

Highly uniform Al₂O₃ thin layers by seed-layer-free Atomic Layer Deposition onto monolayer epitaxial Graphene on 4H-SiC

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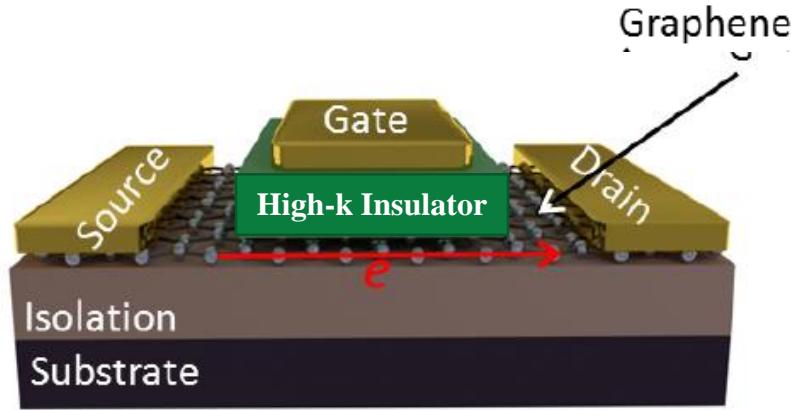


Consiglio Nazionale delle Ricerche

EuroCVD-BalticALD 2019, Luxembourg

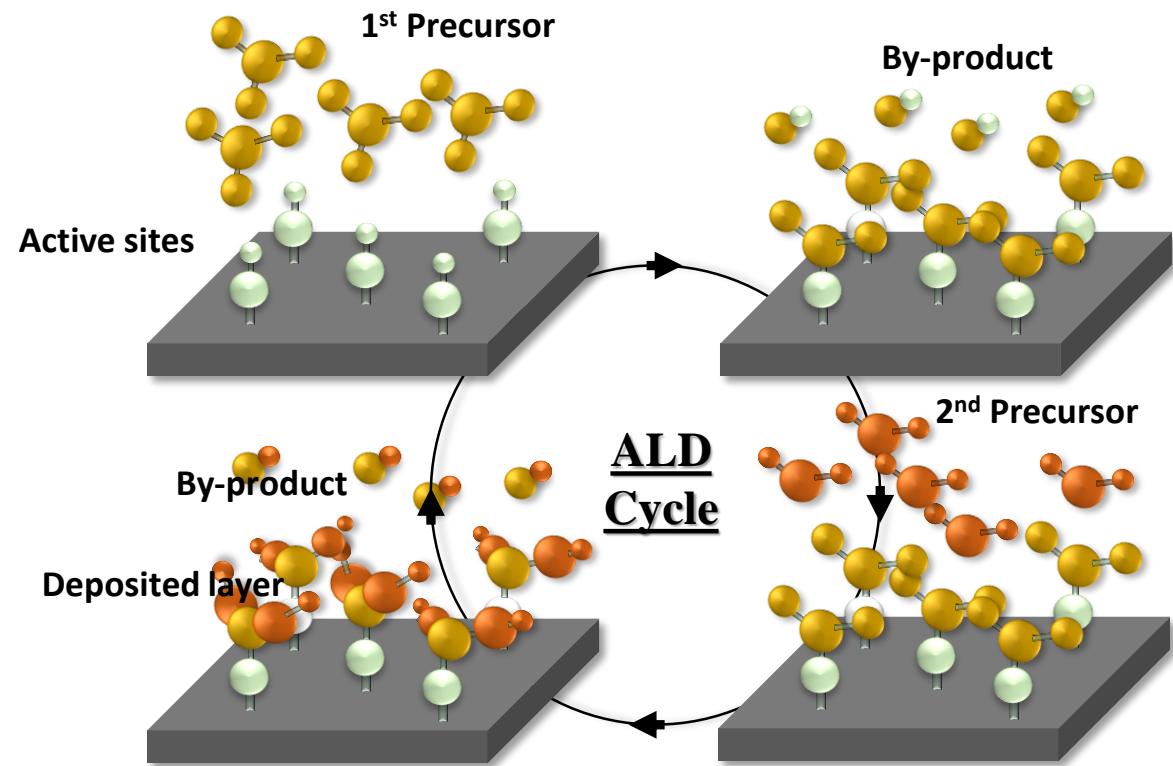
Atomic Layer Deposition (ALD) of high-k insulator on Graphene (Gr)

Graphene based- Field effect transistor (FET)

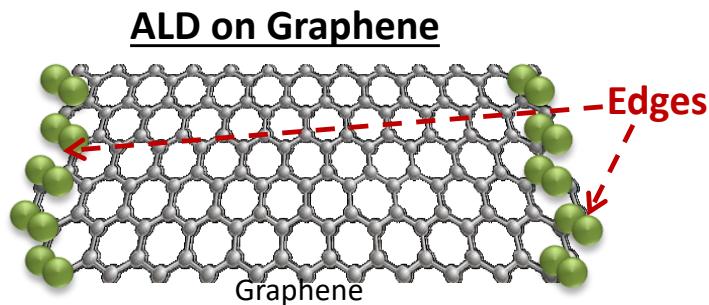


The insulator layer on top of Gr is useful to have a good electrostatic control of channel

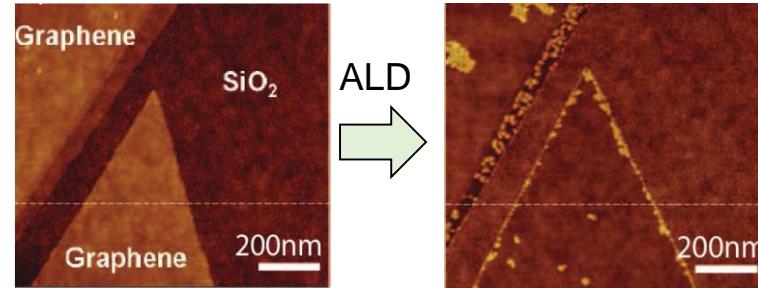
- High-k insulators (Al_2O_3 , HfO_2);
- Ultrathin (< 10 nm);
- Uniform;



