Epitaxial Heterojunctions and Quantum Structures: Expectations and Challenges

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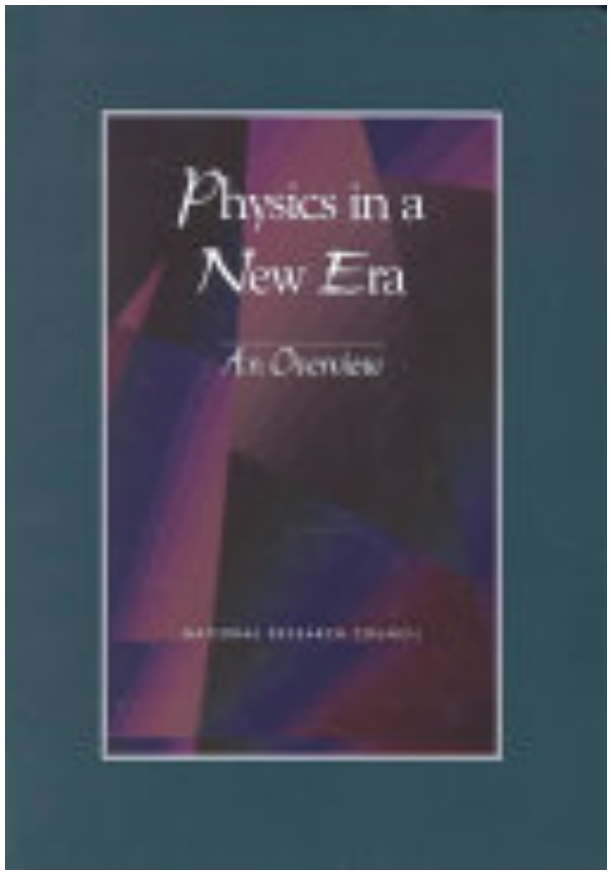


Physics in the New Era

can be separated into four broad categories

–

- Quantum manipulation & new materials
- Complex systems
- Structure & evolution of the universe
- Fundamental laws and symmetries

Emphasis on the unity of the field and the strong commonality that links the different areas, while highlighting new and emerging ones.

Role of Quantum Mechanics from Aerospace Applications to Quantum Computers

PDF version available from the National Academics Press at :

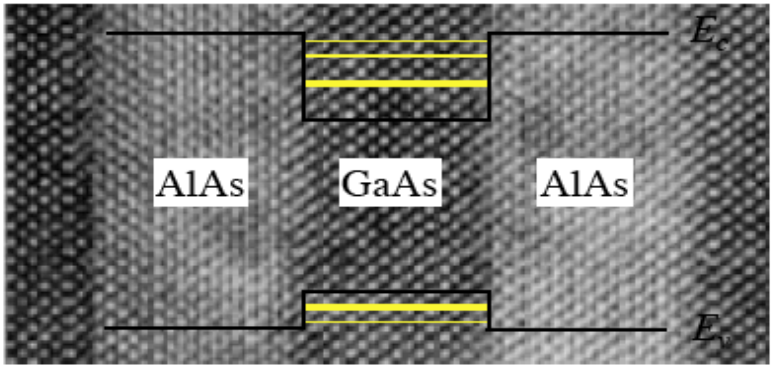
http://www.nap.edu/catalog/10118.html

Is Interface Different ?

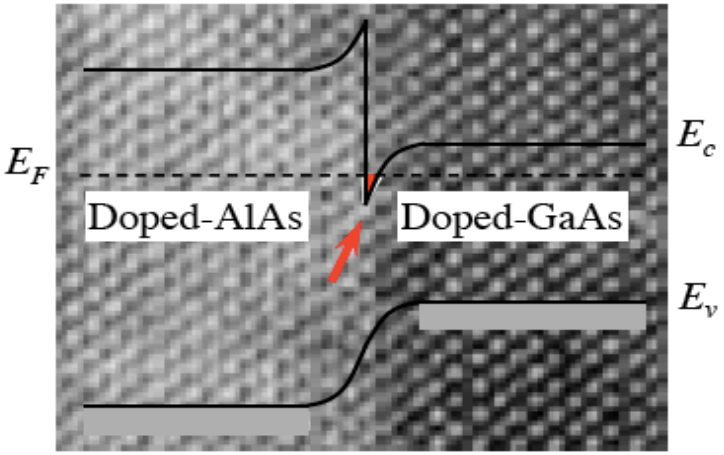
Novel Interface-induced Phenomena appearing.

How do Quantum Effects play role ?

Quantum Well



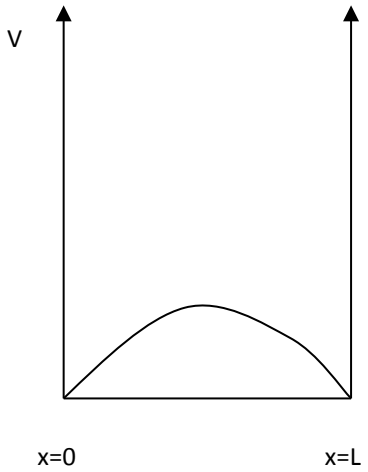
2D electron gas



By controlling symmetries and atomic arrangements at interfaces of complex materials, we will have a tremendous opportunity for searching for novel phenomena which do not exist in natural compounds.

- Quantum confinement → discrete states
- Energy levels for particle in a box
- Schrodinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V(r)\Psi = E\Psi$$



- For 1D infinite potential well

$$\Psi(x) \sim \sin(\tfrac{n\pi x}{L}),\ \mathrm{n} = \text{integer}$$

- If confinement in only 1D (x), in the other 2 directions → energy continuum

$$\text{Total Energy} = \frac{n^2h^2}{8mL^2} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

Structure	Degree of Confinement	dN/dE
Bulk Material	**3D**	$\sqrt{E}$
Quantum Well	**2D**	**1**
Quantum Wire	**1D**	$1/\sqrt{E}$
Quantum Dot	**0D**	**δ(E)**

Centre for Quantum Structures at IACS

- MBE
- PEEM
- VT-STM
- SQUID-VSM
- Micro-Raman
- UHV-Sputtering
- MOKE
- .....

A focused experimental-cum-computational research initiative on charge and spin transport in physically (not chemically) assembled quantum structures and devices.

Plan of my talk :

- Introduction : Modelling & Simulation using DFT
- Modelling of A/B Epitaxial Interfaces heterojunctions

  Ex. DFT estimation of Schottky Barrier Height
- Manifestation of some novel properties in 2D
- Case studies

  Ag on Si(111)

  Silicene on III-V & II-VI Semiconductor Substrates

  h-BN-sheet on Ni(111)

  $MoSe_2$ on Ni(111) and Cu(111) substrates
- Concluding remarks

Modelling and Simulation

- **Materials are complex many-body systems**
- **Equations that describe the physical and chemical behavior of real systems are often too complicated to be solved analytically or even numerically**
- **Key assumptions about reality can be made, often ignoring the complexity**
- **Modelling establishes a relations between physical or chemical quantities**
- **Simulation gives the numerical solution to the model applied to a specific situation**

A/B Epitaxial Heterojunctions & Superlattices

→ **Synthesis via MBE, MOCVD, Laser Ablation (LMBE) & other techniques**

→ **Modeling & Simulation using first-principles DFT**

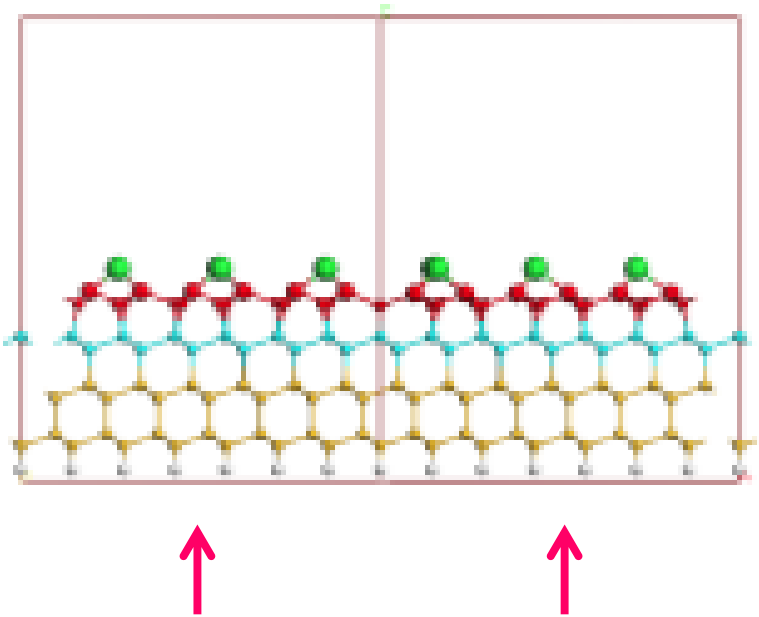
Type of Interface	Physical Quantity
• Metal/Semiconductor	→ Schottky Barrier
• Semiconductor/Semiconductor	→ Band Offset
• Insulator/Semiconductor	→ Interface State
• Metal/Ceramic	→ Chemical Bonding
• FM/NM/FM metallic multilayer	→ GMR
• Ferromagnet/Semiconductor	→ Spintronics

DFT based Computational Approach

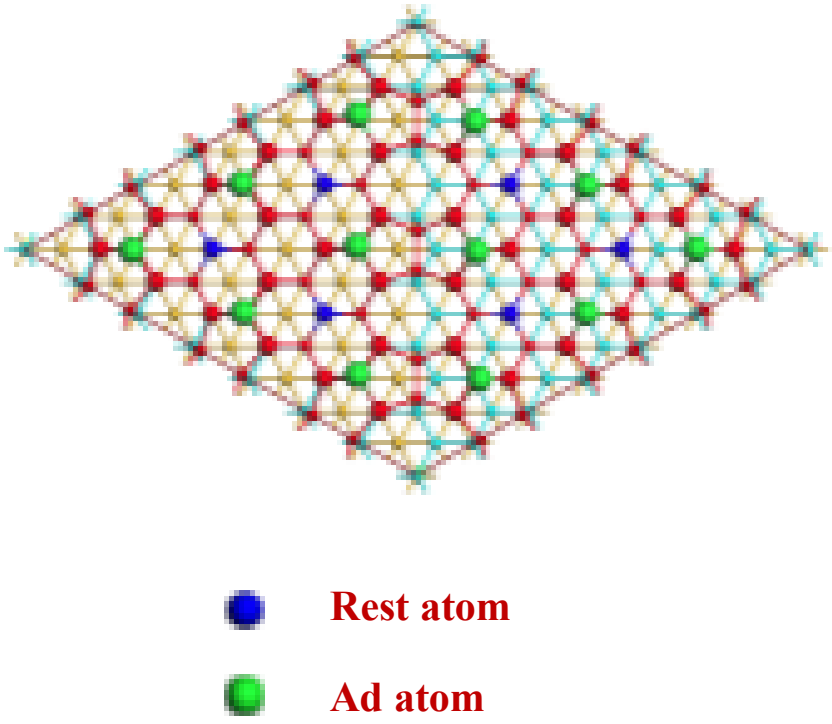
- **First principles Density functional (DFT) calculation in supercell geometry with necessary boundary condition along Z-direction**
- **Local density approximation (LDA/LSDA), GGA, Hybrid functional**
- **Vienna *Ab Initio* Simulation Package (VASP) with Projector Augmented Wave (PAW) potentials for elemental constituents**
- **Plane wave basis with 300 eV cut-off (500 eV cut off in some cases).**
- **Geometry optimization using Conjugate Gradient (CG) method**
- **Self-consistency criteria : Energy minimization up to 10^{-4} eV and "Force" up to 0.001 eVÅ^{-1}. "Force" minimization up to 0.01 eV Å^{-1}**
- **Brillouin Zone (BZ) sampling using Monkhorst-Pack method. K-mesh chosen appropriately**

Si (111)-7x7 Reconstructed surface : a classical problem

Side view of the 7x7 unit cell

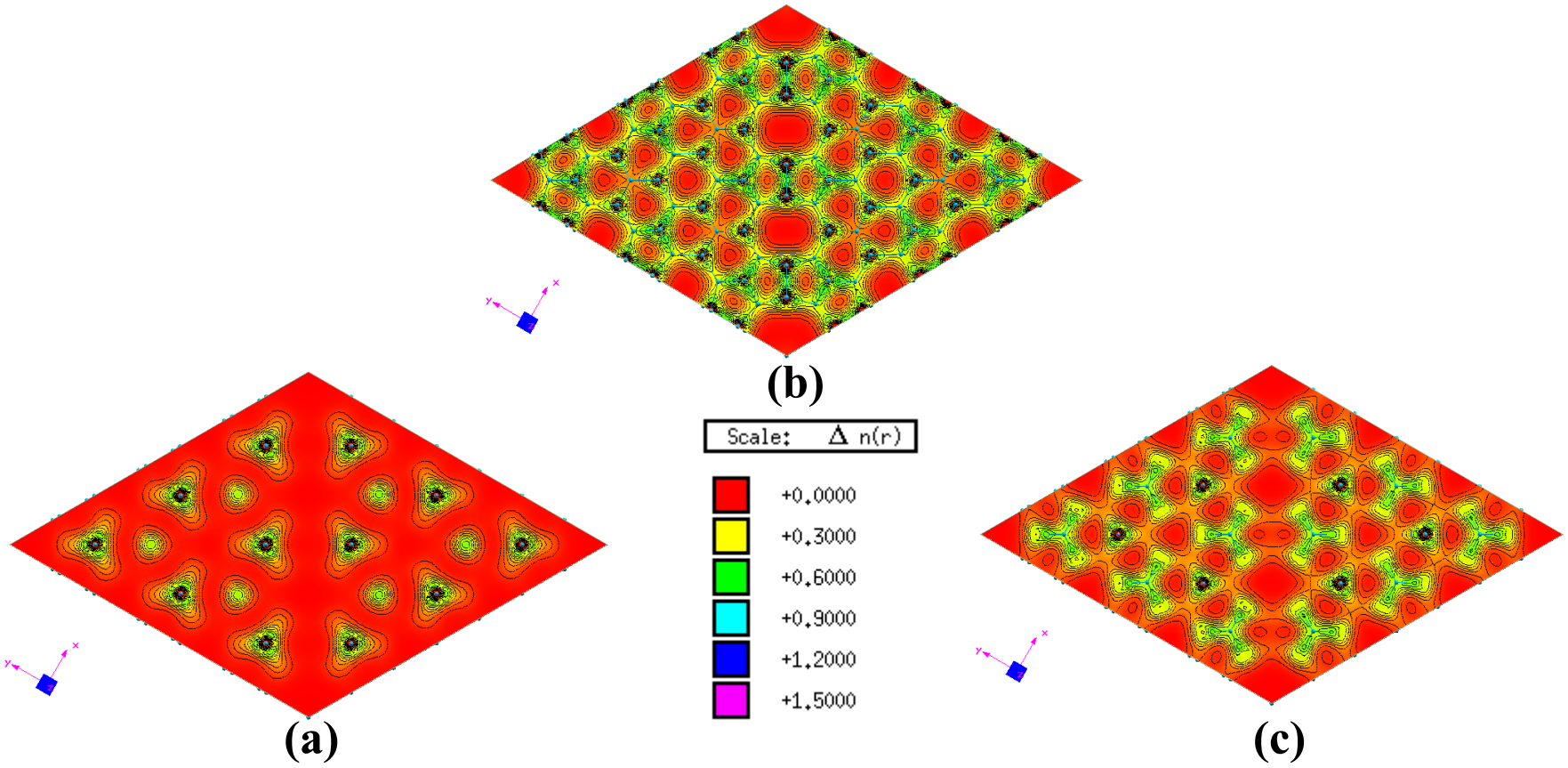


Top view of the 7x7 unit cell



[Binning *et al* , PRL, (1983)]

Charge density contour plot of 7x7 reconstructed Si (111) surface : our DFT based simulation



(a) Position of ad atoms and rest atoms ; (b) formation of dimers ; (c) presence of corner holes clearly seen from the above figure.

