

Surface production of negative-ions in hydrogen plasmas: comparative analysis of different surface materials

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Surface production of negative-ions in hydrogen plasmas: comparative analysis of different surface materials



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Introduction

□ Many low-pressure plasma negative-ion sources rely on the process of surface ionization:

 $H / H_{x}^{+} + surface \rightarrow H^{-}$

- The surface can be an extraction grid, a plasma electrode, the plasma reactor walls...
- In this process the material work function (WF) ϕ is a key parameter: $\phi \ge => H^2 7$ a priori
- Cs has the lowest ϕ : 2.1 eV vs 4-5 eV for most metals
- Cs complicates negative-ion source operation => study of H⁻ surf. prod. on alternative materials

Negative ion (NI) surface production mechanism



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Samples as introduced

- The as-deposited μ c-BDD and μ c-D are hydrogen surface terminated
- PDD has been chemically de-hydrogenated in order to perform post deposition surface analyses
- All samples are first annealed to 400C to desorb impurities



- ✓ Sub-bandgap (<5.5eV) electron emission reveals negativeelectron affinity [1]
- Emission threshold at 4.4eV and band gap of 5.5eV sets the negative-electron affinity to -1.1eV
- ✓ Between 4.4eV and 5.5eV, some electrons from the surface are directly emitted into vacuum (see mechanism I) [1]



based on ref [1]

□ NI yield and correlation with work-function

 $Y_{NI} = P_{iz}(Y_B + Y_S)$

• P_{iz} = surf. ioniz. proba depends exponentially on ϕ for metals • $Y_B = \phi(H_{back}) / \phi(H_x^+) = backscattering yield$ • $Y_s = \phi(H_{sputt}) / \phi(H_x^+) = sputtering yield$

□ Alternative materials under study:

- Electride material C12A7: work function 2.4 eV
- microcrystalline Boron Doped Diamond (µc-BDD)
- microcrystalline non Doped Diamond (μc-D)
- Phosphorous doped diamond (PDD)
- Gadolinium (as a low WF metal reference): tabulated work function 2.9 eV





Hydrogenated diamond Electron affinity χ is negative **γ**< 0

- ✓ The second threshold at 5.5eV reveals another electron emission mechanism [1]
- Photon absorption promotes electron in the conduction band (II)
- \checkmark These electrons have a quite large mean free path (μ m range)
- They reach the surface and be emitted into vacuum due to the negative-electron affinity (III)
- ✓ Negative-electron affinity is not expected for a non hydrogenated diamond layer
- ✓ The sub bandgap emission is therefore probably due to surface reconstruction and surface states
- No effect: temperature phosphorous dopants do not seem to be involved in the emission process
- Vacuum **Conduction Band** ______<u>0.6_eV</u> P level 4 eV 5.5 eV Surf. defects Valence Band
- Electride behaves pretty similarly to PDD
- Emission from surface states (bandgap states) due to surface reconstruction?

Goal of this study

- Monitor material electronic structure changes upon plasma exposure. **Electonic structure** changes due to plasma irradiations have implications on negative-ion emission yield but also on secondary electron emission yield
- Correlate electronic structure changes and negative-ion yields variations



- NI are measured by mass spectrometry
- Surface is analyzed by Photoemission **Yield Spectroscopy (PYS)**



Sample rotation under

vacuum to choose

between negative-ion or

surface analysis

 \otimes

Experimental set-up



- 13.56 MHz RF ICP plasma
- D2 plasmas at 2 Pa and 150 W



Samples after plasma exposure



Correlation between photoemission thresholds and negative-ion fluxes







• A bias pulse at -60V (20µs, 1kHz) is applied to the surface. Negative-ions are self extracted towards the mass spectrometer thanks to this bias pulse

- Negative-ions are measured synchronously to the pulse
- A DC bias can be superimposed to the extraction pulse $V_{Ex} = -60 V$ for the purpose of modifying the surface state and changing the electronic structure

Conclusion

- ✓ In-situ photoemission spectroscopy has been successfully employed to investigate the electronic structure of diamond, before and after plasma exposure
- Electronic structure of electride is more difficult to establish and requires further works
- ✓ Negative-ion flux seem to be uncorrelated from the lowest photoemission threshold
- ✓ Further investigation are required to understand main factors playing a role on negative-ion surface production yield for these materials

References

✓ [1] Takeuchi D, Kato H, Ri G S, Yamada T, Vinod P R, Hwang D, Nebel C E, Okushi H and Yamasaki S 2005 Direct observation of negative electron affinity in hydrogen-terminated diamond surfaces Applied Physics Letters 86 152103



- ✓ Considering the large range of photoemission threshold explored, we can state that for diamond and electride the negative-ion flux is uncorrelated with the lowest photoemission threshold
- \checkmark it can be assumed that the incident particles capture an electron from the valence band having a large density of states. The electron density at the threshold is probably too low to influence negative ion yield
- \checkmark On the contrary the lowest photoemission threshold (work function ϕ) is correlated with the negative-ion flux for Gd metal (low work function metal) in the same experimental conditions

