University of Pisa
Department of Civil and Industrial Engineering
Master Degree in Materials and Nanotechnology

Hydrogen storage in three-dimensional arrangement of epitaxial graphene conformally grown on porousified SiC

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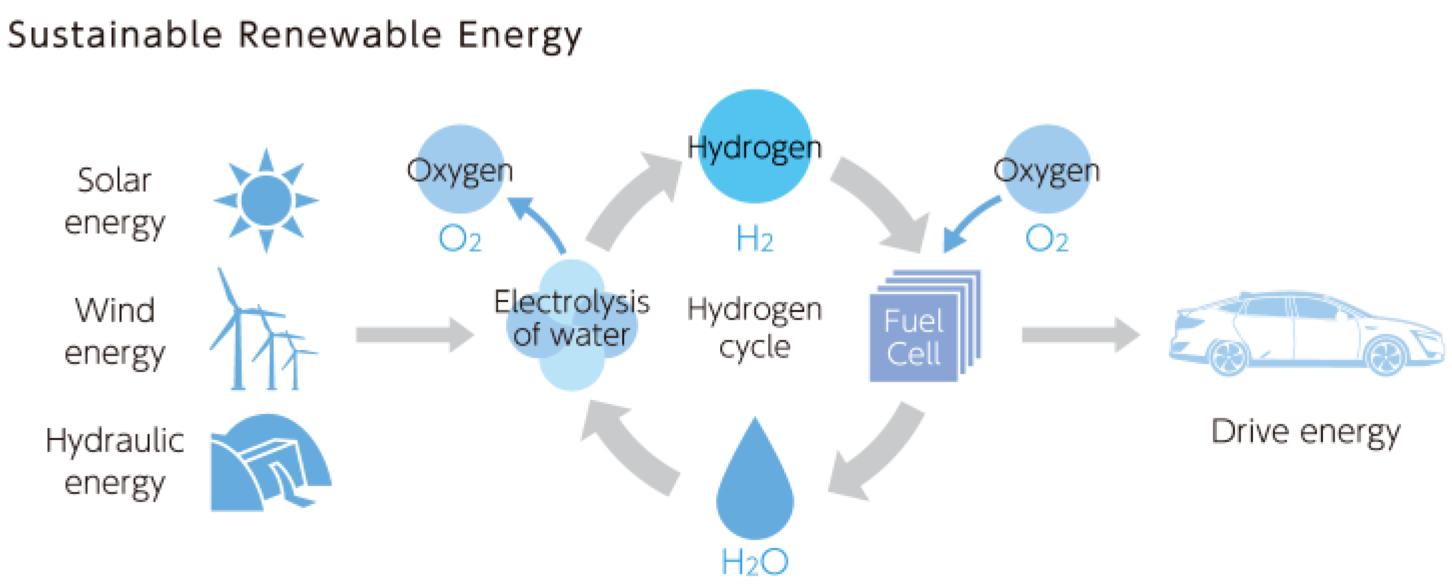
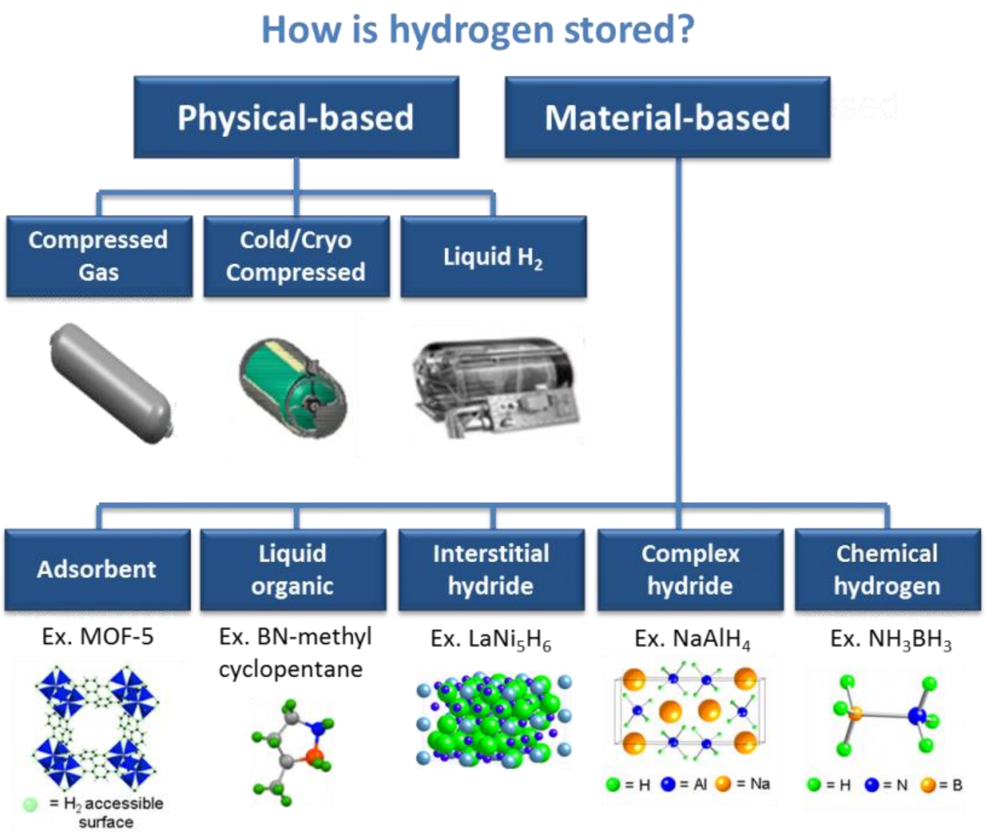
Hydrogen Energy

