Study of the Initial Surface Reactions of Tungsten Nitride Atomic Layer Deposition by In-situ Infrared Spectroscopy

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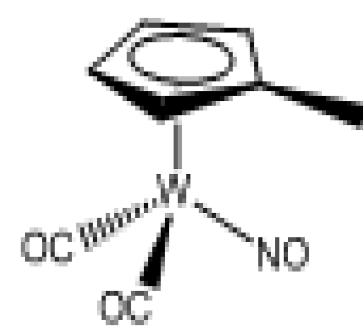
INTRODUCTION

Tungsten nitride (WN)

Highly desirable properties → High melting temperature, relatively low resistivity and chemical inertness for a variety of applications → diffusion barrier for copper metallization or other contact materials.

The surface termination group is one of the main parameters to understand the adsorption of the precursor. Our study shows deposition of WN films in both –OH and –H silicon surfaces at temperatures of 300 °C and lower.

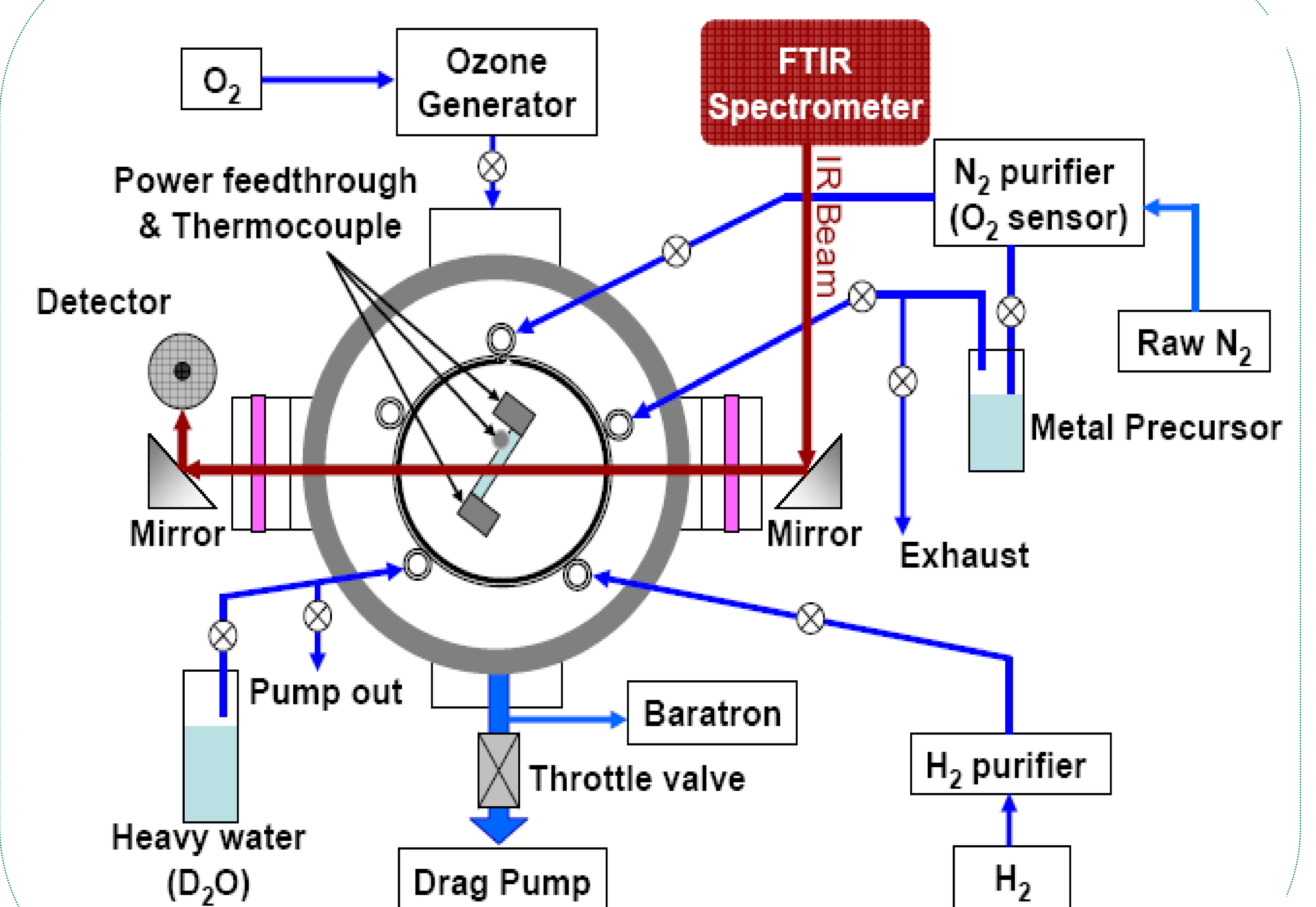
Surface termination → OH/Si, H/Si



Hydrazine (N_2H_4)

