Reactions of Cu(hfac)₂ and Co₂(CO)₈ during Chemical Vapor Deposition of Copper−Cobalt Films

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The reactions of $Co_2(CO)_8$ and submicron cobalt particles with $Cu(hfac)_2$ (hfac = hexafluoroacetylacetonate) were studied in toluene. Reactions between these species in the gas phase were studied in a hot-wall, parallel-plate chemical vapor deposition (CVD) reactor. Similar results were obtained with both methods. The overall chemical reactions can be expressed by the following equations: $2Cu(hfac)_2 + Co_2(CO)_6 \rightarrow 2Cu + 2Co(hfac)_2 + 8CO$ and $Cu(hfac)_2 + Co \rightarrow Cu + Co(hfac)_2$. These results suggested that $Co_2(CO)_8$ is not a good source precursor for CVD of Cu−Co binary films when used in conjunction with copper(II) and some copper(I) hexafluoroacetylacetonate compounds and that chemical etching of cobalt metal by $Cu(hfac)_2$ needs to be taken into account when depositing this binary film with copper(I) and copper(II) hexafluoroacetylacetonate compounds as copper source precursors.

Introduction

Deposition of copper is one of the most important metallization technologies to be employed in the next decade due to the low resistivity and high electromigration resistance of copper.[1,2] In the past three decades, chemical vapor deposition (CVD) processes for high-quality copper have been developed and demonstrated using a variety of Cu(I)hfac[3] and Cu(II)hfac[4] (hfac = hexafluoroacetylacetonate) complexes. However, in order for them to be practically useful, copper films need to be alloyed with other metals to improve copper's interconnect performance with respect to both electromigration resistance and oxidation resistance.[1] Copper−cobalt binary thin films are also technically attractive because giant magnetoresistance has been discovered in this metallic system.[5]

The most common way to deposit alloyed copper films using CVD is to simultaneously deposit copper and another metal from two separate sources.[6−10] However, this route is complicated by the interactions of the different chemical species in the gas phase and on the surface. Growth of palladium was significantly inhibited during codeposition with $Pd(hfac)_2$ and (vtms)Cu-(hfac) (vtms = vinyltrimethylsilane) when compared with the independent CVD kinetics of $Pd(hfac)_2$.[6] One CVD study focused on doping Al interconnects with copper using Cu(I) and Cu(II) compounds with TMAA (trimethylamine alane).[9] The $Cu(hfac)_2$ source exhibited a "massive parasitic reaction" with the Al precursor which hampered control over the composition, while Al−Cu films could be derived with a copper(I) precursor. A study of the codeposition of copper−cobalt with (hfac)-Cu(1,5-Me₂-1,5-COD) (COD = cyclooactadiene) and Co_2-(CO)₈ has been reported.[10] Considerable difficulty in controlling the amount of Co in the film was encountered. This was attributed to thermal decomposition during sublimation of $Co_2(CO)_8$.[10]

Since the most studied Cu(II) compound, $Cu(hfac)_2$,[4] is also the most likely reaction product from the disproportionation reaction of (hfac)Cu(I)L precursors[3] and since $Co_2(CO)_8$ is the most widely studied precursor for cobalt CVD,[11,12] qualitatively understanding the chemical reactions of $Cu(hfac)_2$ with $Co_2(CO)_8$ and cobalt metal is important in terms of screening precursors and controlling the CVD process. Such information can also be helpful in guiding the experimentation on CVD of other copper alloys. In this study, these chemical reactions were studied with both gas-phase and liquid-phase approaches, and consistent results were obtained. A novel parallel-plate, asymmetrically heated, hot-wall

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CVD reactor was designed and used to isolate particles formed by gas-phase reactions during CVD.

Experimental Section

Chemicals and General Procedures. All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves. The species $Cu(hfac)_2$ and $Co_2(CO)_8$ were purchased from Strem Chemical Co. and used directly. The species $Co(hfac)_2$ and $H(hfac)$ were purchased from Aldrich Chemical Co. and used without further purification. Cobalt particles (with particle sizes in the range 0.5–1.5 μm) were purchased from Strem Chemical Co. $H(hfac)$ was used to wash the cobalt particles for 0.5 h before use of the particles. Without this step, chemical reactions were severely hindered. It was postulated that the amount of native surface oxide on these particles was reduced by washing with $H(hfac)$. The acid $H(hfac)$ was chosen for two reasons: (i) introducing extraneous materials could be minimized, and (ii) the reaction of $H(hfac)$ with cobalt particles is slower than other acids such as HCl, which enabled better control over the process. The reactions of $Cu(hfac)_2$ with $Co_2(CO)_8$ and cobalt particles were studied in toluene. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques.[13] Gas-phase reactions were studied in a parallel-plate, asymmetrically heated, hot-wall CVD reactor as described below to allow isolation of aerosol particles formed by gas-phase reactions.

