Mechanistic Studies of Palladium Thin Film Growth from Palladium(II) β-Diketonates. 2. Kinetic Analysis of the Transmetalation Reaction of Bis(hexafluoroacetylacetonato)palladium(II) on Copper Surfaces

Wenbin Lin,[†] **Ralph G. Nuzzo,***[,‡,†] **and Gregory S. Girolami***[,†]

Contribution from the School of Chemical Sciences, Department of Materials Science and Engineering, and the Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

Received December 22, 1994[⊗]

Abstract: The reaction pathways and kinetics for the selective deposition of palladium on copper from the metal−organic precursor $Pd(hfac)_2$ have been established by means of reactive molecular beam−surface scattering where a flux of $Pd(hfac)_2$ (ranging from 10^{13} to 10^{14} molecules cm^{-2} s^{-1}) impinges continuously on the copper surface. The surface selectivity of the deposition process is a consequence of a "redox transmetalation" reaction, which is best described by the stoichiometric equation $Pd(hfac)_2 + Cu \rightarrow Pd + Cu(hfac)_2$. On polycrystalline copper foils, the production and subsequent desorption of $Cu(hfac)_2$ from the surface occurs with unit efficiency at temperatures between 400 and 600 K. At temperatures above 600 K, the yield of $Cu(hfac)_2$ decreases and eventually falls to zero at 800 K as the thermolytic decomposition of the hfac ligands on the surface becomes kinetically competitive. We have devised a steady-state kinetic model of the adsorption of $Pd(hfac)_2$, desorption of $Cu(hfac)_2$, and thermolytic decomposition of hfac molecules that quantitatively fits the decrease in $Cu(hfac)_2$ yield seen at higher temperatures. The transmetalation reaction follows an apparent power rate law that is first order in Cu and first order in hfac coverage; the preexponential factor and the activation energy for the transmetalation reaction are $A' = 2 \times 10^{-10}$ molecules^{-1} cm^2 s^{-1} (or $\sim 1 \times 10^6$ s^{-1} when normalized to the surface atom density of Cu) and $E_a' = 13$ kcal mol^{-1}. The steady-state kinetic model accurately predicts the deposition rate so long as diffusion of the Pd atoms into the Cu bulk is relatively fast; for the precursor fluxes used in the present study, this situation holds on polycrystalline copper foils because the grain boundaries present provide a mechanism for the rapid interdiffusion of Pd and Cu. On a single crystal copper substrate, where the high diffusivity pathway due to grain boundaries is absent, the transmetalation reaction is self-limiting at our precursor fluxes owing to the slower rate of atomic diffusion. The diffusion coefficient (D) for the interdiffusion of palladium and copper on single crystal substrates has been calculated from a kinetic model explicitly incorporating the transport processes and is estimated to be $\sim 10^{-18}$ cm^2 s^{-1} at 358 K. The nature of multicomponent chemical vapor deposition processes that operate under the kinetic control of atomic diffusion is discussed.

Introduction

We have recently shown that bis(hexafluoroacetylacetonato)-palladium(II) selectively deposits palladium on a copper substrate via a novel redox transmetalation reaction; in this reaction, $Pd(hfac)_2$ molecules are reduced by surface copper atoms to give palladium deposits while the copper substrate is etched away as the volatile byproduct $Cu(hfac)_2$.[1−3] This redox transmetalation reaction has made possible a selective CVD alloying technology for copper.

$$Pd(hfac)_2 + Cu \rightarrow Pd + Cu(hfac)_2$$

The preceding paper describes temperature-programmed reaction, X-ray photoelectron (XPS), and reflection−absorption infrared (RAIR) spectroscopic studies of the reaction of $Pd(hfac)_2$ on both single crystalline and polycrystalline copper substrates under ultrahigh-vacuum conditions.[3] In contrast to the results obtained at the higher pressures used for the MOCVD process, these studies show that thermolytic decomposition of hfac groups is the predominant reaction pathway when a clean copper surface is dosed with $Pd(hfac)_2$ and heated in ultrahigh vacuum; the transmetalation reaction becomes a competing reaction pathway only when $Pd(hfac)_2$ is dosed onto a Cu surface bearing a carbonaceous overlayer.[3]

In order to better understand the different results obtained under MOCVD and UHV conditions, we have carried out reactive scattering experiments of $Pd(hfac)_2$ on two different copper surfaces: polycrystalline foils and higher-quality Cu(111) single crystals. In the experiments described below, a constant flux of $Pd(hfac)_2$ molecules to the surface creates conditions that more closely resemble those operative during the deposition of palladium in a MOCVD hot zone. From these reactive scattering experiments, we have established both the energetics and the rate law for the redox transmetalation reaction of $Pd(hfac)_2$ on copper. In addition, we have explored the factors responsible for the different deposition behavior seen on single crystalline and polycrystalline copper substrates; we describe herein the rich interplay between the reactions of the hfac ligands on the surface and the atomic diffusion processes responsible for metal atom transport in the bulk. This study

---

[†] School of Chemical Sciences.

[‡] Department of Materials Science and Engineering.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

(1) Lin, W.; Warren, T. H.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 11634−11635.

(2) Lin, W.; Warren, T. H.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* Submitted for publication.

(3) Lin, W.; Wiegand, B. C.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1996**, *118*, 5977−5987.

S0002-7863(94)04131-4 CCC: $12.00

delineates several subtle but important aspects of chemical vapor deposition processes that occur under the kinetic control of atomic diffusion.

Experimental Section

The experiments reported here were carried out in a diffusion-pumped chamber with a base pressure of $\leq 2.0 \times 10^{-10}$ Torr; a comprehensive description is given in the preceding paper.[3] Integrated desorption mass spectrometry was performed using the protocol described by Dubois,[4] while reactive molecular-beam/surface-scattering experiments were conducted according to the procedures of Bent *et al.*[5] Details of the sample preparation and manipulation procedures are described in the preceding paper. The heating rates used for the reactive molecular-beam/surface-scattering studies were 4 K/s for the single crystal experiments and 7 K/s for the copper foil experiments.

The mass spectrometer was equipped with a nickel skimmer to minimize interference from material desorbing from the sample support apparatus. In the reactive scattering experiments, the effusive $Pd(hfac)_2$ beam was incident on the surfaces at 30−40° from the normal and scattered into the mass spectrometer, which was fixed at an angle approximately 15° off the specular direction (toward the surface normal). The sample was held ∼5 mm from both the mass spectrometer skimmer and the effusive beam source.

$Pd(hfac)_2$ was dosed via an effusive molecular beam doser.[6] The effusive source used was a 3.2-mm-diameter stainless steel tube capped with a Ni disk bearing a 200-μm pinhole. The pressure behind the doser pinhole was monitored with a bakeable capacitance manometer (MKS, 1 Torr full scale). The fluxes were calculated from standard kinematic theory as appropriately applied to the geometry of this experiment (the pressure in the dosing line, the size of the doser orifice, and the distance between and the relative orientation of the doser and the surface) and are believed to be accurate to within a factor of 4 or better. Bis(hexafluoroacetylacetonato)palladium(II) was prepared according to a reported literature method[7] and purified by sublimation before use.

Results and Discussion

Reactive Scattering of $Pd(hfac)_2$ on Copper Foil Surfaces. The reactive scattering experiments involve directing a continuous effusive molecular beam of $Pd(hfac)_2$ toward a copper foil substrate and analyzing the molecules scattered from the surface by mass spectrometry. The incident fluxes used in the experiment reported in the present paper ranged from ca. 3×10^{13} to ca. 2×10^{14} molecules cm^{-2} s^{-1}. The composition of the scattered/desorbing flux was monitored by mass spectrometry as a function of the surface temperature. The $m/e = 201$ [Cu(hfac) − CF_3] and 63 (Cu) signals were used to monitor $Cu(hfac)_2$ and, similarly, the $m/e = 244$ [Pd(hfac) − CF_3] and 106 (Pd) signals were used to monitor $Pd(hfac)_2$.