- Fossil fuels are problematic
- Renewables are intermittent
- Conversion into stable compounds
- Advantages of hydrogen



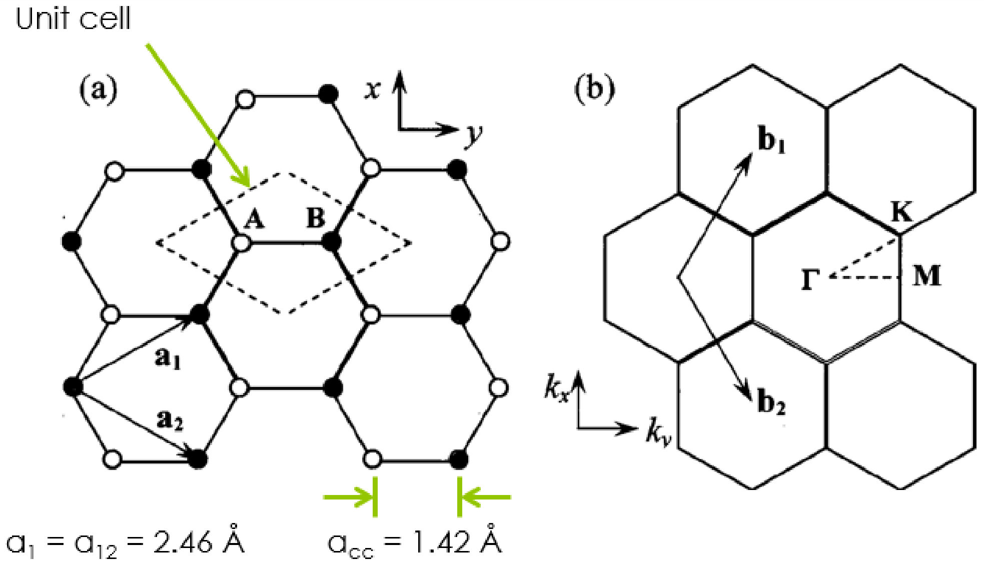
Hydrogen Storage

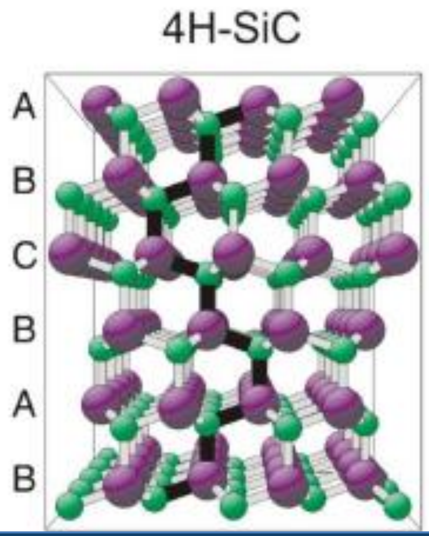
- Compressed (700 bar, large volume)
- Liquid hydrogen (Cryogenic, 22K)
- Solid state (higher volumetric density, less extreme P and T)
  - Physorption
  - Chemisorption

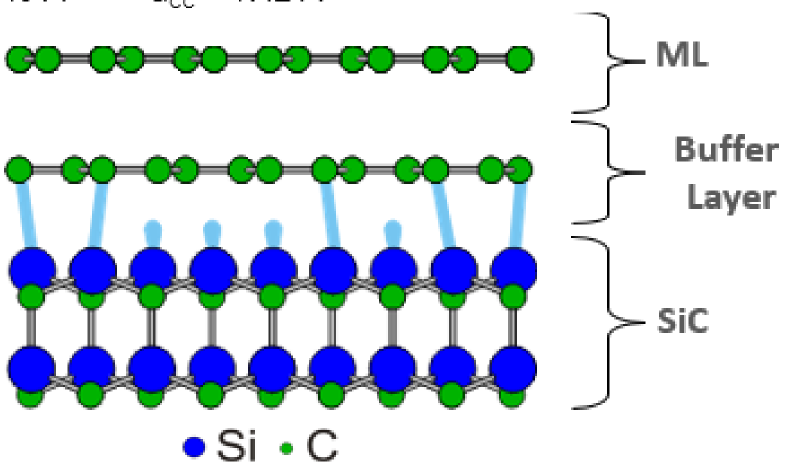


Graphene and Epitaxial Growth

- Hydrogen storage in graphene (cheap, lightweight, inert, functionalization)
- Graphene structure
- Epitaxial graphene (Annealing, Buffer layer)

