Unusual Materials for Hydrogen Storage: From Natural Diamond to Inorganic Nanotubes and Inorganic Fullerene-Like Nanoparticles

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Low, Medium, and Large Scale Requirements
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Part 1: Study of Hydrogen in Diamond: Collaborators

Alon Hoffman (Technion, Israel)

Gérald Dujardin, Genevieve Comtet, (LPPM, Université Paris Sud, Orsay, France) – Synchrotron Radiation Measurements

Roger Azria, (LCAM, Université Paris Sud, Orsay, France) - Electron Stimulated Desorption Measurements

Presentation Outline

1. Exposure of differently oriented <u>undoped</u> natural diamonds (**type IIa-<u>no impurities</u>**) to deuterium activated by microwave (MW) plasma - <u>SIMS analysis</u>;

2. Interaction of activated by Microwave (MW) plasma and in UHV, by Hot Filament atomized deuterium with CVD polycrystalline diamond films – <u>synchrotron radiation photon stimulated ion desorption (PSID) and electron stimulated desorption (ESD) measurements.</u>

Aim of the Research

1. To elucidate, whether hydrogen/deuterium can diffuse into the inner lying atomic layers of natural <u>undoped</u> diamond following exposure to MW plasma.

2. To compare the effects of MW and *in situ* (in UHV) deuteration (using hot tungsten filament) on the structure and electronic properties of diamond.

Interaction of MW Plasma Activated Deuterium with Natural Diamond

Sample Preparation

Samples: <u>undoped</u>, type <u>IIa,</u> natural (100)-, (110)-, and (111)-oriented diamonds

Treatment: exposure to MW Deuterium (99.999 %) plasma:

Gas pressure: 60 Torr;

Sample Temperature: ~ 700 °C

Plasma Power: 900 W

Duration of the treatment: 30-45 min

Analysis

Static SIMS: surface concentration of deuterium

Dynamic SIMS: sputter depth profile

Verification of the Crystalline Perfection

(before and after MW plasma treatment)

LEED pattern: well-defined planes: (111)-1×1:D, (100)-2×1:D, and (111)-facetted structure for the (110)-oriented diamond

EELS: the characteristic diamond bulk and surface plasmon peaks at 33 and 23 eV, respectively, were observed with no traces of spectral features at 6 eV commonly related to amorphous carbon and graphite
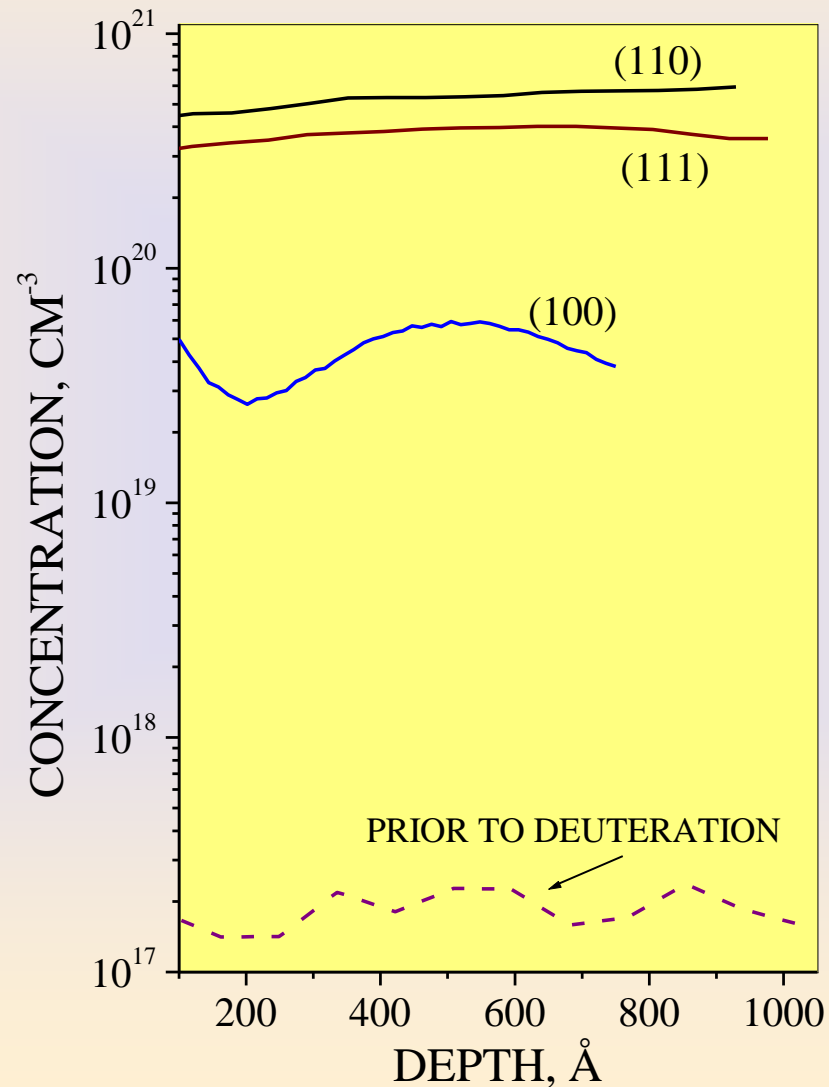
Static SIMS