Figures 1a and 1b show the results obtained by using an incident flux of 5×10^{13} molecules cm^{-2} s^{-1}. The factors responsible for the shapes of these scattering curves are discussed below, but some important characteristics will be pointed out here. At temperatures between 300 and 400 K, both $Cu(hfac)_2$ and $Pd(hfac)_2$ are present in the scattered flux. As the temperature is raised above 400 K, $Pd(hfac)_2$ disappears from the scattered products (Figure 1a) and the only metal-containing ions seen are those due to $Cu(hfac)_2$ and its fragments (Figure 1b). During the temperature ramp, the amount of $Cu(hfac)_2$ desorbing from the surface first crests and then drops until reaching a steady-state limit above 400 K. The absence of $Pd(hfac)_2$ among the scattered products above 400 K and the steady-state production of $Cu(hfac)_2$ at these temperatures strongly suggest that the reaction is flux limited in this regime. The identification of $Cu(hfac)_2$ as the exclusive product generated during the reactive scattering of $Pd(hfac)_2$ on copper has been confirmed by the integrated desorption mass spectrum taken at 450−500 K (Figure 2). All the peaks in the IDMS spectrum can be assigned to cracking fragments of $Cu(hfac)_2$.

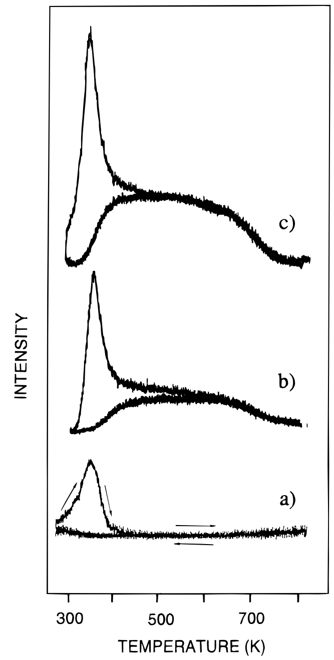

Figure 1. Profiles obtained during the reactive scattering of $Pd(hfac)_2$ on copper foil surfaces: (a) $m/e = 244$, which tracks desorption of $Pd(hfac)_2$, (b) $m/e = 201$, which tracks desorption of $Cu(hfac)_2$, (c) $m/e = 201$ but at twice the incident flux of $Pd(hfac)_2$. For (a) and (b) the flux was 5×10^{13} molecules cm^{-2} s^{-1}; for (c) the flux was 1×10^{14} molecules cm^{-2} s^{-1}. The heating rates were 7 K/s. The arrows indicate whether the traces were obtained upon heating or cooling. In both curves, the lowest signal corresponds to zero flux.

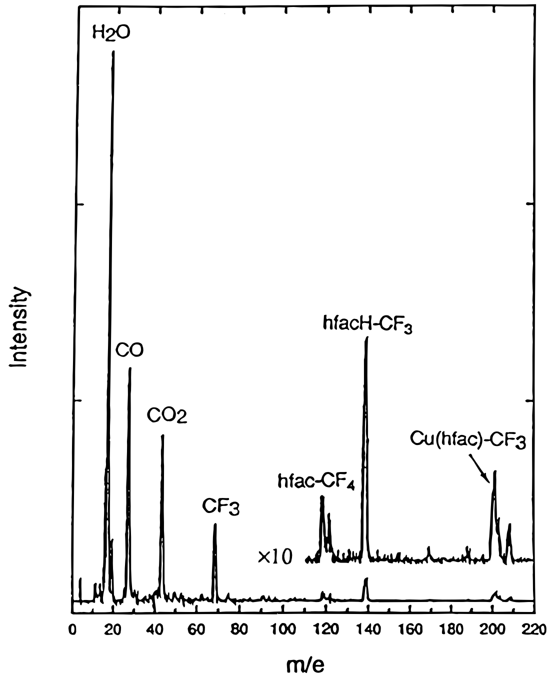

Figure 2. IDMS spectrum of the species desorbing from a copper foil surface during the reactive scattering of $Pd(hfac)_2$. The spectrum was taken at temperatures between 450 and 500 K and the heating rate was 7 K/s. The peaks due to H_2O, CO, and CO_2 are uncorrected for contributions from the background gases.

---

[4] Dubois, L. H. *Rev. Sci. Instrum.* **1989**, *60*, 410−413.

[5] Bent, B. E.; Dubois, L. H.; Nuzzo, R. G. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 327−338.

[6] Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1989**, *111*, 1634−1644.

[7] Siedle, A. R. *Inorg. Synth.* **1990**, *27*, 316−317.

That the reaction is flux limited in the 400−600 K temperature regime was confirmed by scattering experiments carried out at a higher incident flux. This is shown by the data in Figure 1c, which demonstrate that doubling the $Pd(hfac)_2$ flux to 1×10^{14} molecules cm^{-2} s^{-1} doubles the amount of $Cu(hfac)_2$ detected in the scattered products throughout this temperature range. This result is consistent with mass balance experiments conducted at higher pressures (ca. 10^{-3} Torr).[2] In these higher-pressure experiments, $Pd(hfac)_2$ was passed over a heated copper surface and the $Cu(hfac)_2$ produced was collected; the amount of $Cu(hfac)_2$ recovered amounted to 95% of that expected for the transmetalation reaction.[2] Thus, we conclude that the transmetalation process proceeds with high efficiency above 400 K: for every $Pd(hfac)_2$ molecule incident on the surface, one $Cu(hfac)_2$ molecule is produced.

Above 600 K, the amount of $Cu(hfac)_2$ desorbing from the surface begins to decrease and eventually falls to zero at temperatures higher than 800 K. This fall-off is apparently due to the irreversible thermolytic decomposition of the hfac ligands on the copper surface at these temperatures (see below).[3,8]

Interestingly, the heating and cooling curves show significant hysteresis below 400 K. Although in the heating curve the amount of $Cu(hfac)_2$ desorbing from the surface reaches a maximum at a temperature of 330 K and then falls to a steady-state limit, no peak is seen at this temperature in the cooling curve. This behavior can be explained by noting that different hfac coverages are present in the two situations. In the heating curves, the initial surface temperature is below the multilayer desorption temperature for $M(hfac)_2$ (M = Pd or Cu) species,[3,8] and substantial amounts of $Pd(hfac)_2$ from the dosing beam build up on the surface. Subsequent heating of the surface to ca. 330 K promotes the reaction of these molecules with the copper surface and gives rise to a large desorbing flux of $Cu(hfac)_2$ (and some $Pd(hfac)_2$ also). Eventually, this multilayer becomes exhausted and the amount of $Cu(hfac)_2$ desorbing from the surface becomes limited by the flux of $Pd(hfac)_2$ to the surface.

In contrast, when the surface is cooled from 800 K, it is not saturated with hfac-containing species because the high rate of desorption of $Cu(hfac)_2$ at temperatures above 400 K keeps the hfac coverage low. When the surface is cooled, a temperature is reached (∼330 K at this precursor flux) where the rate of $Cu(hfac)_2$ desorption slows even though transfer of hfac ligands from $Pd(hfac)_2$ to open sites on the copper surface is still facile; only then does the hfac coverage increase significantly. Therefore, at temperatures just above 330 K, the hfac coverage is high in the heating cycle but low in the cooling cycle. Because the rates of the surface reactions responsible for the assembly of $Cu(hfac)_2$ molecules are dependent on the hfac coverage (and because this process becomes rate limiting at low temperatures—see below), the amount of $Cu(hfac)_2$ that desorbs from the surface between 330 and 400 K differs when approached from the high- and low-temperature limits.

