

Chemical Fluid Deposition of Metals from Supercritical Fluids

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We recently reported a new technique called chemical fluid deposition (CFD) that can be used to deposit metal films from supercritical fluids (SCF) onto planar surfaces and patterned substrates. This technique produces metal films which meet the requirements of the microelectronics industry for device fabrication.

In this presentation, we concentrate on the deposition of copper and its application to semiconductor devices. We present three different routes to copper using CFD: H₂-assisted reduction,[1] thermal disproportionation [2] and alcohol-assisted reduction[3] of copper β-diketonate compounds.

INTRODUCTION

Chemical Fluid Deposition (CFD) involves the chemical reduction of organometallic compounds in SCFs to yield high purity deposits.[4] Typically, the reaction is initiated upon the addition of H₂ or other reducing agent. The advantages of CFD over conventional deposition techniques are a consequence of the unique properties of SCFs, which lie intermediate to those of liquids and gases. Supercritical CO₂ (scCO₂) has been used in most of the depositions because it is non-flammable, non-toxic and it has convenient critical parameters (T_c=31 °C, P_c=73.8 bar).[5] Furthermore, many organometallic compounds dissolve appreciably in scCO₂. [6, 7] The presence of scCO₂ facilitates desorption of ligand decomposition products, which reduces contamination of the metal film. Although CFD is a solution-based technique, the transport properties of scCO₂ (low viscosity and high diffusivity relative to liquids), the absence of surface tension and its miscibility with gaseous reducing agents such as H₂ promote infiltration into complex geometries and mitigate mass transfer limitations common to liquid phase reductions. To date, high purity Pt, Pd, Au, Rh, Ni, Cu and other metal films have been deposited by CFD from scCO₂ using appropriate precursors.[1, 2, 8-11] CO₂ technology is also under development for other applications in the microelectronics industry [12-14] Nevertheless our technique is not limited to scCO₂ and we have deposited Cu films by CFD from supercritical C₂F₆ (scC₂F₆)[2] and supercritical CF₃H (scCF₃H).

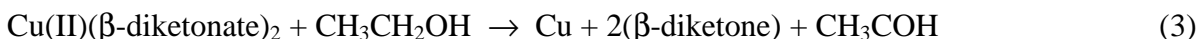
Cu is the preferred material for interconnect structures in integrated circuits due to its low resistivity and superior electromigration resistance.[15] We have previously shown that CFD of Copper β-diketonates provides a single-step route for the deposition of device-quality Cu films. [1-3] Three different reaction mechanisms have been identified: H₂-assisted reduction,[1] thermal disproportionation [2] and alcohol-assisted reduction.[3] H₂-assisted reduction of Cu(II)(β-diketonate)₂ precursors proceeds according to (1).



Deposition from precursors of the type $\text{Cu(I)(}\beta\text{-diketonate)}\text{L}_n$ can proceed by an alternative mechanism, thermal disproportionation, in the absence of H_2 following (2)



Alcohol assisted reduction using EtOH may proceed through Eq. (3)



In this presentation we discuss the utility of the different chemistries for the deposition of copper films.

MATERIALS AND METHODS

Cu films were deposited using a number of Cu(I) and Cu(II) β -diketonates obtained from commercial suppliers. Cu(II) Bis(hexafluoroacetylacetonate) $[\text{Cu}(\text{hfac})_2]$ and Cu(II) Bis(tetramethylheptanedionate) $[\text{Cu}(\text{tmhd})_2]$ were obtained from Strem and Cu(II) ethylacetoacetate $[\text{Cu}(\text{etac})_2]$ from Gelest, Inc. Cu(I)(hexafluoroacetylacetonate)L compounds $[\text{Cu(I)(hfac)L}]$ where L is (2-butyne), (1,5-cyclooctadiene) [COD] or (vinyltrimethylsilane) [VTMS] were purchased from Gelest. Cu(I)(hfac)(2-methyl-1-hexene-3-yne) was obtained from ADCS, Inc.. All compounds were used without further purification. Methanol [MeOH] (+99.9%, Omnisolv, EM Science), ethanol [EtOH] 200 proof (+99.5%, Aldrich), 1-propanol [1-PrOH] (+99.9%, Burdick & Jackson), 2-propanol [2-PrOH] (+99.5%, Mallinckrodt SpectrAR), 1-butanol [1-BuOH] (+99.9%, Mallinckrodt SpectrAR) and 2-butanol [2-BuOH] (+99.5%, Sigma-Aldrich), were used as received. Coleman grade carbon dioxide (99.99+% purity), hexafluoroethane (99.95+ % purity) and ultra high purity hydrogen (99.999+%) were obtained from Merriam-Graves. Trifluoromethane (98+%) was obtained from Aldrich. Test wafers were donated by Novellus Systems.

