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Etch Products of Copper Atomic Layer Etching by Oxidation and Formic Acid Vapor

Running title: Copper ALE Product Determination

Running Authors: Smith et al.

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ABSTRACT

Atomic layer etching (ALE) of metals offers a path to greater control of selectivity, etch rate, and etch profile. However, tailoring a process to meet these demands requires an understanding of the volatile etch product, which is challenging to detect due to low product concentrations and the paramagnetism of many metalorganic products. In this work, several complementary analysis techniques were used to determine the volatile etch product and residual surface species of a Cu ALE process based on plasma oxidation and formic acid vapor etching of the oxidized layer. It was shown that the volatile product was copper formate with a Cu^{2+} paramagnetic center, in concordance with prior density functional theory (DFT) calculations. While copper formate tetrahydrate was formed, it was determined that the tetrahydrate product was confined to the surface, with anhydrous copper formate being the volatile etch product.

I. INTRODUCTION

In an integrated circuit (IC), the interconnects are the metal “wires” that link the transistors and other electrical components. Initially made of Al, interconnects in most modern ICs are made of Cu due to its higher conductivity and greater resistance to electromigration^{1, 2}. When the IC industry initially switched from Al to Cu, difficulties in developing a low temperature gas phase etch of Cu necessitated the use of a dual damascene process to create the interconnects³. In the dual damascene process, the interlayer dielectric (ILD) is deposited and patterned. A barrier layer is then deposited, followed by electrodeposition of Cu. This results in excess, or overburden, Cu that must be removed using a chemical mechanical planarization (CMP) step. The subsequent layers of vias and lines can then be created using the same process.

Even using state of the art lithography tools, edge placement error (EPE, the misalignment between subsequent lithography steps) can cause a metal via to be too close to a neighboring metal line, leading to crosstalk, increased RC delay, and in extreme cases shorts. The fully self-aligned via (FSAV) was proposed as a way to improve device reliability by mitigating the negative impact of EPE⁴. In order to achieve an FSAV, either an area selective deposition of dielectric on dielectric⁵ or a recess etch of the Cu is required, which has been demonstrated using solution phase processing^{4, 6}. Gas phase etching of Cu through atomic layer etching (ALE) could be another means of achieving a recess etch.

To achieve controllable and selective gas-phase etching of Cu, a halogen-free atomic layer etch (ALE) process was developed that relied on alternating cycles of plasma oxidation to oxidize the Cu surface and formic acid vapor to remove the oxidized layer⁷. To understand the mechanisms behind the etching of the oxidized Cu by formic acid, density functional

theory (DFT) was used to explore the possible products, and it was found that an anhydrous dimeric tetra(μ -formato) dicopper(II) “paddlewheel” complex ($\text{Cu}_2(\text{HCOO})_4$) was the most thermodynamically favorable etch product. However, experimental verification of the etch mechanism, particularly identification of the volatile etch product, was not attempted at the time. In the present work, experimental determination of (1) the volatile etch product and (2) the state of the oxidized Cu surface after etching with formic acid vapor are demonstrated, as outlined in Fig. 1.

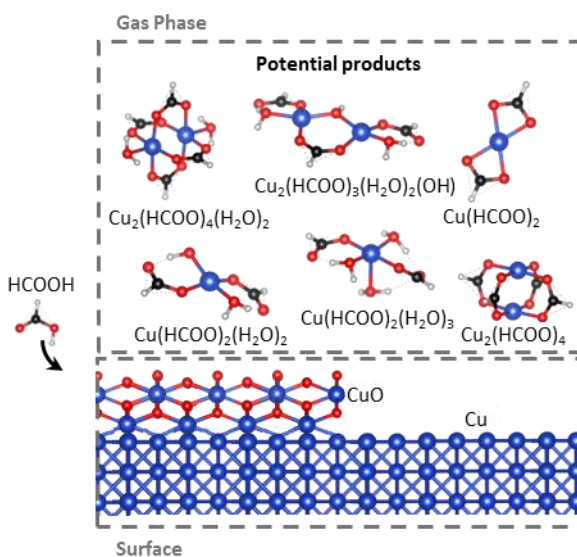


FIG. 1. Many potential volatile products of a Cu ALE process using oxygen plasma and formic acid vapor were examined theoretically using DFT⁷. However, experimental verification of the volatile gas phase product, as well as determination of the state of the surface following etch, are still needed. A variety of complementary techniques are employed in this work to ascertain the volatile product and surface state post etch.

Various means have been used to determine ALE reaction products. However, determination of the volatile products can be particularly challenging because ALE of thin films forms miniscule amounts of product that are difficult to detect, and standard surface

analysis techniques cannot detect the gas phase product. For example, studies using X-ray photoelectron spectroscopy (XPS)^{8,9}, Fourier transform infrared spectroscopy (FTIR)¹⁰, and temperature programmed desorption (TPD)¹¹ revealed useful information about the etched surfaces, but did not conclusively demonstrate the nature of the volatile product. In one approach to determine volatile etch products, a custom quadrupole mass spectrometry (QMS) system was constructed¹² that has been used for a variety of interesting ALE mechanistic studies¹³⁻¹⁵. While this QMS system can clearly identify volatile etch products, it operates at pressures much lower than those used for Cu ALE by formic acid. In this work, the Cu ALE etch products are studied using a range of complimentary techniques and are found to be in good agreement with the prior DFT calculations.

II. EXPERIMENTAL

Ambient pressure XPS (AP-XPS) allows for in situ study of surfaces as they are exposed to vapor or gas¹⁶⁻¹⁸ and is leveraged in this work to observe a CuO surface exposed to formic acid vapor. AP-XPS was performed at the Advanced Light Source (ALS) beamline 9.3.2¹⁹ using an X-ray energy of 700 eV, a take-off angle of 90°, and a sample temperature of 25°C. The sample analyzed was a 45 nm Cu film that was grown on a TiN adhesion layer on a Si substrate, then subsequently plasma oxidized for 10 min in a Unaxis 770 reactor at 500 W ICP power and 35 mTorr O₂. Prior to collecting spectra, the sample was cleaned by dosing the AP-XPS chamber with O₂ gas at a pressure of 100 mTorr, then heating the sample surface to 250°C and holding this for 50 min. The chamber was then pumped to ultra-high vacuum (UHV). Residual formic acid in the chamber from prior experiments meant that not all initial carbon was removed following

the cleaning procedure. Spectra were collected at UHV, and then the chamber was dosed with formic acid through a leak valve to a pressure setpoint ranging from 10^{-5} to 10^{-1} Torr, with spectra collected at each setpoint. It should be noted that the highest pressure in the AP-XPS experiments, 0.1 Torr, is much lower than the partial pressure of formic acid in the vapor chamber used for the actual ALE process, which ranges from 50 to 70 Torr depending on the total pressure used^{7, 20}.

Magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy measurements were performed using a WB Bruker Avance 500 MHz instrument used with a 7.5 mm AMP 4395-001 rotor designed for heterogeneous sample packing²¹. For these experiments, a slurry of ^{13}C -enriched formic acid (Cambridge Isotope Laboratories) and Al_2O_3 powder (Strem Chemicals) was prepared by mixing 319 mg of Al_2O_3 and 40 μL of ^{13}C -enriched formic acid in a 1.5 mL centrifuge tube, then filling half of the rotor volume with the slurry. Al_2O_3 is unreactive with formic acid. A barrier layer of 35 mg of Al_2O_3 was then packed on top of the slurry. CuO powder (Sigma-Aldrich) was added in increments of ~ 245 mg, packing down the rotor contents after each addition, until the rotor was full. While the polycrystalline CuO powder is not a perfect model of the amorphous CuO surface formed by plasma oxidation of Cu ²², it is nonetheless a reasonable approximation as it exposes different CuO crystal orientations to formic acid, with each orientation having different free energies of reaction with formic acid²³. Previously published X-ray diffraction (XRD) data showed no crystalline Cu_2O or CuO peaks, suggesting the oxidized surface was amorphous. Because of the many layers in the rotor, stable spinning was only possible up to a maximum speed of 4 kHz. The rotor was packed at room temperature with the CuO isolated from the formic acid containing

slurry by the Al_2O_3 barrier layer. It was heated to 80°C in the NMR probe, volatilizing the formic acid and causing it to percolate through the rotor. The ^{13}C -enriched formic acid vapor then reacted with the CuO powder in the top of the rotor, with the reaction monitored by ^{13}C MAS-NMR in real time.

A second MAS-NMR instrument, a Bruker 400 MHz ASCEND DNP-NMR, was used with a 2.5 mm thick-walled rotor. This probe and rotor combination allowed for spinning at a higher spinning speed of 34 kHz, which lessened ^1H - ^{13}C and ^1H - ^1H dipolar couplings, reducing peak linewidth and allowing for resolution of paramagnetic peaks²⁴,²⁵. Temperature measurements using the 2.5 mm rotor filled with a KBr reference spinning at 34 kHz showed a rotor temperature of $\sim 74^\circ\text{C}$ ²⁶. For these experiments, the analyte was prepared by mixing 82.8 mg of CuO powder with 5 μL of ^{13}C -enriched formic acid in a 1.5 mL centrifuge tube, then packing the sample into the rotor. A reference powder of $\text{Cu}(\text{HCOO})_2 \cdot 4(\text{H}_2\text{O})$ (Alfa Aesar) was used as a reference for chemical shifts. An anhydrous version of $\text{Cu}(\text{HCOO})_2$ was prepared by dehydrating the tetrahydrate in an oven at 100°C for 5 hours, which was also used as a chemical reference. For both spectrometers used, all ^{13}C spectra were referenced to the second peak of standard adamantane at 38.48 ppm with respect to tetramethylsilane (TMS) at 0 ppm, and all ^1H spectra were referenced to the ^1H peak of adamantane at 1.71 ppm.

The etch products of reacting CuO powder with formic acid (95%, Sigma-Aldrich) were collected by placing a cold trap (Labconco CentriVap Cold Trap) between the custom-built vapor chamber and its roughing pump. The cold trap was cooled to -50°C to condense all vapor phase products for analysis. For the experiment, 100 mg of CuO was loaded into the vapor phase reactor, which was then dosed with formic acid at a

pressure of 350 Torr at a temperature of 80°C for a duration of 30 min, after which the chamber was pumped down to base pressure. This was repeated an additional 9 times, after which the CuO powder was replaced with a fresh 100 mg of CuO powder and the process repeated. A total of 30 cycles were done this way, with the CuO powder replaced every 10 cycles. An additional 30 cycles was then carried out at the same pressure and temperature and replacing the CuO every 10 cycles, but using an exposure time of 10 min. Following the second set of the 30 cycles (60 cycles total and 600 mg of CuO used), the cold trap was removed and the liquid etch condensate extracted and stored in glass vials. The etch condensate was then analyzed with matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS)^{27, 28} and XRD^{29, 30}. For MALDI-TOF MS, the etch condensate was mixed with a matrix and analyzed using a Bruker Ultraflex extreme spectrometer. Three different matrices were tested: 2,5-dihydroxybenzoic acid (DHB), α -cyano-4-hydroxycinnamic acid (CHCA), and 2-(4'-hydroxybenzeneazo)benzoic acid (HABA).

For XRD measurements, a D8 DISCOVER with DAVINCI Design X-ray powder diffractometer, configured in Bragg-Brentano focusing with LynxEye geometry was used. For the sample, 750 μ L of etch condensate was drop-cast on a Si zero diffraction plate (MTI Corporation) in 50 μ L increments. This was then scanned continuously over the course of 133 hours to acquire data with sufficient signal to noise. The powder diffraction pattern was then compared to various references. The anhydrous $\text{Cu}(\text{HCOO})_2$ crystal structure was determined by single crystal XRD of anhydrous $\text{Cu}(\text{HCOO})_2$ prepared by immersing CuO powder in formic acid solution at 80°C for 10 min, pipetting out the solution, drying out the powder, and then collecting spectra on a single crystal

pulled from the powder. The powder diffraction patterns of $\text{Cu}(\text{HCOO})_2$ dihydrate and tetrahydrate were taken from literature data³¹.