Finally, we note that the scattering profiles shown in Figure 1 are very reproducible, provided that the experimental parameters (incident flux, ramp rate, and temperature-scanning limits) remain constant.

The reactive scattering experiments clearly establish that $Pd(hfac)_2$ is converted with high efficiency to $Cu(hfac)_2$ under these conditions. Since the reactive scattering experiments have been carried out under a constant $Pd(hfac)_2$ precursor flux, which more closely mimics the processing conditions obtained at higher pressures, the results described here demonstrate conclusively that the redox transmetalation reaction is responsible for the deposition of palladium from $Pd(hfac)_2$ on copper substrates under MOCVD conditions.

The deposition chemistry reported herein for the $Pd(hfac)_2$/Cu system has a close connection to the industrially important semiconductor processing method referred to as tungsten-plug CVD.[9−11] In this process, a vapor of WF_6 is passed over a patterned silicon substrate, the majority of which is covered with a thick SiO_2 layer. In exposed gate regions, WF_6 reacts with the silicon to deposit tungsten selectively via a transmetalation reaction which liberates SiF_4 as a coproduct. All CVD transmetalation processes in which deposition and etching occur simultaneous must have several common features: the compositional profile of the solid substrate must vary with time, and in the absence of bulk interdiffusion, the rate of the deposition must eventually fall to zero as the available surface atoms of the substrate are covered by those of the source material. These mechanistic features will be discussed in the next sections.

Evidence of Rapid Interdiffusion of Palladium and Copper on Polycrystalline Substrates. For the redox transmetalation reaction of $Pd(hfac)_2$ on copper, three distinct transport reactions are necessary to ensure kinetic competence. The first is simply that of the transport of the Pd reagent to the surface (i.e., the rate of transmetalation has to be zero in the limit of zero flux). The second transport term involved in the global kinetics is that related to assembly of $Cu(hfac)_2$ on the surface and its desorption into the gas phase. The third transport term, and by far the most complex to analyze, describes the atomic diffusion of Pd and Cu atoms. It is well-known that the grain boundaries present in polycrystalline substrates considerably accelerate interdiffusion processes,[12] but it is important to determine experimentally whether interdiffusion of Pd and Cu is in fact fast under the reaction conditions present during the scattering experiments used to obtain the data in Figure 1.

On copper foils, at $Pd(hfac)_2$ fluxes of $\geq 10^{13}$ molecules cm^{-2} s^{-1} and at temperatures above 400 K, the production of $Cu(hfac)_2$ does not slow as $Pd(hfac)_2$ exposure continues (Figure 1). The steady-state desorption of $Cu(hfac)_2$ seen in the reactive scattering experiments implicitly requires that the rate of interdiffusion of copper and palladium be comparable with the rate at which copper atoms are replaced by palladium atoms via the redox transmetalation reaction: i.e., that fresh copper atoms must be continually brought to the surface and that palladium atoms must be diffusing into the bulk. If the surface were *not* being replenished with Cu, the production of $Cu(hfac)_2$ in the reactive scattering experiments would be self-limiting and, at this flux, would slow considerably after several seconds of exposure to the beam. Significantly, no self-limiting behavior was noted even in experiments carried out at higher fluxes.

The rapid interdiffusion of palladium and copper under these conditions ($T > 400$ K; Cu foil substrates) is further supported by XPS studies of copper foils dosed with a monolayer coverage of $Pd(hfac)_2$. These studies show that, at sufficiently high temperatures, the intensities of the XPS peak due to Pd atoms (generated from thermolytic decomposition of $Pd(hfac)_2$) rapidly decrease over time as interdiffusion takes place.[3]

Because the rate of the redox transmetalation reaction on copper foil substrates above 400 K is not limited by either the rate of bulk interdiffusion or the rate of assembly of $Cu(hfac)_2$ molecules on the surface, the rate-limiting process under our conditions must be the transport of the Pd reagent to the surface: i.e., the flux of $Pd(hfac)_2$. Scattering studies carried

---

[8] Girolami, G. S.; Jeffries, P. M.; Dubois, L. H. *J. Am. Chem. Soc.* **1993**, *115*, 1015−1024.

[9] Powell, C. F.; Oxley, J. H.; Blocher, J. M., Jr. *Vapor Deposition*; John Wiley & Sons: New York, 1966; pp 256−257.

[10] Voorhoeve, R. J. H.; Merewether, J. W. *J. Electrochem. Soc.* **1972**, *119*, 364−368.

[11] Tsao, K. Y.; Busta, H. H. *J. Electrochem. Soc.* **1984**, *131*, 2702−2708.

[12] Gupta, D.; Cambell, D. R.; Ho, P. S. In *Thin Films: Interdiffusion and Reactions*; Poate, J. M., Tu, K. N., Mayer, J. W., Eds.; John Wiley & Sons: New York, 1978; Chapter 7.

out on single crystals give quite different results, however, because bulk interdiffusion becomes rate limiting (see below).

Kinetic Analysis of the Reactive Scattering of Pd(hfac)$_2$ on Copper Foil Surfaces. We will show in this section that the reactive scattering curves can be analyzed to obtain estimates of the activation parameters for the transmetalation reaction. As noted earlier, the amount of Cu(hfac)$_2$ generated in the reactive scattering experiments begins to decrease at 600 K and eventually falls to zero at temperatures above 800 K. We know from the results described in the preceding paper that this fall-off is attributable to the onset of the thermolytic decomposition of surface-bound hfac ligands. It should therefore be possible to model the shape of the reactive scattering curve at temperatures above 400 K in terms of a competition between the decomposition of hfac ligands and the transmetalation reaction of Pd(hfac)$_2$ with Cu surface atoms.[13]

With a few assumptions, we have been able to fit the shape of the reactive scattering curve in this temperature regime to such a kinetic model. Our first assumption is that the rate of adsorption of Pd(hfac)$_2$ is equal to the flux to the surface. This assumption, in order to be valid, requires that the sticking probability of Pd(hfac)$_2$ (and the hfac groups it generates) be equal to 1. This is a reasonable approximation since very little Pd(hfac)$_2$ is seen in the scattered flux at these temperatures.

Second, we assume that the rate of hfac decomposition follows first-order kinetics with the same activation parameters as found in the TPR experiments discussed in the preceding paper.[3] This is a reasonable assumption since the same surface and the same adsorbates are involved.

Third, we must make an assumption about the order of the rate law for hfac desorption (in the form of Cu(hfac)$_2$ molecules). As noted in the previous paper, Cu(hfac)$_2$ molecules readily desorb from a pretreated copper surface at temperatures above 320 K. Therefore, at temperatures above 400 K, the rate of Cu(hfac)$_2$ desorption should be equal to the rate at which Cu(hfac)$_2$ molecules are assembled on the surface. In the Appendix, we analyze a kinetic scheme in which we assume that the rate of Cu(hfac)$_2$ assembly is second order[14] in hfac coverage. Although this kinetic scheme allows us to fit the reactive scattering data in Figure 1, we can rule out this possibility on two grounds: the preexponential factor for the assembly of Cu(hfac)$_2$ is not physically reasonable, and the model predicts incorrectly that the decomposition of hfac groups on the surface should be inhibited at high Pd(hfac)$_2$ fluxes.

