Aerosol-Assisted Chemical Vapor Deposition (AACVD) of Binary Alloy (Ag_xPd_{1-x}, Cu_xPd_{1-x}, Ag_xCu_{1-x}) Films and Studies of Their Compositional Variation

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Atmospheric pressure chemical vapor deposition (CVD) of Ag–Pd, Cu–Pd, and Ag–Cu alloys using aerosol precursor delivery over a range of preheating temperatures, 70–80 °C and substrate temperatures, 250–300 °C is described. The precursors were (hfac)Ag(SEt_2), (hfac)Cu^I(1,5-COD), Cu$(hfac)_2$, Pd$(hfac)_2$, and Pd$(hfac)_2$(SEt_2) dissolved in toluene with 10% H_2 in Ar as carrier gas. The films were characterized by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction. The X-ray diffraction results showed the Ag Pd films consisted of Ag Pd alloys, the Cu/Pd films were composed of Cu–Pd alloys, and the Cu/Ag films were composed of the α- and β-phases of Ag–Cu alloys. Control experiments using involatile $AgNO_3$ and volatile (hfac)Ag(SEt_2) as precursors to Ag films were consistent with a chemical vapor deposition (CVD) process. Reactivity studies between precursors and H_2 suggested Pd$(hfac)_2$ is likely to undergo a small amount (<2%) of decomposition during the aerosol-assisted CVD experiments, and Pd$(hfac)_2$(SEt_2) was used to eliminate this problem. Compositional variation studies in Cu–Pd and Ag–Pd alloy systems were also conducted by mixing Cu$(hfac)_2$/Pd$(hfac)_2$ and (hfac)Ag(SEt_2)/Pd$(hfac)_2$(SEt_2) in different ratios in toluene solution. The films were characterized by X-ray diffraction and the results showed the composition of the films was dependent upon the solution stoichiometry. The possible rate-limiting steps are discussed, and it is proposed that the deposition rate is limited by the feed rate of the precursors to the reactor. These predictions were consistent with a study of deposition rate as a function of substrate temperature at constant feed rate in the (hfac)Ag(SEt_2)/Pd$(hfac)_2$(SEt_2) system, which showed no variation in the deposition rate over a 75 °C temperature range. It was concluded that conditions of feed-rate or diffusion-rate limited deposition are useful approaches to control film composition.

Introduction

Metal alloy thin films have many applications ranging from interconnects in semiconductor device manufacture[1] to gas-permeable membranes in separations technology.[2] Chemical vapor deposition (CVD) is an attractive method of deposition of metal alloy films because conformal coverage and uniform deposition can be obtained.[3] The key to success for CVD of alloys is the selection of suitable precursors that avoid unfavorable reactions prior to or during deposition. However, the quality of films obtained by CVD with conventional delivery is often limited by the low volatility and low thermal stability of the precursors. To alleviate this problem, a number of groups are developing precursor transport methods, including liquid delivery,[4-6] supercritical fluid transport (SCT) CVD,[7] spray metal–organic (MO) CVD,[8-15] and aerosol-assisted (AA) CVD.[16-28]

Aerosol delivery of precursors provides a viable alternative route to conventional delivery.[29] In this method, the precursor is first dissolved in a solvent. The solution is passed through an aerosol generator, where micron-sized aerosol droplets are generated in a carrier gas and are transported into a preheating zone where both the solvent and the precursor evaporate. The precursor vapor reaches the heated substrate surface

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Table 1. Summary of Deposition Conditions

alloy	precursors (mmol)	preheating temp (°C)	substrate temp (°C)	deposition rate (Å/min)	composition (XRD)
Ag/Pd	$Pd(hfac)_2(SEt_2)$/(hfac)$Ag(SEt_2)$ 0.370/0.370	70	250	220	Ag/Pd 0.50/0.50
Cu/Pd	$Pd(hfac)_2$/$Cu(hfac)_2$ 0.229/0.229	80	275	230	Cu/Pd 0.15/0.85
Ag/Cu	(hfac)$Ag(SEt_2)$/$Cu(hfac)_2$ 0.500/0.499	80	275	180	mixture of phases

where thermally induced reactions and film deposition take place. Aerosol delivery enables a high mass-transport rate of the precursor to the substrate which can result in a high deposition rate but does not require high precursor vapor pressure at room temperature or long-term thermal stability of the precursor at elevated temperature. In addition, this system also has the potential to be operated under conditions where the precursor delivery rate and the composition of precursors in solution and droplets do not change with time, which allows reproducible deposition of multicomponent films, such as alloys.

This method has not been studied extensively for CVD of metals.[29] The CVD of low-resistivity Cu films has been achieved from toluene solutions of (hfac)Cu^{I}(1,5-COD), where 1,5-COD is 1,5-cyclooctadiene and hfac is 1,1,1,5,5,5-hexafluoroacetylacetonate, at rates of ~800 Å/min and low temperature (140 °C).[27] Palladium films have been deposited at a preheating temperature of 80 °C and substrate temperatures of 200–250 °C from $Pd(hfac)_2$.[26] In addition, pure Ag films also have been obtained at a substrate temperature as low as 120 °C, using the precursor (hfac)$Ag(SEt_2)$, which has low volatility and low thermal stability and is not suitable for CVD with conventional precursor delivery.[26] Preliminary results of the AACVD of $Ag_{0.4}Pd_{0.6}$ films have been reported in which (hfac)$Ag(SEt_2)$ and $Pd(hfac)_2$ were dissolved in a 1:1 molar ratio in toluene.[26]

In this work, we report our recent results on AACVD of binary alloys, including Ag–Pd, Cu–Pd, and Ag–Cu alloys and on reactivity studies of precursors with each other and with H_2 in solution. Also, to investigate how the composition of an alloy can be controlled or affected by the composition of precursors in solution, we have studied the relationship between film and solution composition for Ag–Pd and Cu–Pd alloy systems. The Ag–Pd alloy system exists as a solid solution over the whole composition range, and the change of the alloy lattice parameters is directly proportional to the composition of alloy. As a result this is a convenient system to quantitatively monitor the change of alloy composition by X-ray diffraction. Finally, we have examined the temperature dependence of the deposition rate to gain insight into the rate-limiting step for film growth.