Experimental: 10 keV Cs^+ beam

Ion current: 1×10^{-12} A

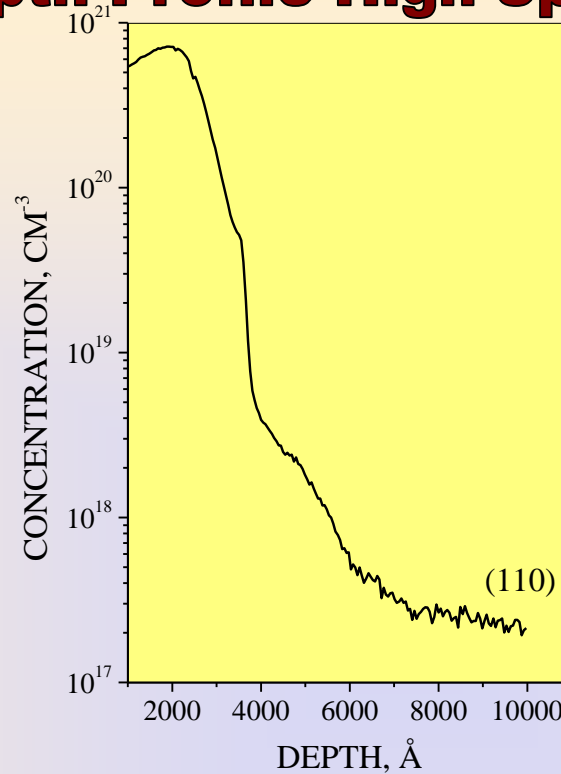Maximal ion dose: 4×10^{12} cm^{-2}
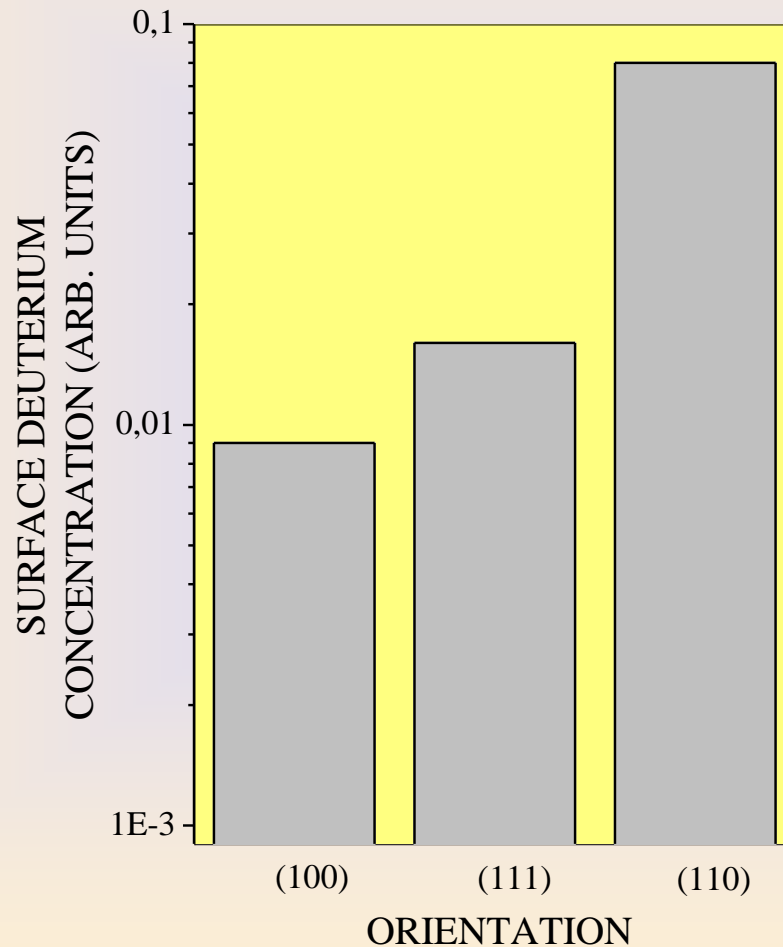
The _highest_ concentration of deuterium is on the **(110)-oriented** surface.

Depth Profile SIMS Analysis

Experimental: 10 keV Cs$^+$ beam;

Ion current: 1×10^{-8} A

Depth Profile-High Sputter Rate

Figure: Concentration (CM^{-3}) vs Depth (Å) profile, labeled (110). Y-axis ranges from 10^{17} to 10^{21} CONCENTRATION, CM^{-3}; X-axis DEPTH, Å from 2000 to 10000.

➤Deuterium atoms activated by MW plasma **diffuse** into undoped <u>type IIa</u> diamond crystal to doses of 10^{19}-10^{21} cm^{-3}

➤**No change** in hydrogen concentration **when hydrogenated samples have been stored for days or weeks**

➤Relative amounts of deuterium in the **bulk**, as well as in the **near-surface** region of differently oriented diamonds *retain these on the very surface*:

10^{20}-10^{21} cm^{-3} for the (110)-oriented surface

~ 10^{20} cm^{-3} for the (111)-oriented surface

~ 10^{19} cm^{-3} for the (100)-oriented diamond

➤The diffusion depth of deuterium is ~ 8000 Å (0.8 μm)

Interaction of Activated Deuterium with Polycrystalline Diamond Films: MW Plasma vs. Hot Filament Activation

Sample Preparation

Substrates : *p*-doped Si wafers, treated with diamond/ethanol slurry

Deposition: using MW CVD

CH_4:H_2 (1.5:98.5) gas mixture

Gas pressure: 70 Torr (400 sccm gas flow rate)

Temperature: ~ 850 °C (MW power: 1200 W)

Deposition time: 4.5 hours

Film Thickness: ~ 10 μm

Crystallite Size: 2-5 μm

Post-Deposition Deuteration (*Ex situ*):

exposure to MW Deuterium (99.999 %) plasma:

⅋ **<u>Gas pressure</u>**: 60 Torr

⅋ **<u>Sample Temperature</u>**: ~ 800 °C

⅋ **<u>Plasma Power</u>**: 900 W

⅋ **<u>Duration of the treatment</u>**: 30-45 min

Deuteration (*In situ*):

⅋ **Annealing of the film to 1000 °C in UHV**

⅋ **Verification of the complete hydrogen desorption** (by PSID)

⅋ **Exposure to deuterium gas flowing through a hot (1800 °C) tungsten filament**, while keeping the sample at **the room temperature**:

☞ Gas Pressure: 1.5×10^{-5} Torr (while pumping)

☞ Duration: 60 min

Analysis

SIMS measurements - *difficult to perform* due to high surface roughness

We applied the following techniques:

1. **Photon stimulated ion desorption (PSID) of D^+:**

   using synchrotron radiation: 280-310 eV

   measuring the total yield of escaping D^+ ions after *in situ* annealing to 25–1000 °C

2. **Electron stimulated desorption (ESD) of D^- (H^-):**

   using low energy electrons (5–35 eV)

   measuring:

   ⇨ ion yield

   ⇨ ion kinetic energy distribution (KED)

