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Abstract.

Gas seeding is often used in tokamaks to reduce the power load onto the divertor target plates. Nitrogen is the preferred seeding species because of its favourable radiative properties as well as its apparent beneficial effect on plasma confinement. However, nitrogen molecules are chemically reactive with hydrogen and its isotopes to form stable ammonia compounds. Since ammonia is a polar molecule, sticking on metal surfaces can be expected, increasing as a consequence the tritium retention which could pose a serious risk for ITER operation and maintenance. It is, therefore, important to understand the adsorption mechanism of ammonia on surfaces, investigate when the surface saturation occurs and whether ammonia adsorbs as a molecule or undergoes a dissociation on the surface. In this contribution, ammonia sticking on different fusion-relevant materials is presented. The results show a pressure-dependent ammonia sticking on tungsten, boron and stainless steel followed by a partial desorption from these surfaces while on gold and beryllium, ammonia molecules weakly adsorb and completely desorb. A detailed explanation of the two interaction mechanisms is addressed. Furthermore, the time dependence of ammonia desorption as well as the chemical state of non-desorbed residuals were investigated with X-ray Photoelectron spectroscopy. Tungsten, boron and stainless steel surfaces showed a continuous dissociation process from NH_3 to NH_2, NH, N and surface nitrides.

μ

$\times$ —

—

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α ν

f $f - f$ f f f f f

$\pm$ $\circ$

$\circ$

$\circ$

f $\dfrac{- n f}{\rho \, \mu^{\frac{1}{2}}}$ m $-C$ m

ρ

ρ μ μ $\times$

f $f \, \alpha P$ C P

α

α

$\times$ $-$ ρ η

$$f \quad \frac{-nf \ \rho \ \eta \ ^{\frac{1}{2}}}{\pi f \ \rho \ \mu q \ ^{\frac{1}{2}}}$$

$$f \quad - \ . \ C \ C \ \rho$$

$$-$$

$$C \quad a \quad b \ \rho$$

$$-$$

$$f \quad - \ . \ C \ C \ \rho \quad - \ . \ C \ \rho \ a \quad b \ \rho \quad B \ \rho \quad B \ \rho$$

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To determine B_1 and B_2 values, we measured Δf_r for 3 noble gases Ar, He and Ne on a bare gold crystal. As these gases cannot adsorb at RT on any surface we can consider $\Delta f_m = 0$ and measure the total frequency shift. Then Δf_r is calculated directly by subtracting pressure and viscosity terms from the total frequency shift (see equation 1). Δf_r is plotted in Figure 1 as function of the gas density. Using a second order polynomial fit, B_1 and B_2 coefficients were extracted, allowing one to calculate Δf_r for NH_3 gas.
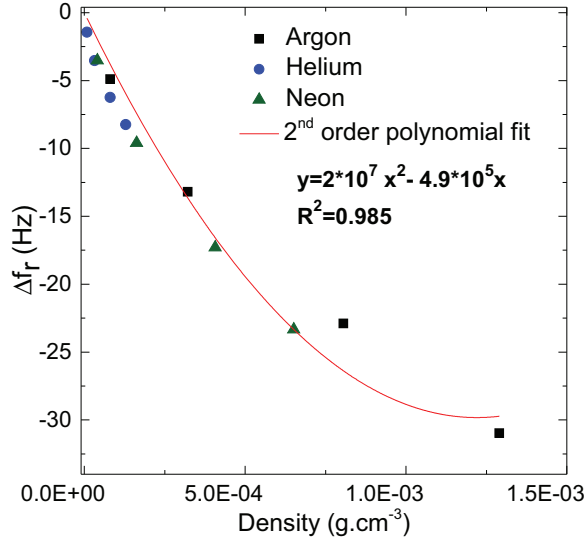
Figure 1: Frequency shift caused by the crystal surface roughness as function of gas density measured for Ar, He and Ne on Au surface fitted with a second order polynomial.

