

ACTIVELY-CONTROLLED OXIDATION OF Cu(100) WITH HYPERTHERMAL O₂ MOLECULAR BEAM

The dissociation process of an oxygen molecule (O₂) on a metal surface is of considerable research interest, both because many important industrial oxidation processes are heterogeneously catalyzed by transition metals (TMs) and because O₂ dissociation is the first step towards the corrosion of various TMs. Among TMs, Cu is one of the most important metals. Cu oxidation process must be elucidated because of the important role of Cu oxides in materials science, for example, high-T_c superconductors of cuprates and solar cells.

A Cu(100) can be oxidized in its bulk when exposed to ambient thermal O₂ molecules at temperatures above 450 K, and Cu₂O films can be grown epitaxially. However, high exposures of 10⁵-10⁶ L O₂ (1L = 1.33 × 10⁻⁴ Pa·s) are required for an oxide-film growth on Cu(100) under a thermal O₂ atmosphere, suggesting the low efficiency of oxidation. Here, we demonstrate actively-controlled oxidation of Cu with a hyperthermal O₂ molecular beam (HOMB) [1-4].

All experiments were performed using the surface reaction analysis apparatus (SUREAC~2000) constructed at beamline BL23SU. After the irradiation of a proper amount of HOMB along the surface normal, high-resolution X-ray photoemission spectroscopy (XPS) spectra were measured at ~300 K using synchrotron radiation (SR) with the photon energy of 760.3 eV.

Figures 1(a) and 1(b) show the oxygen-coverage (θ) dependence of representative O-1s XPS spectra and the O-uptake curve determined from the integration of such O-1s spectra in the 2.3-eV-HOMB irradiation on the Cu(100) surface at ~300 K, respectively. In Region I in Fig. 1(b), the O-1s peak, fitted well with a symmetric single component (see the spectrum at $\theta = 0.47$ ML in Fig. 1(a)), decreases in its full width at half maximum (FWHM) with increasing θ . In $\theta \geq 0.5$ ML (Region II), the oxidation of Cu progresses very slowly as seen in Fig. 1(b). We have tried to separate the O-1s peak into two components (see the spectrum at $\theta = 0.95$ ML in Fig. 1(a)). One component (blue solid line) located at the binding energy of 529.5 eV corresponds to the surface O atoms and has the same line shape as the single component (red solid line) at $\theta = 0.47$ ML, as shown in Fig. 1(a). The other component (blue dashed line in Fig. 1(a)) centered at 530.1 eV with nearly the same FWHM as the surface

