Low-Pressure Chemical Vapor Deposition of Cu−Pd Films: Alloy Growth Kinetics

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We have examined the formation of copper films alloyed with small quantities of palladium. Independent control studies of palladium and copper deposition from palladium bis(hexafluoroacetylacetonate) [Pd(hfac)$_2$] and (hexafluoroacetylacetonato)copper(I)(vinyltrimethylsilane) [(hfac)Cu(I)(vtms)], both in the presence and absence of H_2, were carried out. The growth kinetics for both metals were feed-rate-limited under similar reactor conditions. No significant variation in deposition rate (100 nm/min, Pd; 100−500 nm/min, Cu), morphology, resistivity, and purity of the copper films was observed due to the addition of H_2. Simultaneous introduction of both precursors yielded Cu−Pd alloy films. The absence of pure palladium grains was confirmed by X-ray diffraction analysis which showed binary solid solutions ($Cu_{99.5}Pd_{0.5}$−$Cu_{80}Pd_{20}$) as the only crystalline phases. Auger electron spectroscopy analysis showed a significant reduction in the palladium content of the films as compared to that expected on the basis of the growth rates obtained during independent palladium deposition. Co-deposition of copper and palladium also resulted in a change of the palladium growth kinetics from a feed-rate-limited to a surface-reaction-limited regime ($E_a = 16$ kcal/mol). The Cu/Pd stoichiometry could be varied by controlling both the Pd(hfac)$_2$ partial pressure and substrate temperature. Experiments to investigate the cause of the change in Pd CVD kinetics showed that vinyltrimethylsilane (vtms) severely inhibits Pd growth during independent Pd deposition. The films were also contaminated with C when vtms was added. This study has shown that alloy CVD kinetics can be drastically different from the independent metal deposition kinetics.

1. Introduction

The low resistivity (1.7 $\mu\Omega$cm) and high electromigration resistance of pure copper make it an attractive choice for the replacement of aluminum alloy as an interconnect metal.[1] However, such a proposed copper-based interconnect system suffers from several disadvantages. Major concerns are the high diffusion rate of copper in silicon, SiO_2, and other materials used in integrated circuits, the lack of corrosion resistance toward oxidizing atmospheres, and the poor adhesion to most dielectrics. The diffusion problem can be mitigated through use of barrier layers while the adhesion problem can be solved through use of adhesion layers.

Several schemes have been proposed to improve the corrosion resistance of copper by effecting surface passivation through doping of the copper with other metals. The general approach has been to dope the copper with other metals that segregate or diffuse to the surface and/or the dielectric interface at low annealing temperatures followed by reaction of the dopant metals with NH_3 or O_2 to form their respective nitrides or oxides.[2]

A related aspect of the problem is that the electromigration resistance of copper is only marginally better than of Al−Cu.[3] This implies that other metals need to be added to copper to improve the electromigration resistance. The dopants required for electromigration improvement, oxidation resistance improvement, and minimal resistivity are different, and a tradeoff exists in that the choice of a particular element, e.g., Mg, has been shown to improve the oxidation resistance[4] but has a deleterious effect on electromigration.[3]

The discussion above suggests there is a need to add other dopant metals to copper, preferably during deposition. The strategies of passivation and electromigration improvement described above relied on depositing the alloy films by sputtering of alloy targets, coevaporation from metal sources, or annealing of individually deposited bilayers. Most integrated circuit wiring approaches, however, require a process that can conformally deposit copper films. Chemical vapor deposition (CVD) processes can offer the advantage of conformal

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coverage.[5] Thus, there is a strong motivation to investigate the co-deposition of copper and other prospective dopant metals using CVD. However, the process of co-depositing metal alloys by CVD is complex due to the possibility of the various adventitious interactions of the different species on the surface and in the gas phase.

There have been a few studies on the CVD of Cu alloys by conventional CVD.[6−11] Co-deposition of copper−cobalt and copper−tellurium was reported, but no kinetics studies or reliability tests were conducted.[6] Aluminum−copper co-deposition was demonstrated and interconnect performance was also tested, but this work focused on doping Al interconnects with copper and the kinetics were not examined.[10,11] Copper−tin alloys were deposited from a series of mixed metal precursors of the general form (hexafluoroacetylacetonato)copper(I)-(vinyltrialkyltin) [(hfac)Cu(I)(vinyltrialkyltin)].[8,9] Although this showed the simplicity of a single-source precursor, the films were significantly contaminated with carbon. Furthermore, controlled variation of stoichiometry is difficult with such a technique, and developing similar precursors for other metals is a difficult task.

Alternative delivery methods have allowed CVD of copper alloy films from low-vapor-pressure precursors. In this approach, metal alloy films were deposited by delivering a solution of metal-organic precursors in an organic solvent in the form of an aerosol followed by CVD, a technique called aerosol-assisted (AA)CVD.[12−14] The reaction kinetics, however, were quantitatively different from those for CVD employing traditional delivery methods. In general, there have been no investigations into the kinetics or mechanism of binary metal alloy film formation by CVD.

Although many metals have been identified as prospective dopants for copper, few of them have volatile precursors that deposit the pure metal at low temperatures. Even given a precursor, there are still the critical requirements for the similarity of deposition conditions, absence of premature reaction between precursors, and control of film stoichiometry and resistivity. Nearly all previous studies of copper alloy deposition using CVD processes were feasibility studies of film formation. Considering the major impact of even small quantities of metal dopant atoms in copper on its properties, a more fundamental understanding of the alloy deposition kinetics is required to achieve control over the properties of the films. So far there have been no studies to obtain such an understanding. Therefore it is necessary to understand thoroughly the impact of alloying elements on deposition rate, resistivity, morphology, conformality, and kinetics to be able to deposit alloy films reliably.

