



A Novel Method of Etching Copper Oxide Using Acetic Acid

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The removal of copper oxide using acetic acid at low temperatures was investigated. Acetic acid removes a variety of copper oxides, including cuprous oxide, cupric oxide, and cupric hydroxide without attacking the underlying copper film. The removal of these oxides was determined by X-ray photoelectron spectroscopy. Acetic acid can tolerate up to 4 vol % water dilution without hindering the oxide removal while producing an oxide-free surface. However, if a deionized water rinse is performed after an acetic acid treatment, a surface film of cupric hydroxide forms immediately. An acetic acid treatment at 35°C without a water rinse removes the native copper oxide and produces an oxide-free, streak-free copper surface.

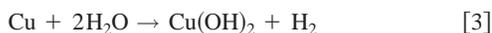
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Since its inception, the integrated circuit (IC) industry has used aluminum extensively as the conductor material for interconnects. In 1997, IBM and Motorola announced plans to use copper interconnects¹ due to the material limitations of aluminum at small (<0.18 μm) IC geometries. At these smaller dimensions, the lower resistivity and higher resistance to electromigration make copper an attractive alternative compared to aluminum.²⁻⁴

A number of challenges exist with the implementation of copper into the IC fabrication process. For instance, the current chemistry used for postplasma etch cleaning of aluminum interconnects attacks copper (*e.g.*, hydroxylamines).⁵ An additional challenge is the selective removal of the native copper oxide that is formed on the copper surface upon exposure to air. The presence of the copper oxide inhibits adhesion of films to copper, and can generate contact resistance when another conductor is deposited on the copper.

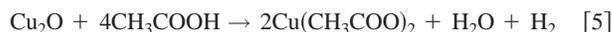
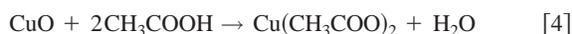
Copper has three different oxidation states: Cu⁽⁰⁾ (metallic copper), Cu^I (cuprous oxide, Cu₂O), Cu^{II} (cupric oxide, CuO). Upon exposure to air, a mixed film of cuprous oxide, cupric oxide, cupric hydroxide (Cu(OH)₂), chemisorbed water, and carboxylate species results.^{6,7} Water with dissolved oxygen activates the copper surface by the following reactions



Provided that no kinetic limitations exist, any three of these oxidation products can be present, since the Gibbs free energies of formation for H₂O, CuO, Cu₂O, and Cu(OH)₂ are -56.7, -31.9, -38.13, -85.5 kcal/mol at 25°C, respectively.⁸ Cuprous oxide, a corrosion product of copper and its alloys, serves as protection against further corrosion, particularly in an aqueous environment.⁹ Prior to subsequent IC processing, this mixture of copper oxides must be removed without attacking or oxidizing the underlying copper.¹⁰

Vapor-phase etching of copper oxide has been performed, but such methods require that the surface be in particular chemical oxidation states to be successful.¹¹ An additional drawback to vapor-phase oxide removal is the complexity of the process, requiring temperatures greater than 200°C and/or vacuum environments.¹² However, liquid-phase removal of copper oxide can also have varying degrees of complexity with the implementation of co-solvents, complexing agents, surfactants, and/or antitarnishing agents.¹³

Copper has excellent resistance to corrosion in the presence of acetic acid.¹⁴ However, acetic acid reacts with copper oxide to form cupric acetate by the following reactions



This paper examines the variety of chemical species found in native copper oxide and the ability of acetic acid to remove the oxide layer at low temperatures. The presence of these species can be differentiated by investigation of the Cu (2p), O (1s), C (1s), and copper Auger electron spectra by X-ray photoelectron spectroscopy (XPS). For copper, the Auger parameters for Cu, Cu₂O, CuO, and Cu(OH)₂ have been tabulated as 1851.2, 1849.1, 1851.8, and 1851.3 eV, respectively.¹⁵ The Auger parameter is determined by summing the binding energy of the Cu (2p_{3/2}) photoelectron and the kinetic energy of the Cu(L₃M₄₅M₄₅) Auger electron.¹⁶

Acetic acid is used to remove copper oxide without attacking the copper film, since acetic acid does not oxidize the copper surface. Acetic acid also has a low surface tension (27.8 dyn/cm), allowing easy removal from a surface.¹⁷ As a result, deionized (DI) water rinsing is not required to remove residual acetic acid and thus copper reoxidation due to a water rinse can be prevented.