Perturbation caused by presence of an interface

- Perturbation dies down asymptotically into the individual solids, a few layers away from the interface
- Most of the interface induced physical properties are dictated crucially by the exact geometry and electronic structure of the interface, between which there is an interplay.
- Model calculations relying only on the electronic structures of the two bulk constituents fail to explain and reproduce the experimental results on these hetero-junctions
- Interface induced dipole at the hetero-junction
  [obtained from plane-averaged electron density ρ(z)] :

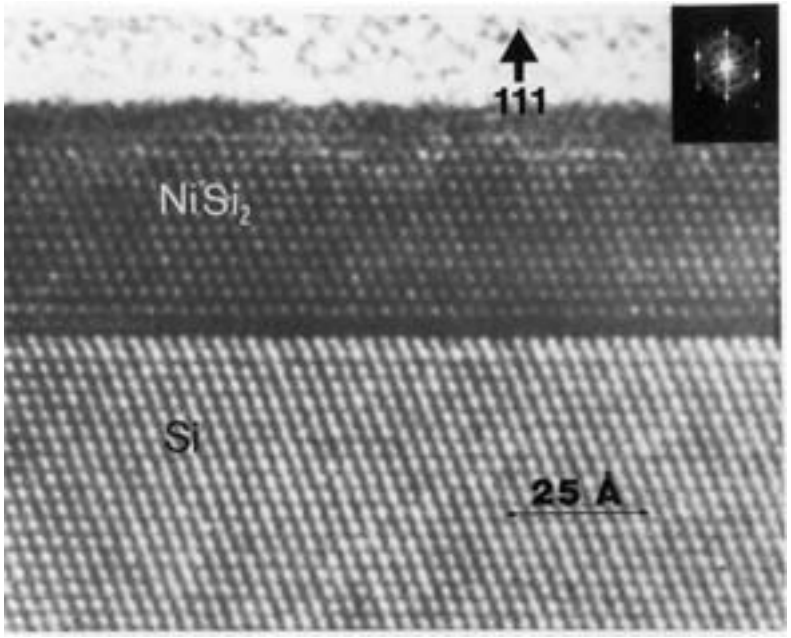
$$\Delta\rho(z) = \rho_{M/S}(z) - \rho_M(z) - \rho_S(z)$$

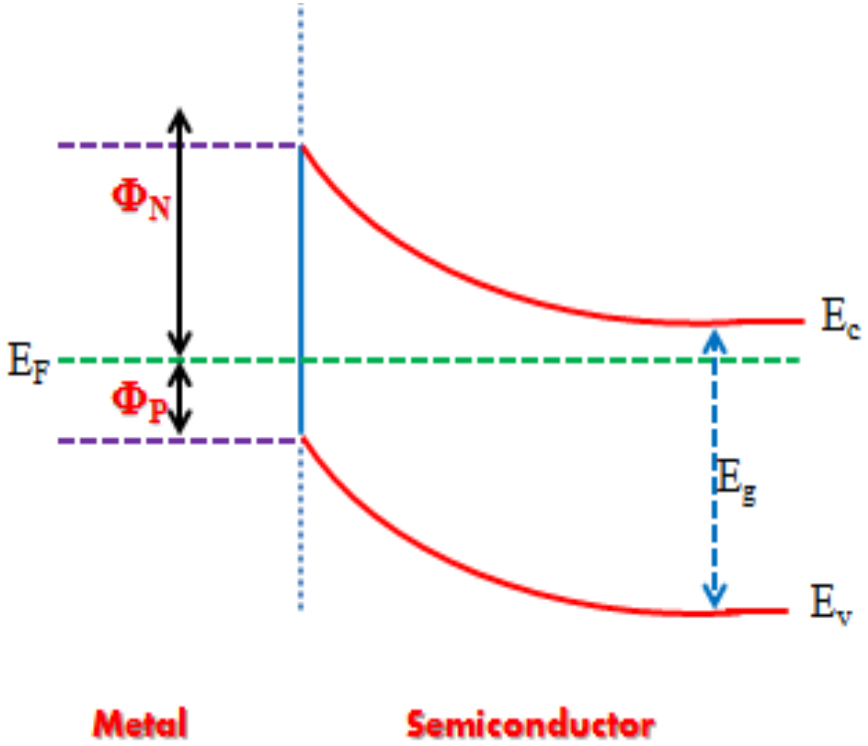
Metal/Semiconductor epitaxial junction

2D Quantum structure : fundamental constituent of electronic devices

- **Localized surface and interface states**
  - → Surface states evolve due to the presence of unsaturated (dangling) bonds at the surface.
  - → Interface states are nothing but the surface states of a semiconductor substrate in presence of an over-layer
- **Metal-induced gap states (MIGS)**
  - → Evolution of localized states due to the spilling over of the electronic states of the metal into the band gap of the semiconductor/insulator.
- **Work function of metal over-layer : A surface property**
  - → Minimum amount of energy required to remove an electron from the highest occupied level (Fermi level) of the metal
- **P-type Schottky barrier height (SBH) (Φ_p)**
  - → Energy difference between the Fermi level of the metal over-layer and the valence band top of the semiconductor substrate.
- **Fermi level pinning**
  - → SBH is found to be nearly independent of the choice of the metal.
  - → While work functions of metals vary over a wide range of energy.

Schottky Barrier Height in Metal/Semiconductor epitaxial heterojunction

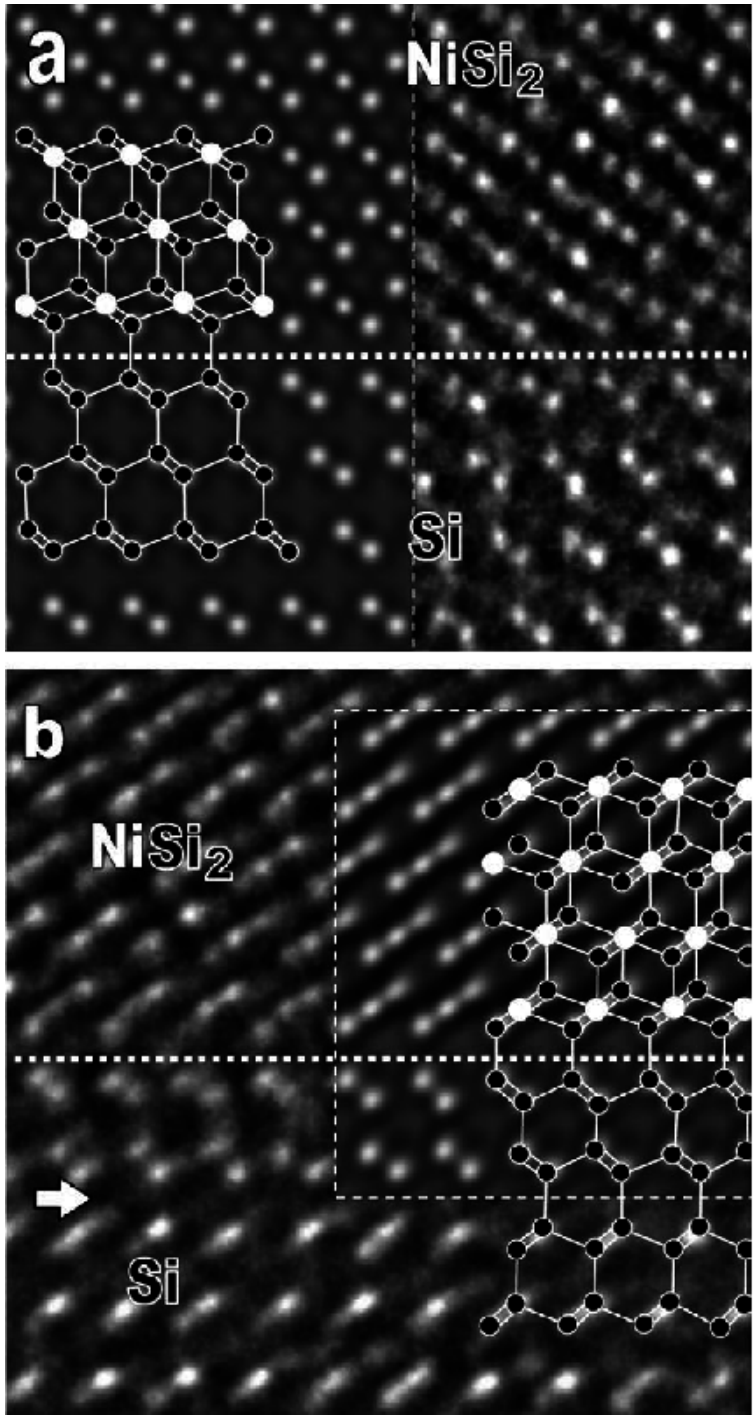




Work Function : $W = E_{vac} - E_F$

p-type Schottky Barrier Height : $\Phi_p = E_F - E_v$

$NiSi_2$/Si (111) A-type→ Φ_p = 0.52 eV , B-type→ Φ_p= 0.38 eV



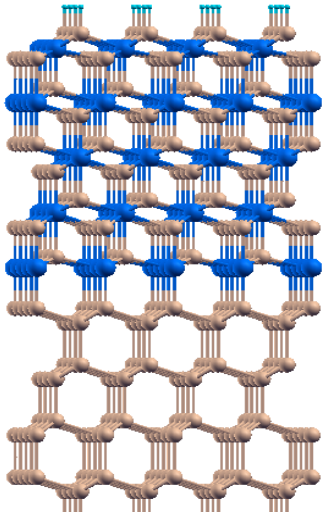
HRTEM image of the $NiSi_2$/Si (111) interface with A-type geometry (a) and B-type geometry (b). The dotted line traces the interface.

The simulated images are inserted in the left side in (a) (thickness = 6 nm, C s = À15 lm and defocus = 4.6 nm) and in a broken-line box in (b) (thickness = 6.4 nm, C s = À15 lm, defocus = 4.2 nm and crystal tilt = 15 mrad).

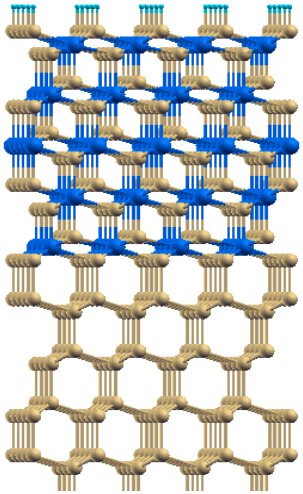
The structure mode of the $NiSi_2$/Si (111) interface is superimposed. The {111} twin boundaries in Si are indicated by an arrow in (b).

Ref: Mi et al, Acta Mater. (2009)

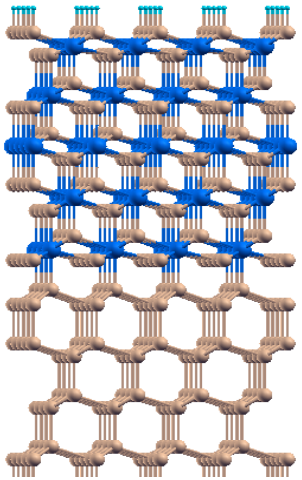
Different type of MSi_2/Si(111) interfaces (M-Ni, Co)



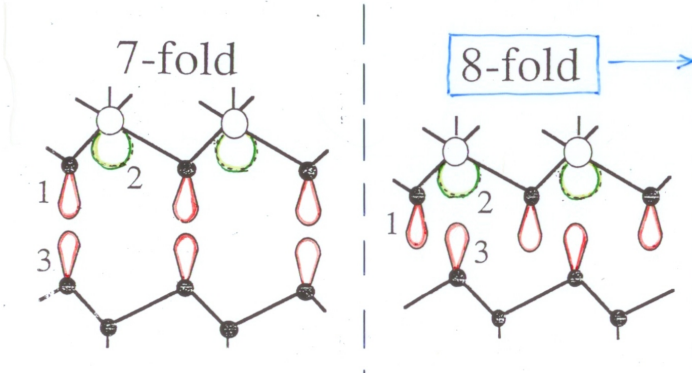
M-atom 5-fold Coordinated



M-atom 7-fold Coordinated



M-atom 8-fold Coordinated.



