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

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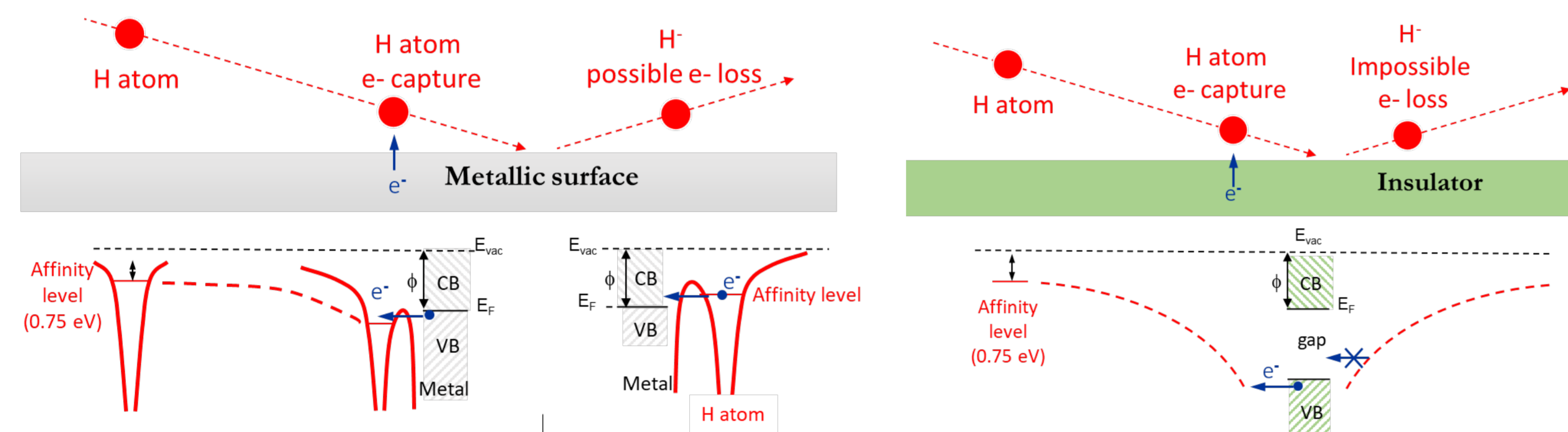
## Introduction

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



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

## Negative ion (NI) surface production mechanism



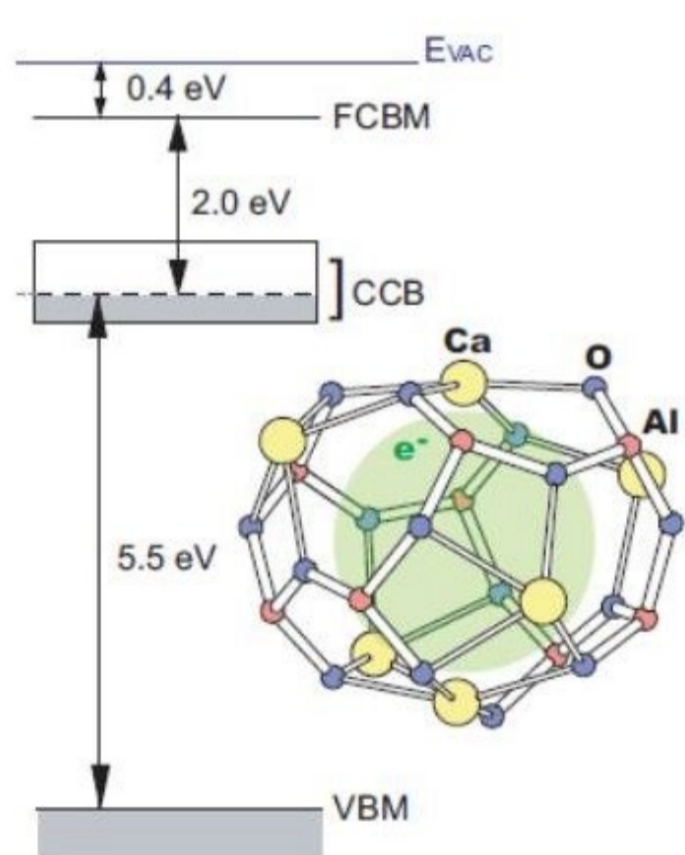
- NI yield and correlation with work-function

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

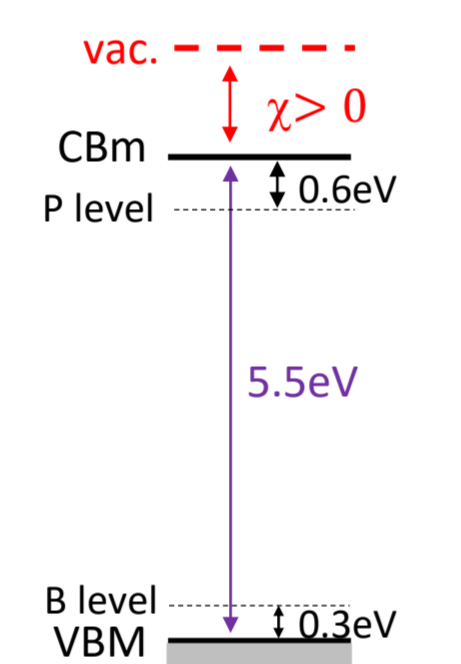
- $P_{iz}$  = surf. ioniz. proba depends exponentially on  $\phi$  for metals
- $Y_B = \phi(H_{back}) / \phi(H_x^+) =$  backscattering yield
- $Y_S = \phi(H_{sputt}) / \phi(H_x^+) =$  sputtering yield