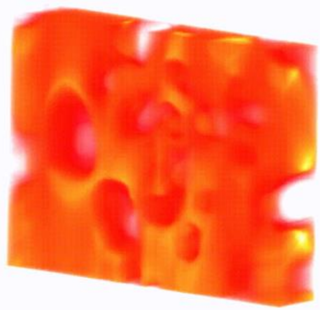




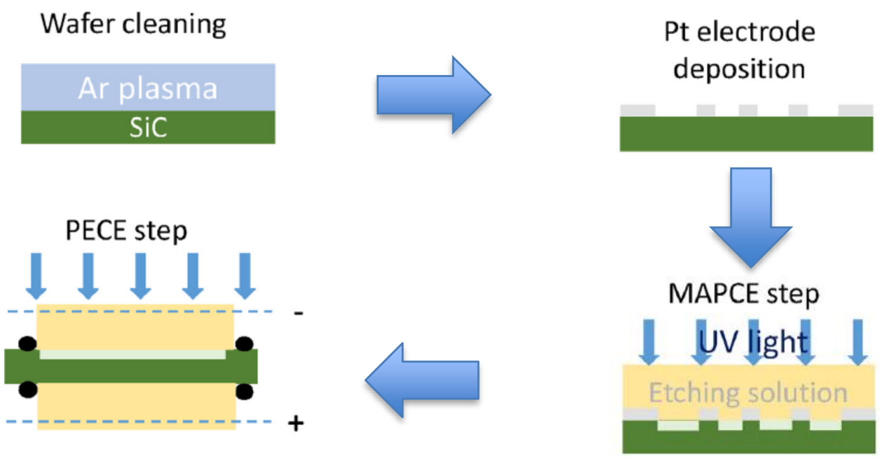


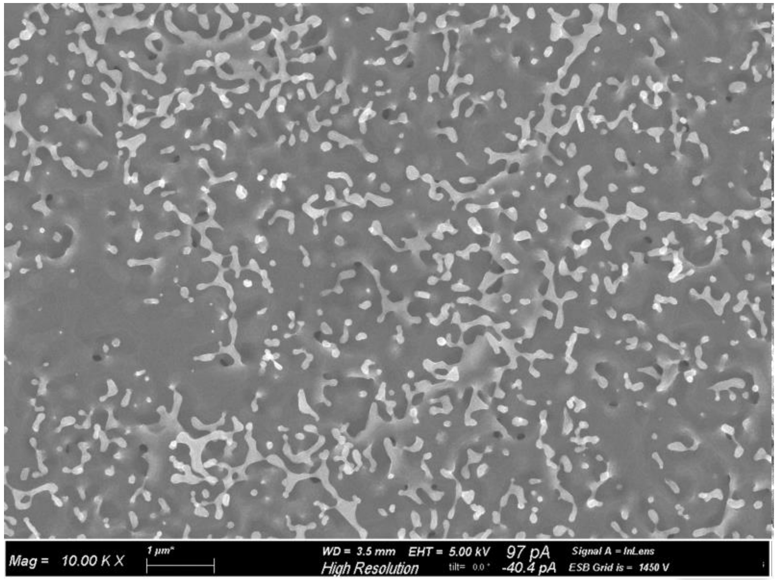
3D Graphene

- Increase surface (graphene foams)
- Photo-Electrochemical etching
- Porous SiC
- 3D graphene (optimal 1370°C)



