Graphitic films of group III nitrides and group II oxides: platform for fundamental studies and applications (**GRIFONE**)

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GRIFONE overview

FLAG-ERA

Joint Transnational Call 2015

- Graphene JTC Scientific area: New layered materials and heterostructures
- The Aim & Scientific concept
  - ➢ The international context & impact
- Work Packages & Consortium partners
- Added value

The Aim & Scientific concept

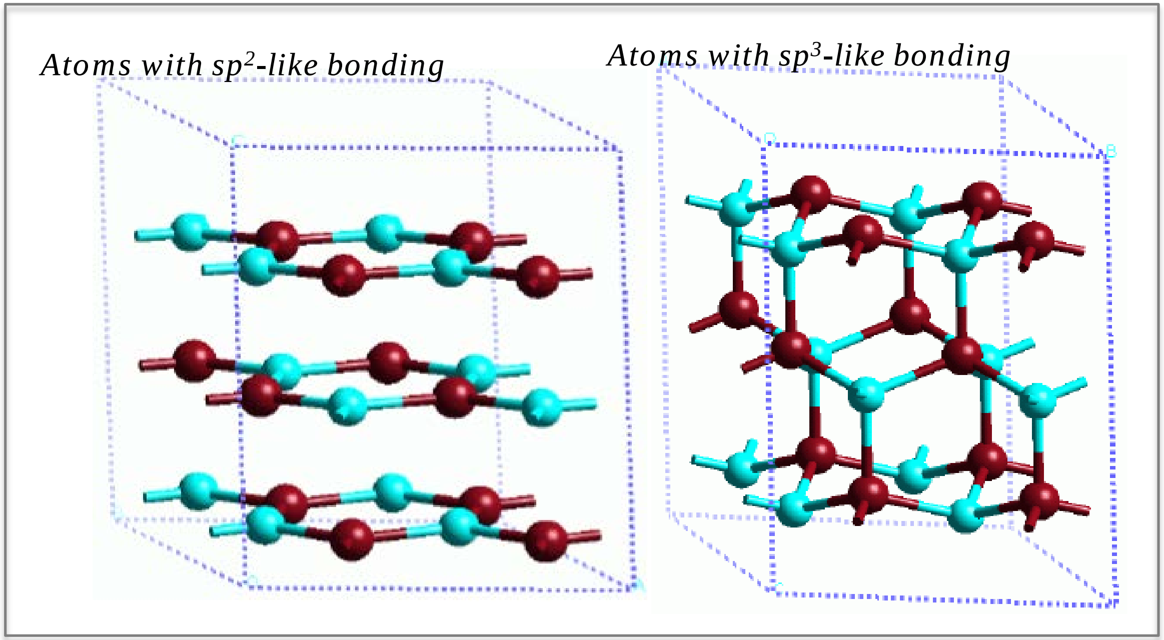
The aim

- Breakthrough in the fabrication of graphene heterostructures with semiconducting materials by developing an innovative material concept for ultrathin graphitic films of group III nitrides and group II oxides

  - We will explore the metal organic chemical vapor deposition (MOCVD) of original and unexplored ultrathin graphitic films, a key to ensure any industrial relevance

graphitic AlN and ZnO: theoretical predictions

- The flat graphitic structure has been calculated to be the lowest in energy for ultrathin films of e.g., AlN, GaN, BeO, ZnO, ZnS, and SiC

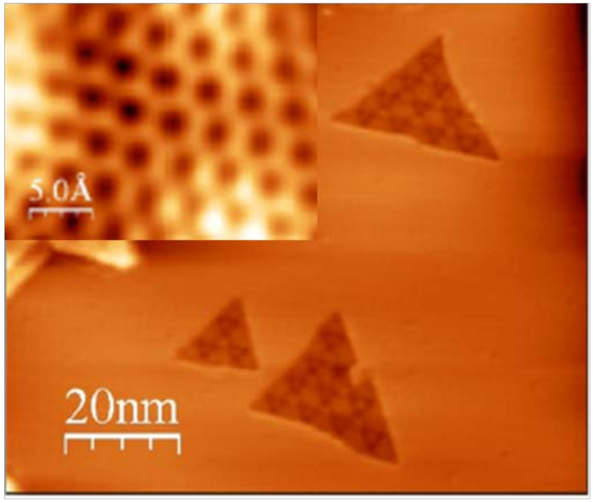


C.L. Freeman et al., Phys. Rev. Lett. 96, 066102 (2006)