- Alternative materials under study:

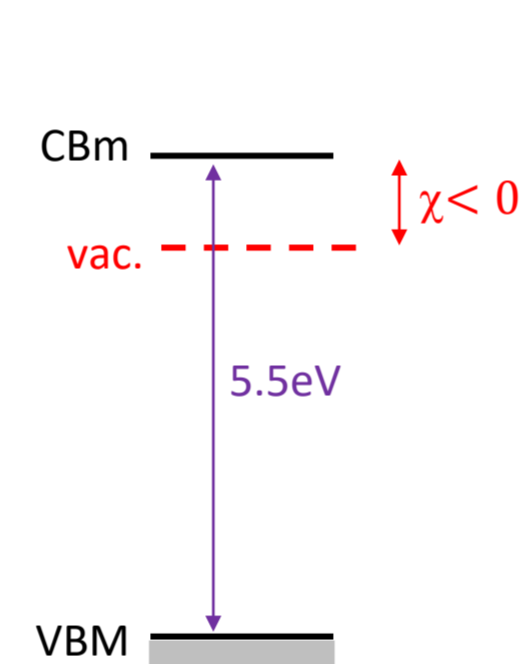
- Electride material C12A7: work function 2.4 eV
- microcrystalline Boron Doped Diamond ( $\mu$ -BDD)
- microcrystalline non Doped Diamond ( $\mu$ -D)
- Phosphorous doped diamond (PDD)
- Gadolinium (as a low WF metal reference): tabulated work function 2.9 eV



Non hydrogenated diamond  
Electron affinity  $\chi$  is positive



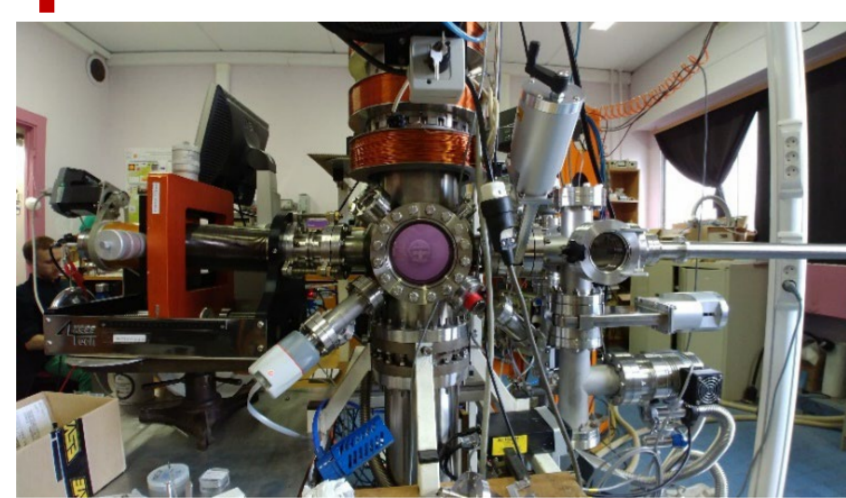
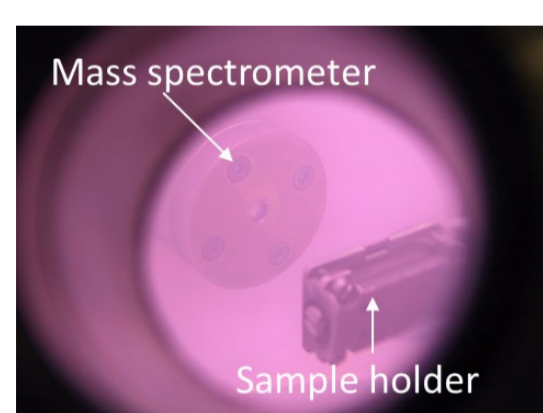
Hydrogenated diamond  
Electron affinity  $\chi$  is negative



