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by

C. Roger, T. S. Corbitt, T. T. Kodas
and M. J. Hampden-Smith

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Department of Chemistry and Center for Micro-Engineered Ceramics

University of New Mexico

Albuquerque, NM 87131.

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AEROSOL-ASSISTED CHEMICAL VAPOR DEPOSITION OF COPPER: A LIQUID DELIVERY APPROACH TO METAL THIN FILMS.

Christophe ROGER[‡], Thomas S. CORBITT[‡], Toivo T. KODAS^{‡*}
and Mark J. HAMPDEN-SMITH^{‡*}

Departments of Chemistry[‡] and Chemical Engineering[‡]
University of New Mexico,
Albuquerque, NM 87131.

Aerosol-Assisted Chemical Vapor Deposition (AACVD) has been used to attain high deposition rates (1000 Å/min, up to 800 Å/min at 140°C) of Cu films at low temperatures (120-200°C) from toluene solutions of (hfac)Cu(1,5-COD) in a warm-wall reactor. The films are crystalline and exhibit resistivities close to bulk (1.7-3.5 μΩcm). Activation energies calculated from the deposition rate as a function of the preheating temperature and the substrate temperature (varying also the nozzle-substrate distance) were 6.8, 8.9 (0.7 cm) and 9.1 (1.7 cm) kcal/mol, respectively.

[‡]Current address: Elf Atochem, N.A., 900 First Avenue, P.O. Box 1536, King of Prussia, PA 19406-0018.

*Authors to whom correspondence should be addressed.

The Chemical Vapor Deposition (CVD) of metal films from metal-organic precursors has potential applications in the microelectronics industry.¹⁻³ Copper is a candidate for metal interconnects because of its low resistivity and good electromigration resistance compared to other metals.⁴ However, CVD requires volatile precursors, rapid precursor transport rates and thermal decomposition pathways that lead to deposition of high-purity films at high rates.⁴ Traditional approaches for CVD of metals have been limited in many cases by the paucity of precursors with high vapor pressures as well as by the relatively low purity of the deposited films.⁴ This latter problem has been solved in many cases by the design of new precursors. In the case of CVD of Cu, the compounds (β -diketonate)CuL, L = Lewis base, deposit high-purity Cu films at low temperatures (150-200 °C) and at high rates (typically 1000 Å/min) via thermally-induced disproportionation (eq. 1).⁴



However, the vapor pressure of these precursors are relatively low leading to slow reactant feed rates. This problem is usually approached by heating the precursors to high temperatures where precursor decomposition in the feed system becomes a problem. For this reason, there is a general need to develop better precursor delivery systems to avoid premature decomposition of the precursors either in the metal-organic precursor container or in the delivery system which, in turn, can improve the deposition rates for coating large wafers.

Here we present a new approach for metal precursor delivery: Aerosol-Assisted CVD (AACVD) of metals (Fig. 1). In this approach, a volatile metal precursor is dissolved in a solvent (1) and is atomized to form droplets (2) which evaporate to give the precursor and solvent vapors (3) which are then transported to the substrate (4) where they react to form the film. This process does not rely on the equilibrium vapor pressure of the precursor at the bubbler temperature, but relies instead on the vaporization of the precursor in the delivery system and reactor to achieve high precursor feed rates. As a result, it is possible to obtain greater precursor partial pressures at the substrate than the vapor pressure at the bubbler and delivery-line temperatures. In addition, two or more precursors can be delivered simultaneously using a single

solution leading to controlled and reproducible film stoichiometry. Liquid delivery with flash evaporation on warm surfaces for CVD of metals,⁵ and aerosol delivery for CVD of ceramics ZnS,⁶ LiNbO₃⁷ and GaAs⁸ have demonstrated qualitative improvements over conventional precursor delivery approaches. However, the advantages of the processes have not yet been quantified.

In this paper, we report quantitative results of a preliminary study of the AACVD of crystalline Cu onto SiO₂ substrates at low temperatures (120-200 °C) which results in higher deposition rates compared to traditional CVD.

The precursor (hfac)Cu(1,5-COD) (hfac = hexafluoroacetylacetonate, 1,5-COD = 1,5-cyclooctadiene) was chosen for this study because it is air stable in the solid state, its use in traditional CVD in both hot-wall and cold-wall reactors has been studied quantitatively,⁹⁻¹⁰ and it can be prepared according to simple literature procedures.¹¹⁻¹² The Aerosol-Assisted CVD reactor is shown in Fig. 2. The deposition reactions were carried out using toluene solutions of (hfac)Cu(1,5-COD) (62.5 g (0.164 mol)/L of toluene) under a nitrogen atmosphere. The toluene solution was kept at room temperature, atomized through a TSI-3076 aerosol generator, and preheated (40-100 °C) to partially vaporized the precursor. The precursor vapor was then reacted on the substrate (120 °C to 200 °C). Copper was deposited on silica substrates¹³ (1-2 cm²) at atmospheric pressure. The deposition rate was calculated from the film thickness obtained by weighing the substrate and confirmed by scanning electron microscopy.