III. RESULTS AND DISCUSSION

A. *AP-XPS Shows Hydrated Surface*

The state of a CuO surface during formic acid vapor etching was studied using AP-XPS. The O 1s, C 1s, and Cu 3p spectra collected during these experiments are shown in Fig. 2(a-c), respectively. In the O 1s region, increasing the formic acid pressure led to the emergence of two peaks at 535.9 and 534.3 eV which correspond to the O-C and O=C oxygen atoms in gaseous formic acid. The attribution of these peaks was verified by backing the oxidized Cu sample away from the detector and collecting spectra of only the formic acid vapor, with these spectra shown in Figure S-1(a) of the supporting information. For the O 1s peak fitting, these two vapor phase formic acid peaks were constrained to have the same area, consistent with the stoichiometry of the formic acid molecule. A peak attributed to adsorbed water at 533.8 eV was also observed as the formic acid pressure increased, similar to the binding energies reported in the literature for water adsorbed on CuO ³² and Cu_2O ³³. Water is a byproduct of the formation of the volatile metalorganic products predicted by DFT.⁷ The AP-XPS spectra confirm that water adsorbates are formed as byproducts of the formic acid and CuO reaction. However, this does not point to the structure of the volatile etch product. In the C 1s region, the peak associated with carbon bonded only to hydrogen or other carbon atoms (C-C/C-H) grew substantially, despite the fact that formic acid has only a single carbon with two oxygen bonds. Reasons for this could include that the X-ray beam decomposes the formic acid or that formic acid displaces

adventitious carbon species from the chamber walls that subsequently adsorb on the sample surface. At a formic acid pressure of 100 mTorr, a gaseous formic acid C 1s peak became visible at a binding energy of 291.1 eV, consistent with AP-XPS C 1s spectra reported in the literature³⁴. The attribution of this peak was also confirmed by collecting spectra with the sample backed away from the detector, shown in Figure S-1(b). No changes were observed in either the full widths at half maximum or the peak positions the Cu 3p region peaks with increasing formic acid pressure. The Cu 3p region is much less studied than the Cu 2p_{3/2} region, and it may be that the chemical shift between CuO and Cu(HCOO)₂ in the 3p region is not significant. From the AP-XPS measurements it was therefore concluded that water is adsorbed on the surface post etch.

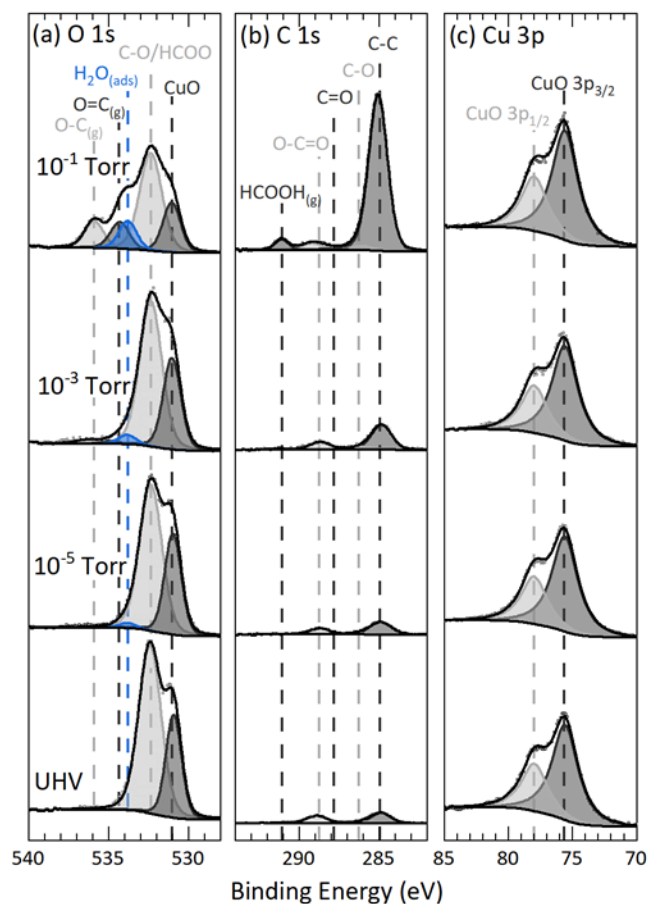


FIG. 2. (a) O 1s, (b) C 1s, and (c) Cu 3p AP-XPS spectra of a plasma oxidized Cu sample treated with formic acid at various pressures. Increasing the formic acid pressure led to the emergence of a peak at 533.8 eV, which was attributed to adsorbed water on the surface.

B. MAS-NMR Shows Paramagnetic $\text{Cu}(\text{HCOO})_2$ Product

The results of the MAS-NMR experiment carried out using the heterogeneous rotor are shown in Fig. 3. At room temperature, there was a clear ^{13}C -enriched formic acid peak at 165 ppm, with all other peaks being satellite spinning sidebands³⁵. These spinning sidebands were separated from the main peak by integer multiples of the spinning speed (4 kHz). When changing the spinning speed, only the peak at 165 ppm remained at a constant position, and all other peaks shifted according to the change in spinning speed, confirming that they were merely spinning sidebands.

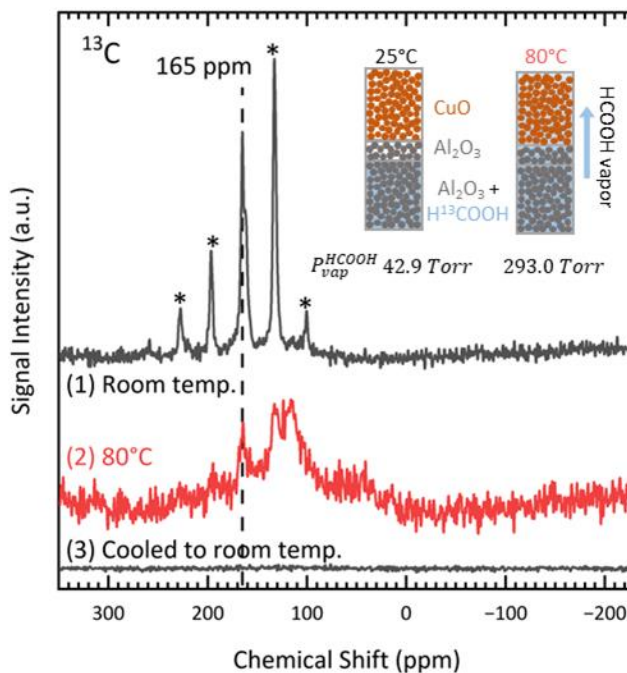


FIG. 3. NMR spectra of a heterogeneously packed rotor at room temperature, after heating to 80°C, and after cooling back down to room temperature. The ^{13}C -enriched formic acid peak has a chemical shift of 165 ppm, and all other peaks in the spectra were spinning sidebands (denoted by asterisks) of this main formic acid peak. When the rotor was heated and the formic acid vapor reacted with CuO, all peaks disappeared due to the formation of a paramagnetic product with a fast relaxation time, confirming the product is Cu^{2+} . (Inset) The rotor is packed at room temperature such that the CuO is separated from the slurry containing the formic acid. Heating the rotor to 80°C volatilizes the ^{13}C -enriched formic acid and causes it to react with the CuO powder in the top of the rotor.