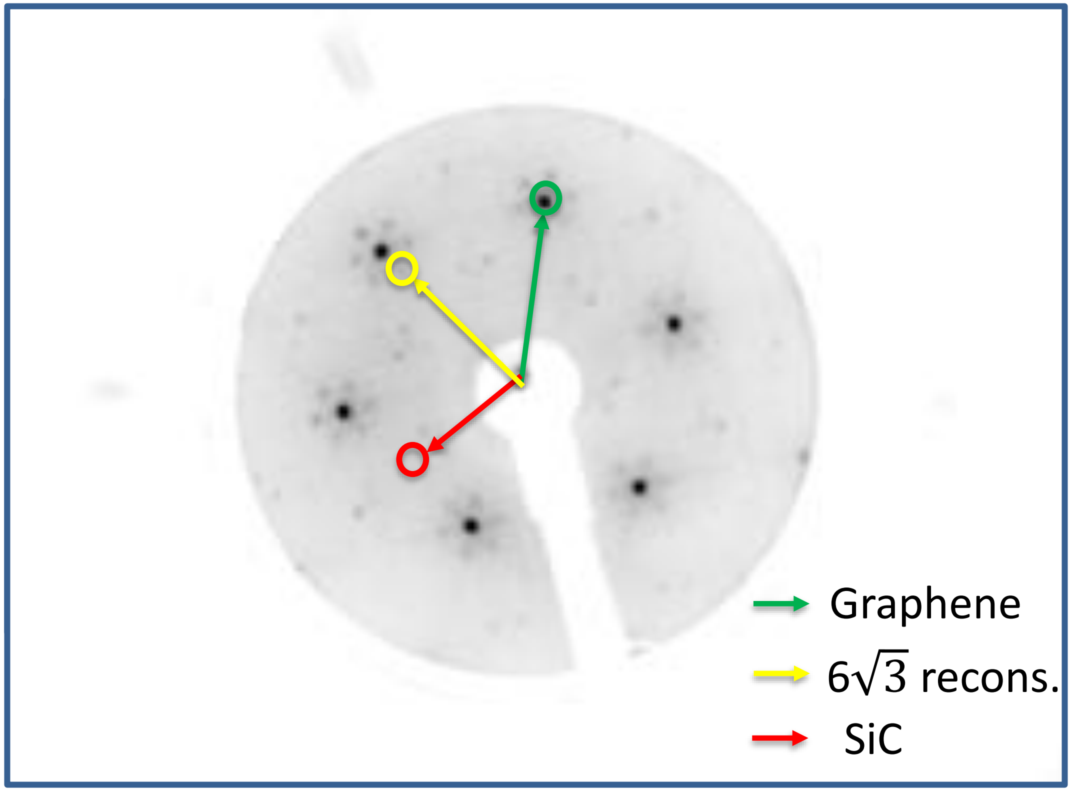
Sara Bals, University of Antrwerp





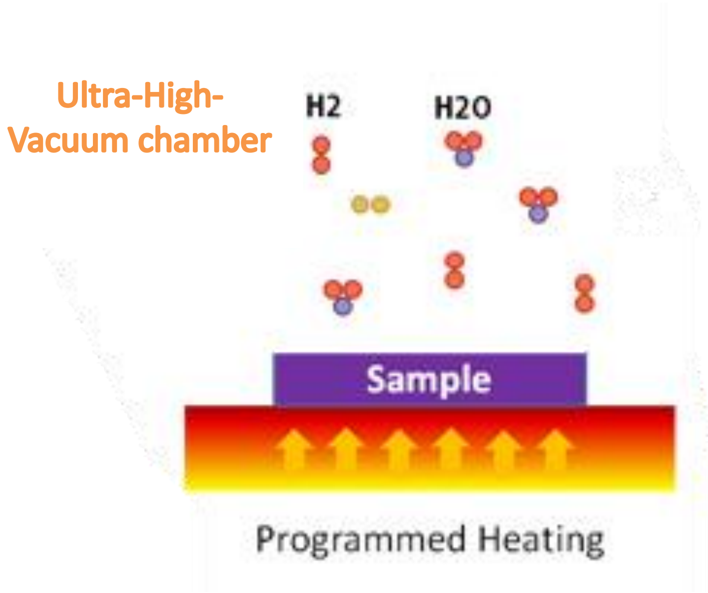
Surface Characterization

- Raman (uniform, high quality graphene)
- STM (atomic resolution)
- LEED (4H SiC, Graphene, Moirè pattern)



Thermal Desorption Spectroscopy (TDS)

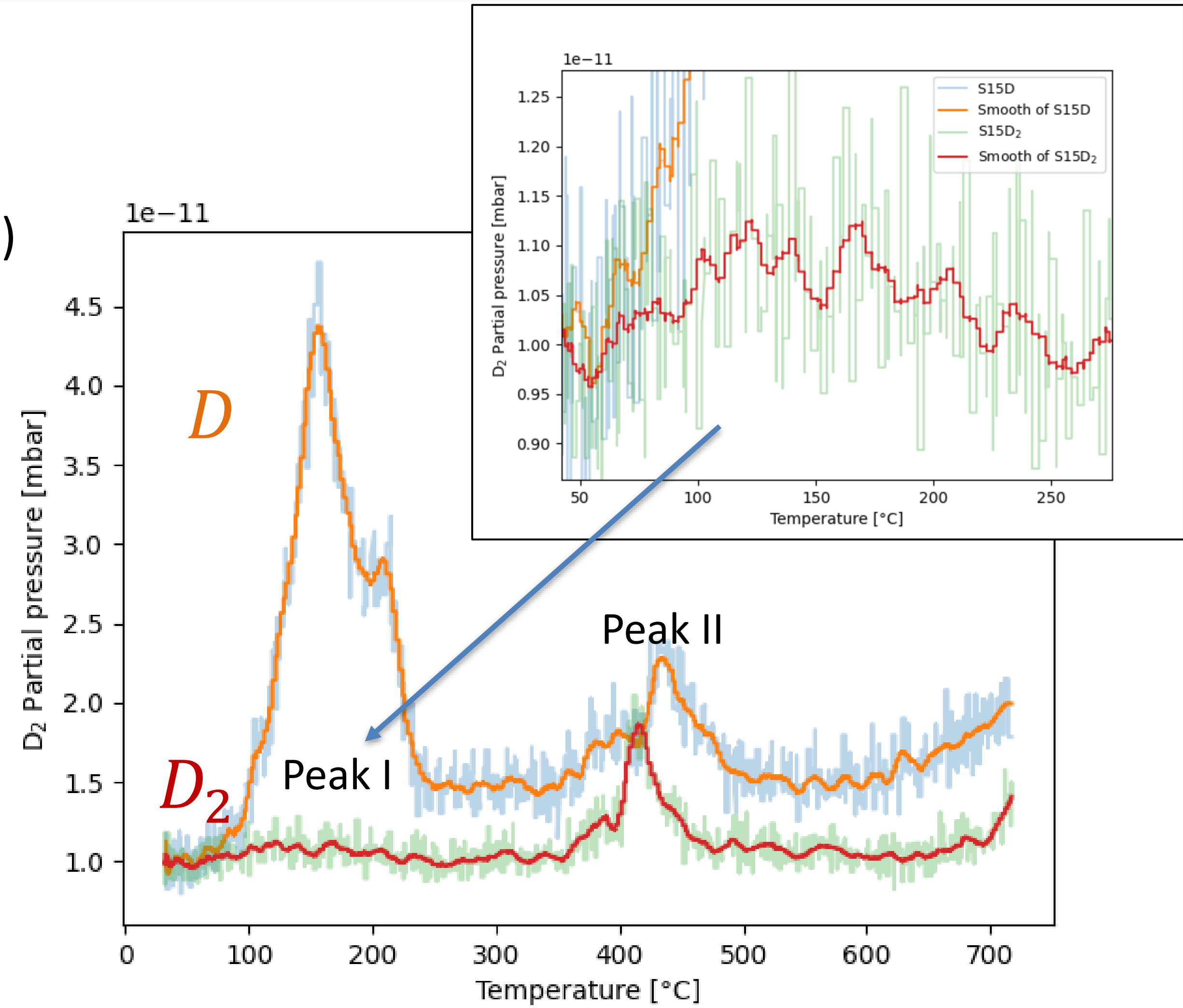
- Principles (hydrogenation, linear heating, PID)
- RGA (m=4)
- 4 different TDS protocols
    - RT exposure TDS
    - LT exposure TDS
    - RT exposure LT TDS
    - Alt. LT exposure TDS