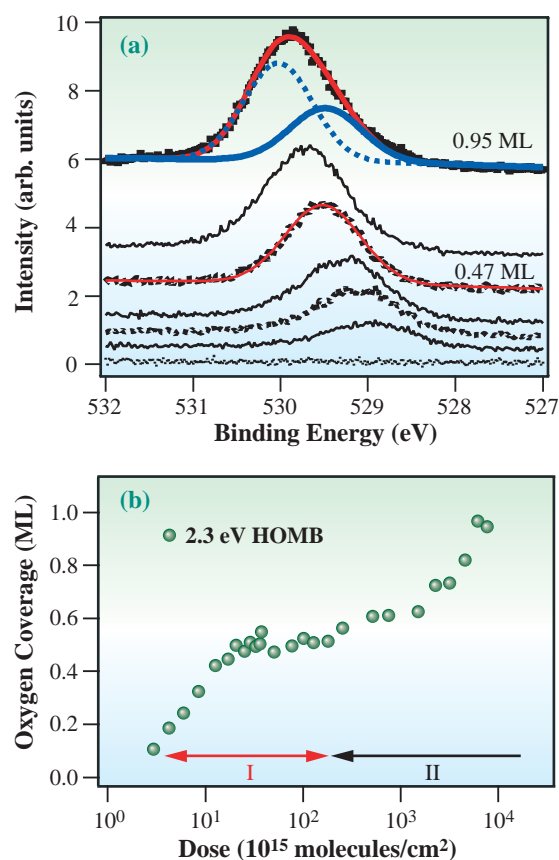


Fig. 1. (a) O-coverage dependence of the O-1s XPS spectra for the 2.3-eV-HOMB incidence along the surface normal on Cu(100) at ~300 K. The spectra correspond to 0, 0.19, 0.32, 0.42, 0.47, 0.73, and 0.95 ML from the bottom. The spectra at $\theta = 0.47$ and 0.95 ML are separated into single (red solid line) and double components (blue solid and dashed lines), respectively. The red solid line at $\theta = 0.95$ ML indicates the sum of the double components. (b) O-uptake curves on Cu(100) for 2.3 eV HOMB incidence. Regions I and II are indicated by the arrows.

component is assigned to the subsurface and/or bulk O atoms that initiate a growth of Cu₂O.

What happens in the slow oxidation into subsurface and/or bulk? We propose that a *collision-induced-absorption mechanism* may explain the slow oxidation process of Cu in Region II. In this mechanism, an incident O₂ molecule collides with a preadsorbed O atom impulsively with a small impact parameter. The energy transfer from the incident particle to a

preadsorbed O atom occurs effectively and as a result, the produced energetic O atom penetrates into the subsurface leaving a vacant site for further dissociative adsorption on the surface.

We directly confirmed this collision-induced-absorption mechanism as follows. Figure 2 shows the O-1s spectra measured with a high resolution after the 3-eV-Ar-beam incidence along the surface normal on the $2 \times 2 \times 2$ R45° surface ($\theta = 0.5$ ML) at ~ 300 K. The symmetric O-1s shape (see the spectrum at $\theta = 0.47$ ML in Fig. 1(a)) turned into an asymmetric shape after the exposure of the $2\sqrt{2} \times \sqrt{2}$ R45° surface to 3-eV Ar. This asymmetric shape is attributed to the

above-mentioned two components; one at 529.6 eV for surface O atoms and the other at 530.0 eV for the subsurface and/or bulk O atoms. This is the first example of the collision-induced-absorption mechanism in the oxidation process, although it is known that the energetic-collision process induces the dissociation of the preadsorbed O₂ molecule at low temperatures.

In summary, oxidation of Cu(100) by HOMB was investigated by high-resolution XPS with SR. We apply for the first time a collision-induced absorption mechanism to the oxidation of Cu into Cu₂O with the HOMB irradiation. Thus, we demonstrated the possibility of the actively-controlled oxidation by HOMB.

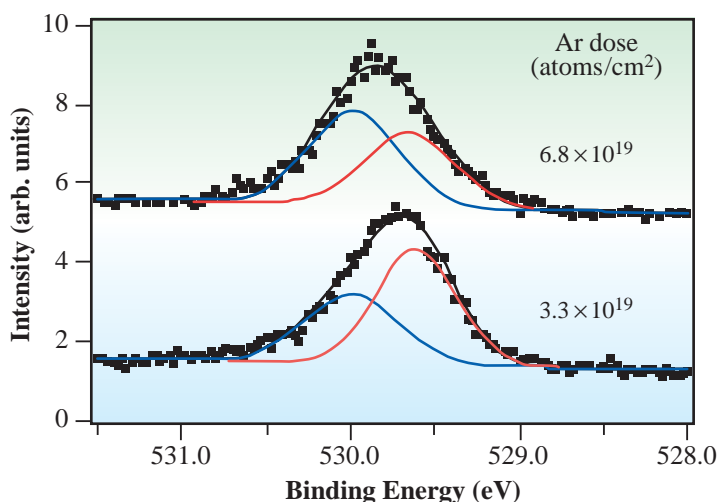


Fig. 2. O-1s XPS spectra measured after the 3 eV Ar-beam incidence along the surface normal on the $2 \times 2 \times 2$ R45° surface ($\theta = 0.5$ ML) at ~ 300 K. The lower and upper spectra correspond to the 3-eV-Ar exposures of 3.3×10^{19} and 6.8×10^{19} atoms/cm², respectively. Each spectrum can be separated into two components of surface (red line) and the subsurface and/or bulk (blue line) O atoms. Black lines indicate the fitted curves corresponding to the sums of the red and blue curves.

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