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Etchant Solutions for the Removal of Cu(0) in a Supercritical CO_2-Based "Dry" Chemical Mechanical Planarization Process for Device Fabrication

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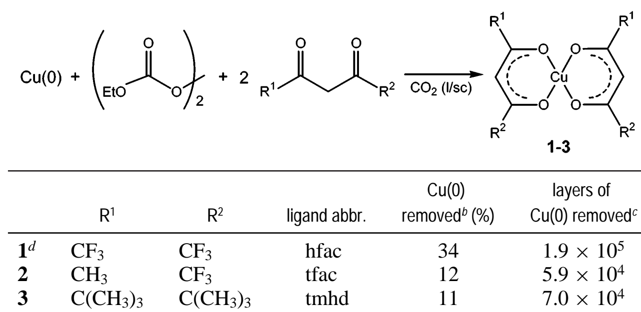
The drive toward miniaturization in the microelectronics industry is fueling the development of smaller and smaller chip geometries. Line widths of 90 nm will be the standard for next generation devices, down from 130 nm line widths, which are common in today's semiconductor devices. Such feature size reduces the tolerance level for defects. Chemical mechanical planarization or polishing (CMP) is a rapidly growing process used in the microelectronics industry to make metal and dielectric layers on silicon substrates smooth and defect free with vertical dimension control.[1] There is a growing interest in using copper as the interconnect metal due to its superior electrical conductivity and better electromigration resistance than current tungsten- or aluminum-based materials.[2] Because of the difficulties involved in patterning copper by conventional dry-etch techniques, CMP has emerged as a new technology for implementing copper in submicron semiconductor devices. During CMP, the chemical slurry removes copper from the wafer surface by a combination of chemical and mechanical means. In the chemical process, the metallic copper is oxidized and chelated, while in the mechanical process, the copper surface is rubbed against a polishing pad until global planarization is achieved.[3] A typical copper CMP slurry contains one or more of the following: chemical etchants (oxidants), chelating agents, buffers, abrasive particles, passivating agents, and cosolvent(s).

Most of the current processes use water as the solvent for the CMP slurry leading to both technical and environmental difficulties. One particular technical drawback of the aqueous-based CMP processes is the incompatibility of porous low-k inorganic and organic interlayer dielectric materials with water. Inefficient water removal can result in higher than expected dielectric constants. Environmental issues include the generation of large quantities of contaminated aqueous waste (containing acids, buffers, abrasives, etc.), which cannot be readily recycled. Nonaqueous CMP processes suffer from similar environmental drawbacks as many of these processes use highly undesirable organic solvents such as carbon tetrachloride.[1] Thus, there exists a great demand for new CMP technologies which circumvent the technical and environmental drawbacks of the current aqueous and chlorinated organic solvents.

In this regard, we present our first efforts to establish a "dry" CMP process based on dense CO_2. The key challenge to realizing this goal is the unprecedented oxidation and removal of an elemental metal film in CO_2, a solvent that has a very low dielectric constant. Both liquid and supercritical (sc) CO_2 have significant potential for replacing current aqueous and organic CMP solvents. We consider CO_2-based processes as "dry" processes, because at standard temperature and pressure CO_2 is a gas. Therefore, CO_2 is amenable for use in tools/chambers that can be easily evacuated and interfaced with vacuum cluster tools which are standard "dry" tools used in manufacturing facilities today. Unlike water, condensed CO_2 has an extremely low viscosity and a low surface tension − characteristics desired for CMP processing. Additionally, the environmental difficulties associated with the use of organic solvents (e.g., solvent toxicity and oxidation) as well as the recyclability of the organic or aqueous solvents are avoided. Condensed CO_2 is easily separated from the other chemicals in the proposed CMP slurry by tuning the pressure and/or temperature.