C. Bacaksiz et al., Phys. Rev. B 91, 085430 (2015)

graphitic AlN and ZnO: experimental manifestation

- Ultrathin h-AlN (12 monolayers) prepared by MBE on Ag(111)



P. Tsipas et al., Appl. Phys. Lett. 103, 251605 (2013)

- Ultrathin h-AlN prepared by ammonia assisted MBE on Si(111)
  - ➢ Maximal thickness of 5-6 monolayers: the effect of structural defects and roughening

V. Mansurov et al., J. Cryst. Growth 428, 93 (2015)

Main objectives

- R&D
  - ➢ semiconductor-quality thin films of wz-AlN (respectively wz-GaN, wz-InN) and wz-ZnO
  - ➢ ultrathin graphitic films of h-AlN and h-ZnO

  on SiC-supported graphene templates by developing chemical vapor deposition processes and applying the modern concept of direct van der Waals epitaxy

- Creating routes for proof-of-concept deposition of van der Waals heterostructures on demand
  - ➢ Ultimate control of the growth kinetics

The international context

nature COMMUNICATIONS

NATURE COMMUNICATIONS | 5:4836 |

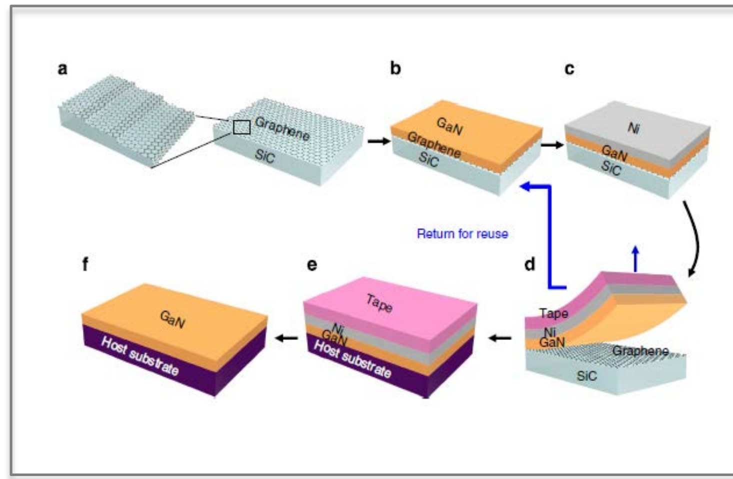
ARTICLE

Received 25 Jun 2014 | Accepted 29 Jul 2014 | Published 11 Sep 2014

DOI: 10.1038/ncomms5836

Principle of direct van der Waals epitaxy of single-crystalline films on epitaxial graphene

Jeehwan Kim[1,*], Can Bayram[1,*], Hongsik Park[1], Cheng-Wei Cheng[1], Christos Dimitrakopoulos[1,†], John A. Ott[1], Kathleen B. Reuter[1], Stephen W. Bedell[1] & Devendra K. Sadana[1]

