Application Note #250201

**KeyWords**
NAP-XPS, ice, thin film,
Peltier cooling, backfilling

SPECS™
A member of SPECSGROUP

# NAP-XPS analysis of an in-situ grown ice film

**NAP-XPS studies of in-situ grown thin ice films are easily possible with standard laboratory backfilling systems equipped with cooling capabilities, e.g., a Peltier cooler, providing fundamental insights into physical, chemical, and biological processes.**

## Introduction

Investigations of thin ice films are important for several scientific and technological reasons due to their relevance across multiple fields:

### Atmospheric and Climate Science

Thin ice films play a crucial role in atmospheric chemistry, particularly in processes that occur in polar stratospheric clouds. These clouds contribute to ozone depletion by providing surfaces for reactions involving chlorine and other compounds. Understanding the behavior of ice films in the atmosphere helps improve climate models, especially in predicting how atmospheric particles interact with gases and influence ozone depletion or the greenhouse effect.

### Astrophysics and Planetary Science

In space environments, ice films are found on the surfaces of planets, moons, and comets. Investigating these films helps us understand the formation and evolution of solar system bodies, particularly in cold environments.

### Surface Science and Nanotechnology

Thin ice films are used as models for studying fundamental properties of water at interfaces, including its structure, dynamics, and interaction with other materials. This knowledge is critical for various surface-related applications in nanotechnology, catalysis, and material science.

### Materials and Coating Technologies

Thin ice films are studied in the context of creating anti-icing surfaces and coatings for various industrial applications. These coatings can prevent ice buildup in industries ranging from power lines to shipping, reducing maintenance costs and improving safety.

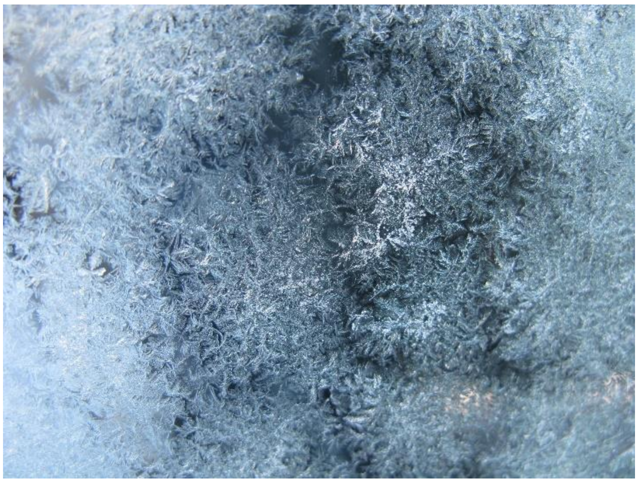

**Fig. 1 Example image of an ice film.[1]**

In sum, investigating thin ice films provides fundamental insights into physical, chemical, and biological processes, enabling advancements in a variety of scientific and practical fields.

## Method

X-ray Photoelectron Spectroscopy (XPS) is a powerful and non-destructive technique for material and surface analysis, which provides quantitative elemental and chemical information. NAP-XPS has been developed to enable routine analysis of real-world samples. The transformation of XPS from a UHV-based method towards environmental conditions has dramatically revolutionized XPS and opens completely new application areas. NAP-XPS is used extensively for in-situ and operando studies of industrially relevant (electro) chemical reactions and catalytic processes, especially at gas-liquid, gas-solid, and liquid-solid interfaces.

In XPS as an analytical technique an electron beam is generated inside the X-ray source and focused on an aluminum anode. The deceleration of electrons on the anode generates X-rays that are monochromated and focused on the sample. The interaction of X-ray photons with the sample results in the excitation of electrons within the material, which are subsequently emitted with a specific kinetic energy. This energy is determined by the binding energy of these electrons and the photon energy of the excitation source.

In solid samples, electrons originating from atoms situated at a depth of approximately 10 nm or less are the only electrons capable of exiting the surface. These emitted electrons propagate through the lens system of the electron analyzer into the hemisphere, which functions as a spherical capacitor, forcing the electrons onto circular paths with radii dependent on their kinetic energy. The trajectory of the photoelectrons ultimately reaches an electron-sensitive detector, where they are amplified and quantified as intensity in counts per second. A photoelectron spectrum is recorded by sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector. Subsequently, a quantitative analysis of the sample surface, providing information regarding its elemental composition, can be derived from these spectra.

