Study of the niobium oxide structure and microscopic effect of plasma processing on the Nb surface

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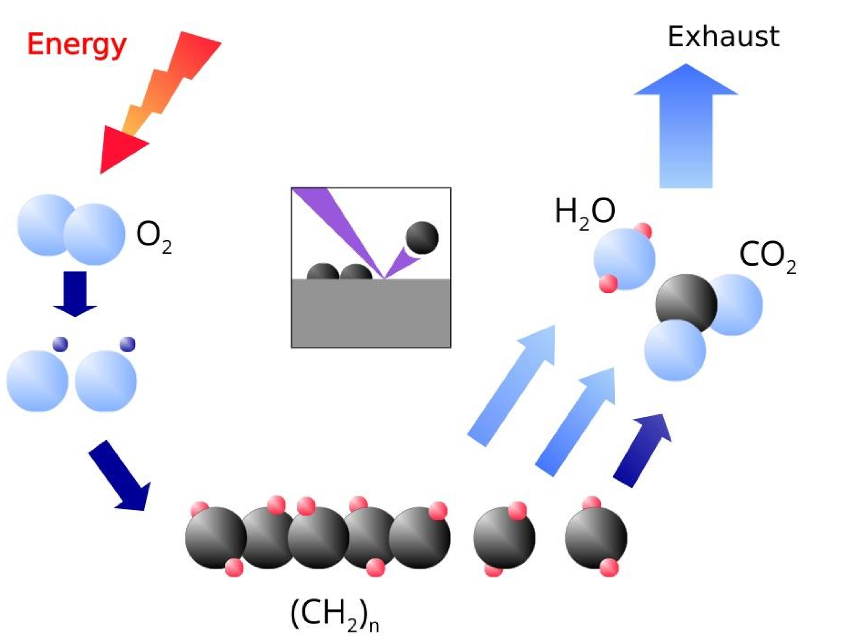
1. Abstract

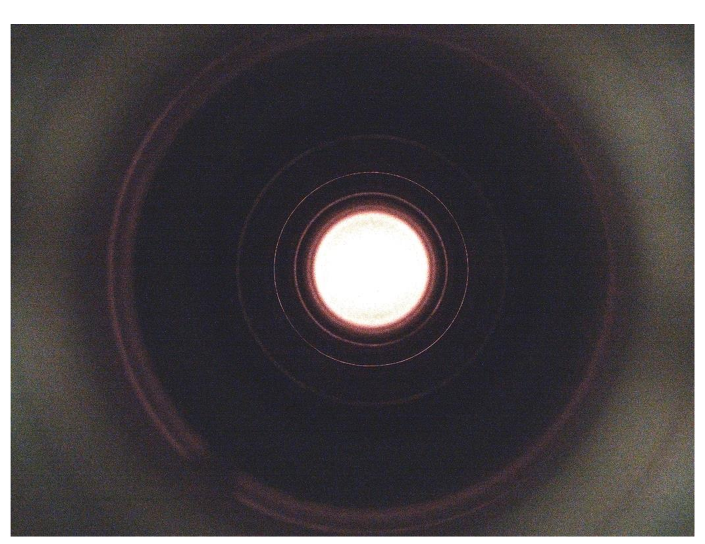
A study of the niobium oxide structure is presented here, focusing on the niobium suboxides. Multiple steps of argon sputtering and XPS measurements were carried out until the metal surface was exposed. Subsequently, the sample was exposed to air for different time intervals and the oxide regrowth was studied. In addition, three Nb samples prepared with different surface treatments were studied before and after being subjected to plasma processing. The scope is investigating the microscopic effect that the reactive oxygen contained in the glow discharge may have on the niobium surface. This study suggests that the Nb_2O_5 thickness may increase. Nevertheless, since the Nb_2O_5 is dielectric, its thickening would not negatively affect the cavity performance.

2. Plasma processing to mitigate FE

- Reducing FE through C_xH_y removal from cavity Nb surface
- Increasing the niobium work function by 10% results in 15% increase in E_{acc}