We have investigated CVD of copper alloyed with palladium as it has been identified as an additive that improves the electromigration resistance of pure copper.[15] Previous work has also indicated possible improvement of the oxidation resistance of copper by forming a solid solution or an intermetallic compound.[16] Moreover, pure palladium films also have applications in integrated circuit (IC) fabrication, to be discussed later. The precursor, $Pd(hfac)_2$, is a typical low-vapor-pressure precursor, and investigating the co-deposition with such a precursor puts severe constraints on the flexibility of choosing the deposition conditions. However, most precursors for the deposition of other metals also possess low vapor pressures.[17]

The biggest obstacle in the CVD of palladium has been the lack of precursors that deposit high-purity films at high deposition rates. This has motivated studies of various precursors for the CVD of palladium films.[18,19] Recently, a complete study of palladium deposition involving the reaction between $Pd(hfac)_2$ and H_2 was reported.[20] The system used for the palladium

$$Pd(hfac)_2 + H_2 \xrightarrow{\Delta} Pd + 2hfacH \qquad (1)$$

deposition reported here is identical.

Once the deposition kinetics and film properties for pure palladium deposition were understood, independent copper deposition from (hfac)Cu(I)(vtms) was studied under the same conditions as would be required for the co-deposition with palladium. Copper growth was studied both in the presence and absence of H_2 because there is still some uncertainty about the role of H_2 during the growth process. The presence of H_2 could result in a facile reduction of (hfac)Cu(I)(vtms) (vtms = vinyltrimethylsilane) as opposed to the disproportionation pathway.[1] These results for independent Cu and Pd CVD were used for comparisons with the composition obtained in the co-deposited films to gain insight into the alloy deposition kinetics. The impact of doping on grain size, surface morphology, crystallinity, and resistivity was also investigated, and comparisons with pure copper films were made to identify any significant changes in film properties.

Experimental Setup

Palladium CVD. The cold-wall low-pressure reactor setup was a modified version of a system described previously and is shown in Figure 1.[21] A base pressure of 1×10^{-5} Torr was obtained with a turbomolecular pump. The palladium precursor chamber was a uniformly heated insulated box. The precursor was loaded into a small vessel inside a N_2 atmosphere drybox and placed in the precursor heater without exposure to air. The temperature could be controlled within

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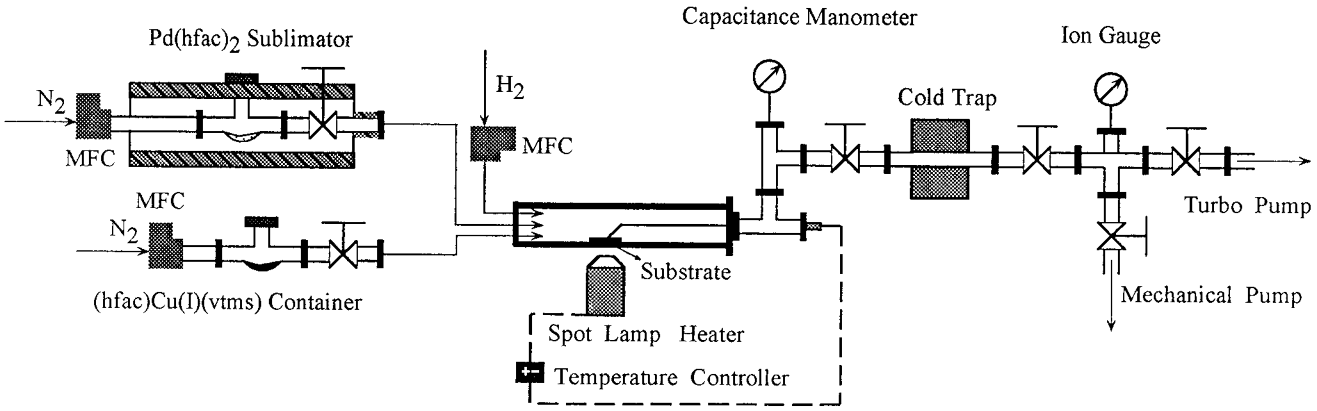

Figure 1. Low-pressure, cold-wall CVD apparatus used for the present study.

Table 1. Summary of Co-deposition Experiments

subs	Pd N_2 flow (sccm)	Cu N_2 flow (sccm)	H_2 flow (sccm)	total press (mTorr)	subs temp (°C)	Pd(hfac)$_2$ temp (°C)	dep rate (nm/min)	ρ ($\mu\Omega$cm)	% Pd
Si	2.8	3.0	0.5	100	100	60	167	2.42	0.1
Si	2.8	3.0	0.5	100	120	60	212	2.33	0.5
Si	2.8	3.0	0.5	100	140	60	389	8.62	5.0
Si	2.8	3.0	0.5	100	160	60	329	11.59	10.0
Si	2.8	3.0	0.5	100	180	60	368	15.87	16.0
Si	2.8	3.0	0.5	100	200	60	403	37.40	21.0
Si	2.8	3.0	0.5	100	100	35	179	2.29	0.0
Si	2.8	3.0	0.5	100	120	35	238	2.87	0.3
Si	2.8	3.0	0.5	100	140	35	469	2.95	0.8
Si	2.8	3.0	0.5	100	160	35	329	4.03	1.7
Si	2.8	3.0	0.5	100	180	35	332	7.33	3.1
Si	2.8	3.0	0.5	100	180	60	368	15.87	16.0
Si	2.8	3.0	0.5	100	180	55	414	13.28	14.3
Si	2.8	3.0	0.5	100	180	50	359	14.86	10.7
Si	2.8	3.0	0.5	100	180	45	383	11.42	7.6
Si	2.8	3.0	0.5	100	180	40	364	8.14	5.0
Si	2.8	3.0	0.5	100	180	35	332	7.00	3.1
patterned	2.8	3.0	0.5	100	100	60			0.2
patterned	2.8	3.0	0.5	100	120	60			0.8
patterned	2.8	3.0	0.5	100	140	60			3.0
patterned	2.8	3.0	0.5	100	160	60			10.0
patterned	2.8	3.0	0.5	100	180	60			18.0
patterned	2.8	3.0	0.5	100	200	60			21.0