Accordingly, the rate of hfac desorption in the form of Cu(hfac)$_2$ molecules is assumed to be first order in hfac coverage. Several different mechanisms would give this rate law: for example, the reaction could be limited by the rate of migration of a reactive intermediate across the surface, or the reaction could occur in a stepwise fashion via an activated "Cu(hfac)" intermediate which either is formed in a rate-limiting step or reacts in a rate-limiting way to produce Cu(hfac)$_2$. The "Cu(hfac)" intermediate must be distinct in some structural sense from that of hfac ligands bound to, for example, terrace sites; one possibility is that the "Cu(hfac)" intermediate consists of hfac groups pinned at surface defect sites. All these mechanisms can afford a power rate law in which the rate of formation of Cu(hfac)$_2$ should be first order in hfac coverage and first order in copper surface atom density.

The rate of hfac desorption is therefore taken to be a second-order reaction overall, but it can be considered as a pseudo-first-order process if we assume that the Cu surface atom density remains approximately constant throughout the reactive scattering experiment. This latter assumption is reasonable in view of our observation that, for copper foils at temperatures above 400 K, the production of Cu(hfac)$_2$ does not decrease with time. The steady-state kinetics means that the bulk interdiffusion process continually brings copper atoms to the surface at a rate equal to the rate at which they are converted to Cu(hfac)$_2$.

The rates of hfac adsorption, hfac decomposition, and hfac desorption in the form of Cu(hfac)$_2$ molecules (i.e., the transmetalation rate) are thus given by:

$$R_{\mathrm{adsorp}}(\mathrm{hfac}) = 2\sigma \tag{1}$$

$$R_{\mathrm{decomp}}(\mathrm{hfac}) = \theta_{\mathrm{h}} n_{\mathrm{h}} A \mathrm{e}^{-E_{\mathrm{a}}/RT} \tag{2}$$

$$R_{\mathrm{trans}}(\mathrm{hfac}) = 2\theta_{\mathrm{h}} n_{\mathrm{h}} \theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' \mathrm{e}^{-E_{\mathrm{a}}'/RT} \tag{3}$$

where σ is the Pd(hfac)$_2$ flux per unit area, θ_{h} and θ_{Cu} are the fractional surface coverages of hfac ligands and copper atoms, n_{h} and n_{Cu} are the numbers of adsorbed hfac molecules and copper atoms per unit area at saturation coverage, A is the Arrhenius preexponential factor and E_{a} is the activation energy for decomposition of the surface-bound hfac groups, A' is the Arrhenius preexponential factor and E_{a}' is the activation energy for formation and subsequent desorption of the Cu(hfac)$_2$ molecules, R is the gas constant, and T is the surface temperature. Note that the factor of 2 in the R_{adsorp} expression reflects the generation of two surface hfac groups for every molecule of Pd(hfac)$_2$ that adsorbs; a factor of 2 also appears in eq 3 for similar reasons.

Conservation of hfac groups demands that $R_{\mathrm{trans}} + R_{\mathrm{decomp}} - R_{\mathrm{adsorp}} = 0$. Thus:

$$2\theta_{\mathrm{h}} n_{\mathrm{h}} \theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' e^{-E_{\mathrm{a}}'/RT} + \theta_{\mathrm{h}} n_{\mathrm{h}} A \mathrm{e}^{-E_{\mathrm{a}}/RT} - 2\sigma = 0 \tag{4}$$

Solving this equation for the quantity ($\theta_{\mathrm{h}} n_{\mathrm{h}}$), we find:

$$\theta_{\mathrm{h}} n_{\mathrm{h}} = \frac{2\sigma}{A \mathrm{e}^{-E_{\mathrm{a}}/RT} + 2\theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' \mathrm{e}^{-E_{\mathrm{a}}'/RT}} \tag{5}$$

Substituting eq 5 into eq 3 gives the transmetalation rate (i.e., the rate of hfac desorption in the form of Cu(hfac)$_2$ molecules); dividing R_{trans} by 2σ gives the expression below, which reflects

---

[13] On polycrystalline copper surfaces at temperatures lower than 400 K, the transmetalation reaction no longer operates under steady-state conditions and the kinetics become complicated: other processes such as Pd/Cu interdiffusion and assembly of Cu(hfac)$_2$ molecules on the surface, which are fast and not rate limiting above 400 K, become slow and rate limiting below 400 K.

[14] Second-order kinetics could result if the desorption of Cu(hfac)$_2$ occurs by means of the sequential reaction of surface-bound hfac ligands with copper atoms:

$$\mathrm{Cu} + \mathrm{hfac}_{(\mathrm{ads})} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cu^*(hfac)}_{(\mathrm{ads})}$$

$$\mathrm{Cu^*(hfac)}_{(\mathrm{ads})} + \mathrm{hfac}_{(\mathrm{ads})} \xrightarrow{k_2} \mathrm{Cu(hfac)}_{2(\mathrm{ads})}$$

$$\mathrm{Cu(hfac)}_{2(\mathrm{ads})} \xrightarrow{\text{fast}} \mathrm{Cu(hfac)}_{2(\mathrm{g})}$$

where Cu(m) is a surface copper atom and Cu*(hfac) is an activated surface species such as one present at a defect site. For most of the temperature range of interest, there is no observable amount of Cu*(hfac)$_{(\mathrm{ads})}$ on the surface; a steady-state approximation for Cu*(hfac)$_{(\mathrm{ads})}$ allows us to derive the rate of desorption of Cu(hfac)$_2$ (i.e., the rate of the transmetalation reaction):

$$R_{\mathrm{trans}} = \frac{k_1 k_2 \theta_{\mathrm{h}}{}^2 n_{\mathrm{h}}{}^2 \theta_{\mathrm{Cu}} n_{\mathrm{Cu}}}{k_{-1} + k_2 \theta_{\mathrm{h}} n_{\mathrm{h}}}$$

If $k_{-1} \ll k_2\theta_{\mathrm{h}}n_{\mathrm{h}}$, then $R_{\mathrm{trans}} = k_{\mathrm{Cu}}\theta_{\mathrm{h}}n_{\mathrm{h}}\theta_{\mathrm{Cu}}n_{\mathrm{Cu}}$ where $k_{\mathrm{Cu}} = k_1$; assuming that the temperature dependence of all of the rate constants can be described by the Eyring equation gives eq 3. If $k_{-1} \gg k_2\theta_{\mathrm{h}}n_{\mathrm{h}}$, then $R_{\mathrm{trans}} = k_{\mathrm{Cu}}\theta_{\mathrm{h}}{}^2n_{\mathrm{h}}{}^2\theta_{\mathrm{Cu}}n_{\mathrm{Cu}}$ where $k_{\mathrm{Cu}} = k_1k_2/k_{-1}$; this is the situation discussed in the Appendix.

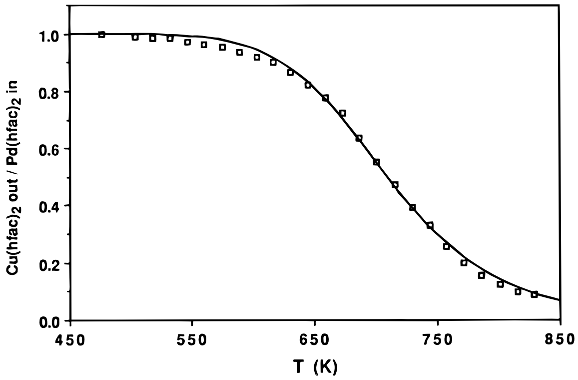

Figure 3. Experimental and calculated rates of $Cu(hfac)_2$ desorption during the reactive scattering of $Pd(hfac)_2$ on a copper foil surface with a $Pd(hfac)_2$ flux of 1×10^{14} molecules cm^{-2} s^{-1}. The experimental points (□) are taken from the high-temperature tail of the reactive scattering curve monitored at $m/e = 201$. The solid curves are the calculated result based on eq 6.