In the first series of experiments, the substrate temperature and the distance between the end of the nozzle and the substrate were kept constant (140 °C and 1.7 cm) while the heating tape and preheating oven temperatures were varied. The deposition rates obtained are presented in Fig. 3. The plot of log(rate) versus 1/RT is linear (between 40 °C and 80 °C, Fig. 3, E) and gives an activation energy of 6.8 kcal/mol. This value corresponds to the enthalpy of vaporization of (hfac)Cu(1,5-COD) (6.4 kcal/mol) that can be obtained from the log(vapor pressure) versus 1/T data reported by Reynolds *et al.*⁹ At preheating temperatures above 80 °C, we observed a dramatic decrease in deposition rate, indicative of gas-phase reactions.^{ref MRS Dubois} At a

preheating temperature of 80 °C and a substrate temperature of 140 °C, the deposition rate of Cu was ~500 Å/min compared to ~200 Å/min obtained in a traditional warm-wall (88 °C) CVD reactor (10 mtorr) at the same substrate temperature (see Fig. 4, B).¹¹ This higher deposition rate can be attributed to a more efficient precursor transport mechanism. The throughput of the aerosol generator (2.0 L/min for a pressure of nitrogen of 20 psi), the concentration of the precursor (0.164 mol L⁻¹), and the rate of disappearance of the solution (14-15 mL/h) allow the calculation of the partial pressure of (hfac)Cu(1,5-COD) of approximately 500 mtorr for the case of complete vaporization. This value can be compared to the equilibrium vapor pressure of this compound at 62 °C (bubbler temperature) which is 52 mtorr. This demonstrates that higher precursor partial pressures at the substrate temperature can be obtained than can be obtained by traditional delivery methods.

In another set of experiments, the preheating temperature was kept constant (60 °C) and the substrate temperature was varied from 120 to 200 °C for two different nozzle-to-substrate distances (0.7 and 1.7 cm) (Figure 4). The plots of log(rate) versus 1/RT (J and É) are linear between 120 °C and 180 °C and the activation energies, calculated using the slopes obtained from the least-squares fits (straight lines), are 8.9 and 9.1 kcal/mol for a nozzle-substrate distance of 0.7 (J) and 1.7 cm (É), respectively. For comparison, the activation energies for CVD of Cu from (hfac)Cu(1,5-COD) in traditional warm-wall (88 °C and 70 °C) CVD reactors (10 mtorr and 18 mtorr) are 26.0¹¹ and 29.8 kcal/mol,⁹ respectively. One possibility for the difference between the activation energy obtained by AACVD at 500 mtorr (if the precursor is fully evaporated) is a change in reaction mechanism. This same trend is observed in the case of (hfac)Cu(VTMS) (VTMS = vinyltrimethylsilane). For this compound, traditional CVD was performed at precursor vapor pressures of 10 and 500 mtorr and gave activation energies of 43 and 10 kcal/mol, respectively.¹⁴

The geometry of the reactor (nozzle-substrate distance) has no influence on the position of the rate determining step (the activation energy of Cu AACVD) but affects the deposition rate. At any given temperature (between 120 and 180 °C), the rate of deposition of Cu for a nozzle-

substrate distance of 0.7 cm is about twice that measured for a nozzle-substrate distance of 1.7 cm. This can be explained by the temperature variation of the rate of precursor evaporation. The closer the nozzle is to the surface, the closer the precursor droplets come to the surface. Because the gas above the surface is heated by the substrate, the closer the droplets connect the surface the more precursor evaporate leading to higher deposition rates. By adjusting the preheating temperatures (heating tape and preheating oven) and the nozzle-substrate distance, deposition rates of Cu on SiO₂ of up to 800 Å/min were achieved at 140 °C. At temperatures above 180 °C (Fig. 4, I) gas-phase reactions occurred and the deposition rate dropped to about 190 Å/min.

The resistivity of the films was measured using a four-point probe and ranged from 1.7 to 3.5 μΩcm (1.67 μΩcm for bulk Cu at 20 °C) consistent with high-purity films. Even at low deposition temperature (120 °C), the Cu films were crystalline as determined by X-ray diffraction. The films had preferred orientations along the (111) and (200) planes.