The experiments were carried out using an 80 ml high-pressure cold-wall reactor shown in Figure 1.[1] The cold wall reactor is a two-flanged stainless-steel high-pressure vessel with an electrically heated stage. The reactor is lined with a ceramic. The temperature of the walls (T1) and the stage (T2) are controlled independently. In these experiments, the walls of the reactor were heated to 60-80 °C by heating cartridges while the stage was heated resistively to 200-300 °C. Metals deposited selectively onto the heated substrate. The experiments were conducted in batch mode.

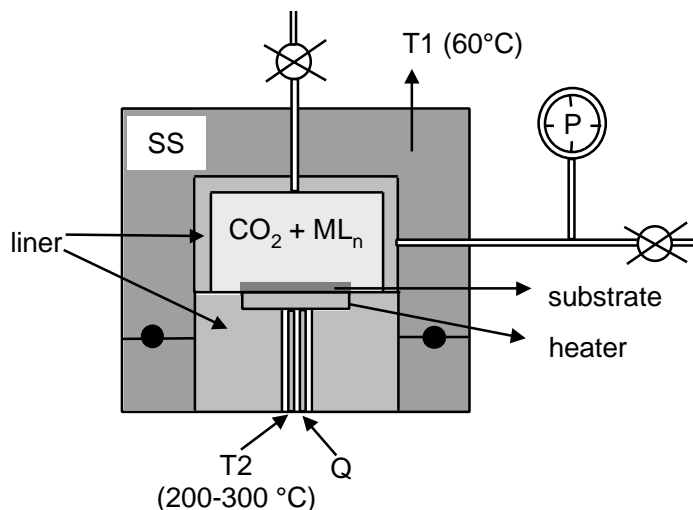


Figure 1. Schematics of the cold-wall reactor.

In a typical experiment the solid precursor and a substrate were loaded into the reactor and the vessel was sealed and purged with N₂. Liquid precursors were introduced using a sample loop. The reactor walls were heated to the desired temperature (60-80 °C) and the reactor was charged with CO₂ up to the selected pressure using a computer controlled syringe pump. The compound was allowed to dissolve for 30-45 minutes. Then the substrate was heated to a temperature between 200–300 °C. For H₂-assisted reductions, deposition was initiated by adding H₂ into the reactor in stoichiometric excess. For the alcohol-assisted experiments, a given volume of alcohol was added to the reactor using a sample loop. In the thermal disproportionation experiments, no reducing agent was introduced into the system. For the experiments with scC₂F₆ and scCF₃H, the reactor was loaded with the SCF from a pressurized high-pressure manifold via a pressure drop. Solubility of the compounds in scCO₂ was assessed using a view cell[5] or a closed loop recirculating system,[16] both methods are available in our laboratory.

RESULTS

H₂-assisted reduction of Cu(II) and Cu(I) β-diketonate compounds in scCO₂ yielded highly reflective Cu films. At temperatures of 200 °C or less deposition was selective for metal surfaces or catalytic seed layers over the bare Si oxide. At temperatures above 225 °C, Cu deposited directly onto the native oxide of Si or Cu diffusion barrier layers such as TiN. [1, 2, 16] An example of Cu deposited by the H₂ reduction of Cu(tmhd)₂ on a patterned test wafer is provided in Figure 2. Exceptional trench filling is evident in features 100 nm wide by 800 nm deep.

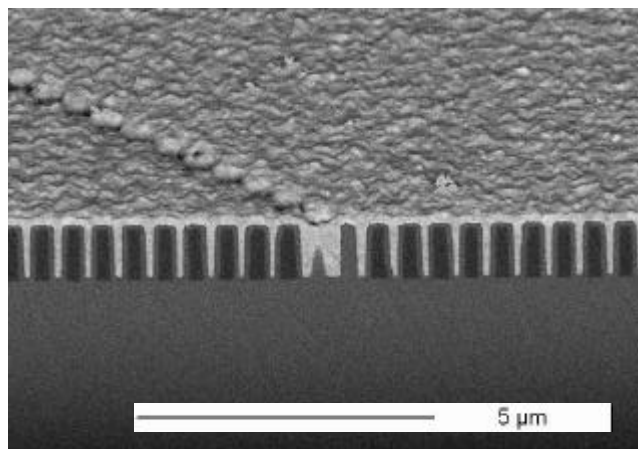


Figure 2. FIB-SEM of a copper layer deposited by H₂-reduction of a solution of Cu(tmhd)₂ in scCO₂ onto a Pd-seeded Si test wafer.