Characterization. Infrared spectroscopy (IR) data were obtained with a Perkin-Elmer 1600 instrument. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) data were acquired on a Hitachi Model S-800 instrument. X-ray diffraction (XRD) data were collected on a Siemens D5000 X-ray diffractometer using Cu Kα radiation (25 kV). A Perkin-Elmer Auger electron spectrometer [for atomic emission spectroscopy (AES)] with a 0–5 kV electron gun (base pressure 5×10^{-10} Torr) was used for analyzing the purity of the deposits. Film thickness was measured by cross-sectional SEM after the substrates were cleaved along the center line in the gas flow direction.

Study of the Reaction between $Cu(hfac)_2$ and $Co_2(CO)_8$ in Toluene. The compound $Cu(hfac)_2$ (2.38 g, 0.005 mol) was dissolved with stirring in 25 mL of toluene for 0.5 h, which gave a deep green solution. The $Co_2(CO)_8$ (0.85 g, 0.0025 mol) was dissolved with stirring in another 25 mL of toluene for 0.5 h, which gave a dark orange solution. These two solutions then were mixed at room temperature with stirring. Upon mixing, a black solution with a solid suspension resulted and evolution of gas (assumed to be carbon monoxide) was observed. After reaction at room temperature for 5 h, the evolution of carbon monoxide ceased and the solution turned deep red with a solid suspension. The solution was filtered. The precipitate was washed with ether and dried in a vacuum. A red powder (0.29 g) was collected. The solvent was evaporated under vacuum for 2 h and about 2.13 g of red orange crystals were left. The product was recrystallized and washed with ether. The red powder filtered from the solution was characterized by XRD as copper. The red orange crystals were characterized by EA (elemental analysis) and IR. Anal. Calcd for $C_{10}H_2O_4F_{12}Co\cdot xH_2O$ ($x = 1.5$): C, 24.02; H, 1.01; F, 45.59. Found: C, 24.35; H, 1.39; F, >43.41. IR (cm^{-1}): 3439 (OH str), 1645 (C=O str), 1260 (CF$_3$ str), 1150 (CH in plane bend), 806 (CH out of plane bend), 750 (C–CF$_3$ str), 672 (C–CF$_3$ str).

Study of the Reaction between $Cu(hfac)_2$ and Co Particles in Toluene. Experiments with two molar ratios were conducted. First, the reaction between equal molar amounts of $Cu(hfac)_2$ and Co particles was studied. The compound $Cu(hfac)_2$ (2.38 g, 0.005 mol) was dissolved with stirring in 25 mL of toluene for 0.5 h, which gave a deep green solution. Commercial cobalt particles (0.30 g, 0.005 mol) were suspended with stirring in another 25 mL of toluene after
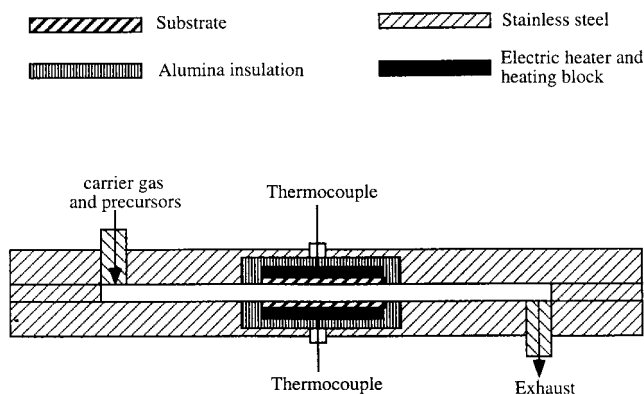
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Figure 1. Schematic of the reactor.

being washed with $H(hfac)$ for 0.5 h. The two solutions were mixed and refluxed at 110 °C. After 24 h, the solution turned black with a solid suspension remaining. The solution was filtered. The precipitate was washed with ether and dried in a vacuum. A red powder (0.30 g) was collected. The red powder filtered from the solution was characterized by XRD as composed of metallic copper and cobalt.

In the other experiment, a large excess of cobalt particles (2.95 g, 0.05 mol) was reacted with the $Cu(hfac)_2$ (2.38 g, 0.005 mol) using the above procedure. After 24 h, the deep green solution turned red with a solid suspension remaining. The solution was filtered. The precipitate was washed with ether and dried in a vacuum. Black powder (2.94 g) was collected. The solvent was evaporated under vacuum for 2 h and 2.15 g of red orange crystals were left. These crystals were recrystallized under vacuum and washed with ether. The presence of copper in the black powder filtered from the solution was identified by EDS. The crystals precipitated from the solution were identified as $Co(hfac)_2$ by IR.

