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In situ X-ray absorption spectroscopic studies of copper in a copper-rich sludge during electrokinetic treatments

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Speciation of copper in a copper-rich chemical-mechanical polishing sludge during electrokinetic treatment has been studied by *in situ* extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy. The least-squares-fitted XANES spectra indicate that the main copper species in the sludge are $Cu(OH)_2$ (74%), nanosize CuO (20–60 nm) (13%) and CuO (>100 nm) (13%). The average bond distance and coordination number (CN) of Cu—O are 1.96 Å and 3.5, respectively. Under electrokinetic treatment (5 V cm^{-1}) for 120 min, about 85% of the copper is dissolved in the electrolyte, 13% of which is migrated and enriched on the cathode. Notably the copper nanoparticles in the sludge can also migrate to the cathode under the electric field. By *in situ* EXAFS, it is found that during the electrokinetic treatment the bond distance and CN of Cu—O are increased by 0.1 Å and 0.9, respectively.

Keywords: copper; electrokinetic; CMP; XANES; EXAFS.

1. Introduction

A grinding slurry containing 5–10% of very fine particles is generally used for chemical-mechanical polishing (CMP) of wafers in the semiconductor industry. Chemicals such as pH buffer (KOH, NH_4OH and organic acid), oxidizer [such as H_2O_2, $Fe(NO_3)_3$ and KIO_3] and surfactants (Zhang *et al.*, 2009) are also used to maintain a desired stability of suspended solids in the grinding slurry. Dispersed powders, dissolved metal ions, or chemicals may be adsorbed on the surfaces of wafers during the CMP process. High-purity water is therefore utilized to remove these foreign materials from wafers. Thus, a large amount of relatively difficult-to-treat sludges is frequently discharged from the CMP wastewater treatment processes (such as coagulation, flocculation, flota-tion, microfiltration and ultrafiltration). Extraction or recovery of copper from the CMP sludges using ion exchange methods has been investigated (Rengaraj & Moon, 2002; Jha *et al.*, 2009). However, scaling up these processes suffers from a relatively low economical attraction.

Electrokinetic treatment has been considered a promising and cost-effective method for *in situ* remediation of contaminated soils (Acar & Alshawabkeh, 1993; Lageman, 1993; Trombly, 1994; Reddy & Ala, 2005). The electrokinetic method has also been used in treatments or recovering of valuable materials from sludge wastes (Kim *et al.*, 2002). However, a fundamental understanding of the electrokinetic process is still lacking in the literature.

Speciation data such as bond distance, coordination number (CN) and chemical identity of select elements in the complex matrix can be determined by extended X-ray absorption fine structure (EXAFS) spectroscopy. X-ray absorption near-edge structure (XANES) spectra can also provide information about oxidation states of an excited atom, coordination geometry, and local bonding environment in complicated solids. Using EXAFS and XANES, it was found that copper oxides (in ZSM-5 or ZSM-48) are involved in the catalytic decomposition of NO and oxidation of chlorophenols in supercritical water (Lin & Wang, 2000; Huang *et al.*, 2003). Mineralization of CCl_4 with CuO was also determined by *in situ* EXAFS (Chien & Wang, 2001). These EXAFS and XANES data turn out to be very useful in revealing speciation of copper and its possible reaction pathway during miner-alization and catalysis.

The main objective of the present work was to investigate speciation of copper in the electrokinetic treatment of the sludge by *in situ* EXAFS and XANES. An *in situ* EXAFS cell was used to reveal the structural change of copper during the electrokinetic process. The molecule-scale data are expected to be useful in understanding the recovering process of copper from the copper-rich CMP sludge wastes.

