Production d'ions négatifs lors de l'interaction plasma-surface

G. Cartry
A. Ahmad, P. Kumar, M. Carrère, J.M. Layet, C. Pardanaud, G. Giacometti, JB Faure, T. Pasquet
PIIM laboratory, Aix-Marseille Université, Marseille, France

A. Gicquel, F. Silva
LSPM, Université Paris-Nord

D. Eon
Institut Néel, Grenoble

R. Engeln
Technical University, Eidhoven
Negative ions in plasmas

- Negative ions are present in plasmas when using electronegative gases: $H_2$, $O_2$, $Cl_2$, $C_2F_6$...

- Negative ions in are usually produced in plasma volume by electron dissociative attachment on molecules:
  - $e + H_2(v) \rightarrow H^- + H$
  - $e + O_2(v) \rightarrow O^- + O$ ...

- Negative ions can also be created on surfaces:
  - $H_x^+ + \text{surface} \rightarrow H^-$
  - $H + \text{surface} \rightarrow H^-$
  - ...

Negative ions in plasmas

- They have impact on discharge kinetics and equilibrium
  - They require new diagnostics
  - They may be at the origin of plasma instability

  N. Plihon et al, JAP 98, 023306 2005
  Chabert et al, PSST, 10 (2001) 478–489

- But they have also potential applications…
Negative ions in plasmas

- They are used as source particles for accelerator

- Negative ion based plasma thrusters are currently under development (I⁻, F⁻…)

- They can be used for material processing (C⁻, C₂⁻, Ag⁻, Si⁻…):
  - ion beam deposition
  - ion implantation
Negative ions in plasmas

- As they are easily neutralized, they can be used to generate neutral beams for:
  - Charge effect free etching (F\(^-\), Cl\(^-\) ions...):
  - Heating of magnetically confined plasmas (H\(^-\), D\(^-\) ions...) for fusion:
Deuterium/hydrogen ions are extracted from a low pressure high density plasma source.

Deuterium/hydrogen ions are accelerated. The beam is neutralized and injected in the tokamak plasma.
Introduction
Cs seeded negative ion sources

- Requirements for ITER: **20 mA/cm$^2$** of D$^-$ negative ions
- At present days, only Cs deposition on surfaces in ion source allows obtaining high negative ion current required for ITER
- Indeed, cesium reduces material work function and strongly increases negative ion surface production yield
Introduction
Cs seeded negative ion sources

- Requirements for ITER: 20 mA/cm$^2$ of D$^-$ negative ions
- At present days, only Cs deposition on surfaces in ion source allows obtaining high negative ion current required for ITER

<table>
<thead>
<tr>
<th>Nowadays, Cesium deposition</th>
<th>Future: cesium free</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantage</strong></td>
<td><strong>Advantages</strong></td>
</tr>
<tr>
<td>High negative ion yield</td>
<td>None of Cs drawback</td>
</tr>
<tr>
<td><strong>Drawbacks</strong></td>
<td><strong>Drawback</strong></td>
</tr>
<tr>
<td>Long term operation stability</td>
<td>None of Cs advantage (low yield)</td>
</tr>
<tr>
<td>Diffusion the in accelerator stage</td>
<td></td>
</tr>
<tr>
<td>High consumption</td>
<td></td>
</tr>
</tbody>
</table>

Need important research effort to develop Cs free negative ion sources
Cs free negative ion sources

Two options

- Develop optimized volume production sources
- Find a material giving a high yield of surface produced negative ions without Cs

Study of $\text{H}^-/\text{D}^-$ surface production on surfaces in $\text{H}_2/\text{D}_2$ plasmas
Experimental set-up

Helicon reactor

- $\text{H}_2$ and $\text{D}_2$ plasma
- $P = 30$-$900$ W
- No magnetic field
- $Pr = 0.2$ – $2$ Pa
Experimental set-up

- Helicon reactor
  - H\textsubscript{2} and D\textsubscript{2} plasma
  - P = 30-900 W
  - No magnetic field
  - Pr = 0.2 – 2 Pa

- Pyrex tube
- Antenna
- Coils
- Mass spectrometer
  - Hiden EQP300
- Pump
Experimental setup

Graphite sample

Positive ion bombardment

Voltage

Mass Spectrometer Hiden EQP 300

Plasma

Negative ions

Measurement of surface produced negative ion distribution function
All distribution functions are shifted by $E_0$ on the energy axis.
H- distribution functions

0.4 Pa H₂, 100W, V_{surface} = -40V, V_p = 47V

\[ E_0 = e (V_p - V_s) \]

- Negative ions are not created at rest on surface
What are the surface production mechanisms?