Control Experiments to Examine Reaction between $Cu(hfac)_2$ and $Co(hfac)_2$. Using the same method as above, commercial $Cu(hfac)_2$ (2.38 g, 0.005 mol) and $Co(hfac)_2$ (2.37 g, 0.005 mol) were mixed in toluene. Upon mixing, a black solution resulted and no evolution of gas was observed. After the mixture was stirred and refluxed at 110 °C for 24 h, the solution remained the same color and clear. The solvent was evaporated under vacuum for 2 h and about 4.42 g of crystals was recovered. These crystals were characterized by XRD. The XRD pattern of these crystals was a superposition of those obtained from commercial $Cu(hfac)_2$ and $Co(hfac)_2$. It was concluded, therefore, that there was no chemical reaction between these two compounds.

Gas-Phase Reaction of $Cu(hfac)_2$ with $Co_2(CO)_8$ and Cobalt Particles. The reactor (Figure 1) was made from stainless steel. Two deposition substrates (width, 3.3 cm; length, 4 cm) were prepared by cleaving the silicon wafers and mounting them on the top and bottom surfaces of the reactor in contact with aluminum heating blocks embedded in alumina insulation. The gaseous precursors and aerosols containing cobalt particles were fed into the rectangular flow channel (width, 3 cm; length, 10 cm; with native oxide) and exhausted from the reactor through $^1/_4$ in. stainless tubings. For studying the reactions between $Cu(hfac)_2$ and $Co_2(CO)_8$, the two vapors were mixed outside of the reactor and then introduced into the reactor. Cobalt particles generated by gas-phase reaction of $Co_2(CO)_8$ outside of the CVD reactor were used for studying the reaction between $Cu(hfac)_2$ and cobalt aerosol particles. The gas-phase reaction of $Co_2(CO)_8$ to form the Co aerosol particles was conducted in a hot-wall tube reactor (inside diameter, 2 cm; length, 15 cm) connected to the parallel-plate, hot-wall CVD reactor. The aerosol reactor furnace temperature was varied in the range 60–200 °C. The particles generated by gas-phase reaction in the hot-wall tube reactor were collected on filter papers (Gelman Sciences 2220) for analysis of the particle purity by AES. The furnace temperature under which cobalt particles of 100% purity (as analyzed by AES) could be obtained was identified. The $Cu(hfac)_2$ and

cobalt particles of 100% purity were mixed and then introduced into the reactor.

Fresh precursors (2.00 g for each compound) were used for each run. The $Cu(hfac)_2$ was sublimed at 100 °C without decomposition in the sublimator. The $Co_2(CO)_8$ was sublimed at 40 °C with slow decomposition in the sublimator.[11] The transport lines leaving the sublimators were held at 20 °C above the sublimation temperatures to prevent condensation of precursors on the tubing walls. Pure hydrogen was used as the carrier gas for $Cu(hfac)_2$ and $Co_2(CO)_8$ at a rate of 20 mL/min [standard temperature and pressure (STP)]. The $Cu(hfac)_2$ delivery rate was 3.92 ± 0.78 mg/min under the sublimation condition as measured by weight loss of the sublimator. The weight loss of the $Co_2(CO)_8$ in the sublimator could not be related to the delivery rate due to decomposition to Co and CO during sublimation. The same amount of carrier gas was used to synthesize cobalt particles ex situ and introduce the resulting aerosol into the parallel-plate reactor. All the experiments were conducted with a total flow rate of 40 mL/min (STP) under atmospheric pressure. Gas flow rates were measured and controlled by flow meters. Resistive heating was used to heat the substrates, sublimators, tube reactor, and transport lines. Temperatures were controlled by temperature controllers (Omega CN9000A). The deposition usually lasted for 1–2 h.

Thermophoretic Conditions in the CVD Reactor. Thermophoresis,[14] the motion of particles in a temperature gradient, was used to collect solid particles on the cold substrate of the parallel plate CVD reactor and identify the occurrence of gas-phase chemical reactions. The top substrate was always heated to a higher temperature. The temperature difference between the two substrates was kept at 30 °C while the spacing between the substrates was kept at 2 mm. A larger temperature difference caused noticeable particle deposition before the gas reached the silicon substrates. The top substrate temperature was varied in the range 230–380 °C while the bottom substrate temperature was varied in the range 200–350 °C, respectively.

Control Experiments To Examine the Deposition Characteristics of Cu(hfac)₂ and Co₂(CO)₈. Experiments were conducted to study the separate deposition characteristics of $Cu(hfac)_2$ and $Co_2(CO)_8$ in the CVD reactor. Sublimation temperatures, carrier gas flow rates, and substrate temperatures were controlled to be the same as mentioned earlier. Pure H_2 gas was used as dilution gas at a rate of 20 mL/min (STP) to maintain the total flow rate at 40 mL/min (STP).