2. Experimental method

The CMP sludges were sampled from a semiconductor plant in southern Taiwan. The samples were dried in air at 300 K for

three days, ground with a mortar and sieved with a 2 mm screen. The sludge samples were packed in an electrokinetic cell and filled with 0.01 M potassium nitrate (99%, Fluka) as a conductive solution. A DC voltage of 100 V was constantly applied to the electrodes (voltage gradient 5 V cm^{-1}). After 120 min of electrokinetic treatment, the sludge was immediately sliced into five portions of equal length. Clay minerals of the sludge were determined using an X-ray powder diffraction (XRD) (Rigaku Model D/MAX III-V) spectrometer which was scanned from 5 to 60° (2θ) at a scan rate of 4° min^{-1}. *In situ* XAS spectra of copper were taken using a home-made *in situ* EXAFS cell (Liu & Wang, 2008) which could be moved precisely to obtain a similar optical path. In the present study the X-ray beam was fixed at a point near the anode section (1.5 cm from the anode).

The *in situ* XANES and EXAFS spectra of copper under the electric field were collected on the wiggler beamline at the Taiwan Synchrotron Radiation Research Center. The electron storage ring was operated at an energy of 1.5 GeV. A Si(111) double-crystal monochromator was used for selection of energy with an energy resolution of 1.9×10^{-4} (eV/eV). The absorption spectra were collected using ion chambers that were filled with helium and nitrogen mixed gases. The beam energy was calibrated against the first inflection point of a Cu foil spectrum at 8979 eV.

The EXAFS data were analyzed using the *UWXAFS3.0* (Stern *et al.*, 1995) and *FEFF8.0* simulation programs (Ankudinov *et al.*, 1998). The isolated EXAFS data were normalized to the edge jump and converted to the wave-number scale. A Fourier transform was performed on k^3-weighted EXAFS oscillations in the range 3.5–11.5 Å^{-1}. To reduce the number of fit variables, the many-body factor (S_0^2) was fixed at 0.9. Fits of model compounds (such as CuO) have an error of ± 0.01 Å in radius and of $\pm 10\%$ in coordination number (CN) for the first-shell atoms and of ± 0.02 Å and $\pm 25\%$ for the second-shell atoms. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter.

The absorption edge was determined at the inflection point (precisely determined by the derivative) of the XANES spectra after pre-edge baseline subtraction and normalization to the maximum pre-edge intensity. Principal component analysis and least-squares fitting were used in the data treatment to optimize the quantitative extraction of relative concentrations of copper species (Scheinost *et al.*, 2002; Beauchemin & Kwong, 2006). XANES spectra of related model compounds were also measured. Analyses were carried out qualitatively by comparing spectra of model compounds with those of the *in situ* spectra. Semi-quantitative analyses of the edge spectra were conducted by the least-squares fitting of linear combinations of model compound spectra to the spectrum of the sample. The height and area of the near-edge band in the copper spectrum were proportional to the amount of copper species. The near-edge $3d$–$4p$ mixing peaks from the experimental absorption edge were fit. A calibration curve could, therefore, be obtained. On average, an

uncertainty limit of 5% corresponds to an error of 2.0% in the fit results.

3. Results and discussion

The X-ray diffraction patterns of the CMP sludge prior to and after the electrokinetic treatment are shown in Fig. 1. Alumina (Al$_2$O$_3$) and Cu(OH)$_2$ were found in the sludge. Little nano-size copper was observed. After 120 min of the electrokinetic treatment, the XRD intensities of Cu(OH)$_2$ were decreased to a great extent, suggesting that most of the Cu(OH)$_2$ species may be dissolved in the aqueous phase. The enhanced disso-lution of Cu(OH)$_2$ can be attributed to the high concentration of H$^+$ near the anode yielded from electrolysis of water. Nevertheless, the chemical structure of copper in the CMP sludge cannot be revealed in detail owing to the complex matrix of the sludge.

To obtain a better understanding of copper in the sludge during the electrokinetic treatment, *in situ* XANES and EXAFS spectra were also measured. In Fig. 2 the pre-edge XANES spectra of copper in the sludge exhibit a very weak $1s$-to-$3d$ transition (8977 eV), which is forbidden by the selection rule in perfect octahedral symmetry (Lin & Wang, 2000; Huang & Wang, 2003; Liu & Wang, 2004). A shoulder at 8986 eV and an intense band at 8992 eV can be attributed to the $1s$-to-$4p_z$ and $1s$-to-$4p_{xy}$ transitions of Cu(II), respectively (Furnare *et al.*, 2005; Strawn & Baker, 2008). After 120 min of the electrokinetic treatment, the first maximum derivative of the XANES spectrum at 8986 eV is not prominent, possibly owing to perturbation of the copper octahedron (CuO$_6$).

