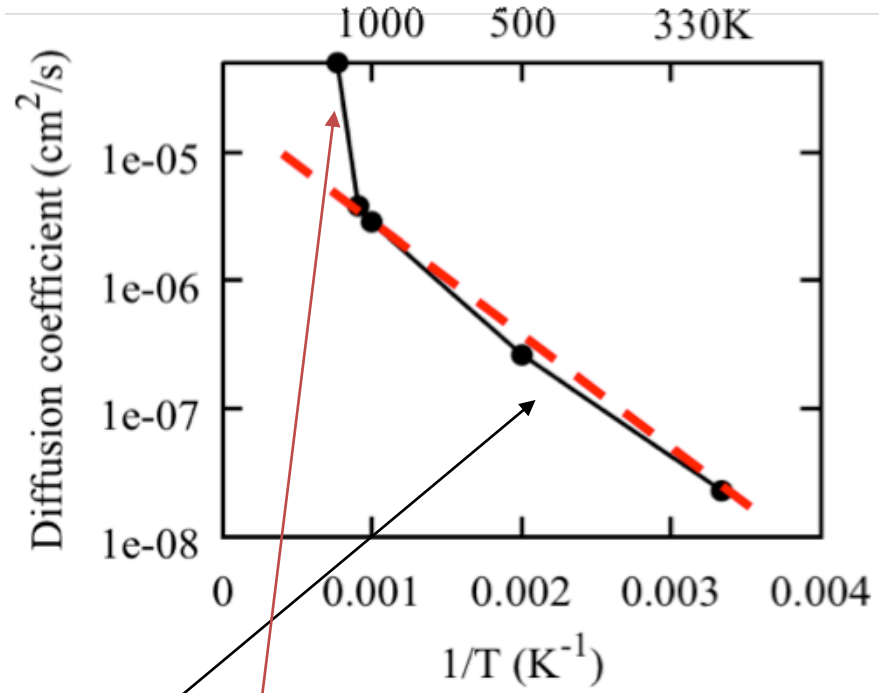
Ga

Subsurface N

2-Dimensional Liquid Phase of Ga Adatom at Growth Temperature

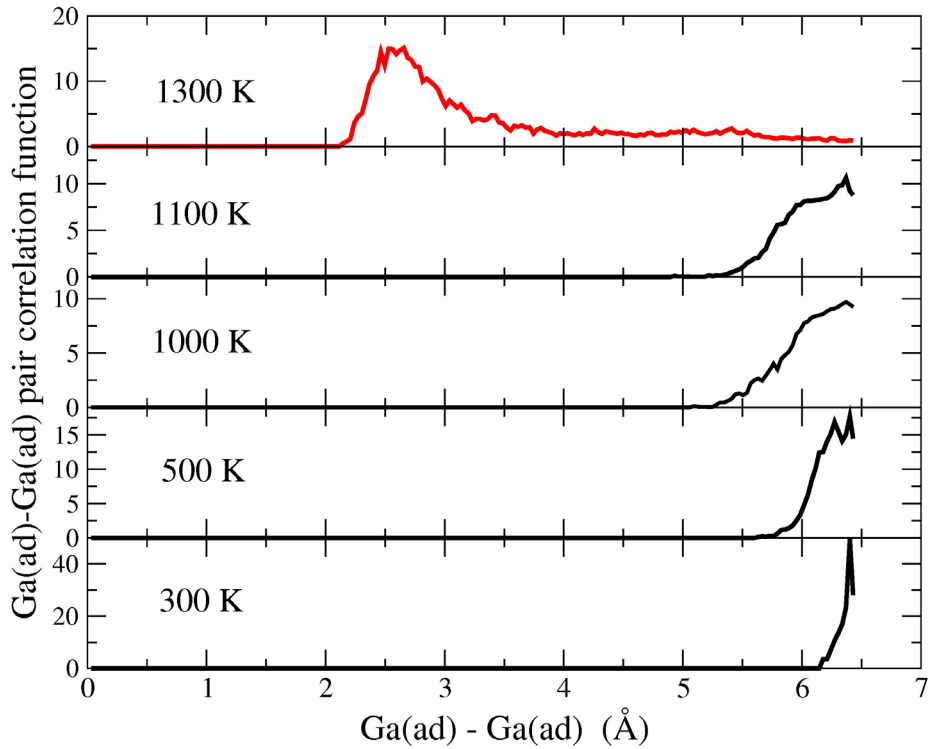
Diffusion Coefficient *D* of Ga adatom on GaN(0001)

$$D = \frac{1}{3}\int_0^{t\to\infty} \left\langle \frac{1}{N}\sum_{I=1}^{N} \mathbf{v}_I(t)\mathbf{v}_I(0) \right\rangle dt$$



- ✓ Arrhenius behavior with 0.28 eV barrier at low temperature
- ✓ Sudden increase in *D* at 1300 K by an order

Pair correlation function of Ga adatom on GaN(0001)



- ✓ At low temperature, peak at 6 Å, characteristic to the adsorption structure
- ✓ At 1300K, peek at 2.6 Å, characteristic to Ga-Ga bond

Further Efforts to Larger-Scale Calculations: Order N Scheme

- ✓ Current scheme of DFT (Kohn-Sham Scheme) scales as cube of the target size N, $O(N^3)$
- ✓ But solving Euler equation in DFT costs $O(N)$ in itself, if we get rid of the orbitals $\{\varphi_i(\mathbf{r})\}$

$$\begin{cases} \left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r};\, n(\mathbf{r}))\right]\varphi_i(\mathbf{r}) = \varepsilon_i\,\varphi_i(\mathbf{r}) \quad (i=1 \sim O(N)) \\ v_{\text{eff}}(\mathbf{r}) = v_{\text{nucl}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{\text{XC}}[n]}{\delta n(\mathbf{r})} \end{cases} \longrightarrow \frac{\delta T_s[n]}{\delta n(r)} + v_{\text{nucl}}(r) + \frac{\delta E_{\text{H}}[n]}{\delta n(\mathrm{r})} + \frac{\delta E_{\text{XC}}[n]}{\delta n(r)} = \mu$$