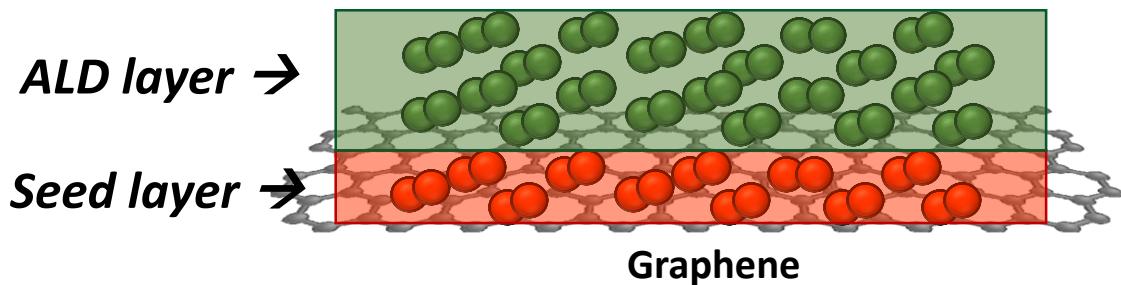
Atomic Layer Deposition (ALD) on Graphene (Gr)



NOT UNIFORM ALD NUCLEATION



Seed-Layer on Graphene to start ALD nucleation



Seed layer

- Spin coated polymers;
- Sputtered metal or metal-oxide;
- H₂O assisted seed-layer;

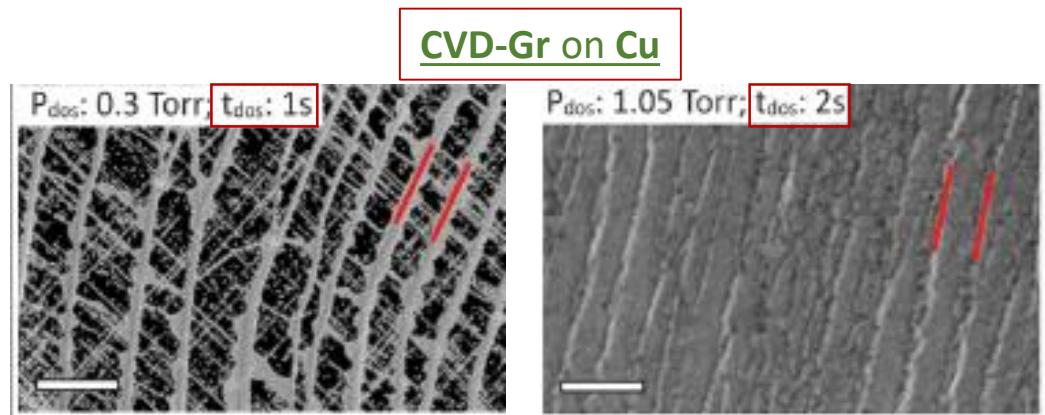
Detrimental effect on ☹

- Electrical properties: charge traps at interface;
- Equivalent Oxide Thickness (EOT) seed-layer/insulator stack

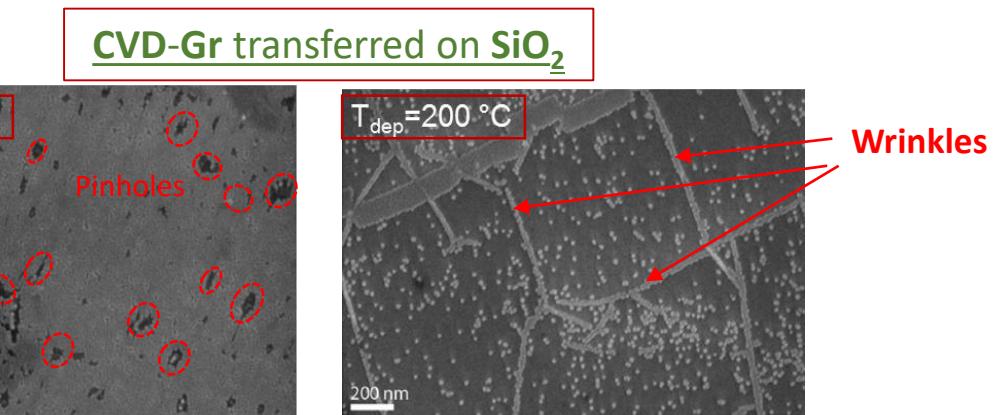
Seed-layer-free ALD on Graphene (Gr)

The uniformity of ALD-covering is function of:

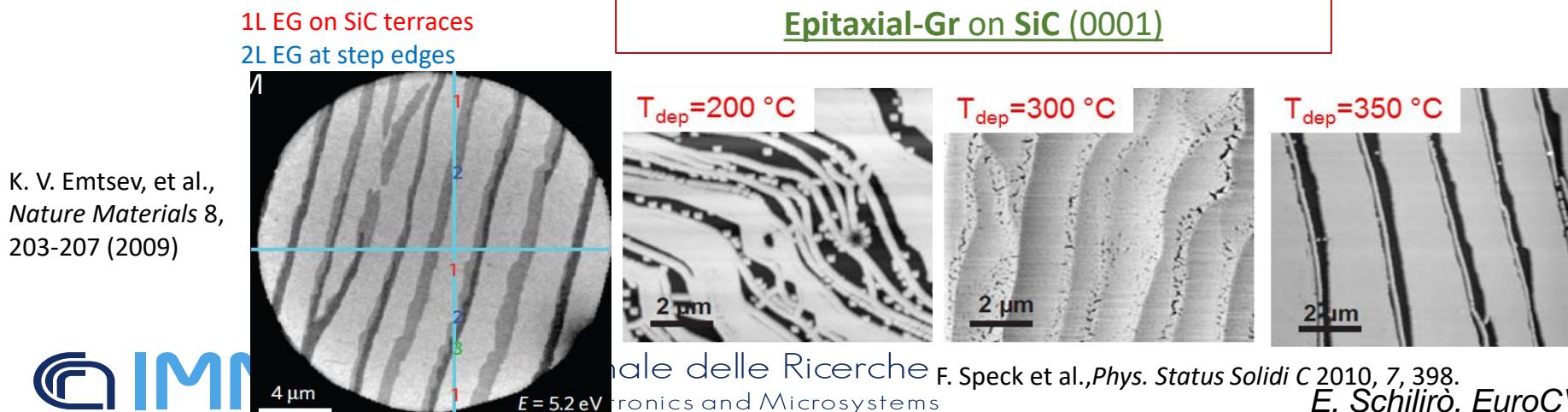
- ALD process parameters: **precursors residence time (t_{dos})** and **temperature (T_{dep})**;
- Graphene properties: **synthesis method and substrate**.