the range 35−150 °C in the precursor chamber. Mass flow controllers were used for the reactant (H_2) and carrier gases (N_2).

The reactor was made of a rectangular quartz tube, and the substrate was heated from underneath by a lamp with a spot size of ~1.5 cm. The substrate (1 cm^2) was placed inside the quartz reactor directly above the heated area. A thermocouple was placed on the substrate and was connected to a temperature controller. The temperature of the substrates could be controlled in the range 35−500 °C. A liquid nitrogen cold trap was placed downstream before the pumping system to prevent any passage of condensable vapors as well as to collect byproducts.

The palladium depositions were performed at a total pressure of 50 mTorr. The precursor was loaded into the sublimation chamber maintained at 60 °C. The deposition experiments were carried out over a substrate temperature range of 80−200 °C. The substrates, p-type silicon(100) with surface native oxide present, were cleaned with standard RCA cleaning solutions,[22] primarily to remove surface organic debris and alkali ion contaminants.

Copper CVD. The experimental setup was identical with that used for palladium. The reactant, (hfac)Cu(I)(vtms), was used as the copper source and was maintained at room temperature. On the basis of prior knowledge about the deposition temperatures for the disproportionation of (hfac)-Cu(I)(vtms), experiments were carried out in the substrate temperature range of 100−200 °C. The substrates, silicon(100) (p-type with native oxide) and tungsten on Si(100), were cleaned using a procedure similar to that used for the palladium depositions. The flow rate of the N_2 used as a carrier gas was fixed at 3.0 sccm which resulted in a (hfac)Cu(I)(vtms) + N_2 total pressure of 50 mTorr. For the depositions in the presence of H_2, the partial pressure of H_2 was fixed at 10 mTorr (0.5 sccm), similar to that for palladium deposition.

Copper−Palladium Alloy CVD. The experimental setup for the separate copper and palladium experiments was modified to accommodate the simultaneous delivery of the two precursors and H_2 coreactant. The substrate was placed close to the mixing region to minimize the time for interaction between the precursors and especially with H_2 in the gas phase. Deposition was investigated in the substrate temperature range of 100−200 °C. The total pressure in the chamber was 100 mTorr. Nitrogen was used as a carrier gas for both precursors, and the partial pressures of the Pd(hfac)$_2$/N_2, (hfac)Cu(I)(vtms)/N_2, and H_2 streams were 40, 50, and 10 mTorr, respectively. The temperature of the Pd(hfac)$_2$ sublimation chamber was varied between 35 and 60 °C to achieve different feed rates and control film stoichiometries. The (hfac)Cu(vtms) was kept at room temperature. Table 1 shows a summary of the data for the co-deposition experiments.

Initial exploratory experiments were performed using a fixed quantity of Pd(hfac)$_2$ (15 mg) in the precursor delivery system. This resulted in alloy films with a decreasing concentration of palladium as a function of growth time. These films could not, therefore, be analyzed for the effect of the palladium content on alloy film oxidation and could not be observed for the variation of palladium composition in the film

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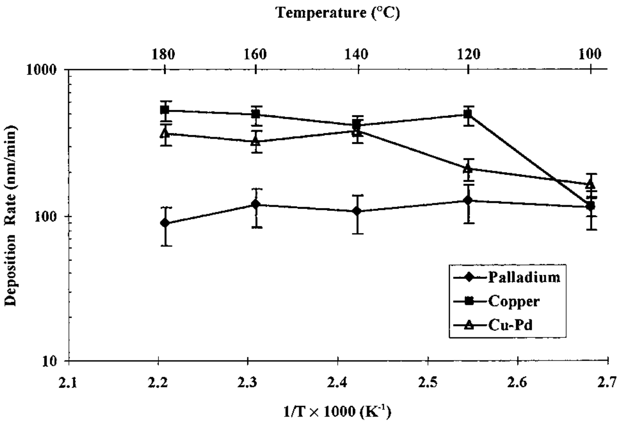

Figure 2. Comparison of the deposition rates of the co-deposited film to copper and palladium. Conditions: $Pd(hfac)_2$ temperature, 60 °C; $Pd(hfac)_2$ + N_2 carrier gas partial pressure, 40 mTorr; (hfac)Cu(I)(vtms) + N_2 carrier gas partial pressure, 50 mTorr; and H_2 partial pressure, 10 mTorr. The $Pd(hfac)_2$ temperature and H_2 partial pressures were the same for both pure palladium and alloy deposition. Error bars represent the maximum variability in data.

as a function of the substrate temperature. The solution to this problem was to do the experiments for a time period short enough to cause minimal variation of palladium within the film and at the same time obtain reasonably thick films (>0.1 μm) to perform reliable resistivity measurements.

