Atomically precise semiconductor-graphene and *h*BN interfaces by Ge intercalation

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Outline

- Method intro
- Si intercalation
- Motivation
- Synthesis
- Surface reconstruction
- Hybridization and film orientation
- Bonding environment
- Electronic properties

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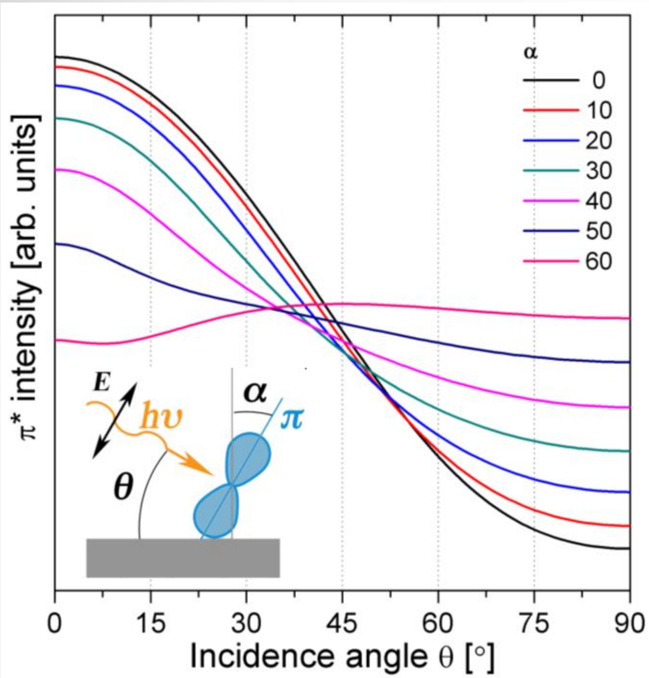
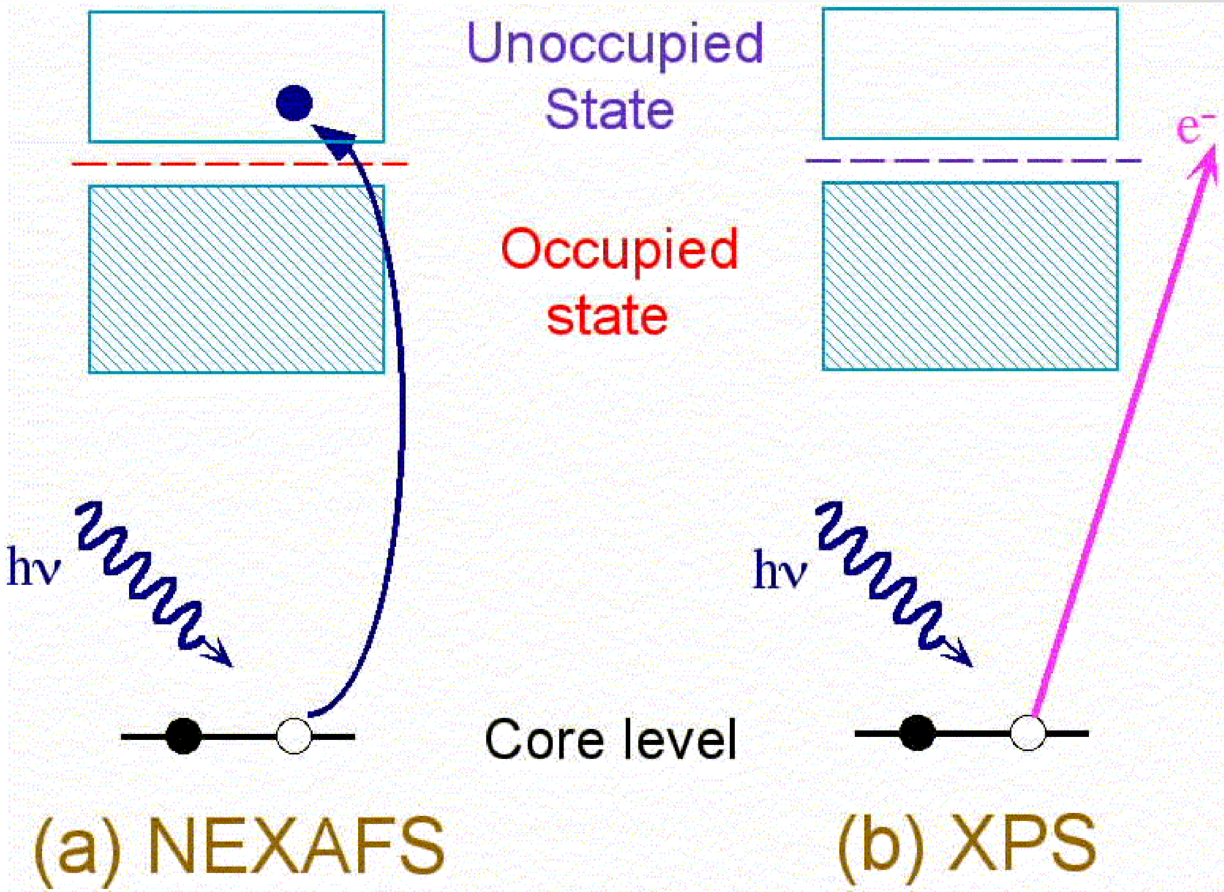
XPS and NEXAFS



