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基礎および産業研究用の実験室系硬 X 線光電子分光

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Laboratory-based Hard X-ray Photoelectron Spectroscopy for Fundamental and Industrial Research

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Hard X-ray photoelectron spectroscopy (HAXPES) is a powerful technique to observe chemical and electronic states of atoms buried inside materials. Recently, a laboratory-based HAXPES system with high throughput has been developed, combining a high-flux Ga ($K\alpha=9.25$ keV) X-ray source and a high-transmission photoelectron analyser. In this article, research using the HAXPES Lab is reviewed, and the data are compared with those using synchrotron light sources. The HAXPES Lab is an attractive option not only for scientists but also for industrialists needing rapid answers for research and development.

KEYWORDS : HAXPES, laboratory, synchrotron, benchmark

1. Introduction

1. 1 Background

From its beginnings in Kai Siegbahn's laboratory in the middle of the 20th century, laboratory photoelectron spectroscopy (PES) has made use not only of the now common soft X-ray sources (e.g. Al and Mg $K\alpha$), but also of hard X-ray sources (e.g. Mo $K\alpha$, Cu $K\alpha$, and Cr $K\alpha$) for the excitation of photoelectrons.[1~3] Hard X-ray photoelectron spectroscopy (HAXPES) is defined by the

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use of X-ray excitation sources with energies above 2 keV. After a very small number of initial explorations of the use of laboratory sources available in the hard X-ray regime for PES,[4, 5] it was the advent of synchrotron sources that truly accelerated the development of HAXPES. Lindau, Pianetti and colleagues performed the first reported synchrotron-based HAXPES experiments at SPEAR, a synchrotron facility in USA, in the 1970s.[6, 7] The following decades saw the development of the technique across the globe, with synchrotron-based HAXPES beamlines being established at a number of synchrotrons, but particularly at SPring-8, Japan. The continued growth of experimental opportunities and the user community itself has resulted in a total of 24 operating user end stations at 12 synchrotrons in Asia, Europe and North America.[8] HAXPES continues to impact a wide range of scientific areas, but has found particularly widespread application in the areas of energy and environment as well as thin films and devices.

The main drivers for the move towards the use and subsequent success of synchrotron sources for HAXPES were limitations in X-ray line widths of available laboratory sources limiting achievable energy resolution and the dramatic reduction in photoionisation cross sections when using hard X-rays necessitating the incredible brilliance of synchrotrons. However, after many decades of HAXPES being a predominantly synchrotron-based technique, recent years have seen the development of a number of laboratory systems. This new generation of laboratory-based HAXPES systems uses predominantly Cr ($K\alpha = 5.42$ keV) and Ga ($K\alpha = 9.25$ keV) X-ray sources. The first systems of this generation were based on monochromated Cr sources and built in Japan.[9, 10] To overcome the limitations imposed by low photoionisation cross sections they chose to combine a monochromated, high-flux X-ray source together with a wide acceptance objective lens and a high-energy hemispherical analyser, an approach still used in systems now.

Today, several commercial systems are available, and a number of custom-built systems are operated successfully. An in-depth overview of both types of existing systems is presented in a recent review by Kalha *et al.*[8]

The present publication focuses on the HAXPES Lab, an integrated HAXPES laboratory system available from Scienta Omicron AB, which first came to market in 2018.[11] The core technologies and examples of measurements are discussed.

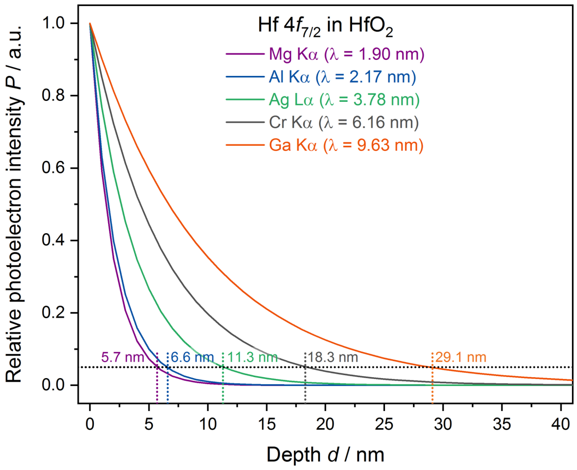

Fig. 1. (color online). Relative photoelectron intensity P as a function of depth d for the Hf $4f_{7/2}$ core level in HfO_2 using available laboratory X-ray sources. The legend gives the inelastic mean free paths λ (IMFPs) for Hf $4f_{7/2}$ at different excitation energies. The calculation method is explained elsewhere.[11]