Heating the rotor to 80°C volatilized the ^{13}C -enriched formic acid and allowed it to react with the CuO powder at the top of the rotor. It was verified that the formic acid was not leaking out through the rotor seals by filling the rotor entirely with formic acid- Al_2O_3 slurry and Al_2O_3 and observing that heating did not cause a reduction in signal. Therefore, the loss in signal must be due to the reaction of formic acid with the CuO forming a paramagnetic product with an unresolvable peak at slow spinning speeds. Cu in the +1 oxidation state is diamagnetic and therefore would not cause the peak broadening/disappearance that was observed. This implies the product contains paramagnetic Cu^{2+} , which features very broad NMR peaks due to enhanced relaxation³⁶. The DFT calculations suggested that Cu^{2+} products were more thermodynamically favorable than Cu^{1+} products⁷, and the present experiments confirm these predictions. Although this heterogeneous rotor packing method did not reveal the exact nature of the product for this ALE chemistry, other ALE processes involving metals in oxidation states that are diamagnetic (e.g., Al^{37} , Hf(IV)^{38} , Zn(II)^{39}) could benefit from product identification using this NMR rotor packing method.

In order to spin at higher speeds and determine the identity of the paramagnetic product, a smaller, homogeneously packed rotor was used. The ^{13}C and ^1H NMR spectra of these very fast MAS-NMR experiments are shown in Fig. 4(a-b), respectively. In the ^{13}C NMR spectra, both the anhydrous and tetrahydrate $\text{Cu}(\text{HCOO})_2$ reference powders had peaks at -14.0 ppm and -166.9 ppm, corresponding to the two formate ligands. Literature reports on manganese(III) acetylacetonate ($\text{Mn}(\text{acac})_3$) have shown that the paramagnetic shifts of ligands with the same chemical structure but in different magnetic environments because of the central paramagnetic center can have different chemical shifts²⁵. In the case of $\text{Mn}(\text{acac})_3$ the CH_3 carbons on each of the three acac ligands were found to have chemical shifts of -47 , -113 , and -530 ppm despite all being part of chemically identical acac ligands. In the present work, the two chemically similar formate ligands in $\text{Cu}(\text{HCOO})_2$ manifest as two distinct peaks because they are in different magnetic environments due to the paramagnetic Cu^{2+} center. A similar phenomenon is observed in the ^1H spectra where both the anhydrous and tetrahydrate $\text{Cu}(\text{HCOO})_2$ powders have two ^1H peaks at 374.6 and 284.4 ppm. The only difference between the two ^1H spectra is that the tetrahydrate has a strong water peak at 5.9 ppm.

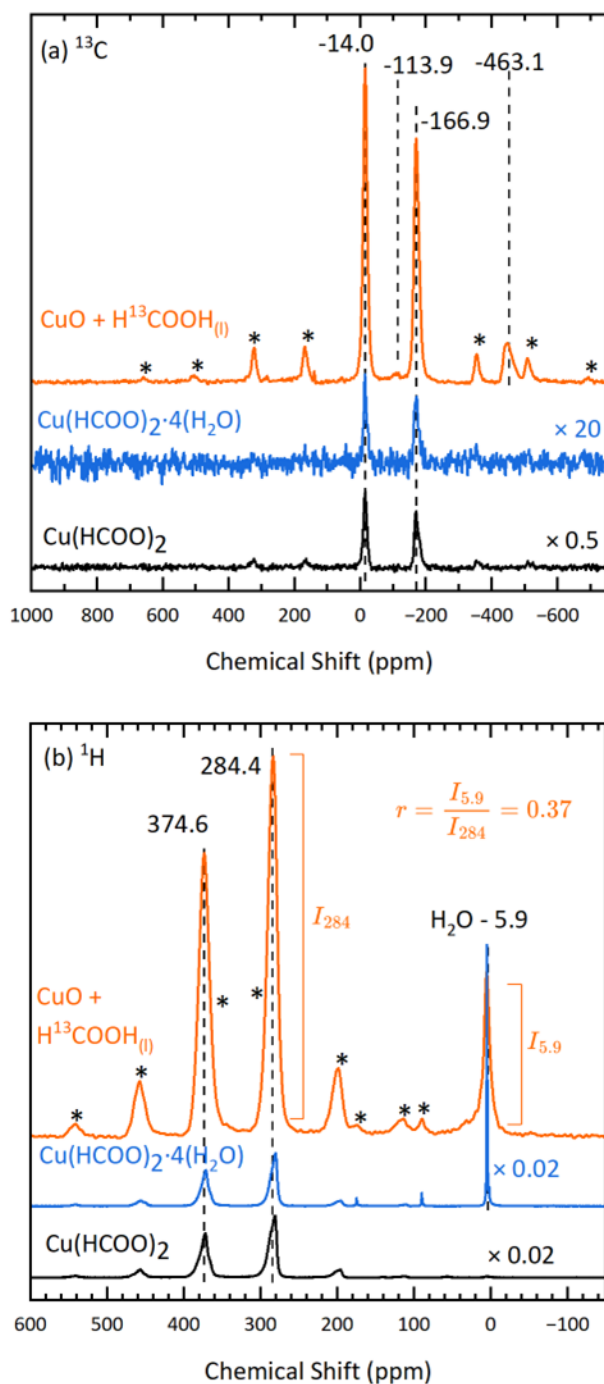


FIG. 4. (a) ^{13}C and (b) ^1H NMR spectra of $\text{Cu}(\text{HCOO})_2$ powder, $\text{Cu}(\text{HCOO})_2 \cdot 4(\text{H}_2\text{O})$ powder, and CuO mixed with ^{13}C -enriched formic acid. Formic acid reacted with CuO form $\text{Cu}(\text{HCOO})_2 \cdot x(\text{H}_2\text{O})$. The integrated intensity of the water peak suggests the product is a mix of the tetrahydrate and anhydrate.