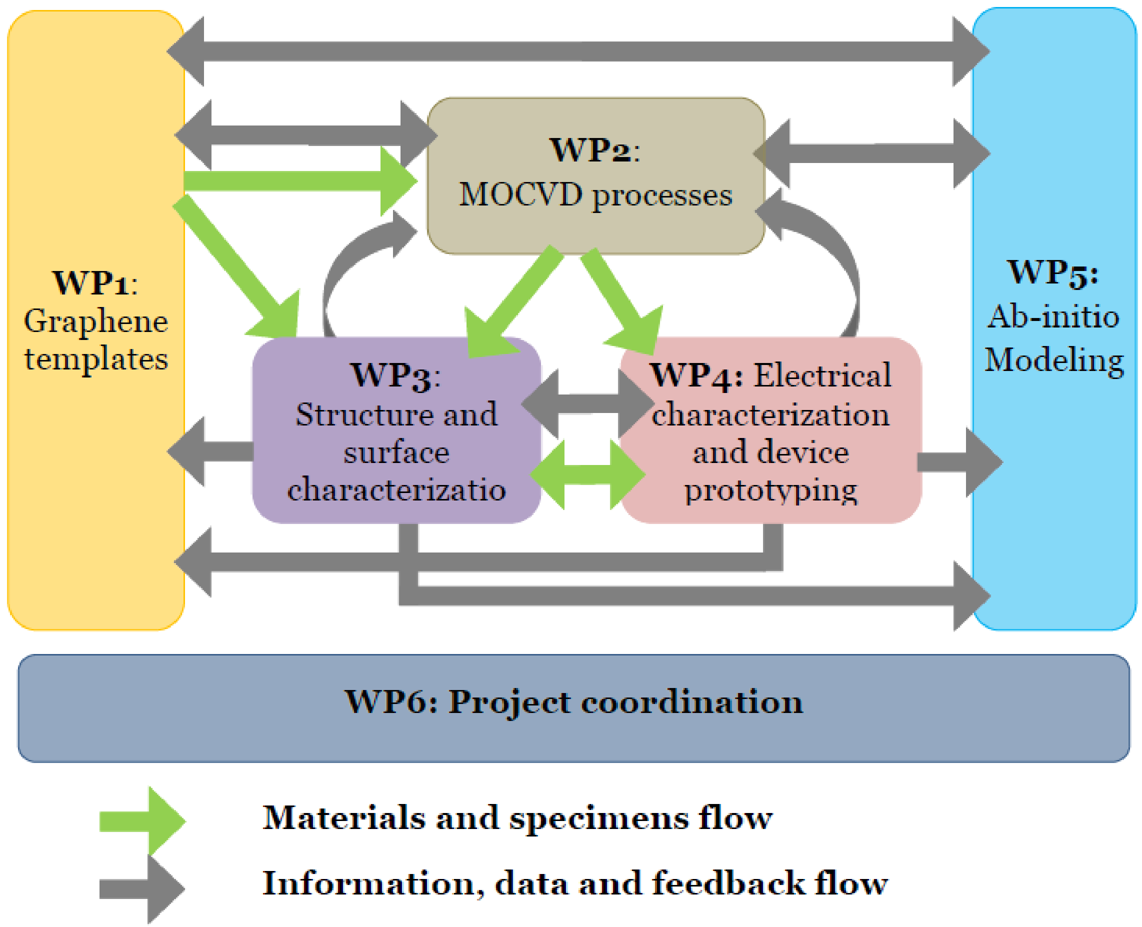


Impact

- Material solutions for flexible electronics and reduced thermal resistance in high power/high-frequency electronics
  - ➢ The virtue of post-growth release and transfer onto arbitrary substrates
  - ➢ Meeting the demand for thermally optimum operation and reliability of the GaN devices
- Opportunities for research in novel electronic/optoelectronic devices based on ultrathin graphitic films
  - ➢ h-AlN and h-ZnO have band gaps larger than 2.0 eV
- Hydrogen storage
  - ➢ The estimated binding energy of adsorbed H_2 on h-AlN and h-ZnO meets the desired energy range of 0.1–0.2 eV/H_2 for efficient hydrogen uptake
- Room-temperature semiconductor-based spintronics
  - ➢ The fluorination of h-AlN may render them ferromagnetic

