Revisit of XPS Studies of Supersonic O₂ Molecular Adsorption on Cu(111): Copper Oxides

Koki Hayashida, Yasutaka Tsuda, Takashi Yamada, Akitaka Yoshigoe, and Michio Okada

ABSTRACT: We report the X-ray photoemission spectroscopy (XPS) characterization of the bulk Cu₂O(111) surface and "8" and "29" oxide structures on Cu(111) prepared using a 0.5 eV O₂ supersonic molecular beam. We propose a new structural model for the "8" oxide structure and also confirm the previously proposed model for the "29" oxide structure on Cu(111), based on the O 1s XPS spectra. The detection angle dependence of the O 1s spectra supports that the nanopyramidal model is more preferable for the (√3 × √3)R30° Cu₂O(111). We also report electronic excitations that O 1s electrons suffer.

1. INTRODUCTION

To date, copper-based catalysts play important roles in various heterogeneous catalytic processes such as CO oxidation,¹–⁵ methanol synthesis,⁶–⁹ and so on. It was demonstrated that partially oxidized Cu improved the catalytic properties.¹⁰–¹⁵ Cu-based catalysts have been also the most effective for the Rochow reaction,¹⁶ which synthesizes dimethylchlorosilane for producing useful organosilicon products.¹⁷ Various types of Cu-based catalysts are designed and tested, including copper oxides.¹⁸,¹⁹

The oxidation of Cu has been intensively studied to obtain a fundamental aspect of the surface and bulk oxidation process.¹⁰,¹¹ At low temperatures, a molecularly adsorbed species forms on the Cu surface, while at room temperature, O₂ dissociates and reacts.¹² At low O surface coverages on Cu(111), O adatoms are preferentially adsorbed on the FCC threefold hollow sites.¹³,¹⁴ As the O coverage is further increased, disordered oxide structures are formed.¹⁵–¹⁷ The formation of honeycomb oxide phases, exhibiting five to seven defects and O vacancies, were also reported.¹⁸–²⁰ When the surface is saturated with O atoms at ~673 K, the "29" oxide structure with a long periodicity is formed.²¹,²²–²⁴ Moreover, the "8" oxide structure,²³ which was first reported by Judd et al., was not reproduced for a long time, was produced and studied using a hyperthermal molecular beam,²⁴–²⁶ which relaxes to the "29" structure after annealing to 620 K.²⁷ Here, the "29" and "8" structures are referred to as such because their unit cell areas are 29 and 8 times larger than the underlying Cu(111) unit cell. These structures are considered to be precursors to bulk Cu₂O growth, which begins to take place at high oxygen exposures, typically >10⁶ Langmuirs (1 Langmuir = 1 × 10⁻⁶ Torr·s).²⁷

Among these known copper oxide reconstructions, structural models for only the honeycomb and corresponding defective oxides,²⁸,²⁹,³⁰ for example, the "29" structure, and the Cu₂O(110)-like "8" structure,³¹ have been theoretically calculated and experimentally unraveled. The "8" structure can be produced only by energetic O₂ molecules²⁴–³⁶ so that the experimental approaches have been limited for elucidating its surface properties. Most of these oxide structures are Cu₂O(111)-like films that were distorted so that they could be commensurate with the underlying Cu(111) substrate.²⁰,³¹ The perfect Cu₂O(111) surface consists of connected hexagonal rings with a periodicity of 0.6 nm.³² The rings are

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made up of linear O−Cu−O bonds, which buckle, resulting in raised and depressed O atoms; however, when grown on Cu(111), this oxide film must distort to be commensurate with the Cu(111) substrate and take on the symmetry of the "29" oxide. Very recently, a new model, i.e., a nano-pyramidal model, was developed for the (√3 × √3)R30°Cu2O(111) surface. Here, we report on the X-ray photoemission spectroscopy (XPS) characterization of the bulk Cu2O(111) surface and "8" and "29" oxide structures on Cu(111) prepared using a 0.5 eV O2 supersonic molecular beam (SSMB) source. We reproduce the "8" structure, which can be prepared with energetic molecules. We discuss the obtained XPS results in comparison with the previously proposed structural models.