Experimental Section

All manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves. Silver(I) nitrate and $Pd(hfac)_2$ were purchased from Aldrich Chemical Co. and used without further purification. The $Cu(hfac)_2$ was purchased from Strem Chemical Co. and used directly. The precursors (hfac)Cu(1,5-COD), (hfac)$Ag(SEt_2)$, and $Pd(hfac)_2(SEt_2)$ were prepared by the methods described previously.[30–33] The carrier gas used throughout was 10% H_2 in Ar. Silica substrates were obtained by oxidation of silicon wafers by water vapor at 1100 °C for 4 h and used as received from Sharp Microelectronics Technology, Inc. Nuclear magnetic resonance spectra were recorded on a Bruker AC-250P NMR spectrometer by using the protio impurities of the deuterated solvents as reference for the ^1H NMR. Deposition rates were calculated from the weight gain of the substrate using a microbalance after CVD and confirmed by SEM or by direct measurement of the film thickness from SEM only. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were obtained with a Hitachi S-800 instrument. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer 7700 thermogravimetric analyzer. X-ray diffraction data were collected on a Siemens D5000 X-ray diffractometer.

(A) AACVD Procedure for Binary Alloys. A typical procedure was as follows: In a 50 mL flask, $Pd(hfac)_2(SEt_2)$ (0.266 g, 0.370 mmol) and (hfac)$Ag(SEt_2)$ (0.150 g, 0.370 mmol, 1.00 equiv) were dissolved in 20 mL of toluene. Film deposition was conducted using this solution with a carrier gas of 10% H_2 in Ar. The solution was kept at room temperature, atomized through a TSI-3076 aerosol generator operated at 20 psi corresponding to a gas flow rate of ~2 L/min at STP, and the droplets were introduced into a preheating tube (60–70 °C). The precursors vapor was directed toward a lamp-heated SiO_2 substrate at 250 °C and atmospheric pressure. After 20 min, reflective films were formed. At a preheating temperature of 70 °C and a substrate temperature of 250 °C, a deposition rate of 220 Å/min was obtained. The solution consumption rate is approximately 0.5 mL/min. The film was characterized by SEM, EDS, and X-ray diffraction. The EDS results indicated the existence of Ag and Pd. The X-ray diffraction results showed the formation of an alloy of AgPd. Previous studies using X-ray photoelectron spectroscopy (XPS) and present studies using Auger electron spectroscopy (AES) confirmed the purity of these films. The experimental conditions are tabulated in Table 1. All experiments were conducted at 1 atm with 10% H_2 in Ar using toluene as solvent.

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(B) Control Experiments To Distinguish AACVD from Droplet or Particle Deposition. *(i) AACVD from Precursor of (hfac)Ag(SEt$_2$).* A Schlenk flask was charged with 1.00 g of (hfac)Ag(SEt$_2$) and 20 mL of pyridine or toluene (concentration = 0.123 M). After the precursor was dissolved, AACVD experiments were conducted with a preheating temperature of 70 °C and a substrate temperature of 200 °C, using 10% H_2 in Ar as carrier gas. After 25 min, reflective, silver-colored films were obtained at deposition rates of 300 and 550 Å/min, in pyridine and toluene solvents. The different deposition rates may reflect the influence of the solvent properties on the deposition process. The films were characterized by SEM, EDS, and X-ray diffraction. The EDS and X-ray diffraction data indicated the formation of crystalline silver films on the substrates.

(ii) AACVD from Precursor of AgNO$_3$. Silver(I) nitrate, 0.420 g, was dissolved in 20 mL of pyridine or water (C = 0.123 M). The AACVD experiments were carried out under exactly the same conditions as described in section (i) of part B. After 25 min., no deposition was observed on the substrate in each case. These films were also characterized by SEM, EDS and X-ray diffraction. The results indicated no silver or silver-containing material existed on the substrates.

(C) Reactivity Studies of Precursors with Carrier Gas (10% H_2 in Ar). It is crucial to study the reactivity between precursors and carrier gas to avoid any side reaction in solution before deposition. The following experiments were conducted.

(i) Reactivity Studies with H_2. A small amount of Pd(hfac)$_2$ (~5 mg) was dissolved in each of two NMR tubes in toluene-d_8. Hydrogen was passed through the solutions at room temperature and at 70 °C to simulate the operating temperature of the preheating region of the AACVD apparatus. The reaction was monitored by ^{1}H NMR spectroscopy and through observation of the color change of the solution. At room temperature, after 2 h, evidence for a reaction was observed, while at 70 °C, a reaction was observed within only ~2−3 min, as determined by formation of a drak cloudy solution or a metal mirror on the wall of the tube. ^{1}H NMR spectra revealed the formation of hfacH. The metal mirror was characterized as Pd metal by powder X-ray diffraction and energy-dispersive spectroscopy. Similar experiments were carried out with Pd(hfac)$_2$(SEt$_2$) and (hfac)Ag(SEt$_2$).

(D) Composition Variation Studies of the AACVD of Alloys. Palladium(II) bis(1,1,1,5,5,5-hexafluoroacetylacetonato) (0.714 g) and 1.09 g of Cu(hfac)$_2$ were dissolved in 30 and 50 mL of toluene, respectively (concentrations for both were 0.0457 M). These solutions were introduced into another flask using calibrated pipets in different ratios, keeping the total volume 10.0 mL. A series of solutions in the following molar ratio (Pd/Cu) were prepared: 5/95, 15/85, 25/75, 30/70, 50/50, 80/20. The AACVD experiments were conducted as described in section A at a preheating temperature of 70 °C and a substrate temperature of 275 °C on SiO$_2$ substrates. The films were examined by X-ray diffraction, and the results showed alloys formed in each case and the composition of the film was affected by the solution stoichiometry.

Using the same method, Pd(hfac)$_2$(SEt$_2$) and (hfac)Ag(SEt$_2$) were mixed in toluene in different molar ratios (Ag/Pd): 0/100, 25/75, 50/50, 75/25, 100/0, respectively. The AACVD was conducted using the procedure described above at a preheating temperature of 70 °C and substrate temperature of 250 °C on SiO$_2$ substrates.

(E) Studies To Determine Whether the Deposition of Ag−Pd Alloy from Pd(hfac)$_2$(SEt$_2$) and (hfac)Ag(SEt$_2$) Is Feed-Rate Limited. Using the same method described above, Pd(hfac)$_2$(SEt$_2$) and (hfac)Ag(SEt$_2$) were mixed in toluene in the same molar ratio with individual concentrations of 0.0123 M. The AACVD was conducted using the procedure described above at a preheating temperature of 70 °C and substrate temperatures of 235, 250, 265, 275, 285, and 310 °C on SiO$_2$ substrates, taking care to keep all other parameters identical. The deposition time was 19 min for all six experiments.