Work packages & Partners

Work Packages



Linköping University, Sweden

WP1. Graphene templates

R. Yakimova

WP2. MOCVD processes

A. Kakanakova

V. Khranovskyy

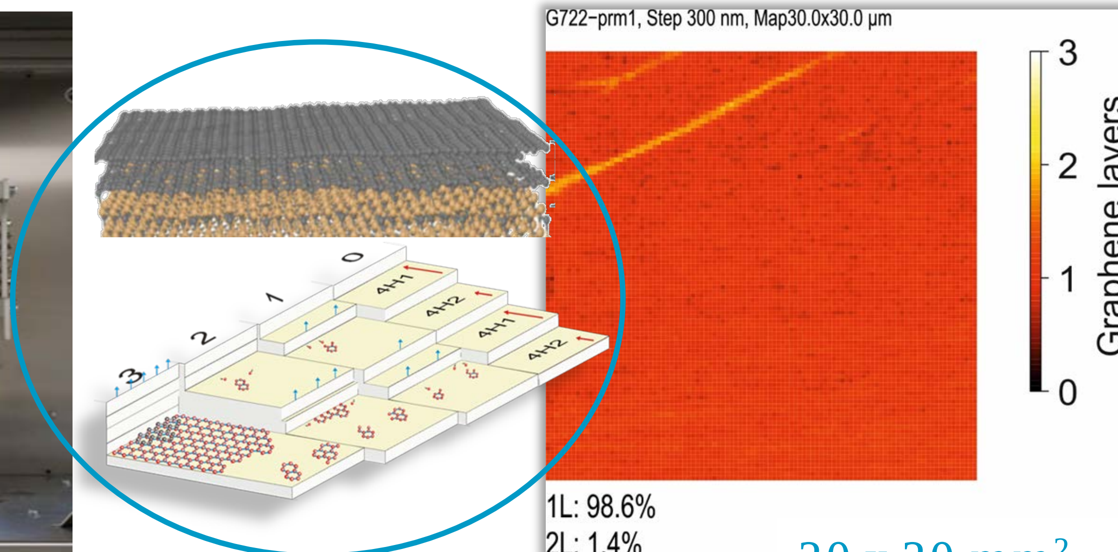
WP5. Ab-initio modeling

G. Gueorguiev

Graphene templates: the growth concept

- LiU unique high temperature method in argon ambience for the preparation of graphene on SiC yielding large area defect free monolayer graphene

Control of the buffer layer formation as a precursor of graphene growth



20 x 20 mm^2

Understanding of the step bunching process on different SiC polytypes

A. Tzalenchuk, et al., Nature Nanotechnology 5 (2010) 186

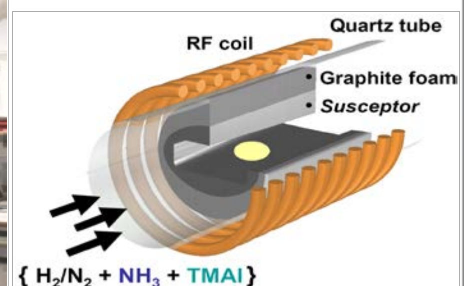
G.R. Yazdi, et al., Carbon 57 (2013) 477

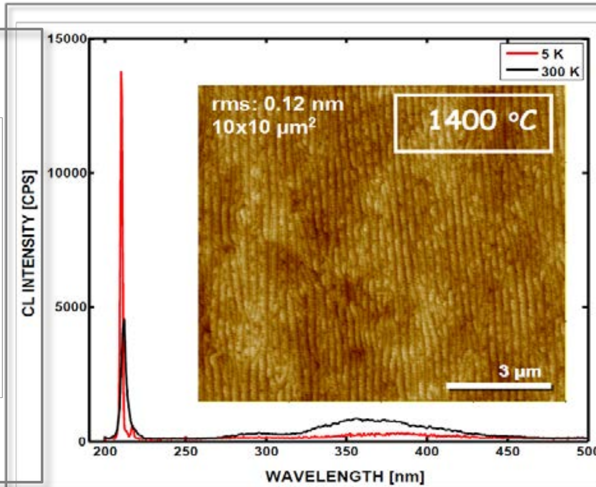
WP1. Graphene templates: objectives

- Having as a start the LiU breakthrough graphene growth process, we will explore SiC structure diversity to create designated templates for heterostructure growth
  - Strain controlled templates by pre-patterning of the SiC substrate in order to control the adsorption activity of graphene; and exploring diverse surface topology
  - Patterned graphene templates of nano-ribbon shape optimized towards best continuity of the MOCVD grown AlN and ZnO

