

# Time- and Depth-resolved Chemical State Analysis of the Surface-to-subsurface Oxidation of Cu by Wavelength-dispersive soft X-ray Absorption Spectroscopy at Near Ambient Pressure

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## 1 Introduction

The X-ray absorption spectroscopy (XAS) in soft x-ray region has an advantage in its significant interaction with light elements in the surface region. It typically requires high-vacuum conditions, however, recently XAS measurements at higher pressures have been realized by using appropriate thin film windows (e.g. Si<sub>3</sub>N<sub>4</sub> windows), and this could enable the observation of surface chemical states during reactions at ambient pressure.

In addition, to follow the chemical reaction, real-time measurement is required, but the absorption intensity is obtained at each energy in a step-by-step fashion using a monochromator, which makes in situ, real-time measurements impossible in conventional XAS. To conquer the drawback of the measurement time, we developed a method to illuminate the sample with dispersed soft x rays and separately collecting the fluorescent x-ray emitted at each position on the sample [1]. In addition, non-destructive depth-resolved measurements [2] have been combined with dispersive XAS, and this enables depth profiles of chemical states having a resolution of 1 nm (that is, the near-surface region) in real time [3].

In this study, we carried out these measurements at higher pressures using Si<sub>3</sub>N<sub>4</sub> windows to separate the vacuum required for equipment operation and the ambient air required for sample oxidation. This enabled us to study the oxidation of less reactive metals. Thus, we report the real-time observation of the surface oxidation of the Cu surface using fluorescence-yield wavelength-dispersive XAS with depth-resolved measurements. We carried out Cu L<sub>3</sub>-edge XAS measurements in real time in air at pressures up to ca. 5000 Pa.

## 2 Experiment

Measurements were carried out using fluorescence-yield wavelength-dispersive XAS to enable the real-time measurement of soft X-ray absorption spectra with depth-resolved analysis [2]. Fig. 1 shows the experimental setup for the wavelength-dispersive measurements. Wavelength-dispersive soft X-rays are illuminated to be absorbed at each position of the sample, and the fluorescence soft X-rays emitted from the sample are collected by the fluorescence X-ray imaging system consisting of two spherical mirrors so that X-ray fluorescence emitted from each position on the sample is focused onto the detector separately. The setups used this study realized time-

resolved measurements with a resolution of ca. 10 s. The top-view in Fig. 1a shows the setup for depth-resolved analysis. The depth-dependent XAS data are obtained simultaneously, allowing the reaction occurring in the depth direction to be monitored with time, as shown in Fig. 1b. Further detail is shown in ref. [3, 4].

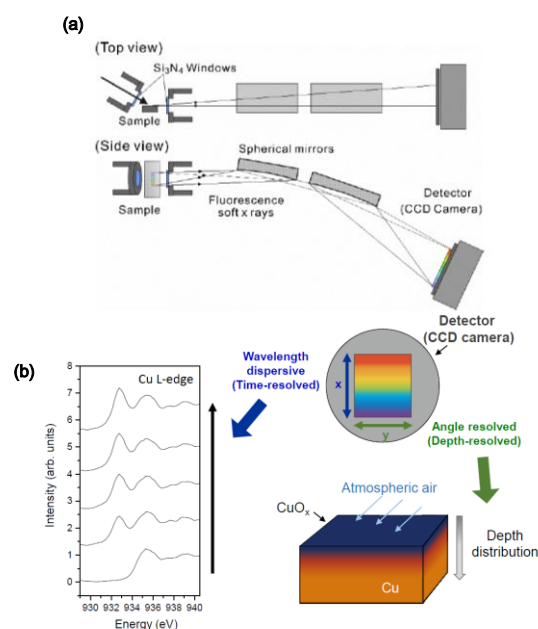


Fig. 1: (a) Schematic of the optical configuration in the side and top views. (b) The spectra around Cu L<sub>3</sub>-edge were obtained in real time, and the depth distribution of the chemical species around the surface was obtained at each time step.

All experiments were performed at beamline BL-16A. A soft X-ray CCD camera was used as the detector. A 10-mm diameter Cu(001) single crystal was placed in the measurement chamber and was cleaned by Ar<sup>+</sup> bombardment. Subsequently, the XAS spectra of the Cu surface were measured continuously while air was introduced from pressures of ca. 10<sup>-5</sup> to 5000 Pa.

## 3 Results and Discussion

In wavelength-dispersive mode, the Cu L<sub>3</sub>-edge XAS spectrum of the Cu surface in air at 500 Pa at room temperature was obtained, as shown in Fig. 2a, and subsequently spectra were obtained as the pressure was increased to 5000 Pa, as shown in Fig. 2b. At 500 Pa, the

intensity of the peak at approximately 932 eV increased markedly with time (Fig. 2a), suggesting oxidation progress, i.e. the formation of CuO on the Cu surface. At 5000 Pa, the intensity of the peak at approximately 934 eV increased, as shown in Fig. 2b, suggesting the formation of Cu<sub>2</sub>O at this pressure.