Can we study them by studying negative ion distribution function?
Surface production mechanism

Backscattering

We first consider backscattering of a positive ion as a negative ion.

Positive ion bombardment

Neutralization = first electron capture

Elastic collision with carbon atoms

Second electron capture and backscattering

The negative ion is created with an initial energy equal at maximum to the $\text{H}^+$ incident energy $E_0 = e(V_p - V_s)$.
Then the $\text{H}^-$ negative ion is accelerated by the sheath and gain the energy $E_0 = e(V_p - V_s)$

- $\text{H}^-$ created on surface via backscattering of $\text{H}^+$ reaches plasma with maximum energy: $E_1 = E_0 + E_0 = 2E_0$
Backscattering: energy considerations

Then the $\text{H}^-$ negative ion is accelerated by the sheath and gain the energy $E_0 = e(V_p - V_s)$.

- $\text{H}^-$ created on surface via backscattering of $\text{H}^+$ reaches plasma with maximum energy: $E_1 = E_0 + E_0 = 2E_0$

- What happens with molecular ion bombardment?

- The initial energy is shared between fragments: the negative ion is created with a maximum energy equal to $E_0/2$ ($\text{H}_2^+$) or $E_0/3$ ($\text{H}_3^+$).
Then the $H^-$ negative ion is accelerated by the sheath and gain the energy $E_0 = e(V_p - V_s)$

- $H^-$ created on surface via backscattering of $H^+$ reaches plasma with **maximum** energy: $E_1 = E_0 + E_0 = 2E_0$

- $H^-$ created on surface via backscattering of $H_2^+$ fragment reaches plasma with **maximum** energy: $E_2 = \frac{1}{2}E_0 + E_0 = \frac{3}{2}E_0$

- $H^-$ created on surface via backscattering of $H_3^+$ fragment reaches plasma with **maximum** energy: $E_3 = \frac{1}{3}E_0 + E_0 = \frac{4}{3}E_0$
Backscattering in H$_2$ plasma

H$_3^+$ dominates (90%)
Backscattering in H$_2$ plasma

H$_2^+$ dominates 90%
Backscattering in H$_2$ plasma

H$^+$ is non negligible

0.12 Pa Ar and 0.02 Pa H$_2$, 900W: H$^+ \sim$ H$_2^+$

- Backscattering explains at least the high energy part of IDF in H$_2$ plasmas
Backscattering explains at least the high energy part of IDF in H$_2$ [1] and D$_2$ plasmas [2]

Is there another negative ion production mechanism?

Another production mechanism?

$E_0 = 10\text{eV}$  

$E_0 = 18\text{eV}$  

$E_0 = 20\text{eV}$  

$E_0 = 23\text{eV}$  

$E_0 = 30\text{eV}$
Sputtering threshold?

0.2 Pa, 100 W

\( H^- \) total intensity vs positive ion energy \( E_0 \)
Sputtering could explain this threshold effect

\[ H_x^+ + H_{\text{adsorbed}} \rightarrow H^- \]
We now consider sputtering of an adsorbed hydrogen atom as a negative ion: \[ H_x^+ + H_{\text{adsorbed}} \rightarrow H^- \]
Sputtering of adsorbed H as H⁻ in H₂ plasmas

- At high temperature, H surface coverage is null, sputtering should not occur

![Graphs showing H⁻ energy distribution at different temperatures and voltages](image-url)
Sputtering of adsorbed H as H\(^-\) in H\(_2\) plasmas

- At high temperature, H surface coverage is null, sputtering should not occur

- Main peak is decreasing strongly when surface coverage goes to 0
- Main peak is due to sputtering
- There is coincidence of energetic tails at high and low temperature. Backscattering is not dependent on temperature
Conclusion on sputtering

- Sputtering explains main peak of negative ion IDFs at room temperature:
  - \( H_x^+ + H_{\text{adsorbed}} \rightarrow H^- \) [1]

- Sputtering represents 75% of the measured negative ion up to 80eV where it decreases strongly

- Similar results are found in \( D_2 \) plasmas [2]

[1] L Schiesko et al, APL, November 2009
Polycrystalline boron doped diamond films were deposited at LSPM laboratory by plasma assisted chemical vapor deposition.

Results on diamond are compared with graphite.
Yield increases by a factor 5 on BDD at elevated temperature!