Film deposition by ALD at a substrate temperature of 300 °C → Film characterization → FTIR, XPS

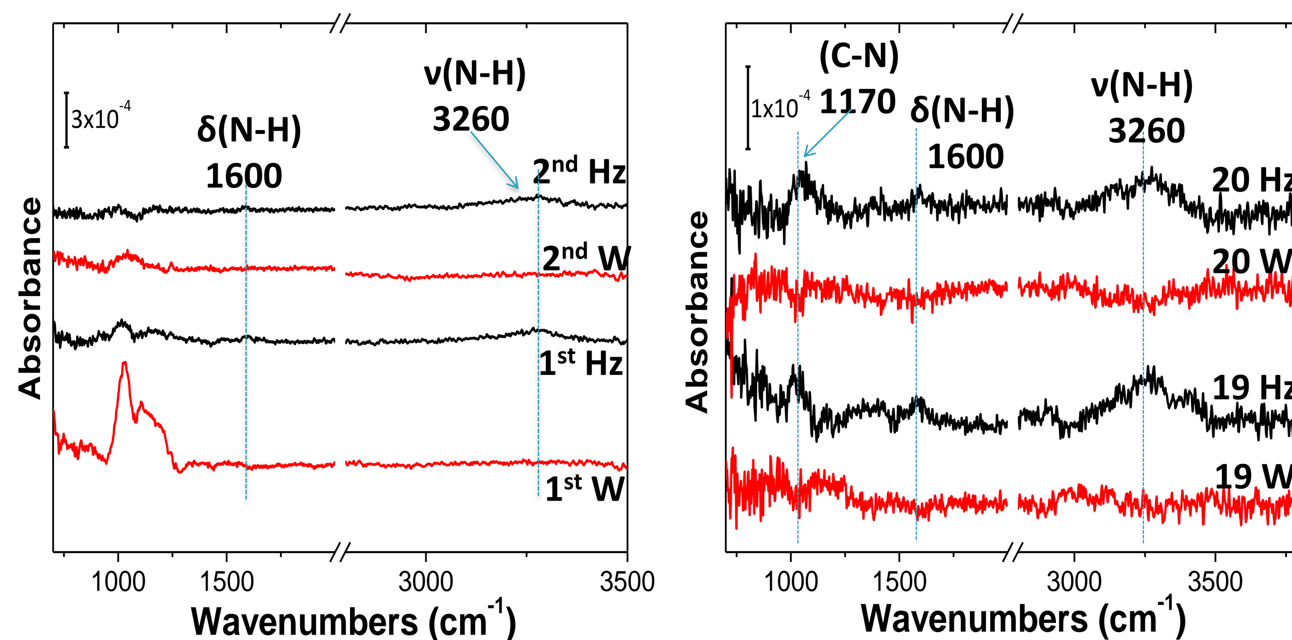
EXPERIMENTAL SETUP



EXPERIMENTS AND RESULTS

Si-OH surface

Differential IR spectra of 20 ALD cycles



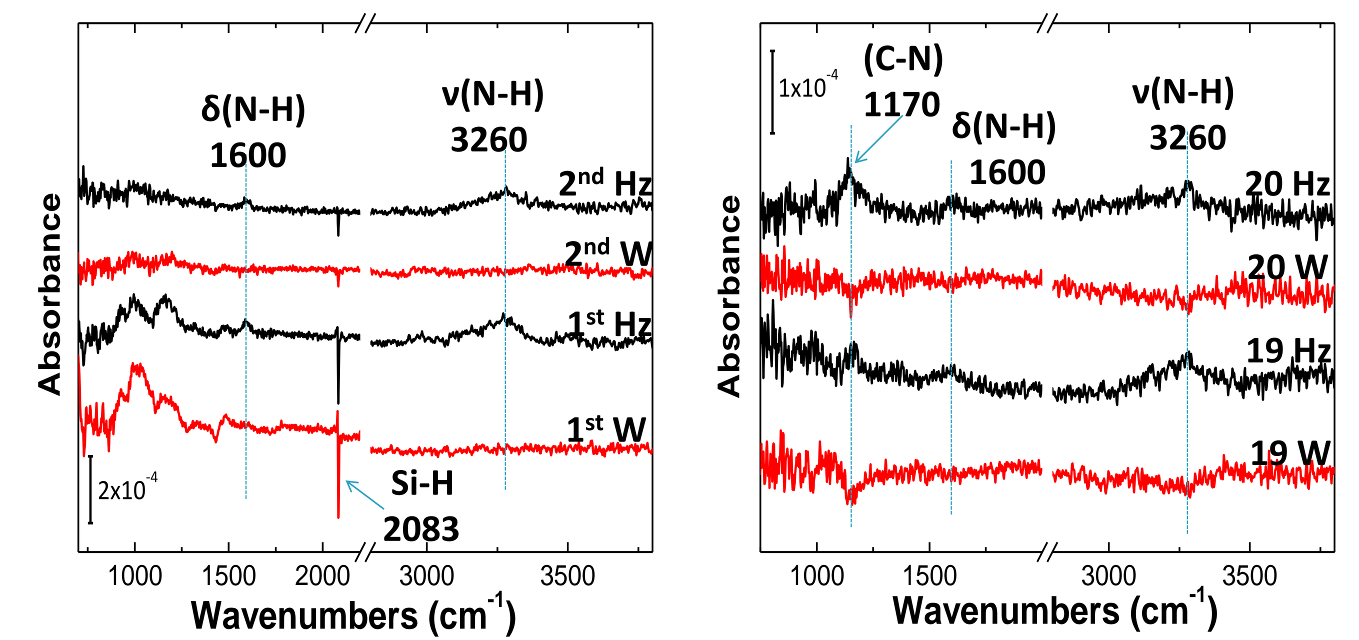
Fourier-Transform Infrared Spectroscopy (FTIR)