A. I. Aria, et al., ACS Advanced Mater. 8, 30564 (2016).



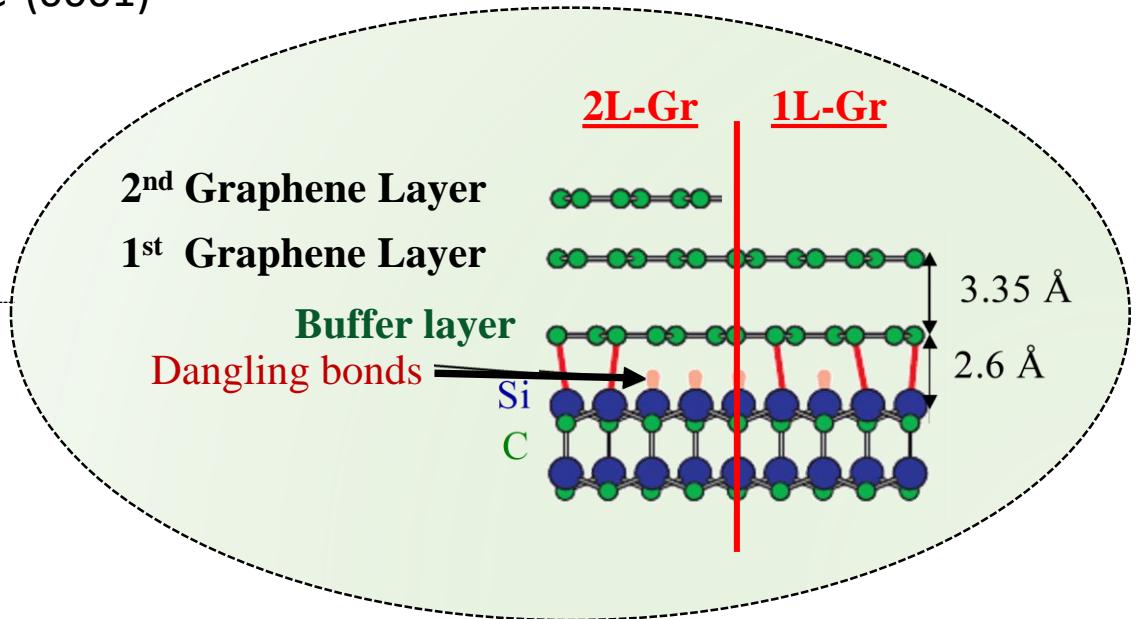
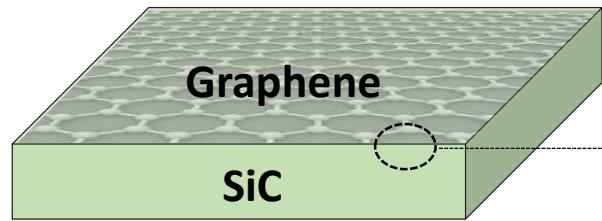
R. H. J. Vervuurt, et al., Chem. Mater. 29, 2090 (2017).



Epitaxial-Gr on SiC

Epitaxial Growth on SiC (0001)

- Thermal decomposition of “nominally” on-axis 4H-SiC (0001) at 2000 °C in inert gas (Ar) at atmospheric pressure



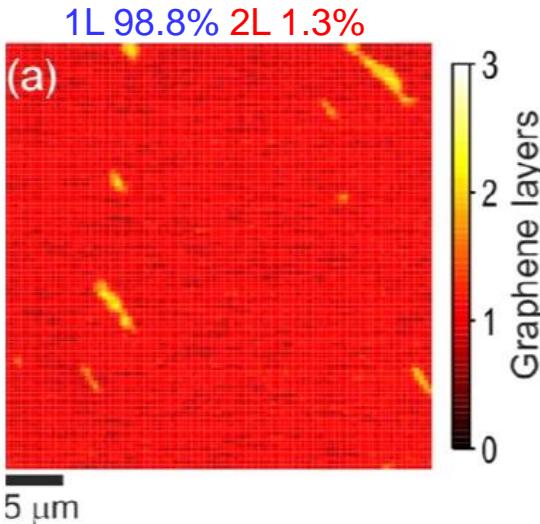
Graphene features

- Varying layer number (depending on growth conditions);
- Buffer layer (partially bounded to SiC);
- N-Type doping (10^{13} cm^{-2}) induced by dangling bonds;

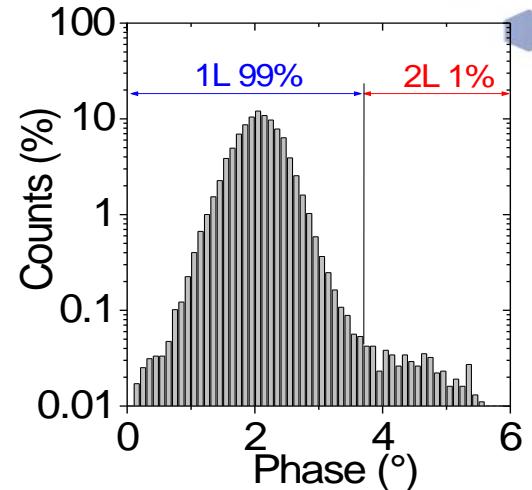
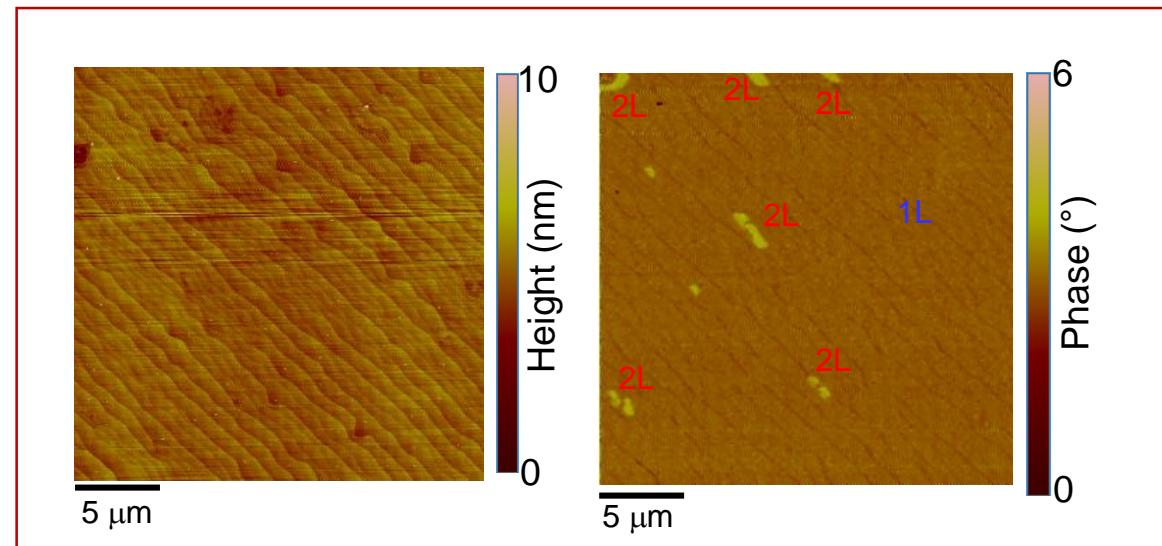
C. Virojanadara, M. Syvajarvi, R. Yakimova, L. I. Johansson, A. A. Zakharov, T. Balasubramanian, Phys. Rev. B 78, 245403 (2008).