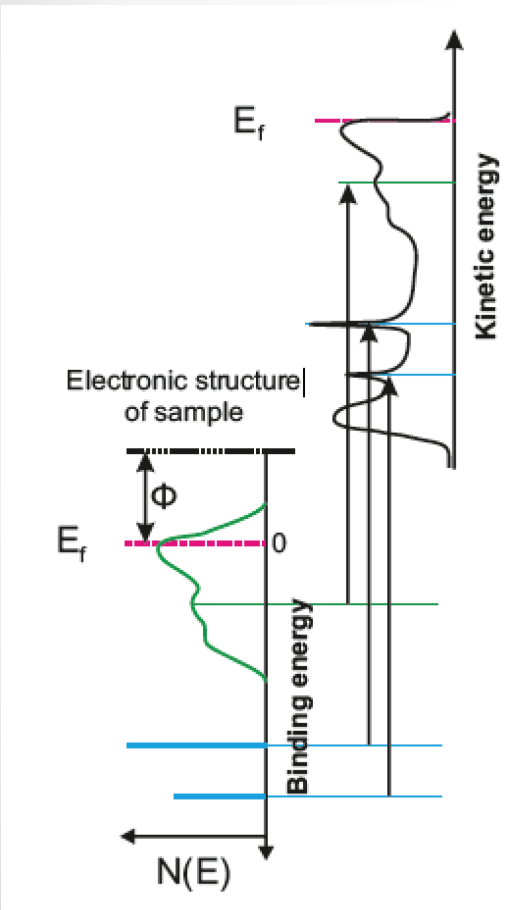
NEXAFS angle dependence

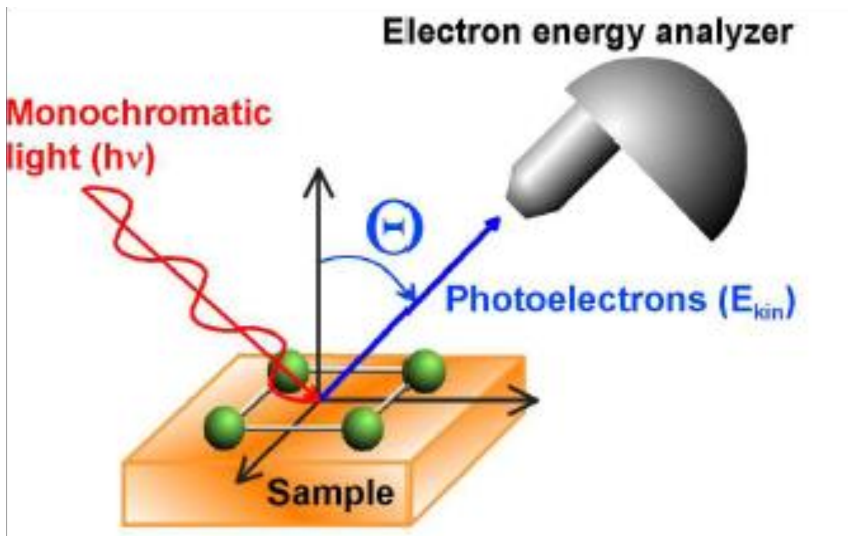


- Corrugation
- Structure
- Bonding environment

- Chemical state
- Bonding environment
- Stoichiometry

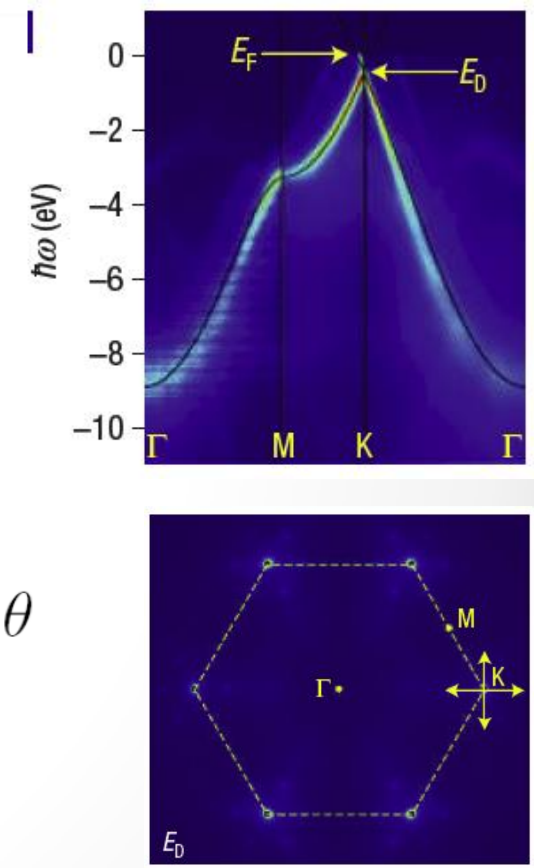
Angle-Resolved Photoemission Spectroscopy