The ^{13}C and ^1H NMR spectra of the mixture of CuO powder and ^{13}C -enriched formic acid can be compared to the reference powders to ascertain the nature of the product. Like the reference powders, the mixture of CuO powder and ^{13}C -enriched formic acid showed prominent ^{13}C peaks at -14.0 and -166.9 ppm and ^1H peaks at 374.6 and 284.4 ppm. This confirms that the product has a stoichiometry of $\text{Cu}(\text{HCOO})_2$. The CuO and ^{13}C -enriched formic acid ^1H spectrum also showed a ^1H water peak at 5.9 ppm.

To determine the hydration of the product, the ratio r of integrated intensities of the ^1H peaks at 5.9 and 284.4 were compared. For the $\text{Cu}(\text{HCOO})_2 \cdot 4(\text{H}_2\text{O})$ reference the value of r was 0.63 . The amount of water x in a sample of $\text{Cu}(\text{HCOO})_2 \cdot x(\text{H}_2\text{O})$ can be therefore be determined as $x = \frac{4r}{0.63}$. For the sample of CuO mixed with ^{13}C -enriched formic acid, the ratio of the peaks at 5.9 and 284.4 ppm was determined to be 0.37 leading to a stoichiometry of $\text{Cu}(\text{HCOO})_2 \cdot 2.3(\text{H}_2\text{O})$. The DFT calculations suggested that a dihydrate product was not thermodynamically favorable under the experimental conditions used and instead suggested that an anhydrous dimer of $\text{Cu}_2(\text{HCOO})_4$ or anhydrous monomer $\text{Cu}(\text{HCOO})_2(\text{HCOOH})_4$ was most thermodynamically favorable⁷. Based on the alignment with the $\text{Cu}(\text{HCOO})_2$ reference powder peaks, the monomeric $\text{Cu}(\text{HCOO})_2(\text{HCOOH})_4$ can be ruled out as the volatile product. What is proposed based on the NMR results and is corroborated with further experiments is that the reaction between formic acid and CuO forms a volatile anhydrous $\text{Cu}(\text{HCOO})_2$ product and leaves the CuO surface terminated with residual $\text{Cu}(\text{HCOO})_2 \cdot 4(\text{H}_2\text{O})$.

NMR captures the signal from volatile and nonvolatile products simultaneously. Although small chemical shifts between the liquid and gas phase have been observed experimentally for diamagnetic compounds²¹, paramagnetic compounds have broad

linewidths that could obscure the slight chemical shift of the vapor phase. Based on the total product stoichiometry of $\text{Cu}(\text{HCOO})_2 \cdot 2.3(\text{H}_2\text{O})$, the proposed mixture of volatile anhydrate and surface tetrahydrate would correspond to 41.3% anhydrate and 58.7% tetrahydrate. The formation of $\text{Cu}(\text{HCOO})_2 \cdot 4(\text{H}_2\text{O})$ on the surface is consistent with the AP-XPS results showing water on the surface following the reaction of CuO with formic acid vapor. Similarly, a literature report using $\text{Cu}(\text{HCOO})_2 \cdot x(\text{H}_2\text{O})$ chemical vapor deposition (CVD) precursors suggested that the hydrated precursor molecule volatilizes first through a dehydration step followed by sublimation of the copper formate, although direct evidence for an anhydrous volatile compound was lacking⁴⁰. To verify the formation of the volatile anhydrous $\text{Cu}(\text{HCOO})_2$, analysis of the etch condensate was pursued.

C. Etch Condensate Analysis Shows Anhydrous Volatile Product

The nature of the volatile product could be studied by analyzing the condensate collected in the cold trap of the vapor phase reactor. Only the volatile product was collected in this manner, allowing for separation of the surface products from the volatile product. However, the process of condensing the volatile product simultaneously with excess formic acid, coupled with ambient exposure prior to ex situ analysis, could lead to chemical and structural changes in the observed product. Understanding these limitations, the structure of the drop-cast condensate containing the volatile product was studied with XRD, with the XRD powder diffraction pattern for the drop-cast condensate shown in Fig. 5. This was compared to the powder diffraction patterns of the anhydrous, dihydrate, and tetrahydrate $\text{Cu}(\text{HCOO})_2$.

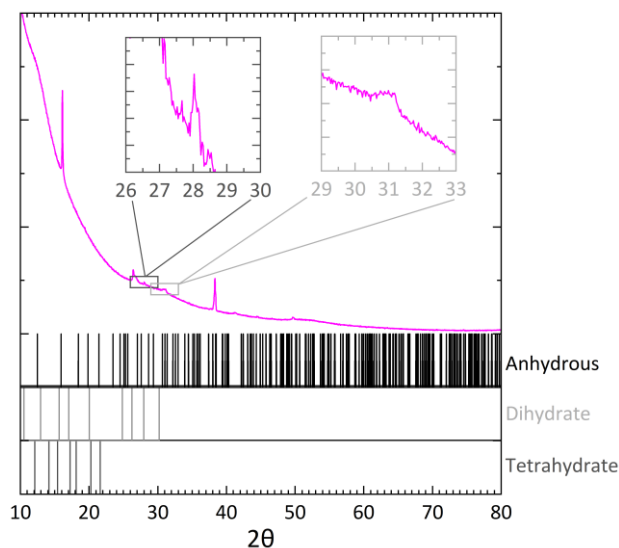


FIG. 5. XRD of the etch condensate drop-cast on a Si zero-diffraction plate compared to anhydrous, dihydrate, and tetrahydrate $\text{Cu}(\text{HCOO})_2$ reference patterns. The dehydrated and tetrahydrate powder diffraction patterns are taken from the literature³¹. The dominant peaks of the XRD pattern most closely align with the anhydrous reference, suggesting the volatile product is anhydrous.