The utility of thermal disproportionation for Cu deposition via CFD using Cu(I) precursors in the absence H₂ was also studied.[2] Attempts to deposit high purity Cu films by disproportionation of the Cu(I)(hfac)L compounds where L is (2-butyne), (COD), (VTMS) or (2-methyl-1-hexene-3-yne) in scCO₂ in the absence of H₂ at 225⁰ C were unsuccessful and yielded highly oxidized Cu films in each case. On the contrary, at the same conditions, H₂-assisted reduction of any of the studied Cu(I)(hfac)L compounds in scCO₂ rendered pure copper. The thermal decomposition of the ligand in absence of H₂ and the presence of trace impurities in the supercritical fluid are likely responsible for the oxidation of the film.

Oxidation of the film during thermal disproportionation was reduced significantly when experiments were conducted in other SCFs such as scC_2F_6 , [2] and nearly suppressed in $scCF_3H$. However, adhesion of the films produced in these fluorinated fluids to the substrate was poor. Differences in the nucleation and growth of copper films in the different SCFs could explain the different degree of oxidation found. Figure 3 shows an X-ray diffraction pattern (XRD) of a film deposited from the thermal disproportionation of $Cu(hfac)(2\text{-butyne})$ in $scCF_3H$ at 225 °C. XRD pattern shows the presence of Cu. A very weak shoulder at $2\theta \text{ ca. } 36$ indicates the presence of some Cu_2O . Furthermore, films deposited at these conditions appeared slightly darker than those produced with H_2 , reflecting the lower purity of the film.

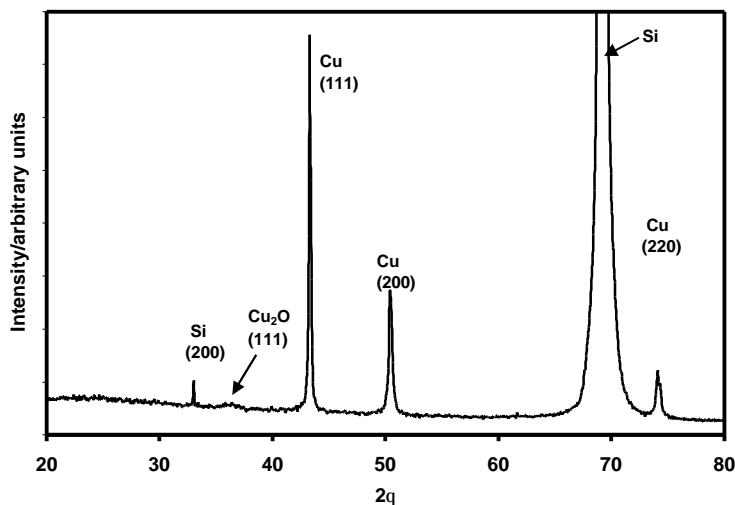


Figure 3. XRD pattern of film deposited by CFD of $Cu(hfac)(2\text{-butyne})$ in $scCF_3H$ at 225 °C without H_2 .

We have also studied the use of alcohols as reducing agents to deposit Cu and compared the films produced with those obtained using H_2 . [3] Since $Cu(II)$ precursors including $Cu(hfac)_2$ and $Cu(tmhd)_2$ are soluble in ethanol, the alcohol can be used as both a liquid carrier for the precursor and as a reducing agent. Highly reflective copper films were deposited via CFD of $Cu(tmhd)_2$ and $Cu(etac)_2$ compounds using ethanol as the reducing agent at temperatures slightly higher than those employed in the H_2 assisted experiments. Deposition of Cu occurred as a result of the reduction of the $Cu(II)$ compound by ethanol, which was oxidized to acetaldehyde. Resistivities of the films deposited using $Cu(tmhd)_2$ and ethanol are as low as $2.0 \mu\Omega\text{-cm}$, which is very similar to those deposited using H_2 .