Highly uniform Epitaxial-Gr onto on-axis 4H-SiC(0001)

Reflectance map



Atomic Force Microscopy map

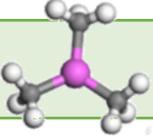


I. G. Ivanov, J. Ul Hassan, T. Iakimov, A. A. Zakharov, R. Yakimova, E. Janzén, Carbon 77, 492 (2014).

E. Schilirò, R. Lo Nigro, F. Roccaforte, I. Deretzis, A. La Magna, A. Armano, S. Agnello, B. Pecz, I. G. Ivanov, R. Yakimova, F. Giannazzo, Adv. Mater. Interfaces 1900097, 1-11 (2019)

- The red contrast is associated to 1L-Gr (98.8%) and the yellow elongated patches to 2L-Gr (1.2%).
- The small elongated patches with higher phase contrast correspond to 2L-Gr.

ALD of Al_2O_3 on Gr: process parameters

Al precursor	O source	T dep.	Pulse period	Carrier gas	Numbers cycles	Al ₂ O ₃ thickness
TMA 	H ₂ O	250°C	20 ms	N ₂ (80sccm)	190	→ 15 nm

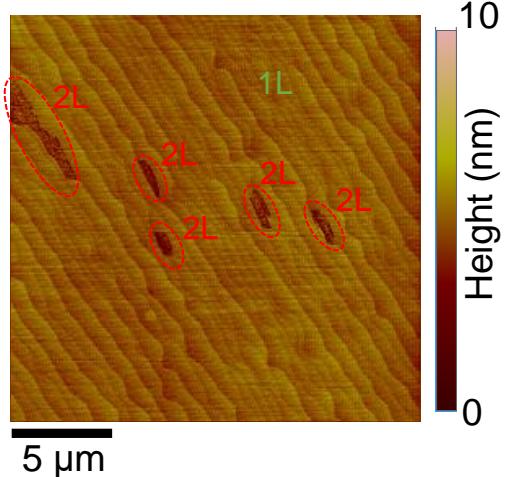
SENTECH Si PEALD LL Reactor



Al_2O_3 grown on Epitaxial-Gr onto on-axis 4H-SiC(0001)

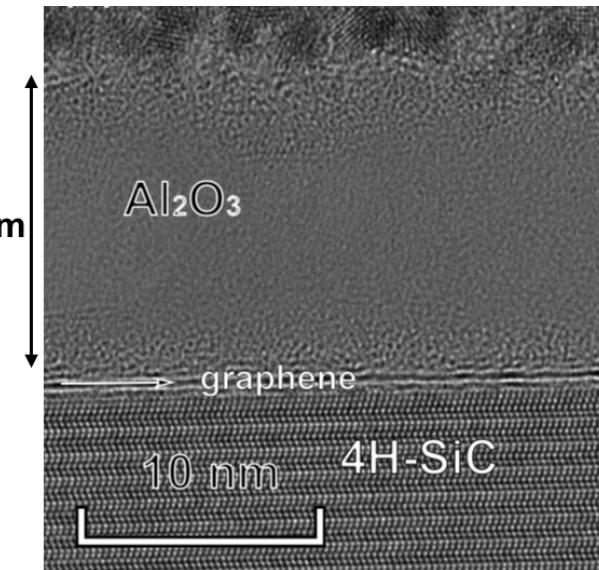
Morphological and structural properties

AFM map



Highly uniform Al_2O_3 coverage on 1L EGr
Low uniform Al_2O_3 coverage on 2L EG.

Cross-section TEM

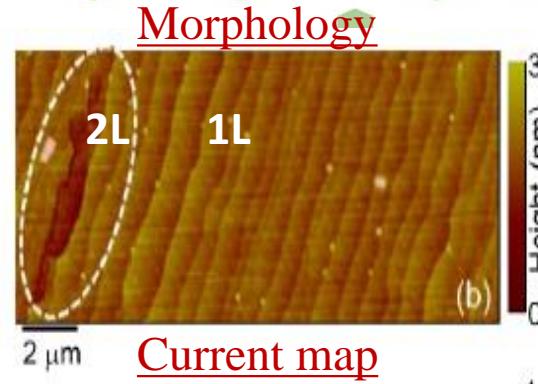
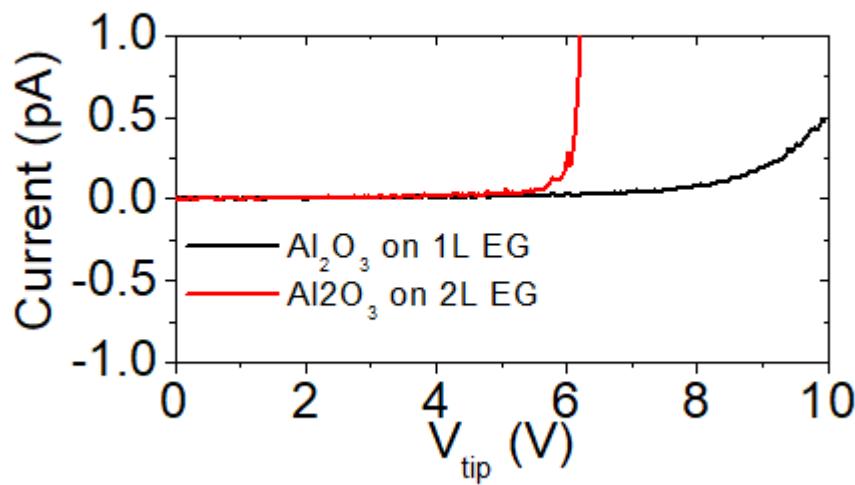
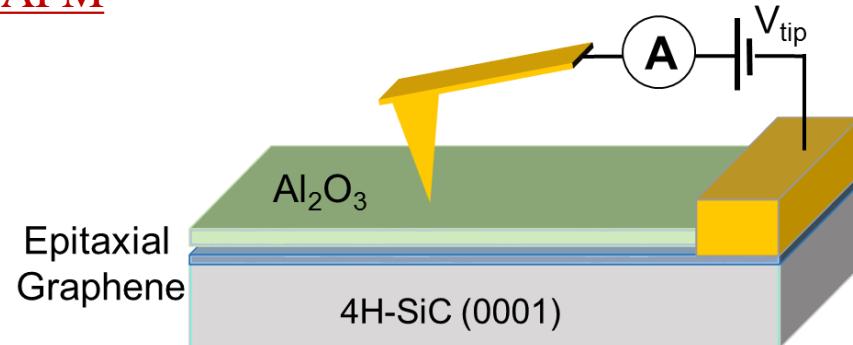