The XANES spectra of copper are also expressed mathe-matically by linear combination XANES fit vectors, using the absorption data within the energy range 8970–9040 eV (Fig. 2). XANES spectra of copper model compounds [nanosize CuO, CuO, Cu^{2+} (10 mM, pH = 6), Cu(NO)$_3$, CuCO$_3$, CuSO$_4$, CuCl$_2$, Cu(OH)$_2$, Cu$_2$O and Cu foil] (see Fig. 3) were also measured on the wiggler beamline. It is found that Cu(OH)$_2$ (74%), nanosize CuO (13%) and CuO (13%) are the main copper
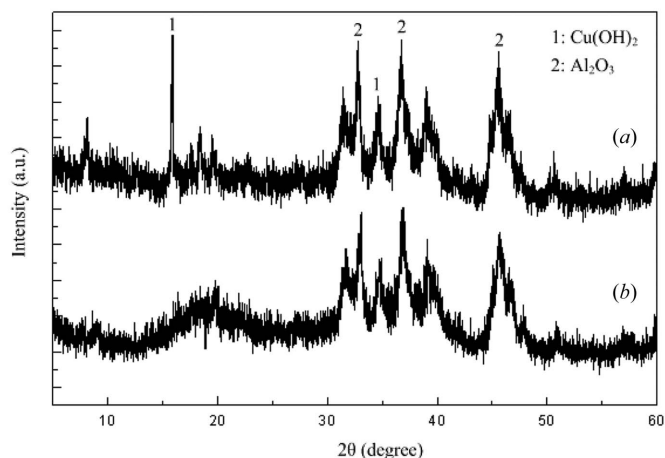

Figure 1
XRD patterns of the CMP sludge (*a*) prior to and (*b*) after (120 min) the electrokinetic treatment.
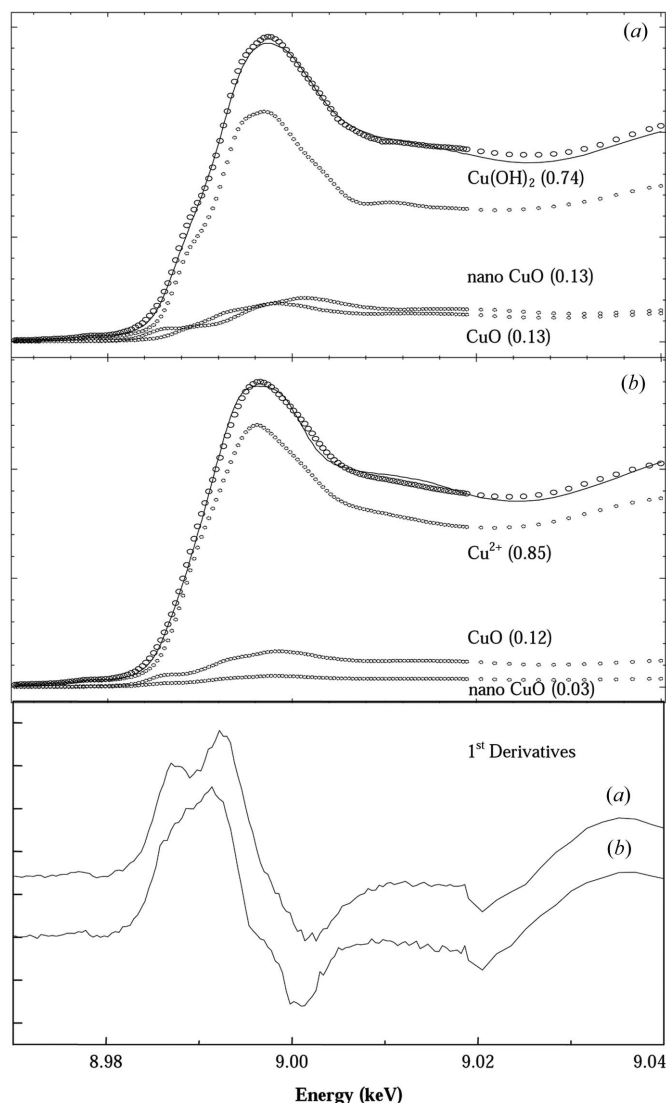
Figure 2
In situ XANES spectra and their first derivative of copper in the CMP sludge (*a*) prior to and (*b*) after (120 min) the electrokinetic treatment. Solid lines and circles represent experimental data and the least-square fits, respectively.