Experimental

Glacial acetic acid (99.7%, JT Baker, 9508-01) was used without further purification. Experiments at atmospheric conditions were conducted in a Pyrex beaker using a stir bar rotating at 500 rpm for agitation. Removal of copper oxide with acetic acid proved feasible at room temperature, but to ensure reproducibility, experiments were conducted at 35°C to establish a controllable, reproducible temperature value. Post-acid-exposed surfaces were not rinsed with DI water, but were dried with a nitrogen gas flow.

Silicon (100), 1-10 Ω-cm, 4 in. wafers were used as substrates for the copper oxide removal experiments. Copper was dc sputtered (5.1 ± 0.5 nm) onto RCA-cleaned silicon surfaces. Experiments were conducted on 1 cm² samples cleaved from the substrate. XPS measurements were conducted on a PHI 1600 model equipped with Al Kα radiation source (1486.7 eV) and a hemispherical analyzer. XPS spectra were obtained at a takeoff angle of 60°, pass energy of 11.75 eV, and an operating vacuum of <5 × 10⁻⁹ Torr unless otherwise noted. Atomic force microscopy (AFM) data was acquired using a Digital Instruments Nanoscope IIIa.

Results and Discussion

Copper forms a thin oxide upon exposure to air or any oxygen-containing ambient. To obtain a thin copper oxide in these experiments, the copper films were exposed to cleanroom air immediately after deposition to allow a native copper oxide surface to form. Samples were immersed in acetic acid at 35°C for times from 5 to 10 min. Upon removal, the samples were dried with a nitrogen flow to displace the acetic acid from the surface. Visually, a shiny copper surface was observed without streaking or hazy residue.

Prior to acetic acid treatment, XPS Cu 2p analysis shows a typical native copper oxide, Fig. 1a, with strong shake-up peaks characteristic of cupric compounds.^{6,18} From tabulated XPS data,¹⁵ the Cu(OH)₂ peak at 935.1 eV is easily identified as the pronounced

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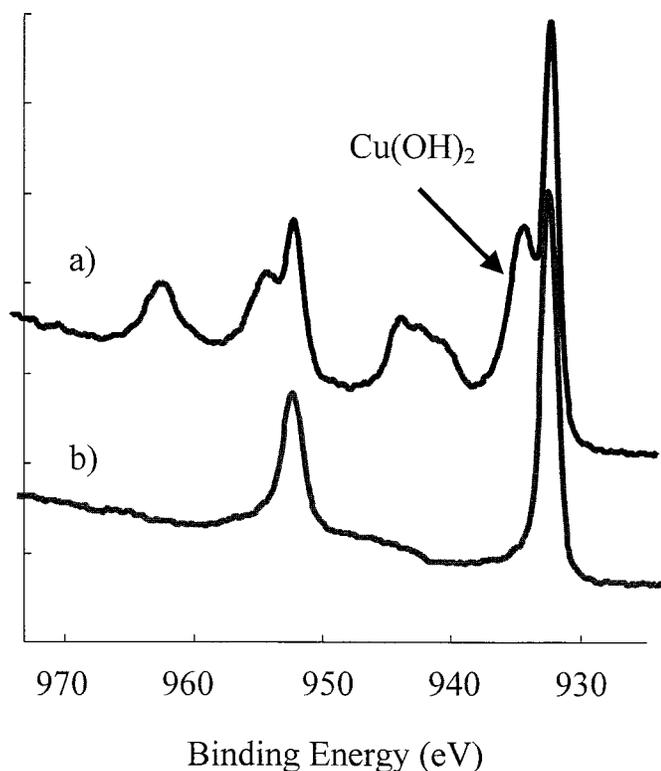


Figure 1. Cu 2p XPS spectra for (a) original native copper oxide and (b) copper surface after 5s acetic acid treatment at 35°C.

shoulder on the peak centered at 932.6 eV. The latter peak contains contributions from $\text{Cu}^{(0)}$ (932.6 eV), Cu_2O (932.5 eV), and CuO (933.7 eV). From the O 1s peak, Fig. 2, the various oxides initially present can be deconvoluted: underlying SiO_2 (532.0 eV), $\text{Cu}(\text{OH})_2$ (531.2 eV), Cu_2O (530.3 eV), and CuO (529.6 eV).