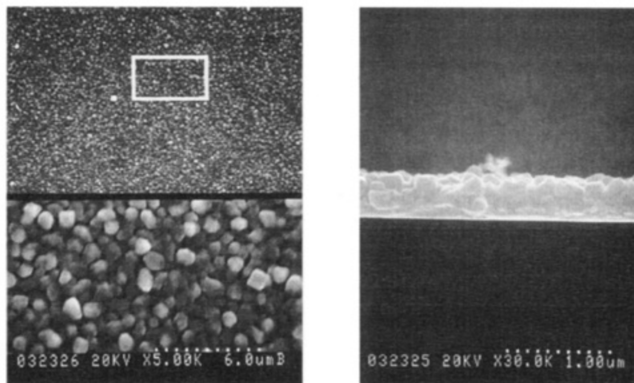

Figure 1. Scanning electron micrographs of a Cu$_{0.15}$Pd$_{0.85}$ film grown from Pd(hfac)$_2$ and Cu(hfac)$_2$ on SiO$_2$ substrate at a preheating temperature of 80 °C and a substrate temperature of 250 °C.

Results and Discussions

This section is organized as follows. An overview of the AACVD results for deposition of three binary alloys, Ag−Pd, Cu−Pd, and Ag−Cu derived from precursors mixed in a 1:1 molar ratio is presented. The reactivity of the precursors toward each other and hydrogen is then described. Studies of the influence of solution composition on film composition are presented. Finally, the temperature dependence of the deposition rate is discussed.

Aerosol-Assisted Chemical Vapor Deposition (AACVD) of Alloys Between the Elements of Ag, Pd and Cu. *(i) AACVD of Ag−Pd Alloys:* A preliminary report of the deposition of Ag$_{0.4}$Pd$_{0.6}$ from (hfac)Ag(SEt$_2$) and Pd(hfac)$_2$ in toluene with a carrier gas of 10% H_2 in Ar has previously been communicated.[26] These results are reviewed briefly here for comparison to the results described below. The precursor (hfac)Ag(SEt$_2$) cannot be sublimed intact suggesting that it cannot be used as a precursor for CVD of Ag with conventional precursor delivery.[32] However, it was shown to be suitable for AACVD of Ag from 120 to 300 °C under N_2.[26] The precursor Pd(hfac)$_2$ has also been used to deposit Pd films above 200 °C under H_2.[26,34] Therefore, they were chosen as precursors for deposition of Ag−Pd alloy films in our previous experiments.

(ii) AACVD of Cu−Pd Alloys: The precursors used for deposition of Cu−Pd alloy were Pd(hfac)$_2$ and Cu(hfac)$_2$. The Cu−Pd alloy thin films were grown on SiO$_2$ substrates over a range of preheating temperatures, 70−80 °C and substrate temperatures, 250−300 °C under 10% H_2 in Ar. After 25 min, reflective gray films were obtained and characterized by SEM, EDS, and X-ray diffraction. The SEM pictures showed smooth, uniform texture with grain sizes of 0.1−0.2 μm (see Figure 1). The EDS results indicated palladium and copper were present in the film. At a preheating temperature of 80 °C and a substrate temperature of 275 °C, a deposition rate of 230 Å/min was obtained. The X-ray diffraction data, shown in Figure 2, indicated the formation of Cu$_{0.15}$Pd$_{0.85}$ alloy.

The compounds Pd(hfac)$_2$ and (hfac)Cu(1,5-COD) were also used as precursors for AACVD of Cu−Pd alloys. The deposition was carried out at a preheating temperature of 70 °C and a substrate temperature of 250 °C.

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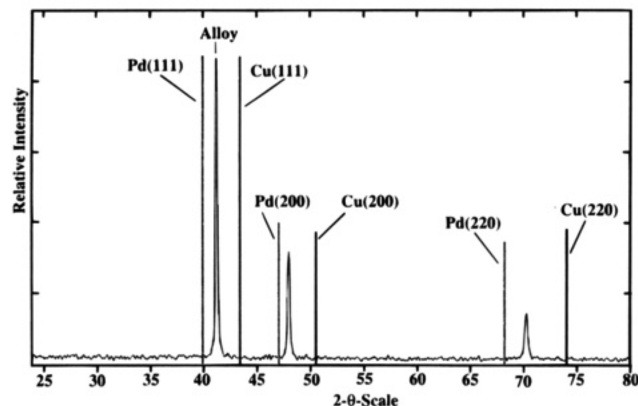

Figure 2. X-ray diffraction data for a $Cu_{0.15}Pd_{0.85}$ alloy film deposited from $Pd(hfac)_2$ and $Cu(hfac)_2$ at a preheating temperature of 80 °C and a substrate temperature of 250 °C on SiO_2 substrate.

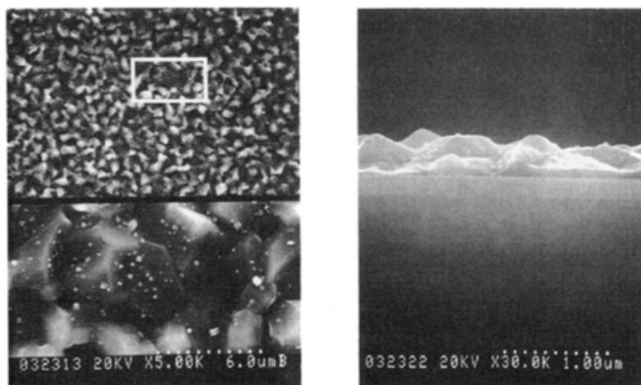

Figure 3. Scanning electron micrographs of the film grown from (hfac)Cu(1,5-COD) and $Pd(hfac)_2$ on SiO_2 substrate at a preheating temperature of 70 °C and a substrate temperature of 250 °C.

