

**CLEANING OF COPPER SURFACE USING
VAPOR-PHASE ORGANIC ACIDS**

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In ULSI fabrication with interconnection using copper and low dielectric constant (low-k) materials, surface damages such as oxidation and roughing of copper by post-plasma-etch process have been crucial to degrade device performances. Vapor phase cleaning of copper surface are advantageous, because of high reactivity of copper and processes without exposure to atmospheric ambient. Thus, we have examined vapor phase treatments of copper surface using various carboxylic acids (e.g., formic acid, acetic acid, and n-valeric acid etc.).

Samples were prepared as follows; initially a copper films (about 1000 nm thickness) was deposited on bare Si substrate by sputtering. The film was oxidized under atmospheric ambient at 200°C, and then, was exposed to carboxylic acid vapor using an apparatus shown in Fig.1.

When the surface of oxidized copper film was exposed to acetic acid vapor at 200°C, the surface was changed to be shiny and greenish-blue volatile products were collected by a liquid nitrogen trap. These products dissolved in methanol were analyzed by electro-spray-ionization mass-spectrometry (ESI-MS). Intense positive ions were detected at m/z 214 and 216 as shown in upper part of Fig. 2. The ion intensity ratio of the two is roughly 7:3, which corresponds to the isotropic abundance of ⁶³Cu/⁶⁵Cu. These results indicate a complex ion consisting of copper (II) acetate, Cu(CH₃COO)₂, and protonated methanol derived from solvent. To confirm this, deuterium-labeled acetic acid, CD₃COOD, was used instead of CH₃COOH. An ESI-MS spectrum of the volatile products is shown in bottom part of Fig.2. Comparing with these spectra, the intense two peaks is observed at six higher m/z of those. This concluded that one of the volatile products is copper (II) acetate. Additionally, higher mass components including binuclear copper complexes were observed at m/z 333,335, and 337[the ratio is 5.4/4.7/1] derived from ⁶³Cu⁶³Cu, ⁶³Cu/⁶⁵Cu, and ⁶⁵Cu/⁶⁵Cu (not shown Fig.2).

Next, we compared reactivity between acetic acid and formic acid. Using infrared reflection-absorption-spectroscopy (IR-RAS), absorption peak of carboxylate ion on the surface was detected at around 1630 cm⁻¹. Figure 3 shows time evolution of the 1630 cm⁻¹ peak intensity when carboxylic acid vapor was exposed. In the case of using the formic acid, formation of surface carboxylate ion is several times faster than that of using acetic acid. Dehydrogenation, which relates pKa(acid dissociation constant), causes formation of carboxylate ion. The formation ratio is close to that of pKa between formic acid and acetic acid.

In conclusion, we found that vapor of simple organic acids eg., formic acid, and acetic acid, can remove oxidized copper. In this vapor phase cleaning process, the following processes are considered. The acid gas adsorbes on surface of oxidized copper and proton is transferd, followed by carboxylate ion formation. These carboxylate ions form several complexes of copper carboxylates. These complexes volatilize because of their large vapor pressures.

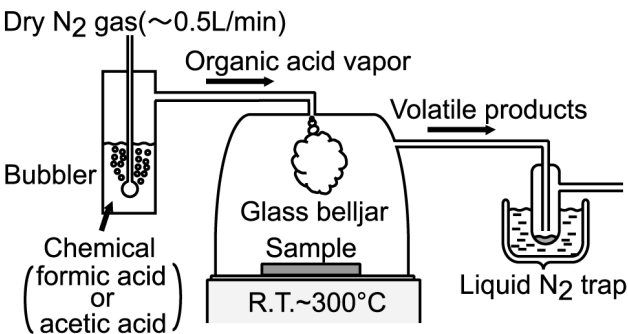


Fig. 1 Schematic view of the experimental apparatus.

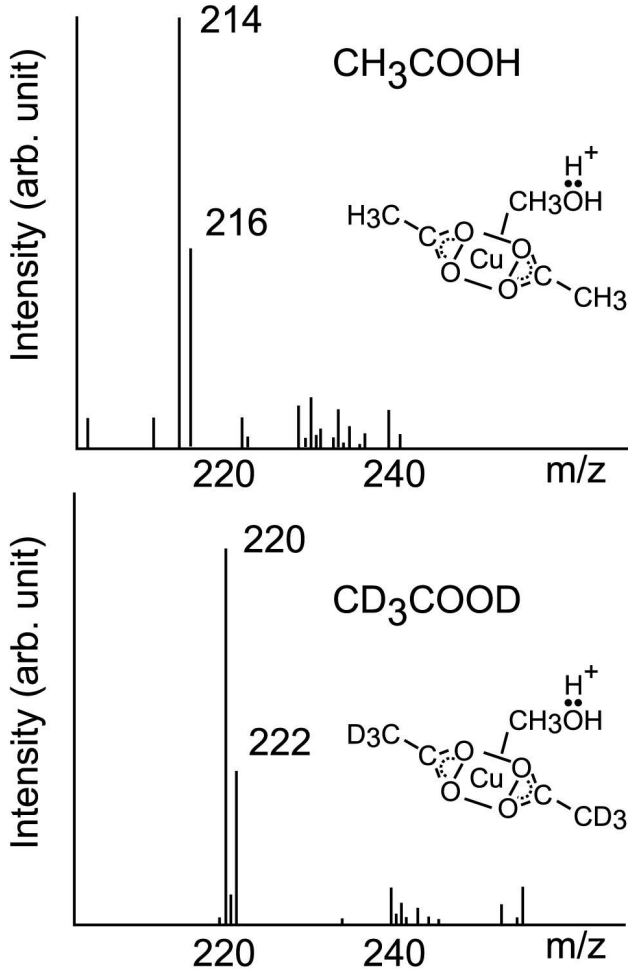


Fig. 2 ESI-MS spectra of the reaction products of acetic acids (upper) and deuterium-labeled acetic acid (bottom).

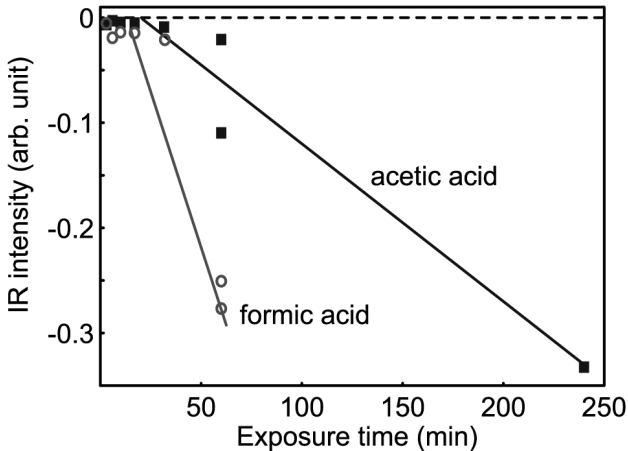


Fig. 3 Time evolution of infrared absorption at 1630cm⁻¹.