1. 2 Bulk sensitivity

HAXPES allows the study of bulk materials, buried layers and interfaces, and samples without the need of extensive surface preparation, due to the increase in probing depth with increasing photon energy. **Fig. 1** illustrates the dramatic increase in inelastic mean free path (IMFP), and therefore probing depth, when going from soft to hard X-ray regimes. Here, probing depth is defined as the region from which 95% of the total signal originates, therefore it is 3λ. For the case of Hf $4f_{7/2}$, it is noted that the probing depth for Ga $K\alpha$ source (29.1 nm) is 60% larger than that for Cr $K\alpha$ source (18.3 nm). In addition to the increase in bulk sensitivity, higher photon energies make deeper core levels accessible to measurements, which can add valuable information, particularly considering core line shapes, including satellite features.[12, 13] Furthermore, the use of hard X-ray excitation sources makes it is easier to avoid the overlap between target signals and other core level and Auger spectra.

1. 3 HAXPES Lab

A major challenge in laboratory-based HAXPES is the significant reduction in photoionisation cross sections compared to the soft X-ray regime. The HAXPES Lab system tackles this challenge by combining a high-flux, monochromated MetalJet 9.25 keV Ga liquid metal X-ray source by Excillum AB with a high-transmission EW4000 energy analyser by Scienta Omicron AB. The MetalJet

X-ray source is based on a Ga alloy liquid metal-jet anode,[14] which is liquid at room temperature and can be continuously regenerated, thereby supporting higher electron-beam power and generating higher X-ray flux compared to conventional solid metal anodes. The EW4000 combines a state-of-art wide angle electron lens with a conventional hemispherical analyser. High transmission is obtained through the spherical aberration correction by a spherical mesh at the entrance of the electron lens.[15]

2. Buried interface analysis of microelectronic components

2. 1 Background

The single-phase, solid solution $Hf_{0.5}Zr_{0.5}O_2$ (HZO) is a promising material for ferroelectric capacitor integration in memory cells, thanks to its low crystallization temperature, fully compatible with back end of line technology.[16] The maximum ferroelectric polarization is obtained for a film thickness of ∼10 nm. The formation of chemically distinct interface layers to the TiN electrodes, with distinct electric properties with respect to the HZO, can therefore play an important role in ultimate device performance. For example, an interface layer may destabilize the ferroelectric state in the HZO, favor leakage by modifying the Schottky barrier height, or reduce the total capacitance of the stack.

Understanding these challenges requires techniques capable of accessing buried interfaces in a non-destructive manner. HAXPES is an ideal tool probing the local chemistry and electronic structure of buried interface layers, providing key information such as the depth distribution of oxygen vacancies or the oxidation states present in interface layers.

To benchmark the performance of HAXPES Lab with respect to a typical synchrotron radiation HAXPES set-up, a 12 nm TiN/10 nm La : $HfZrO_2$/12 nm TiN/SiO_2/Si sample, shown schematically in **Fig. 2**(a), was used.

2. 2 Experimental details

HZO was grown by atomic layer deposition (ALD), and the bottom and top TiN electrodes were deposited using physical vapor deposition (PVD) sputtering. The sample was then annealed to stabilize the polar orthorhombic phase of HZO. More details for the sample preparation are explained elsewhere.[17]

The synchrotron HAXPES experiments were performed at the BL15XU beamline at SPring-8 (Japan) using 8 keV photons and a Scienta R4000 analyser. Laboratory-based measurements were performed using the Scienta Omicron HAXPES Lab at the Scienta Omicron premises in Taunusstein (Germany).

Identical dwell times, energy step sizes, spectral ranges, and incidence and detection angles were used for both experiments. Only the number of scans per spectrum was varied to obtain reasonable signal to noise (S/N) ratios for all spectra and the energy resolution of the analyser was adjusted using the slit width.