X-ray Standing Wave (XSW) experiments compared with DFT Supercell calculations of the interfaces, modelled by considering five layers of MSi_2 on eight bilayers of Si (111)

Relative stability of different types of interfaces

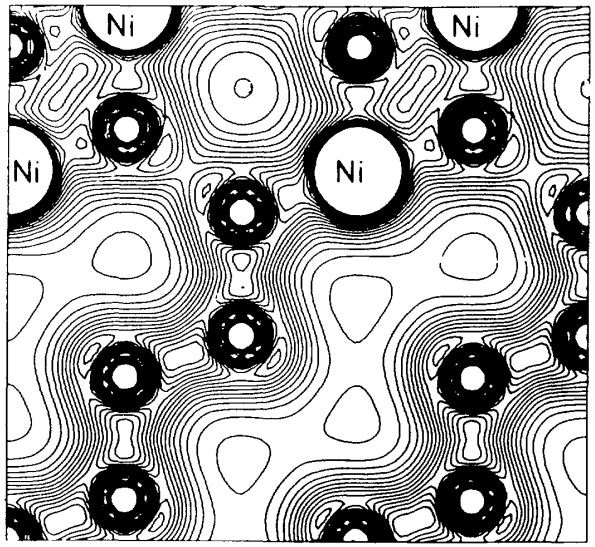
Binding energy - $\Delta E_B = E_{Tot} - (E_H + E_{Co/Ni} + E_{Si})$ eV

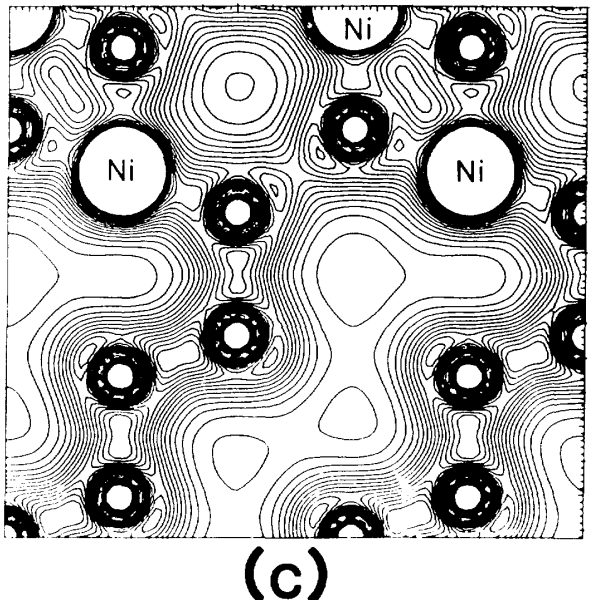
Type of interfaces	$NiSi_2$/Si (111)	$CoSi_2$/Si (111)
5-fold coordinated	4.5472 eV	4.6677 eV
7-fold coordinated	4.5713 eV	4.7021 eV
8-fold coordinated	4.5581 eV	4.7093 eV

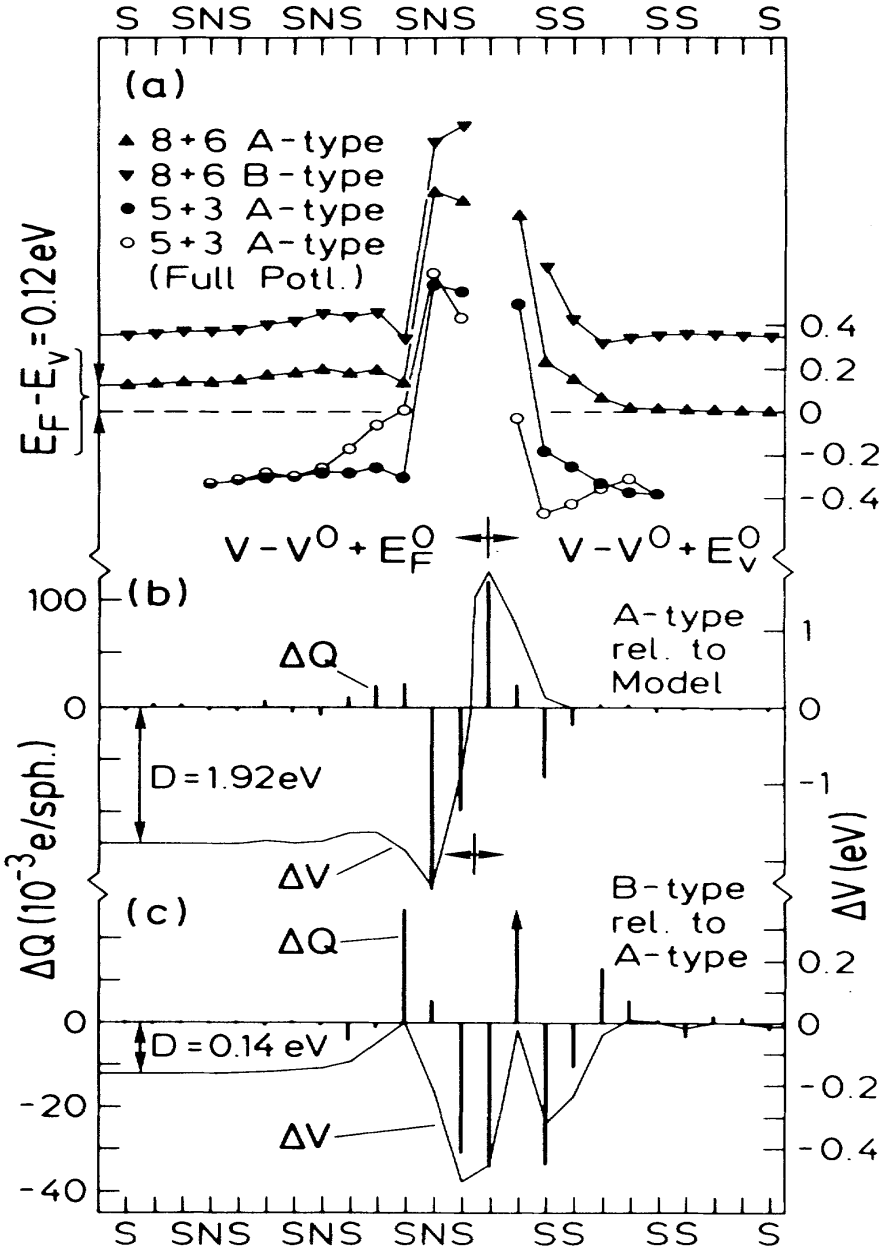
Interface geometries that energetically favorable :
$NiSi_2$/Si (111) interface → 7-fold
$CoSi_2$/Si (111) interface → 8-fold
Result consistent with available results

DFT estimated SBH in A- and B-type NiSi2/Si(111) epitaxial interface,

G.P. Das, P.E.Bloechl, O.K. Andersen, N.E. Christensen, O. Gunnarsson, PRL (1989)







Electronic Structure

Ag overlayer on Si(111)

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citable using Digital Object Identifier – DOI)

Phys. Status Solidi B, 1–7 (2012) / DOI 10.1002/pssb.201248542

physica status solidi b
www.pss-b.com
basic solid state physics

First principles electronic structure of coincidence site epitaxial Ag/Si(111) interface

A. H. M. Abdul Wasey[1], R. Batabyal[1], J. C. Mahato[1], B. N. Dev[1], Y. Kawazoe[2], and G. P. Das[*,1]

Supercell model and Interface Relaxation

Lattice Parameters:

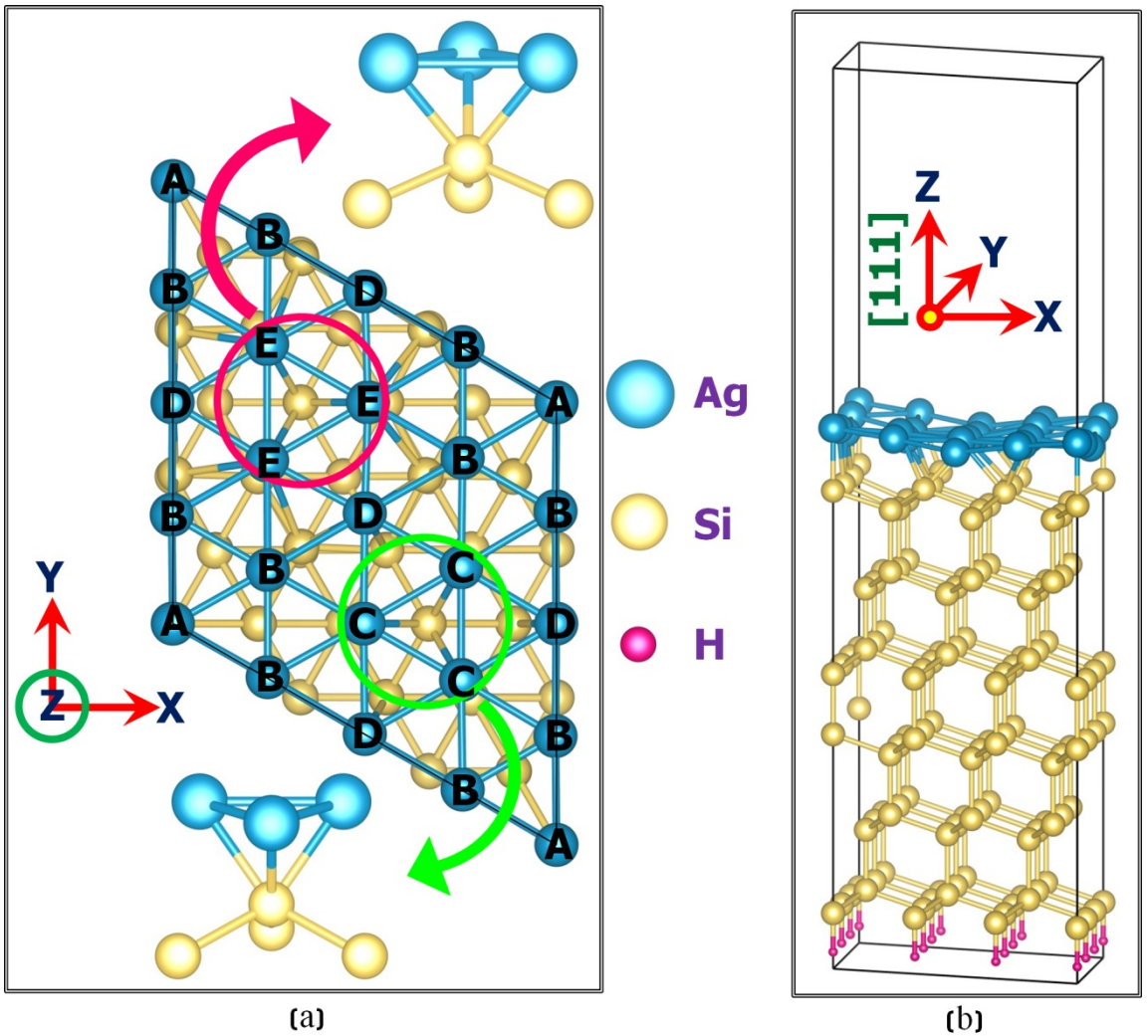
Ag → 4.09Å

Si → 5.43Å

→Nearly 25% lattice mismatch can be adjustable by placing 4×4 unit cells of Ag on 3×3 unit cells of Si

→Resulting mismatch is now~ 0.3%

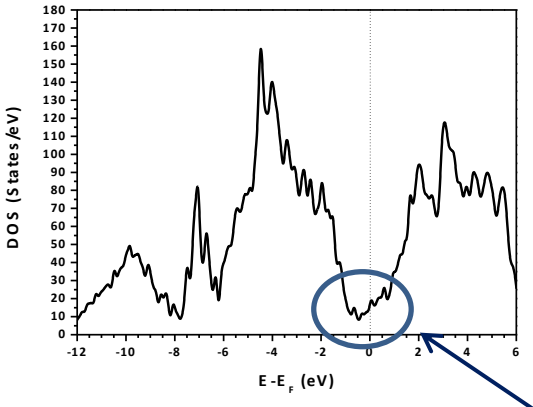
Modeling of Ag/Si(111) : One atomic layer of Ag on six double layers of Si(111) surface whose most bulk like layer has been passivated with H atoms.



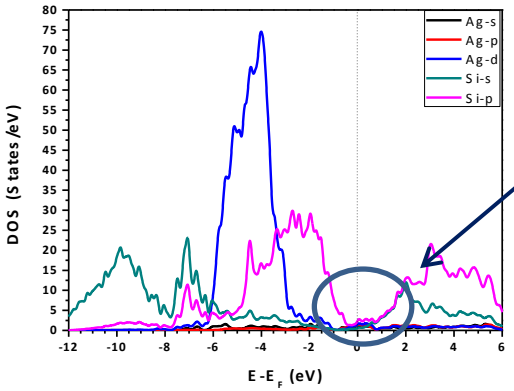
(a) (b)

(a)Top view of optimized geometry of the Ag/Si (111) supercell. Capital letters are assigned according to their height w.r.t. a common reference plane well below the interface. According to height A>B>C>D>E (b) Side view of the optimized gr st geometry.