PSID measurements

MW-deuterated

HF *(In situ)*-deuterated
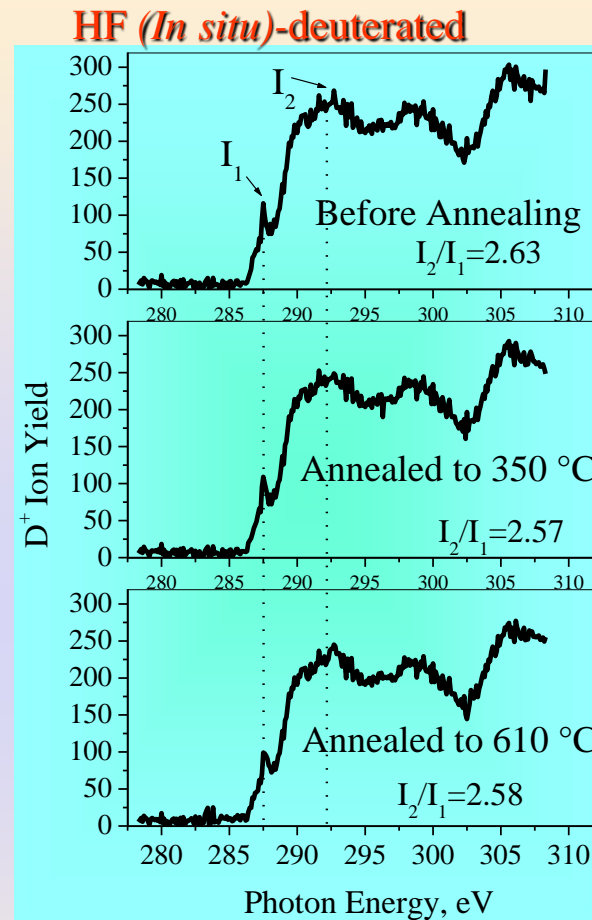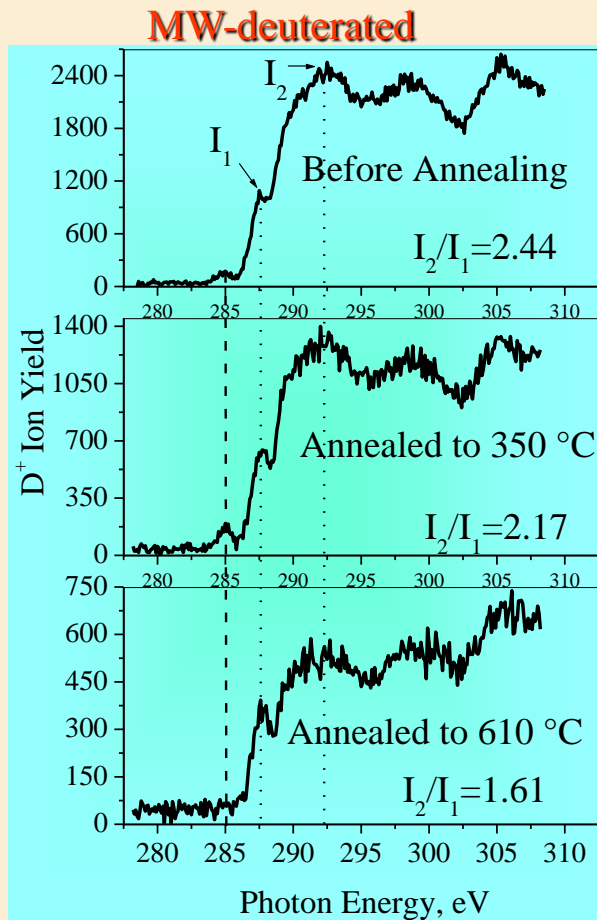
Assignement of the spectral feautures: [Reference: *Hoffman et al.*, Phys. Rev. B **62**, 8446 (2000)].

I_1 (287.5eV)-excitation energy of C-H (ads) bonds: *direct* (via core-hole relaxation) and *indirect* (via secondary electron excitations) processes;

I_2 (~ 292 eV) - due to excitation of C-C bonds (mainly *indirect* processes);

**285 eV** – valence band excitations due to *sec. electrons* in sp^2-bonded carbon;

302.4 eV (dip) – second absolute band gap of diamond (*indirect* processes).

MW-deuterated films: effect of annealing:

☞ integral desorption yield *decreases*

☞ I_2/I_1 peaks ratio *decreases*

HF (*in situ*)-deuterated films: effect of annealing:

☞ integral desorption yield *is lower* than for a <u>MW-deuterated film</u>

☞ integral desorption yield *remains nearly constant*

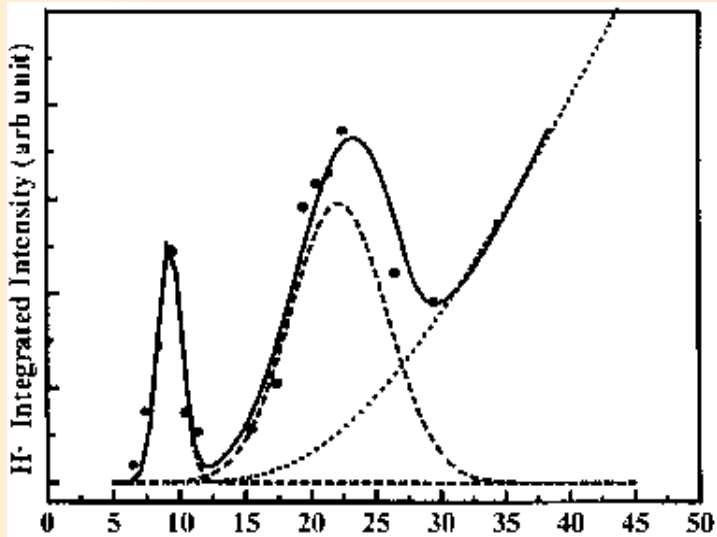☞ I_2/I_1 peaks ratio *remains nearly constant*
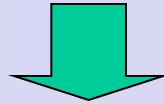
MW-deuterated films:

❧ deuterium concentration decreases upon moderate heating

❧ dynamics of the desorption changes in favor of direct processes (*not driven by SEE*)

HF (*in situ*)-deuterated films:

❧ deuterium is stable upon annealing

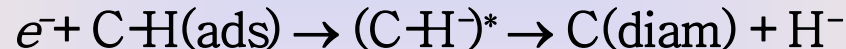❧ dynamics of the desorption processes remains unchanged

ESD measurements

☙ The peak **around 9 eV** is attributed to a **dissociative electron attachment (DEA)** process through a Feshbach resonance:

$$e^- + C-H(ads) \rightarrow (C-H^-)^* \rightarrow C(diam) + H^-$$

☙ The **monotonic increase** is associated with a **dipolar dissociation (DD)** process:

$$e^- + C-H(ads) \rightarrow [(C-H)^* + e^-] \rightarrow C^+(diam) + H^- + e^-$$

☙ The **structure around 22 eV** is due to **sub-surface deuterium giving DEA process** after the incident electrons have lost energy (13 eV) in electronic inter-band excitation of the diamond

Reference: *Hoffman et al.*, Phys. Rev. B **63**, 045401 (2001).