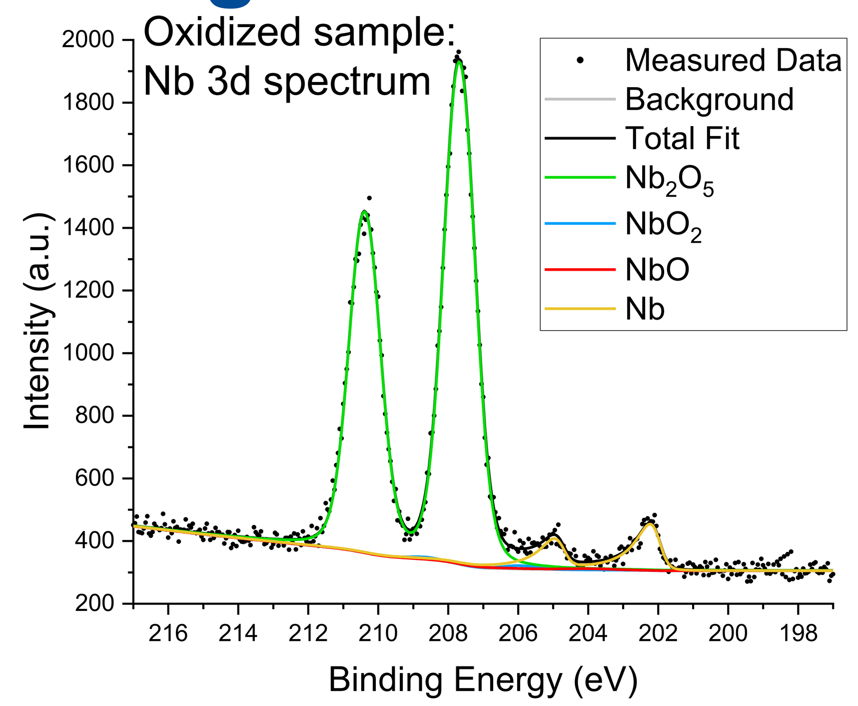
$$O_2 + C_xH_y \rightarrow CO + CO_2 + H_2O$$



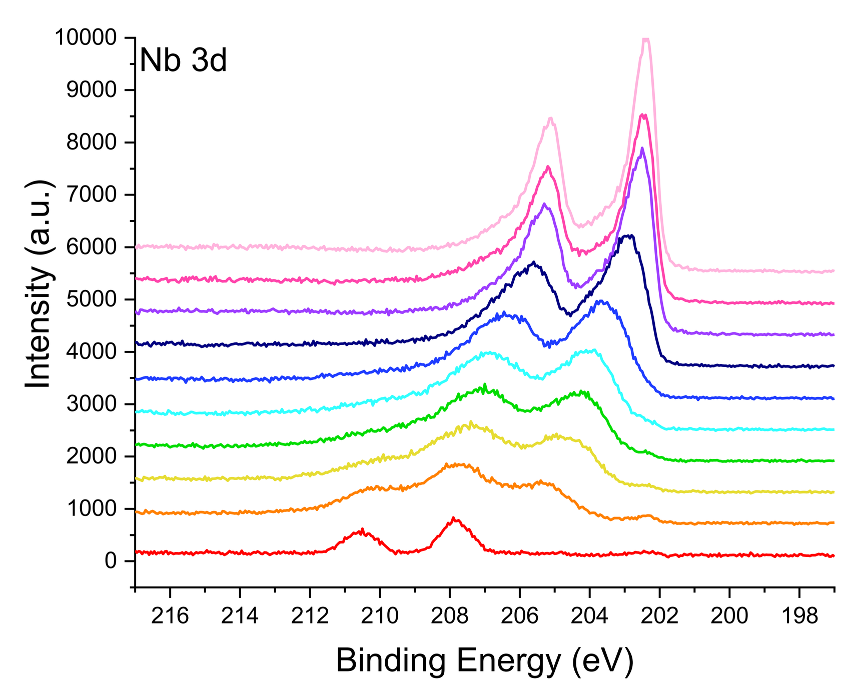
M. Doleans *et al*, NIMA 812 (2016)
P. Berrutti, B. Giaccone *et al.*, J. Appl. Phys. 126, 023302 (2019)
B. Giaccone *et al.*, Phys. Rev. Accel. Beams 24, 022002

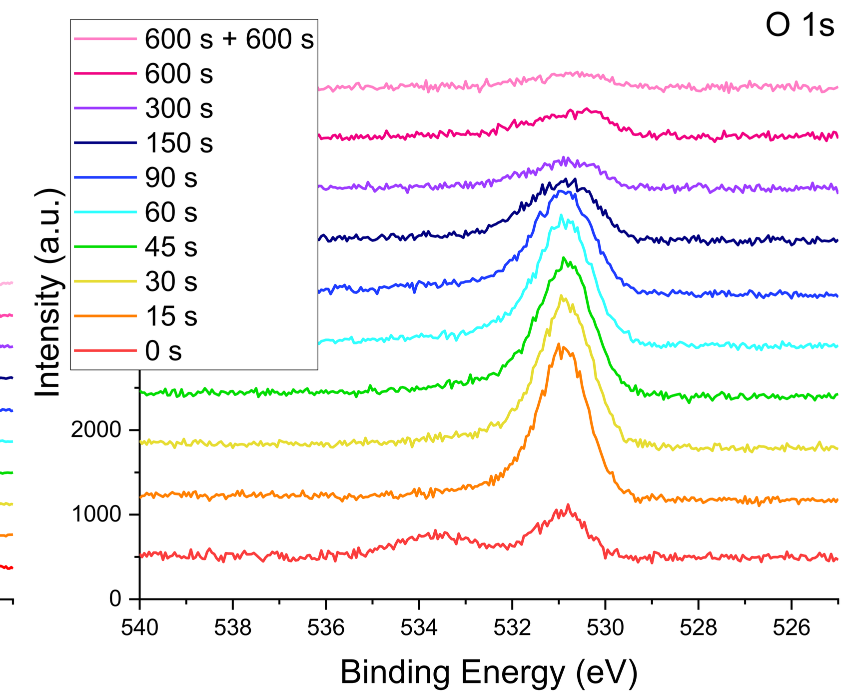
3. Argon ions sputtering on oxidized Nb sample