$$k_{||} = 0.51 \text{Å}^{-1} \sqrt{E_{kin}[eV]} \sin\theta$$

$$E_{kin} = \hbar\omega - \Phi - |E_B|$$



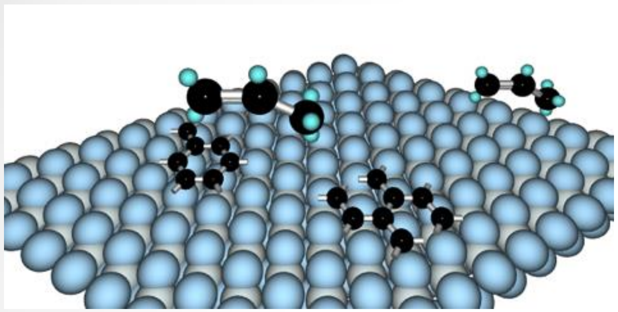
A. Bostwick et al.,
Nat. Phys. (2007), **Vol. 3**

Motivation

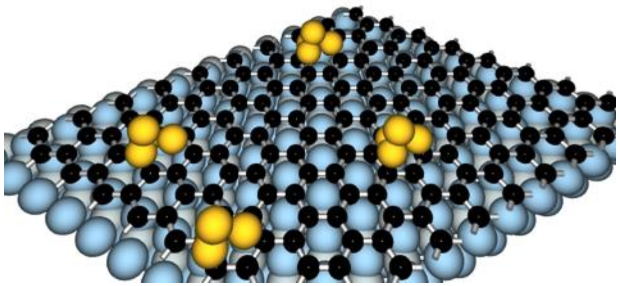
- CVD allows to achieve highest quality on large scale (Ni, Co, Cu substrates etc.)
- Graphene on metals is complicated by charge transfer, puddles, hybridization etc.
- Post-growth transfer inevitably leads to contamination and breakage of graphene sheets.
- Intercalation of metals, semiconductors, oxygen, hydrogen to reduce impact of the substrate.
- Interface structure will strongly affect electronic properties of 2D film.
- Method to produce graphene on semiconductor surfaces with defined interface is needed.