Figure 3
X-ray absorption near-edge structure spectra of copper model compounds.

Figure 4
Time dependence for (*a*) dissolution and (*b*) migration of Cu(II) in the sludge during the electrokinetic treatment.

species in the sludge. Most of the $Cu(OH)_2$ is dissolved in the aqueous phase (aqueous Cu^{2+}) after 120 min of the electrokinetic treatment. Interestingly, fractions of the nanosize CuO in the sludge are decreased by about 10%. It seems that the nanosize CuO has a greater mobility than the bulky CuO under the 5 V cm^{-1} electric field. This difference may be due to at least two possibilities: (i) the greater dissolution rate of the nanosize CuO, and (ii) the nanosize CuO may be migrated to the cathode directly. About 85% of the copper species are dissolved in the aqueous phase, 13% of which are migrated and enriched on the cathode after 120 min of the electrokinetic treatment.

Combined data of the time-dependent copper concentration and *in situ* XANES, the time-dependent dissolution and migration of Cu(II) in the sludge during the electrokinetic treatment are shown in Fig. 4. The dissolution and electromigration rates of copper [mainly Cu(II)] in the sludge are 4.0
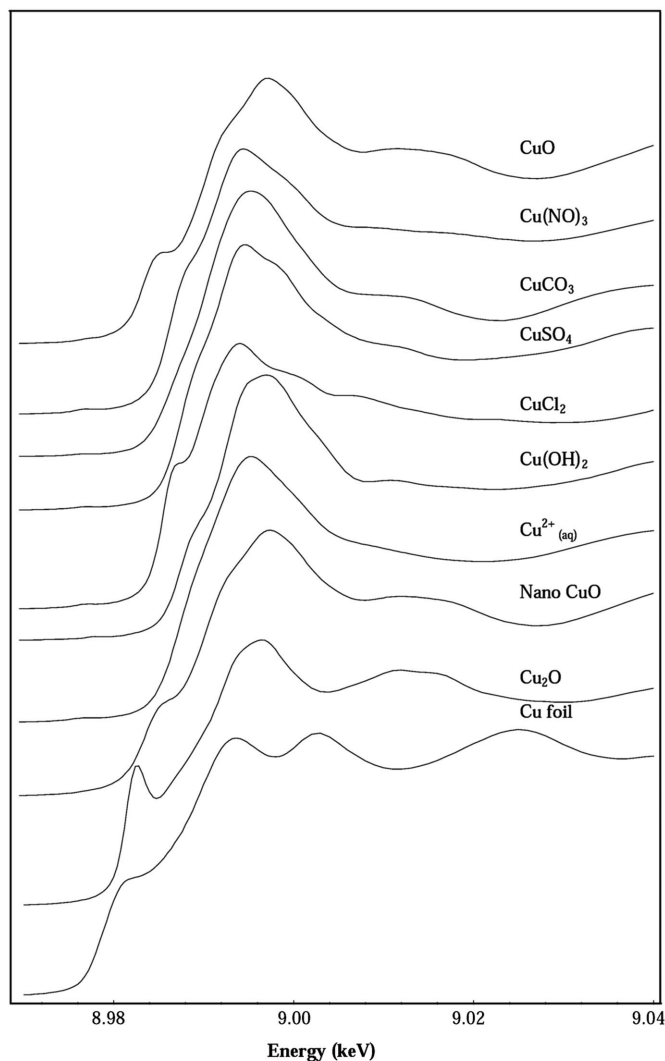
and 0.4 mmol h^{-1} g^{-1}, respectively. It seems that electromigration may be the rate-determining reaction in the electrokinetic process. The relatively slow electromigration of
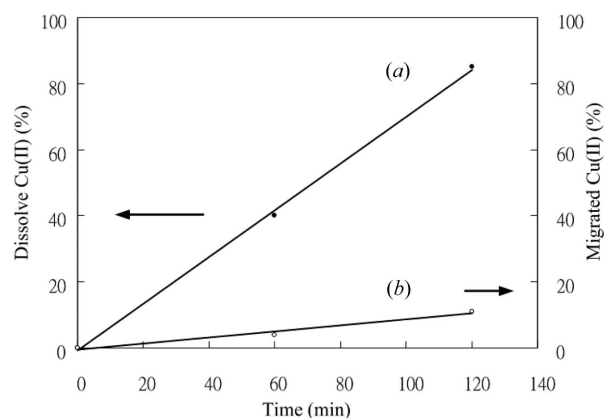
copper in the sludge may be due to re-adsorption of Cu^{2+} on the sludge.