- Sample preparation: 800 ˚C x 3h + 20 μm EP + 5 min HF rinse
- After surface treatment: 1 week to fully oxidize prior to XPS measurement



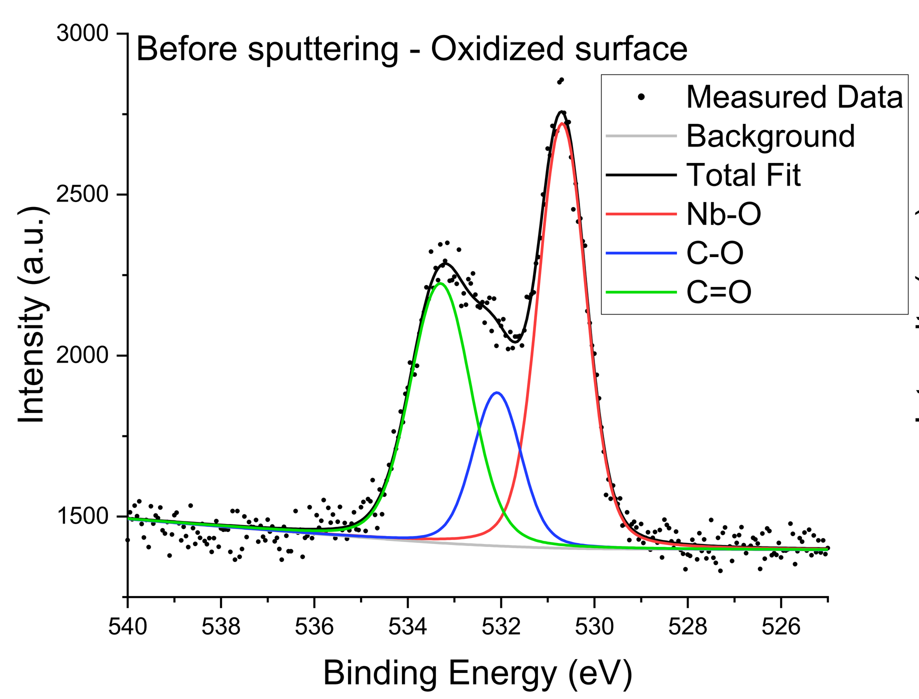
Spectra acquired during sputtering

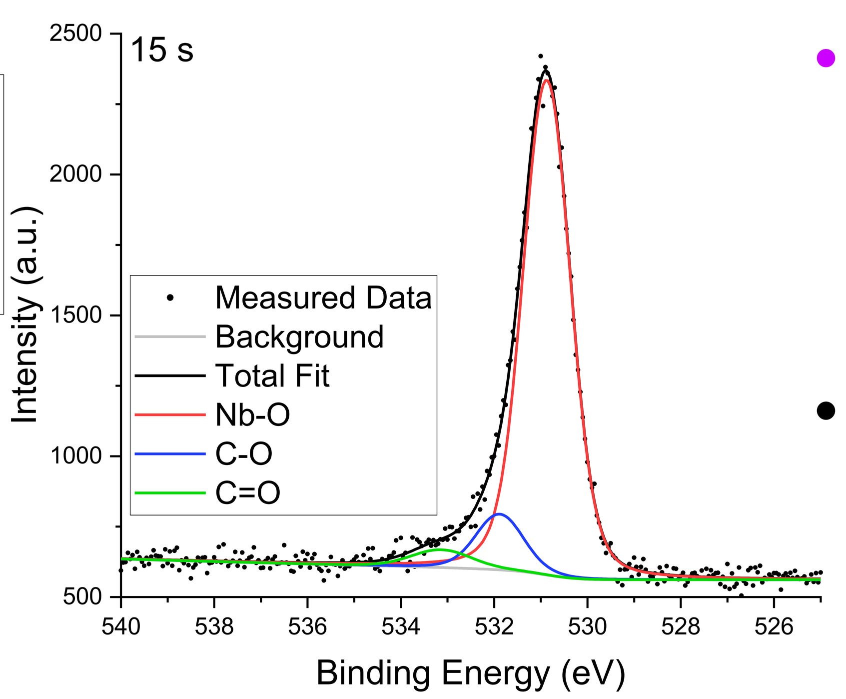




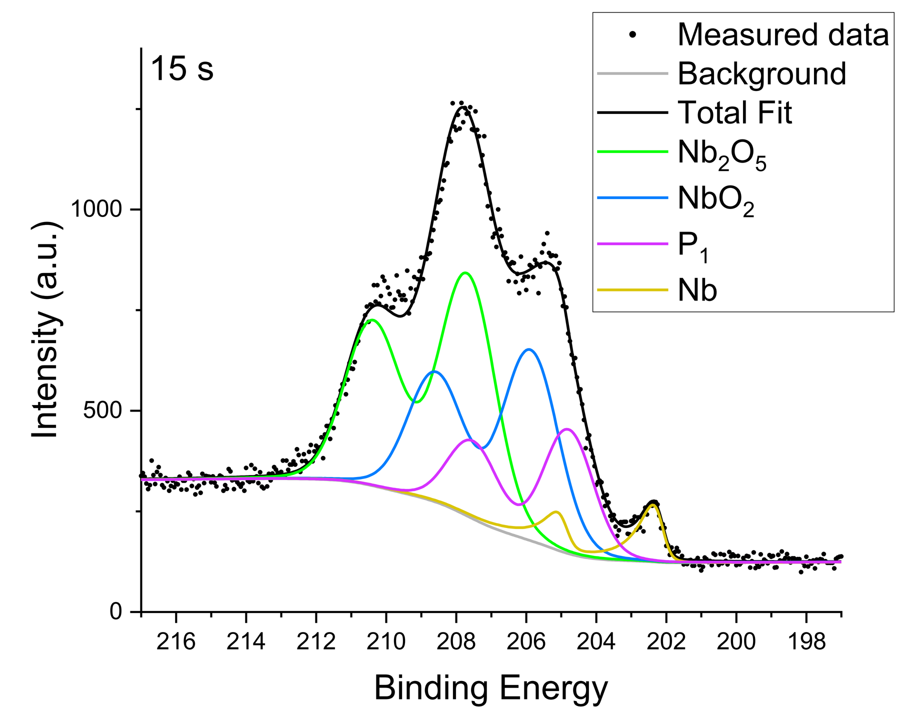
- Nb 3d: shift towards lower energy values as the oxidation state decreases
- O 1s: initially three peaks are detected: niobium oxide, C-O, C=O. The niobium oxide peak is due to Nb_2O_5 plus the suboxides