A Peltier element, also known as a Peltier cooler or thermoelectric cooler, works based on the Peltier effect. It consists of two different types of semiconductor materials (n-type and p-type) arranged in pairs and sandwiched between two ceramic plates. When an electric current flows through the Peltier element, it creates a temperature difference: one side absorbs heat and becomes cold, while the other side releases heat and becomes hot. This happens because electrons move from the n-type to the p-type material, absorbing heat energy on one side and releasing it on the other. By reversing the direction of the current, the hot and cold sides can be swapped.

## Experimental Section

SPECS NAP-XPS systems can operate in (near) ambient conditions up to several dozens of Millibars.[2-4] This NAP-XPS capability allows in-situ surface studies of a multitude of samples in very different environments. Here we present results of a surface chemical analysis of a thin ice film that was grown in-situ on a stainless-steel sample plate. This growth was done inside of the analysis chamber in an atmosphere of water vapor at a pressure of 3 mbar and a temperature of -6 °C using a Peltier cooler. Oxygen core-level spectra were acquired in scan mode with a step width of 0.1 eV, a dwell time of 0.1 s, and a pass energy of 20 eV in a loop (15x, 15 s each) with a total measurement time of 4 minutes.

## Results

Figure 2 shows the O 1s core-level spectra of the first three loops measured during the initial growth of the thin ice film. Initially in loop one the water vapor related peak around 536 eV is the main peak together with a broad shoulder at lower binding energies corresponding to steel-related oxygen species of the sample plate surface.

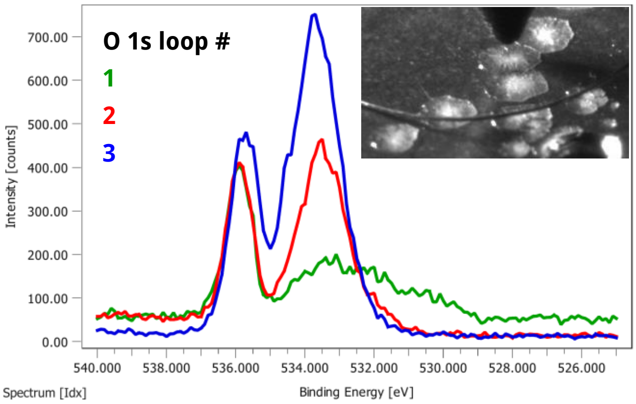

**Fig. 2 O 1s core-level spectrum of an ice film grown in-situ on a sample plate at 3 mbar of water vapor using a Peltier cooler at -6 °C (loop #1, 2, and 3). The inset shows the ice film growing from islands and the analyzer nozzle during measurements.**

After the first loop a second peak arises around 533-534 eV which becomes the dominant feature in loop three, which represents the oxygen atoms bound in the ice film. The inset of Fig. 2 shows the formation of single islands growing on the sample plate during the measurement before formation of a complete ice film.

Figure 3 is showing the O 1s detail spectrum taken in loop number three including a simple two component peak fit with one component representing the solid water species from the ice film located at 533.6 eV and a second component originating from the gaseous species of the surrounding water vapor located at 535.7 eV.

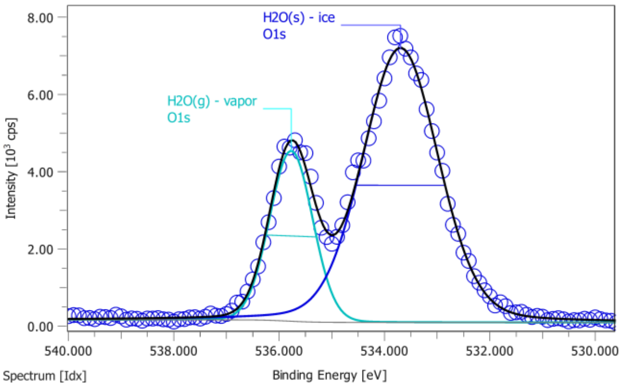

**Fig. 3 Same O 1s core-level spectrum as in Fig. 1 from loop #3 including a simple two component peak fit using one component for solid water (ice) located at 533.6 eV and a second component for gaseous water (vapor) located at 535.7 eV.**

The development of these two peak components over time is shown in Figure 3. The ice film remains stable while cooling for 90 seconds (loop# 3-8) and then disappears gradually starting from loop nine when the Peltier device is switched off.