MOCVD of group III nitrides at LiU

- SiC substrates
- (500-700 ºC) up to (1400-1500 ºC)
  - ➢ High temperatures are implicit for the control of the AlN nucleation & deposition



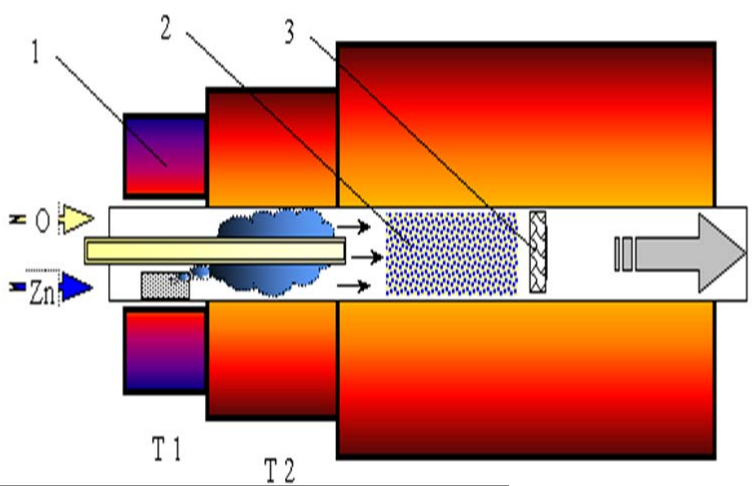


A. Kakanakova-Georgieva et al., Cryst. Growth & Design 9 (2009) 880

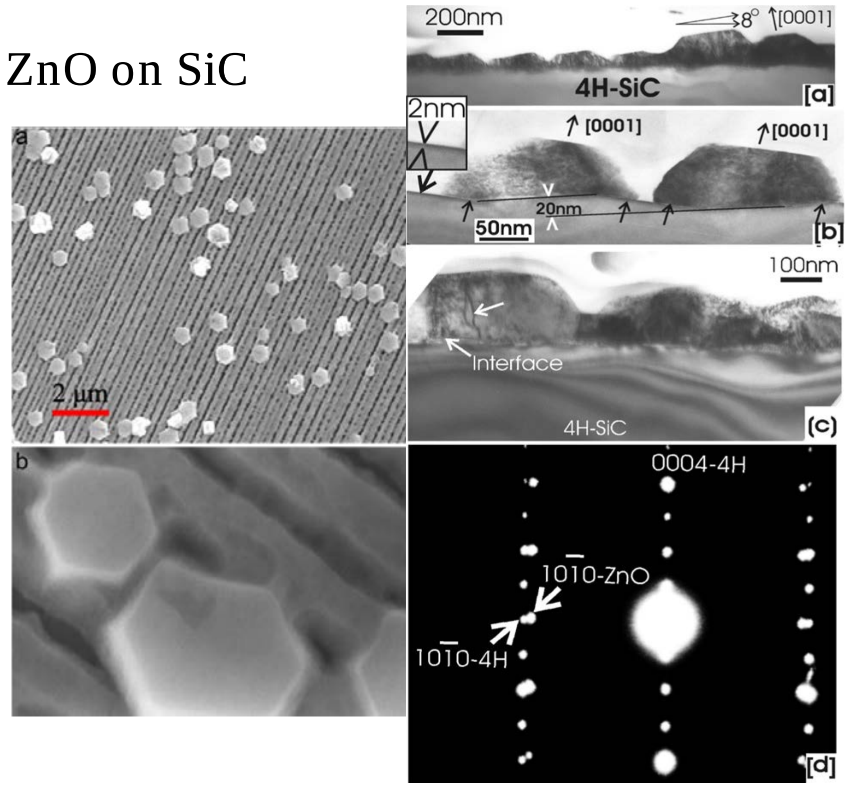
D. Nilsson et al., J. Phys. D: Appl. Phys. 49 (2016) 175108