Kinetic Energy Distribution of Deuterium Anions
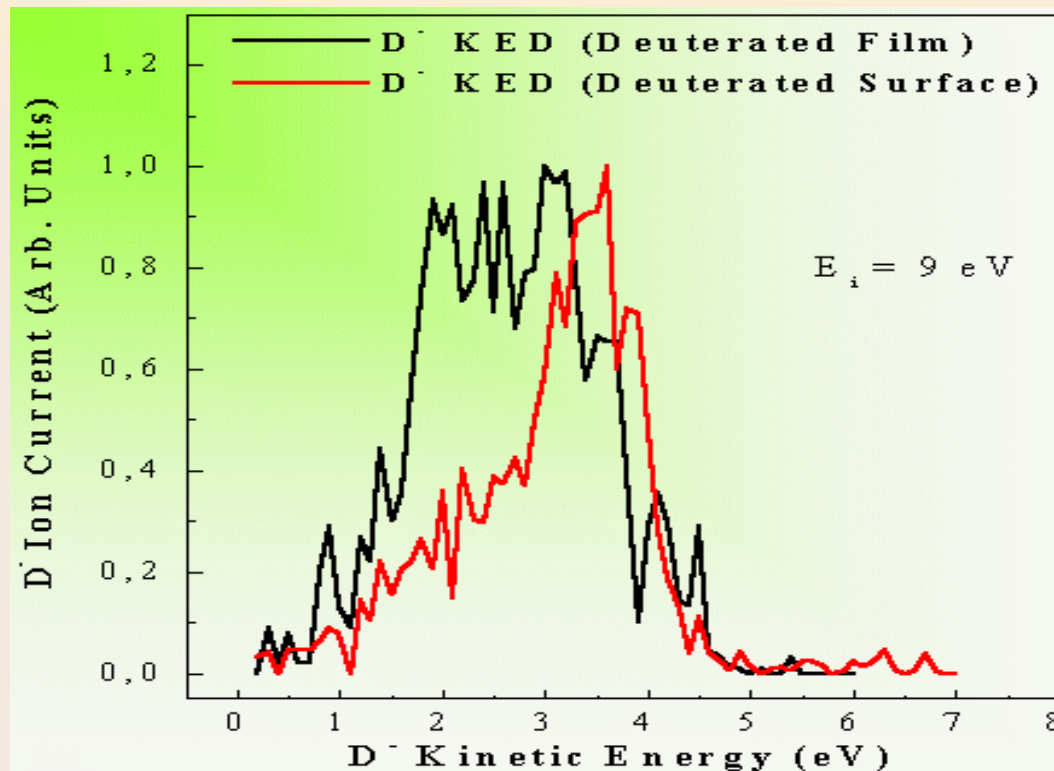
🔊 In the «surface» case (HF-deuterated), the D⁻ KED displays a peak at a high kinetic energy and a low-intensity tail

🔊 In the «film» case (MW-deuterated), deuterium is located in the sub-surface, as well as on the surface itself. This results in energy losses due to *collisions and phonon coupling before D⁻ ions escape from the film*

Hydrogen in Diamond: Conclusions

Natural Diamond:

❧ Deuterium activated by MW plasma diffuses into undoped type IIa natural diamond to the concentrations of 10^{19}–10^{21} cm^{-3}

❧Both bulk and surface concentrations of deuterium are the highest for the (110)-oriented surface, and the lowest for the (100)-oriented one. D

❧Diffusion depth of deuterium is in the order of 0.8 μm

❧Hydrogen can be stored for long periods (days, weeks, may be moore)

Polycrystalline Diamond Films:

❧ Deuteration performed *in situ* (by Hot Filament) does not result in bulk diffusion of deuterium atoms, in contrast to the MW plasma treatment

❧ Bulk deuterium (hydrogen) is not thermally stable, and desorbs upon moderate heating to 350 °C

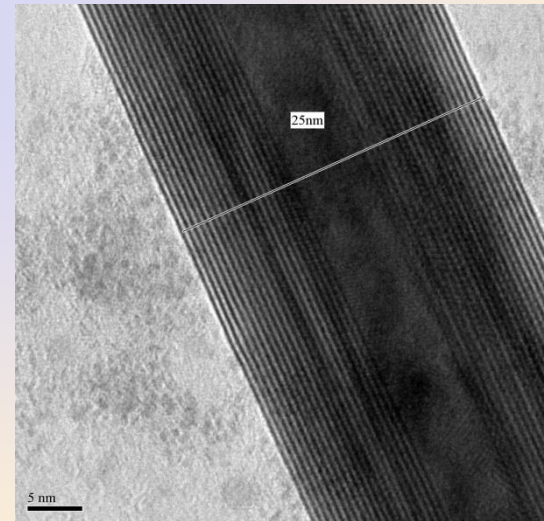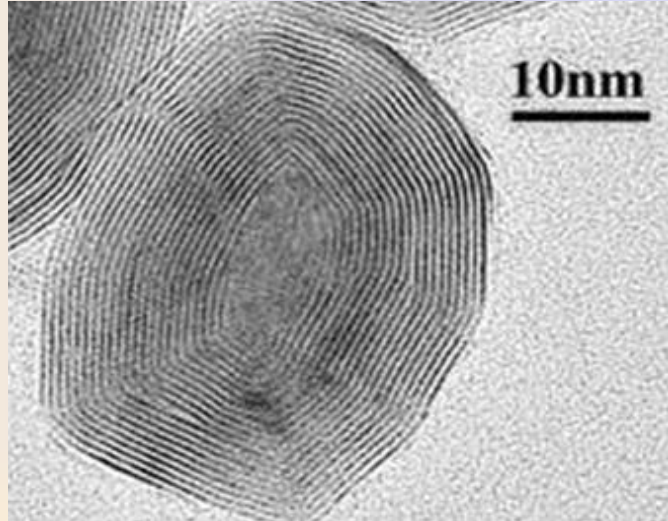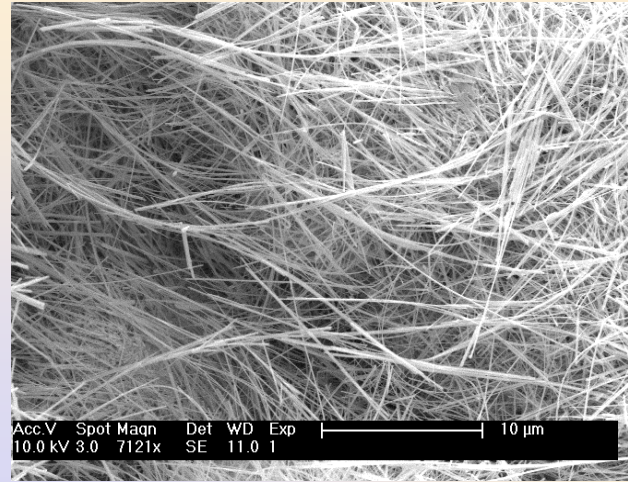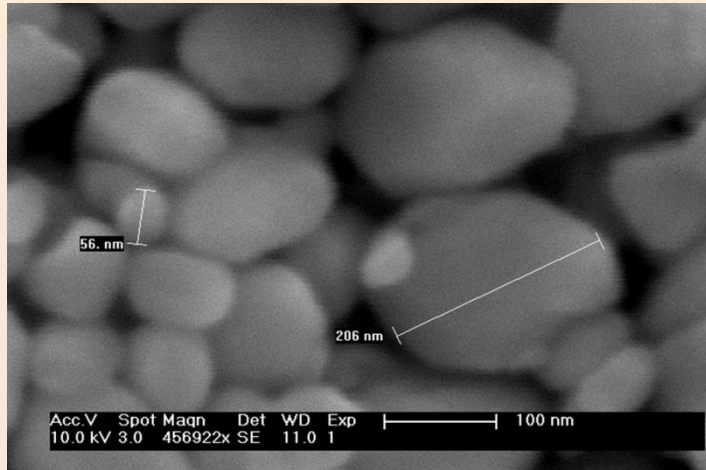❧ Chemisorbed deuterium (hydrogen) atoms are stable up to high temperatures.