4. Results and discussion

4.1. Interaction of NH_3 with different materials

NH_3 adsorption/desorption cycles done at 50 mbar will first be presented on Au and W surfaces and compared to a reference Ar adsorption/desorption cycle done on Au (non-reactivity and zero adsorption at RT). The results of adsorption cycles of (a) Ar on Au bare crystal, (b) NH_3 on Au bare crystal and (c) NH_3 on W coated Au crystal are shown in Figure 2. The QMB total frequency shift as a function of time is represented by the black curve while the blue dashed line represents the calculated sum of Δf_P, Δf_ν and Δf_r. As can be seen, the sum of the three terms is higher for Ar than NH_3 due to the higher density of Ar ($\rho_{Ar} > \rho_{NH3}$). In fact, while Δf_P does not depend on the gas nature, Δf_ν and Δf_r both increase with the gas density. The typical behaviour of a non-adsorbing gas ($\Delta f_m = 0$) is shown in Figure 2a. A sudden frequency decrease is observed when Ar was introduced. The vertical slope corresponds to the phase when the gas pressure is rising until reaching the constant value of 50 mbar. As the desired pressure is attained, the total frequency variation stabilizes and corresponds to the sum of pressure, roughness and viscosity effects on the QMB (blue dotted line). By pumping

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the gas from the vacuum chamber, these effects disappear and the QMB returns to its initial resonance frequency. As seen in Figure 2b, NH_3 exhibits a different trend on Au. The total frequency shift is much higher than the sum of Δf_P, Δf_ν and Δf_r. According to equation 1, this observation indicates that the observed frequency is mainly due to adsorbed mass on the surface. When the gas was fully pumped from the chamber, the QMB returns to its initial resonance frequency value, indicating a total desorption of NH_3 molecules from the Au surface. The QMB coated with W behaves differently as can be seen in Figure 2c. In fact, the measured total frequency shift caused by the NH_3 adsorption is around 3.5 times higher on W than on Au indicating that more NH_3 can adsorb on the W surface. Moreover, after the pumping of the chamber, the initial resonance frequency was not reached and, as the base pressure is recovered, there is no residual NH_3 in the vacuum chamber. This indicates that the partial frequency recovery can only be caused by remaining NH_3 molecules on the QMB, i.e. a partial NH_3 desorption.
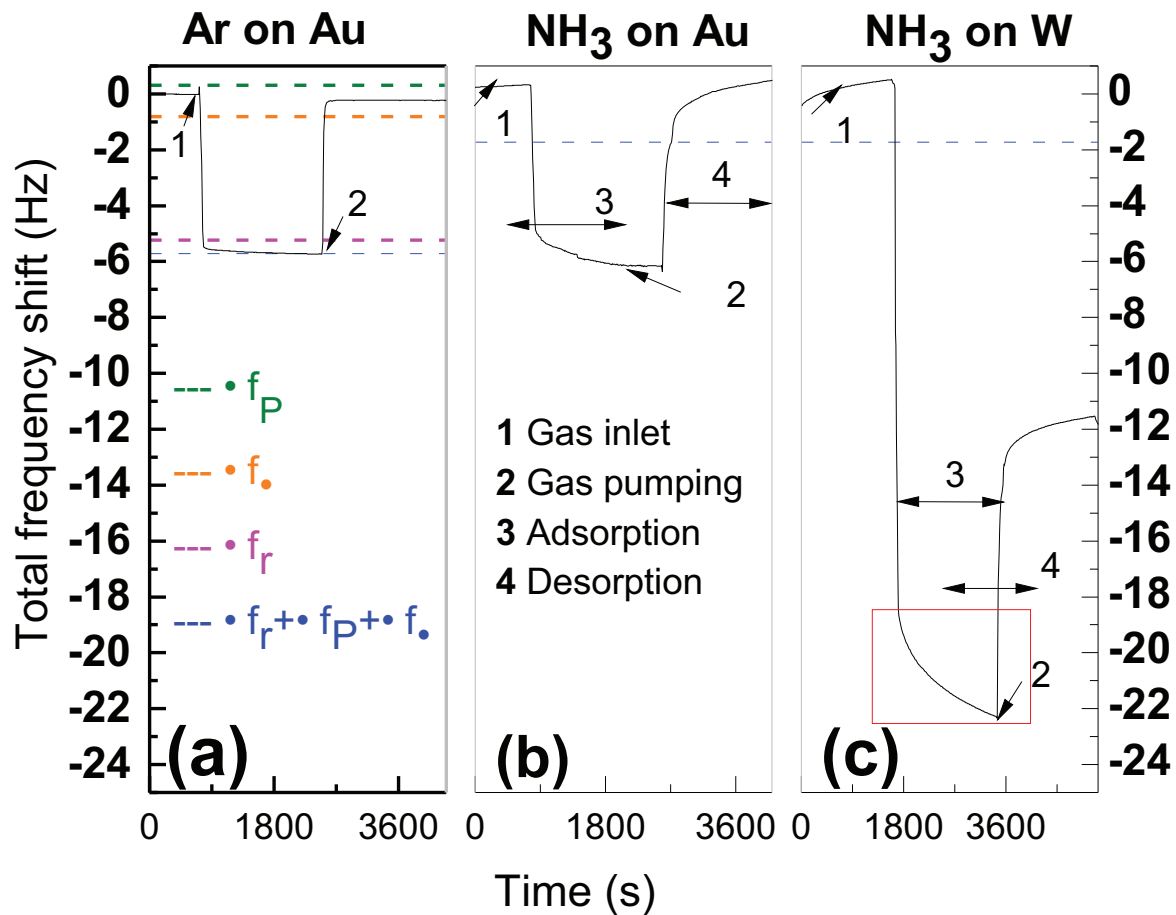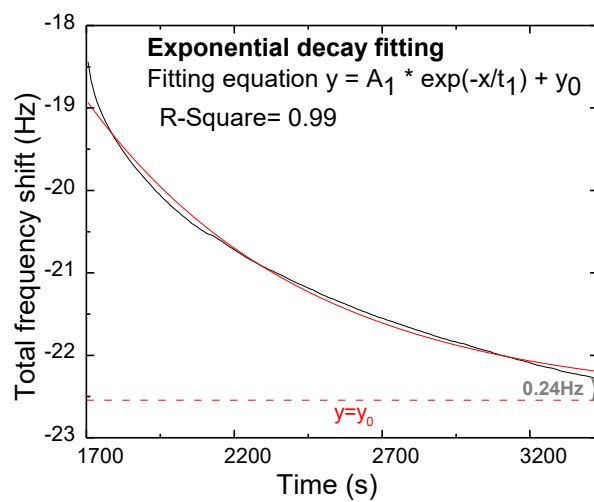