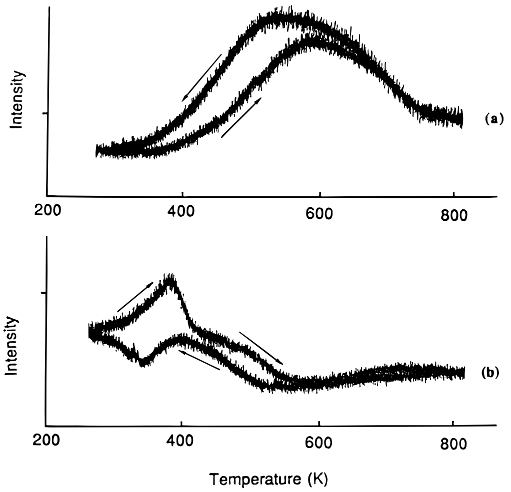

Figure 4. Profiles obtained during the reactive scattering of $Pd(hfac)_2$ on Cu(111) single crystal surfaces: (a) $m/e = 201$, which tracks desorption of $Cu(hfac)_2$; (b) $m/e = 244$, which tracks desorption of $Pd(hfac)_2$. The heating rates were 4 K/s. The arrows indicate whether the traces were obtained upon heating or cooling.

the partitioning of hfac groups along the transmetalation and decomposition channels:

$$\Phi = \frac{\mathrm{Cu(hfac)_2\ flux\ out}}{\mathrm{Pd(hfac)_2\ flux\ in}} = \frac{2\theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' \mathrm{e}^{-E_a'/RT}}{A\mathrm{e}^{-E_a/RT} + 2\theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' e^{-E_a'/RT}} \tag{6}$$

Equation 6 contains two unknowns, the activation parameters for the transmetalation process, A' and E_a'. Most of the other parameters in eq 6 are known accurately. We take $n_{\mathrm{Cu}} = 1.77 \times 10^{15}$ atoms cm^{-2} and $\theta_{\mathrm{Cu}} = 1$, as discussed above. The activation parameters for decomposition of the hfac ligand, $A = 1.3 \times 10^{13}$ s^{-1} and $E_a = 36.8$ kcal mol^{-1}, are taken from the studies described in the previous paper.[3] Note that the efficiency of the transmetalation reaction Φ is independent of the flux of $Pd(hfac)_2$ to the surface, as long as the flux is low enough to keep $\theta_h \ll 1$.

Least-squares fits of the reactive scattering data corresponding to the curves in Figures 1b and 1c were carried out with eq 6 as the fitting equation. Figure 3 shows the results for the data in Figure 1b: the squares are the experimental data showing the flux of $Cu(hfac)_2$ desorbing from the surface as monitored at $m/e = 201$, and the solid curve is the least-squares fit obtained using eq 6. The preexponential factor and the activation energy for the transmetalation reaction derived from the least-squares analysis are $A' = 2 \times 10^{-10}$ $molecules^{-1}$ cm^2 s^{-1} (or $\sim 1 \times 10^6$ s^{-1} when normalized to the surface atom density of Cu) and $E_a' = 13$ kcal mol^{-1}. Essentially identical activation parameters were obtained upon analysis of the data in Figure 1c.

Errors in activation parameters can be large owing to a mutual compensation effect; consequently, we have explicitly examined the quantitative sensitivity of the model by varying the value of E_a' and refitting the data with a new value of A'. It is clear from these efforts that a range of values can fit the data but that the quality of the fit degrades substantially if E_a' is varied by more than 3 kcal mol^{-1} or if A' is varied by more than an order of magnitude. Overall, however, the fits to the data are excellent and serve to confirm the mechanistic assumptions implicit in the kinetic model.

At this point, we can estimate the coverage of hfac groups on the surface at various temperatures. The saturation coverage of hfac, n_h, is taken to be 5.0×10^{14} molecules cm^{-2} (which is based on the estimated area of ca. 20 Å^2 occupied by an upright hfac group, as judged from space-filling models). The flux of $Pd(hfac)_2$ to the surface, σ, is difficult to determine exactly since this number is sensitively dependent on the exact distance and angle between the doser and the surface. For the reactive scattering data analyzed in Figure 3, the flux is estimated to be 1×10^{14} molecules cm^{-2} s^{-1}.[15] By substituting the activation parameters and other constants above into eq 5, the calculated hfac coverage (as a fraction of n_h) varies from 0.25 at 500 K to 0.03 to 600 K to 0.003 at 700 K. Note that at 400 K and at lower temperatures, the model predicts that the coverage should be ∼1; this result agrees with the infrared studies of hfac-dosed surfaces described in the previous paper.[3]

The kinetic model also correctly predicts how the rate of $Cu(hfac)_2$ desorption depends on the $Pd(hfac)_2$ flux to the surface. The calculated rates of $Cu(hfac)_2$ desorption (based on eq 3 and the kinetic parameters derived above) show the same flux dependence as the experimental reactive scattering curves (Figures 1b and 1c): doubling the $Pd(hfac)_2$ flux doubles the rate of $Cu(hfac)_2$ desorption in the steady-state regime ($400 < T < 600$ K). This result shows that the simple kinetic model is adequate to describe the rather complicated reactive scattering behavior.

It is most striking that the kinetic parameters suggest that the transmetalation reaction is exceedingly facile: the activation energy of ∼13 kcal mol^{-1} is quite modest. The best fit value of A' is consistent with a constrained transition state, but it is also entirely consistent with a process that takes place at selected surface sites such as defects or step edges.[16] Similar preexponential factors have been measured for the closely analogous reactive etching of Ge (as $GeCl_2$) by Cl_2 gas.[17,18]

Reactive Scattering of $Pd(hfac)_2$ on Cu(111) Single Crystal Surfaces. Evidence of Slow Interdiffusion of Palladium and Copper. To gain a better understanding of the atomic transport processes involved in this deposition system, we have also carried out reactive scattering experiments of $Pd(hfac)_2$ on Cu(111) single crystal surfaces. Not surprisingly, very different behavior is seen. Figure 4 shows the reactive scattering signals

---

(15) This value of the flux was calculated from standard kinematic theory as applicable to the geometry of our experimental apparatus. This value agrees qualitatively with estimates of σ deduced from the time necessary to saturate the surface with $Pd(hfac)_2$ in a TPRS experiment. In Figure 1, the $Pd(hfac)_2$ multilayer desorption feature seen near 300 K shows that a multilayer has built up even in the time needed to heat the surface from 250 K; at a ramp/cool rate of 7 K/s, this corresponds to a total time of exposure of less than 10 s. The saturation coverage of hfac groups on the surface, n_h, is approximately 5.0×10^{14} molecules cm^{-2} (see text); accordingly, the flux is on the order of 10^{14} molecules cm^{-2} s^{-1}.

(16) D'Evelyn, M. P.; Madix, R. J. *Surf. Sci. Rep.* **1984**, *3*, 413−495.

(17) Madix, R. J.; Schwarz, J. A. *Surf. Sci.* **1971**, *24*, 264−287.