Electronic structure of the Ag/Si (111) system



Total DOS

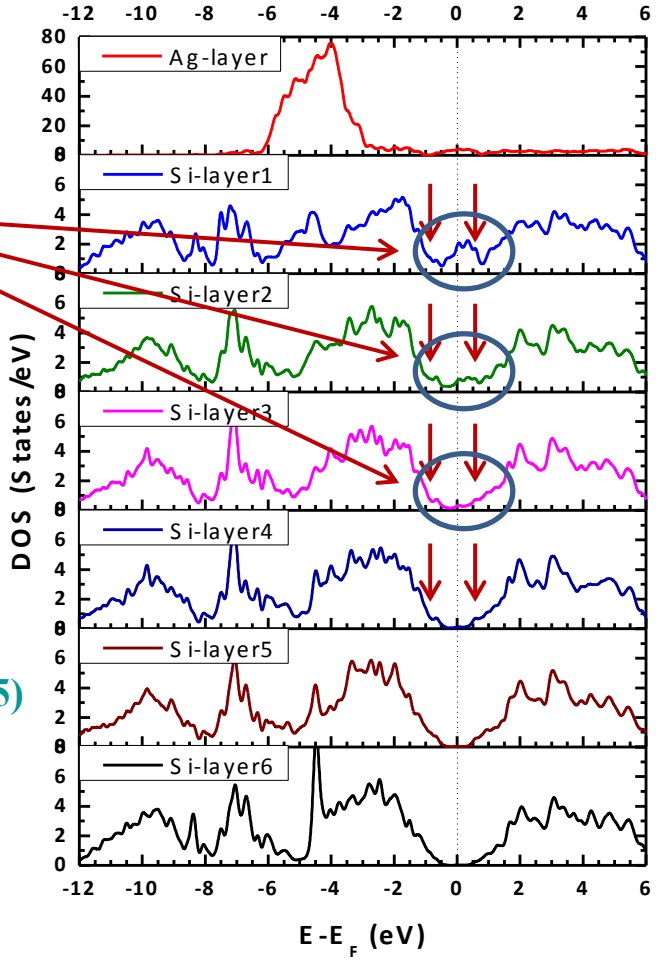


Partial DOS (PDOS)

Metal-induced gap states (MIGS)

Gap states

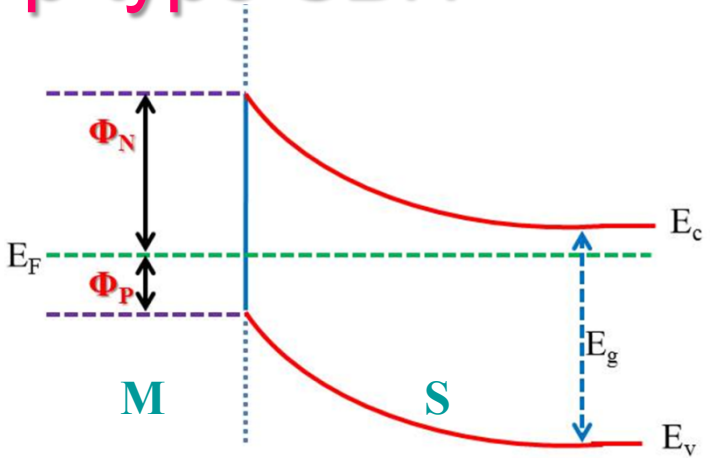
MIGS: V. Heine (1965)



Layer projected DOS (LPDOS)

- Interface states can be observed from the LPDOS
- Evolution of localized states around Fermi level at occupied and unoccupied part
- Signature of metal-induced gap states: due to spilling over of the Ag states into the Si-band gap.

Work function and p-type SBH



Work function of Ag surfaces

Orientations	WF_GGA	WF_LDA	WF_Expt *
Ag(100)	4.34	4.68	4.64
Ag(110)	4.02	4.51	4.52
Ag(111)	4.59	4.72	4.74

*Michaelson, JAP, (1977)

GGA	LDA
Work function of Ag/ Si (111)	
4.34 eV	4.57 eV

Estimated p-type SBH ~ 0.50 eV

Abdul Wasey *et. al.* (2012)

p-type SBH of Ag/Si (111)

Calculated p-type SBH = 0.54 eV

Smith *et. al.* (1971)

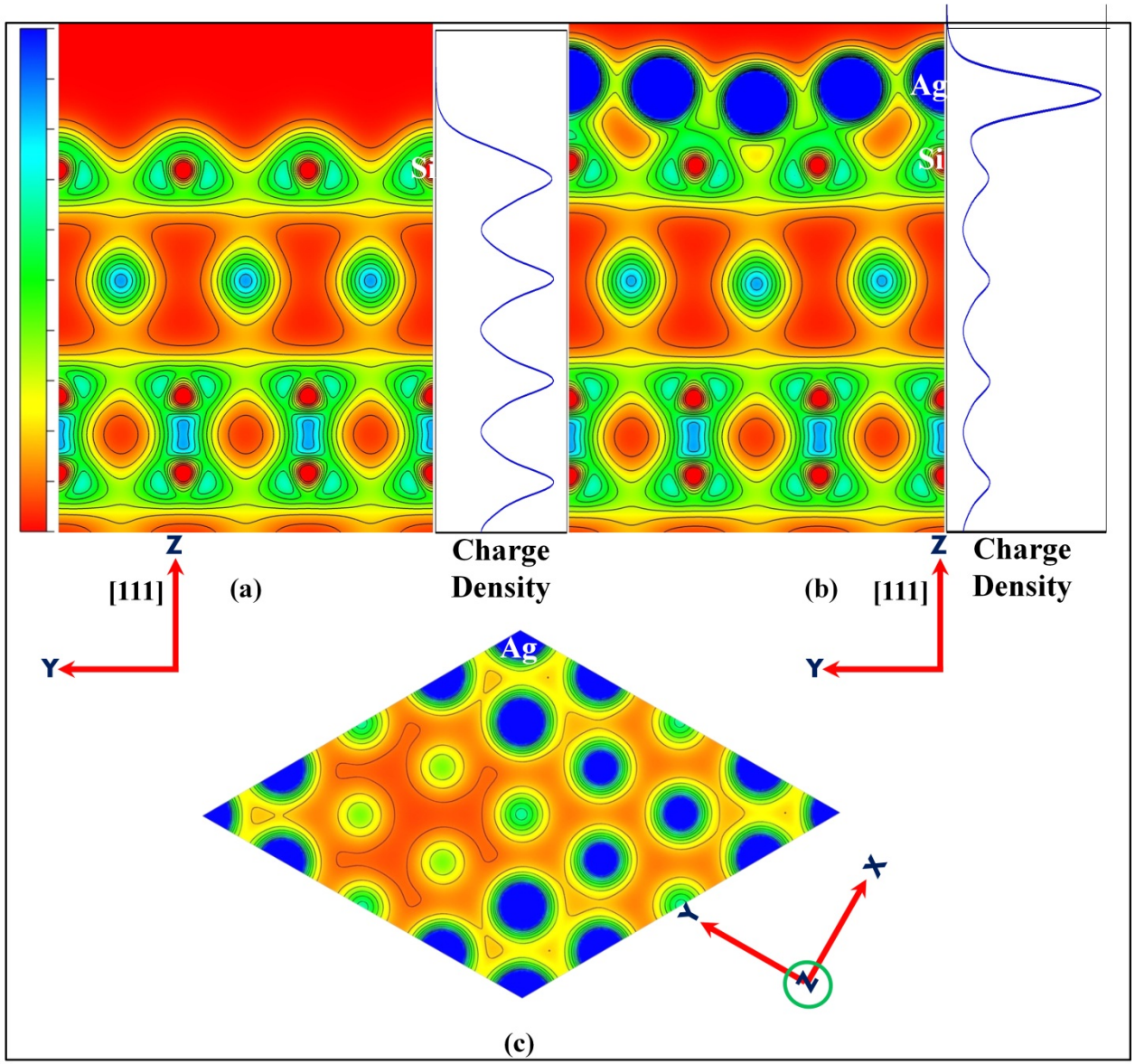
Calculated n-type SBH 0.56 eV

Turner *et. al.* (1968)

Estimated work function values match very well with the experiment.

Estimated p-type SBH of Ag/Si (111) agrees well with the experimental Results of Smith *et. al.* and Turner *et. al.*

Charge density of Si (111) slab before and after deposition of Ag over-layer



(a) Charge density plot of Si (111) slab

(b) Charge density of Si (111) slab after deposition of Ag over-layer.

Fig (a) and (b) also shows the corresponding planar averaged (average in X-Y plane) charge density plot along z axis

(c) Charge density plot projected on X-Y i.e. in (111) plane passing through the Ag layer. All the Ag atoms are not at same height →signature of slight buckling in the Ag over-layer.

In summary

- As a benchmark of our DFT calculations, within the local density approximation (LDA) we have simulated Si (111)-7×7 reconstructed surface.
- We have carried out electronic structure calculation of Ag monolayer on Si (111) and studied the interface relaxation and found an interesting asymmetry in the over-layer as a consequence of the influence of the subsurface Si atoms.
- We have found signature of MIGS in the LP-DOS, caused by the spilling over of the Ag states into the Si-band gap.
- We have estimated the work function of the metal over-layer and p-type SBH of the M/S junction and compared our results with available experimental results.

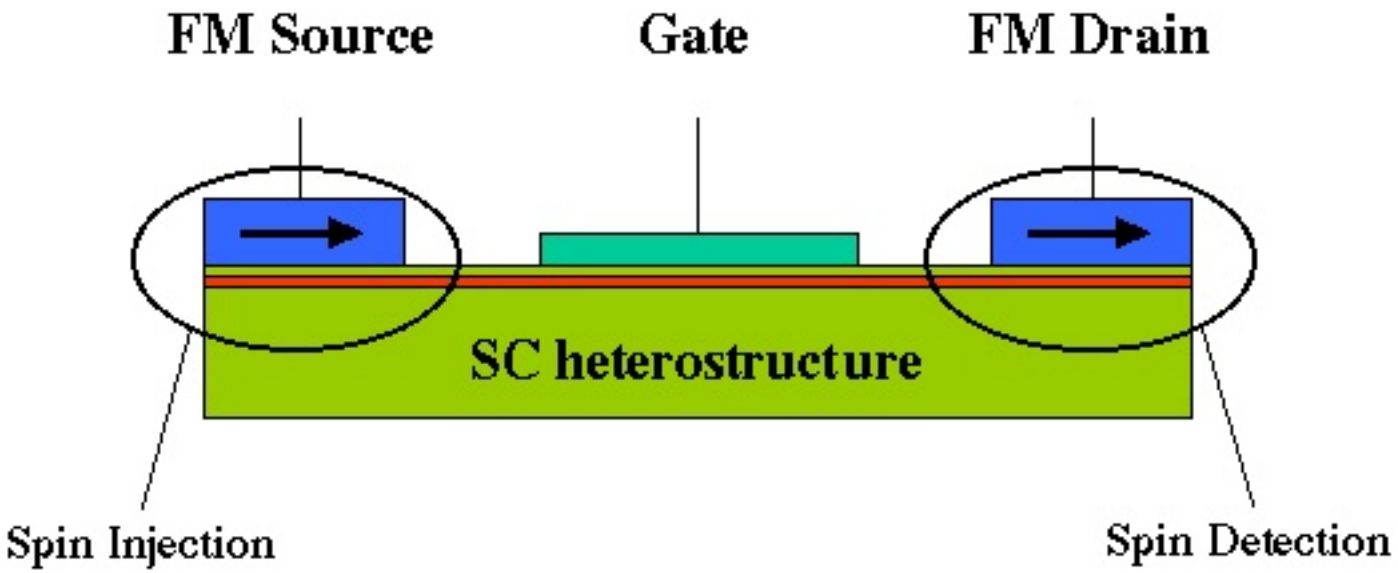
Spin-based electronics

Controlled transfer or injection of spin-polarized current from a ferromagnet into a normal metal or a semiconductor

- Metallic Multilayer Systems : GMR, TMR
  (Nobel Prize in Physics to Fert and Gruenberg)
- All-semiconductor structures : DMS, DMO
  (Hideo Ohno, Plenary Talk in AsiaNANO)
- Hybrid structures combining metallic ferromagnets and semiconductors
  Ex. Fe/MgO/Fe → TMR ratio ~ 400% → 500% at RT !!! (Yuasa, Japan)

Each has its own merits as well as limitations, and are being vigorously pursued by experimentalists & theorists.

Datta-Das Spin-FET (APL 56, 665 1990)



According to the principle of Datta-Das Spin-FET, electrons would be injected from the source, which would align the spins so that their axes were oriented the same way as those in the source and drain. These spin-polarized electrons would shoot through the heterostructure at relativistic speed (~ 1% of c) towards the drain.

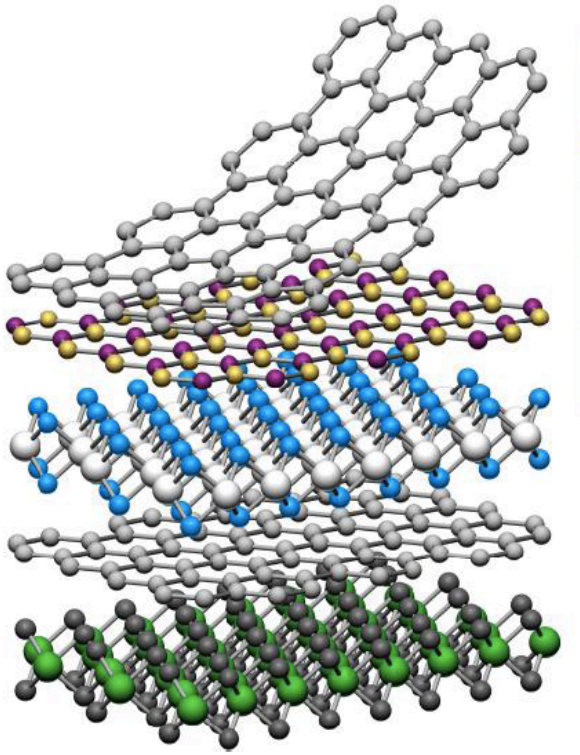
2D materials span a whole range of electronic behavior

Sr No.	3D	2D
1.	Graphite	Graphene
2.	Silicon	Silicene
3.	Germanium	Germanene
4.	Phosphorous	Phosphorene
5.	III-V e.g. c-BN	III-V Sheet e.g. h-BN
6.	III-IV-V Semicond	III-IV-V Sheets
7.	TMDC	Layered TMDC

Graphene → Conductor

h-BN → Insulator

MoS_2 → Semicond



Their sandwitch structures i.e. growth one above the other leads to novel flat-pack assembly known as **"van der Waals heterostructures"** that lead to new functionality in electronic devices due to novel substrate induced screening.