2. EXPERIMENTAL SECTION

We performed all experiments with the surface reaction analysis apparatus (SUREAC 2000) built at BL23SU in SPring-8 with a base pressure of <2 × 10⁻⁸ Pa. Briefly, our surface reaction analysis chamber has an electron energy analyzer (OMICRON EA125-SMCD) and a Mg/Al Kα twin-anode X-ray source (OMICRON DAR400). We also have a quadrupole mass spectrometer, for monitoring the molecular beam, located opposite the O2 SSMB source. We cleaned the Cu(111) (from SPL) and Cu2O(111) (from SurfaceNet GmbH) samples by repeated sputtering with 1.5 keV Ar⁺ and 20 min annealing at 773 K, until the low-energy electron diffraction (LEED) shows (1 × 1) and (√3 × √3)R30°, respectively, and no impurities were detectable by synchrotron radiation XPS (SR-XPS). We generated O2 SSMB by the adiabatic expansion of gas mixture of O2 and He from a nozzle with a small orifice at 300 K, obtaining a 0.5 eV O2 SSMB with a flux density of 4.9 × 10¹⁴ molecules cm⁻² s⁻¹. First, we irradiated the clean Cu(111) surface with 3.0 × 10¹⁸ molecules cm⁻² O2 SSMB (along the surface normal) at 300 K to produce the "8" structure. Second, the "8"-structure surface was annealed up to 620 K to produce "29" structure. We measured three kinds of oxide surface ("8", "29", and bulk Cu2O(111)) with LEED and SR-XPS. The SR-XPS measurements were performed at 300 K using four kinds of photon energies of 742, 903, 1111, and 1496 eV. The SR beamline is much improved compared to that at the previous report in 2008. The high-intensity focused X-ray beam enables us to measure the high-resolution XPS spectra in a short time with high S/N ratios and to perform the fine-peak deconvolution. The peak fitting was performed with UNIFIT 2002 software. All of the spectra were fitted with the Voigt function, defined as the convolution of a Lorentzian with Gaussian line shape. The background was subtracted by the Shirley method, as seen in Figure S1 in Supporting Information I. The simulated LEED patterns were drawn using the commercially available LEEDLab software.

3. RESULTS AND DISCUSSION

3.1. "8" Structure on Cu(111). Figure 1a–c shows the observed and simulated LEED patterns and the O 1s spectrum measured at surface normal and photon energy of 742 eV. Background subtracted using the Shirley method. (d) New ball model of the "8" structure.
is almost consistent with the expected O coverage of 0.5 ML for the “8” structure model. The O 1s peak can be separated into three components (A–C), which have the peak-shape parameters as shown in Table 1. The peaks A and B, having almost the same areal intensity, correspond to the surface and subsurface O atoms, respectively. The peak area is proportional to the number of subsurface and surface oxygen atoms. The previously proposed structural model,40 having only one kind of surface oxygen atoms, is not consistent with the O 1s spectrum, indicating the two kinds of O atoms (peaks A and B). Thus, we propose a new surface structure as shown in Figure 1d. The surface Cu atoms construct a square lattice. The O 1s binding energy (BE) of peak A (529.5 eV) agrees well with that (529.5 eV) of surface O atoms adsorbing on Cu(100).54 Moreover, the O 1s BE of the peak B (529.9 eV) also agrees well with that (530.1 eV) of the subsurface O atoms.54 The relative areal ratio of the peaks A and B is also consistent with the newly proposed “8” structure model in Figure 1d. No obvious photon energy dependence of the O 1s profile (peak A vs peak B) is observed (Supporting Information V: Table S2 and Figure S7) so that subsurface O atoms may be located at the position where the O 1s electrons are not attenuated significantly. The subsurface O atoms of the square-like “8” structure are located on various sites on the substrate Cu(111). This inhomogeneity of the adsorption sites makes the peak B broader (see Table 1) and smaller in height. The Cu L3M4,5M4,5 Auger electron spectrum (AES) in Figure S2 suggests the slight growth of the Cu oxide (Cu2O) precursor. The broad component C will be discussed later.