Graphene synthesis

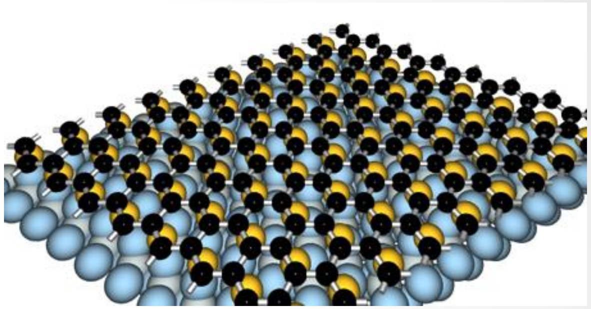
Step I
CVD



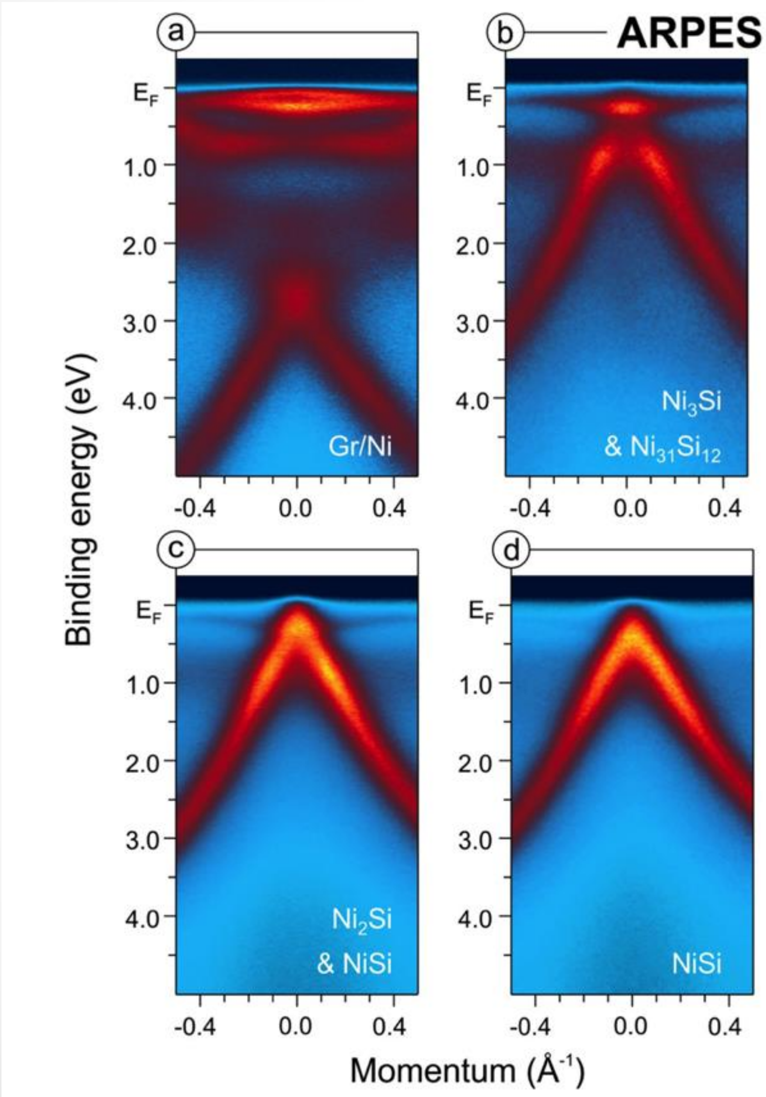
Step II
Ge deposition



Step III
Ge intercalation



Si intercalation

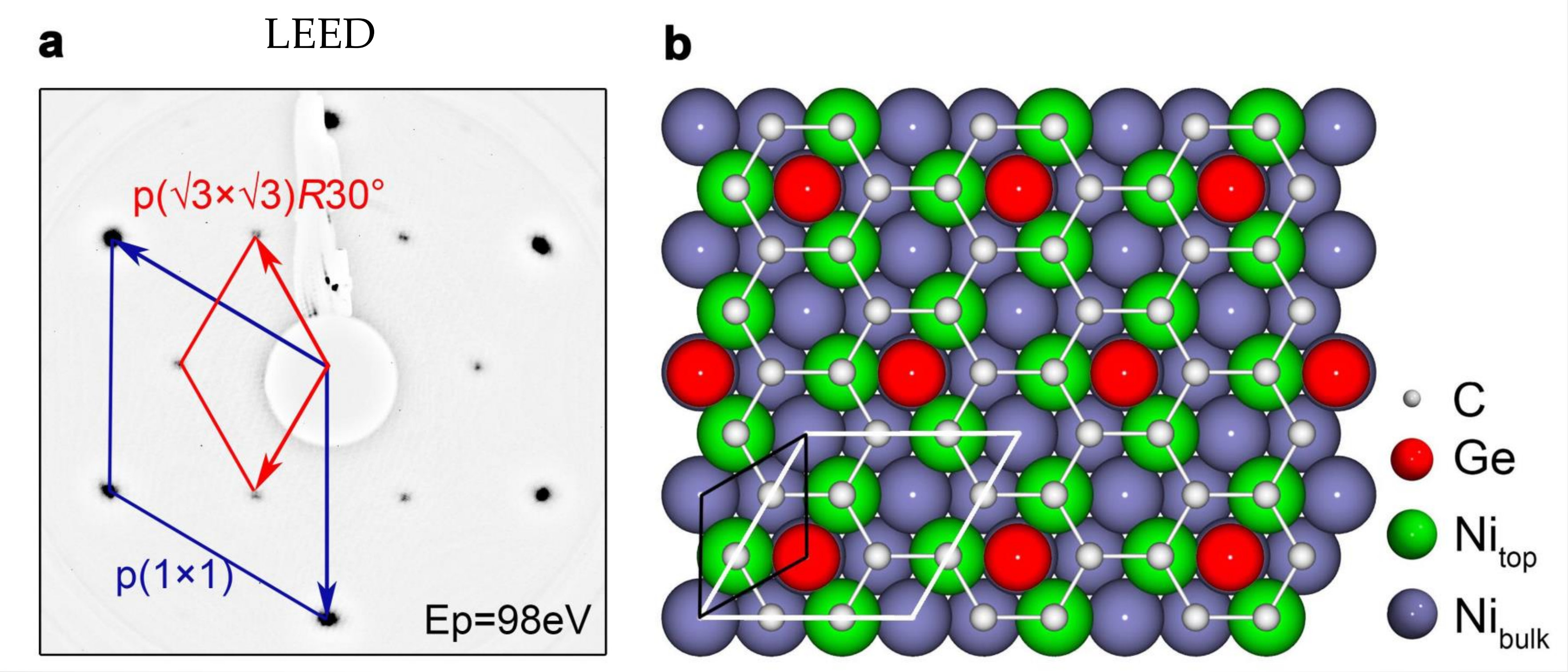


Vilkov, O. et al. Controlled assembly of graphene-capped nickel, cobalt and iron silicides. Sci. Rep. 3, 2168; (2013).