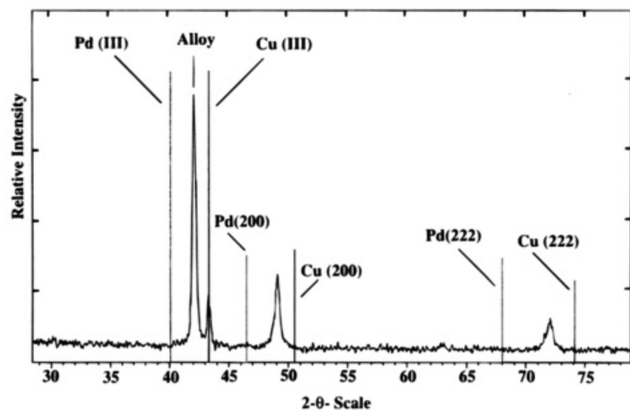

Figure 4. X-ray diffraction data for the film deposited from (hfac)Cu(1,5-COD) and $Pd(hfac)_2$ showing the presence of $Cu_{0.44}Pd_{0.56}$ and oriented Cu(111), at a preheating temperature of 70 °C and a substrate temperature of 250 °C on SiO_2 substrate.

The deposition rate at a substrate temperature of 250 °C was 350 Å/min. The resulting films were characterized by SEM, EDS, and X-ray diffraction. The SEM micrograph in Figure 3 showed a rough texture with grain sizes of less than 0.6 μm. The X-ray diffraction results indicated the film was composed of the $Cu_{0.44}$-$Pd_{0.56}$ alloy and a small portion of oriented Cu(111) (Figure 4). The composition of 0.44:0.56 suggests that the mechanism of film formation was CVD; droplet or particle deposition would have given film compositions of 0.5:0.5.

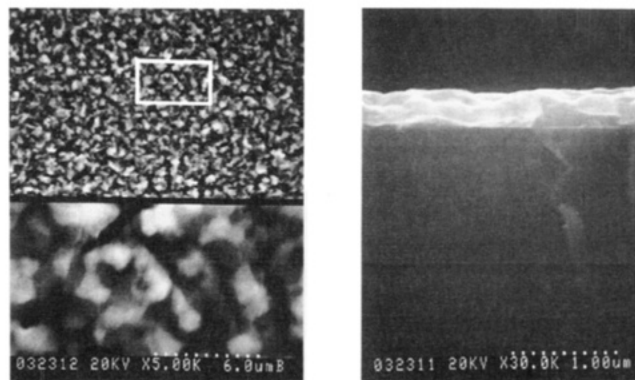

Figure 5. Scanning electron micrographs of an Ag-Cu alloy film grown from $(hfac)Ag(SEt_2)$ and $Cu(hfac)_2$ on SiO_2 substrate at a preheating temperature of 80 °C and a substrate temperature of 275 °C.

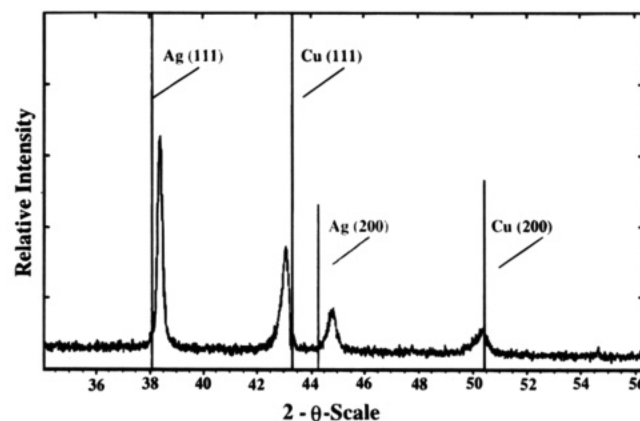

Figure 6. X-ray diffraction data for the Ag−Cu alloys film deposited from $(hfac)Ag(SEt_2)$ and $Cu(hfac)_2$ at a preheating temperature of 80 °C and a substrate temperature of 275 °C on SiO_2 substrate.

(iii) AACVD of Ag−Cu Alloys: Literature reports showed that $Cu(hfac)_2$ can deposit pure Cu films above 250 °C under H_2, but forms Cu films with significant amounts of carbon contamination above 350 °C in the absence of H_2.[35,36] Therefore the deposition of Ag−Cu was carried out using $(hfac)Ag(SEt_2)$ and $Cu(hfac)_2$ as precursors and 10% H_2 in Ar was used to lower the deposition temperature and reduce the impurity incorporation. AACVD experiments were conducted at a preheating temperature of 80 °C and a substrate temperature of 275 °C under H_2. After 15−30 min, reflective, silvery-yellow films were obtained, with a deposition rate of 180 Å/min. The SEM studies of the film morphology showed a rough texture (see Figure 5). The EDS results showed the presence of Ag and Cu. Shown in Figure 6 is the X-ray diffraction data of the film. The peaks close to the 2θ positions expected for authentic Ag(111) and Cu(111) are the β-phase(111) and α-phase(111) of Ag−Cu alloys, consistent with the Ag−Cu phase diagram.[37] This indicated that the film was composed of the α- and β-phases of Ag−Cu alloys.

Control Experiments To Distinguish AACVD from Spray Pyrolysis or Particle Deposition. To establish whether aerosol-assisted precursor delivery is

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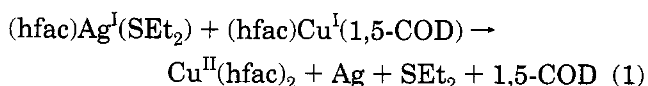
a CVD process rather than a droplet or particle deposition process, a series of experiments was conducted in which an involatile silver source was used as a control. Silver(I) nitrate was chosen as a involatile source of Ag, and (hfac)Ag(SEt_2) was chosen as a volatile source. To compare these experiments under identical conditions, pyridine was used as a solvent. Parallel experiments were also carried out using the same precursor but different solvents (pyridine or toluene for (hfac)Ag(SEt_2) and pyridine or H_2O for $AgNO_3$). The AACVD experiments using solutions of these precursors were carried out under identical CVD conditions, a preheating temperature of 70 °C, substrate temperature of 200 °C, and the same concentration. The lack of gain in weight, as well as X-ray diffraction, SEM and EDS results indicated that for the $AgNO_3$ solutions there was no deposition on the substrate after 25 min. However, in the case of (hfac)Ag(SEt_2), the X-ray diffraction, EDS, and SEM data showed the deposition of silver metal on the same substrate with deposition rates of 300–550 Å/min. If the Ag films were deposited by droplet or particle deposition on the heated surface of the substrate, silver, or silver-containing material should have been detected on the substrate in the $AgNO_3$ experiments. However, no deposition was observed, suggesting that thermophoresis prevents deposition.[38] In contrast, for the case of the volatile (hfac)Ag(SEt_2) compound, the silver films observed are likely to be derived from diffusion of the precursor vapor to the substrate and subsequent reaction. Therefore these results support the deposition of silver from (hfac)Ag(SEt_2) via a CVD process.