(18) Madix, R. J.; Susu, A. *J. Vac. Sci. Technol.* **1972**, *9*, 915−919.

due to the $Cu(hfac)_2$ and $Pd(hfac)_2$ species as a function of the surface temperature. The precursor flux used in these experiments was ca. 1×10^{14} molecules cm^{-2} s^{-1}. The amount of $Cu(hfac)_2$ present in the scattered flux first increases as the surface temperature is increased. When the surface temperature is higher than ca. 600 K, the rate of $Cu(hfac)_2$ desorption begins to decrease because the thermolytic decomposition of surface-bound hfac groups becomes a competing pathway.

The reactive scattering of $Pd(hfac)_2$ on Cu(111) surfaces differs from the reactive scattering on polycrystalline copper foils in two ways. First, the heating and cooling curves between 400 and 600 K show significant hysteresis: more $Cu(hfac)_2$ is present in the scattered flux during the cooling cycle than during the heating cycle. Second, the low-temperature peak near 330 K observed in the reactive scattering of $Pd(hfac)_2$ on polycrystalline Cu surfaces (Figure 1) is absent in Figure 4a. These heating and cooling curves are reproducible in subsequent cycles.

Both of the differences mentioned above can be explained if we assume that the interdiffusion of palladium and copper on a single crystal substrate is slow relative to the rate of reaction. If we assume that the rate constant for the transmetalation reaction is insensitive to the surface composition, the hysteresis seen in Figure 4 can be attributed (at least in part) to differences in the concentration of copper atoms present at the surface during the heating and cooling cycles. At the beginning of the heating cycles, the rate of diffusion of Pd atoms into the Cu(111) single crystal is slow compared to the rate at which Pd atoms are added to the surface (resulting from the transmetalation reaction). The surface copper concentration (and therefore the rate of the $Cu(hfac)_2$ production) will decrease until the temperature becomes high enough to promote a more rapid interdiffusion of palladium and copper. In contrast, at the beginning of the cooling cycle, the rate of diffusion of Pd atoms into the Cu(111) single crystal is fast relative to the rate of Pd deposition and the surface Cu concentration will be higher compared to that at the same temperature during the heating cycle. Therefore the rate of $Cu(hfac)_2$ production at 400−600 K during the cooling cycle is higher than the rate of $Cu(hfac)_2$ production at the corresponding temperatures in the heating cycle.

The absence of a “burst” of $Cu(hfac)_2$ desorbing near 330 K in Figure 4a can also be explained by assuming that interdiffusion of palladium and copper is the rate-limiting step in the overall transmetalation reaction kinetics on single crystal substrates. During the cooling cycle, the surface Cu concentration decreases and eventually becomes negligible below ca. 350 K. Upon further cooling, the transmetalation reaction is slow because the surface is depleted of copper (even though the rate constant for the reaction of $Pd(hfac)_2$ with Cu to give Pd and $Cu(hfac)_2$ may still be appreciable). As a consequence, subsequent heating will not result in the desorption of large amounts of $Cu(hfac)_2$ at ca. 300 K as seen in the reactive scattering of $Pd(hfac)_2$ on polycrystalline Cu substrates. As might be expected for the analysis just given, the quantitative aspects of the hysteresis should depend very sensitively on the absolute value of the precursor flux as well as the heating/cooling rates employed. Control experiments have confirmed that these sensitivities exist.

The amounts of $Pd(hfac)_2$ seen in the scattered flux (Figure 4b) further support the interpretation given above. For example, the heating and cooling curves between 400 and 600 K show hysteresis effects that are complementary to those seen by monitoring the desorbing $Cu(hfac)_2$ flux: the amount of $Pd(hfac)_2$ in the scattered flux is *higher* in the heating cycle than in the cooling cycle. This behavior is also a consequence of the lower surface concentration of copper present during the heating cycle: more of the $Pd(hfac)_2$ scatters from the surface without reacting when the copper surface atom density is low.

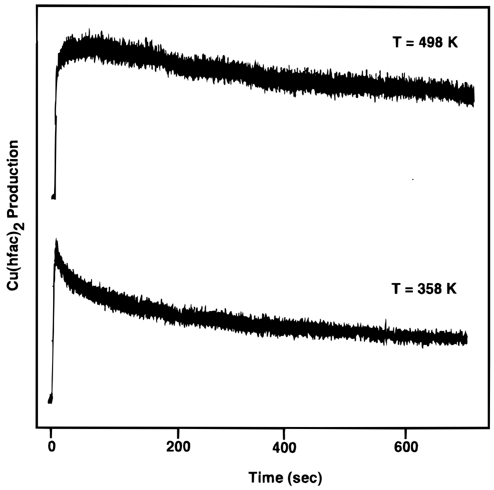

Figure 5. Profiles obtained by monitoring the *m/e* = 244 signal of the scattered products generated during the reactive scattering of $Pd(hfac)_2$ on a Cu(111) single crystal surface at 358 and 498 K. The $Pd(hfac)_2$ flux is 3×10^{13} molecules cm^{-2} s^{-1}.

At temperatures between 280 and 400 K, the $Pd(hfac)_2$ reactive scattering profile shows a second hysteresis effect in which the cooling curve shows a negative peak while the heating curve shows a positive peak. We believe that this hysteresis is due to the adsorption of $Pd(hfac)_2$ on the surface (presumably the surface is now mostly covered by Pd). When the surface is cooled below 380 K, the residence times of the $Pd(hfac)_2$ molecules become sufficiently long to allow the buildup of a physisorbed multilayer; at lower temperatures, the $Pd(hfac)_2$ beam is completely adsorbed onto the crystal and the scattered intensity falls to zero. Subsequent heating results in the desorption of this $Pd(hfac)_2$ multilayer.

Finally, it is clear that on Cu(111) substrates interdiffusion of Pd and Cu becomes fast relative to the transmetalation reaction only at temperatures above 600 K: this is evident from the fact that the heating and cooling curves superimpose in this temperature regime.

In order to confirm that diffusion of Pd atoms into the bulk of Cu(111) single crystal is an important rate-limiting factor at low temperatures, we have also carried out the reactive scattering of $Pd(hfac)_2$ on Cu(111) at constant temperature. Figure 5 shows two reactive scattering curves obtained with a constant flux of 2×10^{14} molecules cm^{-2} s^{-1} and at constant temperatures of 358 and 498 K; these values are just above the “turn-on” temperature for the transmetalation reaction and just below the temperature at which hfac decomposition begins to become kinetically important. The data in Figure 5 show that the desorbing $Cu(hfac)_2$ signal decays over time, and that a more rapid decay is seen at the lower temperature.

The decay in the production of $Cu(hfac)_2$ over time is expected from the simple boundary conditions of the experiment: the surface concentration of copper, θ_{Cu}, is largest at $t = 0$. The decay shows that the surface concentration of Cu atoms decreases (and the Pd coverage increases) as the transmetalation process continues. Given that the crystal constitutes an essentially infinite reservoir of Cu atoms, the system *must* develop a time-varying composition gradient for Pd and Cu (see below). The decay should be most rapid if the deposited palladium atoms remain at the surface; the decay should be very slow if palladium and copper atoms from the bulk of the Cu(111) single crystal are able to interdiffuse. Irrespective of the interdiffusion rate, however, the production of $Cu(hfac)_2$ will reach zero at infinite time (i.e., when all the copper atoms are replaced by palladium).

The rapid decrease in $Cu(hfac)_2$ flux seen at 358 K strongly suggests that the diffusion of Pd atoms into the bulk of the Cu(111) single crystal must be relatively slow. At 498 K, even though similar trends are seen, the desorbing $Cu(hfac)_2$ signal decays more slowly owing to the more rapid interdiffusion rate at higher temperatures. A kinetic analysis of the decay curves is presented in the next section; this analysis affords estimates of the diffusion coefficient for the interdiffusion of Pd and Cu.