In both cases, the IR spectra shows:

- A nucleation period during the first ALD cycles (no ligand exchange).
- Absorption of the W precursor is observed after the first exposure in the 1260-950 cm^{-1} range.
- A ligand exchange is observed after ~8 cycles:
  - ν and δ(N-H) at 3270 and 1600 cm^{-1}
  - C-N bonds at 1170 cm^{-1}

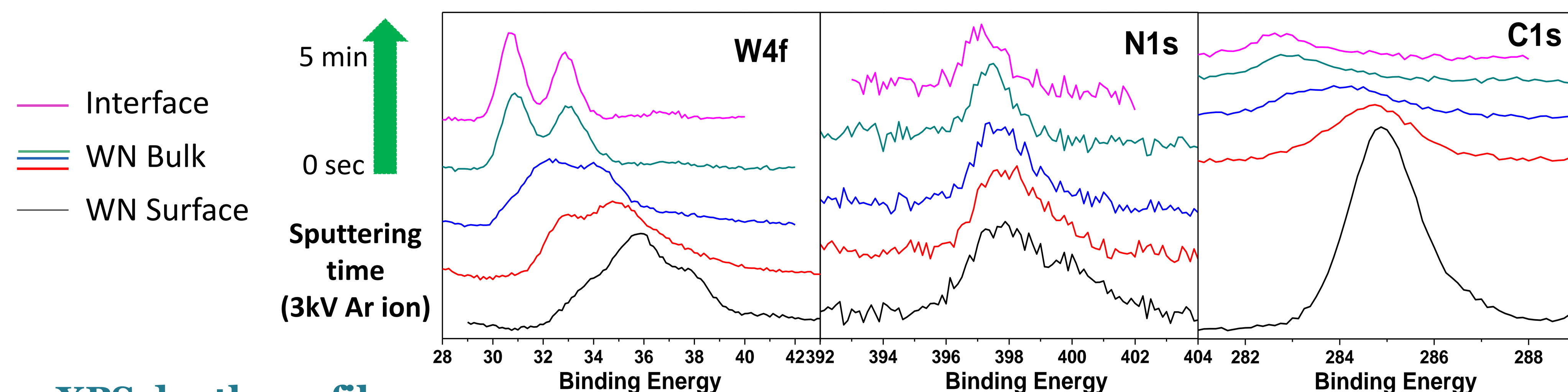
Si-H surface

Differential IR spectra of 20 ALD cycles



- Complete loss of the Si-H bond at 2083 cm^{-1} after 5 cycles.

X-ray Photoelectron Spectroscopy (XPS)



W4f N1s C1s

Binding Energy

XPS depth profile

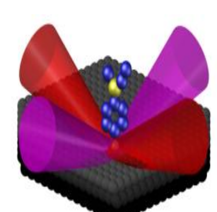
- Oxidation of film upon exposure to air (black).
- W 4f → WN at 32.8 and 34.8 eV (bulk).
- N 1s → WN at 397.4 eV (bulk).
- Lowest BE peaks of W→ metallic W.

XPS spectra in good agreement with IR

SUMMARY AND CONCLUSIONS

- According to IR data, a similar process is observed on both surfaces. There is a nucleation period during the first cycles.
- On the Si-H surface, only 12% of the Si-H sites react after the first pulse of W precursor. After the first 4 cycles, ~50% of Si-H bonds react, saturation point is reach after ~8 cycles.
- XPS data showed formation of WN films after 30 cycles with low C and O impurities.

This study provides insight into the surface chemistry of the precursor's initial reactions necessary to enable future process development and deposition of W-based materials for a wide range of applications.



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