Control Experiments of Thermophoretic Deposition of Cobalt Particles. Cobalt particles generated by gas-phase reaction of $Co_2(CO)_8$ at 150 °C outside of the paralle-plate CVD reactor were introduced into the CVD reactor in order to define the particle deposition range on the substrates. Precursor sublimation temperature, carrier gas flow rate, and substrate temperatures were controlled to be the same as mentioned earlier. Pure H_2 gas was used at a rate of 20 mL/min (STP) to dilute the resulting aerosol and maintain the total flow rate at 40 mL/min (STP).

Results and Discussion

CVD Reactor Design. Reactions in solution usually differ from those in CVD processes. However, in some cases, liquid-phase experiments provide useful insight and help in the design of new reactants for CVD.[8] Studying the reactivity of metal–organic precursors in solution is also critical for depositing alloys with aerosol-assisted CVD.[8]

To verify that the reactions discovered in solution also occurred in the CVD process, a parallel-plate, hot-wall CVD system was designed and employed in this study.
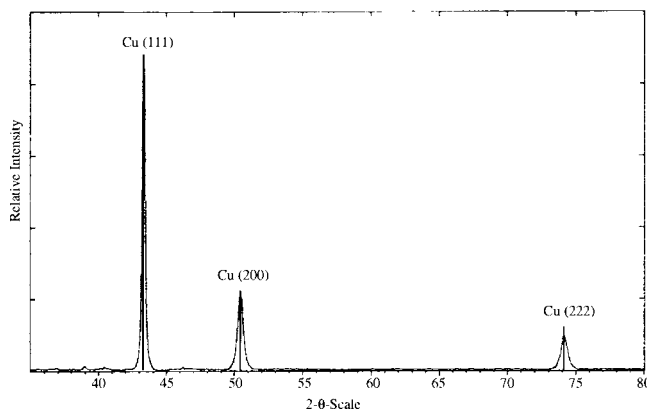
Figure 2. XRD data for the copper powder recovered from the solution reaction between $Cu(hfac)_2$ and $Co_2(CO)_8$.

Hot-wall reactors have been used to identify reaction products at high conversion ratios and yields of the reaction products.[15-17] However, analysis of reaction pathways in chemical vapor co deposition with multiple source precursors is made complex by the coexistence of various chemical species and of solid products (e.g., particles). The reactor used in this work had the same advantage of high precursor conversion and product yield as can be achieved with conventional hot-wall reactors but had each wall held at a different temperature. The use of a colder CVD surface as a particle detector for gaining insight into multiphase CVD processes was suggested and exploited in a theoretical work on multiphase CVD process[18] but has not yet been implemented experimentally. By keeping the substrates at different temperatures, particles can be collected in situ on the lower temperature substrate by thermophoresis.[14] The function of this "detector" was to collect and detect aerosol particles formed in the gas phase. Thermophoresis is also the fundamental principle upon which particle precipitation-aided CVD for single-component films is based.[19,20]

Study of the Reaction between Cu(hfac)₂ and Co₂(CO)₈ in Toluene. The reaction between $Cu(hfac)_2$ and $Co_2(CO)_8$ was investigated in solution. The two precursors were dissolved and mixed in toluene. The color change of the solution and evolution of gas showed that a reaction occurred. The reaction products were isolated and identified. The red powder filtered from the solution was characterized by XRD (Figure 2) as metallic copper. The SEM micrograph in Figure 3 showed that the average size of the particles was around 1 μm. The red orange crystals precipitated from the solution were characterized by EA and IR as $Co(hfac)_2$. EA results agreed with theoretical values for this compound. IR results compared well with the previously published data of this compound.[21]

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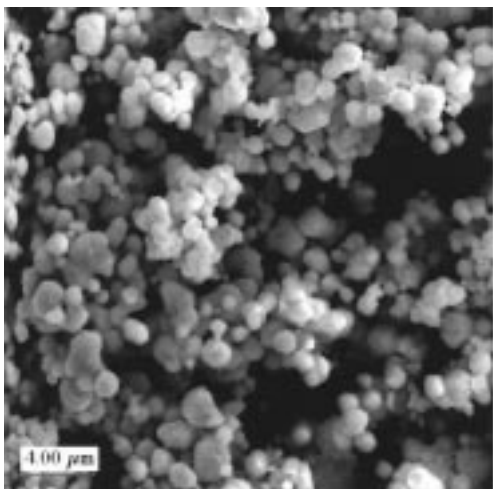
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Figure 3. SEM of the copper particles recovered from the solution reaction between $Cu(hfac)_2$ and $Co_2(CO)_8$.