In summary, Aerosol-Assisted Chemical Vapor Deposition of crystalline, low resistivity copper films from toluene solutions of (hfac)Cu(1,5-COD) has been demonstrated. High deposition rates were obtained at low temperatures (up to 800 Å/min at 140 °C). The rate of deposition of Cu as a function of the preheating temperature enabled determination of the enthalpy of vaporization of the precursor. An activation energy of ~9 kcal/mol has been determined for the AACVD of Cu at a maximum partial pressure of 500 mtorr total. We are now investigating the deposition rates as a function of the partial pressure of the precursor (by varying the aerosol generator throughput or the precursor solution concentration). The AACVD from relatively non-volatile precursors and AACVD of mixed-metal films will also be reported shortly. For example, crystalline Ag films have been deposited onto SiO₂ from low volatility precursors including (hfac)₂Ag₂(toluene) and (hfac)Ag(thioxane)¹⁵ at temperatures as low as 200 °C.¹⁶

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Figure 4. Plots of log of deposition rate versus $1/RT$ ($T = \text{substrate temperature}$) for the AACVD at preheating temperature of $60\text{ }^{\circ}\text{C}$ for a nozzle-substrate distance of 0.7 cm (J) and 1.7 cm (É and I) and traditional warm-wall ($88\text{ }^{\circ}\text{C}$) CVD at 10 mtorr (B).²⁸

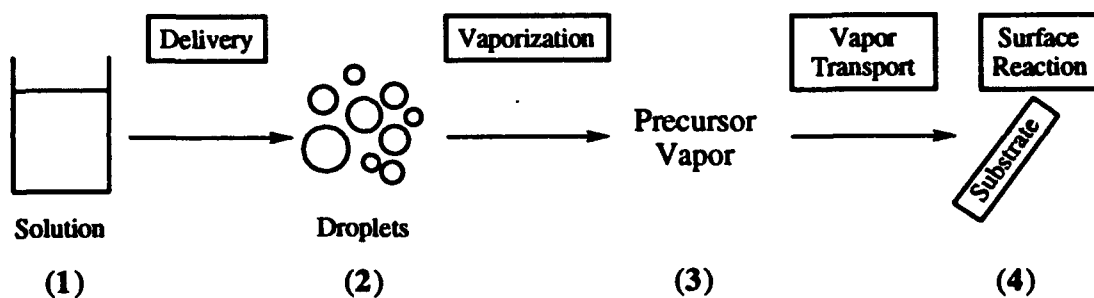


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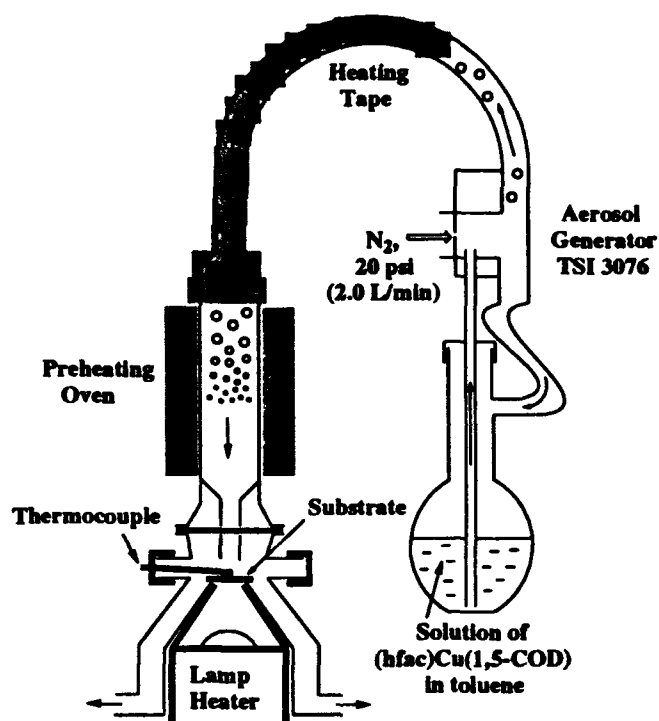