The *in situ* EXAFS spectra of copper in the sludge were also recorded and analyzed in the k range 3.5–11.5 Å^{-1}. A >95% reliability of the Fourier-transformed EXAFS data fitting for copper was obtained. In all EXAFS data analyses, the Debye–Waller factors ($\Delta\sigma^2$) are less than 0.01 Å^2 (Table 1). The k^3-weighted Cu K-edge χ spectra and corresponding radial structure functions of the sludge prior to and after the electrokinetic treatments are shown in Fig. 5. The feature centered at about 1.49–1.55 Å arises from the first-shell Cu—O bonding, while the feature at 2.31–2.42 Å may be attributed to the second-shell Cu—(O)—Cu bonding. Fits of the *in situ* spectra to the EXAFS equation can identify bond distance and CN of copper in the sludge during the electrokinetic treatment. Table 1 shows that copper in the sludge possesses a Cu—O bond distance of 1.96 Å and a CN of 3.5. In the second shells the bond distance and CN of Cu—(O)—Cu are 2.49 Å and 0.9, respectively. Prolonging the treatment time to 120 min, the bond distance and CN of Cu—O are increased to 1.97 Å and 4.4, respectively. The observation indicated that

Table 1
In situ speciation data of copper in the CMP sludge during the electrokinetic treatment.

R: bond distance; CN: coordination number; σ^2: Debye–Waller factor.

Contact time (min)	Shells	R (Å)	CN	σ^2 (Å^2)
0	Cu—O	1.96	3.5	0.006
	Cu—(O)—Cu	2.49	0.9	0.008
60	Cu—O	1.96	3.6	0.006
	Cu—(O)—Cu	2.51	0.9	0.008
120	Cu—O	1.97	4.4	0.006
	Cu—(O)—Cu	2.66	0.7	0.008
Model compounds	Shells	R (Å)	CN	σ^2 (Å^2)
Bulk CuO	Cu—O	1.95	6.0	0.006
	Cu—(O)—Cu	3.04	12	0.008
Nano CuO	Cu—O	1.94	3.2	0.006
	Cu—(O)—Cu	2.58	4.9	0.008