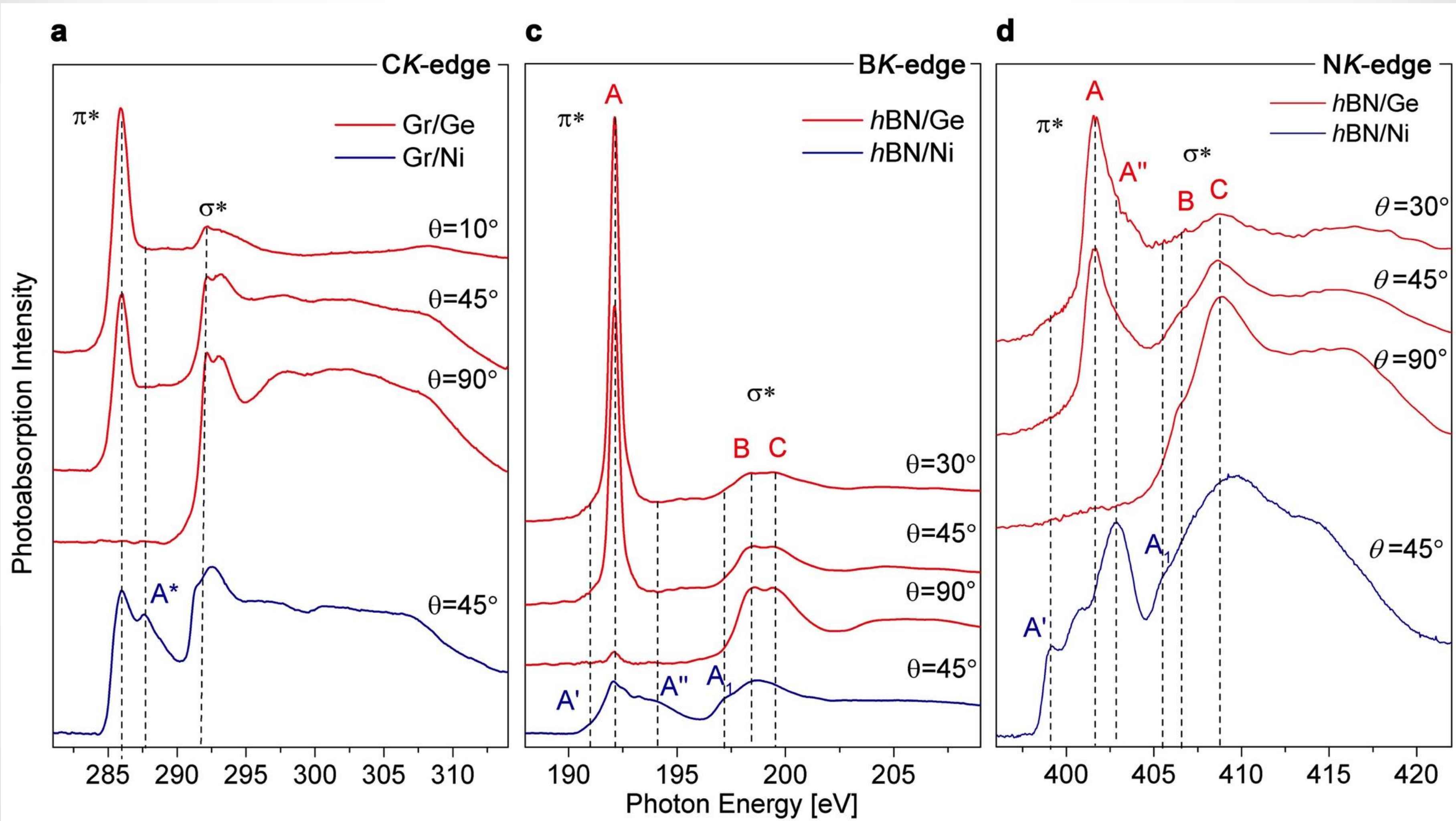
- Si has large solubility in Ni
- Always makes a mixture of silicides