Measured Al_2O_3 thickness (12 nm), lower than the nominal one: lower Al_2O_3 growth rate on EG in the early stages of the deposition process.

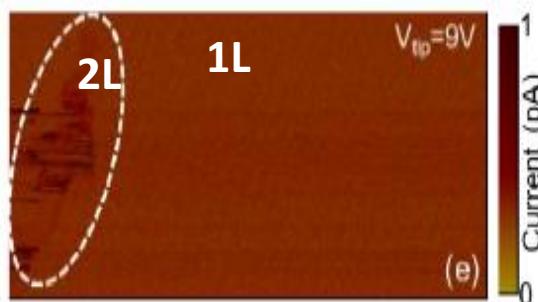
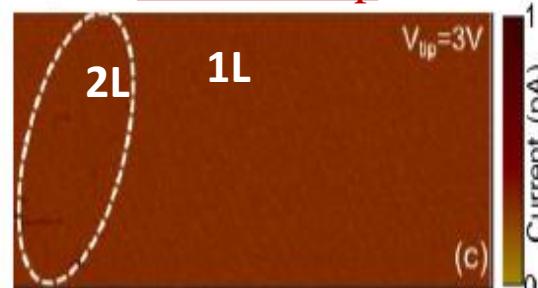
Al_2O_3 grown on Epitaxial-Gr onto on-axis 4H-SiC(0001)

Electrical properties

Conductive-AFM



Current map



Local I-V_{tip} characteristics of Al_2O_3 on 1L and 2L EG regions.

Slow current increase for $V_{\text{tip}} > 8\text{ V}$ in Al_2O_3 on 1L EG:
 $E_{\text{BD}} > 8\text{ MV/cm}$ evaluated for the Al_2O_3 thickness $t_{\text{ox}} \approx 12\text{ nm}$

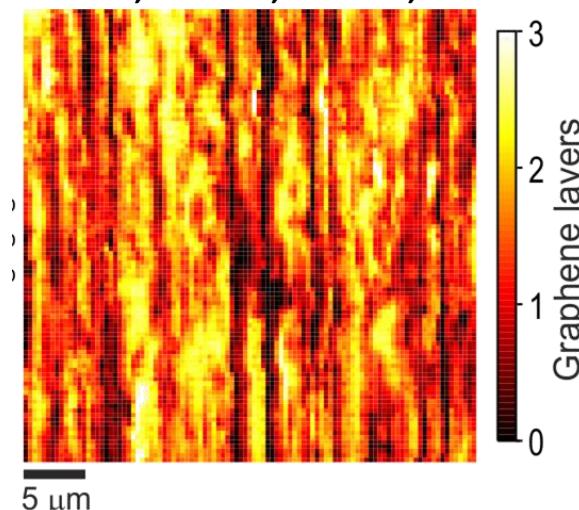
Abrupt current rise at $V_{\text{tip}} \approx 6\text{ V}$ for Al_2O_3 on 2L EG:
 $E_{\text{BD}} \approx 6\text{ MV/cm}$ for the local Al_2O_3 thickness $t_{\text{ox}} \approx 10\text{ nm}$ in these regions

Al_2O_3 grown on few layer Epitaxial-Gr onto on 4° off-axis 4H-SiC(0001)

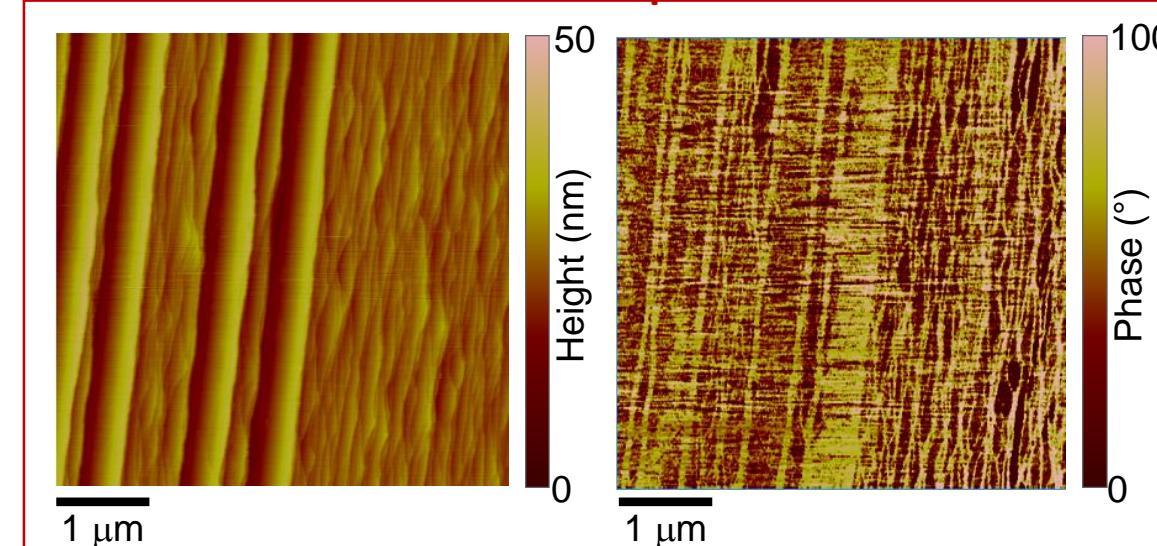
Substrate: Few layer EGr on off-axis SiC