2. 3 Results and discussion

The survey and Hf $3d_{5/2}$ core level spectra from the HAXPES Lab and the synchrotron experiments are shown in **Fig. 2**(b) and (c) together with the total acquisition time t_{acq} and the total spectrometer energy resolution ΔE, as

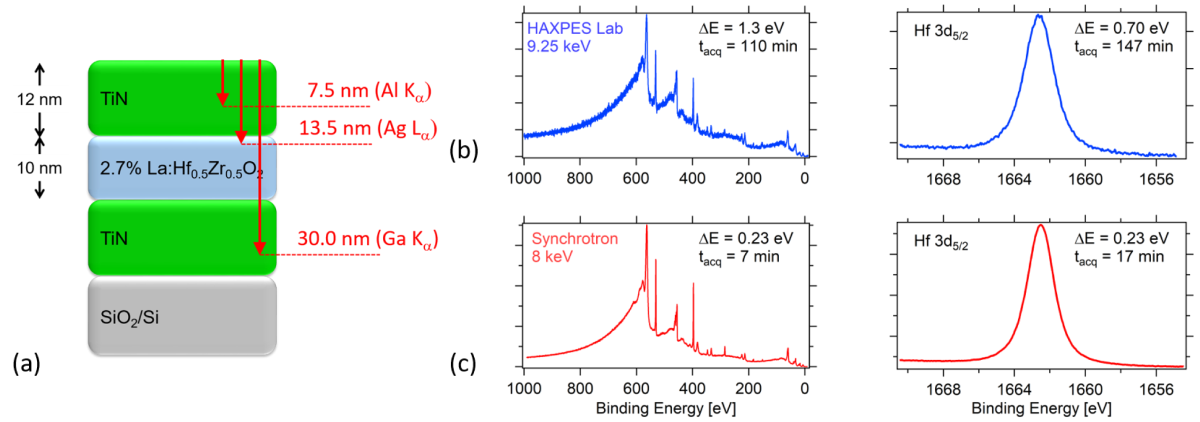

Fig. 2. (color online). (a) Schematic of 12 nm TiN/10 nm La : $HfZrO_2$/12 nm TiN/SiO_2/Si test sample. The approximate probing depths of Hf 3*d* electrons excited by Al Kα, Ag Lα and Ga Kα are shown by the red arrows. The graphs show the survey (left) and Hf $3d_{5/2}$ core level (right) spectra obtained using (b) HAXPES Lab and (c) synchrotron radiation. For each spectrum, the energy resolution ΔE and the total acquisition time t_{acq} are indicated.

estimated from the fitting to Fermi edge of a gold foil.[17] The two survey spectra agree well, but there are some differences in relative intensity of the peaks and background. They may be due to the differences in ΔE and probing depth at two excitation energies (8 keV and 9.25 keV) as well as slight variation in the photoionisation cross-sections.

The S/N ratio of the synchrotron measurements is better. There is also a factor 3 in energy resolution and a factor 8 in total acquisition time, with respect to the HAXPES Lab. However, the full-width half-maximum of the Hf $3d_{5/2}$ peak only broadens from 1.84 to 2.00 eV for the laboratory spectrum as a result of the poorer resolution. This is because the natural linewidth of the $3d$ emission is quite significant with respect to the spectrometer resolution. As a result the analysis retains the ability to identify changes such as the reduction of Hf^{+4}, a signature of the oxygen vacancy concentration, with typical core level shifts of 1–2 eV.[18] The increase in acquisition time is not a major disadvantage given the long-term stability of the Ga Kα source (greater than three days). The 0.70 eV resolution in the laboratory should be sufficient for most analyses of the interface chemistry and band line-up.

These results demonstrate that HAXPES Lab can be used successfully to probe chemical states in this system.

3. Electrochemical and thermal stress study of Li-ion battery cathodes

3. 1 Background

For layered oxide cathodes in lithium-ion batteries, aluminum doping has widely been shown to improve performance, particularly at high degrees of delithiation. While this has led to increased interest in Al-doped systems, including $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), the aluminum surface environment has not been thoroughly investigated despite the known benefits of Al-based coatings (Al_2O_3/$LiAlO_2$) as effective solutions to improve high voltage performance and power output.[19~21] Spectral contamination in surface sensitive X-ray photoelectron spectroscopy (XPS) studies due to the overlap between the Ni $3p$ ($3s$) and Al $2p$ ($2s$) core levels often makes it difficult to determine how the surface Al species react with the electrolyte for Ni-rich oxide cathodes using traditional soft X-ray laboratory-based XPS.[22]

Here, we summarize a recent report employing the HAXPES Lab system for determining the evolution of aluminum species at the surface of NCA.[22] HAXPES studies of electrochemically and thermally stressed NCA electrodes were able to directly measure the deep Al $1s$ core level to correlate reactions between the Al ions and HF and POF_3 associated with decomposed $LiPF_6$ products. A direct comparison is reported here between synchrotron based HAXPES and HAXPES Lab.