RT exposure TDS

- Room temperature D_2 and D hydrogenation
- Two peaks (1 eV and 1.8 eV)
- Due to chemisorption

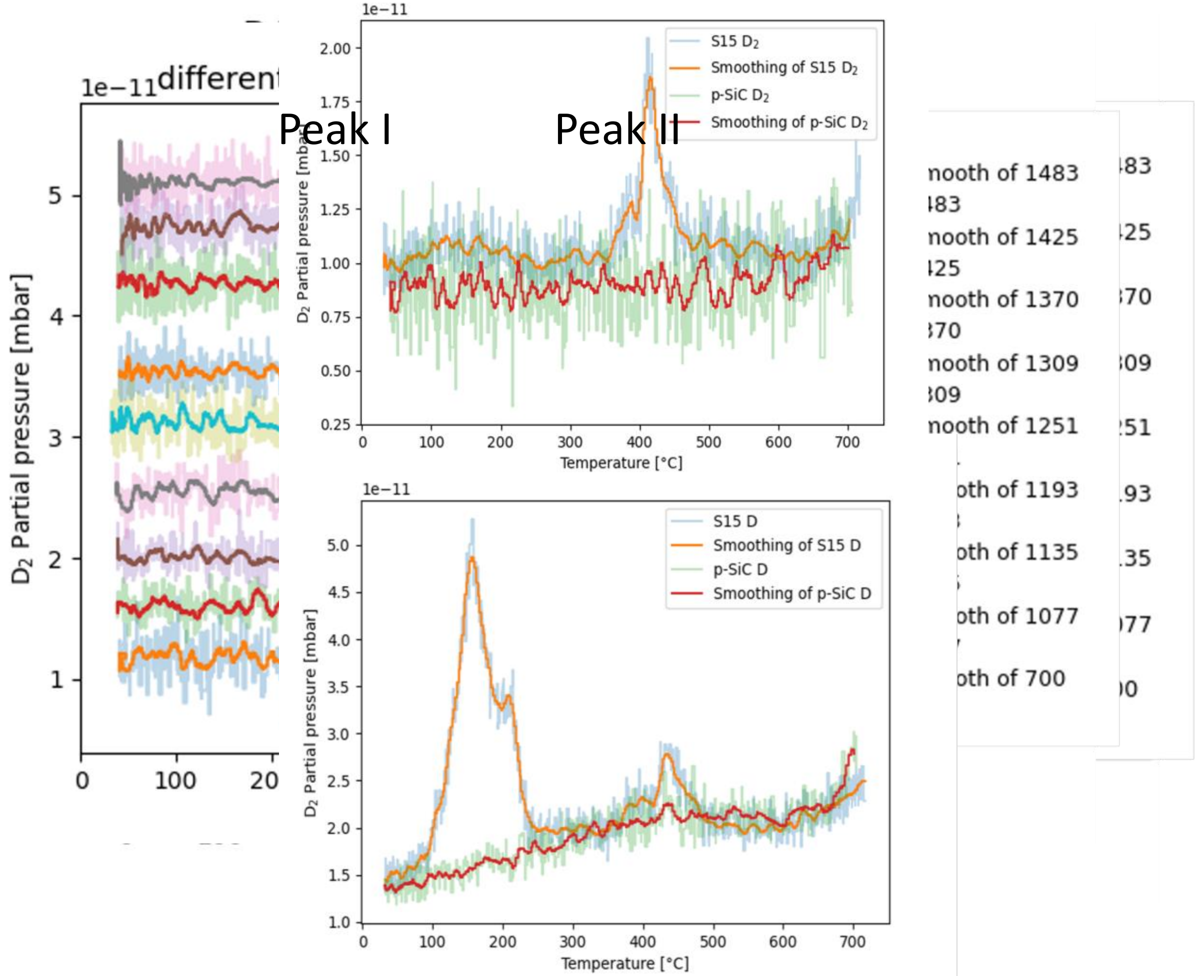
- **Presence of a splitting mechanism**



Multiple Annealing RT deposition TDS

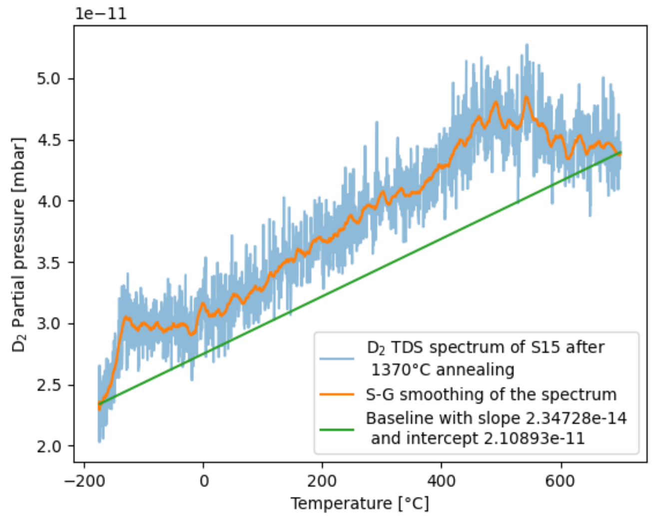
- Porous SiC does not store deuterium
- **Graphene required for storage**

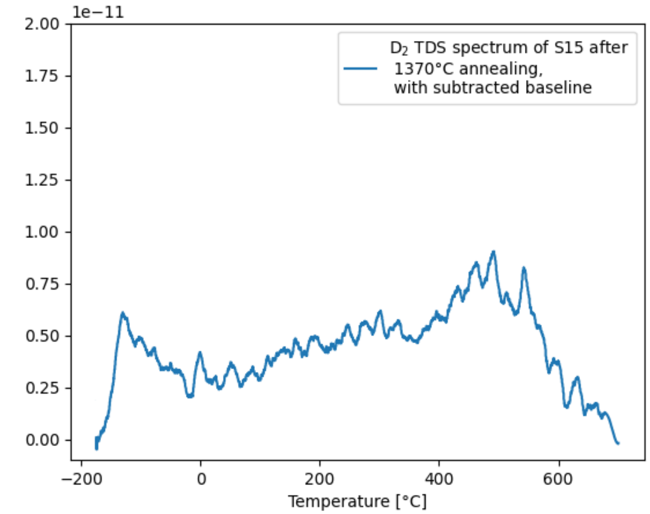