Study of Hydrogen in Tungsten Sulfide Nanoparticles: Collaborators

Alla Zak – HIT and Weizmann Institute, Israel – synthesis

Shaul Michaelson, Alon Hoffman - Technion, Israel - hydrogenations
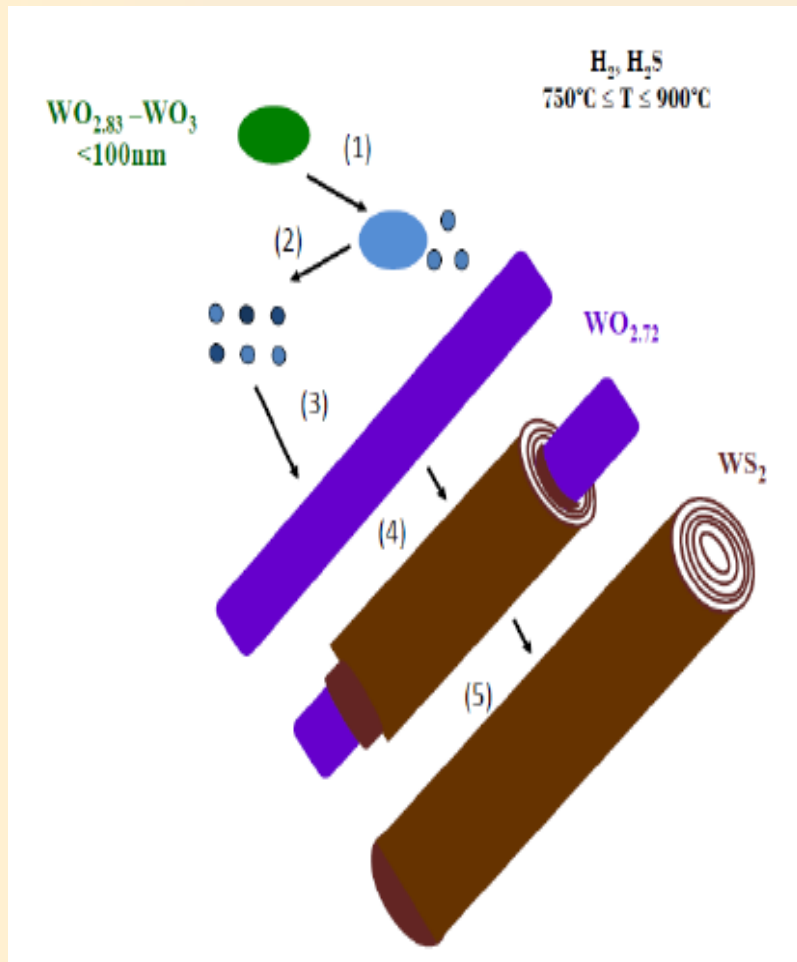
Hoi Ri Moon – UNIST, Korea – volumetric measurements

The Substrate Materials

WS$_2$–Inorganic Fullerenes
(IF)

WS$_2$–Inorganic Nanotubes
(INT)

How to Prepare?

1. The nanosize precursor mixture of non-volatile oxide $WO_{2.83}$–WO_3 phases undergoes mild reduction by hydrogen gas producing a volatile oxide phase (with $2.72 < O/W < 2.83$).

2. The oxide vapor undergoes additional partial reduction to the non-volatile phase, which serves as a nucleation center for the nanowhisker growth into stable suboxide phase of $WO_{2.72}$ ($W_{18}O_{49}$).

3. Sulfidization starts from the surface and middle of the oxide nanowhiskers, and oxygen to sulfur exchange progresses towards the end of the nanowhiskers (fast step) and inwards (slow-diffusion controlled reaction). This process leads to a gradual consumption of the oxide core creating a hollow multiwall WS_2 NT.

Conversion of the WO₃ oxide nanoparticles into inorganic fullerene like nanoparticles of WS₂

seconds — minutes — hours
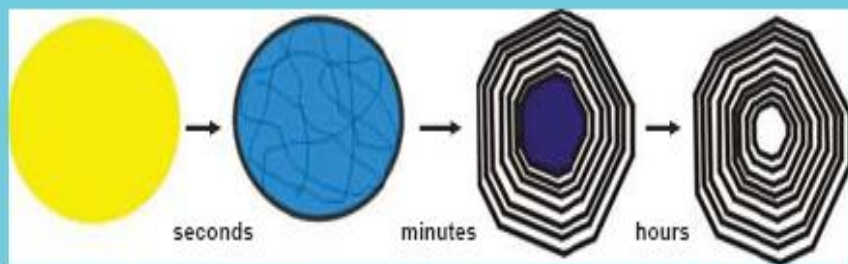
Precursor: WO₃ nanoparticle

the WO₃ suboxide nanoparticle, covered with few layers of disulfide

WS₂ closed-cage structure with a suboxide core encapsulated

Fully converted WS₂ inorganic fullerene-like nanoparticle

➢Fast reaction of the H_2S and H_2 with the surface of semi-spherical oxide NP (the precursor) leads to the quick formation of a few closed WS_2 layers encapsulating the oxide core.