Figure 2: Total frequency shift as a function of time for adsorption/desorption cycle at 50 mbar of a) Ar on Au, b) NH_3 on Au and c) NH_3 on W surfaces.

Taking a closer look on the adsorption phase, one can notice that even though the

Exponential decay fitting

Fitting equation $y = A_1 * \exp(-x/t_1) + y_0$

R-Square= 0.99

$y=y_0$

0.24Hz

Total frequency shift (Hz)

Time (s)

$\times$ $-$

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increases with the pressure, (ii) the frequency shift after the gas pumping i.e the non-desorbed mass remains larger for a higher pressure and (iii) no saturation was reached up to 800 mbar.
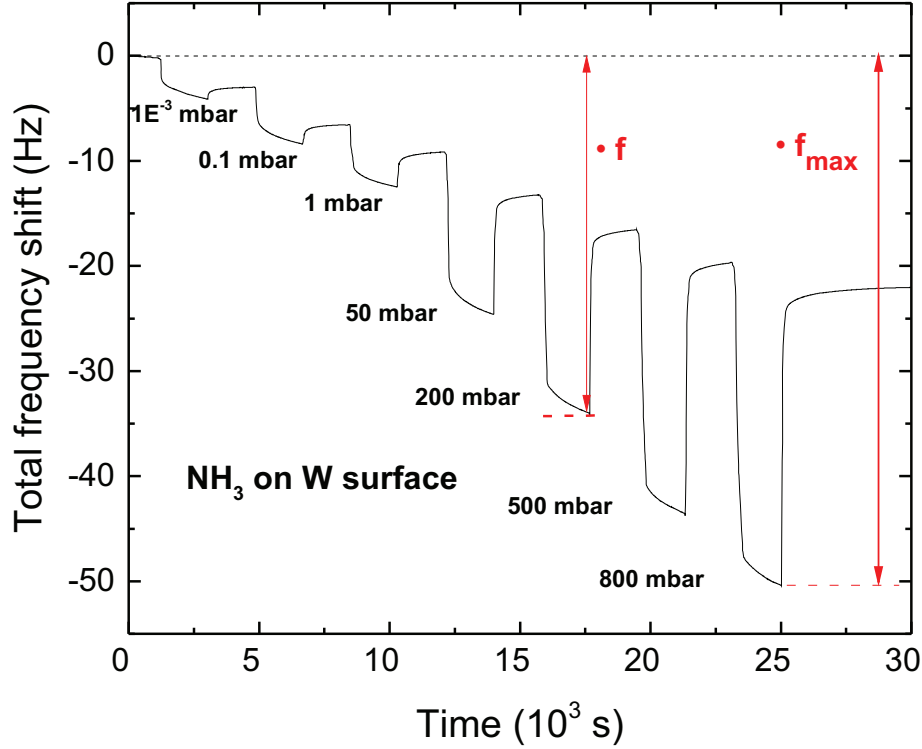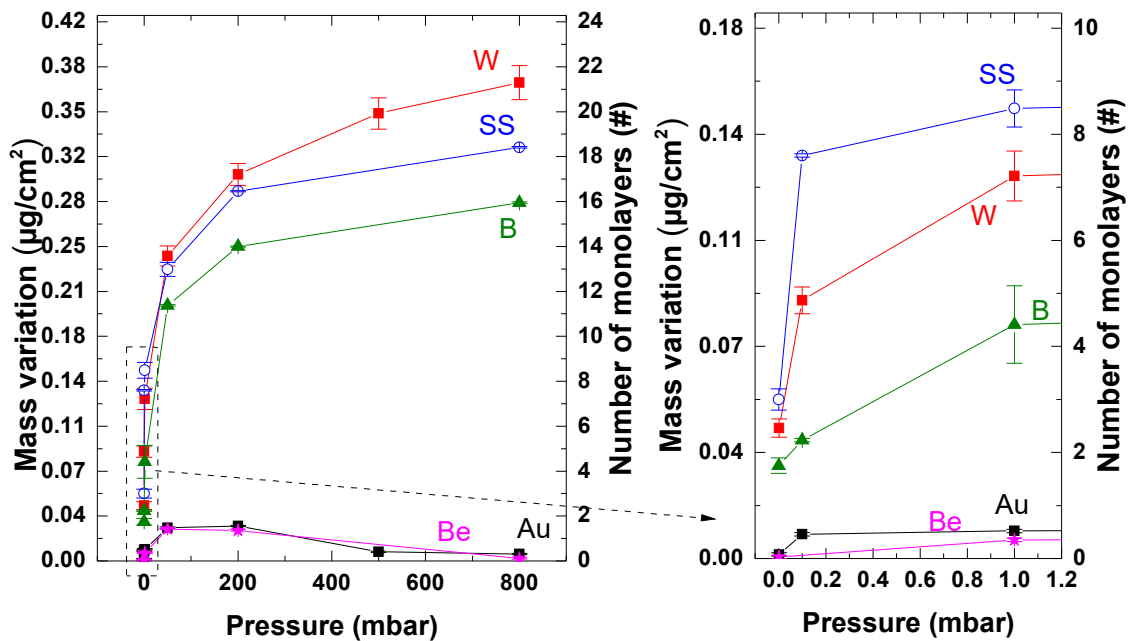

Figure 4: Total frequency shift Δf as a function of time for the adsorption/desorption consecutive pressure cycles of NH_3 on a W surface.