O1s core level spectra

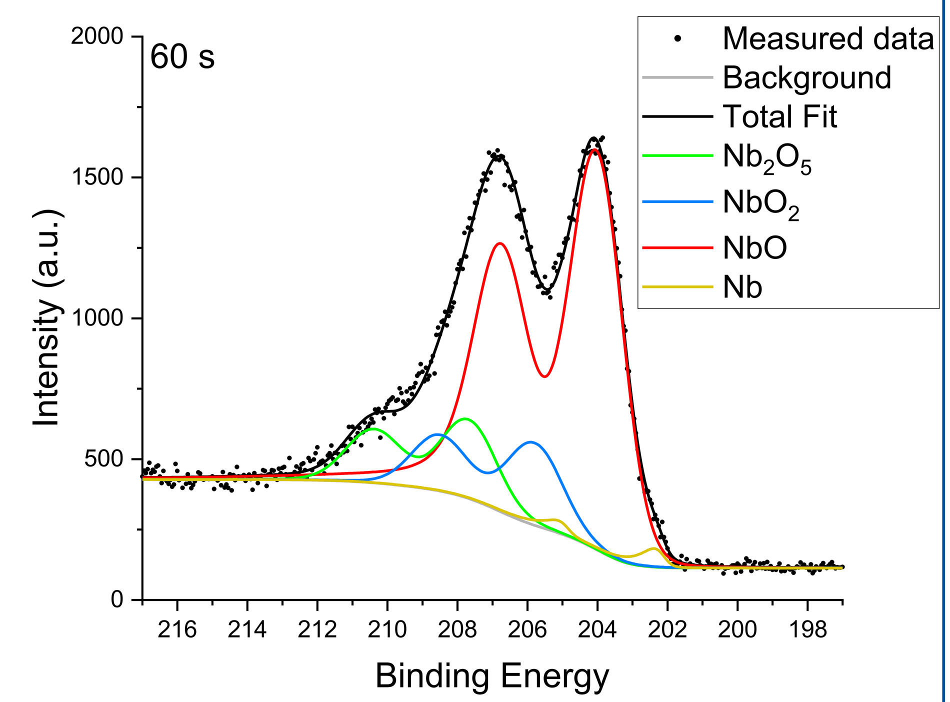




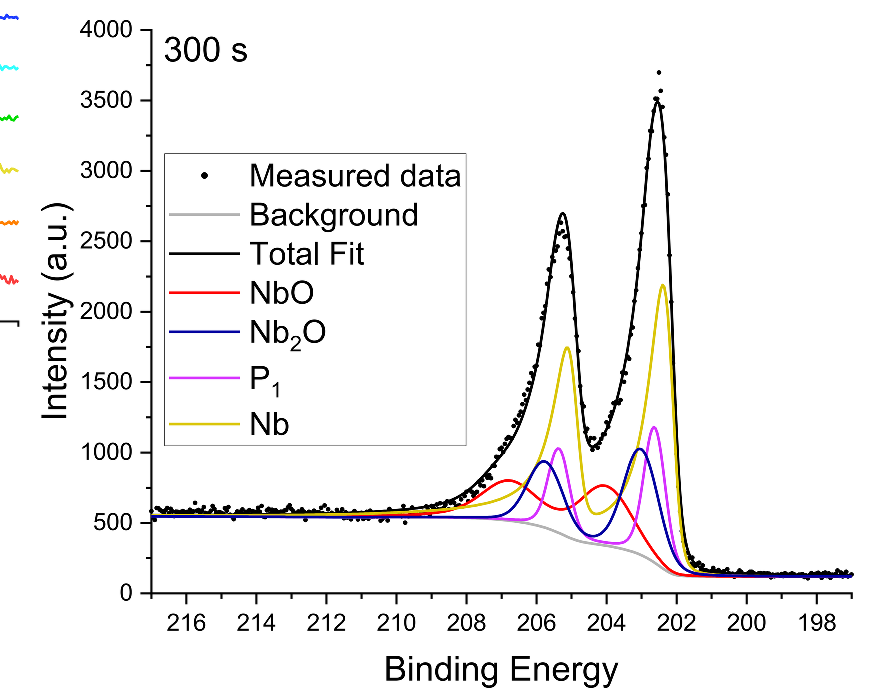
Nb 3d core level spectra



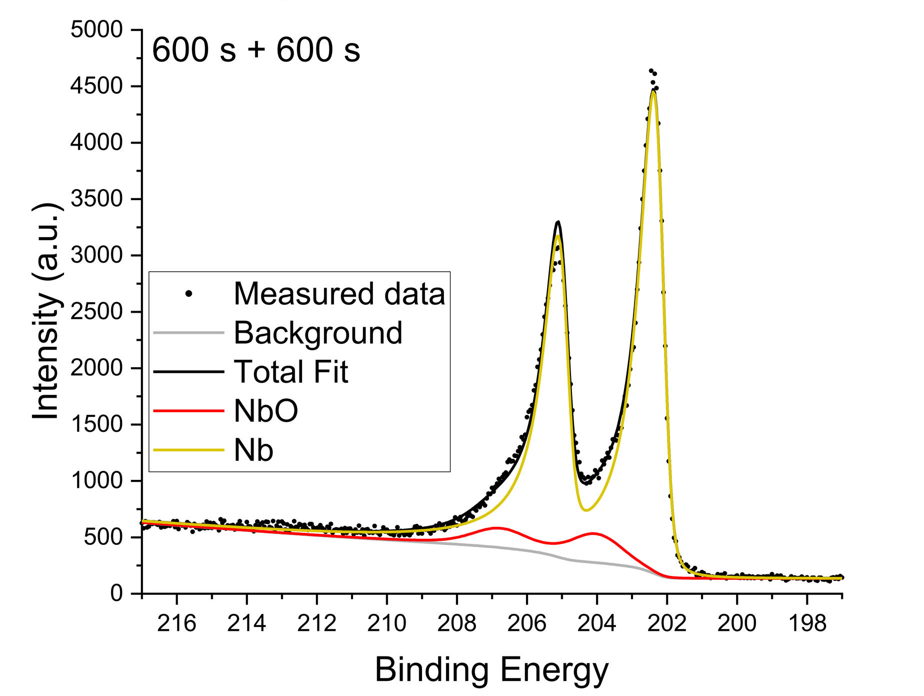
- Nb peak: 202.2 eV
- P_1: NbO_{1+x} peak: 204.8 eV
- NbO_2 peak: 205.9 eV
- Nb_2O_5 peak: 207.7 eV



- Nb peak: 202.2 eV
- NbO peak: 203.8 eV
- NbO_2 peak: 205.8 eV
- Nb_2O_5 peak: 207.8 eV



- Nb peak: 202.2 eV
- P_1: $Nb_{2+x}O$: 202.6 eV
- Nb_2O peak: 203 eV
- NbO peak: 203.8 eV



- Nb peak: 202.2 eV
- NbO peak: 203.8 eV

- P_1 here identifies a nonstoichiometric oxide peak whose energy decreases at each sputtering step as its chemical state is modified by the Ar ions.
- After 600 s of sputtering: sample kept under vacuum for 12 h, followed by additional 600 s of sputtering and final measurement prior to oxide regrowth in air.

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4. Oxide growth through air exposure