Ge-intercalated graphene and *h*BN

Interface structure

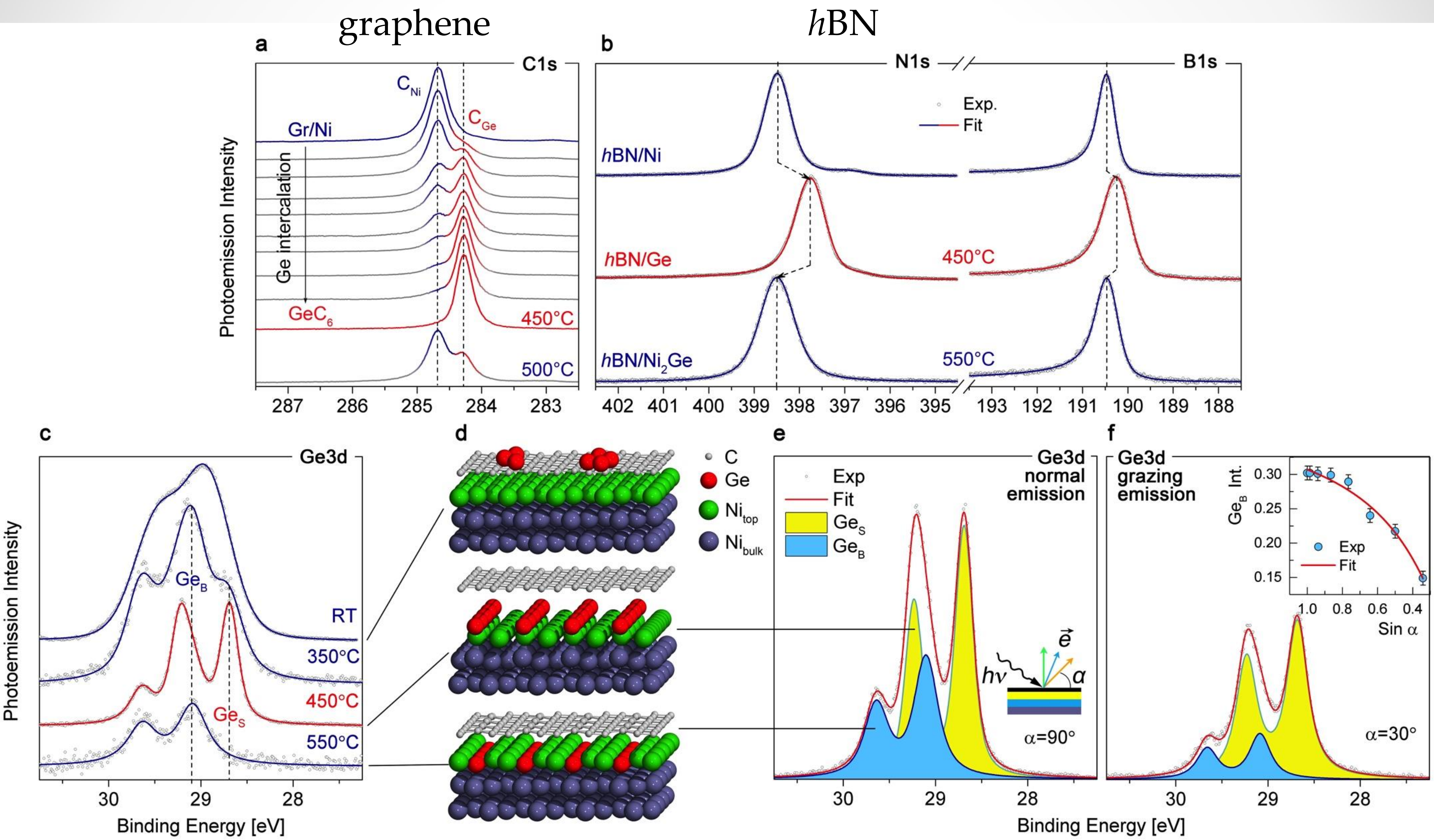


NEXAFS

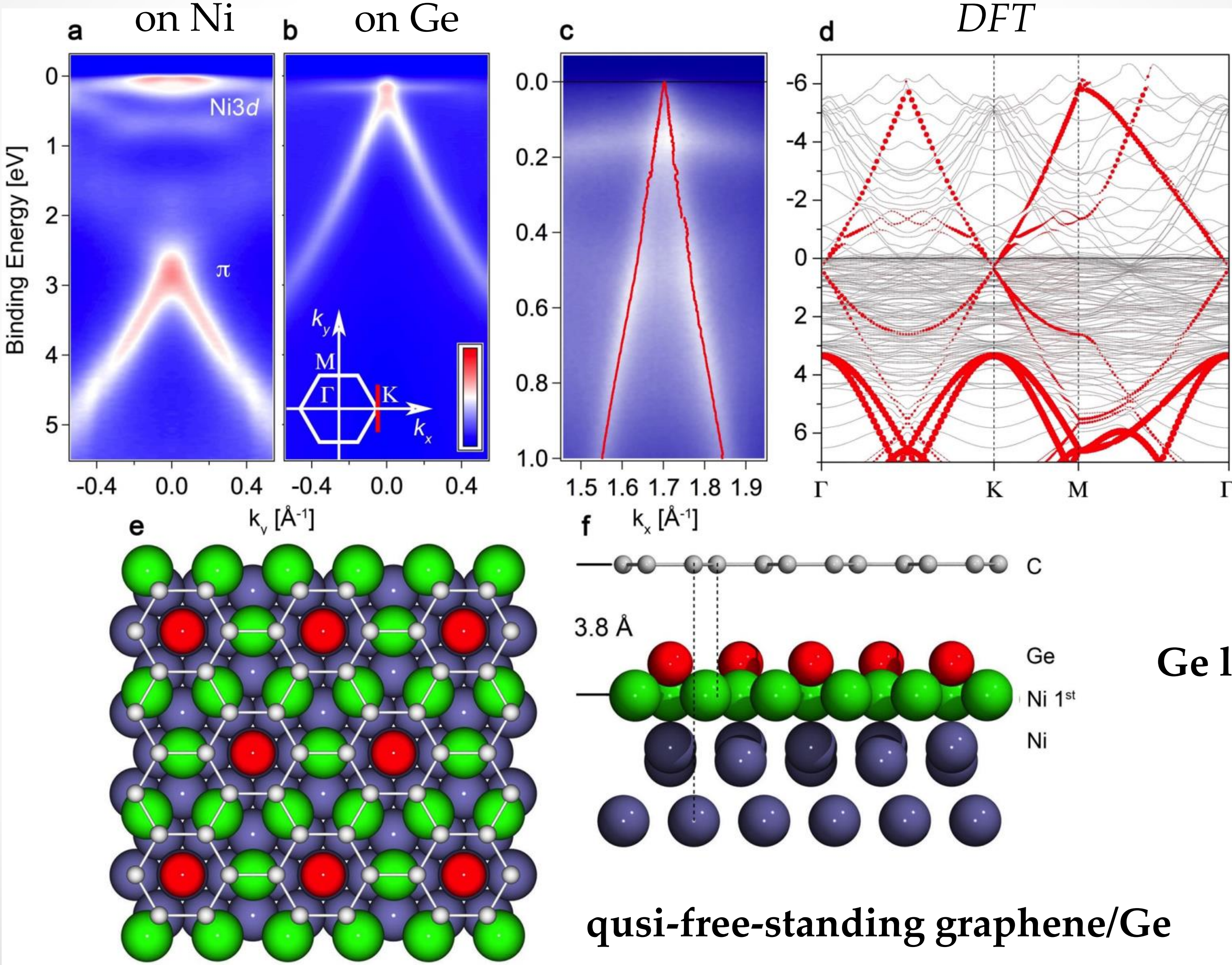


a
c
d
CK-edge
BK-edge
NK-edge
Gr/Ge
Gr/Ni
hBN/Ge
hBN/Ni
π*
σ*
A*
A
A'
A''
A1
B
C
θ=10°
θ=30°
θ=45°
θ=90°
Photoabsorption Intensity
Photon Energy [eV]
285 290 295 300 305 310
190 195 200 205
400 405 410 415 420

XPS


graphene
*h*BN
a
C1s
C_{Ni}
C_{Ge}
Gr/Ni
Ge intercalation
GeC_6
450°C
500°C
Photoemission Intensity
287 286 285 284 283
b
N1s
B1s
Exp.
Fit
*h*BN/Ni
*h*BN/Ge
450°C
*h*BN/Ni_2Ge
550°C
402 401 400 399 398 397 396 395
193 192 191 190 189 188
c
Ge3d
Ge_B
Ge_S
RT
350°C
450°C
550°C
Photoemission Intensity
30 29 28
Binding Energy [eV]
d
C
Ge
Ni_{top}
Ni_{bulk}
e
Ge3d normal emission
Exp
Fit
Ge_S
Ge_B
$h\nu$
$\vec{e}$
α
α=90°
f
Ge3d grazing emission
Ge_B Int.
0.30 0.25 0.20 0.15
Exp
Fit
1.0 0.8 0.6 0.4
Sin α
α=30°
30 29 28
Binding Energy [eV]