- Goal of this study

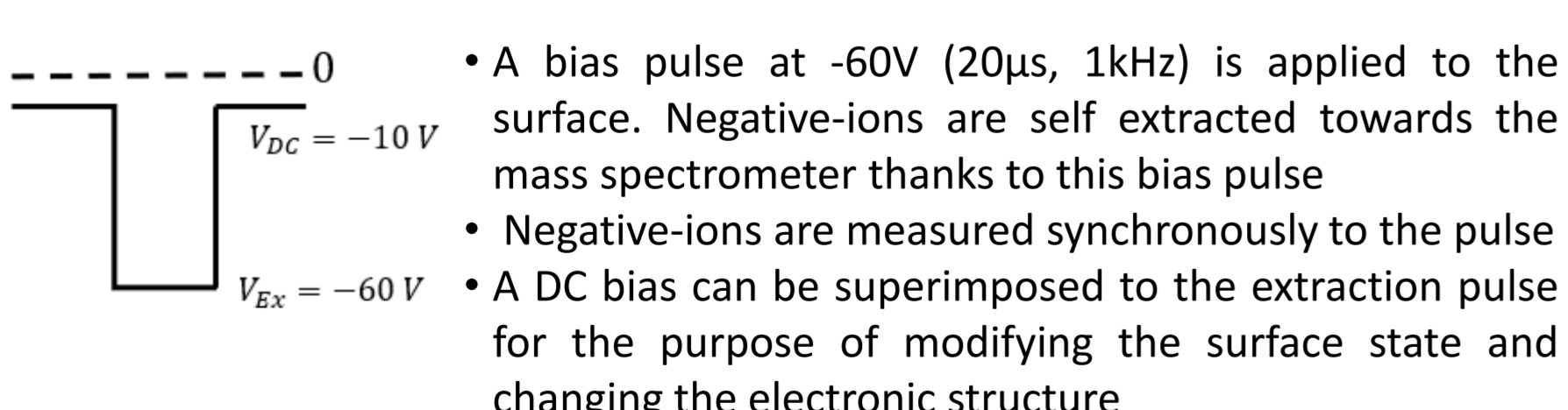
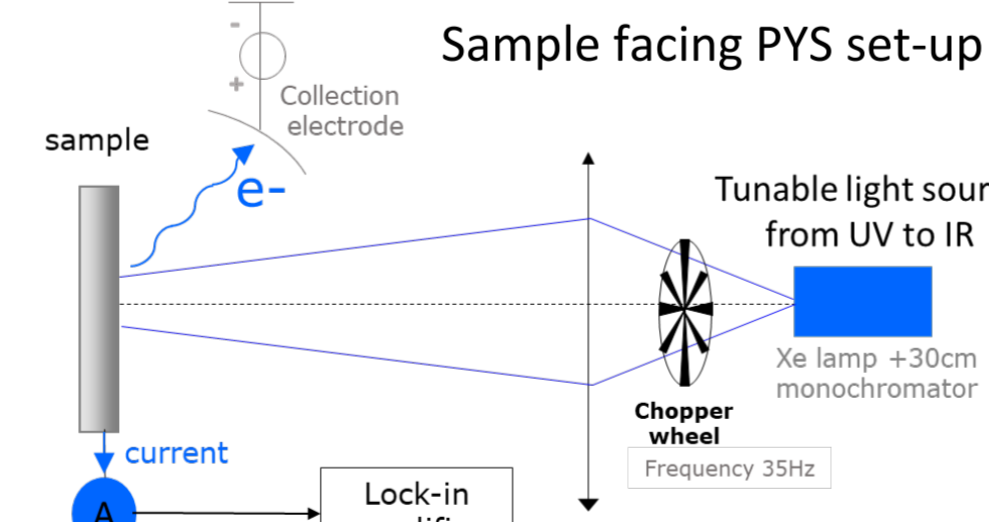
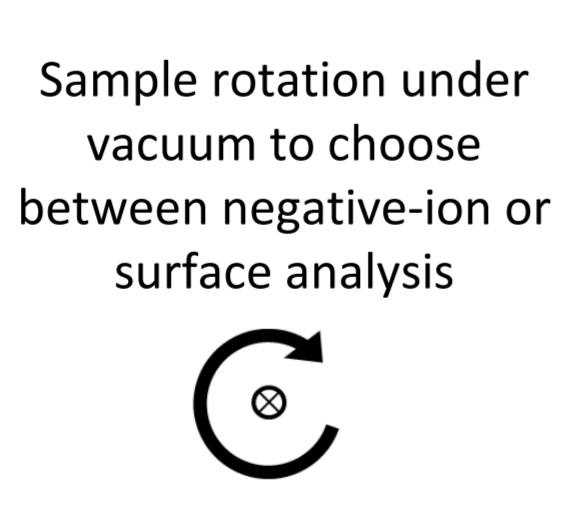
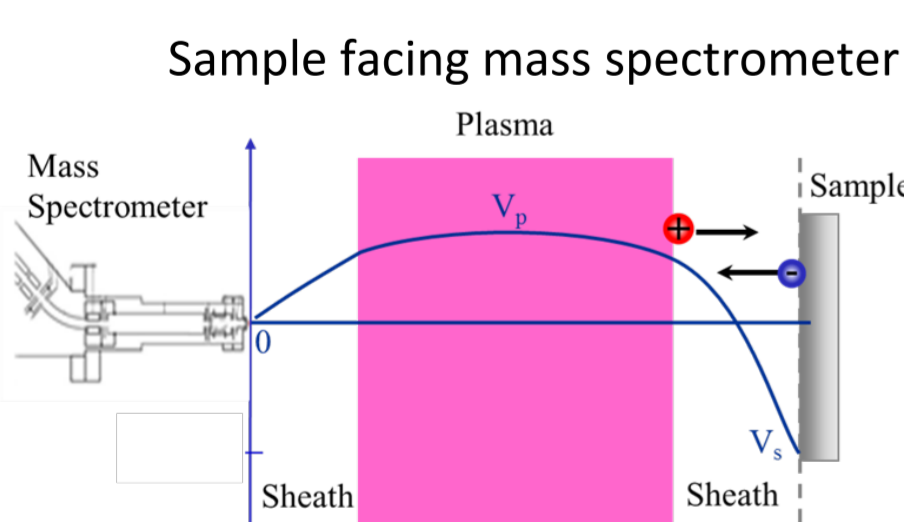
- Monitor material electronic structure changes upon plasma exposure. **Electronic structure changes due to plasma irradiations have implications on negative-ion emission yield but also on secondary electron emission yield**
- Correlate electronic structure changes and negative-ion yields variations