The frequency change for each pressure was then extracted and the maximum value of the NH_3 adsorbed mass was calculated according to the procedure described in section 3, after subtracting the roughness, viscosity and pressure effect. In order to convert this mass uptake into a number of monolayers (ML) adsorbed on the surface, the following calculations were done. Assuming one ML is equal to 6.2×10^{14} molecules/cm^2 [?], the number of ML adsorbing on a surface can be calculated by dividing the number of gas molecules per surface area N_{NH3} by one ML. N_{NH3} can be calculated using the following equation:
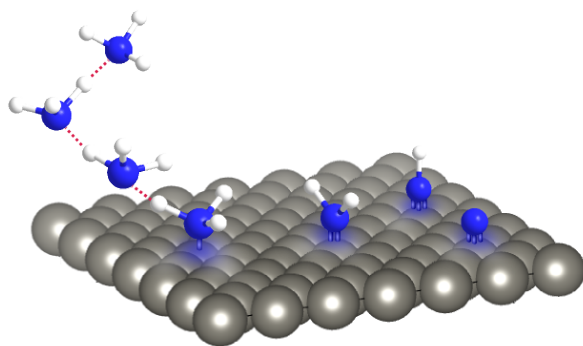
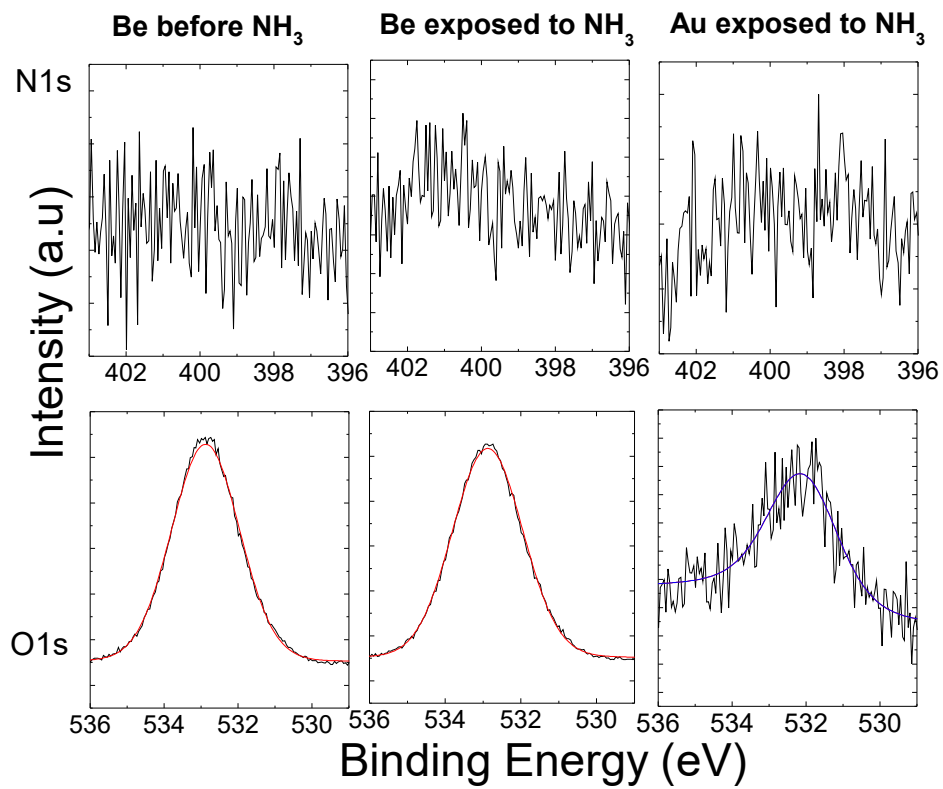$$N_{NH_3} = \frac{\Delta m}{M} \times N_A \qquad (8)$$

where M is the gas molar mass and N_A is the Avogadro number. We should note however that the number of ML can be overestimated as we assume a flat surface and neglect the effect of surface irregularities (steps, kinks...) on adsorption. Figure 5 represents the mass and number of ML of NH_3 adsorbed on Au, Be, B, SS and W surfaces.