An emerging paradigm in materials science and device physics

Electronic & Magnetic properties of Silicene on III-V and II-VI Semiconductor Substrates

APPLIED PHYSICS LETTERS **103**, 123113 (2013)

Exploring semiconductor substrates for silicene epitaxy

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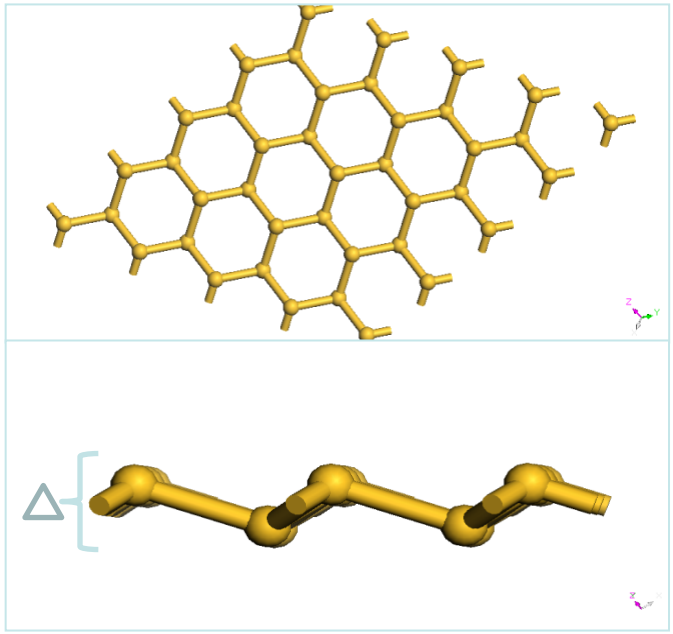
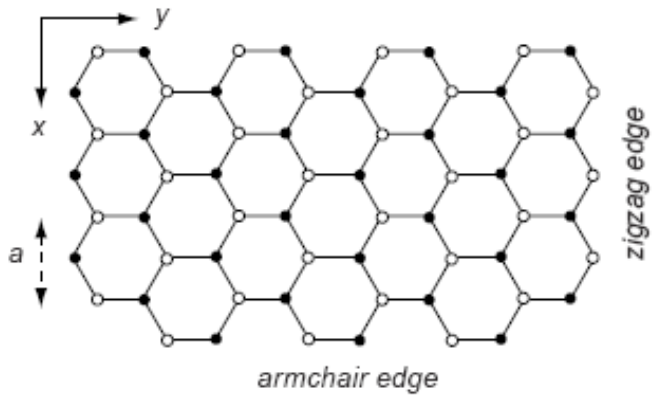
(Received 28 May 2013; accepted 29 August 2013; published online 20 September 2013)

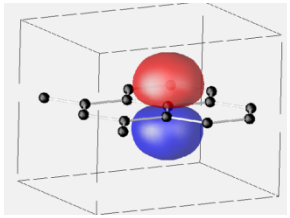
We have carried out first-principles density functional theory based calculations on electronic properties of silicene monolayer on various (111) semi-conducting surfaces. We find that the relative stability and other properties of the silicene overlayer depend sensitively on whether the interacting top layer of the substrate is metal or non-metal terminated. The nature of silicene-monolayer on the metal terminated surface can be metallic or even magnetic, depending upon the choice of the substrate. The silicene overlayer undergoes n-type doping on metal terminated surface while it undergoes p-type doping on nonmetal terminated surfaces of the semiconductor substrates. [http://dx.doi.org/10.1063/1.4821993]

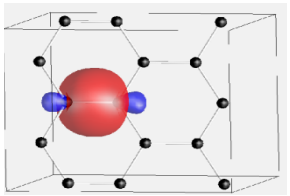
Silicene: The Silicon analogue of Graphene

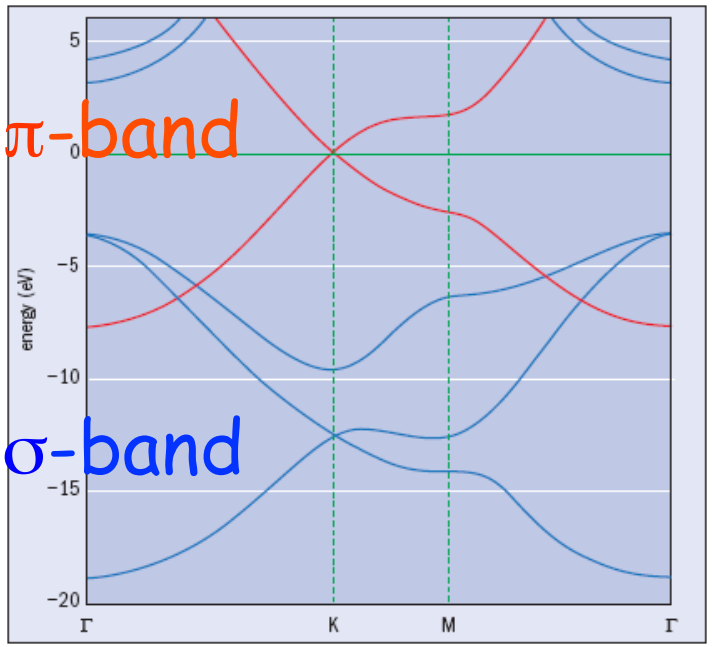
sp^2 bonded single layer of Silicon with graphene-like hexagonal honeycomb structure







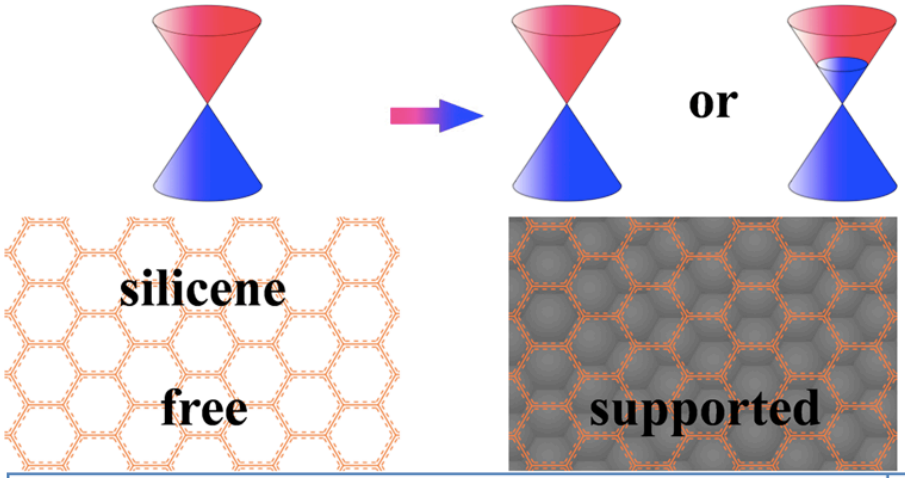


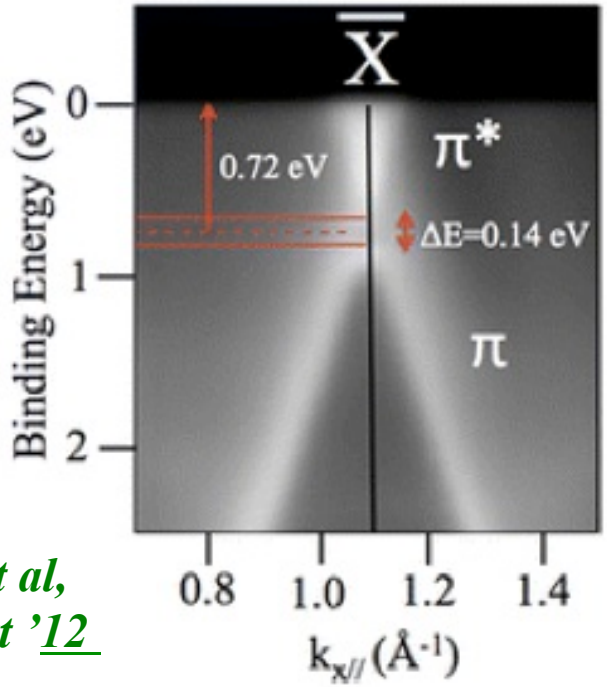


Larger Si-Si bond-length
→weaker π-π overlap
→Low-buckled geometry (Δ ≈ 0.45 Å)
→Partial sp^2 hybridized

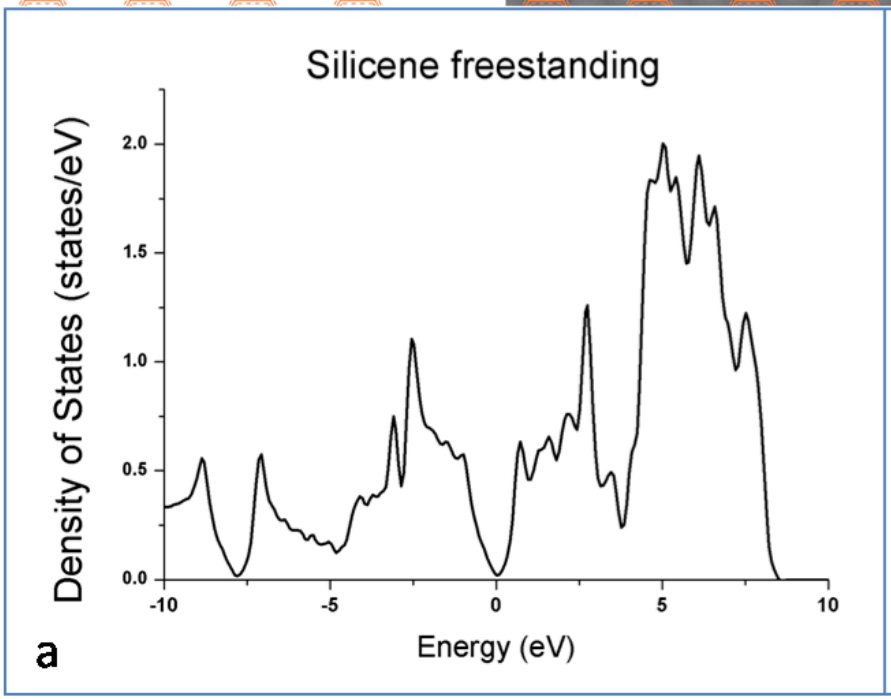
Silicene: Free Standing vs. Supported

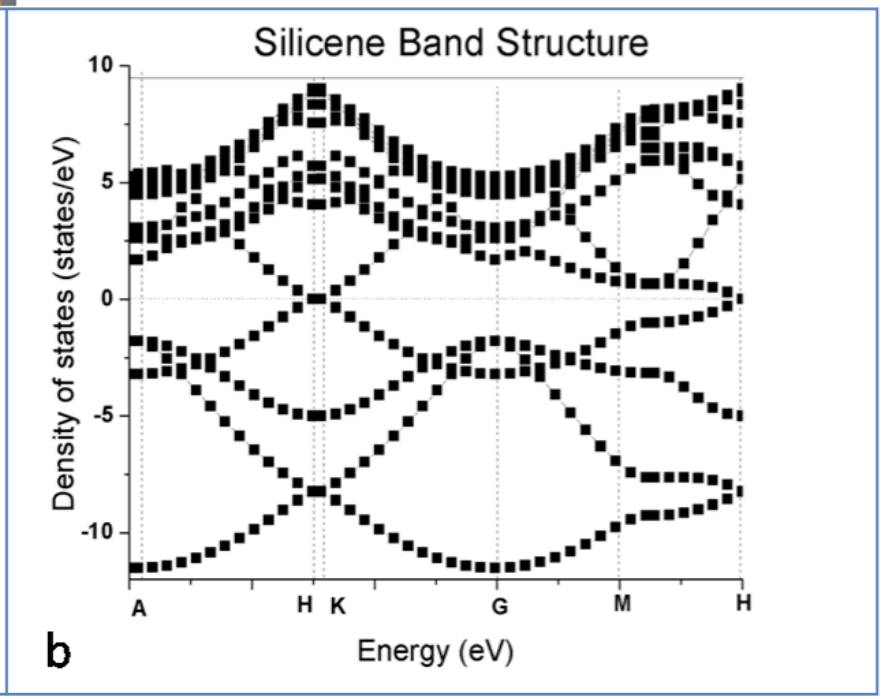
Linear Band Dispersion + Dirac Cone feature





Padova et al, Nano Lett '12





Silicene successfully synthesized on metallic/insulating substrates

→ Metal Substrates : Ag(111), Ir(111), …

→ Insulating Substrates : h-BN, SiC, ZrB2, …

→ Graphene substrate

→ Semiconducting Substrates : III-V, II-VI, IV Semiconductors

Criteria :

- **Limited intermixing between Si and Substrate**
- **Possibility of retaining linear band dispersion near E_F**

For example, Silicene @ Ag (111) substrate

- **Low Biinding Energy ~ 0.52 eV/atom.**
- **DFT calculations yield Dirac Cone ~ 0.3 – 0.5eV below E_F**
- **Results in √3 superstructure, (absent in Graphene or h-BN)**