Auger electron spectroscopy (AES) data were collected with cylindrical mirror analyzer (PHI 10-155), with an electron beam energy of 3 keV, at a base pressure of 10^{-9} Torr. The Ar^+ ion gun with ion beam current intensity of 10 mA/cm^2 at 1 keV beam energy and 4×10^{-5} Torr pressure was applied for etching the surface impurities and for depth profiling of the films.

The X-ray Diffraction (XRD) measurements were performed on a Siemens 5000 diffractometer using Cu Kα radiation (25 kV).

Results and Discussion

Palladium CVD Control Experiments. The observations for palladium CVD were similar to those reported earlier,[20] therefore, only the results pertinent to the co-deposition kinetics are discussed here. The apparatus was operated at high pumping speeds, and N_2 carrier gas was used to maximize precursor delivery. The most important result was that the deposition was feed-rate-limited (Figure 2) even at high precursor delivery rates and low substrate temperatures. Feed-rate-limited growth at such low substrate temperatures (~80 °C) implied that the reactivity between $Pd(hfac)_2$ and H_2 was high and the potential rate of the surface reaction rate was much greater than the observed feed-rate-limited growth rate (~100 nm/min).

The films were pure (Auger electron spectroscopy) and polycrystalline (X-ray diffraction). The resistivity of the films varied as a function of the substrate temperature. At low substrate temperatures (80−120 °C) resistivity values of ~50 $\mu\Omega$cm were obtained and at higher temperatures (>140 °C) the resistivity dropped to ~20 $\mu\Omega$cm. The resistivity of bulk Pd is 10 $\mu\Omega$cm.

Copper CVD Control Experiments. Nitrogen carrier gas was passed over the copper precursor to achieve high delivery rates. These high pumping speeds maximized precursor delivery, but the low vapor pressure of (hfac)Cu(I)(vtms) resulted in feed-rate-limited deposition over the range 120−200 °C (Figure 2). This was because high pumping speed and the use of a carrier gas were necessary to optimize the Pd precursor delivery rate during co-deposition. Preliminary test runs of co-deposition (described later) showed that very little (hfac)Cu(I)(vtms) was delivered to the substrate when a carrier gas was used for $Pd(hfac)_2$ delivery but no carrier gas was used for (hfac)Cu(I)(vtms). This was due to the low vapor pressure of (hfac)Cu(I)(vtms).

The presence of H_2 did not affect the deposition rate, resistivity, or grain size of the copper films, and AES analysis of the films deposited under either condition showed no impurities. There have been some reports of reduced deposition rates in the presence of H_2 by some researchers[23] and increased deposition rates by others,[24] but recent work suggests that the disproportionation pathway remains unchanged[25] even though the role of H_2 is still unclear. The only conclusion that can be drawn from this study is that the addition of H_2 does not drastically change the surface reaction rate. Because the growth rates in this system were feed-rate-limited, any increase or small decrease in the surface reaction rate due to the addition of H_2 would not be observed. This pathway may also occur in competition with disproportionation.

Resistivity was a strong function of the substrate temperature which confirmed previous reports for films deposited from (hfac)Cu(I)(vtms).[21,26−29] The lowest values (~2.0−2.2 $\mu\Omega$cm) were obtained at a substrate temperature range of 100−140 °C and total pressure of 50 mTorr.

Copper−Palladium Co-deposition. In general, there is reason to expect a change of kinetics and properties during CVD of alloys because the composition of the growing surface is different from that during independent metal deposition. The desorption/adsorption/interaction of $Pd(hfac)_2$, H_2, (hfac)Cu(I)(vtms), hfac, vtms, and other intermediates will be different on the co-deposition surface and may lead to different kinetics. There are also possibilities of transmetalation reactions between the two precursors.[1]

Pd−Cu Alloy Film Characteristics. The properties of the co-deposited films were compared to those observed for the independent metal depositions.[29] Resistivity was a strong function of the substrate temperature and increased significantly with an increase in substrate temperature. Low resistivities (~2.3 $\mu\Omega$cm) could be obtained at low substrate temperatures. Co-deposition resulted in the formation of a pure polycrystalline binary Cu−Pd alloy as shown by AES and XRD. This preliminary analysis demonstrated the technological usefulness of the alloy films and justified further analysis of the alloy films to investigate the growth kinetics.

Pd−Cu Co-deposition Kinetics. Conceptually, if the co-deposition process was simply additive, the alloy

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film deposition rate would be the sum of the growth rates observed earlier for the independent Cu and Pd depositions, especially for the case of feed-rate-limited deposition. Any deviations from this ideal situation may be revealed by observing the overall alloy film growth kinetics.

Average deposition rates were measured by averaging the thicknesses obtained at random points by cross-sectional SEM. This was done to avoid any discrepancies due to the different densities of the alloy films. For the sake of comparison, rates were also calculated by weighing the samples before and after deposition and doing the necessary correction for density after estimating the relative concentrations of Cu and Pd using AES.