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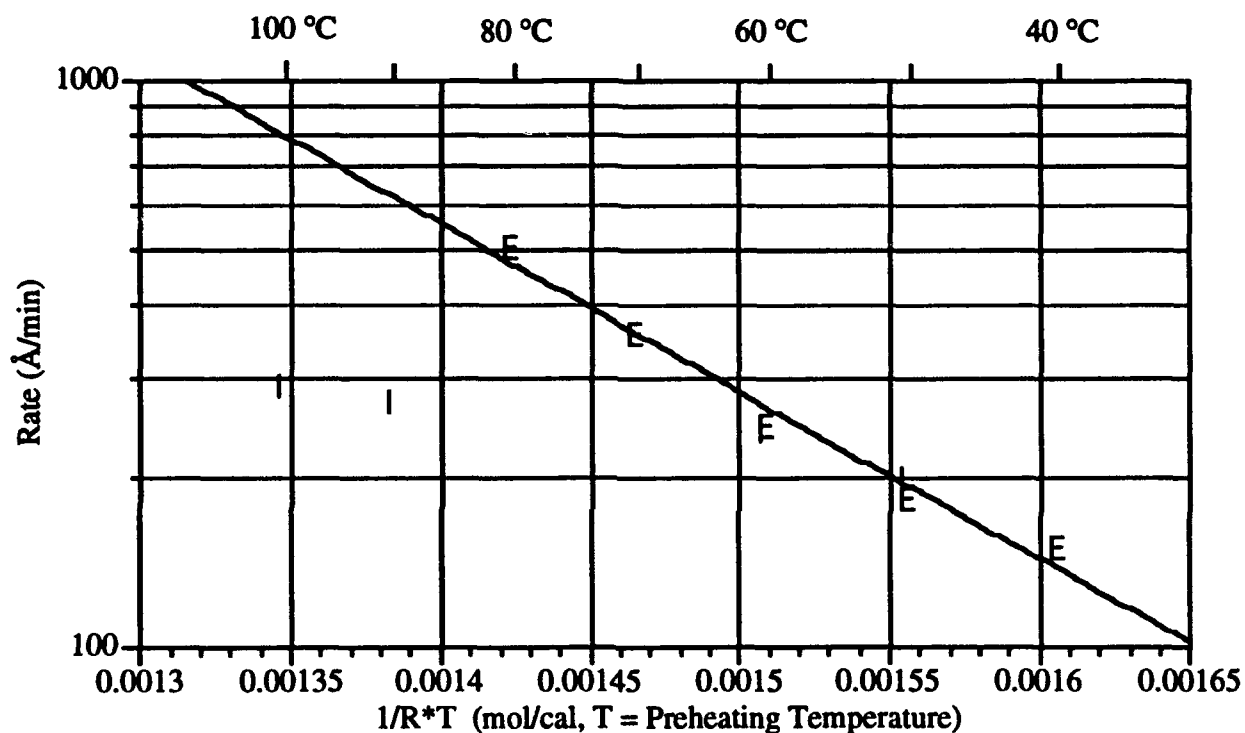


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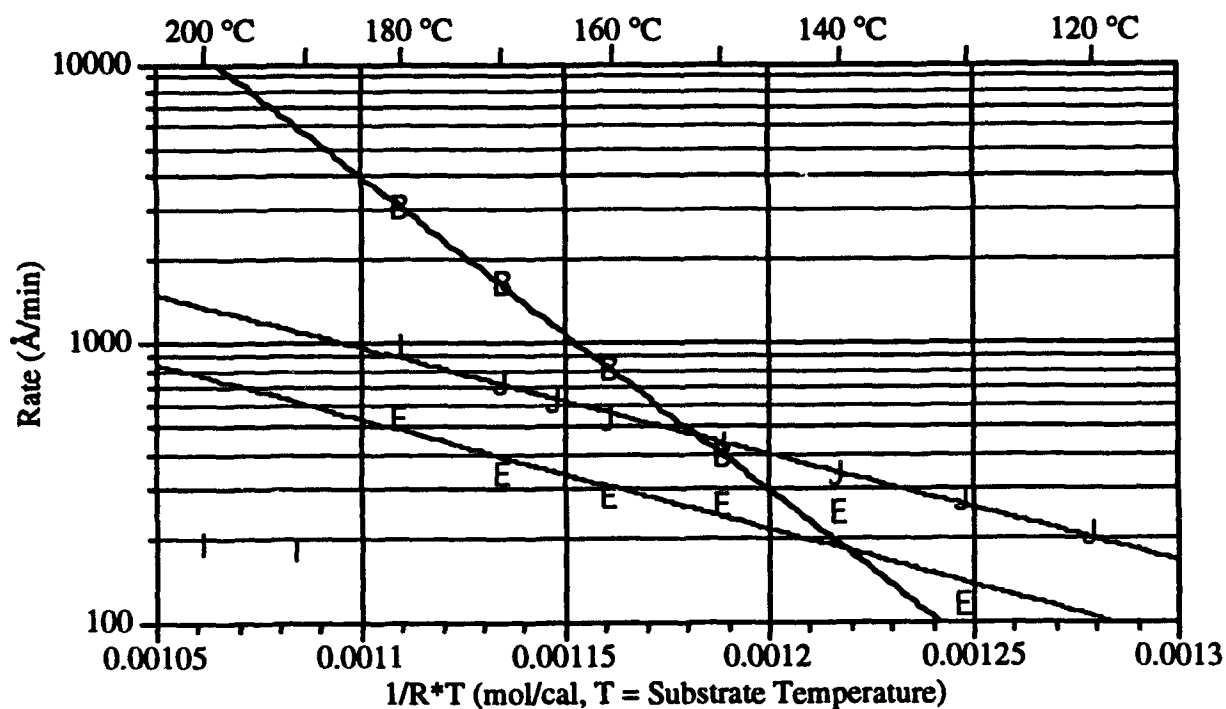


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