Same effect has been observed on non-doped diamond.
H⁻ on other surfaces: metals and semi-conductor

- Similar trends for Palladium, stainless steel, Tantalum, Copper…

![Graph showing H⁻ intensity on different materials]

- Materials: W cleaned, Si cleaned, W oxidized, Si oxidized, HOPG
- Conditions: 0.3 Pa H₂, 300 W, E₀=62V, H₂⁺80%

![Diagram with data points for H⁻ intensity]
H⁻ surface production: conclusions

- Two surface production mechanisms have been identified:
  - Backscattering of an incoming positive ion as a negative ion
  - Sputtering of an adsorbed H/D atom as a negative ion

- Surface production on HOPG and diamond at room temperature is similar
- Surface production increases on diamond at high temperature
- Surface production is low on clean metals (higher on oxidised metals)
Other negative ions, other materials…

H- and cesiated surfaces

- Surface production enhancement with Cs was discovered in the seventies
  Belchenko Yu.I., Dimov G.I. and Dudnikov V.G. 1974 Nucl. Fusion 14 113

- First surface produced source uses a biased cathode as a converter in Cs seeded plasma: high energy H\(^+\) are converted into high energy H\(^-\)
  Holmes, Plasma Physics and Controlled fusion 34 653 (1992)

Similar effect with barium cathode
Other negative ions, other materials...

H- and cesiated surfaces

- In 1989, a high enhancement of negative ion yield is reported in a volume source when Cs is injected (no cathode converter)

- Impact of low energy H atoms on the cesiated extraction grid leads to negative ion formation
  Hemsworth, IEEE transactions on plasma science, 33, (2005)
Other negative ions, other materials…

- Appart from the fusion community, negative ion surface production in plasmas has attracted interest only in the sputtering community.

- It is known for a long time that negative ions can be formed in plasma sputtering process. *R. É. Honig, J. Appl. Phys. 29, 549 (1958).*

- In the seventies, the impact of negative ions on the sputtering process has started to be studied: *Hanak et al, JVST 13, 1976*
  - In this paper there is no direct observation of NI.
  - Ar – O2 plasmas are used to sputter oxydised target ($Y_2O_3$…).
Other negative ions, other materials...

- In 1978, Cuomo et al report an etching of the substrate in the sputtering process rather than deposition of a thin layer.

  Cuomo et al, JVST 15 (1978)

- The etching comes from negative ions accelerated from the cathode and impinging the substrate at high energy.
  - In this paper there is no direct observation of the negative ions formed in the plasma.
  - Ar plasma are used. Rare earth-gold alloys targets are used.
  - The negative ions are probably: Au-, Sm-, O- (impurity)
Other negative ions, other materials…

O⁻ and other negative ions, various surfaces

- From the eighties until now, few tens of papers deal with negative ion surface production in the sputtering process:
  - NI: O⁻, OH⁻, SiO₂⁻, SiO₃⁻, AlOₓ⁻, YOₓ⁻
  - Targets: iron, YBaCuO, Y₂O₃, Al₂O₃
  - Plasmas: Ar, Ar-O₂…

- More recently, some papers focus on the O⁻ negative ion distribution functions
  - O⁻ are created by the sputtering process
  - Usually, simultaneous formation by backscattering is not observed or not commented

- Only one paper deals with NI formation by backscattering
  - H⁻ on stainless steel

Beam experiments

Many different negative ions, many different surfaces

- Charge exchange on surface is studied for a long time under UHV conditions
- Usually incident beams are at grazing incidence

- Negative ions: F\textsuperscript{−}, O\textsuperscript{−}, H\textsuperscript{−}, CF\textsubscript{3}\textsuperscript{−}, C\textsubscript{x}\textsuperscript{−}, Si\textsubscript{x}\textsuperscript{−}…
- Surfaces: Al, Diamond, HOPG, LiF, Si, Mb, Cs, LaB\textsubscript{6}, LiCl, stainless steel…
Conclusions

**NI surface production in plasmas: an unusual phenomena?**

- Depending on the gas, on the wall materials and on the positive ion energy, negative ions can be formed « efficiently » on surfaces

- Materials and gas used in the microelectronic industry could lead to efficient negative ion surface production

**NI surface production in plasmas: a negligible phenomena?**

- Surface production is probably low under non-optimized conditions

- However, high energy negative ions can have an impact on:
  - Thin layers (see sputtering process for instance)
  - Heating of the gas
  - Discharge dynamics…
  - Modelling results
Acknowledgements

- Technical staff: Jean-Bernard Faure, Fred Le Moal, Eric Garabedian...
- Student: Hamouda Ramzy, Timothée Pasquet...
- Fundings:
  - ANR: project ITER-NIS BLAN08-2_310122
  - ANR: project CAMITER BLAN06
  - FR-FCM