Figure 2 shows the comparative Arrhenius plots for copper, palladium, and the co-deposited alloy. The independent palladium deposition rate was feed-rate-limited at ~100 nm/min for a precursor temperature of 60 °C as discussed before. Independent copper deposition rates under the same conditions (total pressure: 50 mTorr, N_2 carrier gas, and high pumping rate) were also feed-rate-limited as seen by the relatively negligible temperature dependence of the deposition rate (Figure 2). The deposition rates for the alloy films were slightly lower than the rates for pure copper films and had no temperature dependence. Thus, the temperature dependence and magnitude of the copper deposition rate did not change greatly upon co-deposition. The alloy deposition rate was feed-rate-limited above 120 °C and possibly in the transition between surface reaction and feed-rate-limited regimes at lower temperatures.

Auger electron spectroscopy composition analyses of the alloy films deposited in the temperature range 100–200 °C for a palladium precursor temperature of 60 °C showed that in contrast to the copper deposition kinetics, the Pd deposition kinetics were changed dramatically. The palladium concentrations of the alloy films increased from 0.5 to 20 at. % between 120 and 200 °C; very little palladium (within AES error) was observed at lower deposition temperatures. This was drastically different from the constant growth rate of ~100 nm/min for the entire substrate temperature range (100–200 °C) for the independent palladium depositions. A constant stoichiometry would be expected for the alloy over the entire deposition temperature range for fixed precursor feed rates if there were no change in the kinetics of the Cu and Pd growth processes during co-deposition. However, these deviations from those expected from the pure metal depositions indicate that the growth of palladium during co-deposition is not identical with deposition of the pure metal.

The compositions obtained from AES measurements were used to calculate equivalent growth rates of copper and palladium in the alloy films. These equivalent growth rates are plotted in an Arrhenius form of log(deposition rate) vs 1/*T* in Figure 3. The plot shows that the copper deposition rate during co-deposition is feed-rate-limited over the entire temperature range (120–200 °C) at a growth rate of ~200 nm/min. The palladium growth rate during co-deposition shows an apparent surface-reaction limitation. From the slope of the least-squares fit an overall surface reaction activation energy of 16 ± 5 kcal/mol was obtained.

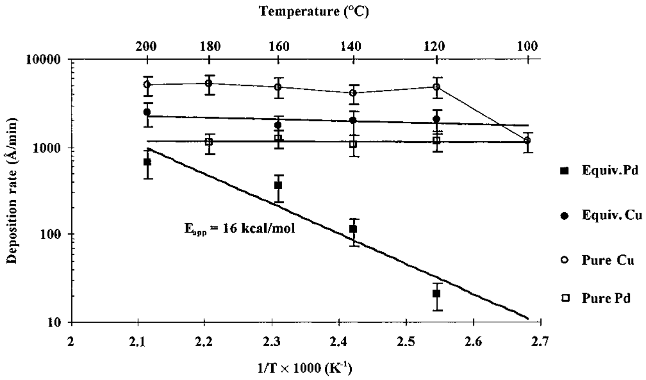

Figure 3. Dependence of equivalent growth rates of palladium and copper during co-deposition on substrate temperature. $Pd(hfac)_2$ temperature was maintained at 60 °C. Error bars represent the maximum variability in data.

These results show that the potential overall rate of the surface reaction for the independent palladium deposition in the absence of (hfac)Cu(I)(vtms) is significantly reduced during co-deposition by at least a factor of 10 at a substrate temperature of 120 °C. For the sake of illustration, the growth rate of pure palladium at a substrate temperature of 120 °C and a feed-rate corresponding to a $Pd(hfac)_2$ temperature of 60 °C resulted in an average deposition rate of ~100 nm/min. Making a comparison with the palladium composition observed in the co-deposited films shows that the equivalent growth rate of palladium in the co-deposited film is 3 nm/min at a substrate temperature of 120 °C.

The other important feature shown in Figure 3 is that the copper deposition rate is only slightly affected by the co-deposition process when compared to that of the independent deposition. The feed-rate-limited behavior of copper growth (~200 nm/min) during co-deposition is consistent with a similar feed-rate limitation for pure copper deposition (~100–500 nm/min). The reason for the small difference between the copper deposition rates in the presence and absence of the $Pd(hfac)_2$ is not known.

The need to deposit films with a wider range of alloy compositions motivated further experimentation by varying the $Pd(hfac)_2$ partial pressure. This was done by varying the Pd precursor temperature between 60 and 35 °C during co-deposition at a fixed substrate temperature of 180 °C. Other conditions were kept identical with previous co-deposition experiments. Auger electron spectroscopy analysis of the alloy films showed that on decreasing the $Pd(hfac)_2$ temperature the palladium content also decreased. Figure 4 shows the variation of the palladium concentration in the alloy films prepared at a substrate temperature of 180 °C with the $Pd(hfac)_2$ temperature. This indicates a dependence of palladium growth rate during co-deposition on the precursor partial pressure (indirectly controlled by the $Pd(hfac)_2$ temperature) when feed-rate limitations do not occur. Thus, the surface reaction is positive order with respect to Pd precursor partial pressure. When the alloy deposition was carried out as a function of the substrate temperature (100–180 °C) for a $Pd(hfac)_2$ temperature of 35 °C, AES analysis showed only a small variation in the palladium concentration (0.5–3 at. %). From previous arguments it was demonstrated that a strong surface-reaction-limited growth of palladium (0.5–20 at. %) occurred during co-deposition

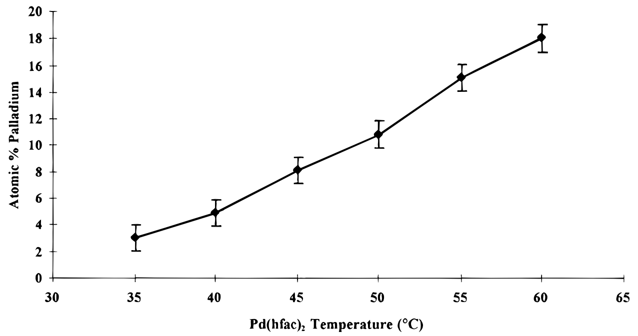

Figure 4. Dependence of palladium content in co-deposited film on Pd(hfac)$_2$ temperature. The films were deposited at a substrate temperature of 180 °C. Error bars represent systematic AES error.

with copper [the Pd(hfac)$_2$ temperature was maintained at 60 °C over the same temperature range]. Hence, decreasing the Pd(hfac)$_2$ precursor source temperature may have resulted in a shift from surface-reaction-limited toward feed-rate-limited operation.