After an acetic acid treatment for 5 s, the oxide-free copper peaks [932.6 eV ($2p_{3/2}$) and 952.4 eV ($2p_{1/2}$)] dominate the Cu 2p spectra, Fig. 1b. Removal of the copper oxides are confirmed again by analyzing the O 1s peak, Fig. 3. Peaks assigned to $\text{Cu}(\text{OH})_2$ and CuO are not detected and the slight Cu_2O peak accounts for less than 2 atom % of the surface, probably due to the ambient air transfer to the XPS. Indeed, angle-resolved depth analysis indicated that this Cu_2O resides on the surface and not within the bulk copper or copper-silicon dioxide interface. Although $\text{Cu}^{(0)}$ and Cu_2O 2p peak locations are essentially the same, the presence of $\text{Cu}^{(0)}$ over Cu_2O can be resolved by use of the Auger parameters. Figure 4a is the original copper-oxide surface with broad peaks due to the different oxides present. However, after the acetic acid treatment, the $\text{Cu}^{(0)}$ peak at 568.1 eV is more prominent and the Cu_2O peak at 570.1 eV is minimal, Fig. 4b.

Although a clean copper surface is obtained within 5 s, experiments were conducted at longer times to determine if acetic acid etches the copper film. With exposure times from 5 to 10 min at 35°C, the ratio of underlying silicon (including the native silicon dioxide) to metallic copper (932.6 eV) remains at 0.83 (± 0.15). If the acetic acid etched the copper film, this ratio (Si/Cu) should have increased with time as the copper film is etched. From these XPS results, it may be concluded that within the timeframe and conditions of this experiment, acetic acid removes copper oxide, but does not etch copper.

In order to minimize data interpretation concerns due to post-acetic acid treatment oxide regrowth, the above results were obtained for samples transferred from the nitrogen-drying step to the XPS vacuum chamber within 30 s. Oxide regrowth was examined by treating the original copper surface for 1 min in acetic acid at

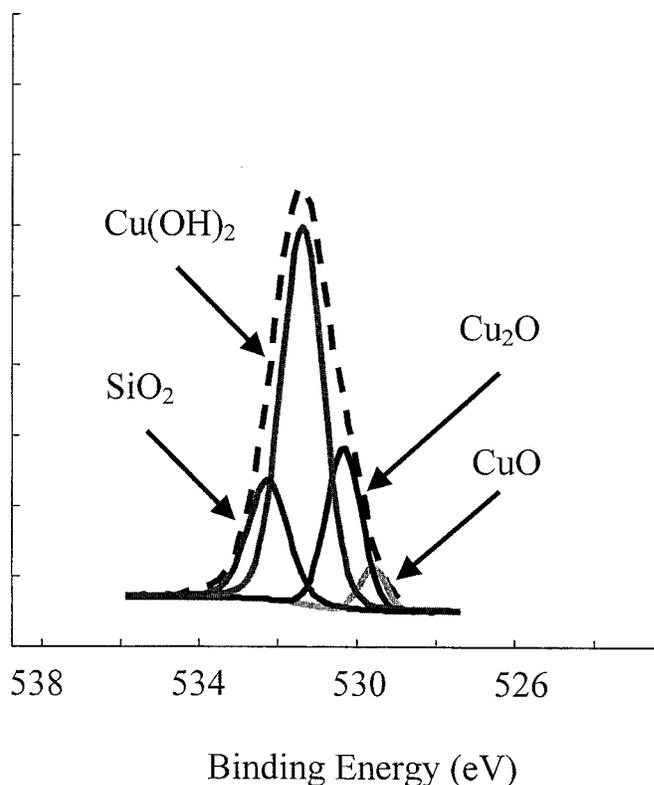


Figure 2. Curve fitting of O 1s XPS spectra for the native copper oxide surface prior to acetic acid treatment. Solid lines represent the various oxide species; the dashed line is the observed O 1s peak.