Reflectance map

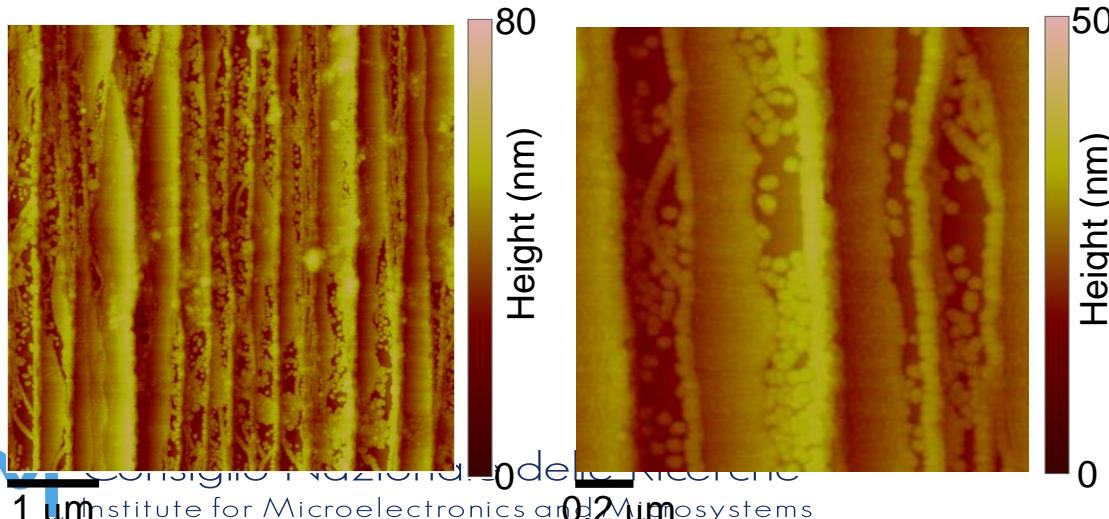
0L=10%, 1L=43%, 2L=43%, 3L=3%



AFM map



ALD- Al_2O_3 on few layer EGr onto on-axis SiC



IMM

1 μm

Scanning Probe Microscopy

and

Micro-

systems

Technology

Research

Center

of

the

University

of

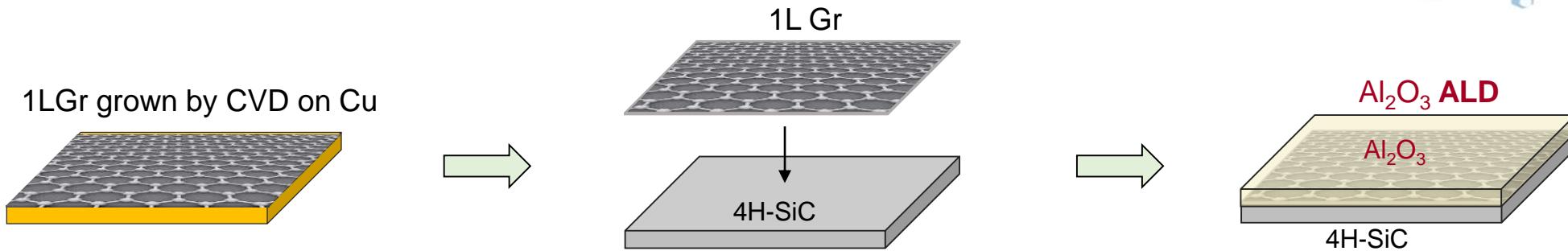
Luxembourg

Institute for Microelectronics and Microsystems

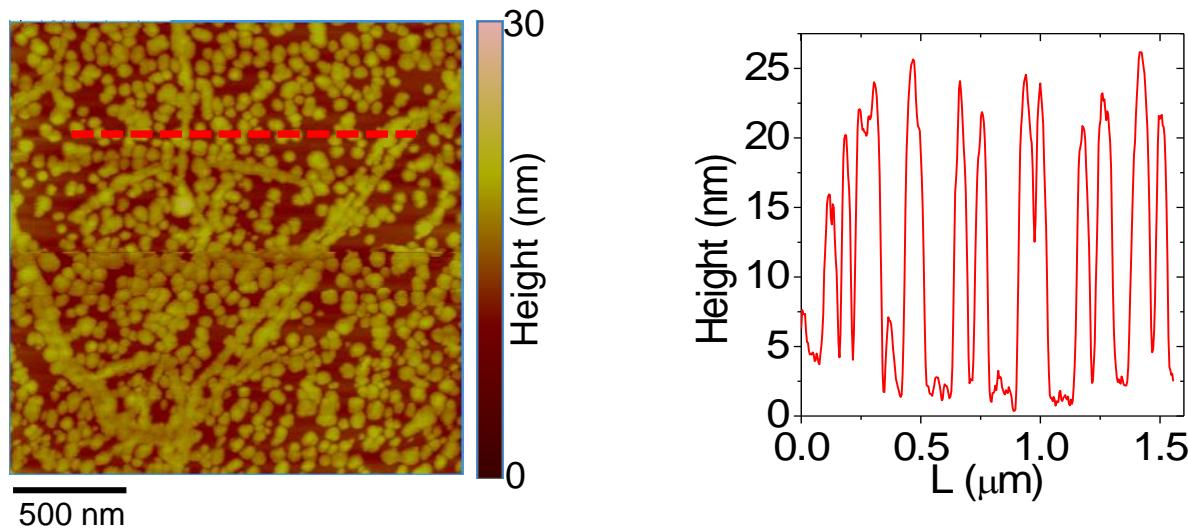
E. Schilirò, EuroCVD-BalticALD 2019, Luxembourg

Al_2O_3 grown on 1L Transferred-Gr onto 4H-SiC(0001)

1) Gr transferred onto SiC



2) T-ALD Al₂O₃: Standard process (without seed-layer), 250°C and 190 cycles.