The diffraction pattern of the drop-cast etch condensate has two sharp peaks at 16.1° and 38.3° that have close analogues with the anhydrous reference (15.9° and 38.0°) that correspond to the (102) and (006) $\text{Cu}(\text{HCOO})_2$ orientations. The condensate also had a weaker peak at 31.2° that corresponds to the (121) peak of the anhydrous $\text{Cu}(\text{HCOO})_2$ at 31.0° . Many peaks from the anhydrous $\text{Cu}(\text{HCOO})_2$ reference were not present in the diffraction pattern of the drop-cast condensate. This is likely because of a combination of a very small amount of etch product and preferential alignment of that small amount along specific crystal orientations of the zero-diffraction plate. There were two additional small peaks in the drop-cast condensate diffraction pattern at 26.4° and 28.1° which were

more aligned with peaks from the dihydrate reference. However, these two peaks are much weaker in intensity than the anhydrous peaks and comprise only a small portion of the product. This XRD analysis therefore suggests the primary volatile etch product of CuO reacting with formic acid is the anhydrous formate.

MALDI-TOF MS was used to further confirm the nature of the volatile etch product. Of the three matrices tested, only spectra collected with DHB showed any peaks matching the Cu isotope pattern. Spectra were collected for the DHB sample in both the positive and negative ion mode, but Cu peaks were present only in positive ion mode. Only one m/z region had peaks that could be associated with the isotope pattern of Cu, with a detailed view of that region shown in Fig. 6. The m/z ratio corresponded to anhydrous $\text{Cu}(\text{HCOO})_2$ as the product. The signal from the DHB matrix overlapped somewhat with the $\text{Cu}(\text{HCOO})_2$ product, with a fitting of all $\text{Cu}(\text{HCOO})_2$ and DHB peaks based on standard isotope ratios illustrated in Fig. 6. Note that all mass values are +1 greater than standard molecular weights because MALDI generates ions through protonation/deprotonation. MALDI-TOF MS thus confirms that the volatile product is anhydrous $\text{Cu}(\text{HCOO})_2$.

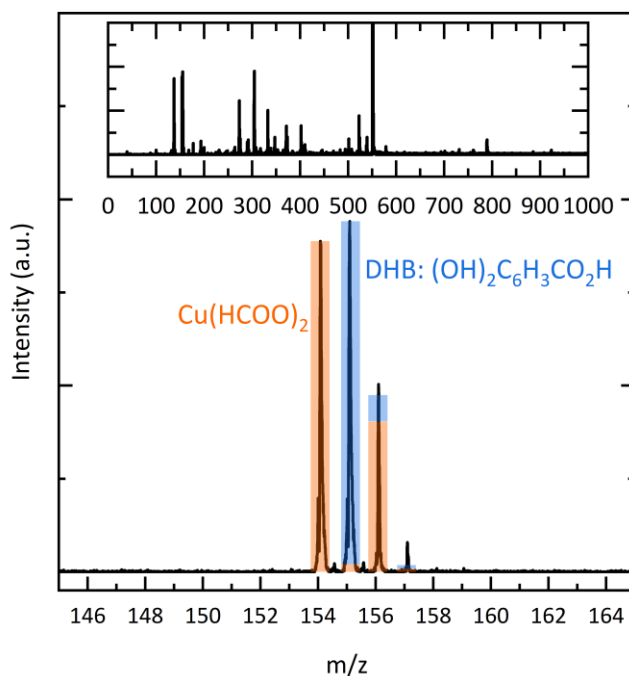


FIG. 6. MALDI-TOF MS spectra of the condensate collected from the volatile products and byproducts of the vapor phase reactor showing anhydrous $\text{Cu}(\text{HCOO})_2$ as the volatile product. DHB was the only matrix that volatilized/ionized the copper etch product, but its signal overlapped with that of the anhydrous $\text{Cu}(\text{HCOO})_2$. The patterns of $\text{Cu}(\text{HCOO})_2$ and DHB based on natural isotope distributions are shown as bars in the figure and closely align with the experimental results. The inset shows the full spectrum.

Based on all of the complementary measurements, the following reaction products are proposed. Formic acid reacts with CuO to form volatile $\text{Cu}(\text{HCOO})_2$ as the primary volatile Cu etch product, as shown by XRD and MALDI-TOF MS. This has the same stoichiometry as the product predicted by DFT., but there was no experimental evidence of the dimer predicted by the DFT calculations⁷. A possible explanation for this is that the dimers revert to monomers in solution phase when the product is condensed in the cold trap. On the surface, the reaction between formic acid vapor and CuO leaves the surface terminated with $\text{Cu}(\text{HCOO})_2 \cdot 4(\text{H}_2\text{O})$. The adsorbed water apparent in the AP-XPS results

supports the conclusion of a residual tetrahydrate on the surface, with MAS-NMR also showing the presence of hydrated $\text{Cu}(\text{HCOO})_2$.

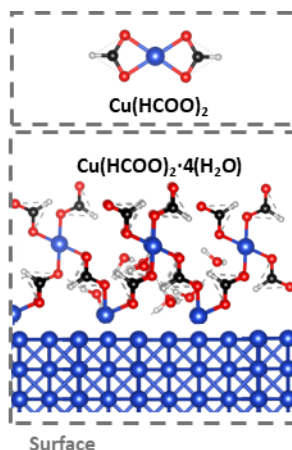


FIG. 7. In the removal half cycle of an ALE process based on plasma oxidation and formic acid vapor, formic acid reacts with CuO to form volatile $\text{Cu}(\text{HCOO})_2$ and H_2O while leaving residual $\text{Cu}(\text{HCOO})_2 \cdot 4(\text{H}_2\text{O})$ on the surface.