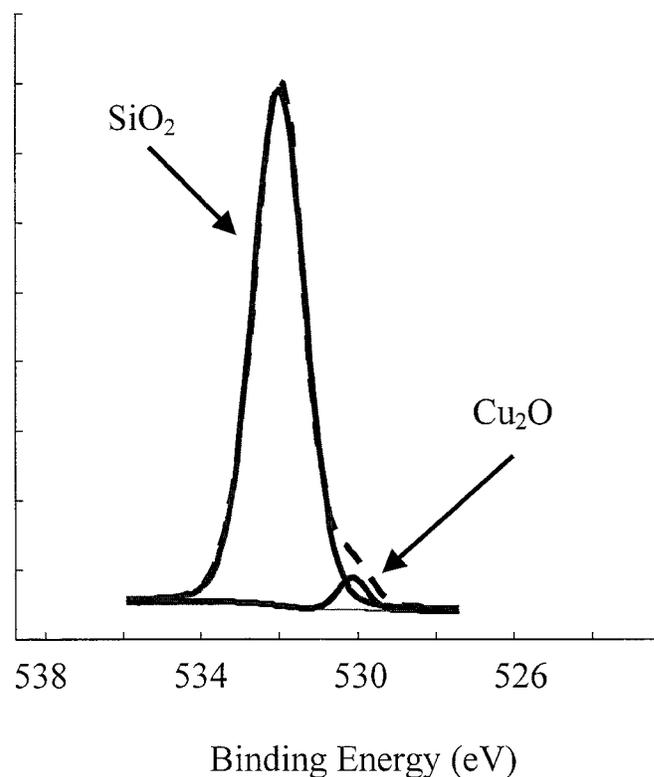


Figure 3. Curve fitting of O 1s XPS spectra detects only SiO_2 and Cu_2O present on the copper surface after 5 s acetic acid treatment at 35°C. Solid lines represent the two oxide species; the dashed line is the observed O 1s peak.

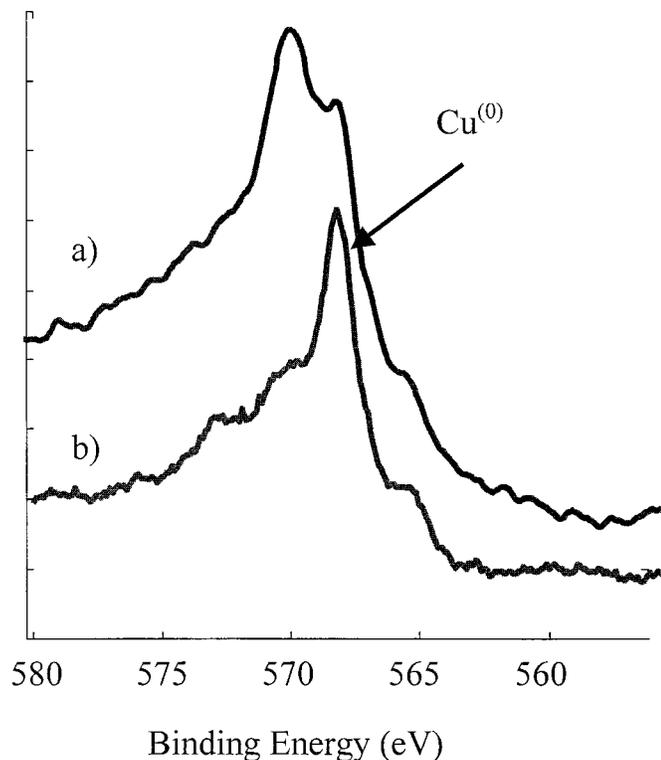


Figure 4. Auger electron spectra of Cu(LMM) for (a) original native copper oxide and (b) copper surface after 5 s acetic acid treatment at 35°C.