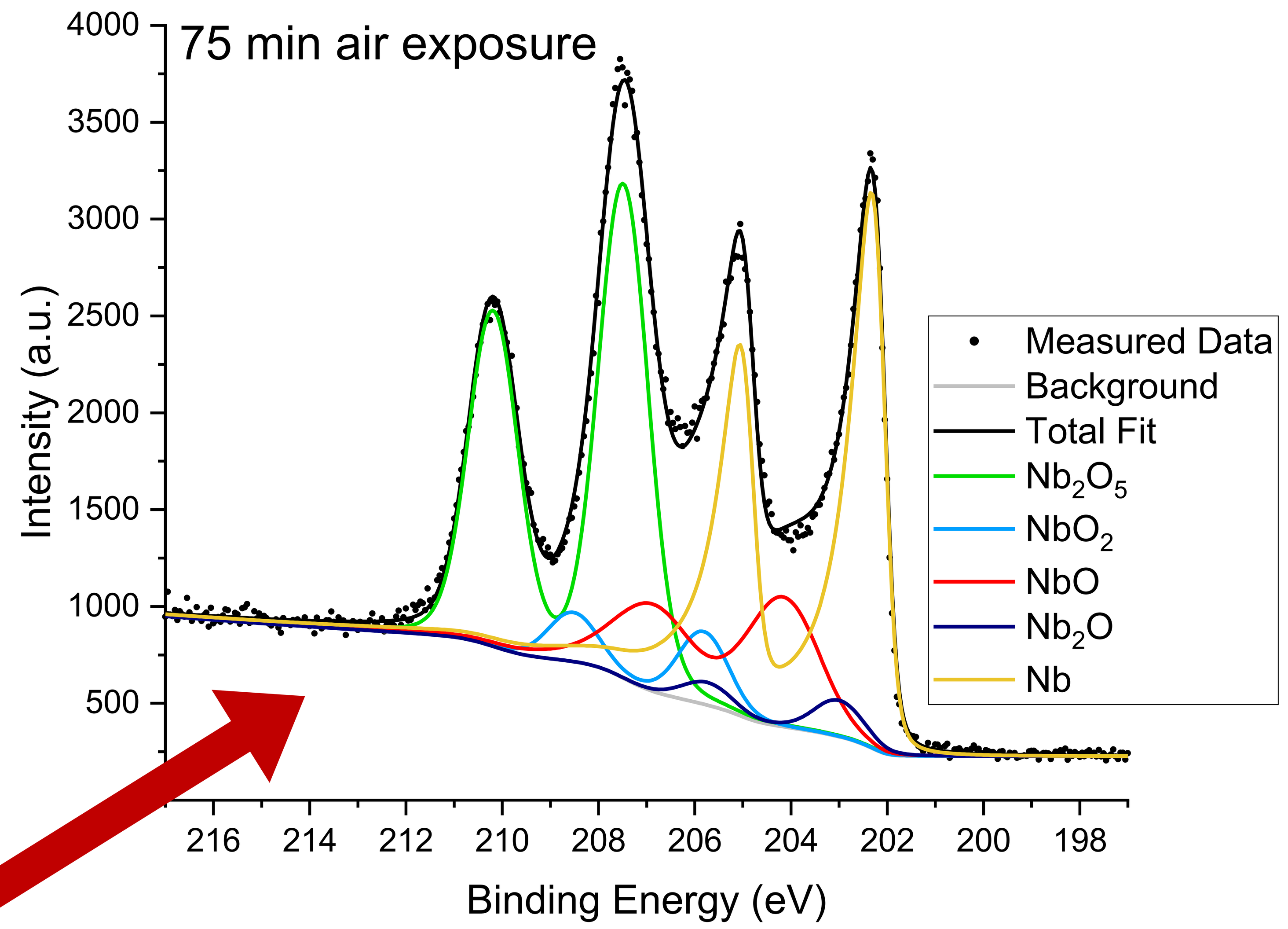
Air exposure steps
15 min in air + 30 min AP*
Additional (15 min in air + 30 min AP)
Total of (30 min in air + 60 min AP) + additional 38 h in vacuum
Additional (45 min in air + 30 min AP)+ 38 h in vacuum

* 'AP': active pumping from atmosphere pressure to 10^{-9} Torr

After 75 minutes of exposure to air: surface has not reached full oxidization.