IV. SUMMARY AND CONCLUSIONS

The volatile and surface products were elucidated for a Cu ALE process that relied on formic acid vapor to etch oxidized Cu surfaces. Using a novel rotor packing method for a heterogeneous MAS-NMR rotor, it was shown that formic acid vapor reacts with CuO powder to form a paramagnetic Cu^{2+} product, but the identity of this product could not be confirmed due to the very fast relaxation time of the products. This rotor packing technique could still be useful for ALE product identification of diamagnetic metals. Very fast MAS-NMR at a spinning speed of 34 kHz confirmed that the etch product had a stoichiometry of $\text{Cu}(\text{HCOO})_2$, although the NMR results were inconclusive as to whether the volatile etch product was anhydrous or hydrated. AP-XPS of an

oxidized Cu surface showed that water adsorbed on the surface with increasing formic acid pressure, suggesting residual $\text{Cu}(\text{HCOO})_2 \cdot 4(\text{H}_2\text{O})$ on the surface after etching. MALDI-TOF MS and XRD analysis of the etch condensate collected in a cold trap downstream of the vapor phase reactor showed that the volatile etch product was anhydrous $\text{Cu}(\text{HCOO})_2$, in line with stoichiometry of the $\text{Cu}_2(\text{HCOO})_4$ product from the DFT predictions, but no dimer was observed.⁷ Based on these results, it is concluded that formic acid vapor reacts with CuO to form volatile anhydrous $\text{Cu}(\text{HCOO})_2$ and leaves the surface terminated with residual $\text{Cu}(\text{HCOO})_2 \cdot 4(\text{H}_2\text{O})$.

SUPPORTING INFORMATION

The Supporting Information contains O 1s and C 1s AP-XPS spectra of the formic acid background gas.

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AUTHOR DECLARATIONS

Conflicts of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- (1) Murarka, S. P.; and Hymes, S. W. Copper metallization for ULSL and beyond. *Crit. Rev. Solid State Mater. Sci.* **1995**, 20 (2), 87-124.
- (2) Pai, P. L.; Ting, C. H. Selective electroless copper for VLSI interconnection. *IEEE Electron Device Lett.* **1989**, 10 (9), 423-425.
- (3) Edelstein, D.; Heidenreich, J.; Goldblatt, R.; Cote, W.; Uzoh, C.; Lustig, N.; Roper, P.; McDevitt, T.; Motsiff, W.; Simon, A.; et al. Full copper wiring in a sub-0.25 μm /m CMOS ULSI technology. In *International Electron Devices Meeting. IEDM Technical Digest*, Washington, DC, USA, 10-10 Dec. 1997, 1997; pp 773-776.
- (4) Briggs, B. D.; Peethala, C. B.; Rath, D. L.; Lee, J.; Nguyen, S.; LiCausi, N. V.; McLaughlin, P. S.; You, H.; Sil, D.; Lanzillo, N. A.; et al. Fully aligned via integration for extendibility of interconnects to beyond the 7 nm node. In *2017 IEEE International Electron Devices Meeting (IEDM)*, San Francisco, CA, USA, 2-6 Dec. 2017, 2017; pp 14.12.11-14.12.14.
- (5) Hausmann, D. M.; Fox, A. R.; Lawlor, C. Selective growth of SiO_2 on dielectric surfaces in the presence of copper US 2019.
- (6) Murdoch, G.; Bömmels, J.; Wilson, C. J.; Gavan, K. B.; Le, Q. T.; Tőkei, Z.; Clark, W. Feasibility study of fully self aligned vias for 5nm node BEOL. In *2017 IEEE*

International Interconnect Technology Conference (IITC), Hsinchu, Taiwan, 16-18 May 2017, 2017; pp 1-4.

(7) Sheil, R.; Martirez, J. M. P.; Sang, X.; Carter, E. A.; Chang, J. P. Precise Control of Nanoscale Cu Etching via Gas-Phase Oxidation and Chemical Complexation. *J. Phys. Chem. C* **2021**, *125* (3), 1819-1832.

(8) Wang, Z.; Opila, R. L. In operando x-ray photoelectron spectroscopy study of mechanism of atomic layer etching of cobalt. *J. Vac. Sci. Technol. A* **2020**, *38* (2), 022611.

(9) Lin, X.; Chen, M.; Janotti, A.; Opila, R. In situ XPS study on atomic layer etching of Fe thin film using Cl₂ and acetylacetone. *J. Vac. Sci. Technol. A* **2018**, *36* (5), 051401.

(10) Chittock, N. J.; Maas, J. F. W.; Tezsevin, I.; Merckx, M. J. M.; Knoops, H. C. M.; Kessels, W. M. M.; Mackus, A. J. M. Investigation of the atomic layer etching mechanism for Al₂O₃ using hexafluoroacetylacetone and H₂ plasma. *J. Mater. Chem. C* **2025**, *13* (3), 1345-1358.

(11) Konh, M.; Janotti, A.; Teplyakov, A. Molecular Mechanism of Thermal Dry Etching of Iron in a Two-Step Atomic Layer Etching Process: Chlorination Followed by Exposure to Acetylacetone. *The J. Phys. Chem. C* **2021**, *125* (13), 7142-7154.

(12) Lii-Rosales, A.; Cavanagh, A. S.; Fischer, A.; Lill, T.; George, S. M. Spontaneous Etching of Metal Fluorides Using Ligand-Exchange Reactions: Landscape Revealed by Mass Spectrometry. *Chem. Mater.* **2021**, *33* (19), 7719-7730.

(13) Lii-Rosales, A.; Johnson, V. L.; Sharma, S.; Fischer, A.; Lill, T.; George, S. M. Volatile Products from Ligand Addition of P(CH₃)₃ to NiCl₂, PdCl₂, and PtCl₂: Pathway for Metal Thermal Atomic Layer Etching. *The J. Phys. Chem. C* **2022**, *126* (19), 8287-8295.

(14) Murdzek, J. A.; Lii-Rosales, A.; George, S. M. Thermal Atomic Layer Etching of Nickel Using Sequential Chlorination and Ligand-Addition Reactions. *Chem. Mater.* **2021**, *33* (23), 9174-9183.

(15) Partridge, J. L.; Abdulagatov, A. I.; Zywootko, D. R.; George, S. M. Limiting or Continuous Thermal Etching of First Row Transition Metal Oxides Using Acetylacetone and Ozone. *Chem. Mater.* **2024**, *36* (15), 7151-7161.

(16) Ogletree, D. F.; Bluhm, H.; Lebedev, G.; Fadley, C. S.; Hussain, Z.; Salmeron, M. A differentially pumped electrostatic lens system for photoemission studies in the millibar range. *Rev. Sci. Instrum.* **2002**, *73* (11), 3872-3877.

(17) Salmeron, M.; Schlögl, R. Ambient pressure photoelectron spectroscopy: A new tool for surface science and nanotechnology. *Surf. Sci. Rep.* **2008**, *63* (4), 169-199.