Overall, this analysis shows that the kinetics of independent metal growth do not remain the same on co-deposition. The growth kinetics can shift regimes as illustrated in the case of palladium. For the pure metal depositions, precursor feed rate was the dominant factor that controlled the deposition rate. Variation in substrate temperature did not have a significant effect. For the alloy deposition, however, temperature was the critical factor controlling palladium growth, and (hfac)-Cu(I)(vtms) feed rate was the critical factor controlling copper growth. It is worth noting that Lin et al.[30,31] have studied the reactions of Pd(hfac)$_2$ on Cu surfaces in the absence of H_2. Formation of Cu(hfac)$_2$ was observed under some conditions. Because the present study was carried out in the presence of H_2 and with a Cu(I) precursor, it is difficult to compare the results of these studies.

These results were important from another standpoint, i.e., the surface-reaction-limited growth kinetics for palladium allowed control of film stoichiometry through variation of the Pd(hfac)$_2$ feed rate, (hfac)Cu-(I)(vtms) feed rate (potentially, because in this case it was not studied), and the substrate temperature. Another conclusion is that by simply varying the substrate temperature very small quantities of palladium could be incorporated in copper under these conditions. This is a requirement for not compromising the resistivity of Cu.

Influence of Nucleation Surface. A better understanding of the system can only be gained if the probable cause(s) for palladium growth inhibition are identified. A series of simple control experiments were carried out using the same reactor setup to get more insight into the alloy film deposition pathway.

For the growth of palladium from Pd(hfac)$_2$ in the presence of H_2, the overall pathway has been identified to be the reduction of adsorbed Pd(hfac)$_2$ by H_2 adsorbed on the surface. Although the actual mechanism is unknown, conceptually the nucleation and growth on a palladium surface may be expected to be different from the nucleation and growth on a copper−palladium alloy surface. The efficiency of H_2 adsorption and film nucleation may be affected by the nature of the deposition surface (Cu, Pd, Cu−Pd alloy), so this aspect was examined in more detail.

Known thicknesses (0.2 μm) of pure copper and palladium were grown separately at a substrate temperature of 140 °C. The co-deposition was done immediately after these films were grown to avoid any possible contamination. AES analysis of the films showed that the composition of the alloy films was the same irrespective of the initial deposition surface. The overall growth rates in all the three cases (native copper, palladium, and SiO_2 surface) were ~400 nm/min. No induction period was observed in any case.

These control experiments showed that the nucleation of palladium and copper was not noticeably different on copper, palladium, or the alloy surface. If the initial palladium growth was strongly promoted by a palladium surface, for example, and no other effect was responsible for inhibition, a high palladium content could have been expected in the alloy film deposited on a native palladium surface. However, surface nucleation on nonnative surfaces is a non-steady-state process and needs to be studied under controlled conditions. Without any information on the relative nucleation times of copper and palladium on different surfaces, it is difficult to draw any conclusion on the actual nucleation behavior of copper and palladium during co-deposition. Thus, these experiments showed simply that the film nucleation and growth resulted in identical film characteristics for copper, palladium, and SiO_2 surfaces.

Effect of Hexafluoroacetylacetone (hfacH) Addition during Pure Pd Deposition. Conceptually, during co-deposition, the surface may have adsorbed species that do not occur during the individual metal depositions. The most probable species present on the surface during co-deposition are "hfac•", Cu(hfac)$_2$, Pd-(hfac)$_2$, (hfac)Cu(I), (hfac)Cu(I)(vtms), vtms, H_2, and "H•". To help understand the roles of the various species present during co-deposition, experiments were carried out in which various other reactants were added. This approach has been used in the past to get a better understanding of the deposition system [e.g., vtms, hfacH,[23] and H_2O[32,33] have been added during copper growth from (hfac)Cu(I)(vtms)].

Hexafluoroacetylacetone is the product formed during the deposition of palladium. In the palladium control experiments, hfacH was added during palladium deposition. The effect of hfacH addition was studied over an hfacH partial pressure range of 10−50 mTorr. The remaining reactor conditions were Pd(hfac)$_2$ + N_2 carrier gas partial pressure, 40 mTorr; H_2 partial pressure, 10 mTorr; and Pd(hfac)$_2$ temperature, 60 °C. These conditions were similar to those used for the independent palladium depositions.