Kinetic Analysis of the Reactive Scattering of $Pd(hfac)_2$ on Cu(111) Single Crystal Surfaces. With a few assumptions, we can model quantitatively the time and temperature dependence of the $Cu(hfac)_2$ desorbing flux in the constant-temperature reactive scattering experiments. Our kinetic model explicitly includes the bulk interdiffusion of palladium and copper. As we will define and detail below, the boundary conditions for this class of diffusion problems do not define a steady state kinetic limit. Rather, one of the most significant features of this model is that the kinetics must of necessity be time varying due to the establishment of a time-dependent Pd/Cu concentration gradient: the surface concentration of copper atoms changes over time owing to the slow diffusion of Pd atoms into the bulk of the Cu(111) single crystal.

First, we assume that for every copper atom that is converted to $Cu(hfac)_2$, one palladium atom is added to the surface; thus the total number of metal atoms in the bulk remains constant. Second, we assume that the diffusion coefficient for interdiffusion of palladium and copper is independent of the composition of the near-surface region. In fact, this may not be a very good assumption: at higher temperatures (1038 °C), the diffusion coefficient is known to change by a factor of 10 as the composition of a Pd/Cu alloy is varied from 100% Cu to 100% Pd.[19,20] Unfortunately, the concentration dependence of the diffusion coefficient for the Pd/Cu system is not known in the temperature range of interest in the present context (350−500 K). In view of this situation, we decided to assume that the diffusion coefficient is composition invariant; this assumption considerably simplifies the mathematical analysis of the kinetic model. Of course, the quantitative accuracy of our model will depend ultimately on the validity of this assumption.

In a mathematical sense, the diffusion-limited transmetalation process is similar to other physical processes that involve both bulk diffusion and a surface reaction of finite rate. Among these are heat loss (or moisture loss) from an infinite plate to a medium of zero temperature (or zero humidity)[21] and chronoamperometric experiments for the irreversible reduction or oxidation of a redox-active analyte in solution at a planar electrode, where the charge transfer kinetics are slow.[22,23] In the former cases, bulk diffusion occurs through a solid; in the latter case, bulk diffusion occurs through a liquid. In a chronoamperometric experiment, the working electrode is initially held at a potential E_1 insufficient to promote the reaction $R \rightarrow O + e^-$, where R and O are the reduced and oxidized forms of the analyte, respectively; the potential of the working electrode is then stepped instantaneously to a potential E_2 sufficient to drive the reaction to completion, and the current is measured as a function of time. In the present context, the parameters relating to the redox transmetalation process are functionally equivalent to the parameters relating to the chronoamperometric experiment as follows (Figure 6):

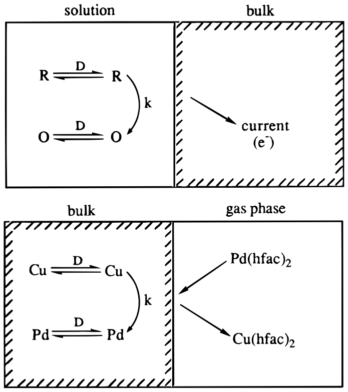

Figure 6. Correspondence between the physical and kinetic processes occurring in a chronoamperometric experiment (top) and the redox transmetalation reaction under diffusion-limited conditions (bottom). The current is monitored as a function of time in the chronoamperometric experiment; the $Cu(hfac)_2$ flux desorbing from the surface is monitored as a function of time in the present study.

bulk concentration of Cu ≡ solution concentration of R

bulk concentration of Pd ≡ solution concentration of O

flux of $Cu(hfac)_2$ desorbing from the surface ≡ current density

For the transmetalation process, the interdiffusion of palladium and copper is governed by Fick's second law of diffusion, which is given by the linear differential equation:

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \qquad (7)$$

where D is the diffusion coefficient and $C(x,t)$ is the copper concentration in the bulk at time t and distance x beneath the surface. In the present case, the boundary conditions are:

$$C(x,0) = C_0 \qquad (8)$$

$$\lim_{x\to\infty} C(x,t) = C_0 \qquad (9)$$

$$J(0,t) = D\left[\frac{\partial C(x,t)}{\partial x}\right]_{x=0} = k_{Cu}h_{Cu}C(0,t)\theta_h n_h \qquad (10)$$

where C_0 is the number of copper atoms per cubic centimeter for pure copper, $J(0,t)$ is the flux of $Cu(hfac)_2$ desorbing from the surface, h_{Cu} is a geometric constant (2.09×10^{-8} cm; equal to $(2/3)^{1/2}$ times the Cu−Cu distance in copper metal) that relates the two-dimensional copper surface atom density to the three-dimensional copper concentration, and θ_h and n_h are defined as before. The first boundary condition merely states that at $t = 0$, the crystal is entirely composed of pure copper; the second boundary condition states that at all times, the crystal is pure copper at large depths. The third boundary condition is eq 3 recast into a slightly different form, with $k_{Cu} = A'e^{-E_a'/RT}$ and $C(0,t) = \theta_{Cu}n_{Cu}/h_{Cu}$.

At sufficiently low temperatures, the hfac coverage will be near saturation ($\theta_h = 1$) and thus approximately constant throughout the constant-temperature reactive scattering experiments. Under these conditions, the constants in eq 10 can be collected to give a simplified version of this boundary condition: $J(0,t) = D\,[\partial C(x,t)/\partial x]_{x=0} = EC(0,t)$, where $E = k_{Cu}h_{Cu}n_h$.

---

[19] Shewmon, P. G. *Diffusion in Solids*; McGraw-Hill: New York, 1963; p 134.

[20] Birchenall, C. E. *Atom Movements*; ASM: Cleveland, 1951; p 122.

[21] Churchill, R. V. *Operational Mathematics*, 3rd ed.; McGraw-Hill: New York, 1972; pp 245−247.

[22] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, 1980; pp 165−168.

[23] Delahay, P. *New Instrumental Methods in Electrochemistry: Theory, Instrumentation, and Applications to Analytical and Physical Chemistry*; Interscience Publisher: New York, 1954; Chapter 4.

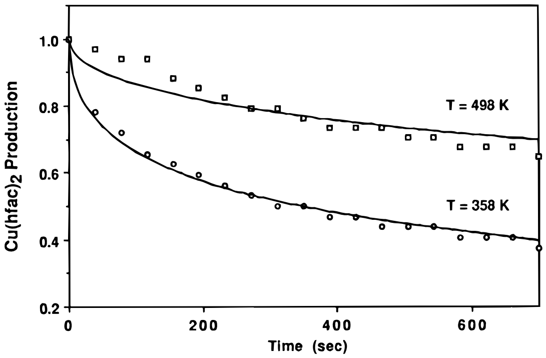

Figure 7. Fits of the desorption of $Cu(hfac)_2$ during the reactive scattering of $Pd(hfac)_2$ on Cu(111) surfaces at 358 and 498 K with a $Pd(hfac)_2$ flux of 3×10^{13} molecules cm^{-2} s^{-1}. The experimental data are indicated by open circles (○), while the solid curves are based on eq 11.

When this simplified version of eq 10 applies, a closed-form solution of the differential equations can be written. Calculation of the Laplace transform of Fick's second law, application of the boundary conditions, and back-transformation give the following solution:[21]

$$J(0,t) = EC_0 \exp(H^2 t)\ \mathrm{erfc}(Ht^{1/2}) \qquad (11)$$

where $H = ED^{-1/2} = k_{Cu}h_{Cu}n_hD^{-1/2}$ and erfc is the complementary error function. Reactive scattering experiments carried out at sufficiently low substrate temperatures satisfy these boundary conditions and can thus be analyzed quantitatively in this way.