- A series of 8 successive annealing steps (1080°C-1480°C)
- No chemisorption signal with D_2
- Catalytic splitting hindered (possibly due to defects)
- Different spectra with D
- Peak II disappears, peak I appears

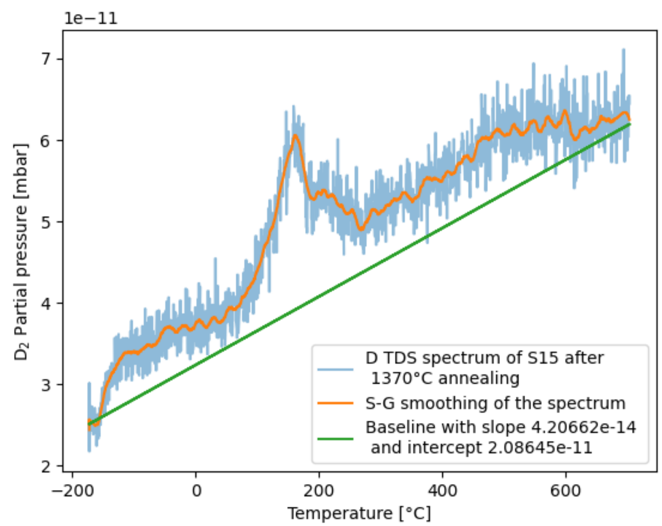


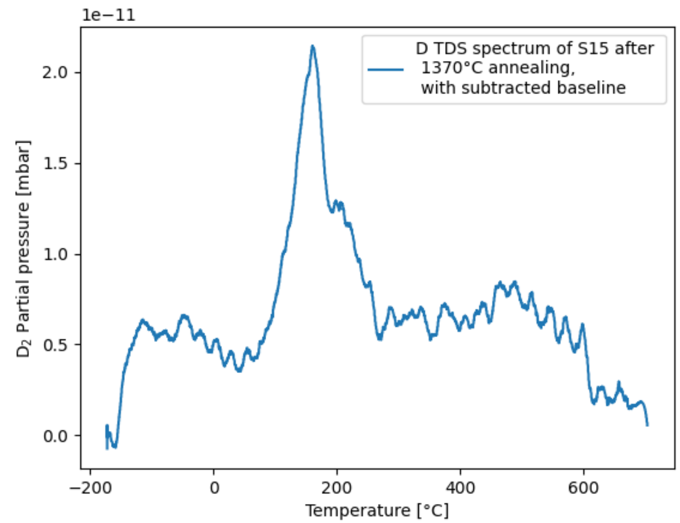
LT exposure TDS

- Sample cooling
- D_2 deposition
- Linear background
- D deposition
- Physisorp. (0.4eV), chemisorption, background increase