35°C and then controlling the time the samples were exposed to ambient air prior to XPS analysis. The O 1s XPS spectra were used to establish the thickness of the oxides present; Fig. 5 shows the various oxygen concentrations present as a function of exposure to ambient air. As depicted in Fig. 2, prior to acetic acid treatments, SiO₂, Cu(OH)₂, Cu₂O, and CuO are present in concentrations of 18, 58, 20, and 4%, respectively. After treatment with acetic acid, clean metallic copper is evident and only a small amount of Cu₂O is found initially (<2%). The copper slowly oxidizes, and at times of air exposure greater than 30 s, forms the three copper oxide moieties.

Although cupric hydroxide forms during the oxide regrowth, after 10 min of air exposure its concentration does not reach the level (15%) of the original copper oxide surface (58%). However, if a DI

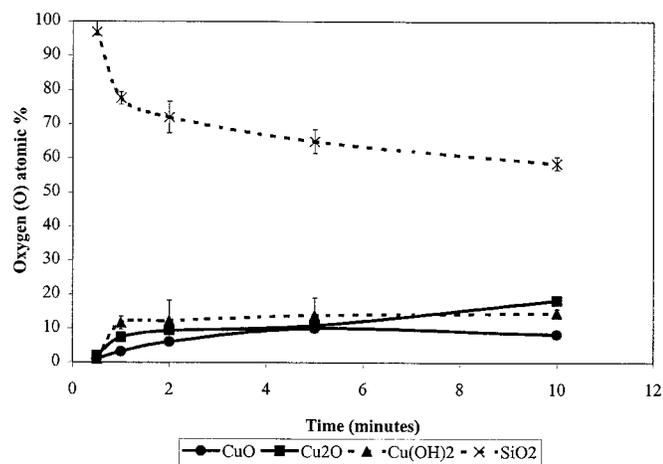


Figure 5. Oxygen (O) concentration attributed to the various oxides present as a function of exposure to ambient air after 1 min acetic acid treatment at 35°C (error bars shown).

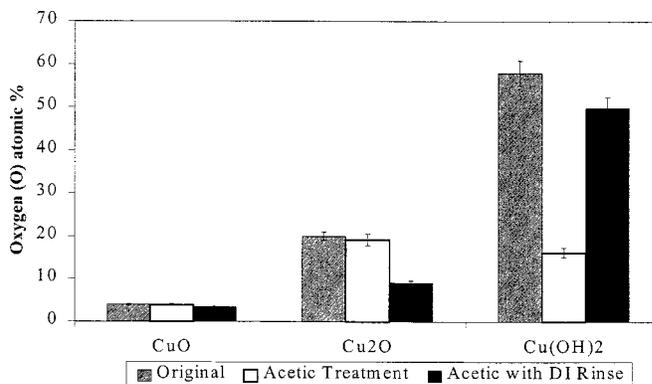


Figure 6. Oxygen (O) concentration present for original copper oxide surface and surfaces exposed to air for 10 min after acetic acid treatment with and without a final DI water rinse (error bars shown). Acid treatments were 5 s at 35°C.

water rinse is employed after the acetic acid treatment and the surface subsequently dried with nitrogen, cupric hydroxide forms immediately; the rinsing step is therefore providing OH⁻. As the surface continues to oxidize, cupric hydroxide remains the dominant species. Figure 6 displays the relative oxide concentration differences between the original copper oxide surface and the acetic acid-treated surfaces with and without a DI water rinse step. All measurements were performed after 10 min of air exposure following the indicated treatment.

Since water (with dissolved oxygen) plays a critical role in establishing the presence and type of oxide on a copper surface, it is important to determine both the effect of dissolved oxygen and the concentration of water that can be tolerated in the acetic acid used for surface treatment. Such information will give insight into the control and reproducibility possible for acetic acid treatments performed under manufacturing conditions. Treatment of copper surfaces by glacial acetic acid that had been purged with nitrogen gas for 30 min does not cause a change in the XPS spectra relative to copper surfaces that had been treated with “unpurged” acetic acid; clearly, the latter solution contains dissolved oxygen.¹⁹ If copper is oxidized by oxygen in the glacial acetic acid, oxidation is minimal, and the acetic acid removes any oxide that forms. Furthermore, dilution of acetic acid with DI water up to 4% by volume did not hinder the oxide removal. At these lower concentrations (<4% vol), the resulting copper XPS spectra were identical to those obtained by treatment with glacial acetic acid. Contrary to experiments conducted with a DI water rinse, cupric hydroxide does not form when small amounts of water are added to the acetic acid bath. At 35°C and 10 min of air exposure, either the small percentage of water added does not oxidize the copper surface or more likely, any oxide that forms is removed by the acetic acid. As more water is added (up to 20% vol), a majority of the copper oxide is still removed. However, XPS analysis indicates that the different oxides are still present upon exposure to these mixtures; quantification of the oxides remaining was not performed.