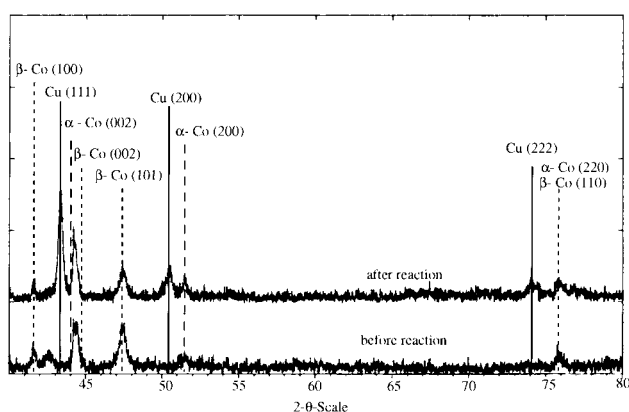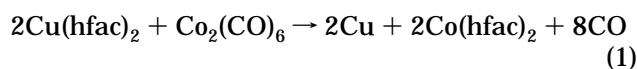**Figure 4.** XRD data for the Cu–Co powder recovered from solution reaction between $Cu(hfac)_2$ and $Co_2(CO)_8$.

The experimental results indicated that $Cu(hfac)_2$ and $Co_2(CO)_8$ reacted in the solution according to the following reaction:

$$2Cu(hfac)_2 + Co_2(CO)_6 \rightarrow 2Cu + 2Co(hfac)_2 + 8CO \tag{1}$$

The yield of Cu powder was 91.3% and the yield of $Co(hfac)_2$ crystals was about 90.1% of the calculated value for eq 1, indicating that this reaction is essentially quantitative.

Study of the Reaction between $Cu(hfac)_2$ and Co Particles in Toluene. The reaction between $Cu(hfac)_2$ and commercial cobalt particles was investigated in solution. The two species were mixed in toluene. The color change of the solution after 24 h showed that a reaction occurred. The reaction products were isolated and identified. The X-ray diffraction results in Figure 4 indicated that the powder resulting from reaction between $Cu(hfac)_2$ and Co particles was composed of metallic copper and cobalt. No change in the particle size was observed with SEM because of the low conversion. The SEM micrograph showed that the average size of the particles was around 1.0 μm, which was about the same as the starting cobalt particles because the reaction had a surplus of Co. The composition of the powder collected and the color of the solution indicated that the reaction was not complete with equal molar amounts of $Cu(hfac)_2$ and Co particles. Complete con-

version of cobalt to $Co(hfac)_2$ could not be achieved by extending the reaction time to 48 h. The experimental results suggested that $Cu(hfac)_2$ and cobalt particles reacted in toluene according to the following reaction:

$$Cu(hfac)_2 + Co \rightarrow Cu + Co(hfac)_2 \tag{2}$$
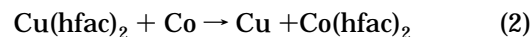
The soluble product and the reaction stoichiometry were examined using a large excess of cobalt particles to completely convert the $Cu(hfac)_2$ to copper. The red crystals precipitated from the solution were identified as $Co(hfac)_2$ by IR. The yield of $Co(hfac)_2$ was about 90.0% of the calculated value for eq 2, again indicating that this reaction is essentially quantitative.

Recently, the surface redox transmetallization reaction between $Pd(hfac)_2$ and Cu solid was discovered.[22,23]

$$Pd(hfac)_2 + Cu \rightarrow Pd + Cu(hfac)_2 \tag{3}$$
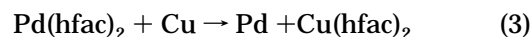
Such a redox transmetallization reaction was suggested to be generally applicable, provided that the redox potentials are favorable. In order for this type of reaction to progress, the reactants on the left-hand side of the equations have to diffuse through the layer of the solid material (Cu for reaction 2 and Pd for reaction 3) deposited. For reaction 3, grain boundaries in the polycrystalline copper foils provide a mechanism for the rapid interdiffusion of Pd and Cu while it was self-limiting on a single-crystal copper substrate due to the absence of grain boundaries.[24] For reaction 2, cobalt and copper are not soluble in each other below 400 °C, unlike copper and palladium.[5] The diffusion rate of cobalt in copper is expected to be much lower than palladium in copper. In this sense, the core of cobalt particles can be protected by deposition of copper on the surface and reaction 2 can be self-limiting.