Reactivity Studies. It is necessary to study the reactivity of metal–organic precursors in solution for deposition of alloys in AACVD experiments. The precursors should not react in solution with each other, with added reagents such as H_2, or with the solvent prior to delivery to substrate, because such a reaction may result in formation of involatile species and change the film composition.

(i) Reactivity Studies of Metal–Organic Precursors. The species Pd(hfac)$_2$ and (hfac)Ag(SEt_2) were used as precursors for deosition of Ag–Pd alloy films in our initial experiments. The reactivity of Pd(hfac)$_2$ and (hfac)Ag(SEt_2) were investigated in solution. The two precursors were dissolved in toluene-d_8 and their behavior monitored by ^{1}H NMR spectroscopy. The spectra showed that a reaction occurred, and after further investigation Pd(hfac)$_2$(SEt_2) and [(hfac)Ag]$_4$(SEt_2) were isolated and fully characterized, which suggested Pd(hfac)$_2$(SEt_2) may represent the active species for the deposition of Pd.[33] In separate experiments it was shown that Pd(hfac)$_2$(SEt_2) and (hfac)Ag(SEt_2) do not react. The details of these experiments will be reported separately.[33]

In the AACVD of Cu–Pd alloy, the precursors Pd(hfac)$_2$ and Cu(hfac)$_2$ used do not react with each other in solution. In addition, solution ^{1}H NMR studies revealed the precursors (hfac)Cu^I(1,5-COD) and Pd(hfac)$_2$ did not react with each other in toluene solution.

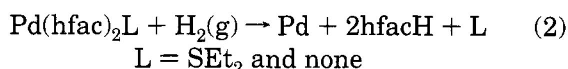
In the Ag–Cu alloy system, when the precursors of (hfac)Ag^{I}L and (hfac)Cu^{I}L were mixed in toluene, a redox reaction occurred within the time scale of the overall AACVD experiment with formation of Ag metal and Cu(hfac)$_2$ according to eq 1. As a result, Cu(hfac)$_2$



$$\text{(hfac)Ag}^{I}(\text{SEt}_2) + \text{(hfac)Cu}^{I}(1,5\text{-COD}) \rightarrow \text{Cu}^{II}(\text{hfac})_2 + \text{Ag} + \text{SEt}_2 + 1,5\text{-COD} \quad (1)$$

was chosen as a source of Cu in these experiments and Cu(hfac)$_2$ and (hfac)Ag(SEt_2) were successfully used for the deposition of Ag–Cu alloy films.

(ii) Reactivity Studies of Precursors with H_2 as Carrier Gas. Hydrogen (10% in argon) was chosen as carrier gas in these AACVD experiments because it generally can lower the deposition temperature and reduce film contamination.[4,35,39] To determine the conditions under which H_2 reacts with the Pd and Ag compounds used in this study, a series of control experiments was carried out. The species Pd(hfac)$_2$, Pd(hfac)$_2$(SEt_2), and (hfac)Ag(SEt_2) were dissolved in toluene-d_8 in separate NMR tubes, and 10% H_2 in Ar was passed through these solutions at room temperature and at 70 °C. Changes in the solution were monitored by ^{1}H NMR spectroscopy as well as through visual observation. The results showed (hfac)Ag(SEt_2) is stable to H_2, and no reaction was observed after bubbling H_2 at 70 °C for 1 h within the limits of sensitivity of ^{1}H NMR spectroscopy. However, a reaction between Pd(hfac)$_2$ and H_2 was observed after 2 h of bubbling H_2 at room temperature, while at 70 °C a reaction was observed after only ~2–3 min. These experiments also revealed that the reaction rate between Pd(hfac)$_2$(SEt_2) and H_2 is slower than that of Pd(hfac)$_2$ and H_2. At room temperature, no reaction was observed after 3 h of bubbling of and H_2. At 70 °C, a reaction was observed only after 20–23 min. The ^{1}H NMR results indicated the existence of free hfacH in the solution. A metallic deposit on the wall of the tube was also evidence of the reaction. The metallic deposit was characterized as Pd metal by X-ray diffraction and EDS. The overall chemical reaction for the decomposition can be expressed by eq 2.



$$\text{Pd(hfac)}_2\text{L} + \text{H}_2(\text{g}) \rightarrow \text{Pd} + 2\text{hfacH} + \text{L} \quad (2)$$
$$\text{L} = \text{SEt}_2 \text{ and none}$$

To determine whether the reactions taking place in solution at 70 °C might lead to decomposition of the precursors in the droplets during the AACVD of Ag, Pd, or Ag/Pd alloy, the residence time of the precursor droplets in the preheater and reactor was calculated. Through measurement of the flow rate of the carrier gas into the aerosol generator as well as the lengths and diameters of connecting and preheating tubes, the residence time was calculated as 10 s. Therefore, because Pd(hfac)$_2$(SEt_2) and (hfac)Ag(SEt_2) showed negligible decomposition for such short heating periods, they should be sufficiently stable to act as precursors for AACVD with H_2 as carrier gas. The Pd(hfac)$_2$ is likely to undergo some decomposition during transport of the droplets in the AACVD experiments. However according to the integration of the protons in the ^{1}H NMR study, the decomposition was not severe during the calculated residence time of 10 s; less than 2% of the Pd(hfac)$_2$ was decomposed after 2 min of bubbling H_2 at 70 °C. Therefore, it is still feasible to use Pd(hfac)$_2$ as a precursor for AACVD of Pd as well as Pd-containing alloys. However, at higher temperatures

(38) Hinds, W. C. *Aerosol Technology*; Wiley: New York, 1982.

(39) Moshier, R. W.; Sievers, R. E.; Spendlove, L. B. U.S. Patent 3,594,216, 1967.