Table 1. Peak-Shape Parameter of Each O 1s Spectrum (Binding Energy and Full Widths at Half-Maximum of Gaussian and Lorentzian Components)

| component   | binding energy (eV) | GP-FWHM (eV) | LP-FWHM (eV) |
|-------------|---------------------|--------------|--------------|
| “8” structure |                     |              |              |
| peak A      | 529.5               | 0.56         | 0.30         |
| peak B      | 529.9               | 0.77         | 0.31         |
| peak C      | 532.7               | 2.83         | 0.10         |
| “29” structure |                   |              |              |
| peak A’     | 529.5               | 0.65         | 0.10         |
| peak B’     | 529.8               | 0.72         | 0.30         |
| peak C’     | 530.2               | 0.76         | 0.33         |
| Cu2O(111)   |                     |              |              |
| peak A”     | 529.2               | 0.67         | 0.10         |
| peak B”     | 530.4               | 0.64         | 0.34         |
| peak C”     | 535.3               | 3.26         | 0.10         |

Figure 2. (a) Observed (primary electron energy of 114 eV) and (b) simulated LEED pattern of the “29” structure and (c) the corresponding O 1s spectrum measured at surface normal and photon energy of 742 eV. Background subtracted using the Shirley method.52 (d) Ball model of the “29” structure.42
assign peak C’ to subsurface atoms of the Cu–O chains. No obvious photon energy dependence of the O 1s profile (peak A’, B’ vs C’) is observed (Supporting Information V: Table S2 and Figure S7). The O 1s electrons from the subsurface atoms are not attenuated due to the open structure. Then, peak B’ is considered to correspond to the surface O atoms of the Cu–O
chains. The relative areal ratio of the peaks A′, B′, and C′ is consistent with the “29” structure model. The estimated O coverage is 0.48 ML, corresponding to the adatom number (N) of N = 2 in the “29” structure model, while theoretical calculation proposed the most stable N = 5 model in Figure 2d. However, in the model structure at N = 2–4, more than three kinds of O atoms of Cu–O chains are proposed, which is inconsistent with the XPS result, suggesting the two O components of Cu–O chains. It is difficult to fit the O 1s XPS spectrum with more than three kinds of components (three kinds of O atoms) of Cu–O chains consistently. Therefore, the N = 5 model is the most probable one. Annealing without O2 supply and the resulting restructuring may lead to the island formation of the “29” structure, making the apparent surface total coverage become smaller due to the desorption. The Cu L3M4,5M4,5 AES in Figure S2 suggests the Cu2O-oxide feature of a “29” structure agrees well with that of an “8” structure. Both “29” and “8” structures are considered to be the precursors for the further growth of Cu oxide. The broad component D′ will be also discussed later.

The valence band spectrum in Figure S3 shows the decrease of the surface state observed for the clean Cu(111) from the “8” structure to the “29” structure. The surface coordination may be stabilized in the transition from the metastable “8” structure to thermally stable “29” structure.

3.3. Bulk Cu2O(O111) Surface. Figure 3a–c shows the observed and simulated LEED patterns and the O 1s spectrum of the clean bulk Cu2O(O111), respectively. The unit cell of the Cu2O(O111) is indicated by the yellow line in Figure 3a,b. In our preparation method, a sharp (√3 × √3)R30° pattern was observed. The O 1s peak can be separated into three components (A′−C′), which have the peak-shape parameters as shown in Table 1. The peaks A′ and B′ correspond to the surface O atoms and bulk O atoms.55 The previously proposed structural models are shown in Figure 3e.41,43,44,56 Figure 3c shows the detection angle dependence of the peak areal intensity ratio (A′/B′). Increasing the ratio with increasing angles is consistent that peak A′ corresponds to the surface-uncordinated O atoms. Moreover, it should be noted that our preliminary experiments demonstrate peak A′ on Cu2O(O111) disappearing after the chemical reactions where the surface O atoms become coordinated, further supporting this peak assignment. In Supporting Information III, we calculate the expected ratio (A′/B′) in a simple way assuming the structural models of Model I33,44 and Model II41,56 in Figure 3e and the calculated electron mean free path.