Table 1. Reaction of Cu(0) and EPDC with Various β-Diketones[a]



	R^1	R^2	ligand abbr.	Cu(0) removed[b] (%)	layers of Cu(0) removed[c]
1[d]	CF_3	CF_3	hfac	34	1.9×10^5
2	CH_3	CF_3	tfac	12	5.9×10^4
3	$C(CH_3)_3$	$C(CH_3)_3$	tmhd	11	7.0×10^4

[a] All reactions were performed in a 10 mL high-pressure cell with a Cu coupon (1 equiv), EPDC (2 M in hexanes, 1 equiv), and a β-diketone (2 equiv) in $scCO_2$ (ca. 8.0 mL), at 40 °C and 214 bar for 20 h. Caution: EPDC can be explosive; use proper safety procedures. [b] Based on the weight loss of copper. [c] Determined using the Cu covalent metallic radius, the area, and the percentage of removed Cu(0). [d] Isolated as the monohydrate.

Herein we give the first report of the development of the chemical aspects of CMP in dense CO_2. Copper coupons (99.999%, 0.1 mm thick) were treated with a "dry", homogeneous solution in $scCO_2$ that contained an oxidant, ethyl peroxydicarbonate (EPDC), and a commercially available β-diketone chelating agent (see Table 1). Representative oxidation and chelation reactions on the copper coupons were performed in a 10 mL high-pressure view cell with $scCO_2$ as the solvent at 40 °C and 214 bar for 20 h. After 20 h, the cell was vented, the copper coupons were rinsed with hexanes and reweighed, and the CO_2 soluble products were analyzed.

Treatment of a Cu coupon with the originally colorless EPDC/chelant formulation in CO_2 results in the formation of a bright green, homogeneous solution after a few minutes (Figure 1). The reactions were monitored in situ using FTIR (Figure 2) and UV/vis spectroscopies. The IR stretching frequencies of the green CO_2 reaction solution correlate well with the formation of $Cu(hfac)_2 \cdot H_2O$ − authentic samples were used as confirmation.[4] For example, for $Cu(hfac)_2 \cdot H_2O$, relevant absorbances in KBr include: 1643

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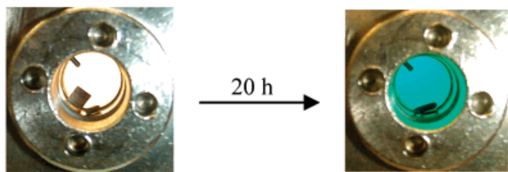

Figure 1. Before and after reaction of Cu(0) (1 equiv) + EPDC (2 M in hexanes, 1 equiv) + hfac (2 equiv) in CO_2 media (40 °C, 214 bar).

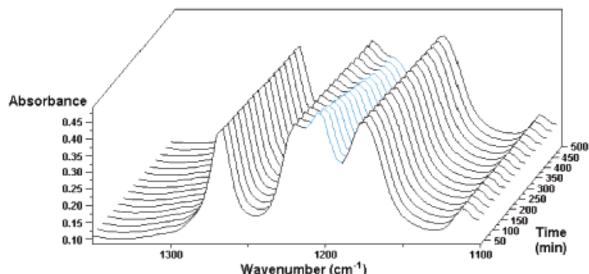

Figure 2. FTIR spectra of Cu(0) + EPDC (7 M in hexanes, 10 equiv) + hfac (20 equiv) in $scCO_2$ media (40 °C, 214 bar). The ligand concentration decreases over time (shown in blue).

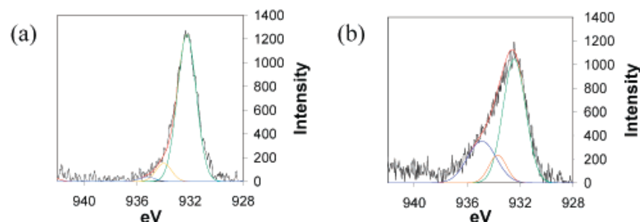

Figure 3. XPS spectra of the copper surfaces (a) before and (b) after treatment with EPDC (2 M in hexanes, 1 equiv) and hfac (2 equiv) for 18 h in $scCO_2$ (40 °C, 214 bar).