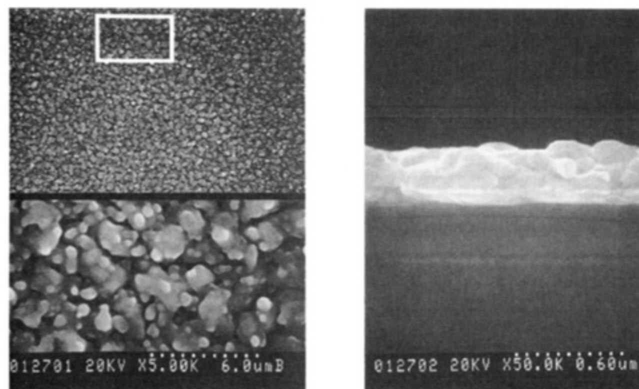


Figure 7. Scanning electron micrographs of a 1:1 Pd:Ag film grown from (hfac)Ag(SEt_2) and Pd(hfac)$_2$(SEt_2) on SiO_2 substrate at a preheating temperature of 70 °C and a substrate temperature of 250 °C.

precursor decomposition and metal particle formation in the droplets is likely to be more extensive and could result in a reduction of the deposition rate.

AACVD of Ag–Pd Alloy Films from (hfac)Ag(SEt_2) with Pd(hfac)$_2$(SEt_2). On the basis of the reactivity studies of (hfac)Ag(SEt_2) with Pd(hfac)$_2$, and Pd(hfac)$_2$ or Pd(hfac)$_2$(SEt_2) toward H_2, Pd(hfac)$_2$(SEt_2) is more suitable than Pd(hfac)$_2$ for deposition of Ag–Pd alloy films in AACVD experiments because it is less reactive toward H_2 and unreactive toward (hfac)Ag(SEt_2). To ensure that Pd(hfac)$_2$(SEt_2) was suitable for CVD, a comparison of the volatility of Pd(hfac)$_2$ and Pd(hfac)$_2$(SEt_2) was carried out by TGA. These studies indicated that Pd(hfac)$_2$ completely sublimed at 115 °C and Pd(hfac)$_2$(SEt_2) completely sublimed at 130 °C under N_2. The TGA experiments carried out under H_2 at a heating rate of 10 °C/min showed Pd(hfac)$_2$ and Pd(hfac)$_2$(SEt_2) decomposed to form Pd metal at 80 and 100 °C, respectively. The observed residual mass for both was slightly lower than the calculated values, which was probably caused by some evaporation of the precursor prior to decomposition. As a result, it is likely that Pd(hfac)$_2$(SEt_2) is a suitable source of Pd for AACVD of Ag–Pd alloy.

Therefore, the deposition of Ag–Pd alloy was reinvestigated using Pd(hfac)$_2$(SEt_2) and (hfac)Ag(SEt_2) precursors mixed in a 1:1 ratio dissolved in toluene using the same method as described previously.[26] After 20 min, reflective films were obtained at a preheating temperature of 70 °C and a substrate temperature of 250 °C under H_2. A deposition rate of 220 Å/min was obtained. The SEM (see Figure 7) study of the film morphology showed a smooth, dense, uniform texture with grain size of less than 0.3 μm. The EDS results showed the presence of Ag and Pd. The X-ray diffraction study, shown in Figure 8, of the film indicated the formation of a 1:1 AgPd alloy. This composition was consistent with a vapor deposition process, limited by the feed rates of the precursors as discussed below.

Compositional Variation Studies. It is known that the properties of an alloy are determined by its composition to a large extent. For example, Ag–Pd alloy membranes containing 23 at. % Ag can reach the maximum value of gas permeability and optimum mechanical properties.[2] Because it is generally hard to control the composition in thin alloy films, we decided to examine the influence of solution stoichiometry on

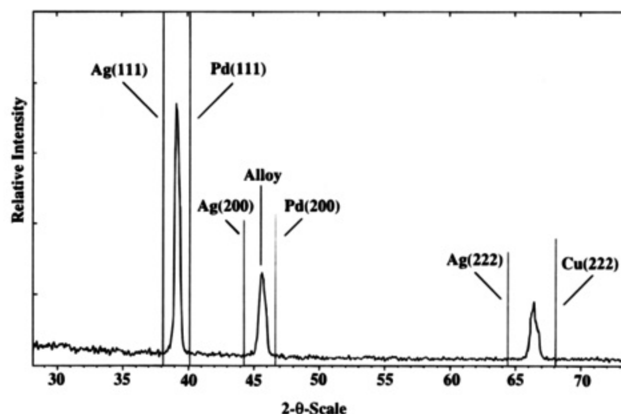


Figure 8. X-ray diffraction data for the 1:1 Pd:Ag alloy film deposited from (hfac)Ag(SEt_2) and Pd(hfac)$_2$(SEt_2) at a preheating temperature of 70 °C and a substrate temperature of 250 °C on SiO_2 substrate.

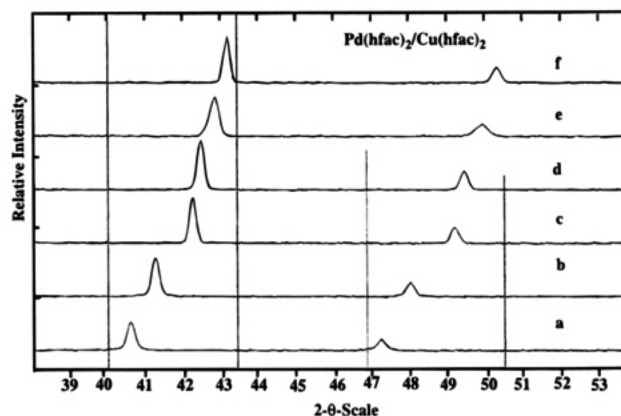


Figure 9. X-ray diffraction data for the compositional variation study of Cu–Pd alloy system deposited from Cu(hfac)$_2$ and Pd(hfac)$_2$ on SiO_2 substrate at a preheating temperature of 80 °C and a substrate temperature of 275 °C; see text for details.

film composition. In addition, we are also interested in understanding physical aspects of the deposition process, such as which step limits the deposition rate under these conditions.

(i) Compositional Variation Studies in Cu–Pd Alloy System. In the first set of experiments, the compositional variation of Cu–Pd alloys was studied. Toluene solutions of Pd(hfac)$_2$ and Cu(hfac)$_2$ (both 0.0457 M) were prepared, and aliquots were removed and mixed accurately in the following ratios: 5/95, 15/85, 25/75, 30/70, 50/50, 80/20, using calibrated pipets. The AACVD experiments were conducted using each solution at a preheating temperature of 70 °C and substrate temperature of 275 °C. The crystallinity and composition of the films were examined by X-ray diffraction. The data indicated the composition of the alloy film was affected by the solution stoichiometry (see Figure 9). By plotting a calibration curve, the films were found to be Pd:Cu in the ratios (solution ratios are given in parenthesis): a, 95:5 (80:20); b, 85:15 (50:50); c, 75:25 (30:70); d, 70:30 (25:75); e, 40:60 (15:85); and f, 12:88 (5:95). These data show that under these deposition conditions, the solution and film stoichiometry are significantly different.