Experimental data in Figure 3d clearly fit well with the calculated values for Model I. This result supports Model I (a nanopyramidal model) where the capped O atom corresponds to peak A′, although our methods are very simple. The BE of peak A′ (529.2 eV) is also consistent with that of adsorbed O atoms (529.5 eV for peaks A and A′). The Cu L3M4,5M4,5 AES in Figure S2 featured the Cu2O oxide. The valence band spectrum in Figure S3, in comparison with that for the clean surface, shows the clear band gap at the Fermi level. The band gap can be obtained using the method proposed in ref 57 (see the details in Supporting Information IV and Figure S6). The obtained value is 2.6 eV, which agrees with the reported value of 2.1–2.6 eV.58–60 Thus, peak C′ corresponds to band-to-band excitations that the O 1s electrons suffer in the exit trajectory, while the peaks around the much higher binding energy of 546.4 eV (see Figures S4 and S5) may be due to the plasmon excitations57,61 of Cu2O. In Figure S5, the shape of the plasmon peak is compared to that of the valence band peak. It is interesting that the shape of both spectra agrees well with each other, suggesting the plasmon excitations reflecting the density of states of the initial band.

3.4. Electronic Properties of Oxidized Cu Surfaces. Now we return to peaks C (“8” structure) and D′ (“29” structure), which have a similar broad feature to peak C′. When we anneal the surface up to 773 K, the peaks C and D′ still survive, and therefore, the peaks C and D′ cannot be due to OH species.52 Thus, we assign the peak C and D′ to d-band-to-Fermi level (E_F) excitations that the O 1s electrons suffer (see Figure S6) in the exit trajectory. The electrons excited from the surface O 1s state are back-scattered from the bulk Cu under the surface and then suffer the energy loss corresponding to d-band-to-E_F excitations. The energy difference between the O 1s peak and the peaks C and D′ is about 3.1 eV, which is almost the energy difference between d-band and E_F (see Figure S6). These features may correspond to the interfacial plasmons between “8” or “29” Cu–O chains and the Cu substrate. The peak areal intensity ratios (peak C, D′, C′/ main O 1s peak) are almost independent of the incident photon energy as shown in Table S1 in Supporting Information V. Thus, the O 1s photo-electron energy (200–970 eV) does not affect the excitation cross sections of occupied d-band electrons.

4. SUMMARY

We performed the X-ray photoemission spectroscopy (XPS) characterization of the bulk Cu2O(O111) surface and “8” and “29” oxide structures on Cu(111) prepared using 0.5 eV O2 SSMB. We proposed the new structural model for the “8” structure and also confirmed the previously proposed model for the “29” structure, based on each O 1s spectrum. From the dependence of detection angle on the O 1s spectra, we concluded that the nanopyramidal model is more preferable for the (√3 × √3)R30° Cu2O(O111). We also identified the electronic excitations that the O 1s electrons suffer during the exit trajectory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04663.

O 1s SR-XPS spectra, Cu L3M4,5M4,5 Auger electron spectra and valence band spectra of “8” and “29” structures and bulk Cu2O(O111), estimation of peak intensity ratio (surface vs bulk) of O 1s from the Cu2O(O111) surface, estimation of IMFP of O 1s electrons, wide range of O 1s and the band gap of the oxide, and peaks in O 1s spectra of “8” and “29” structures and bulk Cu2O(O111) (PDF)

AUTHOR INFORMATION

Corresponding Author

Michio Okada — Department of Chemistry, Graduate School of Science and Institute for Radiation Sciences, Osaka University, Toyonaka, Osaka 560-0043, Japan;

orcid.org/0000-0002-7689-4288; Email: okada@chem.sci.osaka-u.ac.jp

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Authors
Koki Hayashida — Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan
Yasutaka Tsuda — Materials Sciences Research Center, Japan Atomic Energy Agency, Sayo-gun, Hyogo 679-1S48, Japan
Takashi Yamada — Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan; orcid.org/0000-0001-9419-555S
Akitaka Yoshiohe — Materials Sciences Research Center, Japan Atomic Energy Agency, Sayo-gun, Hyogo 679-1S48, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c04663

Notes
The authors declare no competing financial interest.

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