- ✓ $\{\varphi_i(\mathbf{r})\}$ is unnecessary if we know the functional form of the kinetic energy

$$T_s[n] = \int \tau^{\text{TF}}(r)\,F[n]\,dr \longrightarrow \textbf{Orbital-Free DFT (OFDFT)}$$

Enhancement factor

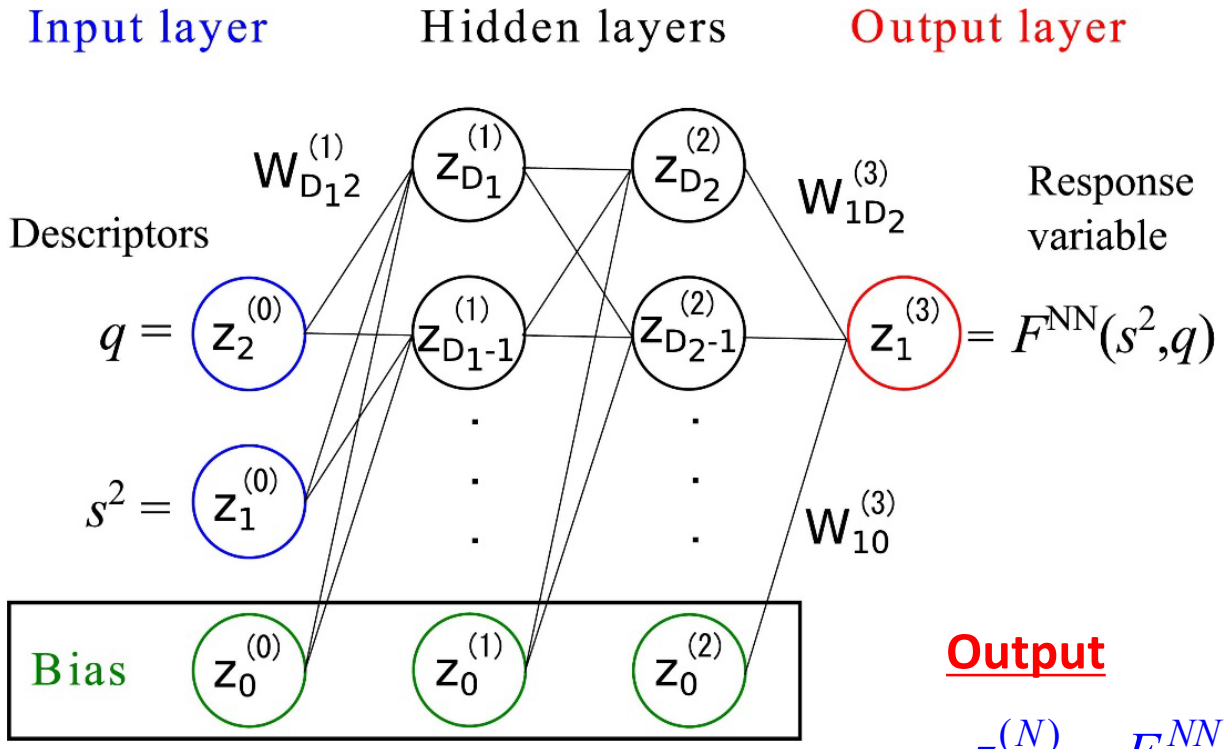
- ✓ We rely on the Neural Network to develop $T_s[n]$

Imoto, Imada, Oshiyama:
Phys Rev Research 3, 033198 (2021)

$$T_s[n] = \int \tau^{\mathrm{TF}}(r)\, F^{\mathrm{NN}}(r;n)\, dr$$

Neural-Network Training

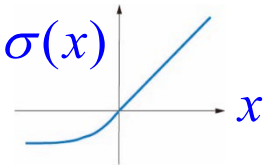
$$L = \frac{1}{N_t}\sum_{m=1}^{N_t}\frac{1}{2}\left[\frac{\delta T_s^{NN}[n]}{\delta n}(r_m) - \frac{\delta T_s^{KS}[n]}{\delta n}(r_m)\right]^2$$



(In the present computation, # hidden layers=3, # neurons per layer =3)

Output from j-th neuron in l-th layer:

$$z_j^{(l)} = \sigma^{(l)}(a_j^{(l)})$$



Input $a_j^{(l)}$ is the output from the previous layer: $a_j^{(l)} = \sum_{k=0}^{D_{l-1}} W_{jk}^{(l)} z_k^{(l-1)}$

Descriptors

$$z_1^{(0)} = s = |\nabla n| \Big/ \left[2(3\pi^2)^{1/3} n^{4/3}\right]$$

$$z_2^{(0)} = q = \nabla^2 n \Big/ \left[4(3\pi^2)^{2/3} n^{5/3}\right]$$

Output

$$z_1^{(N)} = F^{NN}(s^2,q) = \sum_{i=0}^{D_N} W_{1i}^{(N)} \sigma\left(\sum_{j=0}^{D_{N-1}} W_{ij}^{(N-1)} \sigma\left(\sum_{k=0}^{D_{N-2}} W_{jk}^{(N-2)} \sigma(\cdots)\right)\right)$$

Prepare $n(r), s(r)$ ***and*** $q(r)$ ***from the training data (in carbon diamond).***

→ ***Construct F as functionals of n, q and s with the NN parameters*** $W_{ij}^{(l)}$.