Control Experiments To Examine the CVD Characteristics of $Cu(hfac)_2$ and $Co_2(CO)_8$. Initially, the independent CVD characteristics of $Cu(hfac)_2$ and Co_2-$(CO)_8$ were investigated by introducing one precursor vapor into the reactor in the absence of the other. For $Cu(hfac)_2$, an induction period as long as 2 h was observed on both hot and cold substrates at temperatures below 300 °C. No copper deposition could be observed on the cold substrate for 2 h when its temperature was 200 °C. A similar observation was reported in the literature.[25] Typical deposition profiles as measured by cross-sectional SEM are given in Figure 5 for the hot substrate at 350 °C and the cold substrate at 320 °C, demonstrating that all the precursor was consumed. According to previous studies of particle-precipitation-aided CVD, particle formation and thermophoretic deposition would cause more deposition on the cold substrate.[19,20] The deposition profiles obtained suggested that there was no significant gas-phase particle formation during Cu CVD with $Cu(hfac)_2$ under the conditions studied. The purity of the films was

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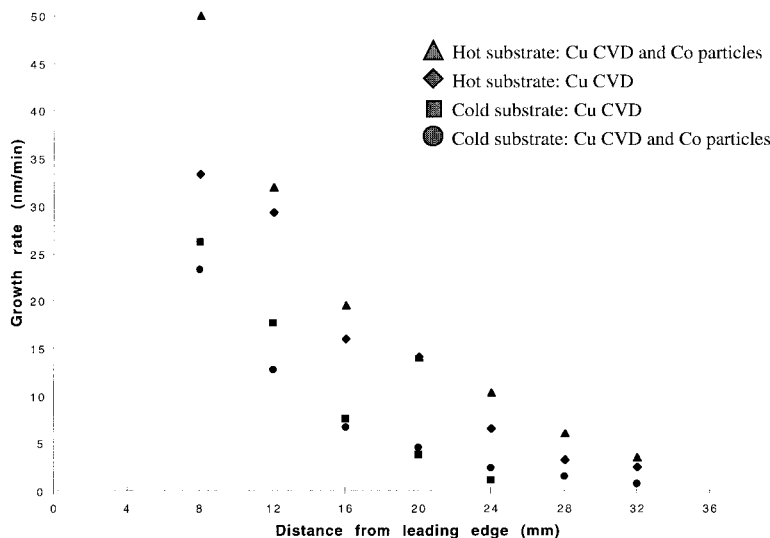
Figure 5. Deposition profiles with hot substrate at 350 °C and cold substrate at 320 °C.

about 98 atom % with 2 atom % carbon contamination as shown by AES data.

For Co$_2$(CO)$_8$, shiny films were observed on the leading edge of both substrates. The thickness profiles of the films are not reported here because (i) a dramatic change in the film thickness occurred 0−2 mm from the leading edge of the substrates and (ii) the films were too thin to be measured accurately by cross-sectional SEM. With an increase in substrate temperature, the deposits appeared more discontinuous and consisted only of sparsely distributed metal islands. Aggregated particles were always observed in the range 4−15 mm from the leading edge of cold substrate and were confirmed as cobalt particles by EDS. No aggregated particles were observed on the hot substrate. AES data showed that the deposit purity was 100 atom %.

Reaction Study of Cu(hfac)$_2$ with Co$_2$(CO)$_8$ in Gas Phase. The gas-phase reactions between the precursors were studied by introducing both precursors simultaneously into the reactor. The cold substrate temperature was 200 °C and the hot substrate temperature was 230 °C. After deposition for 1 h, particles were observed on the cold substrate. These particles were identified as copper by EDS with no evidence for cobalt. On the basis of the results from control experiments that Cu(hfac)$_2$ did not react with hydrogen under these conditions, copper deposition could be a result of reaction 1 rather than reduction of Cu(hfac)$_2$ by H$_2$. The SEM micrograph in Figure 6 showed that the deposited particles were aggregates with primary particle size of about 60 nm, which suggested that most of the particles were deposited from the gas-phase.[14,26] AES data confirmed the absence of cobalt and revealed contamination with carbon (13 atom %) and oxygen (29 atom %).

Red orange powder was formed on the reactor walls upstream and downstream of the substrates. However, the condensate was contaminated by Cu(hfac)$_2$, as indicated by its greenish color when the hot substrate temperature was below 380 °C. No attempt was made to purify the condensate. When the hot substrate
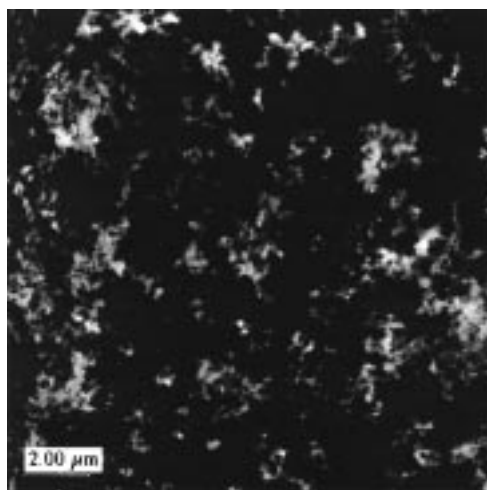
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Figure 6. SEM for the copper particles resulted from gas-phase reaction of Cu(hfac)$_2$ and Co$_2$(CO)$_8$ in the presence of hydrogen. Particles were collected by thermophoresis on a silicon substrate at 200 °C.

temperature was 380 °C and cold substrate temperature 350 °C, nearly 100% conversion of Cu(hfac)$_2$ was achieved. The condensate collected under this condition was analyzed by IR and identified as Co(hfac)$_2$. These results indicated that reaction 1 occurred in the gas phase and possibly on the silicon surface.