(18) Favaro, M.; Xiao, H.; Cheng, T.; Goddard, W. A.; Yano, J.; Crumlin, E. J. Subsurface oxide plays a critical role in CO₂ activation by Cu(111) surfaces to form chemisorbed CO₂, the first step in reduction of CO₂. *P.N.A.S.* **2017**, *114* (26), 6706-6711.

(19) Grass, M. E.; Karlsson, P. G.; Aksoy, F.; Lundqvist, M.; Wannberg, B.; Mun, B. S.; Hussain, Z.; Liu, Z. New ambient pressure photoemission endstation at Advanced Light Source beamline 9.3.2. *Rev. Sci. Instrum.* **2010**, *81* (5), 053106.

(20) Smith, T. G. Mechanistic Studies and Novel Processes for Atomic Layer Etching. PhD, University of California, Los Angeles, 2025.

(21) Chamas, A.; Qi, L.; Mehta, H. S.; Sears, J. A.; Scott, S. L.; Walter, E. D.; Hoyt, D. W. High temperature/pressure MAS-NMR for the study of dynamic processes in mixed phase systems. *Magn. Reson. Imaging* **2019**, *56*, 37-44.

- (22) Smith, T. G.; Morphet, D. R.; Yan, Z.; Cui, D.; Guerin, K. N.; Nwaubani, E.; Nocera, D. G.; Chang, J. P. Depoisoning Catalysts by Atomic Layer Etching. *ChemCatChem* **2025**, e00895.
- (23) Xia, Y.; Sautet, P. Thermodynamics of Atomic Layer Etching Chemistry on Copper and Nickel Surfaces from First Principles. *Chem. Mater.* **2021**, *33* (17), 6774-6786.
- (24) Ishii, Y.; Wickramasinghe, N. P.; Chimon, S. A New Approach in 1D and 2D ^{13}C High-Resolution Solid-State NMR Spectroscopy of Paramagnetic Organometallic Complexes by Very Fast Magic-Angle Spinning. *JACS* **2003**, *125* (12), 3438-3439.
- (25) Wickramasinghe, N. P.; Ishii, Y. Sensitivity enhancement, assignment, and distance measurement in ^{13}C solid-state NMR spectroscopy for paramagnetic systems under fast magic angle spinning. *J. Magn. Reson.* **2006**, *181* (2), 233-243.
- (26) Thurber, K. R.; Tycko, R. Measurement of sample temperatures under magic-angle spinning from the chemical shift and spin-lattice relaxation rate of ^{79}Br in KBr powder. *J. Magn. Reson.* **2009**, *196* (1), 84-87.
- (27) Lay, J. O., Jr. MALDI-TOF mass spectrometry of bacteria. *Mass Spectrom. Rev.* **2001**, *20* (4), 172-194.
- (28) Räder, H.; Schrepp, W. MALDI-TOF mass spectrometry in the analysis of synthetic polymers. *Acta Polym.* **1998**, *49* (6), 272-293.
- (29) Coffey, B. M.; Nallan, H. C.; Ekerdt, J. G. Vacuum ultraviolet enhanced atomic layer etching of ruthenium films. *J. Vac. Sci. Technol. A* **2021**, *39* (1), 012601.
- (30) Murdzek, J. A.; George, S. M. Effect of crystallinity on thermal atomic layer etching of hafnium oxide, zirconium oxide, and hafnium zirconium oxide. *J. Vac. Sci. Technol. A* **2020**, *38* (2), 022608.
- (31) Martin, R. L.; Waterman, H. 269. Magnetic studies with copper(II) salts. Part IV. Remarkable magnetic behaviour of copper(II) formate and its hydrates. *J. Chem. Soc. (Res.)* **1959**, (0), 1359-1370, 10.1039/JR9590001359.
- (32) Trotochaud, L.; Head, A. R.; Pletincx, S.; Karşlıoğlu, O.; Yu, Y.; Waldner, A.; Kyhl, L.; Hauffman, T.; Terryn, H.; Eichhorn, B.; et al. Water Adsorption and Dissociation on Polycrystalline Copper Oxides: Effects of Environmental Contamination and Experimental Protocol. *The Journal of Physical Chemistry B* **2018**, *122* (2), 1000-1008.
- (33) Deng, X.; Herranz, T.; Weis, C.; Bluhm, H.; Salmeron, M. Adsorption of Water on Cu_2O and Al_2O_3 Thin Films. *The J. Phys. Chem. C* **2008**, *112* (26), 9668-9672.
- (34) Jeong, B.; Jeon, H.; Toyoshima, R.; Crumlin, E. J.; Kondoh, H.; Mun, B. S.; Lee, J. Dehydration Pathway for the Dissociation of Gas-Phase Formic Acid on Pt(111) Surface Observed via Ambient-Pressure XPS. *The J. Phys. Chem. C* **2018**, *122* (4), 2064-2069.
- (35) Lowe, I. J. Free Induction Decays of Rotating Solids. *Phys. Rev. Lett.* **1959**, *2* (7), 285-287.
- (36) Pell, A. J.; Pintacuda, G.; Grey, C. P. Paramagnetic NMR in solution and the solid state. *Prog. Nucl. Magn. Reson. Spectrosc.* **2019**, *111*, 1-271.
- (37) Lee, Y.; George, S. M. Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions with $\text{Sn}(\text{acac})_2$ and Hydrogen Fluoride. *ACS Nano* **2015**, *9* (2), 2061-2070.
- (38) Chittock, N. J.; Vos, M. F. J.; Faraz, T.; Kessels, W. M. M.; Knoops, H. C. M.; Mackus, A. J. M. Isotropic plasma atomic layer etching of Al_2O_3 using a fluorine containing plasma and $\text{Al}(\text{CH}_3)_3$. *Appl. Phys. Lett.* **2020**, *117* (16).

- (39) Mameli, A.; Verheijen, M. A.; Mackus, A. J. M.; Kessels, W. M. M.; Roozeboom, F. Isotropic Atomic Layer Etching of ZnO Using Acetylacetone and O₂ Plasma. *ACS Appl. Mater. Interfaces* **2018**, *10* (44), 38588-38595.
- (40) Mouche, M.-J.; Mermet, J.-L.; Romand, M.; Charbonnier, M. Metal—organic chemical vapor deposition of copper using hydrated copper formate as a new precursor. *Thin Solid Films* **1995**, *262* (1), 1-6.

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