→ ***Train the NN (optimize NN parameters*** $W_{ij}^{(l)}$ ***) so as to minimize the cost function L***

TABLE V. Comparison of equilibrium lattice constant (a_0) in Å and bulk moduli (B_0) in GPa obtained by NN and NN[bare] with those obtained by different approximations to KEDF. Numbers in the parentheses are the relative errors in % with respect to the KS values. In β-tin Si, the ratio of another lattice constant c_0 to a_0 (c_0/a_0) is also listed. Some values are left as blanks because the total energy monotonically decreases with respect to the volume expansion.

	diamond		ds-Si		fcc-Si		β-tin Si			3C-SiC		bcc-Li		fcc-Al	
	a_0	B_0	a_0	B_0	a_0	B_0	a_0	c_0/a_0	B_0	a_0	B_0	a_0	B_0	a_0	B_0
NN	3.428	411	5.367	85.4	3.642	143	4.673	0.529	165	3.092	157	3.479	15.5	4.118	79.1
	(-2.53)	(25.7)	(-0.46)	(-14.6)	(-0.22)	(5.93)	(0.17)	(-1.67)	(5.10)	(2.28)	(-36.2)	(-0.83)	(4.03)	(1.68)	(2.06)
NN[bare]	3.130	867	5.187	83.5	3.529	149	–	–	–	2.904	253	3.329	18.9	3.841	129
	(-11.0)	(165)	(-3.80)	(-16.5)	(-3.32)	(10.4)				(-3.94)	(2.85)	(-5.10)	(26.8)	(-5.16)	(66.5)
PGSL0.25	3.430	433	5.384	93.4	3.702	118	4.744	0.529	137	3.073	217	3.496	15.5	4.197	67.4
	(-2.47)	(32.4)	(-0.15)	(-6.6)	(1.42)	(-13.0)	(1.69)	(-1.67)	(-12.7)	(1.65)	(-11.8)	(-0.33)	(3.78)	(3.62)	(-13.0)
LKT	3.343	578	5.336	104	3.644	161	4.643	0.532	186	3.066	227	3.492	15.3	4.144	86.0
	(-4.95)	(76.8)	(-1.04)	(4.00)	(-0.16)	(19.5)	(-0.47)	(-1.12)	(18.5)	(1.42)	(-7.72)	(-0.46)	(2.52)	(2.32)	(10.9)
TF(1/5)vW	–	–	5.708	39.6	3.847	54.0	–	–	–	3.353	63.2	3.384	16.4	4.243	44.0
			(5.86)	(-60.4)	(5.40)	(-60.0)				(10.9)	(-74.3)	(-3.54)	(10.1)	(4.76)	(-43.2)
KSDFT	3.517	327	5.392	100	3.650	135	4.665	0.538	157	3.023	246	3.508	14.9	4.050	77.5

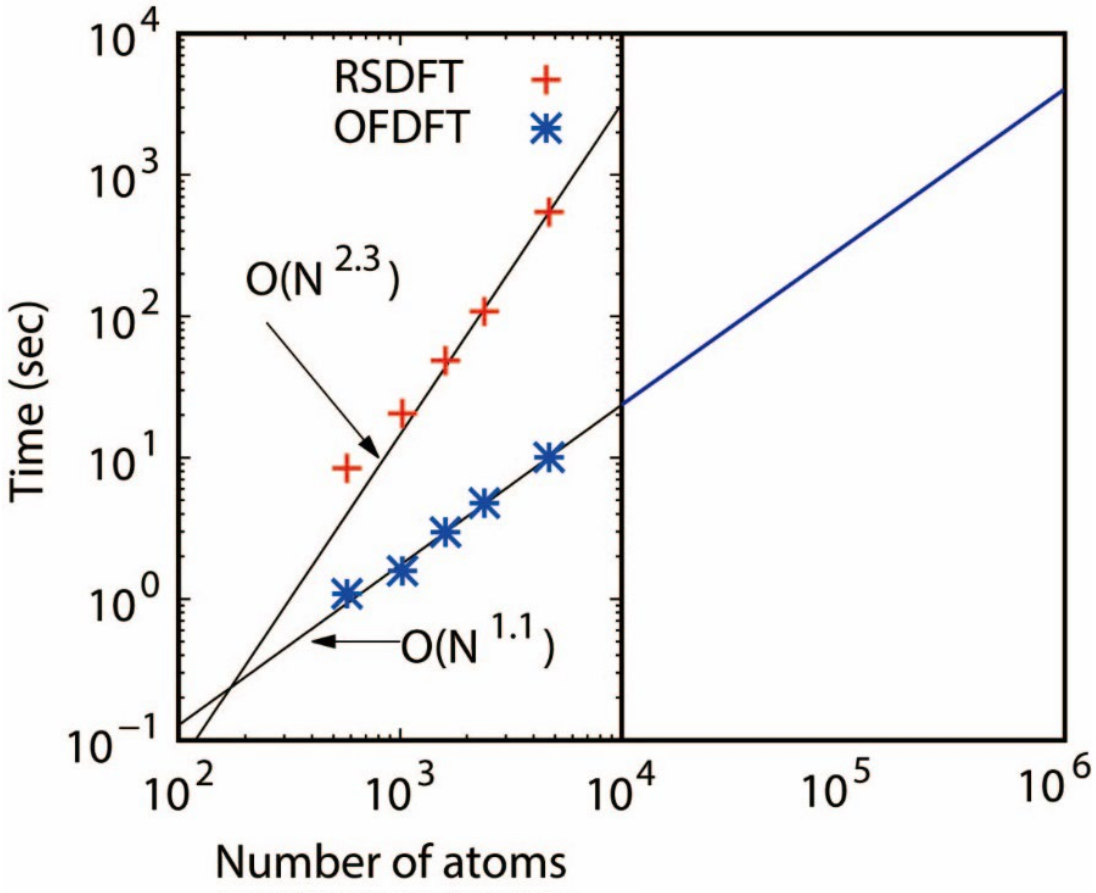
	fcc-Cu		bcc-Na		NaCl		graphene	MARE	
	a_0	B_0	a_0	B_0	a_0	B_0	a_0	a_0	B_0
NN	3.730	169	4.227	7.98	5.678	27.7	2.448		
	(2.33)	(6.96)	(-0.91)	(3.50)	(3.61)	(6.94)	(0.29)	1.39	11.1
NN[bare]	3.887	228	4.045	9.73	5.187	32.4	2.377		
	(6.64)	(44.3)	(-5.18)	(26.2)	(-5.35)	(25.1)	(-2.62)	4.74	38.4
PGSL0.25	3.795	138	4.250	8.00	5.595	22.9	2.433		
	(4.12)	(-12.4)	(-0.38)	(3.75)	(2.10)	(-11.5)	(-0.32)	1.66	12.1
LKT	3.762	175	4.245	7.91	5.596	23.8	2.402		
	(3.21)	(10.7)	(-0.50)	(2.61)	(2.12)	(-8.20)	(-1.59)	1.66	14.5
TF(1/5)vW	3.799	88.4	4.116	8.49	6.056	6.75	2.593		
	(4.21)	(-44.1)	(-3.51)	(10.1)	(10.5)	(-73.9)	(6.24)	6.10	47.0
KSDFT	3.645	158	4.266	7.71	5.480	25.9	2.441		