➢The surface-passivation of the oxide NP by the inert layers of WS_2 prevents coarsening of the NP, making each one of them a nanoreactor of its own. Thus, the oxide core becomes partially reduced to WO_{3-x} and, subsequently, a slow diffusion-controlled reaction leads to fully replacement of the oxygen with sulfur atoms.

➢This outwards-inwards-reaction proceeds in epitaxial-like fashion (layer by layer, using the external sulfide layers as a template) until the synthesis of the hollow IF-WS_2 NP is completed.

➢The size and shape of the fullerene-like NP (IF-WS_2) is determined by the size and shape of the pre-prepared WO_3 NP. The majority of oxide/IF NP range from 150 to 350 nm in diameter being of oval shape.

➢The presence of a hollow core in the IF NP is attributed to the differences in specific gravity of WS_2 and WO_3 (7.5g/cm³ and 7.15g/cm³, correspondingly).

# Why to use them for hydrogen storage?

- High thermal and mechanical stability

- Layered and packed structure

- H_2 could be intercalated in between the layers

- H_2 can diffuse into hollow core or in between the layers through surface defects of IF spherical particles, and in the case of INT – through the open end of the tubes

How to treat them to store hydrogen?

- To expose to molecular hydrogen at high pressure, high/low temperature

- To expose to plasma-activated (MW, RF, DC) hydrogen
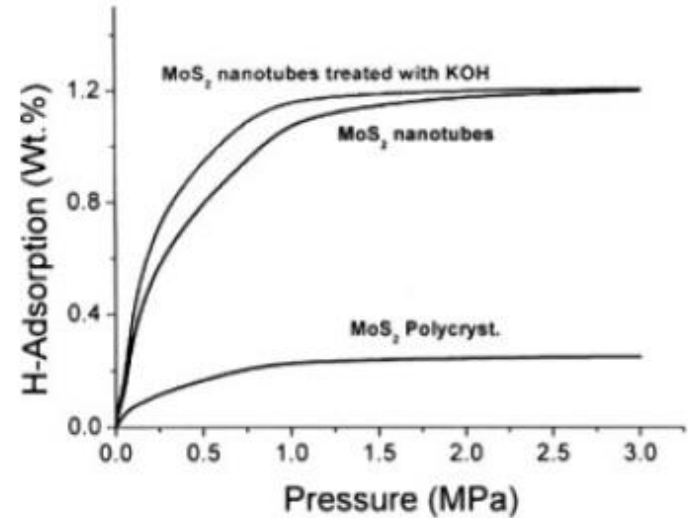
Early Works on Hydrogen Storage in XS₂ Nanotubes

TiS₂
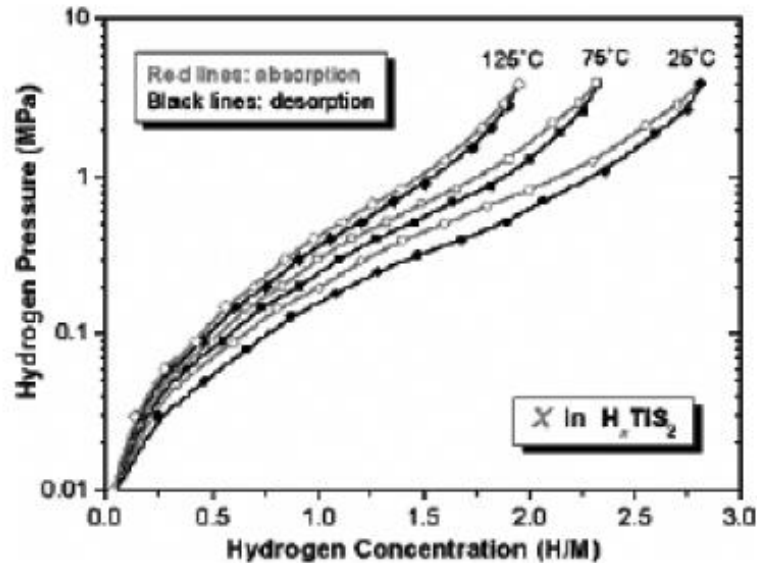
J. Chen, S.-L. Li, Z.-L. Tao, Y.-T. Shen, C.-X. Cui, *J. Am. Chem. Soc.* **2003**, *125*, 5284.

MoS₂

J. Chen, S. L. Li, Z. L. Tao, *J. Alloys Compd.* **2003**, *356–357*, 413.

Max. Wt.%: 2.8%
Molecular weight, TiS₂: 112 g/mol

Max. Wt.%: 1.2%
Molecular weight, MoS₂: 160 g/mol

Recent Results:

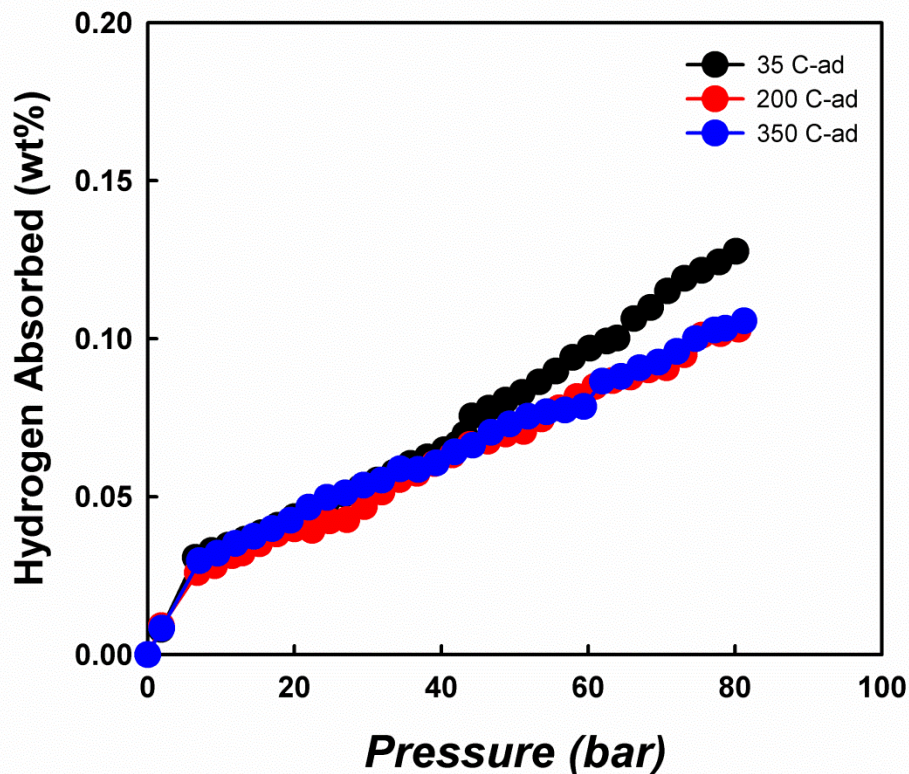## Exposure of WS$_2$-INT to High Pressure Molecular Hydrogen

