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Species formed at cuprite fracture surfaces; observation of O 1*s* surface core level shift

Sarah L. Harmer [a], William M. Skinner [a], Alan N. Buckley [b,*], Liang-Jen Fan [c]

[a] Ian Wark Research Institute, ARC Special Research Centre for Particle and Material Interfaces, University of South Australia, Mawson Lakes, SA 5095, Australia
[b] School of Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia
[c] National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

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ABSTRACT

Surfaces of mineral cuprite prepared by fracture under UHV have been characterised by synchrotron XPS and near-edge X-ray absorption spectroscopy before and after exposure to ambient air. Before exposure of the cuprite, the Cu 2*p* photoelectron and Cu $L_{2,3}$-edge absorption spectra were consistent with Cu^{I} with very little d^9 character. Surface-enhanced O 1*s* spectra from the unexposed mineral revealed a surface species, with binding energy 0.95 ± 0.05 eV below the principal cuprous oxide peak, assigned to under-coordinated oxygen. A second surface species, with binding energy about 1 eV higher than the principal peak, was assigned to either hydroxyl derived from chemisorbed water vapour or surface oxygen dimers produced by restructuring of the cuprite fracture surface. The width of the principal O 1*s* peak was 0.66 ± 0.02 eV. The observed Cu L_3- and O K-edge absorption spectra were in good agreement with those simulated for the cuprite structure. After exposure of the fracture surface to ambient air, the low binding energy O 1*s* surface species was barely discernible, the original high binding energy O 1*s* surface species remained of comparable intensity, new intensity appeared at an even higher ($\sim$1.9 eV) binding energy, and the Cu $L_{2,3}$-edge spectrum indicated the presence of Cu^{II}, consistent with the formation of a thin surface layer of $Cu(OH)_2$.

1. Introduction

The surface chemical composition of cuprite, nominally Cu_2O but more correctly $Cu_{2-x}O$, is of importance for a number of fundamental and technological reasons. Because cuprite is a *p*-type semiconductor with an optical band gap of about 2 eV at ambient temperature [1], it is one of the few metal oxides that are sufficiently conducting to allow O 1*s* and metal core level photoelectron spectra from bulk fracture surfaces to be observed without the peaks being broadened discernibly by non-uniform charging. Also because of its particular semiconducting properties, cuprous oxide is a potentially suitable photocathode for hydrogen production from water [2], however, polycrystalline thin films are more suitable than cuprite single crystals for this application because of the instability of the latter when illuminated in an aqueous solution arising from photoreduction to Cu^0 [3]. Cuprous oxide has several other interesting physical properties, and consequently it has been extensively studied, but mostly as a thin film prepared by one of numerous methods such as oxidation of a Cu metal substrate or as an electrodeposited layer e.g. [1,4,5]. Cuprite is also one of the minerals found in the oxidised zones of copper sulfide deposits, and hence its behaviour as fine particles during the concentration by flotation of a mixed copper sulfide and oxide ore is of commercial importance. Accordingly, in research designed to optimise the flotation of these minerals, the surface chemical composition and reactivity of cuprite in air and air-containing aqueous solutions are of considerable interest.

It is generally accepted that cuprite is normally copper-deficient to some extent [6–8], but thin film cuprous oxide can be much more Cu-deficient than mineral cuprite. Thus, the surface chemistry and reactivity of cuprous oxide thin films are not necessarily the same as those of mineral cuprite or bulk crystalline cuprous oxide. Nevertheless, notwithstanding the importance of cuprite, the nature of its surfaces before and after exposure to air under ambient conditions has been little studied by means of high resolution and surface-enhanced spectroscopic techniques such as synchrotron XPS (SXPS). Cuprous oxide is thermodynamically unstable relative to cupric oxide in the presence of oxygen and water, consequently a surface layer of a Cu^{II}—O species might be expected to form when a fresh cuprite surface is exposed to air under ambient conditions.

In addition to cuprite, few high-resolution surface-optimised SXPS studies have been performed on clean surfaces of other bulk metal oxide semiconductors of band gap less than 2.5 eV. Characterisation of an essentially unaltered and uncontaminated surface

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* Corresponding author. Tel.: +61236854645; fax: +61293856141.
E-mail address: a.buckley@unsw.edu.au (A.N. Buckley).

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requires preparation by fracture under clean UHV, and of the few semiconducting or conducting metal oxides that have been investigated by XPS in this way, most have had the photoemission excited by Mg K_α or mono-chromatised Al K_α radiation. O 1*s* photoelectrons of ~937 eV kinetic energy are not optimised for surface sensitivity; a photon energy within the range 575–600 eV would be required for maximum surface sensitivity of those photoelectrons. Of the investigations in which O 1*s* spectra were determined with a photon energy below 650 eV, such as that of magnetite surfaces by Kendelewicz et al. [9], few have involved the characterisation of a surface prepared by fracture under UHV and not 'cleaned' by means of ion beam sputtering and subsequent annealing. An O 1*s* spectrum from a clean MgO(1 0 0) surface prepared by cleaving a single crystal under UHV was determined at a photon energy of 620 eV by Liu et al. [10], but because of the 7.8 eV band gap of MgO, a flood gun had to be used. The O 1*s* spectrum they obtained was broad (~1.5 eV) and featureless, but asymmetric on the high kinetic energy side possibly because of a surface component (or non-uniform charge compensation). Thus it is not surprising that there have been no reports, to our knowledge, of O 1*s* surface shifts for bulk metal oxides.