Structural Properties of 11 solids

Neural-Network-Assisted Order N - OFDFT Scheme

Imoto, Imada, Oshiyama: Phys Rev Research 3, 033198 (2021)

Computational time measured for SiC 576～4704-atom systems



DFT / CPMD calculations for millions of atoms are feasible with moderate size of computational resources

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  - Power electronics, Non-volatile memories
  - Necessity of quantum-theory based calculations
- Computics: present capability of calculations based on density-functional theory (DFT)
  - On current massively parallel computer architecture not with accelerators yet
- Mechanism of the flash memory: Nitrogen vacancy (V_N) in Silicon Nitride
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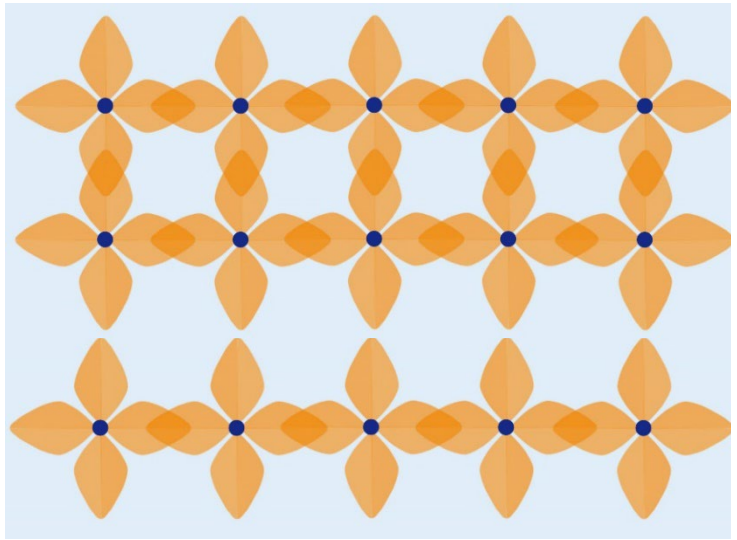
[F. Nanataki, K. Shiraishi & A. Oshiyama: unpublished (2022)]

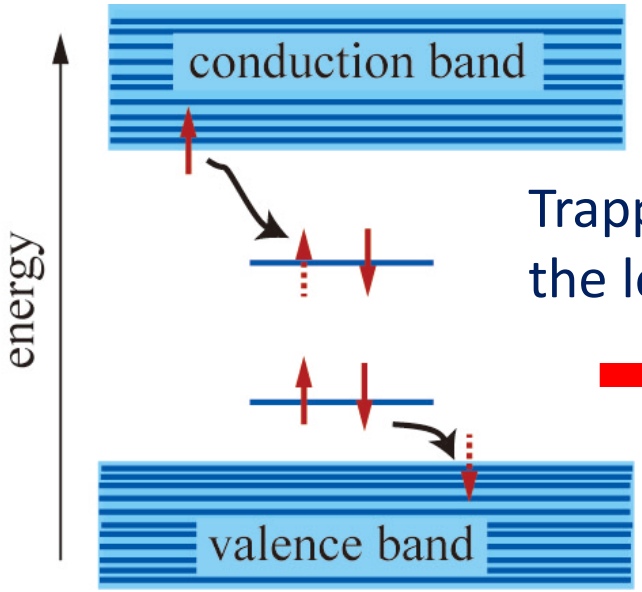
Electron States in Condensed Matters

Extended States vs Localized States

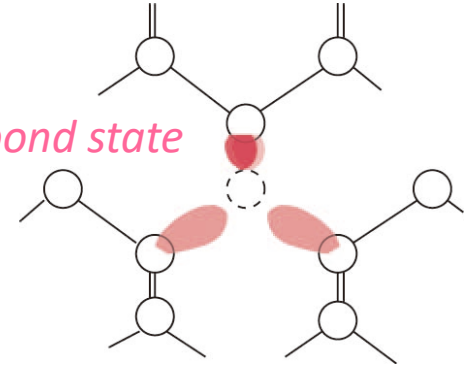
e.g. Bloch states in Crystal



e.g. States induced by imperfection



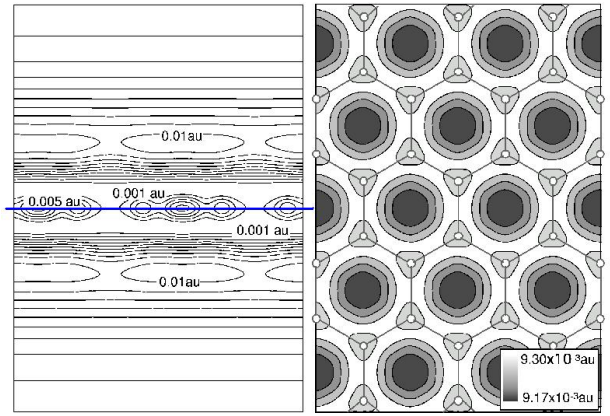
Trapping carriers in the localized region



Vacancy V in xtal

Deterioration of electron devices

Graphene plane



However, controlled electron trapping is storing the information in the localized region: i.e. the memory

V_N in SiN

Interlayer state

or

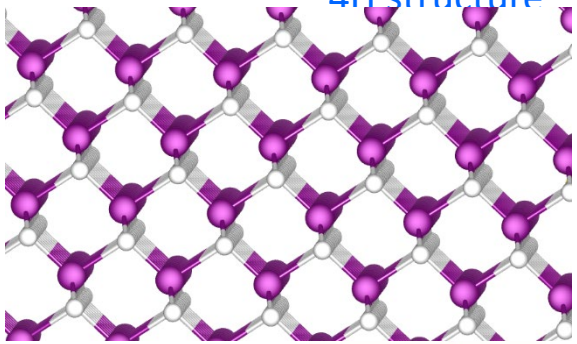
Floating state in sparse material

Floating State and Band-gap Variation in SiC Polytypes

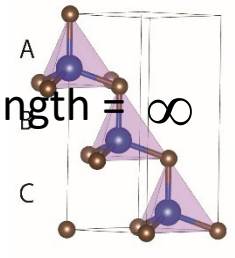
- Polytypes: Sequence of bilayers (A, B & C) have a variety as 2H, 3C, 4H, 6H, 8H, 10H, 15R,,,
  [periodicity and symmetry: Hexagonal/Cubic/Rombohedral]