APMOCVD of group II oxides at LiU

- RT up to 900 °C
- Single source solid state precursor: zinc acetylacetonate $Zn(AA)_2$ and argon as transport gas
- Perfect tool for nanostructures of ZnO on SiC



1. Precursor evaporation zone
2. Precursor decomposition zone
3. ZnO deposition zone



V. Khranovskyy, et al., Nanotechnology 22 (2011) 185603

WP2. MOCVD processes: objectives

Creating routes for the deposition of van der Waals heterostructures on demand

↑

Surface engineered templates

Understanding of surface reactions and diffusion phenomena, and variety of possible bonding types

Preventing the structural relaxation of the precursor ultrathin sp^2-coordinated graphitic films to the wurtzite sp^3-coordinated films

↑

Investigation of the initial nucleation stage of group III nitrides and ZnO on graphene

WP5. Ab-initio modeling: objectives

- To increase the understanding of basic physics and phenomena underlying h-AlN and h-ZnO on graphene
  - Adsorption mechanisms for the precursors on the surface of the graphene by molecular dynamics (in progress)
  - Inter-layer equilibrium distances and inter-layer electronic charge transfers in van der Waals stacks of few-layer h-AlN with graphene: Renato B. dos Santos et al., Nanotechnology 27 (2016) 145601
- Access to High Performance Computer resources within the Swedish National Infrastructure for Computing (SNIC), and to the National Supercomputer Center (NSC) in Linköping

Triolith supercomputer at NSC, Linköping

Research Institute for Technical Physics and Materials Science of the Hungarian Academy of Sciences

WP3. Structural Characterization

B. Pécz, I. Cora and L. Tóth

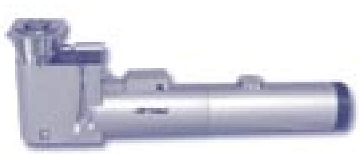
Thin Film Physics Dept. (Energy Research Center)

B. Pécz, I Cora and L. Tóth

TEM

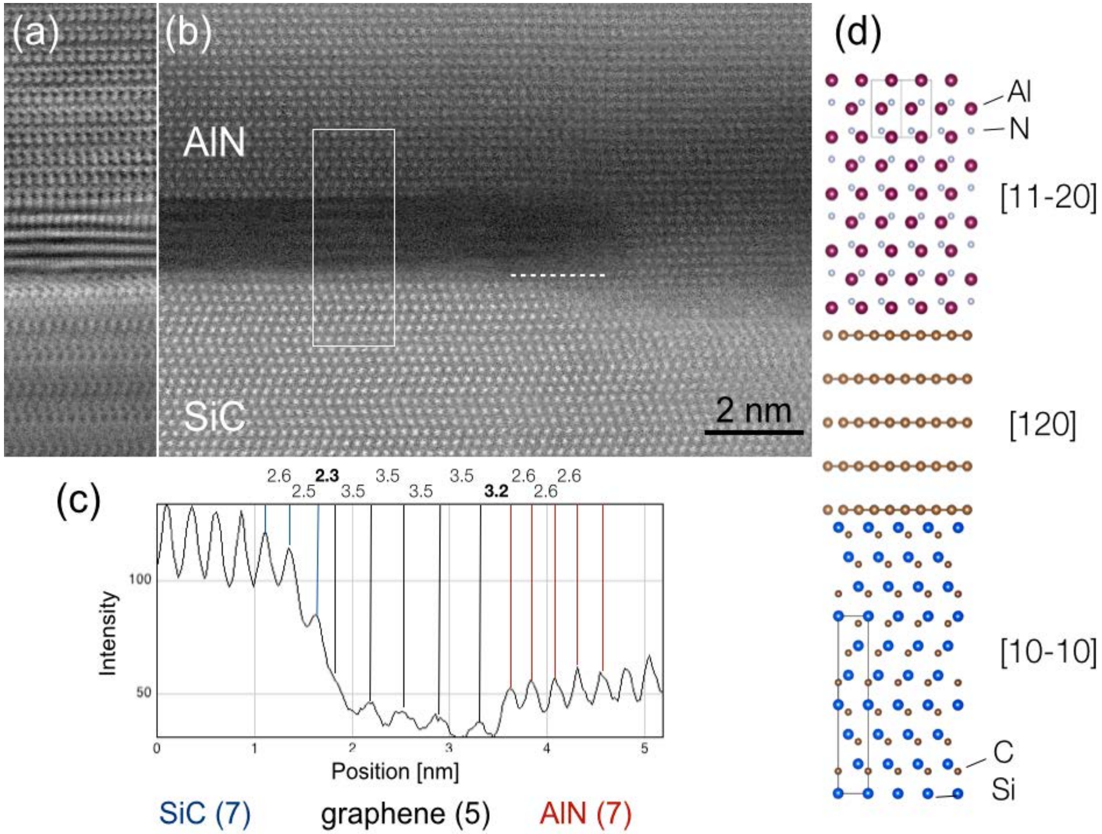
High resolution (0.17 nm) and analytical microscopes