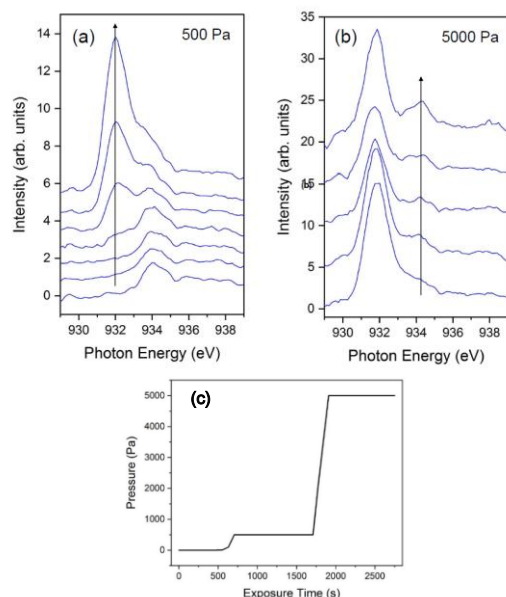


Fig. 2: (a) Cu L<sub>3</sub>-edge XAS spectra of Cu sequentially recorded (from bottom to top) in wavelength-dispersive XAS mode in air at (a) 500 Pa and increased to (b) 5000 Pa. (c) Change in chamber pressure with time as ambient air was introduced.

Next, we examine the depth-resolved spectra using six probe depths ( $\lambda$ ) from 0.6 to 1.6 (Fig. 3a). The depth-resolved spectra were obtained at each time step and numerically fitted to the standard spectra of Cu, CuO, and Cu<sub>2</sub>O (Fig 3b). Please refer ref. [4] for further detail. As shown, in the initial stages (before 500 s and below ca. 500 Pa), Cu was dominant but some Cu<sub>2</sub>O was present around the surface. Once the air pressure reached 500 Pa, the amount of CuO rapidly increased, reaching a ratio of 0.6–1. The composition ratio is larger at smaller probing depth, which directly suggests that CuO was formed mainly around the surface. From these results, the chemical composition was strongly depth dependent, therefore, we analyzed the data and quantified the depth-dependent composition  $C^i(z)$  (see ref. [4]). Fig. 4 shows the contour map of the  $C^i(z)$  profile corresponding to exposure time. From Fig. 4a, Cu is dominant at depths below 1 nm until the pressure reaches 500 Pa, and during this time, Cu<sub>2</sub>O exits around the surface as shown in Fig. 4c. At 500 Pa, CuO appears, especially at depths above 1 nm, and the CuO-rich region gradually expands into the bulk, as shown in Fig. 4b. Subsequently, the amount of CuO decreases after the pressure is increased up to 5000 Pa, eventually remaining only at the surface. In contrast, Cu<sub>2</sub>O appears at depths below 1 nm at 5000 Pa, as shown in Fig. 4c. These data suggest a unique oxidation mechanism: CuO forms on the top surface and subsequently Cu<sub>2</sub>O forms in the subsurface layers (> 1 nm from the surface), accompanied

by the interdiffusion of Cu from inner layer and that of Cu<sub>2</sub>O to inner layer. The reported technique has applications for the analysis of surface phenomena at ambient pressure, whose understanding is crucial in many fields, from chemistry to structural engineering.

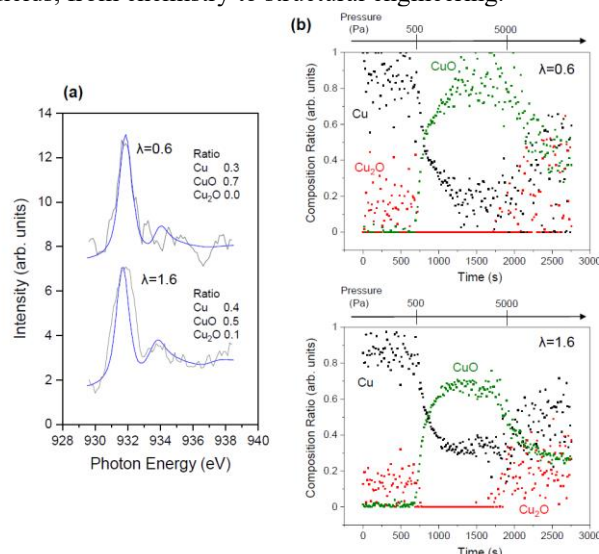


Fig. 3: (a) Example spectra obtained at probing depths ( $\lambda$ ) of 0.6 (the most surface sensitive) and 1.6 nm (the deepest region) ca. 1970 s from the beginning of measurement. CuO and Cu<sub>2</sub>O ratios were estimated by fitting to the standard spectra. (b) Ratio of Cu, CuO, and Cu<sub>2</sub>O with respect to time at  $\lambda = 0.6$  and 1.6 nm.

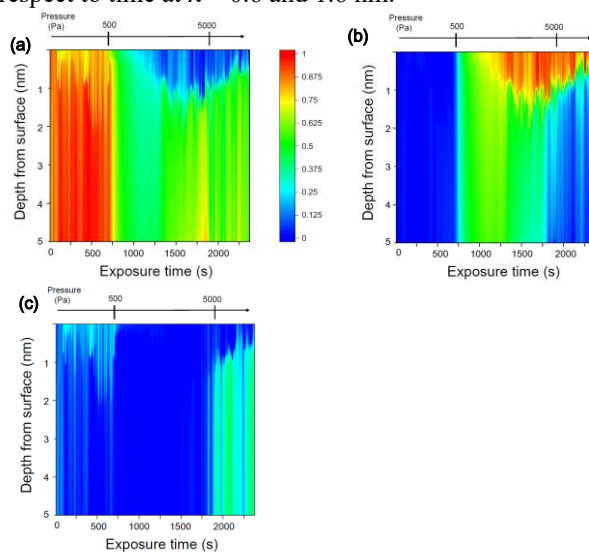


Fig. 4: The contour map of the  $C^i(z)$  profile for (a) Cu, (b) CuO and (c) Cu<sub>2</sub>O, with respect to exposure time.

## References

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