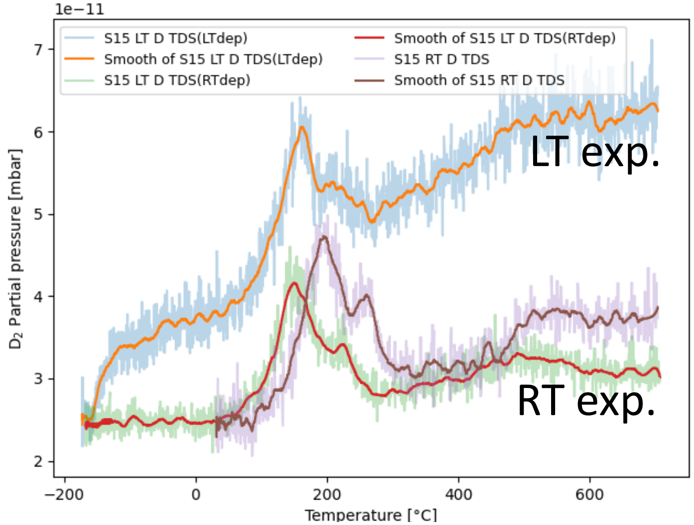


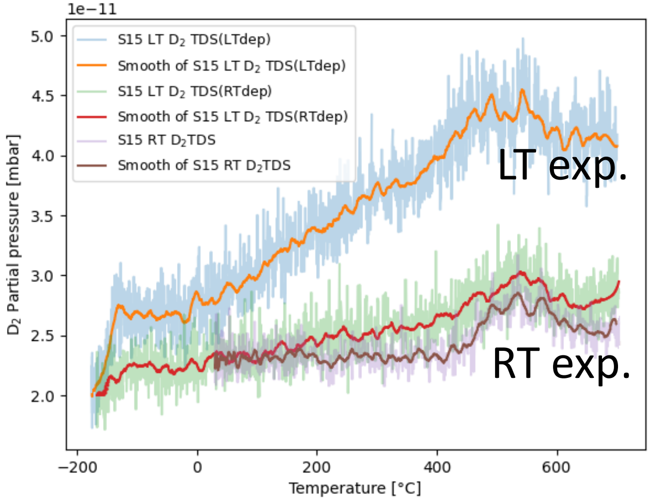




RT exposure LT TDS

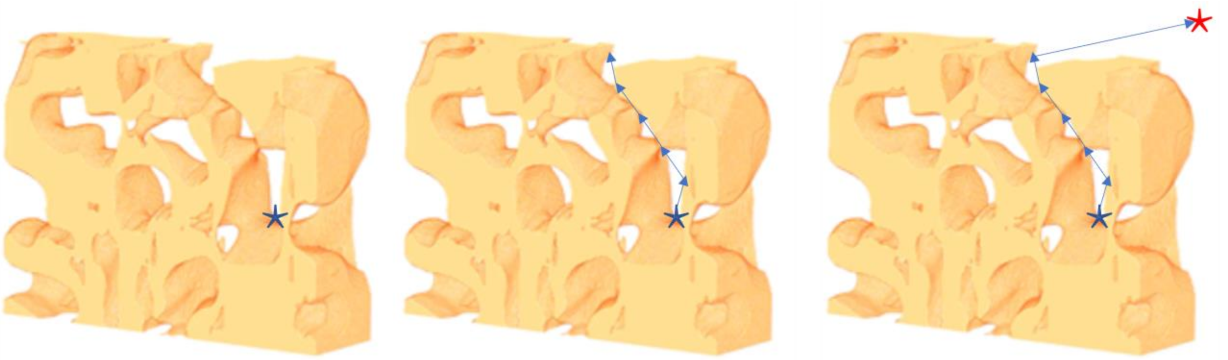
- Modified procedure to exclude physisorption
- Background increase and physisorption peak disappear
- **Background trend due to physisorption**
- Also present at high energies





Delayed Emission Model

- Energies are too high for physisorption
- Continuous and not dicrete emission
- Time lag between emission and detection
- Consistent with LT TDS



Desorption

$$T = T_0$$
$$\tau = \tau_0$$

Delay

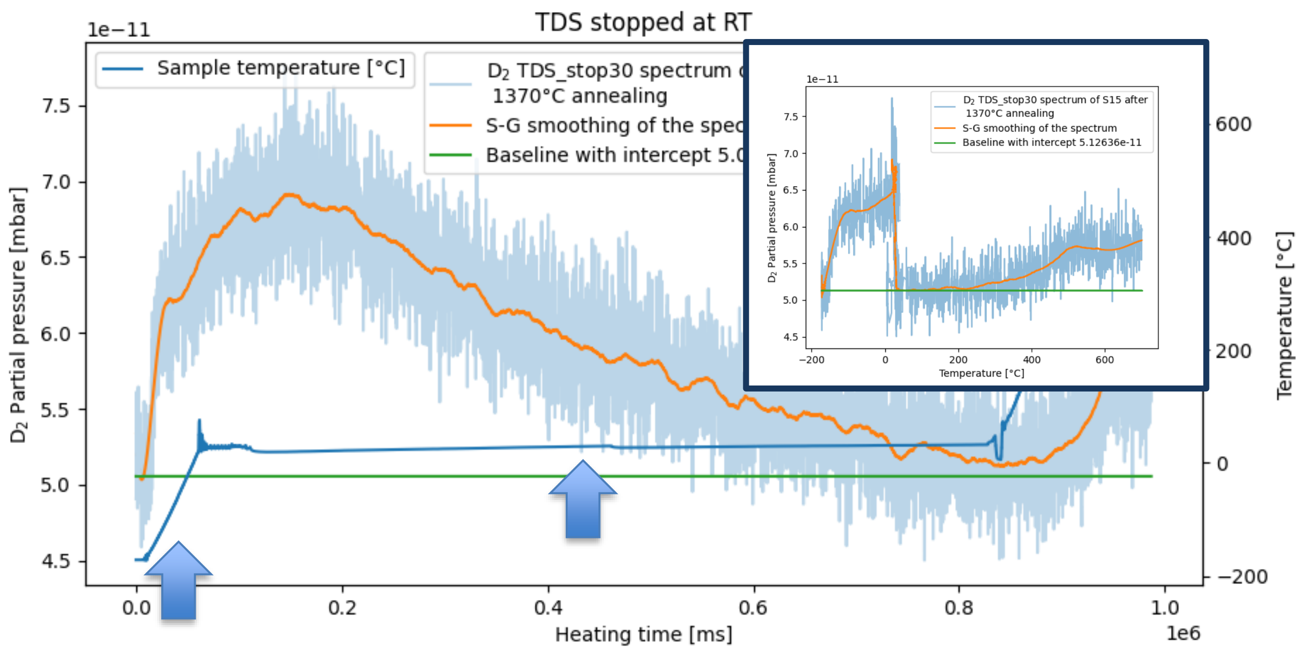
$$T = T_0 + \beta\tau_d$$
$$\tau = \tau_0 + \tau_d$$

