Exploring Pathways Towards Heterostacks of Graphene and Hexagonal Boron Nitride

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Collaborators

Current:
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External Collaborations

Single-Crystal Metal Films
Michael Weinl
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Matthias Schreck
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FNS
Fonds national suisse
Schweizerischer Nationalfonds
Fondo nazionale svizzero
Swiss National Science Foundation
Preparation of artificial 2D materials and devices

K. S. Novoselov and A. H. Castro Neto
Our approach: single-crystalline metal substrates at the four-inch wafer scale

Goals:

- single domain growth of h-BN and graphene using UHV-CVD
- explore growth modes of heterostacks
- transfer and stack single layers with defined lattice orientation

4” Si(111) wafer with 150 nm Rh(111) film (from Matthias Schreck, University of Augsburg)

… same for Ir(111), Ni(111), Ru(0001), Pt(111)…
Contents

• single-layer CVD growth on metal surfaces
• single crystal substrates for wafer scale 2D films
• CVD growth of g/h-BN heterostack on (111) surfaces
• transfer of single crystal 2D films
Growth of a $h$-BN monolayer on Ni(111)

CVD under UHV conditions

base pressure: $2 \times 10^{-10}$ mbar
borazine exposure: $5 \times 10^{-6}$ mbar

Borazine+Ni(111) → $h$-BN on Ni(111)+3H$_2$ at 1050 K

Coverage Θ (ML)

Borazine exposure (L)

XPS B 1s

Nagashima, Oshima et al., PRB 51, 4606 (1995)
h-BN on Ni(111)

- perfect monolayer growth on Ni(111) upon exposure to ~100 L of borazine
- good match of lattice constant (mismatch = +0.8%)
- atomic and electronic structure well known

recipe by Nagashima et al., PRB 51, 4606 (1995)
X-ray photoelectron Diffraction (XPD) experiments:

Chemically sensitive structure probe (probing depth ~ 1nm)
Can identify different phases at the interface

N 1s (1342 eV)  
B 1s (1550 eV)

XPD signals:
- forward scattering:
  - B to N n.n.
  - N to B n.n.
- interference fringes
- absence of peaks near center => single layer

A (12x12) h-BN/Rh(111) superstructure

Single h-BN layer
- 13x13 h-BN on 12x12 Rh units
- periodicity: 3.2 nm
- not a simple moiré pattern
- ‘pores’ of ca. 20 Å diameter of strongly bonded h-BN
- ‘wires’ of weakly bonded h-BN

A boron nitride nanomesh!

LEED:
superstructure

Single-layer model for h-BN nanomesh

(NB) = (top, fcc)
Pentanone as a precursor for graphene growth

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Single-crystalline metal films on 4” Si wafers

Group of Matthias Schreck
Institut für Physik, Universität Augsburg

Single-crystalline Ir films for epitaxial diamond growth

-7.1%  
-25.4%  
-5.3%

Dia  
Ir  
YSZ  
Si

PVD, 800°C, micrometers

e-beam evaporation, 650°C, 100 nm

PLD, 750°C, 20-40 nm

Works for (001) growth ...

Single-crystalline metal films on 4” Si wafers

... but also for (111) growth:

XPD -> twin-free diamond nucleation

XRD pole figures
-> twin free, low mosaicity

M. Fischer, M. Schreck et al.,
Single-crystalline metal films

... and also for Rh(111) growth:
The four-inch wafer growth chamber at UZH

Quality control of h-BN growth across wafer surface

Use LEED superstructure as a quality measure for h-BN film (after transfer through air + annealing)

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CVD growth beyond the monolayer: g/h-BN/Cu(111)

LEED: lattice constants

Careful analysis of LEED spots:

- each layer has a different lattice constant
- the peak positions are consistent with the intrinsic lattice constants of h-BN and graphene (2.50 Å and 2.46 Å)

=> Only small angle domains in both layers (~ 2°).
Characterisation by quantitative XPS

Composition and coverage:

After borazine exposure:
fairly stoichiometric, single layer of h-BN

After pentanone exposure:
h-BN still stoichiometric, single layer,
intensities slightly attenuated by single graphene layer on top

S. Roth et al., Nano Lett. 13, 2668 (2013)
XPD from the heterostack – a puzzle!

SSC theory (free-standing) ⇒ Single layer of h-BN ⇒ Single graphene layer
Both well ordered.

But:
Why no forward scattering of the B and N signal through the graphene layer?
Answer:
Because the layers are incommensurate!

S. Roth et al., Nano Lett. 13, 2668 (2013)
**XPD: commensurate vs. incommensurate overlayer**

**Commensurate**
- Strong forward scattering signal
- [211]

**Incommensurate**
- Forward scattering signals smear out completely
- [211]

S. Roth et al., Nano Lett. 13, 2668 (2013)
Confirmation: STM sees a moiré pattern

Moiré pattern on most of the terraces
Periodicity ~ 9 nm

Regular ribbons (>100 nm x 9 nm, ca. 0.8 nm high):
=> formation of grafolds?

K. Kim et al.,

S. Roth et al., Nano Lett. 13, 2668 (2013)
ARPES data: the $\pi$ bands of h-BN and graphene

In the heterostack, we observe the $\pi$ bands of both individual layers.

- h-BN maintains a large band gap
- graphene shows linear dispersion up to $E_F$
- the two layers are electronically decoupled (exhibit slightly different BZ)

S. Roth et al., Nano Lett. 13, 2668 (2013)
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A refined ‘bubbling’ method using hydrogen intercalation

Approach similar to that used for graphene in

Schematic potentiostat set-up for the bubbling transfer process.

Solution: 0.1 M HClO₄

Hydrogen intercalation prior to bubbling weakens the bonding to the metal substrate.
XPS analysis of transferred h-BN monolayer

![XPS analysis graph](image-url)
Conclusions

Single-layer CVD growth on metal surfaces:
• We can grow large domains of high quality h-BN and graphene

Single crystal substrates for wafer scale 2D films:
• Single layer quality approaching that of single crystal substrates
• Scalable approach

CVD growth of g/h-BN heterostack on (111) surfaces:
• Growth beyond single layer difficult to control
• Quality inferior to single layer growth

Transfer of single crystal 2D films:
• Transfer of h-BN single layers appears to be more difficult than graphene – optimization in progress (collaboration within Flagship)
• Can get aligned flakes
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