There was no deviation of the deposition rate from those obtained for palladium growth without the addition of hfacH. There was also no significant change in the morphology or resistivity of the palladium films due

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to the addition of hfacH. Auger electron spectroscopy analysis showed no evidence for impurities over the entire hfacH partial pressure range (10−50 mTorr). This showed that the presence of excess hfacH does not affect the surface reaction or the adsorption/desorption of Pd(hfac)$_2$ and H$_2$. However, one important fact that is unknown is whether hfacH deprotonates on a palladium surface under these conditions to form hfac$_{(ads)}$ and H$_{(ads)}$.

$$\mathrm{hfacH_{(g)}} \leftrightarrow \mathrm{hfacH_{(ads)}} \tag{2}$$

$$\mathrm{hfacH_{(ads)}} \leftrightarrow \mathrm{hfac_{(ads)}} + \mathrm{H_{(ads)}} \tag{3}$$

One interpretation of these observations may be that under these conditions the equilibrium of eq 2 may be far to the left and/or eq 3 may not occur on a palladium surface. Therefore, addition of hfacH to the system may not actually result in higher surface hfac$_{(ads)}$ coverage and thus no effect on palladium growth would be observed. The data are also consistent with the idea that hfac$_{(ads)}$ present on the surface is not responsible for the inhibition of palladium growth.

The species hfac and hfacH could also be derived from (hfac)Cu(vtms) and H$_2$. The role of hfacH in copper CVD has been discussed elsewhere.[34]

Effect of Vinyltrimethylsilane (vtms) Addition during Pure Pd Deposition. Vinyltrimethylsilane is the neutral ligand that dissociates from the Cu precursor after the adsorption of (hfac)Cu(I)(vtms). Moreover, addition of vtms during pure copper growth has been shown to decrease the deposition rate.[20] This motivated control experiments of vtms addition during independent palladium growth.

Controlled quantities of vtms were supplied during the deposition of pure palladium. The vtms partial pressure was varied between 10 and 50 mTorr at 180 °C. Palladium deposition was studied in the substrate temperature range 100−180 °C. The other conditions were unchanged compared to those of the independent palladium depositions. Variation of the vtms partial pressure at fixed substrate temperatures did not show any effect on the growth rate. However, keeping the vtms partial pressure constant at 50 mTorr and varying the substrate temperature showed a drastically different behavior. A strong temperature dependence was observed over the range 140−180 °C. At lower temperatures the growth rate was very slow (<10 nm/min) relative to the experiments without vtms present.

The results are shown in the form of an Arrhenius plot of palladium growth rate vs inverse temperature in Figure 5. The flat line represents the palladium growth behavior observed in the absence of vtms. Addition of vtms changed this feed-rate-limited behavior to a surface-reaction-limited behavior. The slope of the least-squares fit revealed an apparent activation energy of 15 kcal/mol. Depositions above 180 °C indicated a flattening of the curve due to the onset of a feed-rate limitation. Increasing the substrate temperature further above 200 °C resulted in a drop in the deposition rate probably due to precursor depletion because of homogeneous gas-phase reactions. This is also consistent with a similar observation during palladium deposition in the absence of vtms.

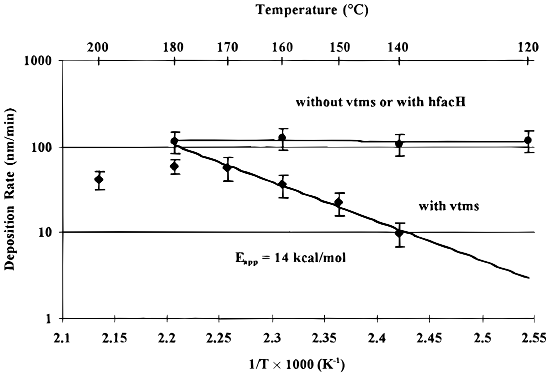

Figure 5. Palladium growth-rate dependence on temperature in the presence of vtms: Conditions: Pd(hfac)$_2$ temperature, 60 °C; vtms partial pressure, 50 mTorr; Pd(hfac)$_2$ + N$_2$ carrier gas partial pressure, 40 mTorr; and H$_2$ partial pressure, 10 mTorr. Error bars represent the maximum variability in data.

The palladium films deposited in the presence of vtms were contaminated with C (~7 at. % as determined by AES). There was also a significant impact on the surface morphology due to vtms addition. Figure 6 shows SEM images of palladium films prepared in the absence and presence of vtms. The films were deposited at a substrate temperature of 180 °C, and total pressure was 100 and 50 mTorr respectively in the absence and presence of vtms. The films deposited in the presence of vtms appeared more specular than those deposited in the absence of vtms, due to the smoother grain texture [Figure 6 (a and b)].

The data are consistent with the idea that vtms can inhibit palladium growth from Pd(hfac)$_2$ and H$_2$ on a palladium surface during independent palladium deposition. The origin of the carbon impurity due to vtms addition may be either hfacH or vtms, but insufficient information was available to draw conclusions as to the source.

The ability to inhibit Pd deposition suggests a possible solution to the problem of the high reactivity of Pd(hfac)$_2$ and H$_2$ in the gas-phase identified earlier. It may be possible to control the reactivity of the palladium precursor by the addition of known quantities of another species without a dramatic change in deposition characteristics. This may be a feasible general alternative if the mechanism of inhibition due to vtms addition is understood. With this understanding other similar reactants may be investigated to achieve a "controlled inhibition" of palladium growth. Specifically, vtms is not a good choice due to the carbon impurities present, but other functional groups may not have a deleterious effect on palladium deposition.

Conclusions

Table 2 summarizes the information obtained from the different experiments. For pure copper growth from (hfac)Cu(I)(vtms), addition of H$_2$ does not reduce significantly the potential surface reaction rate. Because the growth rates in this system were feed-rate-limited, any increase or small decrease in the potential surface reaction rate due to H$_2$ addition could not be observed. The impact of H$_2$ addition on the surface reaction may be observed only if the reactor is operated in the surface-reaction-limited regime.