We explore Semiconductor substrates for silicene growth

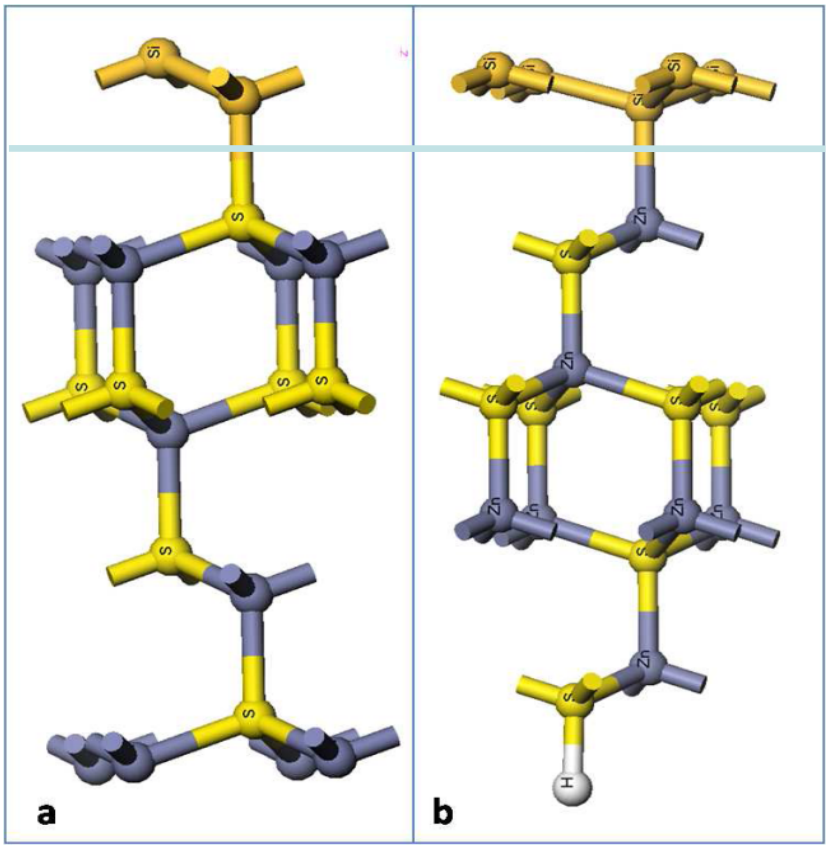
(111)- Semi-conductor substrates

- II-VI → ZnS, ZnSe
- III-V → AlAs, AlP, GaAs, GaP
- IV → Ge

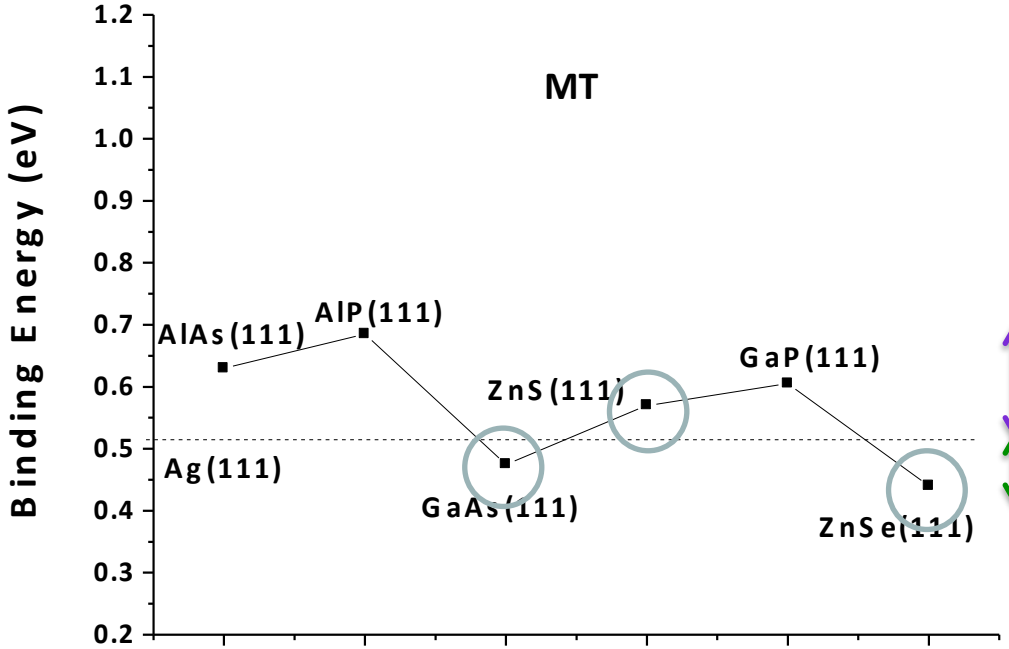
Metal or Non-metal terminated

Case-I Metal terminated	Case-II Non-metal terminated
Metal	Non-metal
Non-metal	Metal
Metal	Non-metal
Non-metal	Metal
Metal	Non-metal
Non-metal	Metal

H-passivated



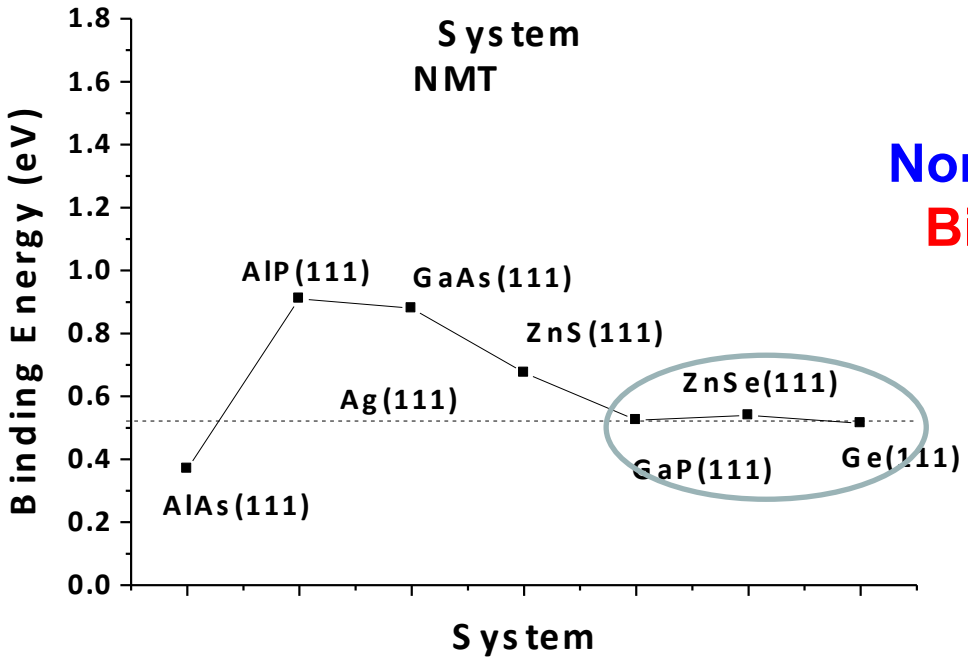
Behavior of silicene on different semiconductor substrate (111) surface



Metal Terminated (MT) Surface

Binding Energy → 0.44 –0.68 eV

→ **Silicene@Ag(111) B.E.= 0.52eV**



Non-Metal Terminated NMT Surface

Binding Energy → 0.37 – 0.91 eV

→ **Silicene@Ag(111) B.E.= 0.52eV**

Silicene on MT Surface :

Case-I : Magnetic Moment gets quenched e.g. AlAs, AlP, GaAs

Case-II : Magnetic Moment gets enhanced e.g. GaP, ZnS

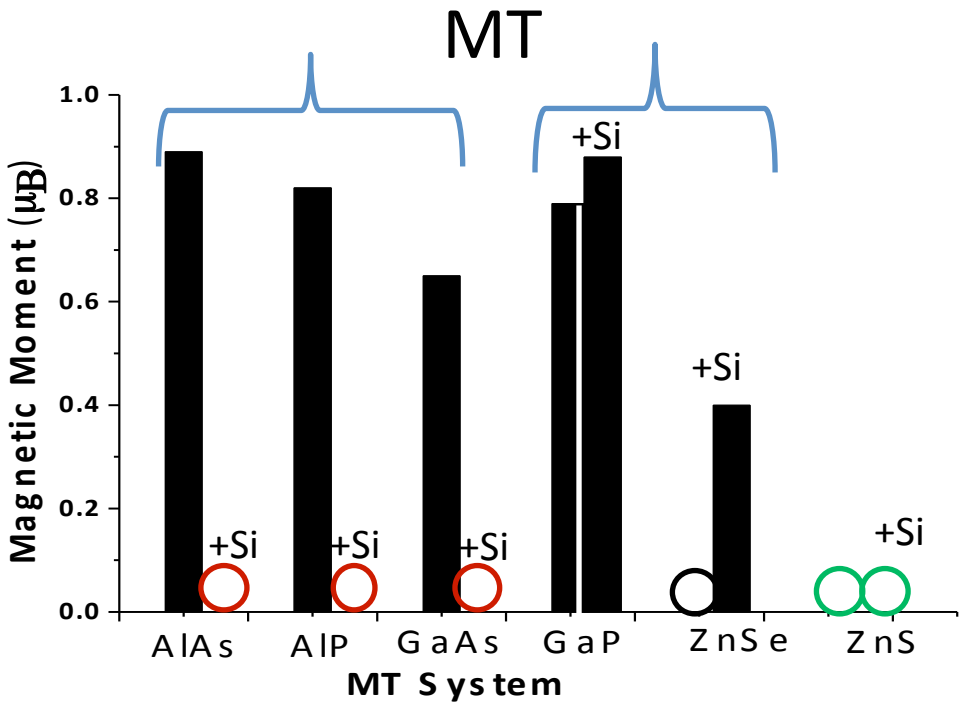
Case-III : No Magnetic Moment before or after e.g. ZnS

Silicene Inclusion

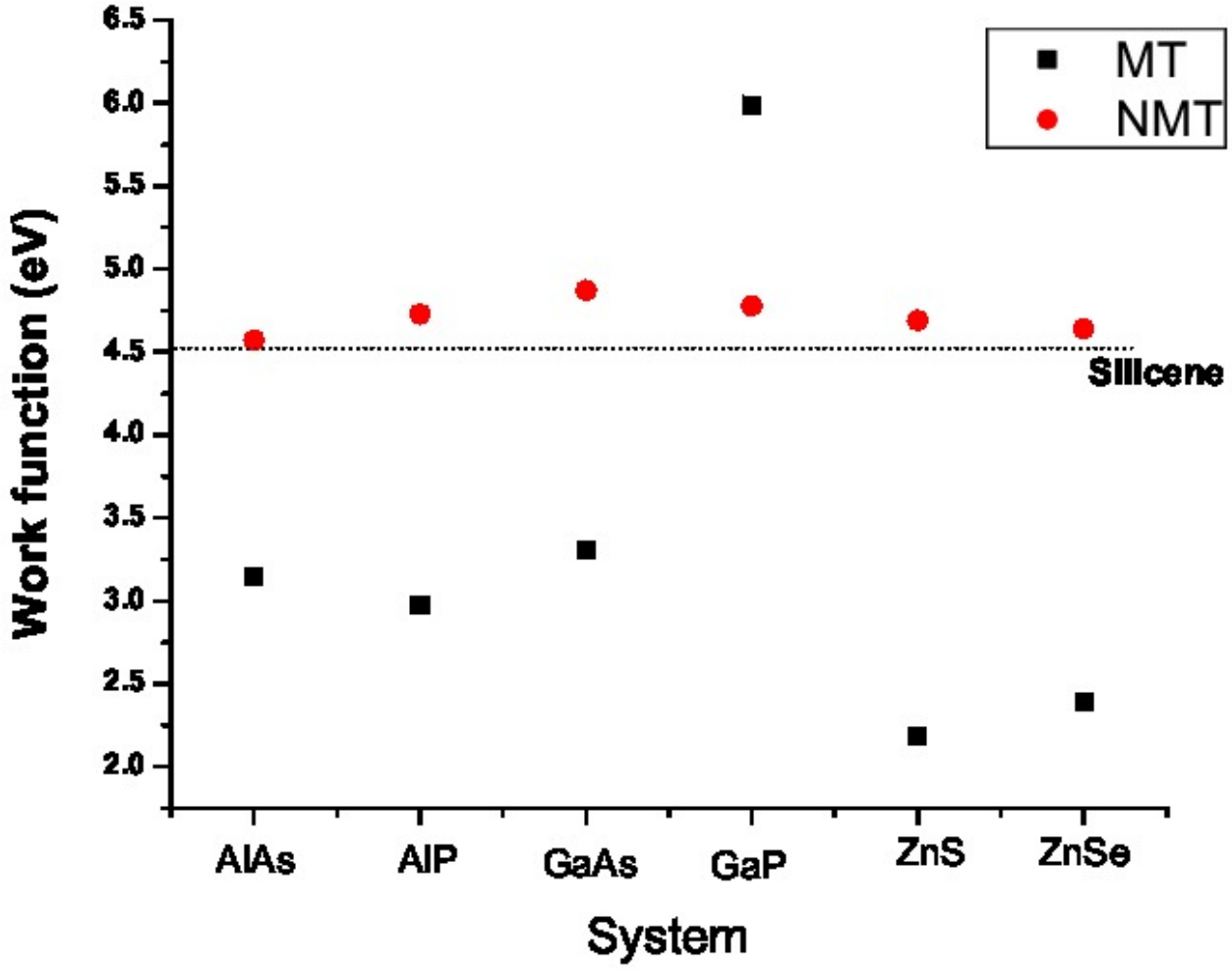
AlAs
AlP
GaAs — **Magnetism quenched**

GaP
ZnSe — **Magnetism enhanced**

ZnS — **Ever 'Zero'**



Work functions of various III-V and II-VI semiconducting surfaces (Φ_s) :
Comparison with that of free standing Silicene monolayer (Φ_{fl})



$\Phi_s > \Phi_{fl}$
p-type doping

$\Phi_s < \Phi_{fl}$
n-type doping

Take home message :

- Binding Energy of Silicence on MT surface is 0.56±0.12 eV, similar to that of Silicene on Ag(111).
- Silicene on NMT surface of all semiconducting substrates leads to enhancement in Magnetic Moment.
- Silicene on MT surface can be metallic, semi-metallic or magnetic depending on the choice of substrate.
- It undergoes substrate induced p-type doping on NMT substrates while p-/n-type doping on MT substrates depending on the direction of charge transfer.

Oxidative Catalysis

h-BN monolayer on Ni(111) substrate

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Letter

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h-BN Monolayer on the Ni(111) Surface: A Potential Catalyst for Oxidation

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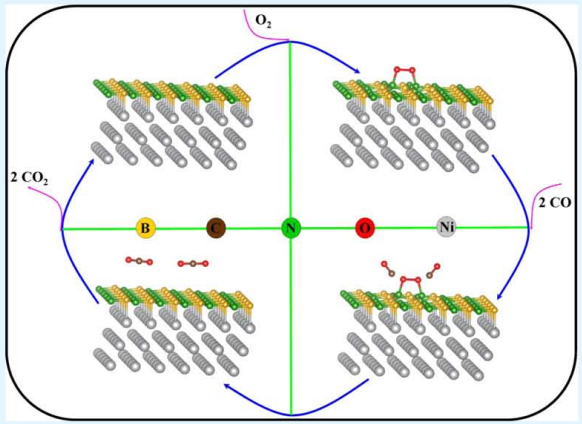
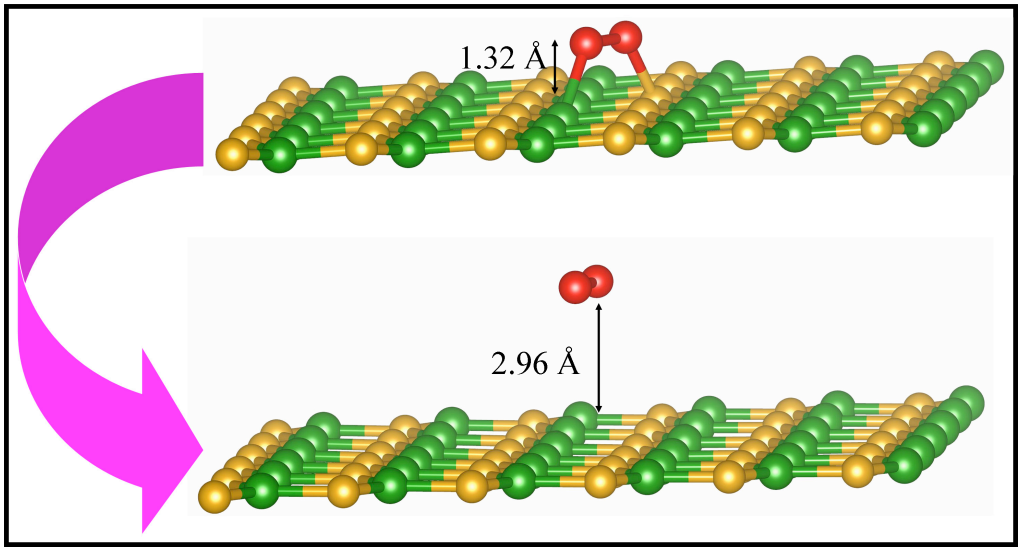
ABSTRACT: The hexagonal boron nitride (*h*-BN) is traditionally considered to be inert. In sharp contrast to the inert behavior of free-standing hexagonal boron nitride (*h*-BN), we propose the catalytic property of *h*-BN monolayer on Ni(111) substrate using first-principles density functional theory investigation. The interaction of O_2 molecule with the *h*-BN/Ni(111) substrate results in nondissociative adsorption of the molecule along with elongation of the O−O bond. This can be considered as the activated state of the O_2 molecule. Further interaction of this complex viz O_2−*h*-BN/Ni(111) with an incoming CO molecule leads to the spontaneous formation of CO_2. Interestingly, the CO adsorption on the *h*-BN/Ni(111) substrate was found to be unfavorable, thereby implying the oxidation of CO selectively through Eley−Rideal (ER) mechanism.