3C structure from [101]

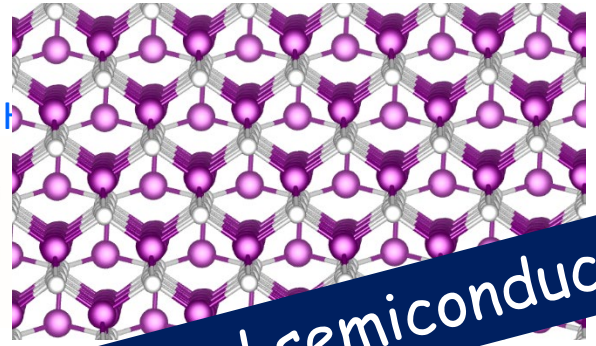
4H structure



3C structure



Length = ∞



Length = $7a_0/2\sqrt{2}$

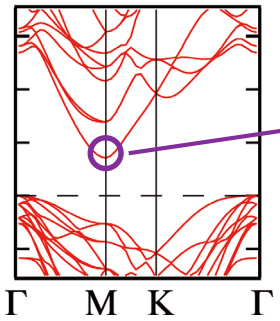
Packing efficiency of tetrahedrally-bonded semiconductors is 0.34

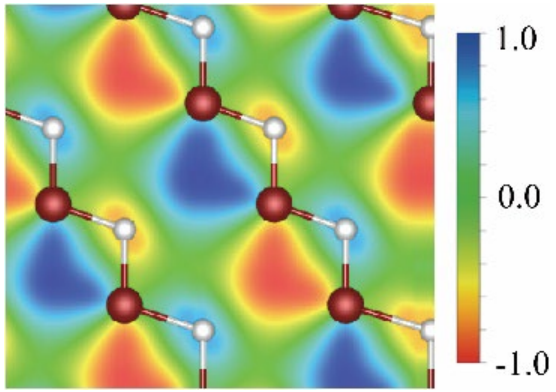
- Band Gaps: 2.2 eV (3C), 2.86 eV (6H), 3.26 eV (4H)
  Bonds and Bands: the bonding sp^3 [illegible], the anti-bonding sp^3 = the conduction band

Matsushita, Oshiyama, ..., ibid., (2014); Nano Lett (2017); JPhysSocJpn (2017)

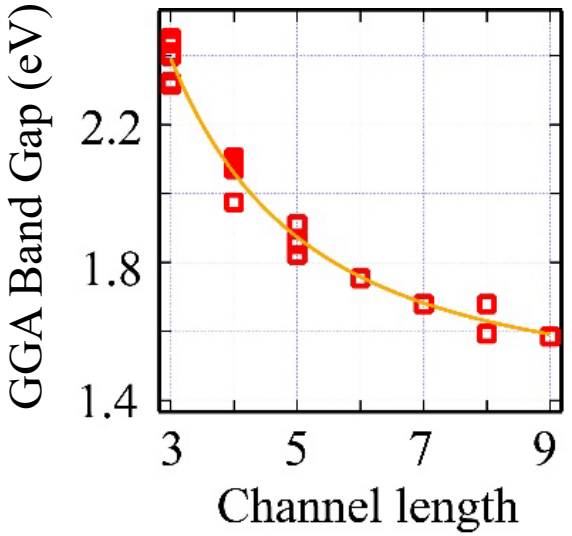
- Conduction [illegible] FLOATING!