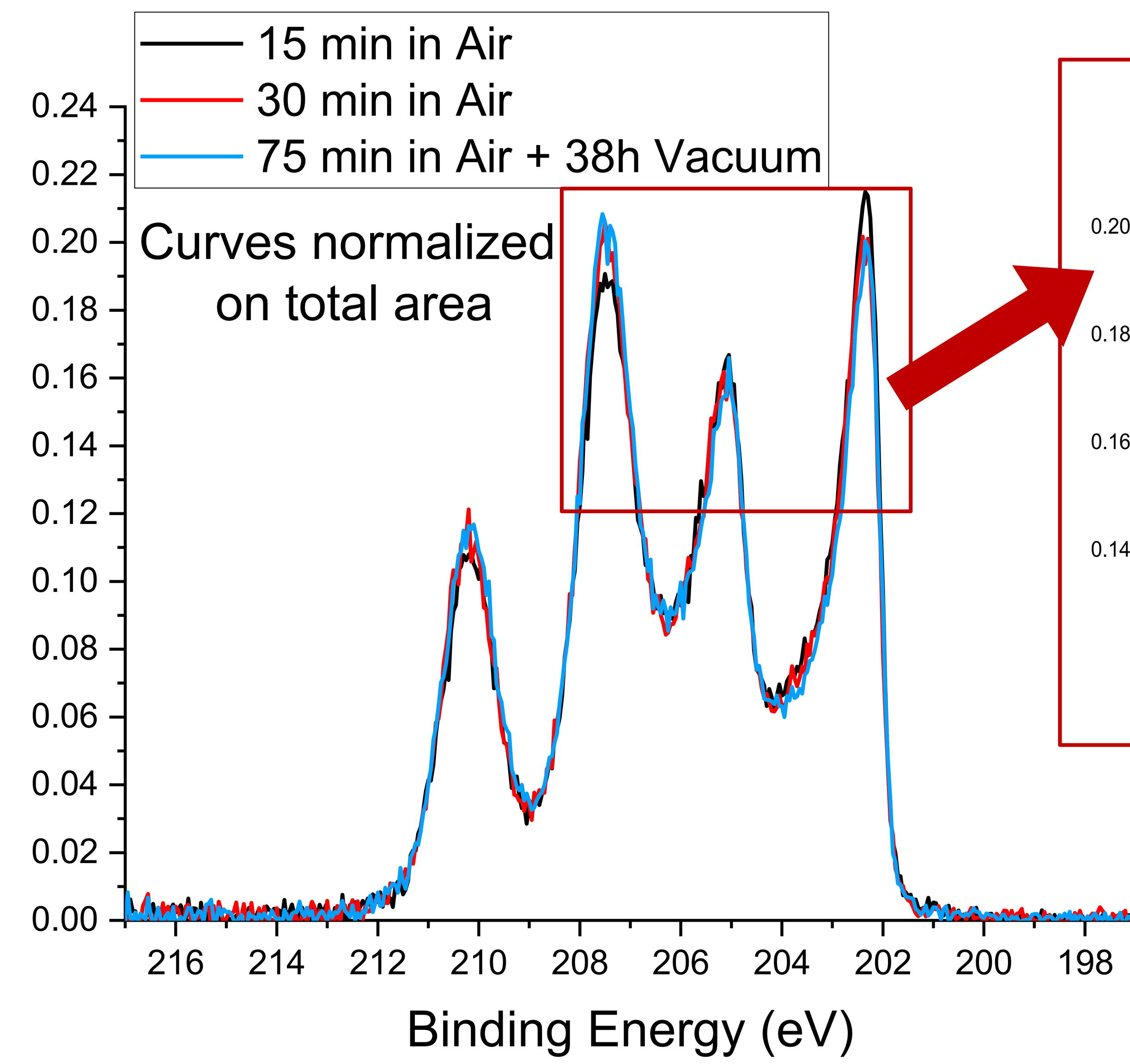
Multiple suboxides were identified through curve fitting: NbO, NbO_2, Nb_2O

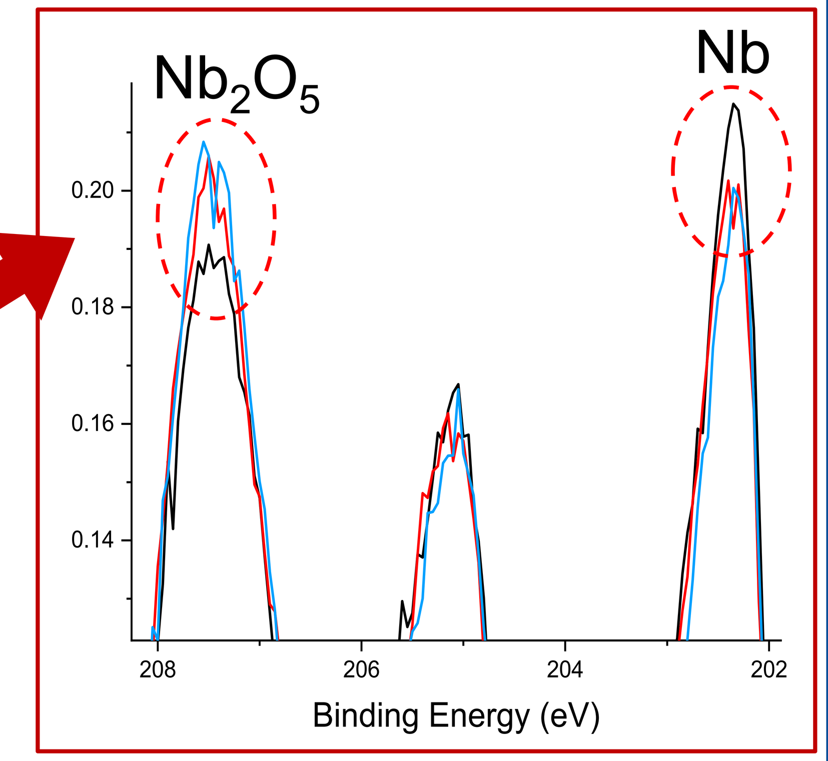
The initial measurements taken on the oxidized sample showed possible traces of NbO and NbO_2, but no Nb_2O was detected.