## Experimental set-up

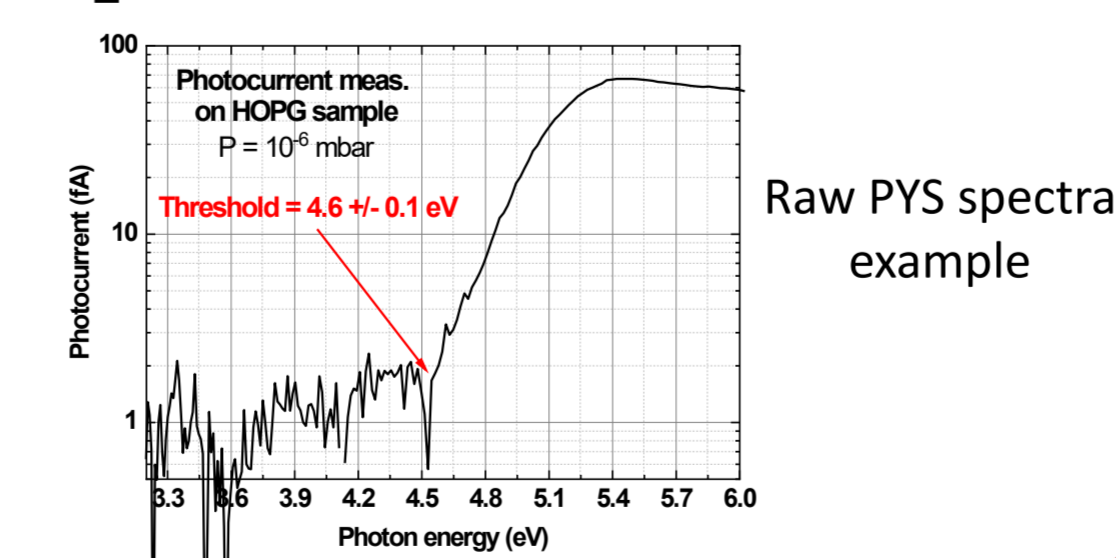


- NI are measured by mass spectrometry
- Surface is analyzed by Photoemission Yield Spectroscopy (PYS)

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



- A bias pulse at -60V (20 $\mu$ s, 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 for the purpose of modifying the surface state and changing the electronic structure