3C-SiC





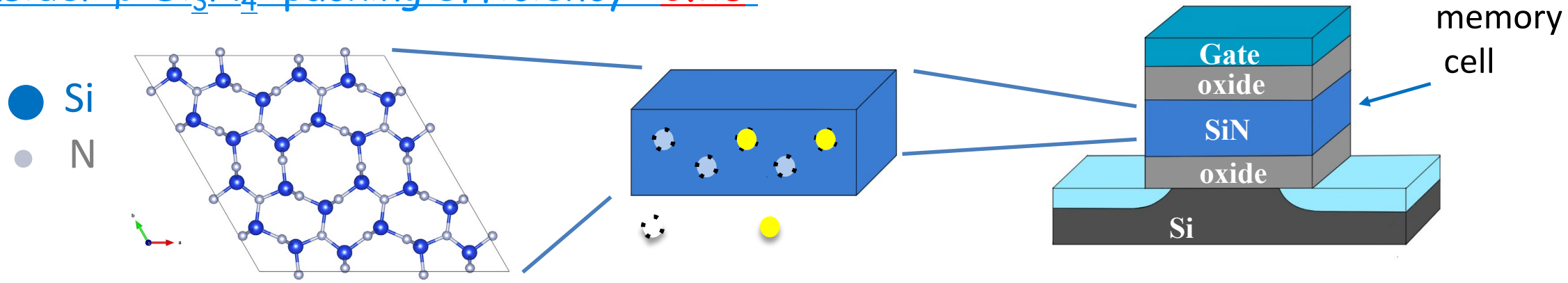
Amplitude of the orbital



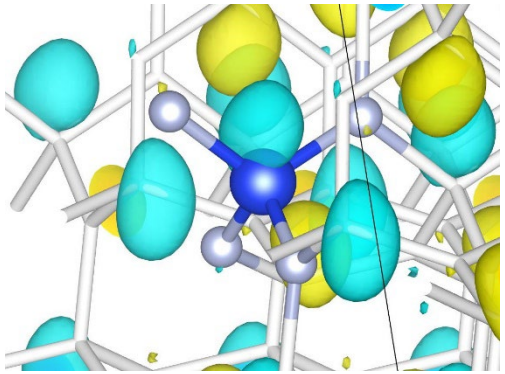
Quantum Confinement in the channel

Floating State in Silicon Nitride

Consider β-Si_3N_4: packing efficiency =0.28

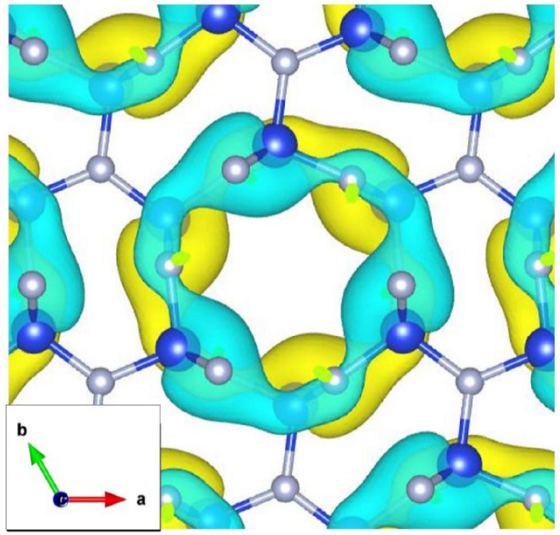


Conduction-band State is FLOATING

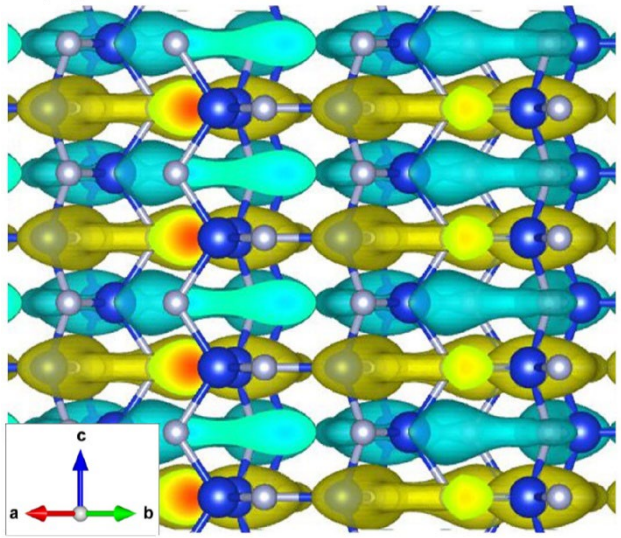


Highest amplitude is at back of Si, not along bonds

Then, is distributed in the internal space

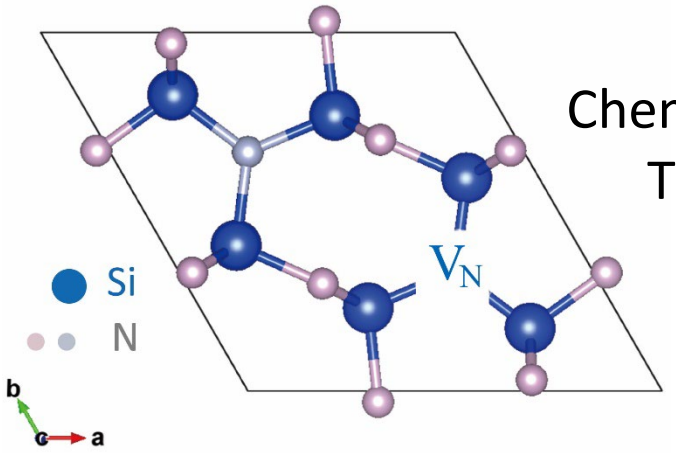


View from [0001] (c axis)

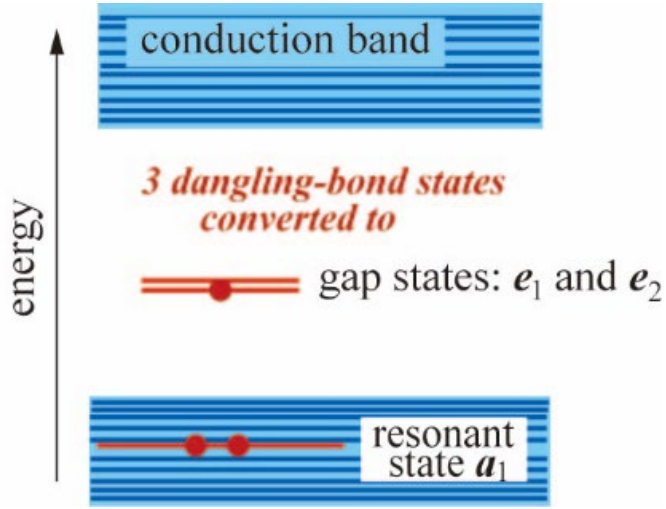


Side view perp to [0001]

Nitrogen Vacancy V_N in Silicon Nitride



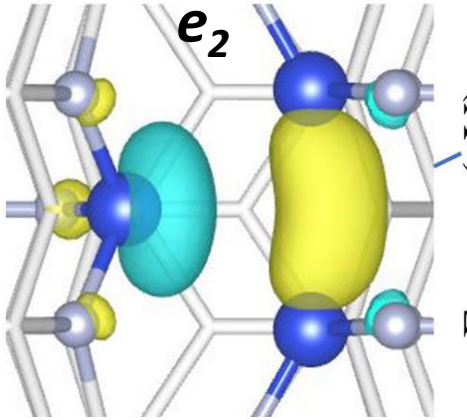
Chemically, V_N induces 3 Si dangling bonds.
They are converted to a singlet a_1
and a doublet e under C_{3v} symmetry.