(ii) Compositional Variation Studies in Ag–Pd Alloy System. To obtain quantitative information for compositional variation, the Ag–Pd alloy system was chosen because the change of composition of the alloy can be

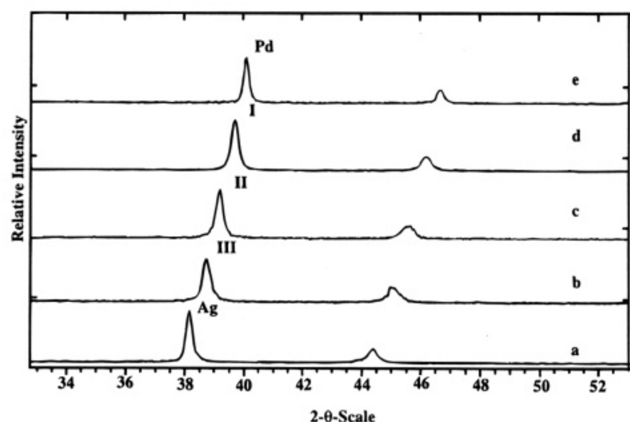


Figure 10. X-ray diffraction data for the compositional variation study of Ag–Pd alloy system deposited from (hfac)-Ag(SEt_2) and Pd$(hfac)_2$(SEt_2) on SiO_2 substrate at a preheating temperature of 70 °C and a substrate temperature of 250 °C.

quantified by X-ray diffraction. The Ag–Pd alloy was deposited at a preheating temperature of 80 °C and a substrate temperature of 250 °C using (hfac)Ag(SEt_2) and Pd$(hfac)_2$ precursors. Their toluene solutions were prepared and mixed in the following molar ratios (Ag/Pd): 0/100, 25/75, 50/50, 75/25, and 100/0. The AACVD experiments were carried out using these solutions at a preheating temperature of 80 °C and a substrate temperature of 250 °C under H_2. The X-ray diffraction data from each film were obtained. Assuming the change of the alloy lattice parameter obeys Vegard's law, that is a linear relationship between composition and lattice parameters, then the composition of the alloy films calculated from the peak positions in the different patterns is Ag/Pd (molar ratio): 0/100, 30/70, 40/60, and 70/30, and 100/0, respectively.[40] The lack of correspondence between solution and film composition is likely to be the result of the reaction between these precursors in solution described earlier.

The compositional variation studies of Ag–Pd alloy also were carried out using toluene solutions of (hfac)-Ag(SEt_2) and Pd$(hfac)_2$(SEt_2) according to the method described above. The two precursors were mixed in toluene in the following molar ratios (Ag:Pd): a, 0:100, b, 25:75; c, 50:50; d, 75:25; and e, 100:0. The AACVD experiments were conducted using each solution at a preheating temperature of 70 °C and a substrate temperature of 250 °C and 10% H_2 in Ar as carrier gas. The X-ray diffraction data from each film are shown in Figure 10. The composition of the alloys b–d calculated from the peak positions in the diffraction patterns are Ag/Pd (molar ratio): 25/75, 50/50, and 75/25, respectively, the same as the ratios in solution. Therefore the composition of the alloy is identical to that of the precursor solution in this case. Again, this composition is in agreement with the result expected for feed-rate-limited or transport-limited deposition.

Speculation of the Rate-Limiting Step for Deposition in These Experiments. As with other CVD experiments, the deposition rate can be limited by any of several steps which can be considered to occur in series. These steps include precursor feed in droplets to the reactor, precursor evaporation from the droplets, precursor transport to the heated substrate and the reaction on the heated substrate surface. These steps are identified in Figure 11. We have previously carried out AACVD experiments with (hfac)Cu(1,5-COD) under conditions where the substrate temperature was held constant and the preheating temperature was varied.[27] The deposition rate data obtained, when plotted as a function of (the reciprocal of the) preheating temperature, revealed a slope that gave an enthaply similar to the enthalpy of vaporization of the precursor. When the preheating temperature was held constant and the substrate temperature was varied, the rate data also gave an enthalpy close to the enthalpy of vaporization. A further key result was that the calculated partial pressure of the precursor assuming complete evaporation was greater than its vapor pressure at this temperature suggesting that only a fraction of the precursor evaporated from the particles. As a result, we concluded that under those conditions, the deposition rate was most likely to be precursor evaporation-rate limited in the sense that the deposition rate was related to the partial pressure of the precursor which was fixed by the vapor pressure. Increasing the preheating temperature increased the vapor pressure, thereby increasing the deposition rate. Similarly, increasing the substrate temperature increased the temperature of the gas above the substrate resulting in increased vapor pressure. However, surface reaction-limited deposition cannot be ruled out by these observations because the rate of the surface reaction depends on the precursor partial pressure which can vary as a function of substrate temperature under these conditions.

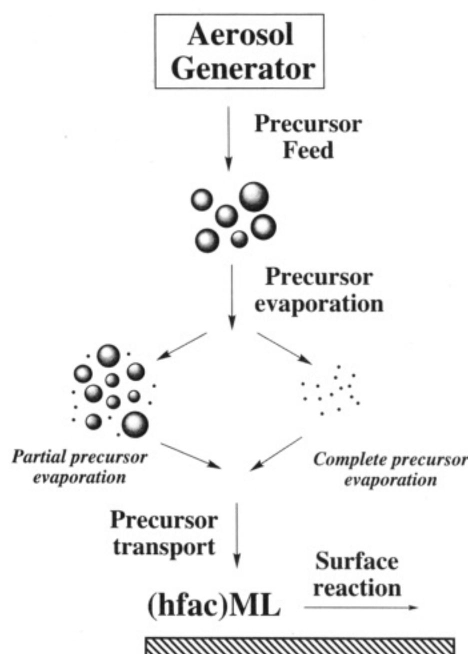


Figure 11. Schematic representation of the steps that are likely to be rate-limiting in the deposition of films by AACVD.