## Conclusion

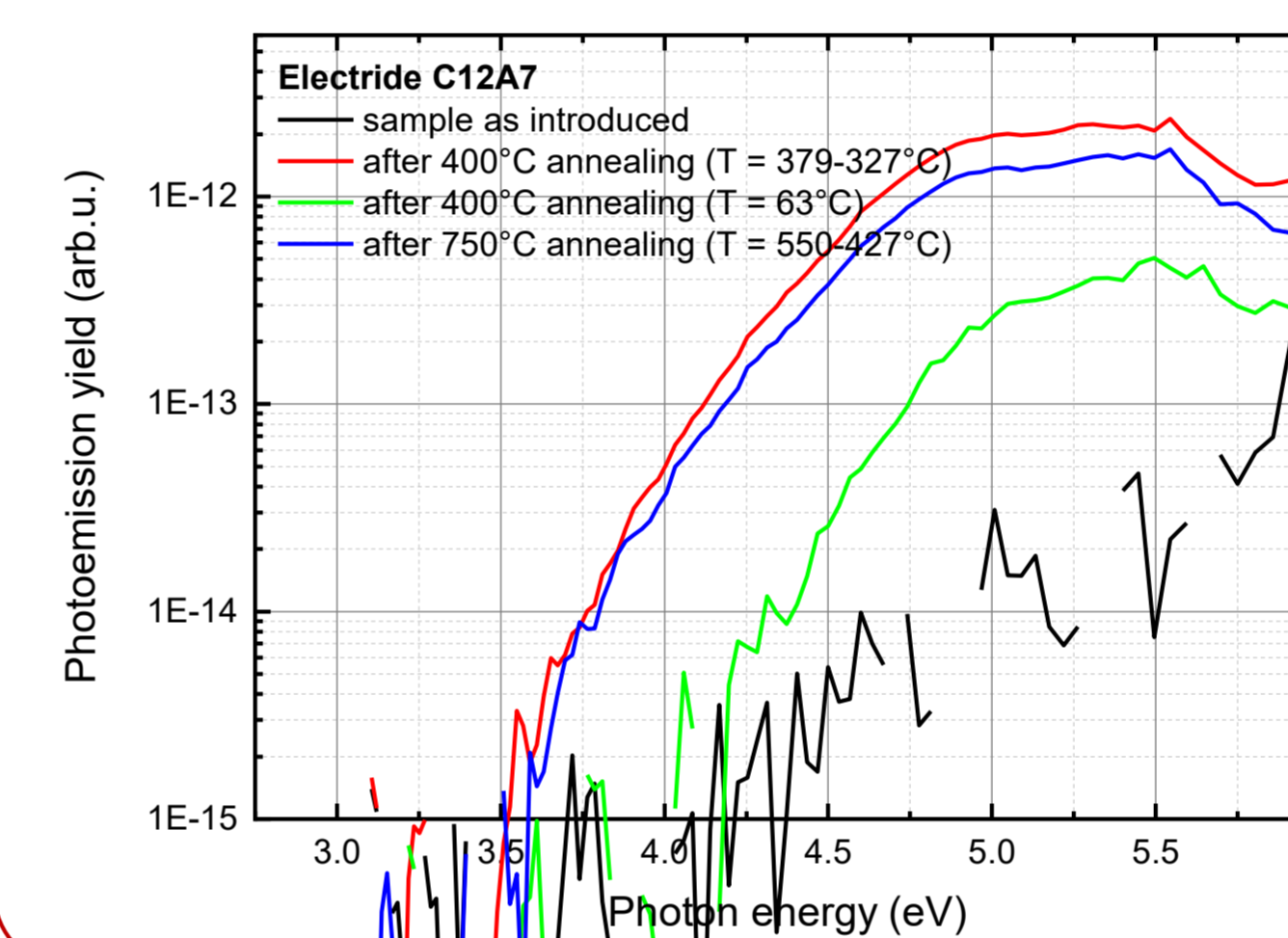
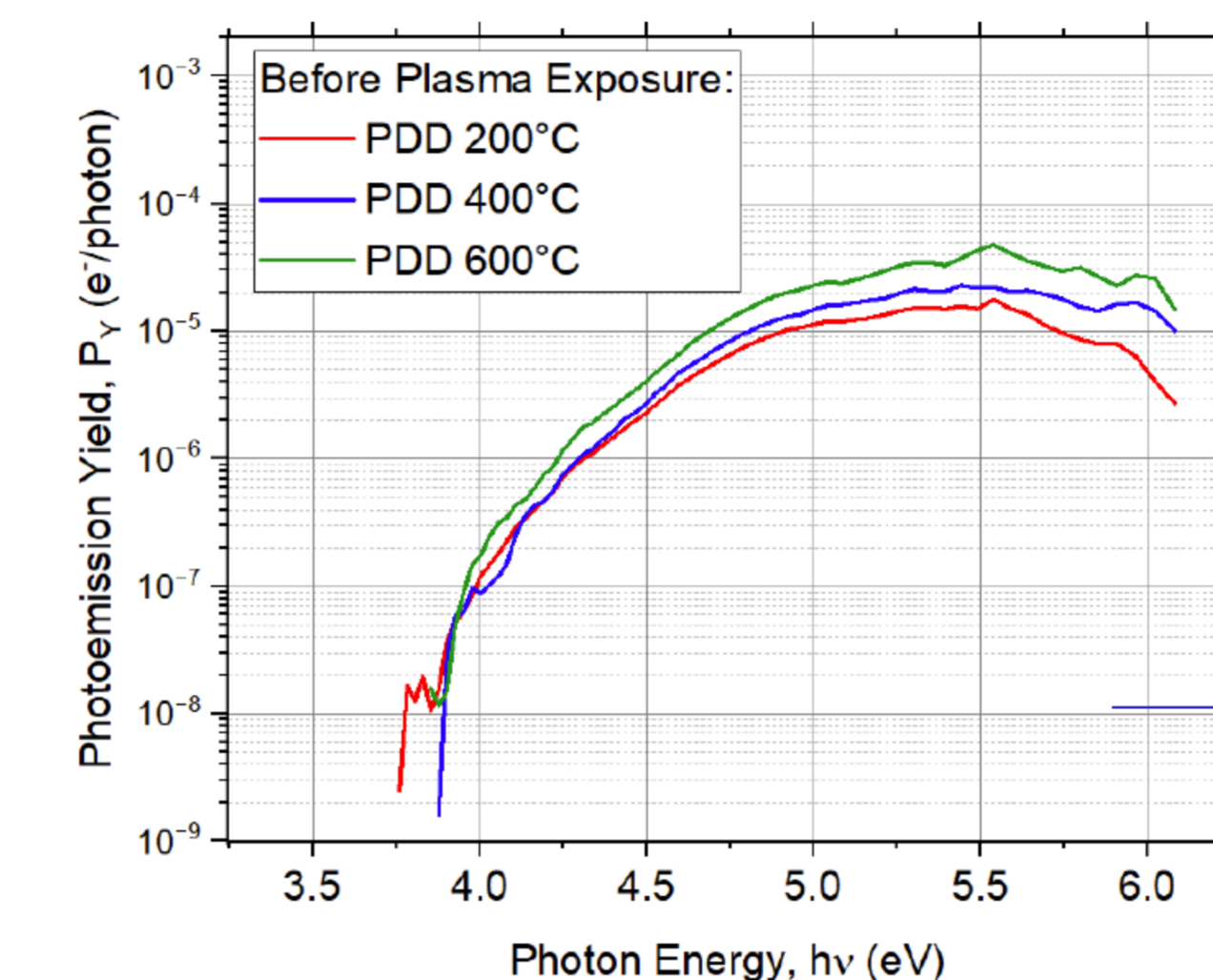
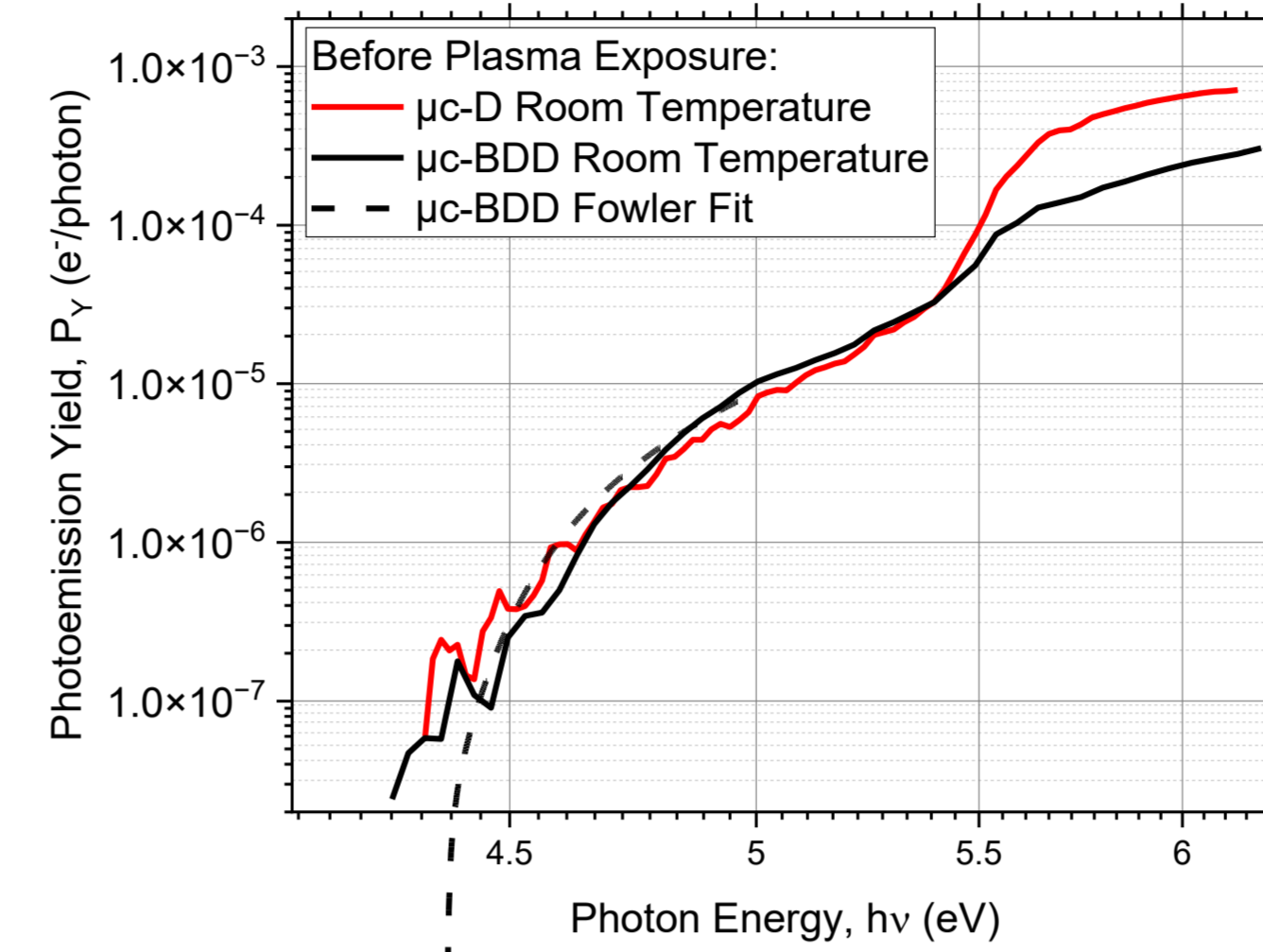
- In-situ photoemission spectroscopy has been successfully employed to investigate the electronic structure of diamond, before and after plasma exposure
- Electronic structure of electride is more difficult to establish and requires further works
- Negative-ion flux seem to be uncorrelated from the lowest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