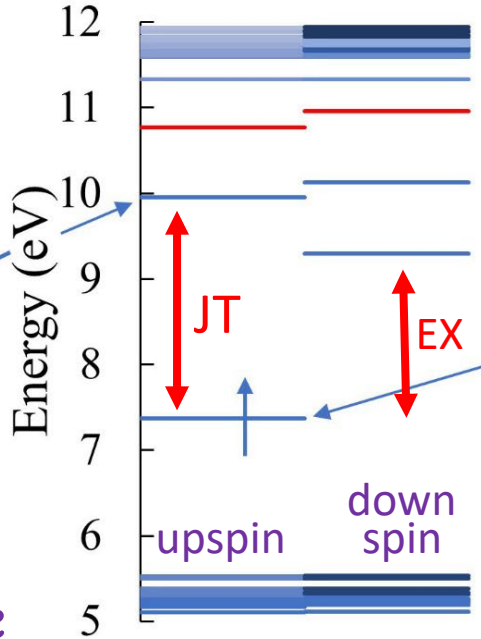


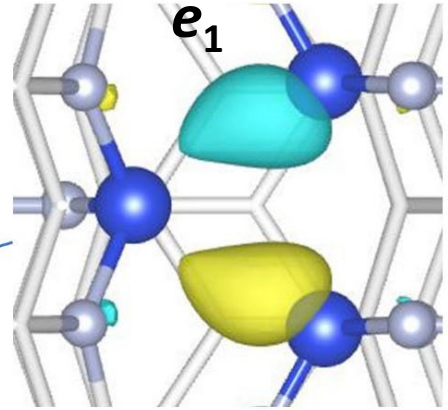
Level Structure near the gap for neutral V_N

- ✓ e_1 and e_2: different nodal planes
- ✓ *Symmetry-lowering Jahn-Teller splitting*
  ⇦ Covalency
- ✓ *Exchange spin splitting*
  ⇦ Ionicity

, depending on its charge state



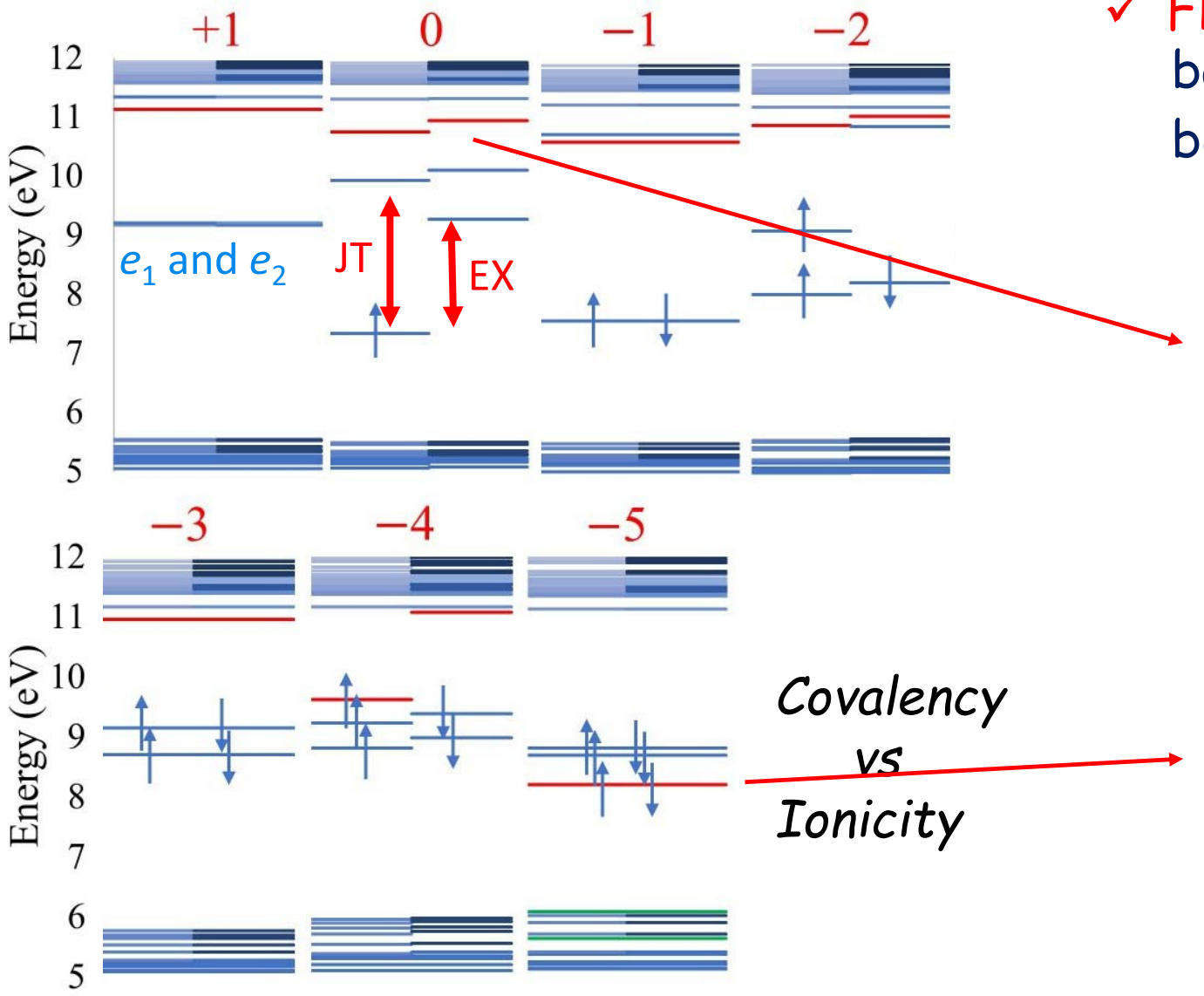




by DFT:
Hybrid
Approx

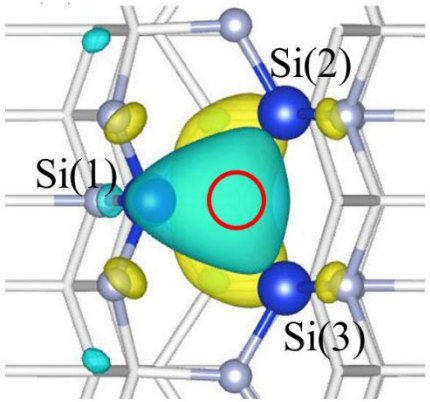
Jahn-Teller and Exchange Splitting ,,,,and Localized Floating Character

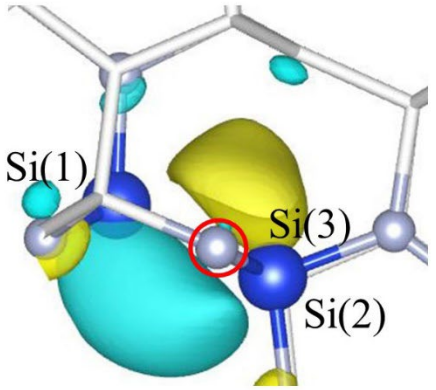
(Kohn-Sham) Electronic Levels: from V_N^{+1} to V_N^{-5}