Outgassing conditions: 120 ^{o}C annealing under vacuum for 8 h

After each isotherm: 350 ^{o}C annealing under vacuum for 8 h

Adsorption time: 10 min
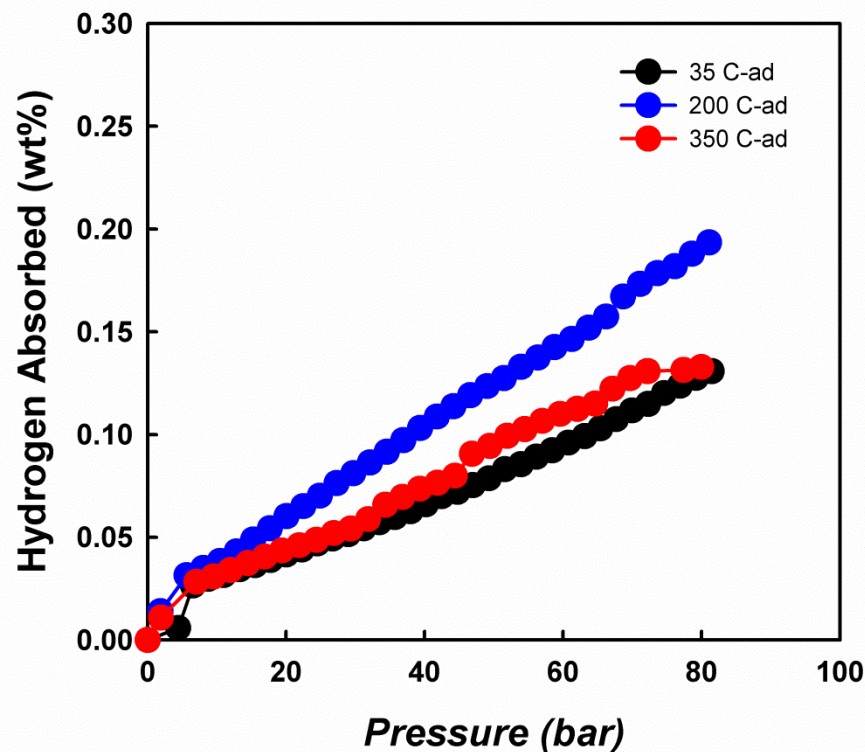
20 sec (time interval between data collection)

Verification of the substrate material: XRD and SEM

adsorption temperature	wt%
35 °C	0.13
200 °C	0.10
350 °C	0.11

Recent Results:

Exposure of WS$_2$-IF to High Pressure Molecular Hydrogen

adsorption temperature	wt%
35 °C	0.13
200 °C	0.19
350 °C	0.13

M.W. (WS$_2$) = 248 g/mol

Recent results: Exposure of WS_2-INT to Low Pressure MW-Plasma Activated Hydrogen

Goal: to get a sufficient energy (per an activated gas molecule) and large atomic flux to the substrate!

Conditions:

400 W, 60 Torr, 200 sccm, 5 min

Sample: tablet of 5 mm in diameter

$$Flux = \frac{6 \times 10^{23} \, \text{mol}^{-1}}{22.4 \times 10^{-3} \, \text{m}^3 / \text{mol}} \cdot v_T \cdot A \cdot t = 2.5 \times 10^{25} \times 1500 \cdot 2 \times 10^{-5} \cdot 300 \cdot \frac{60 \, \text{torr}}{760 \, \text{torr}} = 1.5 \times 10^{25} \, (\text{atoms}) \, (\text{eq. 1})$$

And the energy per an atom is (Eq. 2):