Detection

$$T = T_0 + \beta(\tau_d + \tau_{ex})$$
$$\tau = \tau_0 + \tau_d + \tau_{ex}$$

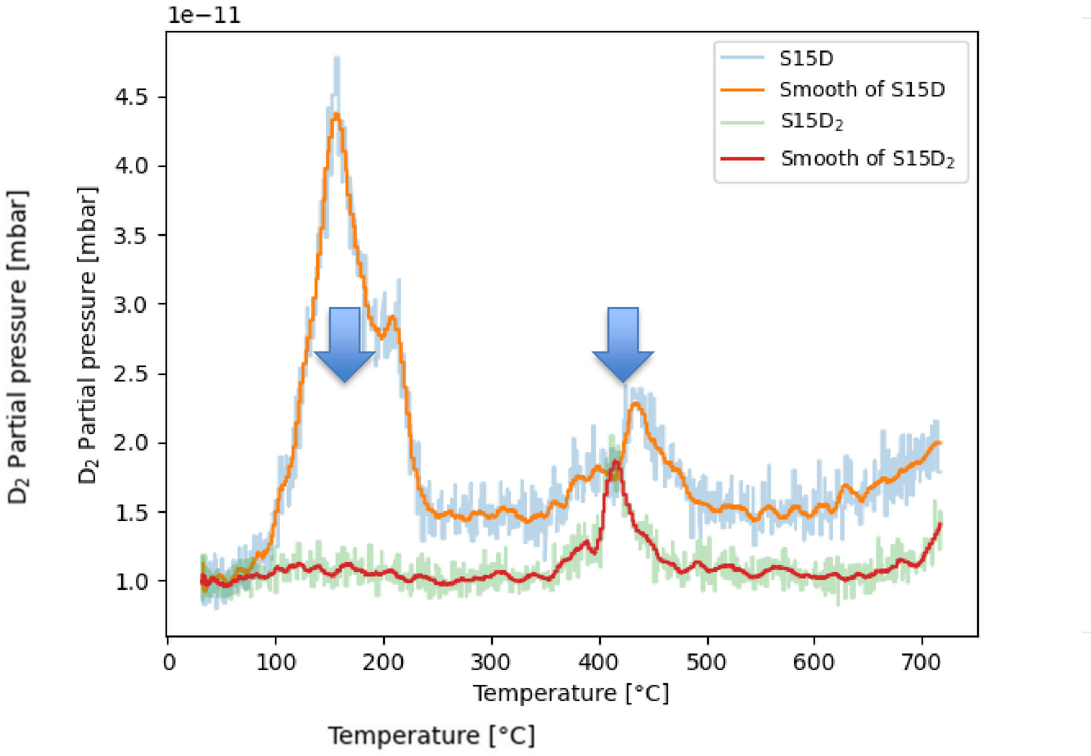
Alternative LT exposure TDS

- Testing the Delayed emission model
- Different TDS plots
- Different heating program
  - Ramp I
  - Temperature Hold
  - Ramp II
- **Consistent with the delayed emission model**
- Common TDS spectrum



Signal Attribution

- Comparison with flat epitaxial graphene
- No chemisorption with D_2
- **Defects introduced by etching**
- SiO_2 and structural defects reported and catalytically active
- **Peak II due to buffer layer**
- **Peak I likely due to dimers**
- Coherent with multiple annealing data



Conclusions

- Synthesis and characterization of a novel 3D graphene structure
- Proof of hydrogen chemisorption, in particular after D_2 hydrogenation
- Effect of the three-dimensionality on hydrogen desorption
- Attribution of chemisorption peaks to phyiscal phenomena

Outlook

- Optimization
  - Material (edges, defects, buffer layer)
  - Hydrogenation procedure (Times)
- Functionalization with active metals (Ti)
- Production of sensors
- Use in electrodes for PEC water splitting

Thank you for your attention