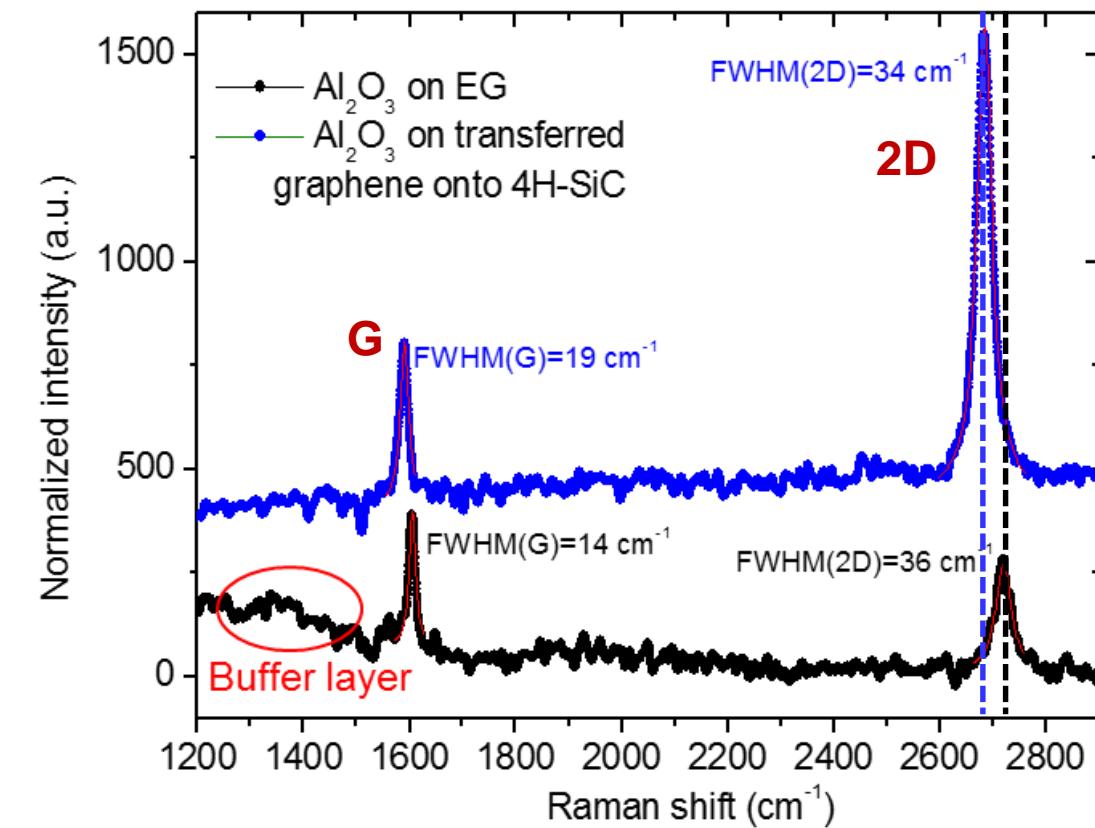


Inhomogeneous ALD nucleation,
giving rise to the growth of 3D
Al₂O₃ islands

E. Schilirò, R. Lo Nigro, F. Roccaforte, I. Deretzis, A. La Magna, A. Armano, S. Agnello, B. Pecz, I. G. Ivanov, R. Yakimova, F. Giannazzo, Adv. Mater. Interfaces 1900097, 1-11 (2019)

Al_2O_3 /1LEpitaxial-Gr and Al_2O_3 /1LTransferred-Gr on-axis 4H-SiC(0001): Comparison

Raman Spectroscopy



Transferred 1LGr: Compressive strain ($e=-0.07\%$)
Low p-type doping ($5 \times 10^{12} \text{ cm}^{-2}$).

Epitaxial 1LGr: Blue shift of G and 2D → Compressive strain ($e=-0.37\%$)
Lower 2D/G → High n-type doping (10^{13} cm^{-2}).

The high n-type doping and strain of EG (originating from the buffer layer) can be responsible of the enhanced Al_2O_3 nucleation on EG

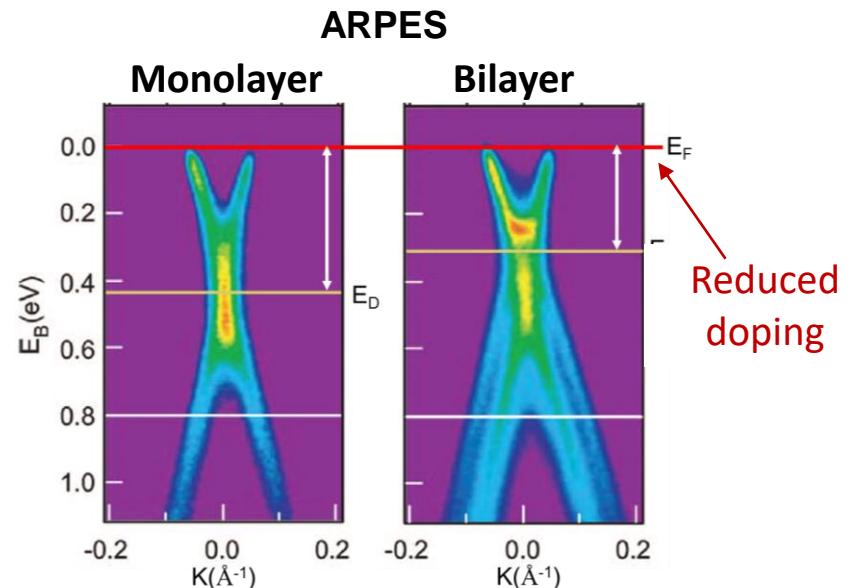
E. Schilirò, R. Lo Nigro, F. Roccaforte, I. Deretzis, A. La Magna, A. Armano, S. Agnello, B. Pecz, I. G. Ivanov, R. Yakimova, F. Giannazzo, Adv. Mater. Interfaces 1900097, 1-11 (2019)