Deposition of copper from $Cu(tmhd)_2$ solution in $scCO_2$ were carried out using a series of alcohols (MeOH, 1-PrOH, 2-PrOH, 1-BuOH and 2-BuOH) at equivalent deposition conditions, precursor concentrations and alcohol loadings. Sterically hindered alcohols were less effective at the same conditions. Deposition with 2-BuOH required higher alcohol concentrations while attempted depositions with 2-PrOH were not successful. The different efficiencies of the alcohols for $Cu(tmhd)_2$ reduction can not be explained by the alcohols susceptibility to oxidation alone, as oxidation of 2-PrOH to acetone is thermodynamically favored. Steric considerations for the interaction of the alcohol with the surface and/or with the precursor seem to be important. The higher acidity of 2-BuOH versus 2-PrOH in the gas phase [17] could explain the difference between the sterically hindered alcohols. It is possible

that 2-PrOH could serve as reducing agents for other β -diketonate compounds with less severe steric constraints.

CONCLUSION

Chemical Fluid Deposition is an effective method to deposit device quality copper films. H_2 -assisted reduction of Cu(II) and Cu(I) β -diketonate compounds in $scCO_2$ rendered high purity Cu films. Deposition was conformal to the surface topology for features as narrow as 100 nm and high aspect ratios. Thermal disproportionation of Cu(I) β -diketonate compounds in $scCO_2$, scC_2F_6 and $scCF_3H$ yielded poor quality copper films. Different degrees of oxidation of the copper films were observed in the different SCFs. Alcohol-assisted reduction of Cu(II) β -diketonate compounds proceeded readily at temperatures slightly higher than the H_2 -assisted experiments. Quality of the films produced using ethanol as reducing agent was very similar to that of the films produced using H_2 . Sterically hindered alcohols were less effective at the same conditions. Differences in reduction efficiencies between primary and secondary alcohols were observed which suggest that steric effects may play an important role. Differences in acidity among the different alcohols are also important.

ACKNOWLEDGMENTS

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REFERENCES

- [1] Blackburn, J. M., Long D.P., Cabañas, A. and Watkins, J.J., *Science*, Vol 294, **2001**, p. 141.
- [2] Cabañas, A., Blackburn, J.M. and Watkins, J.J., *Microelectronic Engineering*, Vol 64, **2002**, p. 53
- [3] Cabañas, A., Shan, X. and Watkins, J.J., *Chemistry of Materials*, submitted, **2002**.
- [4] Watkins, J.J. and McCarthy, T.J., University of Massachusetts, U.S. Patent # 5,789,027, 1998.
- [5] McHugh M.A. and Krukonis, V.J., *Supercritical Fluid Extraction: Principles and Practice*, Butterworths, Boston, 1986.
- [6] Smart, N.G., Carleson, T., Kast, T., Clifford, A.A., Burford, M.D. and Wai, C.M., *Talanta*, 44, **1997**, p.137.
- [7] Lagalante, A.F., Hansen, B.M., Bruno, T.J. and Sievers, R.E., *Inorganic Chemistry*, 34, **1995**, p. 5781.
- [8] Watkins, J.J., Blackburn, J.M. and McCarthy, T.J., *Chemistry of Materials*, 11, **1999**, p. 213.
- [9] Blackburn, J.M., Long, D.P. and Watkins, J.J., *Chemistry of Materials*, 12, **2000**, p. 625.
- [10] Long, D.P., Blackburn, J.M. and Watkins, J.J., *Advanced Materials*, 12, **2000**, p. 913.
- [11] Fernandes, N., Fisher, S.M., Poshusta, J.C., Vlachos, D.G., Tsapatsis, M. and Watkins, J.J., *Chemistry of Materials*, 13, **2001**, p. 2023.
- [12] Goldfarb, D.L., de Pablo, J.J., Mealey, P.F., Simons, J.P., Moreau, W.M. and Angelopoulos, M., *J. Vac. Sci. Technol. B*, 18, **2000**, p.3313.
- [13] Sundararajan, N., Yang, S., Ogino, K., Valiyaveetil, S., Wang, J., Zhou, X. and Ober, C.K., *Chemistry of Materials*, 12, **2000**, p. 41.
- [14] Mount, D.J., Rothman, L.B. and Robey R.J., *Solid State Technology*, 45, **2002**, p. 103.

[15] Kotas T.T. and Hampden-Smith, M.J., The Chemistry of Metal CVD, VCH, Weinheim, **1994**.

[16] Blackburn, J.M., Cabañas, A., Zong, Y, Quinn, J.D. and Watkins, J.J., in Advanced Metallization Conference (AMC) (Y. S.-D. A.J. Mckerrow, S. Zaima, T. Ohba, ed.), MRS, Montreal, Canada, 2001, p. 177.

[17] Gas phase acidity defined as ΔG for $\text{ROH}(\text{g}) \Rightarrow \text{RO}^-(\text{g}) + \text{H}^+(\text{g})$ taken from the compilation of data given by NIST (<http://webbook.nist.gov/>).