In this study, we can make some qualitative predictions for the deposition of Ag–Pd alloy deposited from Cu$(hfac)_2$ and Pd$(hfac)_2$. The extent of precursor conversion is approximately 9.5% based on the mass of alloy deposited compared to the mass transported into the reactor. This is an appreciable fraction for a *cold-wall reactor*, especially when compared to the precursor conversion used to ensure surface reaction-limited deposition of $<1\%$, and is consistent with feed-rate limited deposition. The extent of precursor conversion is gener-

(40) Xu, C. Y.; Hampden-Smith, M. J.; Kodas, T. T. In *Mater. Res. Soc. Symp. CVD of Refractory Metals and Ceramics*; Boston, Fall 1994.

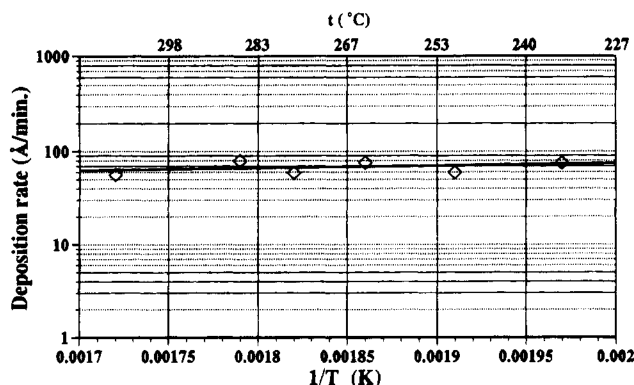


Figure 12. Plot of log deposition rate vs inverse of substrate temperature for deposition of Ag−Pd alloy from (hfac)Ag(SEt_2)$_2$ and Pd(hfac)$_2$(SEt_2) on SiO_2 substrate at a preheating temperature of 70 °C.

ally lower in a cold-wall reactor compared to a hot-wall reactor because in a cold-wall reactor a smaller faction of the precursor contacts a heated surface. The estimated partial pressures of each precursor is approximately 220 mTorr based on the amount of material delivered to the reactor assuming that all the precursor evaporates in the preheating zone at 70 °C. Comparison of these values to the literature data for the vapor pressure of these species at the same temperature (Cu(hfac)$_2$ 1.5−2.0 Torr 70 °C;[41] Pd(hfac)$_2$ 1.4 Torr at 70 °C[42]) shows that the estimated precursor partial pressure is significantly lower than the vapor pressure of these species at this temperature. As a result, this system is qualitatively different from the case with (hfac)Cu(1,5-COD) where only partial evaporation of the precursor occurred. This further supports the idea that the deposition rate is limited by the feed rate of the precursors. We speculate that the surface reaction is unlikely to be rate limiting because in the case of Cu(hfac)$_2$, much higher deposition rates have been observed at similar substrate temperatures and under similar conditions.[41] Similarly, calculated droplet evaporation rates[38] are rapid and show droplet evaporation cannot be rate limiting.

On the basis of this information, the deposition rate is likely to be precursor feed-rate limited but could also be transport-rate limited. This is in contrast to the previous results for (hfac)Cu(1,5-COD)[27] where a higher delivery rate of the precursor did not result in a higher deposition rate because the feed rate of the vapor was limited by the (lower) vapor pressure of this compound.

To test these ideas, a series of experiments was carried out in which the feed rate of the droplets, containing (hfac)Ag(SEt_2) and Pd(hfac)$_2$(SEt_2), to the reactor was kept constant and the only variable was the substrate temperature (preheater temperature = 70 °C). The results of this study are presented as a plot of log deposition rate vs reciprocal temperature in Figure 12. The slope of this plot shows the deposition rate did not vary significantly as a function of substrate temperature which is consistent with the proposal that the deposition is feed-rate limited or transport-rate limited and is in contrast to the previous results for (hfac)Cu(1,5-COD) where a significant dependence of the rate on the substrate temperature was observed. Because both the feed and transport steps have weak temperature dependencies and would give a film composition close to that of the precursor solution composition, we cannot distinguish between these two possibilities. Finally, this series of experiments also showed that the same composition was obtained reproducibly.

(41) Griffin, G. L.; Maverick, A. W. In *The Chemistry of Metal CVD*; Kodas, T. T., Hampden-Smith, M. J., Eds.; VCH: Weinheim, 1994.
(42) Zharkova, G. I.; Igumenov, I. K.; Tyukalevskaya, N. M. *Sov. J. Coord. Chem. (Engl. Trans.)* **1988**, *14*, 67−74.

Conclusions

Aerosol-assisted chemical vapor deposition (AACVD) of crystalline, Ag−Pd, Cu−Pd, and Cu−Ag alloy films from toluene solutions of (hfac)Ag(SEt_2)/Pd(hfac)$_2$(SEt_2), Cu(hfac)$_2$/Pd(hfac)$_2$, (hfac)Cu(1,5-COD)/Pd(hfac)$_2$, and (hfac)Ag(SEt_2)/Cu(hfac)$_2$ precursors over a range of preheating temperatures, 70−80 °C and substrate temperatures of 250−300 °C has been demonstrated. The reactivity studies between precursors as well as between certain precursors and H_2 revealed that Pd(hfac)$_2$(SEt_2) was more suitable for deposition of Pd than Pd(hfac)$_2$. A study of the composition of the films as a function of stoichiometry of the precursors in solution has been conducted. The compositional variation study shows the composition of the films is influenced by the solution stoichiometry. Observations of low deposition rates and low feed rates led to the idea that the deposition was likely to be feed-rate or transport-rate limited under the conditions employed. This prediction was consistent with a study of deposition rate as a function of substrate temperature at constant feed rate in the (hfac)Ag(SEt_2)/Pd(hfac)$_2$(SEt_2) system, which showed no variation in the deposition rate over a 75 °C temperature range. *Taken together*, these observations support feed-rate or transport-rate-limited deposition but not surface reaction-limited deposition.

An important conclusion to be drawn from these experiments is that to control film composition (to be the same as the solution composition), it is useful to carry out the deposition under conditions where the rate-limiting deposition step is not strongly influenced by the chemical characteristics of the precursors, such as evaporation rate or surface reaction rate. The reason is that two or more precursors are unlikely to have identical vapor pressures or surface reaction kinetics, and as a result, if either of these steps are rate limiting, the compositions are unlikely to be the same as the solution stoichiometry. In contrast the feed and transport steps are largely independent of the precursor properties. It is also important to realize that a change in parameters, such as substrate temperature, feed rate, or preheating temperature could change the nature of the rate-limiting deposition step.

Further studies to determine the generality of AACVD of alloys and determination of kinetic parameters and the influence of the positions of the rate-limiting steps on film composition are in progress.

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