Large capacity for sample preparation



GIF tridiem

High-quality GaN over patterned graphene/SiC samples



Typically 3 layers of graphene, but sometimes 5 are observed

➢ A. Kovács, M. Duchamp, R.E. Dunin-Borkowski, **R. Yakimova**, P. L. Neumann, H. Behmenburg, B. Foltynski, C. Giesen, M. Heuken and **B. Pécz**, *Graphoepitaxy of High-Quality GaN Layers on Graphene/6H–SiC*, Advanced Materials Interfaces, 2 (2015) DOI: 10.1002/admi.201400230

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WP4. Electrical Characterization

F. Giannazzo, G. Fisichella

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Available equipment

Class10 - Clean Room devices processing capability

Lithography
- Optical and e-beam lithography
- Nanoimprinting (Hot embossing, UV NIL)

Annealing
- Furnaces annealing and rapid annealing

Etching
- IC Plasma etch with F and Cl chemistries

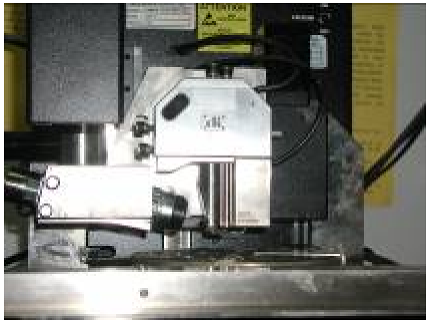
Metal deposition
- Sputters and UHV-e-beam evaporator

Dielectric deposition
- Thermal and plasma atomic layer deposition (ALD)

Scanning probe microscopy

with nanoscale electrical characterization techniques

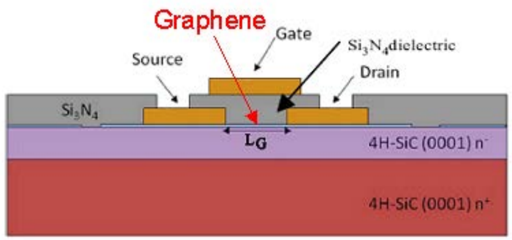
- DI 3100 AFM: Tapping/contact, CAFM, SCM, SSRM, TUNA, KFPM
- Multimode: CAFM at Variable temperature (0 -200 °C)
- Park XE-150: non-contact AFM