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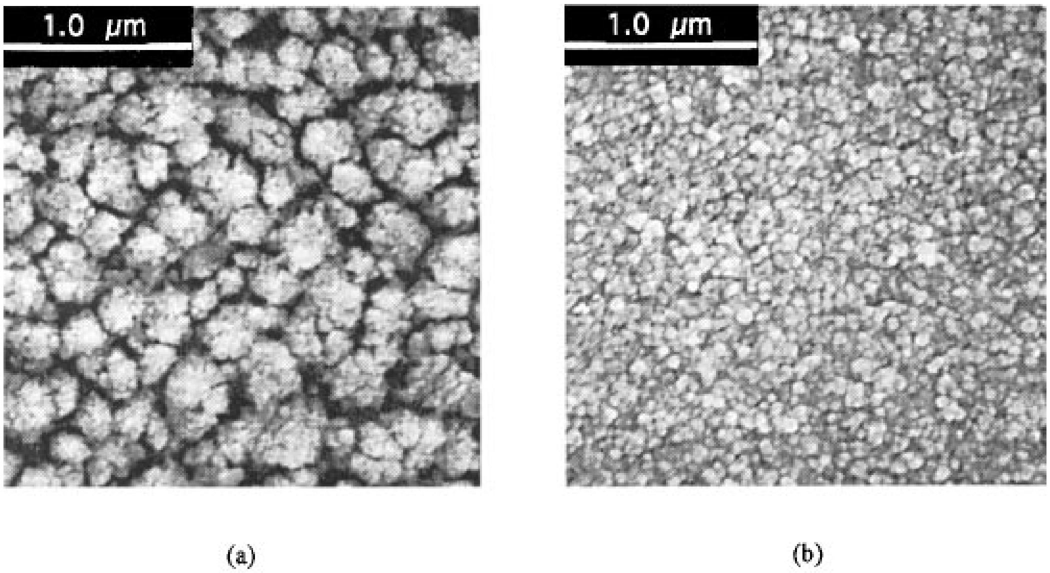

Figure 6. Comparison of surface morphology of palladium films grown at a substrate temperature of 180 °C (a) in the absence of vtms and (b) in the presence of vtms.

Table 2. Experimental Strategy for the Systematic Study of the Cu−Pd System

experimental strategy	motivation	deposition rate (nm/min) (substrate temperature)	E_{app} (kcal/mol)	implications/limitations
individual palladium CVD: $Pd(hfac)_2 + H_2$	deposition kinetics of film formation from typical low-vapor-pressure precursor	100−400 (80−200 °C)	0	feed-rate-limited behavior, high deposition rates, no impurities, low residence time of reactants required
individual copper CVD under similar reactor conditions: (hfac)Cu(I)(vtms)	deposition kinetics in limited operation window, impact of H_2, comparison to previous work	100−500 (100−200 °C)	∼0	transition regime of feed rate and reaction limited, no effect of H_2, deviations from previous work due to different reactor conditions
co-deposition by simultaneous introduction of (hfac)Cu(I)(vtms), $Pd(hfac)_2$, and H_2	kinetics of alloy deposition, impact on film stoichiometry, deviations from individual kinetics, reliability improvement	100−400 (100−180 °C)	∼0	inhibition of palladium growth, marginal increase in deposition rate (within experimental error), film stoichiometry dependent on substrate temperature and $Pd(hfac)_2$ partial pressure
analysis of palladium content in co-deposited film	dependence of palladium growth during co-deposition on substrate temperature and precursor feed rate	10−80 (140−180 °C)	16	apparent reaction limited growth, kinetics significantly different from pure deposition
analysis of copper content in co-deposited film	dependence of copper growth during co-deposition on substrate temperature	∼110 (100−180 °C)	0	marginally lower deposition rates (feed-rate-limited), no major impact on kinetics
co-deposition on initial pure palladium and copper surfaces	dependence of nucleation surface on co-deposition kinetics, probable inhibition cause	100−400 (100−200 °C)	∼0	no significant impact of different surface on film composition or deposition kinetics
individual palladium deposition in the presence of hfacH	impact of excess hfac on the surface reaction steps	∼100 (100−180 °C)	0	no effect on purity or growth rate compared to deposition in the absence of hfacH
individual palladium deposition in the presence of vtms	influence of vtms on deposition kinetics	∼10−80 (120−180 °C)	14	deposition rate severely inhibited by vtms, apparent surface reaction limited kinetics due to some inhibition mechanism, surface coverage of vtms on Pd or adduct formation possible explanations, C contamination

For the Cu−Pd alloy films the inhibition of palladium growth is responsible for the similarity of film properties with those of pure copper and the reduced Pd deposition rate. The control studies suggest that the inhibition of palladium during co-deposition may be due to the interaction of vtms with $Pd(hfac)_2$ on the surface or in the gas phase, but there are many other factors which may also play a role such as the actual adsorption/desorption characteristics of both the precursors and H_2 on the alloy surface and the interactions and reactions of all the species on the surface and in the gas phase.

The most significant conclusion from this study is that the deposition kinetics can be significantly changed on co-deposition from two metal-organic precursors compared to the individual metal deposition kinetics. The major practical impact for Cu−Pd is that even though independent palladium growth occurs at high rates, the co-deposition of palladium and copper can result in highly controlled growth of palladium with the possibility of forming Cu−Pd alloys with low Pd concentrations.

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