## References

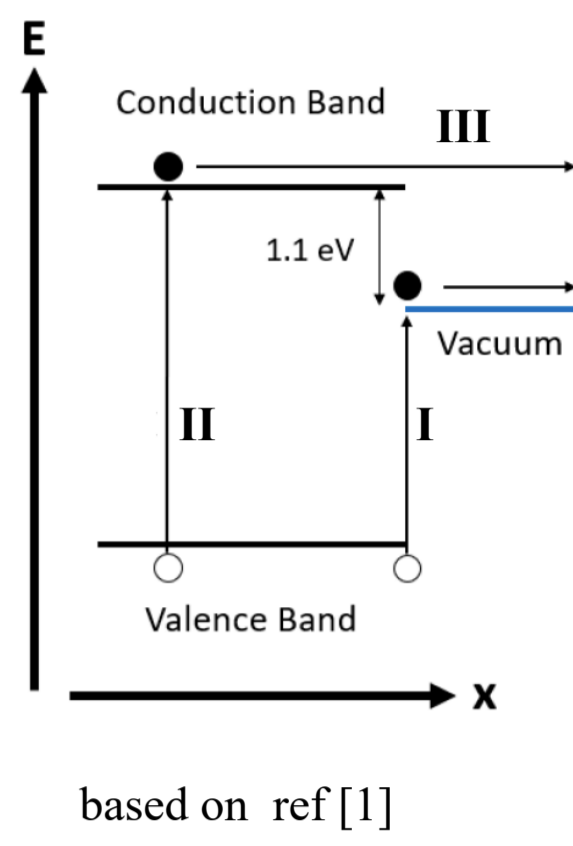
- [1] Takeuchi D, Kato H, Ri G S, Yamada T, Vinod P R, Hwang D, Nebel C E, Okushi H and Yamasaki S 2005 Direct observation of negative electron affinity in hydrogen-terminated diamond surfaces Applied Physics Letters 86 152103

## Samples as introduced

- The as-deposited  $\mu$ -BDD and  $\mu$ -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

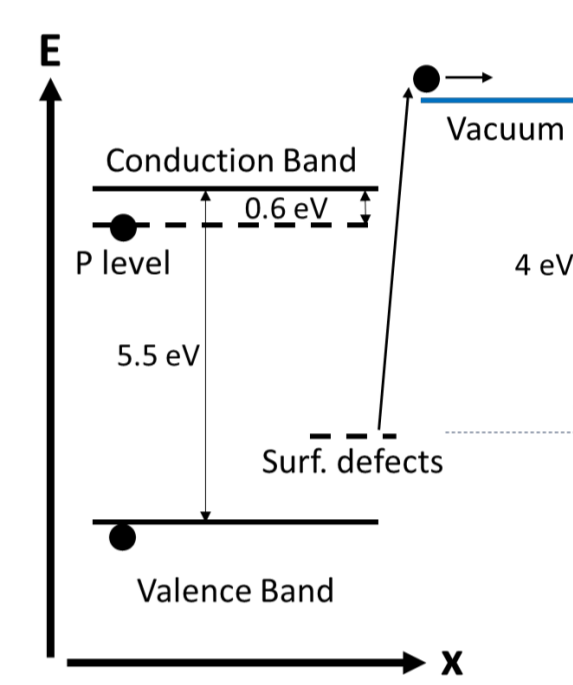


- Sub-bandgap (<5.5eV) electron emission reveals negative-electron affinity [1]
- Emission threshold at 4.4eV and band gap of 5.5eV sets the negative-electron affinity to -1.1eV
- Between 4.4eV and 5.5eV, some electrons from the surface are directly emitted into vacuum (see mechanism I) [1]