Ratio of the areas extracted through curve fitting

Air exposure time	Nb_2O_5/Nb	NbO_2/Nb	NbO/Nb	Nb_2O/Nb
15 min	0.87	0.12	0.36	0.08
30 min	0.99	0.14	0.41	0.11
75 min	1.00	0.15	0.40	0.07





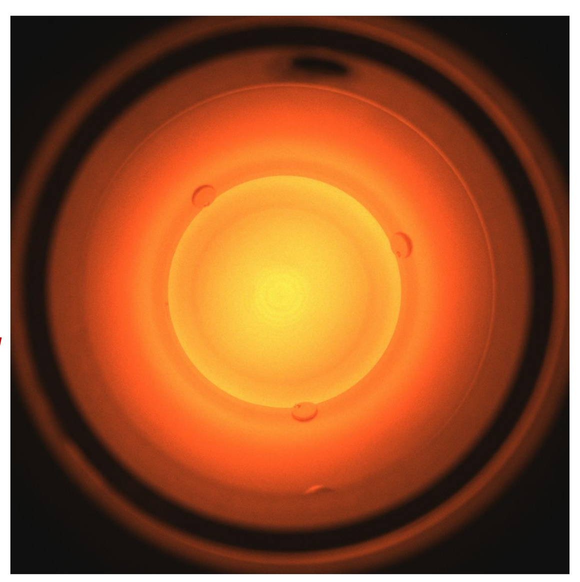
As the air exposure time increases: increase of Nb_2O_5 peak, decrease of Nb metal peak. Ratio of suboxide area over metal Nb area remains constant.

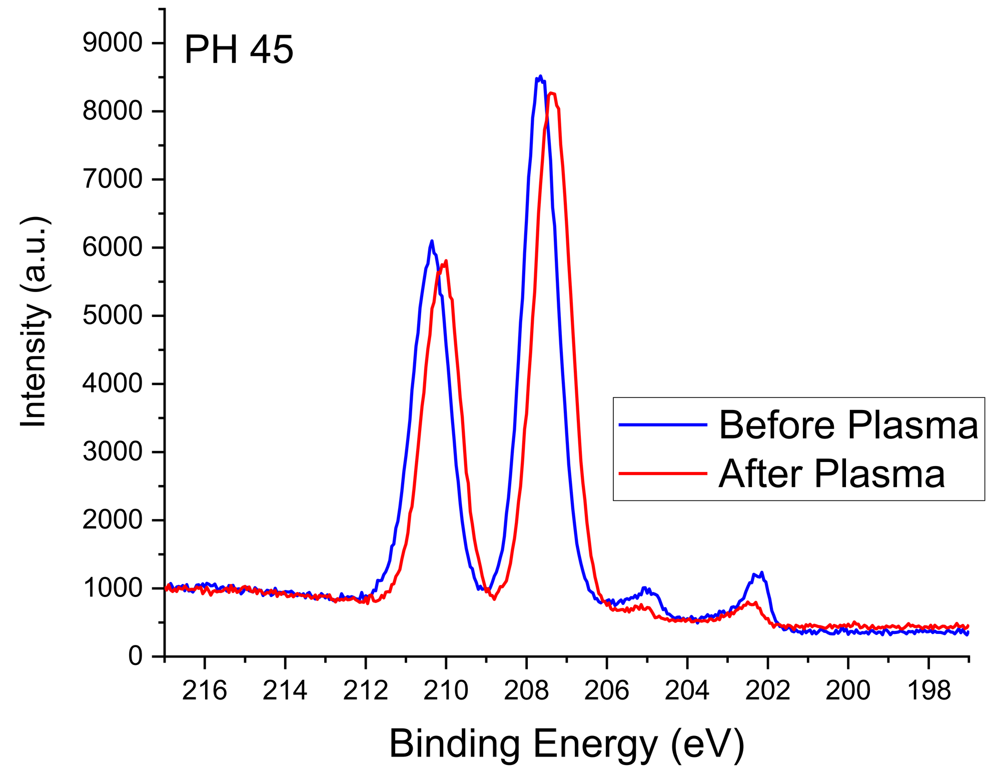
5. XPS analysis on plasma processed Nb samples

Sample preparation:

- PH 45: 800 ˚C x 3h + 20 μm EP
- PH 35: 2/6 N doping + 5 μm EP + 5 min HF rinse
- PH 40: 2/0 N doping + 7 μm cold EP

Samples were positioned on cavity iris and plasma processed for 6h.





- Similar results obtained on all three samples, independently of the surface treatment
- No particular change was observed in the suboxide spectra

- ΔE between Nb and Nb_2O_5 is decreased after plasma processing
- Relative intensity of Nb and Nb_2O_5 is modified: ratio of Nb_2O_5 area over Nb area consistently increases after plasma processing

6. Conclusions

- Sputtering and oxide regrowth: studied niobium oxide structure, identified multiple suboxides and extracted parameters for data analysis
- Plasma processed samples:
  - Consistent change in Nb_2O_5/Nb area ratio suggesting **oxide thickening**
  - **Reduction in ΔE between Nb_2O_5 and Nb peaks: reproducible but not fully understood yet.** May be caused by oxygen vacancies in Nb_2O_5 lattice.

No major impact on cavity performance

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