Impact of graphene doping on the adsorption of the ALD precursors

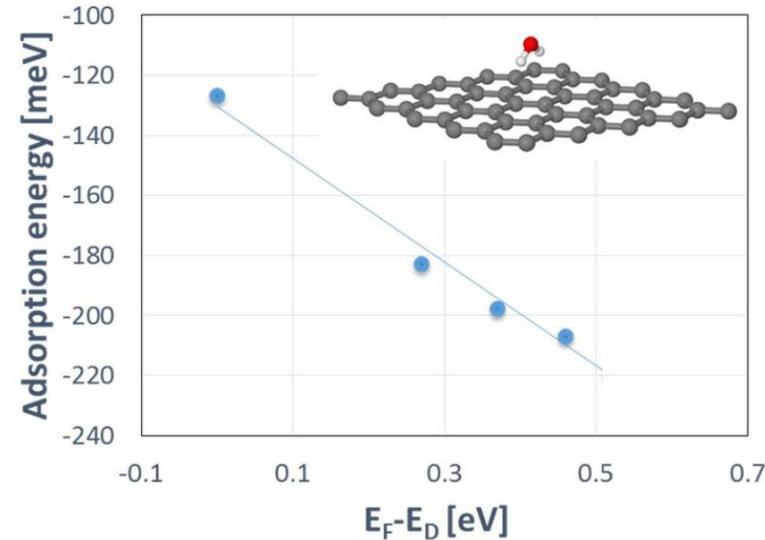
DFT calculations: adsorption energy E_a of H_2O molecules (ALD precursor) on Gr surface as a function of doping (E_F-E_D)

$E_a \approx 127$ meV for $E_F-E_D=0$ eV (neutral graphene)

$E_a \approx 210$ meV for $E_F-E_D=0.45$ eV ($n=1.5 \times 10^{13} \text{ cm}^{-2}$)



D. S. Lee, et al., Nano Lett. 8, 4320-4325 (2008).



The less efficient Al_2O_3 nucleation on 2L EG partially related to the reduced doping of 2L EG with respect to 1L EG

Summary

- Uniform Al₂O₃ films deposited by seed-layer-free thermal ALD on highly homogeneous 1L EG on on-axis 4H-SiC(0001).
- Highly uniform insulating properties of the Al₂O₃ thin films shown by nanoscale resolution C-AFM current mapping: breakdown field >8 MV cm⁻¹ for Al₂O₃ on 1L EG.
- The optimal nucleation behavior on 1L graphene is not related to the SiC substrate, but it is peculiar of the EG/SiC interface.
- Ab-initio DFT calculations showed an enhanced adsorption energy for water molecules on highly n-type doped 1L graphene, indicating the high doping of EG induced by the buffer layer as the origin of the excellent Al₂O₃ nucleation.

Acknowledgements

 **IMM**
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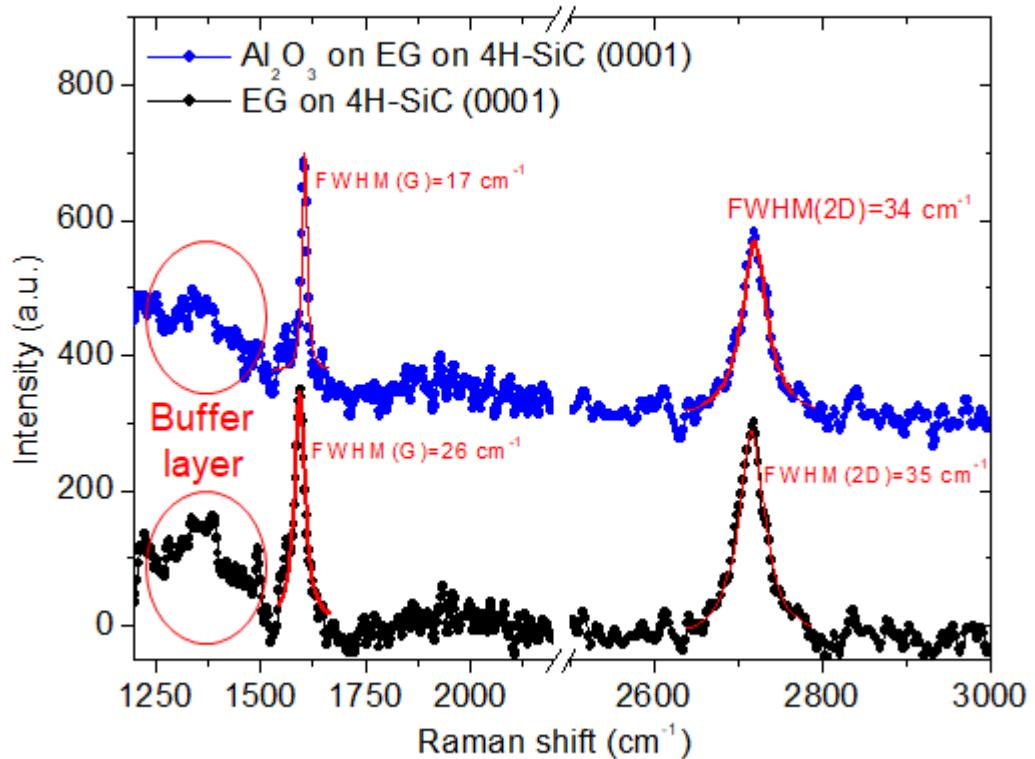
EU projects



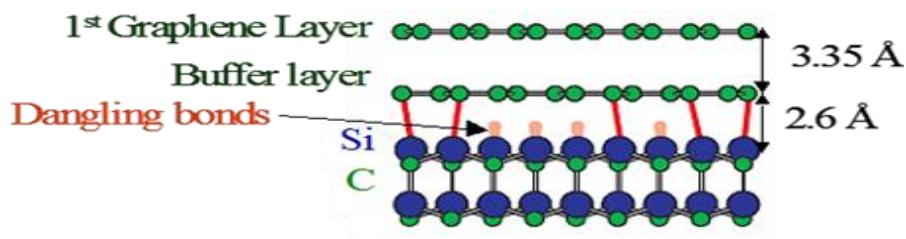
 GRIFONE

Al_2O_3 grown on Epitaxial-Gr onto on-axis 4H-SiC(0001)

Raman Spectroscopy



The features in the 1200–1500 cm⁻¹ range associated to the buffer layer at the EG/SiC interface.



- G and 2D peaks fitted with single Lorentzian : FWHM(G) and FWHM(2D) consistent with 1L EG
D. Su Lee, C. Riedl, B. Krauss, K. von Klitzing, U. Starke, J. H. Smet, Nano Lett. 8, 4320 (2008).
- Small changes of Pos (G) and Pos(2D) after Al_2O_3 deposition:
EG doping and strain not affected by the ALD process.

E. Schilirò, R. Lo Nigro, F. Roccaforte, I. Deretzs, A. La Magna, A. Armano, S. Agnello, B. Pecz, I. G. Ivanov, R. Yakimova, F. Giannazzo, *Adv. Mater. Interfaces* 1900097, 1-11 (2019)