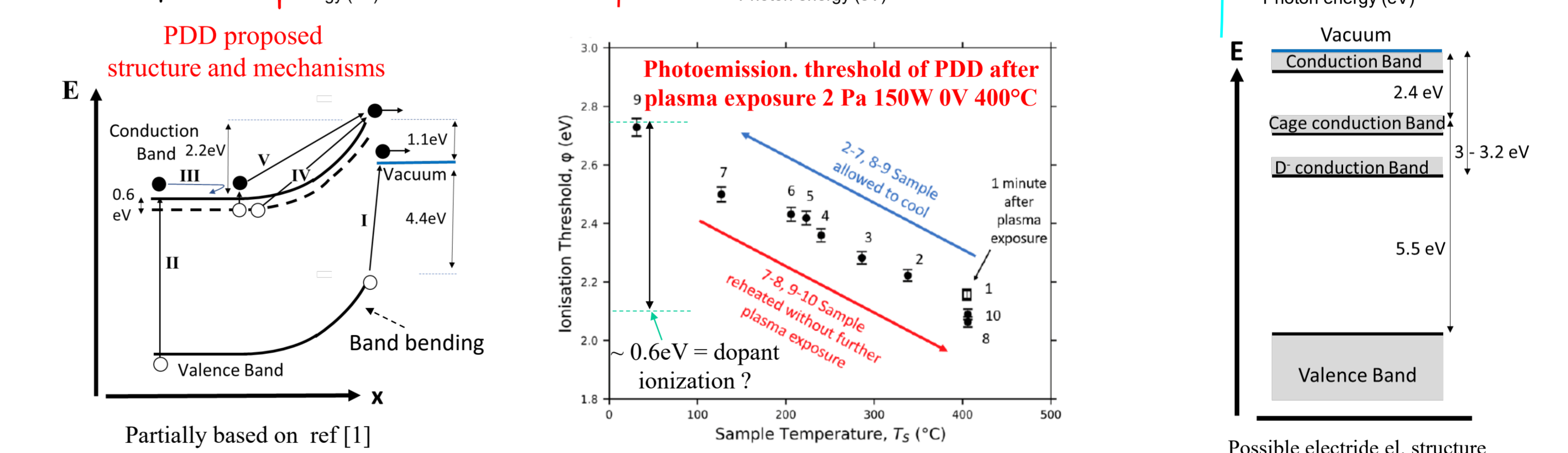
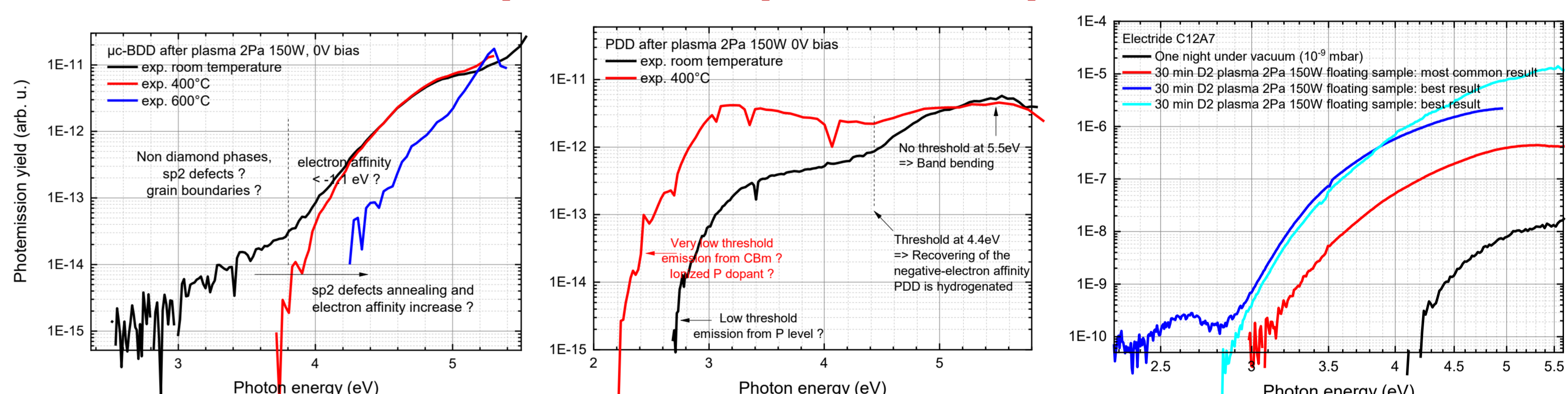
- The second threshold at 5.5eV reveals another electron emission mechanism [1]
- Photon absorption promotes electron in the conduction band (II)
- These electrons have a quite large mean free path ( $\mu$ m range)
- They reach the surface and be emitted into vacuum due to the negative-electron affinity (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 temperature effect: phosphorous dopants do not seem to be involved in the emission process

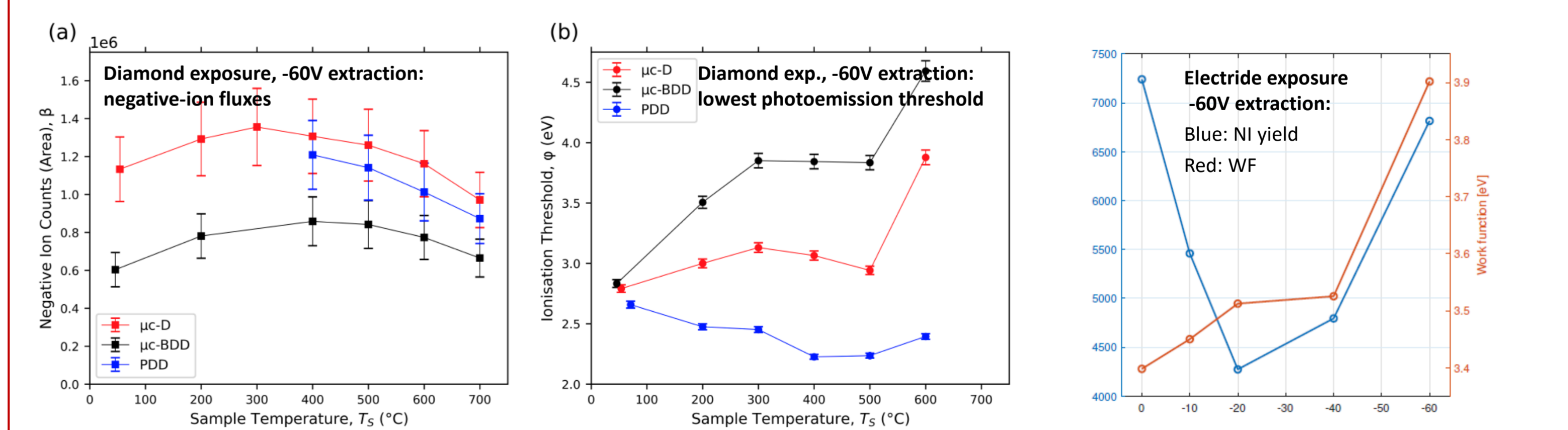


- Electride behaves pretty similarly to PDD
- Emission from surface states (bandgap states) due to surface reconstruction?

## Samples after plasma exposure



## Correlation between photoemission thresholds and negative-ion fluxes



- 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
- 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
- On the contrary the lowest photoemission threshold (work function  $\phi$ ) is correlated with the negative-ion flux for Gd metal (low work function metal) in the same experimental conditions