Gas-Phase Reaction of Co$_2$(CO)$_8$. The gas-phase reaction of Co$_2$(CO)$_8$ in the hot-wall tube reactor was studied in order to generate a pure cobalt aerosol. Below 120 °C, the particles were contaminated with carbon and oxygen, indicating incomplete decomposition of the precursor. Cobalt particles of 100% purity were synthesized at a furnace temperature of 150 °C and above, as shown by AES data. Cobalt particles synthesized at 150 °C were used for studying its chemical reaction with Cu(hfac)$_2$ vapor.

Thermophoretic Deposition of Cobalt Particles. Cobalt particles synthesized at 150 °C were introduced into the reactor with the cold substrate at 320 °C and hot substrate at 350 °C. The particles were deposited in the range 4−15 mm from the leading edge of the cold substrate. No particles were observed on the hot substrate. Particle morphologies were examined by

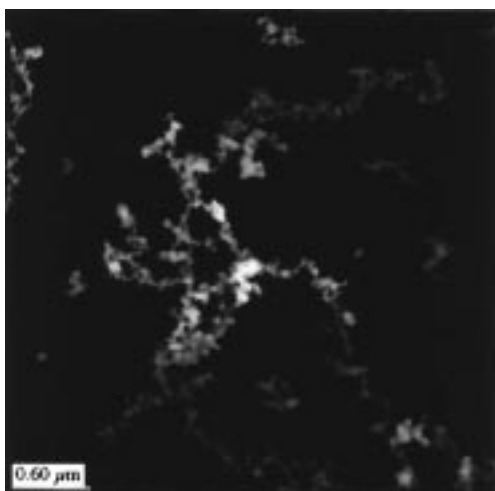**Figure 7.** SEM for the cobalt particles generated by gas-phase reaction of $Co_2(CO)_8$ in the presence of hydrogen. Particles were collected by thermophoresis.

SEM. Figure 7 shows that the cobalt particles synthesized at this temperature were aggregates and had a primary particle size of about 60 nm.

Reaction Study of $Cu(hfac)_2$ with Co Particles in Gas Phase. The cobalt aerosol produced outside the CVD system was introduced in hydrogen carrier gas into the CVD reactor along with $Cu(hfac)_2$. The elemental compositions of the deposits on both substrates were examined by EDS. Cobalt deposition on either substrate could not be detected by EDS when the hot substrate temperature was at or below 380 °C (the cold substrate temperature was below 350 °C). Copper was identified by EDS as the only component in the deposits. AES data showed that the amount of cobalt on the substrate was below the detection limit. Red orange powder was collected from the reactor walls downstream of the substrates in all the experiments. The condensate was analyzed by IR and identified as $Co(hfac)_2$. These results indicated that reaction 2 also happened in the gas phase and possibly on the silicon surface.

A qualitatively different reaction rate and conversion was observed for reaction 2 in the gas phase compared to the liquid phase. In our CVD experiments, the gas-phase residence was estimated to be 6 s before reaching the substrate. Cobalt particles were converted to $Co(hfac)_2$ vapor by reaction 2 in this short period and could not be deposited by thermophoresis as particles. On the other hand, at least 8 h were needed to see signs of reaction (color change) in solution and $0.5-1.5$ μm cobalt particles could not be reacted completely in 48 h. The cobalt particles used in the gas-phase reaction were more than 10 times smaller than the commercial particles used in the solution reaction. The self-limiting nature of the reaction between $Cu(hfac)_2$ and micron-sized cobalt particles was discussed in the preceding section. In order for reaction 2 to proceed, either the surfaces of the solid need to be refreshed or a large portion of atoms must be located at the surface of the solid. The effects of reducing particle size need to be stressed in explaining the experimental observations. Two explanations are possible: (i) The smaller the particles, the greater the surface area per unit mass and the higher the reactivities of the particles.[26] This suggests that the cobalt particles generated by the gas-

phase reaction have a higher proportion of atoms accessible to $Cu(hfac)_2$ and possibly a higher reactivity than micron-sized cobalt particles. (ii) The reactant $Cu(hfac)_2$ must diffuse into the particles in order to achieve complete reaction, which means that a shorter time is required for diffusion in smaller particles. Other possible factors may include the different diffusivity and reactivity of $Cu(hfac)_2$ in the vapor phase than in the liquid phase. Overall these results suggested that the effects of reaction 2 on composition control in CVD of Cu−Co films need to be considered when using hexafluoroacetylacetonate compounds as copper source.