KEYWORDS: *hexagonal-BN monolayer, heterostructure, catalysis, DFT*

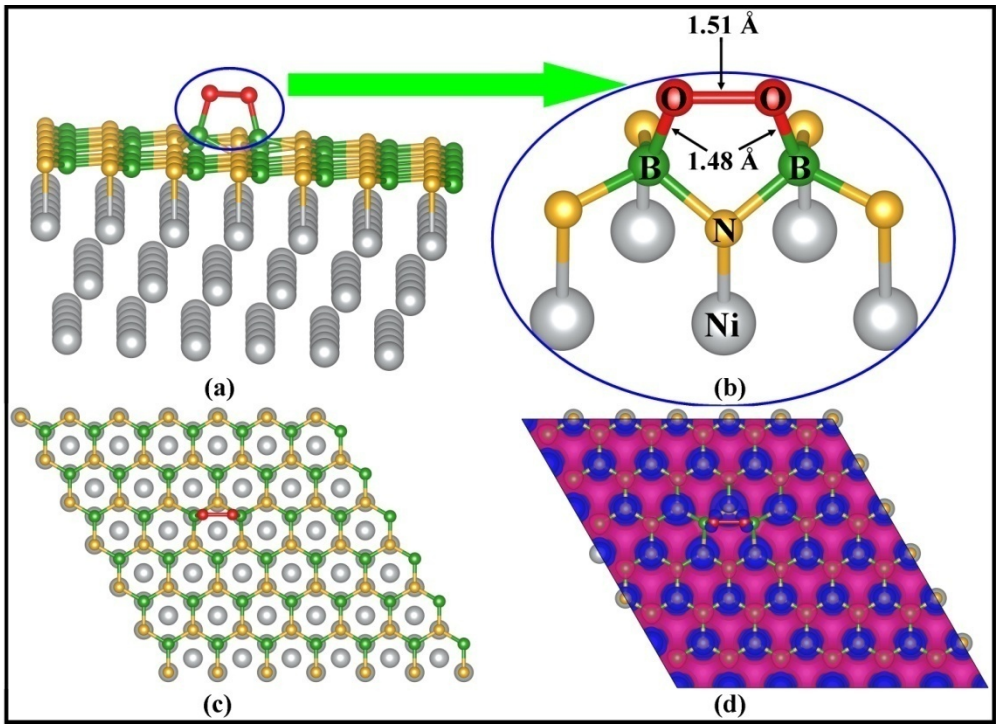
Catalysis

Free standing
h-BN sheet
→ Inert towards O_2



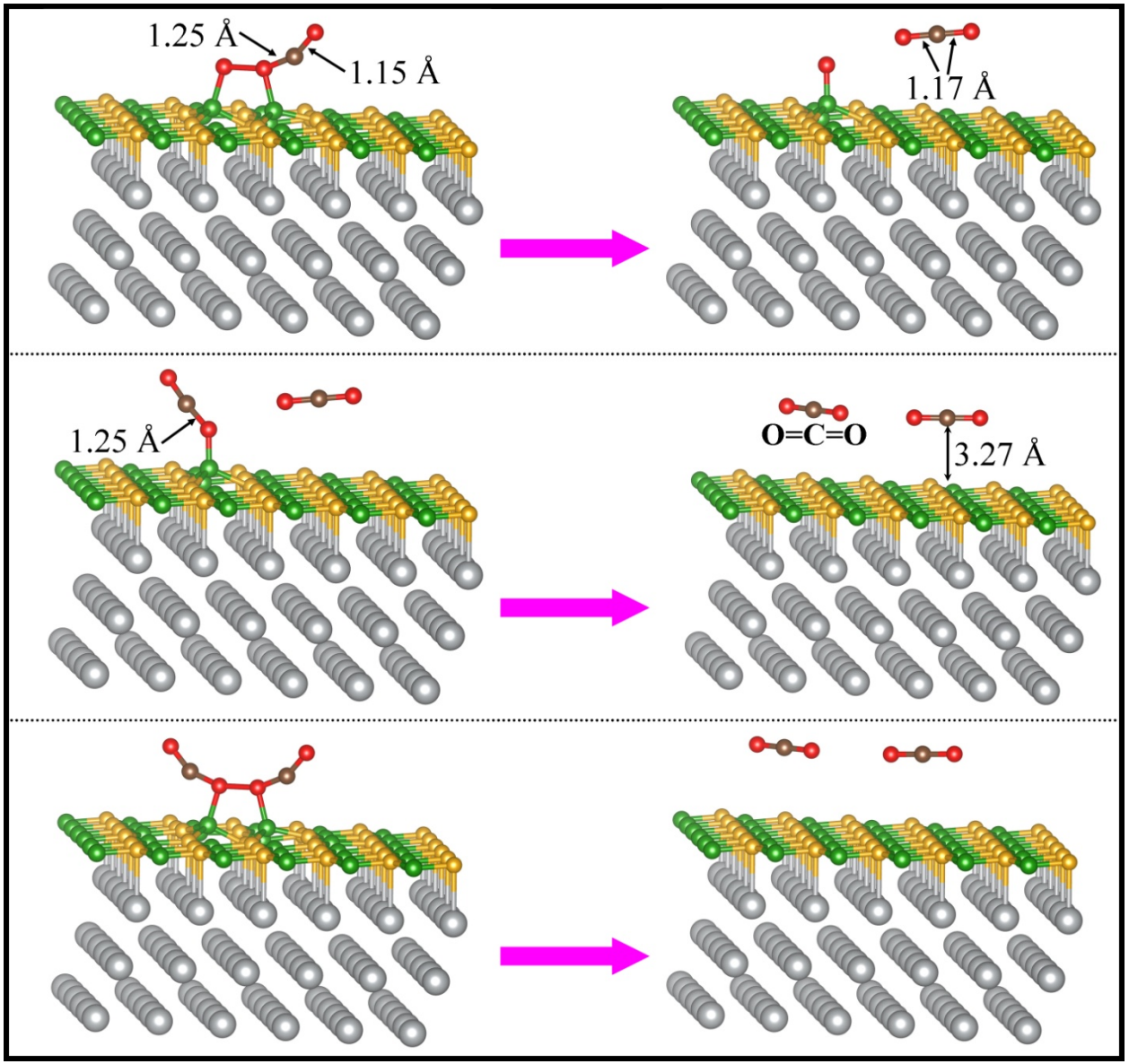
h-BN@Ni(111)
→ O_2 gets adsorbed

Surbstrate induced modulation of
electronic structure



Interaction of CO molecule with O_2--*h*-BN/Ni(111)

- *CO* interacts with adsorbed O_2
- Produces CO_2 spontaneously
- For each *CO* oxidation 2.5 eV of energy is released
- *h*-BN/Ni(111) surface is now free from any gas molecules
- *h*-BN/Ni(111) surface behaving as a catalyst for *CO* oxidation

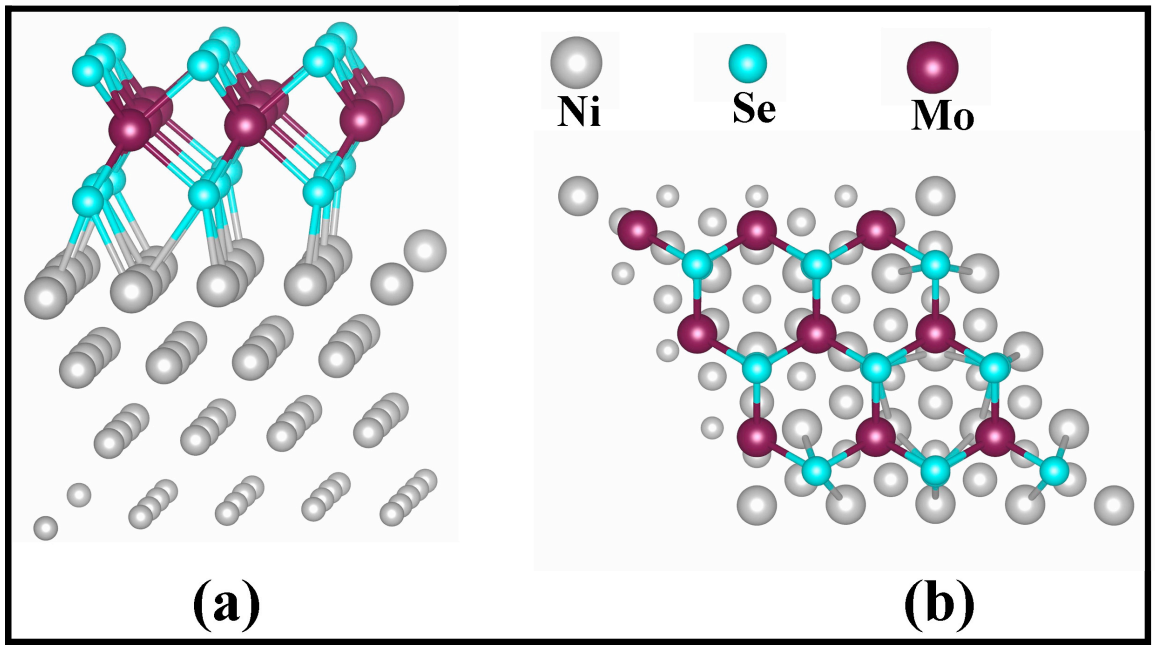


Wasey *et al* [ACS-AMI (2013)]

AIP ADVANCES **4**, 047107 (2014)

Substrate induced modulation of electronic, magnetic and chemical properties of $MoSe_2$ monolayer

A. H. M. Abdul Wasey, Soubhik Chakrabarty, and G. P. Das[a]
Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India



Optimized ground state geometries of $MoSe_2$/Ni(111) system. (a) Side view and (b) top view of the $MoSe_2$/Ni(111) heterostructure. Ni atoms closer to the interface are shown by bigger gray spheres.

$MoSe_2$ monolayer

→ A direct gap Semiconductor (E_g ~1.5 eV)

→ Important for Opto-electronic and Solar cell applications

$MoSe_2$/Ni(111) hetero-junction

Lattice parameters

$MoSe_2$ → 3.32 Å

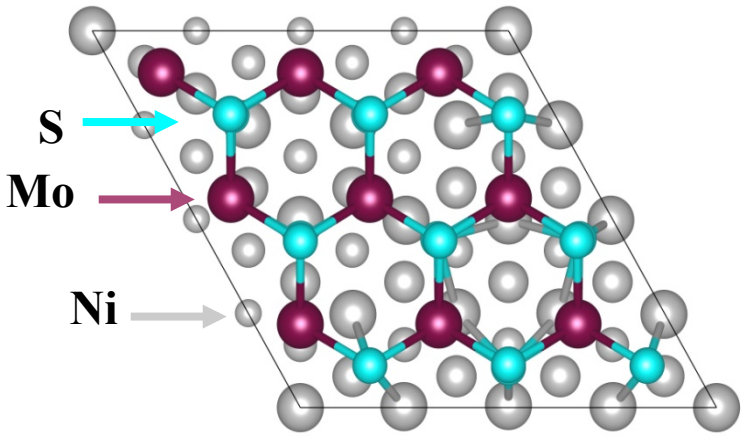
Ni(111) → 2.46 Å

Nearly 35% mismatch!!!

Coincidence site epitaxy

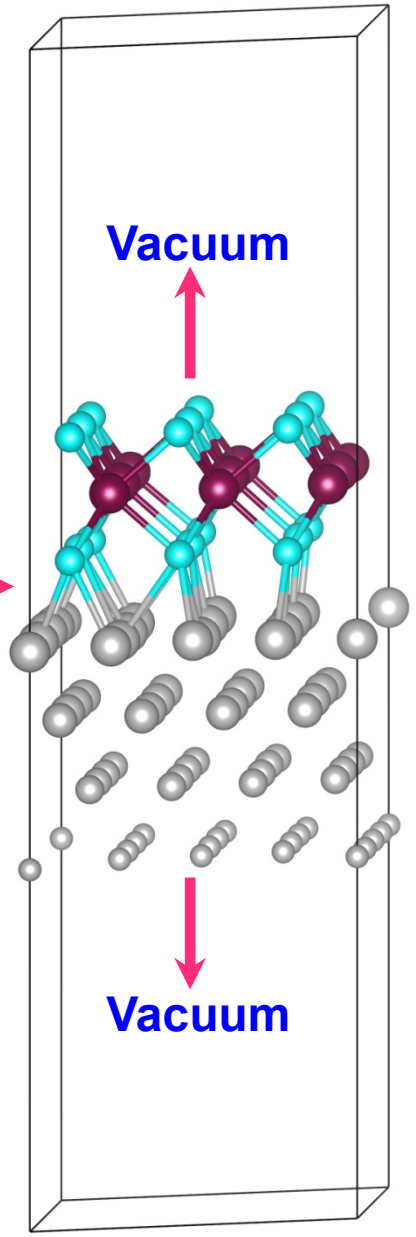
3×3 Surface unit cells of $MoSe_2$ on
4×4 Surface unit cells of Ni(111)-->-
Resulting mismatch ~1% only.