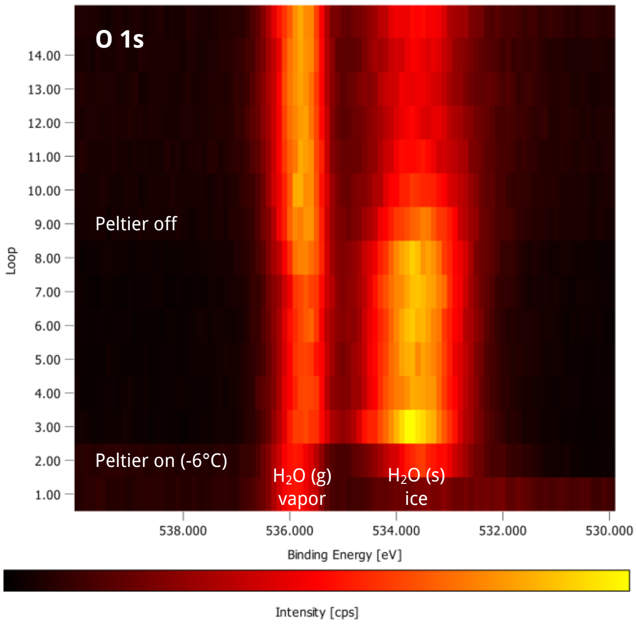

**Fig. 4 Evolution of the O 1s core-level spectrum of the ice film measured in a loop (15x, 15 s each) with a total time of 4 minutes.**

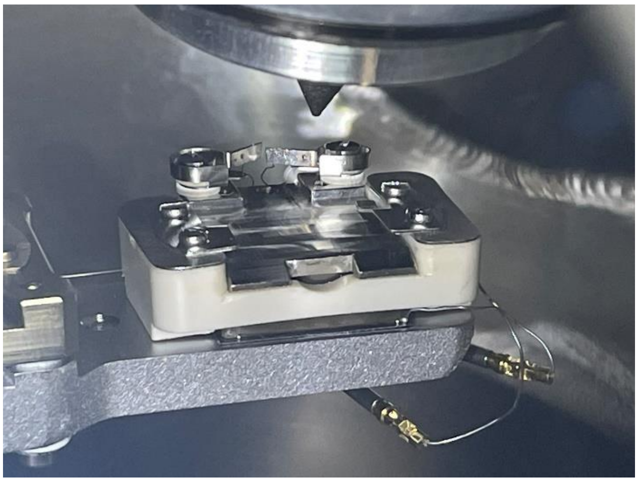

**Fig. 5 Picture of the manipulator head with Peltier cooler option for backfilling NAP-XPS systems from SPECS.**

## Conclusion

Detailed investigations of thin ice films are essential for various scientific and technological reasons due to their relevance across multiple fields.

SPECS NAP-XPS systems can operate in environmental conditions up to several dozens of Millibars.[2-4] This NAP-XPS capability allows in-situ surface studies of a multitude of samples in very different environments. Here we presented results of a surface chemical analysis of a thin ice film that was grown in-situ on a stainless-steel sample plate in an atmosphere of gaseous water at a temperature of -6 °C using a Peltier cooler.

Examining such thin ice films provides fundamental insights into basic and advanced physical, chemical, and biological processes, enabling advancements in a variety of academic and industrial fields and addressing both scientific challenges and practical problems.

---

[1] Image designed by wirestock found on Freepik.

[2] FlexPS NAP Backfilling

[3] ProvenX-NAP

[4] ProvenX-DeviSim NAP

Thanks are due to Dr. Sara Baja and Dr. Ane Etxebarria (Universidad del Pais Vasco, San Sebastian, Spain) for their kind support, cooperation, and organization of the PECAS 2024 workshop.