

## Real-Time Observation of Surface Chemical Reaction with 33-ms Time Resolution by Means of Wavelength-Dispersive X-Ray Absorption Spectroscopy

A wavelength-dispersive near-edge X-ray absorption fine structure (NEXAFS) technique has been developed in the soft X-ray region, which enables real-time observation of surface chemical reactions with 33-ms time resolution. Continuous data acquisition is achieved for a single event of the reaction without repetition. The time evolution of the coverages of surface adsorbates is observed during the CO oxidation reaction on Ir(111). We have demonstrated that surface chemical reactions, which complete in several seconds, can be quantitatively traced by this spectroscopic technique.

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is one of the most powerful techniques to investigate the chemical state and amount of surface adsorbates, owing to the characteristic spectral features depending on chemical species. It takes several minutes, however, to obtain a NEXAFS spectrum by the conventional method, in which the photon energy is scanned step by step at each data point, making it difficult to trace fast surface reactions. Recently, a wavelength-dispersive NEXAFS technique has been developed in the soft X-ray region [1], and several kinds of surface chemical reactions have been investigated at a time resolution of several seconds. In the present report, we demonstrate that the time resolution has been improved to 33 ms, owing to the brilliant soft X-rays from an undulator [2].

All of our experiments were performed in an ultrahigh vacuum chamber, which was connected to the undulator beamline, BL-16A [3]. An Ir(111) single crystal was cleaned by repeated cycles of Ar<sup>+</sup> sputtering, annealing at 1200 K and O<sub>2</sub> treatment in 3×10<sup>-7</sup> Torr at 650 K. The clean Ir(111) surface was first dosed with O<sub>2</sub> at 350 K in order to prepare the atomic-O covered Ir(111) surface. The O/Ir(111) surface was then exposed to CO and the NEXAFS spectra were continuously recorded at every 33 ms (30 Hz) during the CO oxidation process. The horizontally polarized X-rays from an APPLE-II type undulator were used, and the magic-angle incidence condition was adopted, in which the angle between the electric vector and the sample surface is 55°.

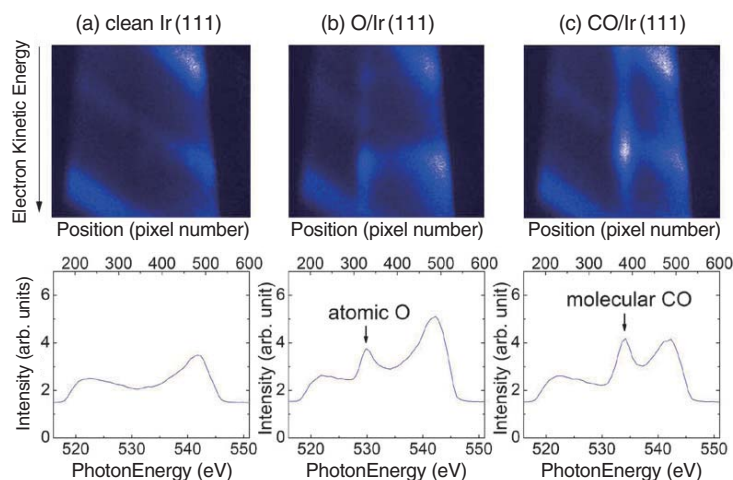


Figure 1 Two-dimensional image on the electron detector (top) and Auger-electron-yield NEXAFS spectrum obtained by integrating the image along the electron kinetic energy (bottom). The position on the sample corresponds to the photon energy.

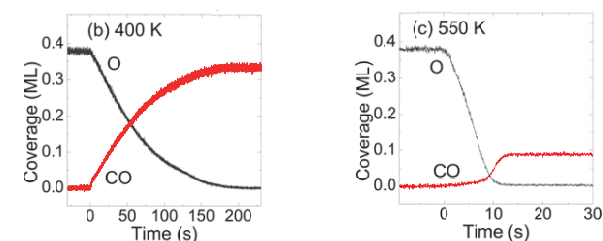
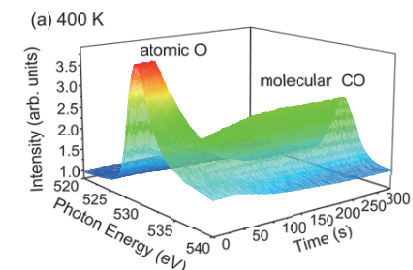


Figure 2 Three-dimensional plot of O K-edge NEXAFS spectra taken at every 33 ms during exposure of the O/Ir(111) surface to 4×10<sup>-7</sup> Torr CO at 400 K (a) and time evolution of O and CO coverages during the reaction at 400 K (b) and 550 K (c).

The principle of the wavelength-dispersive NEXAFS technique is described elsewhere [1]. In short, the wavelength-dispersed X-rays, in which the wavelength gradually changes depending on the position, illuminate the sample surface, and the Auger electrons emitted at each position on the sample are separately and simultaneously collected by a position-sensitive electron analyzer (SES-2002, Gammadata-Scienta). Since the number of Auger electrons is proportional to the X-ray absorption intensity, the NEXAFS spectrum can be obtained by plotting the Auger electron intensity as a function of the position on the sample, which corresponds to the photon energy. Typical images on the detector are shown in Fig. 1, which were taken around the O K edge, together with obtained NEXAFS spectra. Oblique lines in the image correspond to the photoemission peaks, while a smooth structure in the NEXAFS spectrum is mainly due to inhomogeneity of the electron detector. Such a structure appears also in the O/Ir(111) and CO/Ir(111) data, but can be cancelled by dividing the spectrum by that for clean Ir(111).

A set of NEXAFS spectra taken during the CO oxidation reaction at 400 K is shown in Fig. 2(a) as a three-dimensional plot. Only a peak corresponding to atomic O is found before the reaction, but it rapidly decreases when the surface is exposed to CO, and another peak grows, which is attributed to molecular CO. We fit each NEXAFS spectrum by using the O/Ir(111) and CO/Ir(111) data as references, and estimate the coverages

of atomic O and molecular CO on the surface at each moment. The obtained time evolutions of O and CO coverages during the reactions at 400 and 550 K are shown in Figs. 2(b) and 2(c), respectively. The reaction proceeds much faster at 550 K than at 400 K as expected, and the rate constants are estimated to be 8.3×10<sup>-2</sup> and 2.7×10<sup>0</sup>/ML·s at 400 and 550 K, respectively. From the rate constants at 375, 400, 425 and 550 K, the activation energy of the reaction is estimated to be 0.71±0.06 eV. We have thus demonstrated that surface chemical reactions, which complete in several seconds, can be quantitatively traced by the spectroscopic technique.

### REFERENCES

- [1] K. Amemiya, H. Kondoh, A. Nambu, M. Iwasaki, I. Nakai, T. Yokoyama and T. Ohta, *Jpn. J. Appl. Phys.* **40** (2001) L718.
- [2] K. Amemiya, Y. Kousa, S. Nakamoto, T. Harada, S. Kozai, M. Yoshida, H. Abe, R. Sumii, M. Sakamaki, and H. Kondoh, *Appl. Phys. Lett.* **99** (2011) 074104.
- [3] K. Amemiya, A. Toyoshima, T. Kikuchi, T. Kosuge, K. Nigorikawa, R. Sumii and K. Ito, *AIP Conf. Proc.* **1234** (2010) 295.

### BEAMLINE

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