Surface-optimised O 1*s* spectra from thin oxide films prepared *in situ* have been reported. Of particular note is the study of the under-coordinated atoms exposed at the $RuO_2(1\,1\,0)$ surface produced by exposing a single crystal Ru(0 0 0 1) surface to O_2 at elevated temperatures [11]. The photon energy used for the O 1*s* spectrum was 665 eV and the total resolution was 0.38 eV. For the 'almost complete' RuO_2 film, the 3-fold coordinated lattice O 1*s* binding energy was 529.50 eV, but a small (intensity <10%) component at 528.79 eV (−0.71 eV shift) was assigned to under-coordinated O at the surface (the bridging O atoms coordinated to 2 rather than 3 Ru atoms). This assignment was supported by DFT calculations [11,12]. Although not specified [11], the O 1*s* linewidth appeared to be ~0.75 eV, and a shoulder arising from the low binding energy component was just discernible in the spectrum.

In the work reported here, surfaces of relatively pure mineral cuprite were prepared by fracture under clean UHV and surface-enhanced photoemission spectra obtained using synchrotron radiation before and after the fracture surfaces were exposed to air under ambient conditions. Partial electron yield NEXAFS spectra were also obtained at essentially the same time on the same specimen surfaces. *Ab initio* calculations were undertaken to enable simulation of the Cu L_3- and O K-edge absorption spectra to confirm interpretation of the corresponding experimental spectra, and to obtain densities of states that were as representative as possible of the ground-state electronic structure. Some previously reported partial density of state calculations for cuprite had displayed significant differences within the first few eV above the Fermi level (E_F).

2. Experimental details

2.1. Cuprite mineral

The cuprite used in the investigation was a massive, crystalline specimen from the Red Dome Mine, Chillagoe, Queensland, Australia. Bulk analysis of the mineral by ICP-MS confirmed the high purity of the sample investigated; no minor element was present at a concentration greater than 0.6 mg kg^{-1} and only a few had a concentration above 0.1 mg kg^{-1}. For the preparation of a fracture surface, a sample of approximate size 3 × 3 × 5 mm was mounted in a vice-like specimen holder designed for use in the double blade cleaving stage attached to the rotary distribution chamber of the Australian Synchrotron Research Program (ASRP) soft X-ray spectroscopy end-station.

2.2. Spectroscopic measurements

The vacuum in the rotary distribution chamber during surface preparation by fracture and in the analysis chamber during surface characterisation was $<3 \times 10^{-10}$ torr. The SXPS and NEXAFS spectroscopic measurements were carried out in the ASRP soft X-ray spectroscopy end-station while connected to beam-line 24A at the NSRRC in Hsinchu, Taiwan or 14ID at the Australian Synchrotron (AS). BL24A is a bending magnet, wide range beam-line incorporating a grating monochromator. The synchrotron was operated in continuous top-up mode. BL14ID is also a wide range, grating monochromator beam-line, but it has an elliptically polarising undulator source. On BL14ID, the beam linewidth would have been less than 0.1 eV at 600 eV, ~0.2 eV at 1100 eV and ~0.3 eV at 1500 eV. The ASRP end-station, constructed by OmniVac and PreVac, is equipped with a SPECS Phoibos 150 electron energy analyser and an OmniVac UHV-compatible partial yield detector based on a multichannel plate behind retarding grids. Electron analyser pass energies of 2 or 5 eV were used for O 1*s* spectra, and 5, 10 or 20 eV for other narrow range spectra. Binding energies are reported relative to a Cu $2p_{3/2}$ value of 932.6 eV for Cu metal. The Cu $L_{2,3}$-edge NEXAFS spectra are shown with the true photon energy established via the absorption current monitored concomitantly by a Cu metal mesh in the beam-line, but un-normalised by the flux incident on a Au mesh also in the beam-line. The O K-edge spectra are also shown un-normalised to avoid spectral artefacts caused by oxygen-containing species on each mesh. During operation of the NEXAFS detector, negative grid potentials of 0.4 and 1.1 kV were used for O K-edge partial electron yield (PEY) and total fluorescence yield (TFY) spectra, respectively, while 0.75 and 1.5 kV were used for the corresponding Cu $L_{2,3}$-edge spectra.

2.3. Fitting of core photoelectron spectra

The CasaXPS (Version 2.3.5) software was used to fit photoelectron spectra. The background in narrow range spectra could be accommodated either by a linear or Shirley function. In agreement

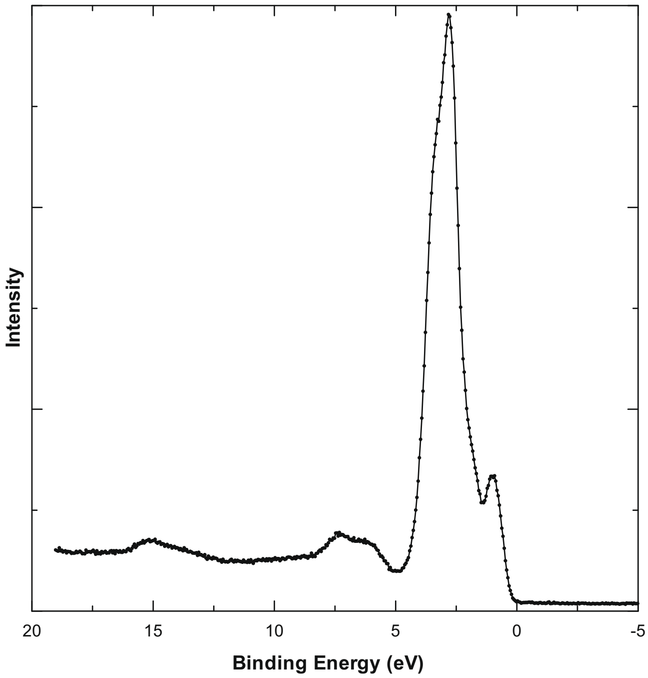

Fig. 1. Cuprite valence band spectrum determined at a photon energy of 610 eV.