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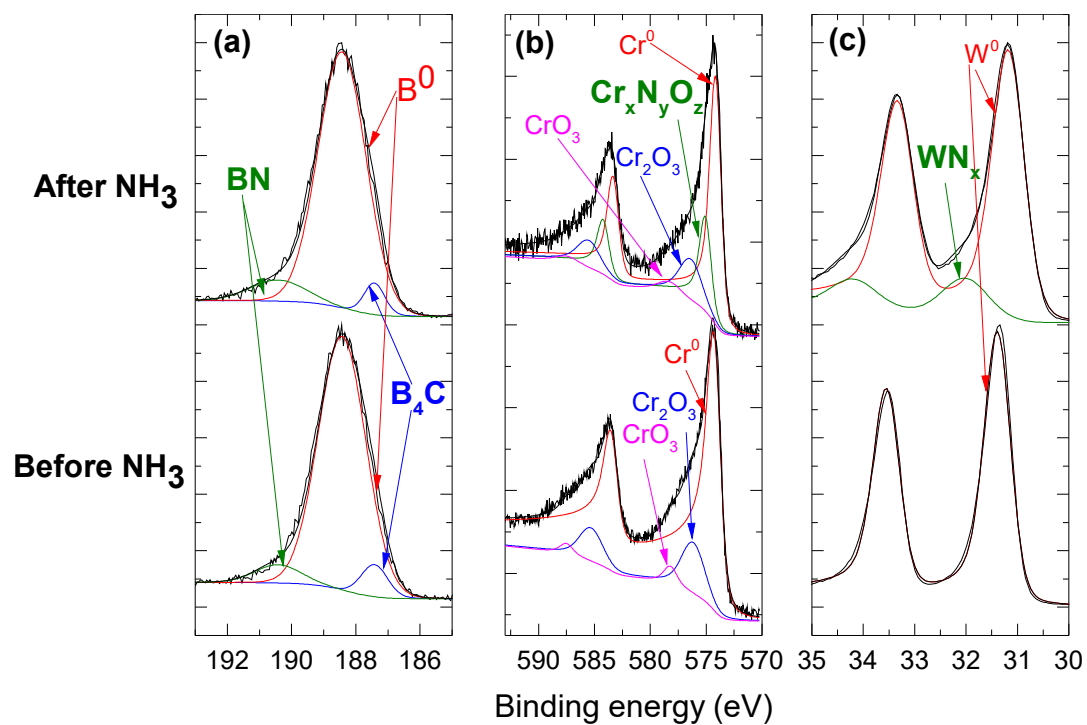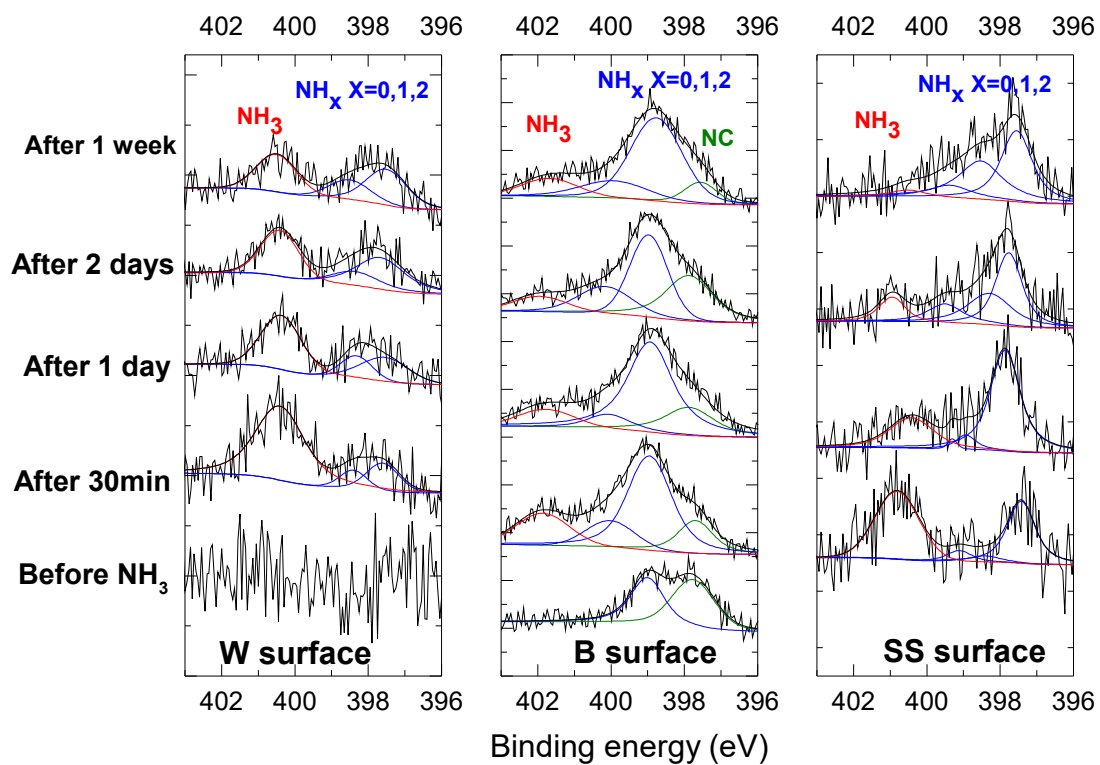
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Intensity (a.u)

N1s

Be before NH$_3$ **Be exposed to NH$_3$**   **Au exposed to NH$_3$**

O1s

Binding Energy (eV)

Binding energy (eV)

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