An XPS survey spectrum of the copper surface both before and after acetic acid exposure detects only copper, oxygen, silicon, and carbon. Carbon contamination, like the formation of a native oxide, is unavoidable during ambient air exposure. Prior to acetic acid treatment, the C 1s XPS spectrum displays two separate peaks attributed to adventitious carbon and carboxylate species, as shown in Fig. 7a. This observation is in agreement with previous studies on copper oxide surfaces.⁷ After an acetic acid treatment, the carboxyl peak diminishes, Fig. 7b. Interestingly, acetic acid is not detected on the copper surface (289.3 eV), even though a DI water rinse is not performed, confirming that acetic acid does not react with the metallic copper surface, at least to the detectability limit of XPS (~0.1 atom %).

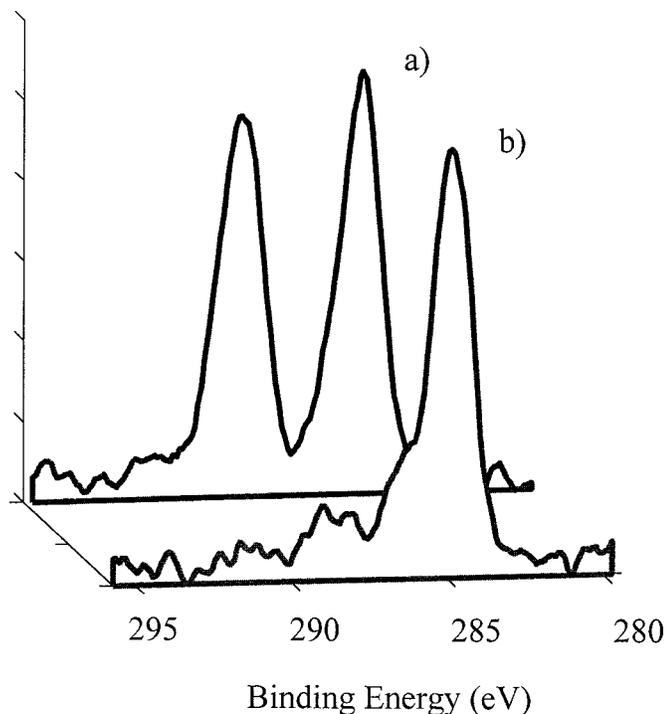


Figure 7. C 1s XPS spectra for (a) original copper oxide surface and (b) copper surface after acetic acid treatment.

Preliminary AFM results indicate that the copper surface may roughen slightly during copper oxide removal if long acetic acid exposure times are used. The original copper surface had a root mean square (rms) roughness of (0.52 ± 0.10) nm, while the rms roughness was (0.67 ± 0.18) nm after 10 min of acetic acid exposure. Additional studies with initially smoother copper surfaces are required in order to establish whether measurable roughening occurs due to acetic acid exposure.

Conclusions

A method for the removal of copper oxide from a copper surface using acetic acid at low temperatures has been investigated. The underlying copper is not oxidized or attacked by the acetic acid and

dilution with water up to 4 vol % does not hinder the oxide removal. Based upon XPS results, the resulting copper surface remains free of oxide for approximately 1 min of air exposure after the acetic acid treatment. Also, a DI water rinse may not be required, since nitrogen drying produces a streak-free, shiny surface. If a DI water rinse is employed, cupric hydroxide forms immediately on the copper surface, whereas acetic acid produces an oxide-free surface.

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