nanosize copper in the sludge may migrate to the cathode, which leads to the increases of the average bond distances and CNs.
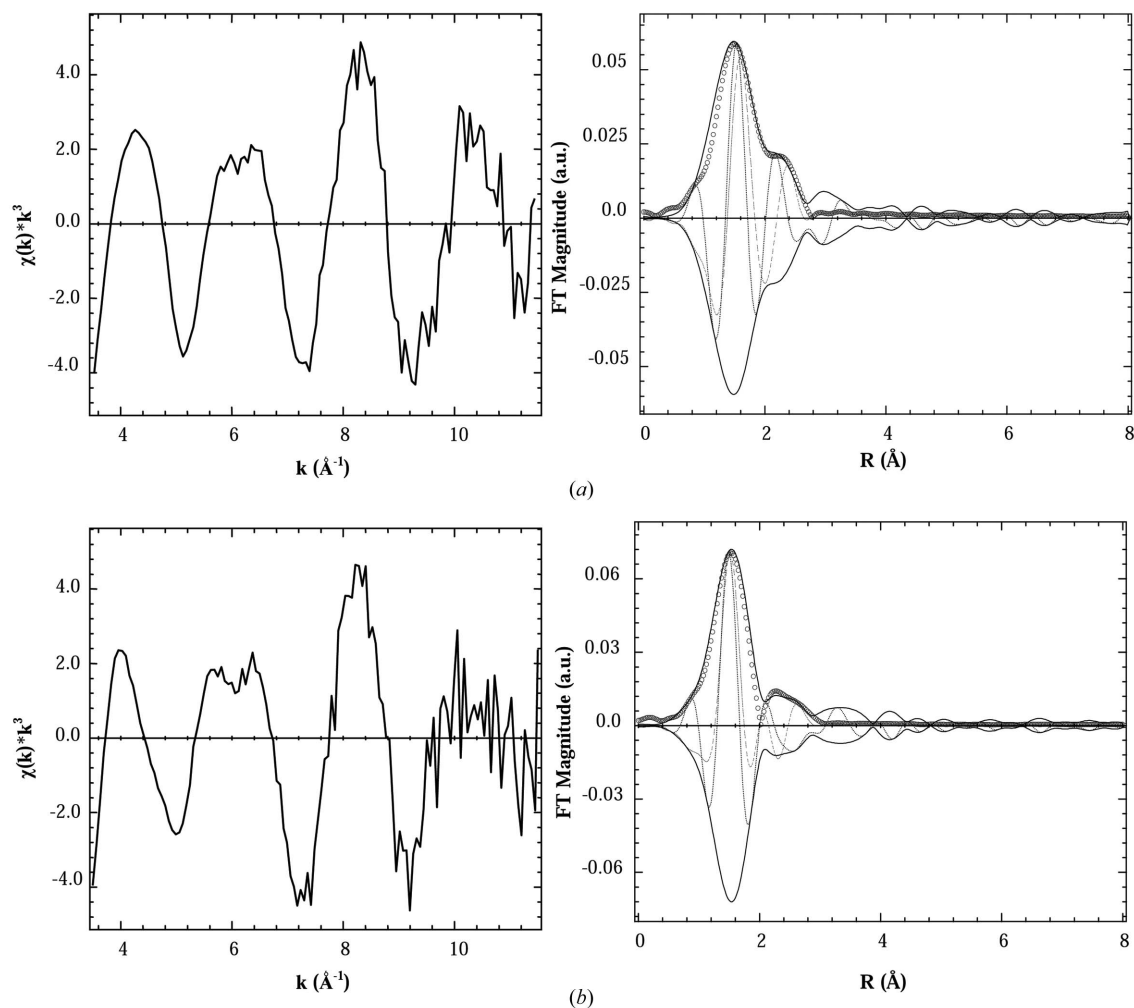

Figure 5
Normalized k^3-weighted Cu K-edge χ (left panels) and corresponding Fourier transforms (right panels) of the CMP sludge (*a*) prior to and (*b*) after (120 min) the electrokinetic treatment. Dotted and solid lines denote the fitting and experimental data, respectively.

4. Conclusion

Using XANES, it is found that the main copper species in the sludge are $Cu(OH)_2$ (74%), nanosize CuO (13%) and CuO (13%). Copper in the sludge possesses a Cu—O bond distance of 1.96 Å and a CN of 3.5. About 85% of the copper is dissolved in the aqueous phase, 13% of which is migrated and enriched on the cathode after 120 min of the electrokinetic treatment. The dissolution and electromigration rates of copper [mainly Cu(II)] in the sludge are 4 and 0.4 mmol h^{-1} g^{-1}, respectively, during the electrokinetic treatment. Notably the copper nanoparticles in the sludge can also migrate to the cathode under the electric field. By *in situ* EXAFS, it is found that during the electrokinetic treatment the bond distance and CN of Cu—O are increased by 0.1 Å and 0.9, respectively. This work also exemplifies the utilization of *in situ* EXAFS and XANES for revealing speciation, dissolution and electromigration of copper recovered from a sludge using the electrokinetic method.

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