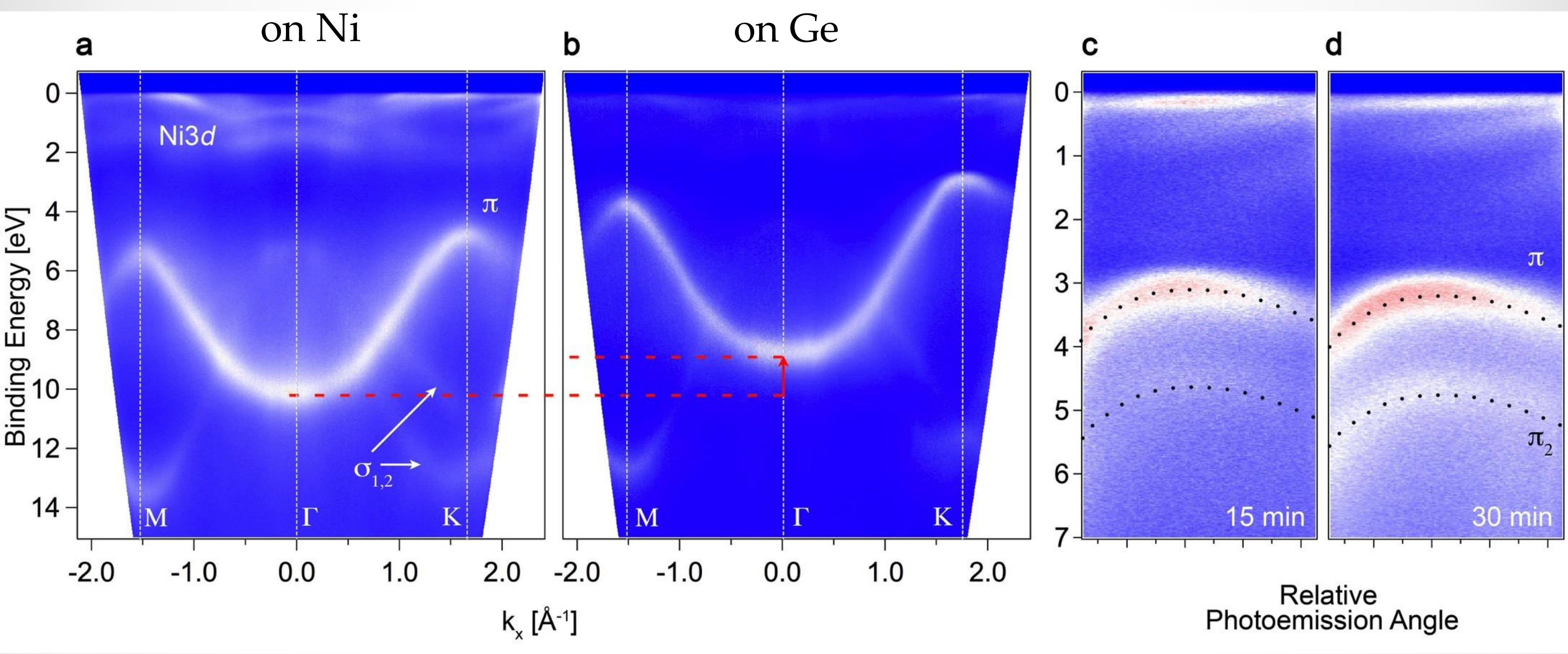
graphene/Ge ARPES



Ge layer

qusi-free-standing graphene/Ge

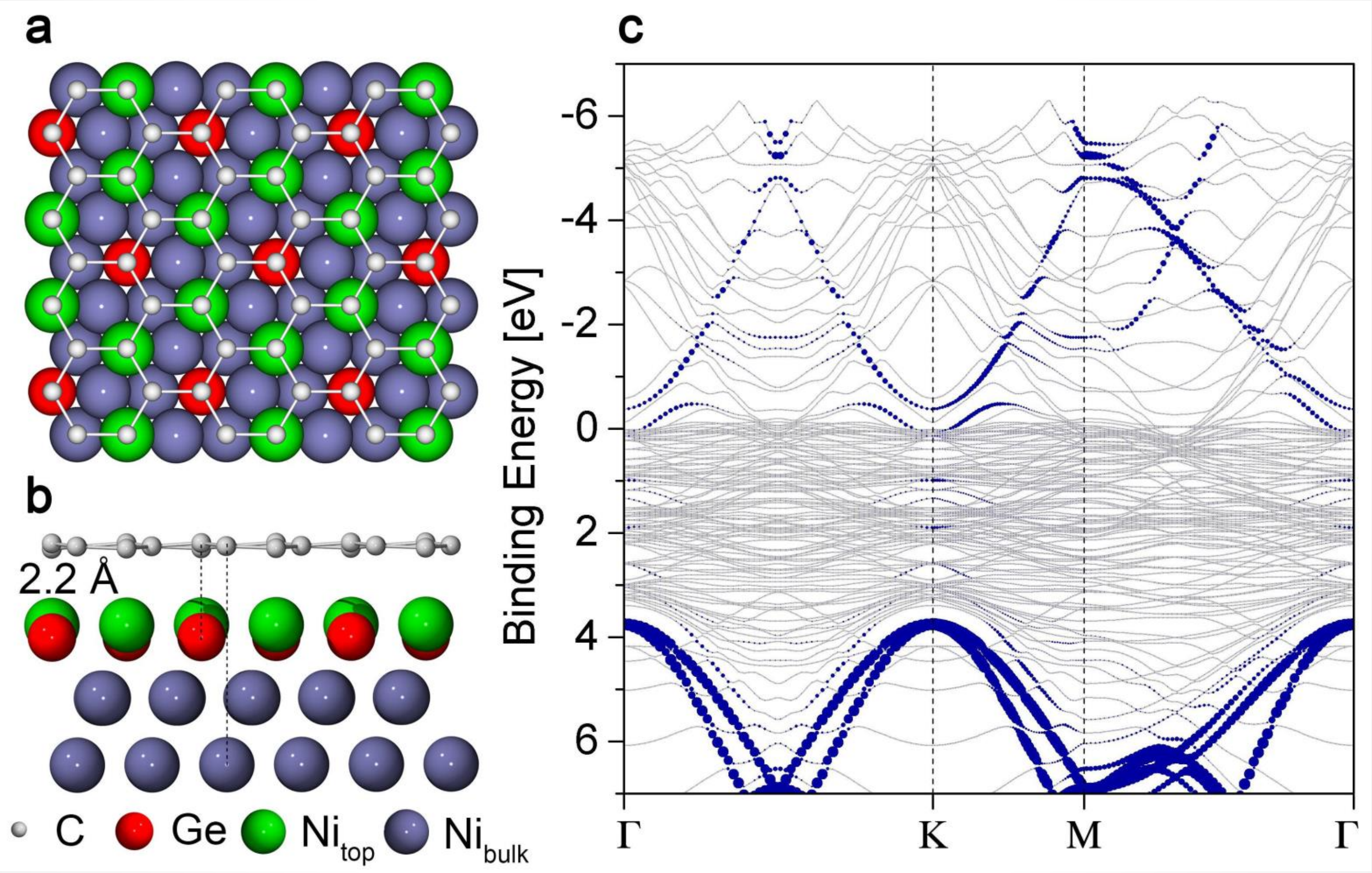
*h*BN/Ge ARPES



Δ=1.29 eV

Further annealing leads
to the second π-band at higher BE

graphene/Ni_2Ge DFT



Ni_2Ge alloy (*top-fcc*)

NO Dirac cone

Conclusion

- New bottom-up approach to synthesize atomically precise graphene–Ge and hBN–Ge interfaces with GeC_6 and GeB_3N_3 stoichiometry.

- $p(\sqrt{3}\times\sqrt{3})-R30^\circ$ reconstruction was observed for both graphene–Ge and *h*BN–Ge systems after intercalation.

- Ge restores the graphene and *h*BN band structure making them quasi-free-standing.

- Intercalation leads to formation of atomically thin Ge layer.

- Further annealing leads to alloying of Ge with Ni and does not result in quasi-free-standing graphene or *h*BN.