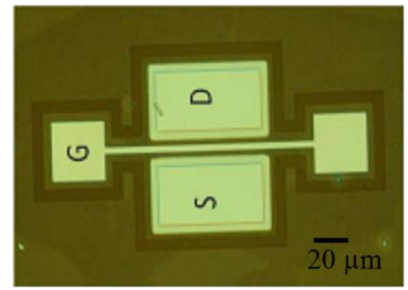


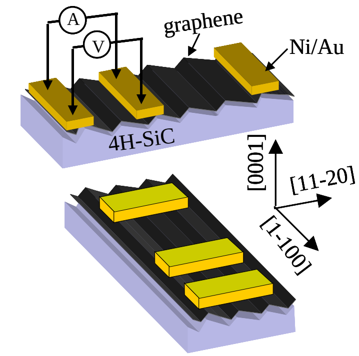
Electrical characterization

I-V, C-V also at variable temperature
- Hall measurements

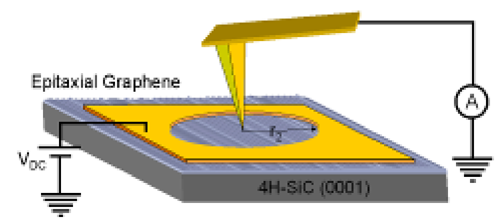
Micro and nanoscale electrical characterization of epitaxial graphene on SiC



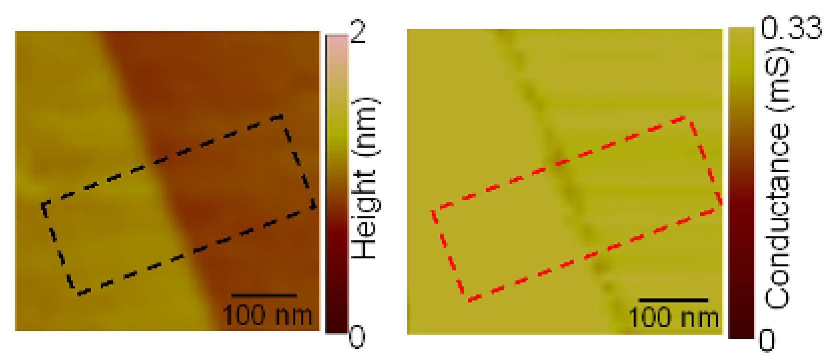




Extensively employed to locally probe the electronic properties of epitaxial graphene, clarifying the impact of the substrate morphology (i.e. SiC terraces and steps) on the local graphene resistivity and doping/workfunction



- S. Sonde, et al., PRB **80**, 241406(R) (2009)
- S. Sonde, et al., APL **97**, 132101 (2010)
- F. Giannazzo, et al., PRB **86**, 235422 (2012)
- G. Nicotra, et al., ACS Nano **7**, 3045 (2013)
- F. Giannazzo, et al., J. of Crystal Growth **393**, 150–155 (2014)
- G. Nicotra, et al. PRB **91**, 155411 (2015)
- F. Giannazzo, Nanotechnology **27**, 072502 (2016)



Role in the GRIFONE project

Nanoscale electrical characterization (CAFM and SCM measurements)

correlation between local morphology and vertical conduction properties

-Thickness uniformity and defectivity of h-AlN (h-ZnO);
- Local barrier height between h-AlN (h-ZnO) and graphene

Correlation with high resolution structural analyses (TEM) and Raman spectroscopy

Test devices fabrication and electrical measurements

- Capacitors: *metal/h-AlN(h-ZnO)/Gr*
- Top gated field effect transistors: *h-AlN (h-ZnO) as gate insulators and Gr as channel material*

Development of basic processes:
-selective area growth of h-AlN (h-ZnO) on Gr (with Linkoping);
-optimal metal contacts on h-AlN (h-ZnO)

- *Electrical characterization*
- *Structural analyses (with MFA) to understand eventual failures in the devices behaviour*

GRIFONE: added value

- Highly complementary consortium
- Creating material platform for bottom-up growth approach to explore innovative van der Waals heterostructures of thin wurtzite sp^3-coordinated films, and ultrathin sp^2-coordinated films of group III nitrides and group II oxides with graphene