$$Power = \frac{400}{1.67 \times 10^{-19}} = 2.5 \times 10^{21} \left(\frac{\text{eV}}{\text{s}} \right); \quad N/t = \frac{200 \, \text{sccm}}{22400 \, \text{cc}/\text{mol}} \cdot \frac{6 \times 10^{23} \, \text{mol}^{-1}}{60 \, \text{s/min}} \approx 1 \times 10^{20} \, \frac{\text{atoms}}{\text{s}}$$
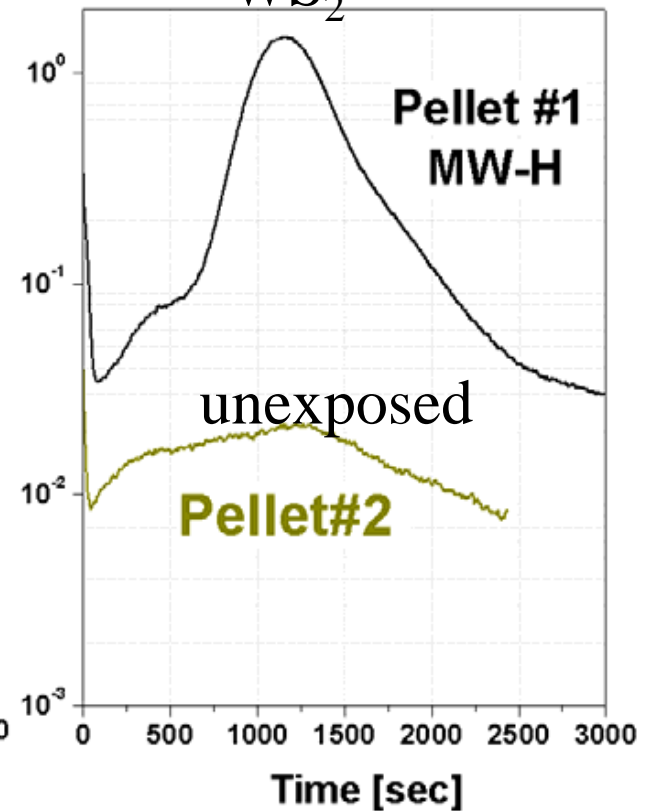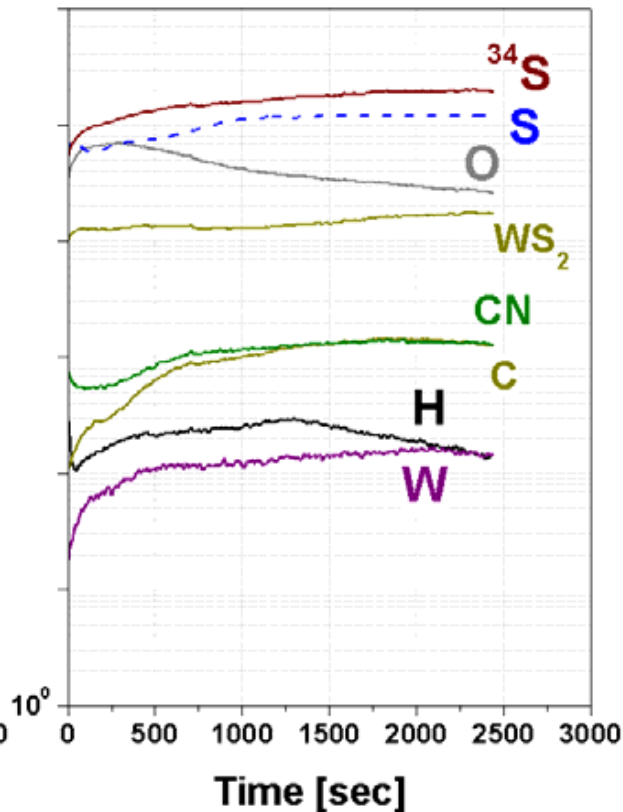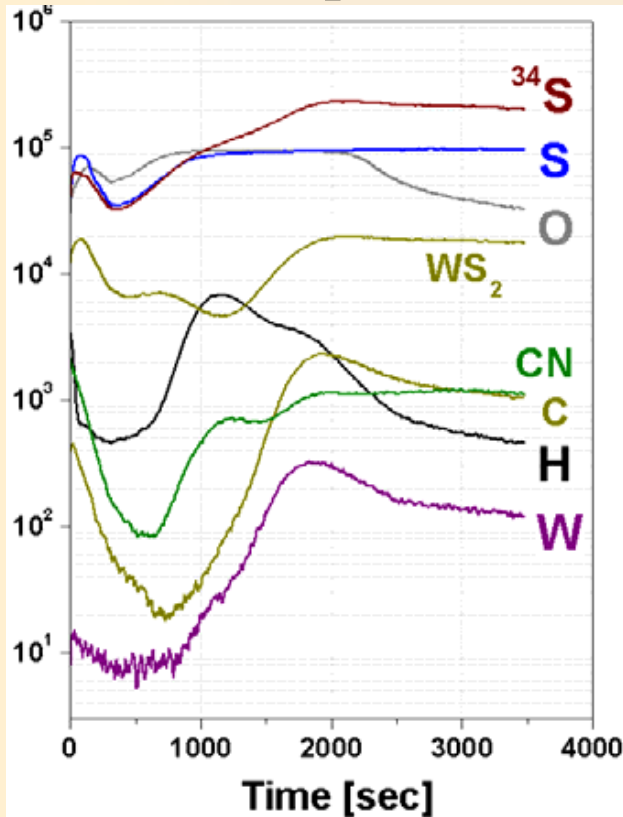
$$Energy = \frac{2.5 \times 10^{21}}{1 \times 10^{20}} = 25 \left(\frac{\text{eV}}{\text{atom}} \right) \, (\text{eq. 2})$$

# TOF SIMS for hydrogen detection

MW-exposed

Unexposed

Both: normalized to WS₂

SEM verified: no visible damage to the structure

➤ Hydrogen signal increase: **×70** (as related to the unexposed sample)
➤ Hydrogen concentration in the unexposed sample: ~0.015 wt.%
➤ Estimated hydrogen concentration in the MW-exposed WS₂-INT: **~ 1 wt.%:**
to be verified by XRD and PCT hydrogen desorption

The Ongoing Research: RF/DC Plasma: Testing the Influence of Particles Energy and Momentum
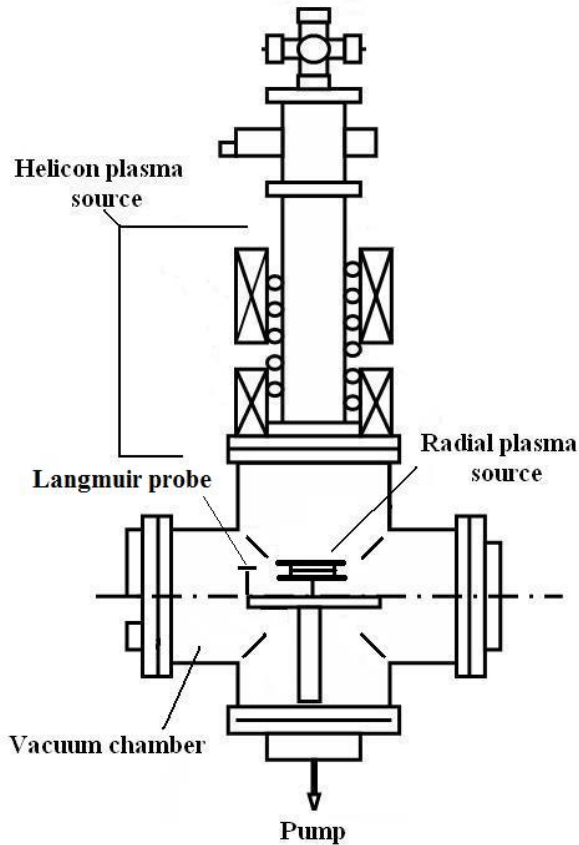
- Different gas flow rate and pressure

- RF plasma: better control on the energy of particles in plasma

- DC plasma: better control over the momentum of particles

In Situ Diagnostics of Hydrogen Adsorption/Desorption in the Plasma System

- After hydrogenation the vacuum chamber will be pumped down to ~10^{-5} Torr.

- The sample will be heated to ~500 °C.

- The hydrogen desorption will be monitored by measuring the gas pressure versus the time, $P(t)$.

- Using data of $P(t)$ and the pumping speed data $S(P)$, we will calculate the mass of the gas absorbed by the sample as $m = M \int_0^T S \dfrac{P}{kT} dt - m_0$, where m_0 is the mass of the gas absorbed by experimental setup and M is the molecular mass of hydrogen.

Hydrogen in WS$_2$-INT and WS$_2$-IF: Conclusions

➢Molecular high pressure-room/high temperature hydrogen absorbs into WS$_2$-INT and WS$_2$-IF to modest 0.13-0.19 wt.%.

➢Increasing temperature does not really favor hydrogen absorption.

➢Very short (5 min) MW-plasma activated hydrogen exposure results in up to ~1 wt.% absorption of hydrogen in WS$_2$-INT (rough estimation).

➢Multiple cycles of exposure-release can be performed and no deterioration of the substrate material has been detected.