3. 2 Experimental details

Powder cells were assembled and were charged to 4.75 V at 25 mAh/g at 60℃ with a 10 h constant voltage. A reference electrode charged to 3.6 V at 25℃ was used to better reflect the pristine electrode Al environment. Full details regarding sample preparation, electrochemical performance, along with additional characterization of these electrodes are reported elsewhere.[22]

All electrodes were dissembled and transferred to the HAXPES instruments in inert environments, using a combination of gloveboxes and vacuum suitcases. synchrotron-based HAXPES measurements were performed at beamline I09 at the Diamond Light Source Ltd. (DLS), UK using a photon energy of 6 keV.[23] The laboratory-based HAXPES was performed using the prototype of the Scienta Omicron HAXPES Lab.[11]

3. 3 Results and Discussion

Fig. 3 plots the Al $1s$ core-level region of the binder-free NCA electrodes at 3.6 V and under stressed conditions for both synchrotron and HAXPES Lab. There is excellent agreement between the two instruments regarding the initial line shape of the Al $1s$ associated with the bulk Al^{+3} environment of the layered oxide. Both instruments confirmed the emergence of an additional Al-O-F species following the electrochemical and thermal stress. The emergence of this feature is interpreted as evidence for the Al surface species acting as HF scavenger (moisture trap), like what has been reported for Al_2O_3 coatings by Myung *et al.*[24] The destabilization of the $LiPF_6$ salt in the presence of trace water (aggravated by the thermal stress) generates HF resulting in the observed $AlF_3{\cdot}xH_2O$ surface species in our HAXPES measurements. These assignments are supported by NMR studies, reported elsewhere.[22] Differences in the chemical shifted peak likely reflect differences in the composition of the $AlF_3{\cdot}xH_2O$ surface species associated with sampling depth regions for the two energies. The HAXPES Lab results confirm that these new species are part of the cathode subsurface associated with the cathode-electrolyte interface.

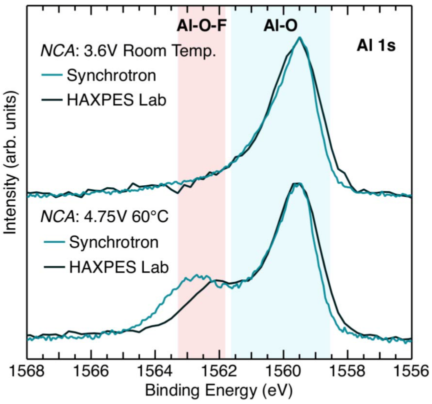

Fig. 3. (color online). HAXPES measurements of the Al 1*s* for commercial NCA electrodes using both synchrotron (I09) and HAXPES Lab. Data reproduced from Ref. 22.

Our results reveal that studies like the one presented here are no longer restricted to synchrotron HAXPES and that further cathode-electrolyte studies can now be performed within a laboratory setting.

4. Standardization

There have been ongoing efforts in the development of databases and calibration methods to support the uptake of HAXPES as a standard tool for surface and bulk analysis. To support measurements and analysis, databases of standard samples are available online from a laboratory system at Hyogo Science and Technology Association(25) and from BL46XU in SPring-8.(26) The HAXPES Lab system is also available through open access routes to support the research in industry.(25) For quantitative analysis of HAXPES data, relative sensitivity factors (RSFs) have been determined in the hard X-ray regime.(27) These RSFs together with transmission functions provided by Scienta Omicron allow researchers to perform accurate quantitative analysis.

Angle-resolved measurements with a 2D detector has been developed as a standard method for depth analysis. Spencer *et al.* have shown that HAXPES Lab is capable of tuning the sampling depth by angle-resolved measurements, similar to photon-energy dependent measurements in synchrotron facilities.(28)

5. Summary

HAXPES Lab has a significantly improved throughput due to the recent developments in the instruments. In this review, it is demonstrated that HAXPES Lab provides access to bulk electronic states as in synchrotron facilities. The flux of the Ga source is still lower than those at synchrotrons,(11) but laboratory facilities have the advantage of short lead times compared to synchrotron beamlines. The Ga source stability allows in part to compensate the lower flux and will significantly increase the accessibility of HAXPES to a much wider user community than those used to synchrotron experiments. In particular, industrialists needing rapid answers for research and development could find the HAXPES Lab an attractive option.

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