(ν(C⋯O)), 1611 (ν(C⋯C)), 1562 and 1534 (ν(C⋯O) + CH bend), 1355 (ν(C⋯C) + C−CF_3 stretch), 1211 (CF_3 stretch), 1142 and 1104 (CH in plane bend), and 804 (CH out-of-plane bend + C−CF_3 stretch) cm^{-1}. UV/vis spectra of the bis(β-diketonate)-copper(II) products in CH_2Cl_2 contain d−d transitions between 660 and 680 nm, as well as intraligand $\pi-\pi^*$ and/or LMCT bands at higher frequencies (380−390, 345−375, and 345−360 nm).[5] These spectra correlate well with authentic samples.

The % removal of copper has been summarized in Table 1. The results indicate that Cu(0) removal increases in the order tmhd = tfac < hfac. This trend is consistent with the estimated solubilities of complexes **1**−**3** in $scCO_2$. Increases in the fluorine content of the ligands enhance the solubilities of the resultant complexes due to the strong interaction between fluorine and CO_2.[5]

As the surface structure is particularly important in the CMP process, we have monitored the effect of oxidation and chelation using a PHI 5400 X-ray photoelectron spectrometer (XPS) with a Mg Kα source at a power of 350 W. Shifts were corrected with a binding energy scale fixed at the C(1s) binding energy of 284.6 eV. The copper $2p_{3/2}$ XPS spectrum of the copper coupon (blank) indicates that the surface consists primarily of Cu(I), in the Cu_2O form, centered at a binding energy of 932.6 eV.[6,7]

Treatment of a Cu coupon with the EPDC (1 equiv) and hfac (2 equiv) over 18 h results in a depletion of the Cu_2O on the surface, and an increase of Cu(II), as CuO (binding energy 933.7 eV) and CuL_2 (binding energy 934.9 eV) species where L = OH^- or diketonate ligand. Figure 3 demonstrates the effect of the "dry" CO_2 etchant formulation on the surface of the copper coupon. Spectrum (a) shows the major species on the surface of the copper coupon to be Cu_2O (88%). This can be compared to the surface of the copper coupon treated with the "dry" CO_2 etchant solution formulation (spectrum (b)) which is 62% Cu_2O. Further XPS analyses of the copper coupons after reaction with EPDC and ligand in $scCO_2$ show little change in the surface composition between hfac and tmhd ligands. A 10% decrease in Cu_2O is observed for the reaction with tfac.

Surface roughness was examined using atomic force microscopy (AFM) and scanning electron microscopy (SEM). AFM analyses were performed on a copper coupon before and after treatment with the "dry" CO_2 etchant formulation. Notably, the blank had a nonuniform surface with a rms roughness of 15−23 nm. The copper surface after reaction with the hfac gave a heterogeneous surface comprised of smaller areas of extremely smooth surface interdispersed with rougher patches. This material had an rms roughness value of ca. 50−175 nm. The surface of the coupon reacted with tmhd appeared to be uniformly covered with small divots and had a rms roughness value of 60−70 nm. Finally, the copper coupon exposed to the tfac ligand was the smoothest with rms roughness values ranging from 13 to 15 nm. Clearly, the planarization aspects of this new "dry" CO_2 etchant formulation for use in CMP now need to be explored in the context of mass transport limitations as well as during mechanical polishing.

In summary, while others have shown that metal β-diketonates can be formed from metal ions and are soluble in CO_2[5,8] and that metal films can be deposited on substrates from CO_2 media,[9] to the best of our knowledge, no one has previously demonstrated the removal and etching of Cu metal using a CO_2-based process. These results indicate an important step in the development of a "dry" CO_2-based process for CMP.

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