But That's NOT All

✓ Floating states hidden in the conduction bands emerge in the gap (red bars), being localization around V_N

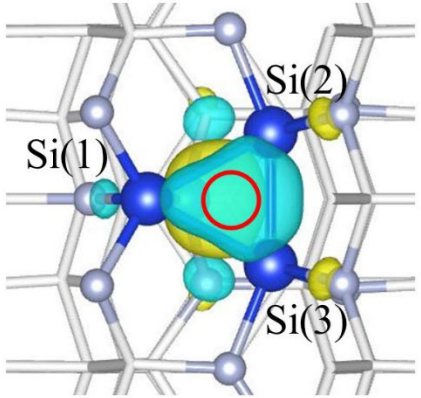


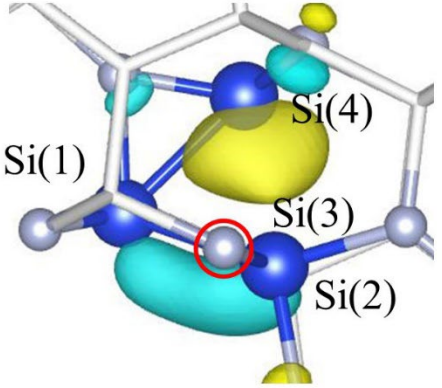


V_N^0

from 2 directions

○ vacant site

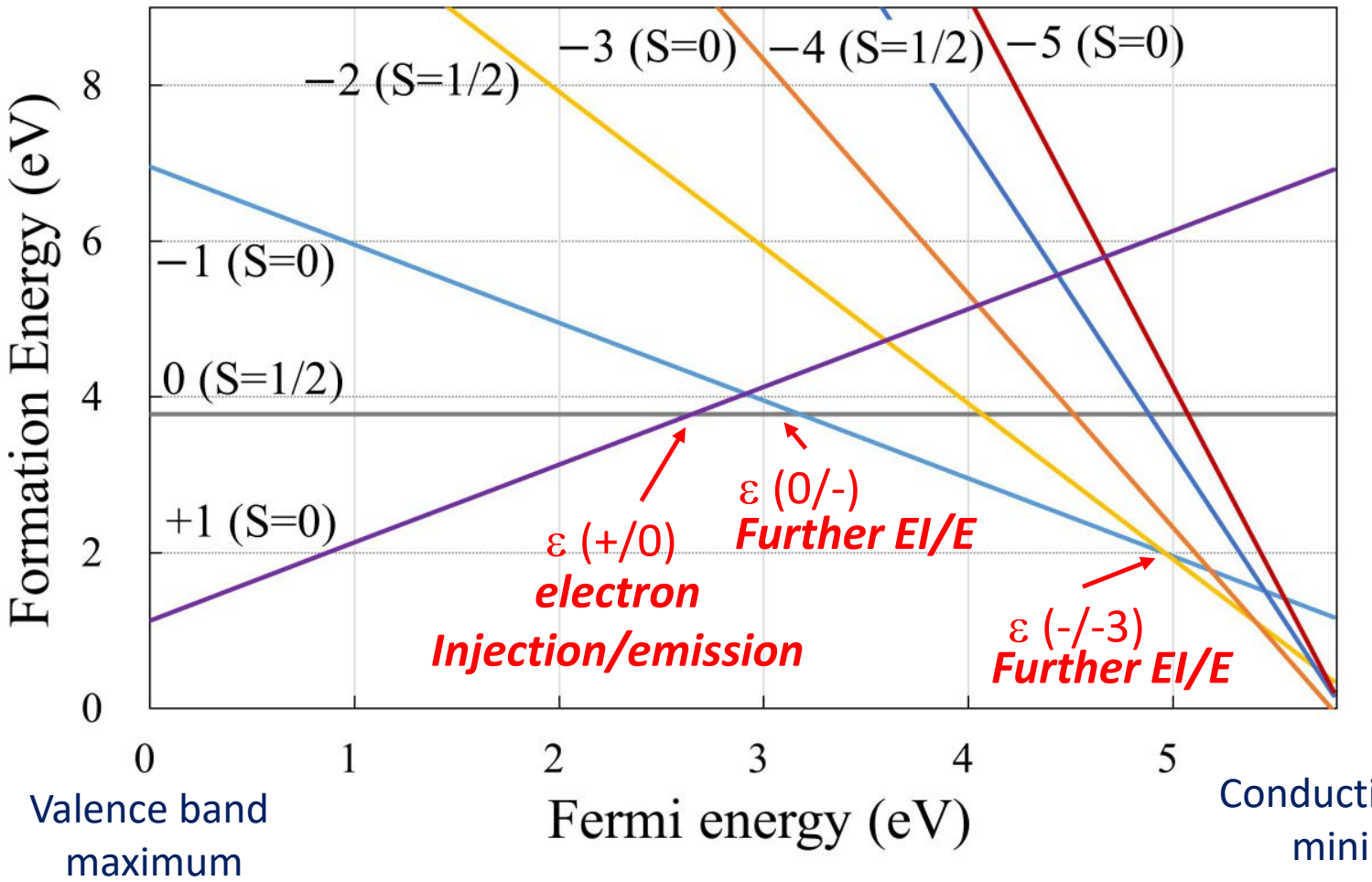




V_N^{-5}

Thermodynamic Level of V_N in SiN

Thermodynamic level ε (q/q'): Fermi-energy position in the gap at which the different charge states q and q' has the same total energy



- ✓ ***This is the level experimentally detected.***
- ✓ ***Control of the Fermi-level position, presumably by device design***
  ⇒ V_N: multi-level memory cell ?

Covalency (Jahn-Teller)
Ionicity (Spin splitting) and
Sparsity (Floating)
make it!

In Summary,

- Importance of Computics Approach based on Quantum Theory for Accurate-Enough Large-Scale Long-Time First-Principles Calculations / Simulations, Contributing to the Development of Energy-Saving Electron Devices

- Ultimate Memory Cells Endorsed by Newly Discovered Floating States?

  Lattice Vacancy in Silicon Nitride