Deposition Profiles and Film Purities. The kinetics of hot-wall Cu CVD with $Cu(hfac)_2$ has been well-studied.[4,27,28] In the case of codeposition of Cu−Co, different deposition kinetics than that seen with single-component CVD might be expected due to the presence of multiple chemical species.[6] In our work, codeposition profiles and purities were compared with those of Cu CVD under the same conditions in order to examine the overall effects of the other chemical species [CO, and $Co(hfac)_2$] on the Cu CVD kinetics. Similar deposition profiles and purities ($\sim$98%) were obtained from codeposition of $Cu(hfac)_2$ with $Co_2(CO)_8$ and Co particles, which means that the chemical species present in the gas phase and on the surface were essentially the same in both cases. This was consistent with the results discussed in the earlier sections. Film thickness profiles obtained from chemical vapor codeposition of $Cu(hfac)_2$ and cobalt particles were compared in Figure 5 with those obtained from Cu CVD. For these runs, the hot substrate temperature was 350 °C and the cold substrate temperature was 320 °C. The overall differences observed were not significant when compared with experimental errors ($\sim\pm$40%). However, a small influence of these species on the kinetics of Cu CVD could not be excluded because concentrations of CO and $Co(hfac)_2$ in the system were low due to the low volatility and thermal decomposition of $Co_2(CO)_8$.[11]

CVD of Cu−Co Films with $Co_2(CO)_8$ as Cobalt Source. The above results indicated another cause for the difficulty in CVD of Cu−Co films with $Co_2(CO)_8$ as a cobalt source and $(hfac)Cu(1,5-Me_2-1,5-COD)$ as a copper source.[10] It was reported that hydrogen was necessary for cobalt incorporation in the film, although decomposition of $Co_2(CO)_8$ and $(hfac)Cu(1,5-Me_2-1,5-COD)$ did not require a reducing agent.[10] The observation can be explained by the reactions reported in this study. Since $Cu(hfac)_2$ is the most likely reaction product from the disproportionation reaction of $(hfac)Cu(I)L$, it can be expected to be present in the gas phase and on the deposition surface. The presence of $Cu(hfac)_2$ in the system is undesirable and should be minimized in order to deposit cobalt from the $Co_2(CO)_8$ because the $Co_2(CO)_8$ could be converted to $Co(hfac)_2$ due to reaction 1. It has been reported that the disproportionation reaction of $(hfac)Cu(I)(1,5-COD)$ to form $Cu(hfac)_2$ could be suppressed by using hydrogen as carrier gas,[29]

(27) Lai, W. G.; Xie, Y.; Griffin, G. L. *J. Electrochem. Soc.* **1991**, *138*, 3499.

(28) Wang, J.; Little, R. B.; Lai, W. G.; Griffin, G. L. *Thin Solid Films* **1995**, *262*, 31.

(29) Griffin, G. L.; Lai, W. G.; Maverick, A. W.; Kumar, R.; Ajmera, P. K. In *Conf. Proc. ULSI− VII*; Rana, V. V. S., Joshi, R. V., Eds; Material Research Society: Pittsburgh, 1991.

although a contradicting result exists for (vtms)Cu-(hfac).[25] When used with (hfac)Cu(1,5-Me$_2$-1,5-COD), deposition of cobalt from Co$_2$(CO)$_8$ in the presence of hydrogen indicated that hydrogen did help to reduce the formation of Cu(hfac)$_2$ from (hfac)Cu(1,5-Me$_2$-1,5-COD).[10] The poor thermal stability of Co$_2$(CO)$_8$ can still be the cause of problems in process reproducibility. Overall, these results suggested that new cobalt precursors need to be used for the current Cu CVD schemes with Cu(II) and Cu(I) hexafluoroacetylacetonate complexes. These precursors should be more thermally stable and be compatible with the chosen Cu compounds.

Conclusions

Chemical vapor codeposition of multicomponent films using separate source precursors is complicated and susceptible to failures. Analysis of such processes can be made difficult due to reactions between precursors, intermediates, and products in the gas phase and on the substrate. In this work, the reactions of Cu(hfac)$_2$ and Co$_2$(CO)$_8$ source precursors were analyzed in a novel parallel-plate, asymmetrically heated, hot-wall CVD reactor which enabled collection of particles formed as a result of gas-phase reactions. This is the first time this type of reactor was used to help identify the reaction pathways in a multicomponent CVD process. Our experimental results demonstrated that the vapor–vapor and vapor–solid reactions during CVD with Cu-(hfac)$_2$ and Co$_2$(CO)$_8$ followed the same pathways as in toluene. However, different reaction rates were observed in the gas phase and liquid phase. The reaction of Cu(hfac)$_2$ with 60 nm cobalt particles in the gas phase was much faster and more complete than the reaction with 0.5–1.5 μm particles in the liquid phase.

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