Binding Energy of $MoSe_2$ ~0.3 eV per $MoSe_2$ formula unit

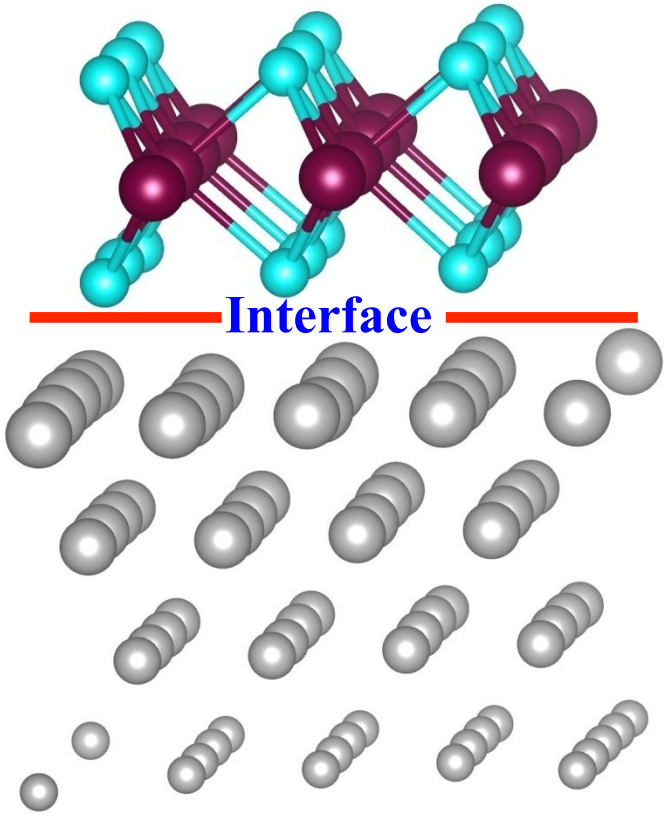


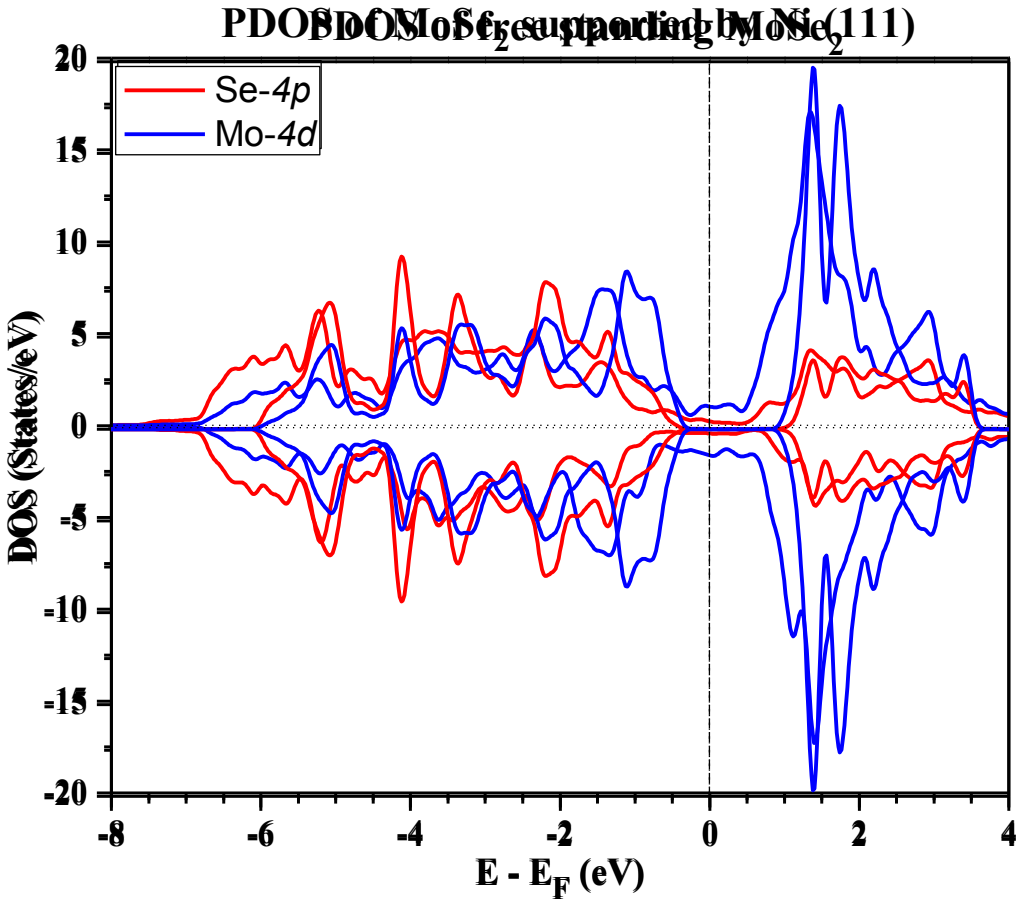
$MoSe_2$/Ni(111) model supercell

(on-top view)



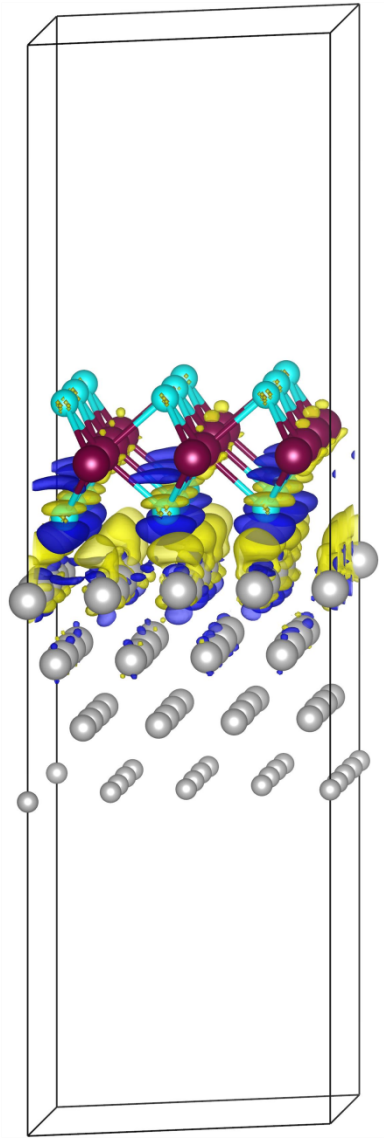
$MoSe_2$/Ni(111): Electronic Structures

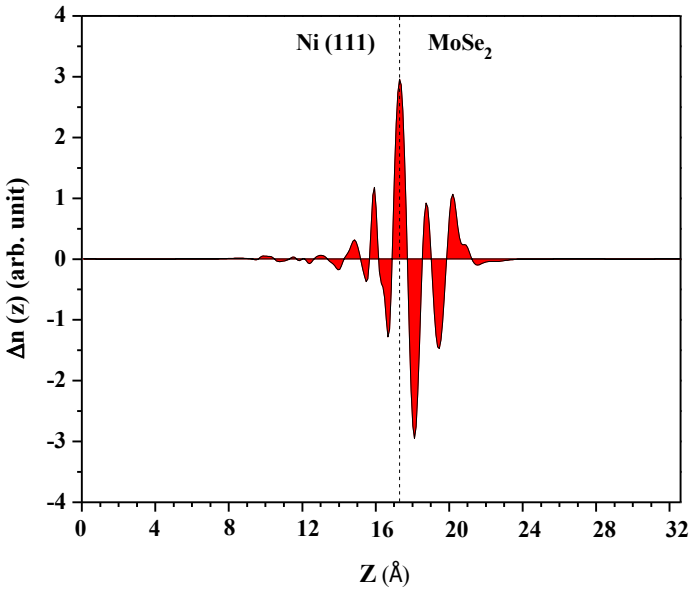


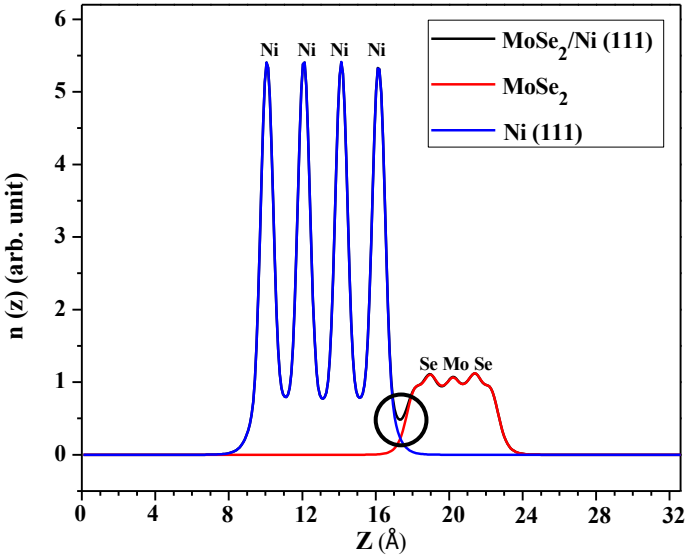


- Overlayer electronic structure gets modified
- Delocalized density of states (DOS) appear around the Fermi level
- Signature of good electron mobility across the Semicond/Metal hetero-junction.
- Substrate induces spin splitting in overlayer DOS

$MoSe_2$/Ni(111): Charge Transfer

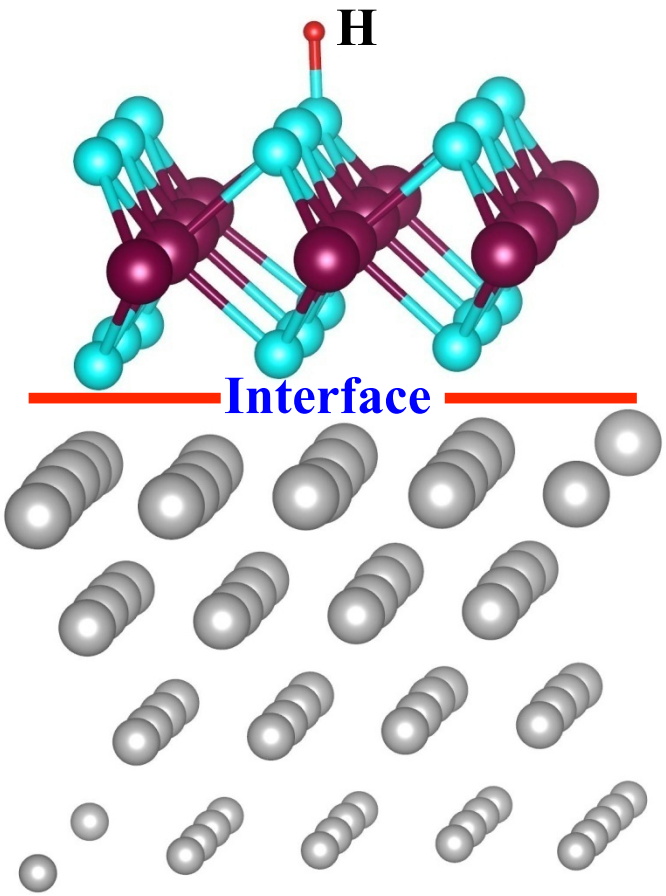


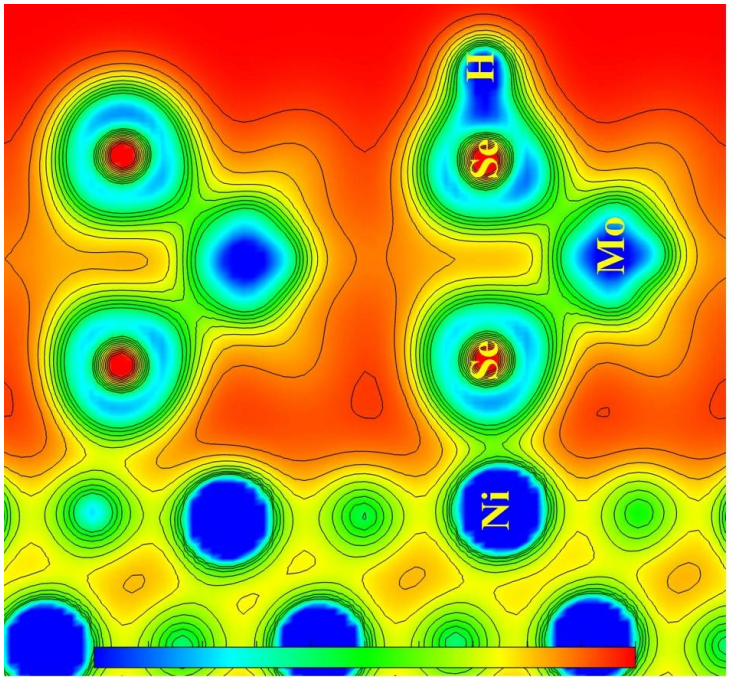




- Charge transfer from metal to $MoSe_2$
- Decrease in work fn (5.45eV to 4.90eV) also characterizes the *n*-type doping
- Signature of chemical modulation

$MoSe_2$/Ni(111): Chemical Modulation





Charge density contour plot showing Se-H bonding

- Binding Energy of H with the surface increases from 0.29 eV to 0.77 eV
- Accumulation of more charges along Se-H bond in case of supported $MoSe_2$
- Chemical reactivity of $MoSe_2$ monolayer gets significantly enhanced due to Ni

To summarize ….

DFT based first principles approach idea for investigating various atomically abrupt epitaxial heterojunctions.

- Interface induced diople crucial for estimating SBH (also Band Offsets in semiconductor heterojunctions)
- Ag overlayer on Si(111) : MIGS, SBH, Work function
- Epitaxial silicene monolayer on III-V, II-VI and Gr-IV semiconductors can behave metallic, semi-metallic, magnetic depending on choice of substrate.
- h-BN@Ni(111) : Oxidative Catalysis
- $MoSe_2$ on Ni(111) & Cu(111) : delocalized interface states leads to increased mobility

Acknowledgments :

All my students and coworkers

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IMR Supercomputer Center


Thank you
for your attention