Figure 7 shows the fit of the constant-temperature reactive scattering data shown in Figure 5a ($T = 358$ K; normalized to the initial rate) to eq 11. The least-squares refinement gives $H = 0.042\ s^{-1/2}$. The fit of the experimental data to eq 11 is excellent: the kinetic model gives an excellent prediction of the shape of the reactive scattering curve shown in Figure 5, and consequently we believe that the model accuracy reflects the physical processes that are important in the transmetalation reaction on single crystal surfaces.

The value of H is related to the diffusion coefficient D by the expression $H = k_{Cu}h_{Cu}n_hD^{-1/2} = A'e^{-E_a'/RT}h_{Cu}n_hD^{-1/2}$. We have not measured the preexponential factor and activation energy for the assembly of $Cu(hfac)_2$ molecules on a single crystal surface, and these kinetic parameters are not necessarily identical to those characteristic of the assembly of $Cu(hfac)_2$ molecules on a polycrystalline substrate. We can, however, use the activation parameters deduced from the kinetic analysis based on eq 6 (see above) of $A' = 2 \times 10^{-10}$ molecules^{-2} cm^4 s^{-1} and $E_a' = 13$ kcal mol^{-1} to make a crude estimate of D and to check whether eq 11 gives physically reasonable results. We also assume that the saturation coverage of hfac groups, n_h, is equal to 5.0×10^{14} molecules cm^{-2} as described before. Given these values, we calculate that $D \approx 10^{-18}\ cm^2\ s^{-1}$ for single crystals at 358 K. In view of the numerous approximations we have made in setting up the model and in assigning values to the various constants, this estimate of the diffusion coefficient must be regarded as being rather imprecise.

As expected, this value of D is significantly smaller than those measured at higher temperatures for polycrystalline copper substrates: Auger depth profiles of films deposited from $Pd(hfac)_2$ at higher pressures (ca. 10^{-3} Torr) showed that D varies from $7 \times 10^{-14}\ cm^2\ s^{-1}$ at 523 K at $1 \times 10^{-12}\ cm^2\ s^{-1}$ at 623 K.[2] The 5 to 6 orders of magnitude difference between these values and the $\sim 10^{-18}\ cm^2\ s^{-1}$ value derived above reflect the acceleration of the diffusion rate by both the presence of defect sites and the 165−265 K increase in temperature.

Attempts to analyze the reactive scattering data at higher temperatures (e.g., $T = 498$ K; Figure 5b) gave poorer results. The least-squares fit of the 498 K data to eq 11 are shown in Figure 7; the best-fit value of H is $0.014\ s^{-1/2}$, which corresponds to $D \approx 10^{-13}\ cm^2\ s^{-1}$. This value of the diffusion coefficient is larger than expected for single crystals at this temperature, which suggests that there may be an underlying problem with this analysis. This is not surprising because the surface hfac coverage at these temperatures is less than 1 and not constant over the course of the experiment (the hfac coverage increases with time as the surface becomes enriched in palladium atoms, which react less quickly with hfac); therefore, the simplified version of eq 10 no longer applies. When θ_h is not constant with time, the differential equations must be solved by first eliminating θ_h from eq 10. This can be accomplished by equating the amount of $Pd(hfac)_2$ adsorbing on the surface to the combined amounts of $Cu(hfac)_2$ and $Pd(hfac)_2$ desorbing from the surface per unit time. This approach affords the following equation:

$$\sigma(1 - \theta_h) = k_{Cu}h_{Cu}C(0,t)\theta_h^{\ 2}n_h^{\ 2} + k_{Pd}h_{Cu}[C_0 - C(0,t)]\theta_h^{\ 2}n_h^{\ 2} \qquad (12)$$

where we have assumed two things: that the sticking probability for the incident $Pd(hfac)_2$ molecules is proportional to the number of open sites on the surface (i.e., sites not covered by hfac groups), and that the surface palladium concentration may be given by $C_0 - C(0,t)$. The rate constants k_{Cu} and k_{Pd} reflect the intrinsic reactivity of surface-bound hfac groups with copper and palladium surface atoms to produce $Cu(hfac)_2$ and $Pd(hfac)_2$, respectively, in the desorbing flux. By solving this expression for θ_h and plugging the result into eq 10, we can obtain a version of eq 10 that can be used as a boundary condition. The resulting expression is nonlinear in $C(0,t)$ and an analytic solution of eqs 7−10 is impossible in this general case; numerical methods must be used to solve the system of differential equations. Since little additional physical insight would be gained by analyzing the higher-temperature reactive scattering data in this way, we have not pursued this latter approach.

Conclusions

These results and those described in the preceding paper have shown that reactions conducted under UHV conditions can provide powerful insights into the mechanisms of macroscopic MOCVD processes—in this case, the surface-selective deposition of palladium on copper from the β-diketonate precursor $Pd(hfac)_2$. Studies of the reactions of $Pd(hfac)_2$ on copper substrates under ultrahigh-vacuum conditions have shown that the decomposition of hfac groups on the surface competes detrimentally at high temperatures with a selective pathway for the deposition of palladium via a redox transmetalation reaction. The activation energies for these two processes are 36.8 and 13 kcal mol^{-1}, respectively.

The decomposition of hfac groups can be inhibited by lowering the reaction temperature but *not* by increasing the incident flux; increasing the flux does not affect the relative amount of decomposition because the rate laws for both decomposition and transmetalation are first order in hfac coverage.

The transmetalation reaction is self-limiting on Cu(111) but not on copper foils owing to the slow interdiffusion of copper and palladium when defect sites are absent. The time dependence of the rate of the transmetalation reaction on single crystal substrates has allowed us to estimate the rate of interdiffusion of copper and palladium; the diffusion coefficient D is equal to $\sim 10^{-18}\ cm^2\ s^{-1}$ on single crystal substrates at 358 K. The ability of the surface microstructure to affect the rates of transport processes (and thus the efficacy of a MOCVD reaction) is powerfully demonstrated for this class of reaction by the detailed kinetic and spectroscopic data reported herein.

These results should prove broadly relevant to the mechanisms of other chemical vapor deposition processes that involve simultaneous deposition onto and etching of a surface.

Appendix

Reactive Scattering Model Assuming that the Transmetalation Reaction Is Second Order in hfac Coverage. At least two different mechanisms for the assembly of Cu(hfac)$_2$ molecules on the surface predict that the rate of hfac desorption (in the form of Cu(hfac)$_2$ molecules) should be second order in hfac coverage. One possibility is that the reaction is inherently termolecular. Alternatively (and more likely), the assembly of Cu(hfac)$_2$ molecules could occur in a stepwise fashion in which Cu(hfac) intermediates are formed on the surface and then react with a second hfac molecule to form the product; similar sequential reaction mechanisms have been observed for the assembly of other MX$_2$ species on surfaces.[18] If we make a steady state approximation for the surface coverage of Cu(hfac), the rate of formation of Cu(hfac)$_2$ should be second order in hfac coverage and first order in copper surface atom density.

The rates of hfac adsorption, hfac decomposition, and hfac desorption in the form of Cu(hfac)$_2$ molecules (i.e., the transmetalation rate) are thus given by:

$$R_{\mathrm{adsorp}}(\mathrm{hfac}) = 2\sigma \tag{A1}$$

$$R_{\mathrm{decomp}}(\mathrm{hfac}) = \theta_{\mathrm{h}} n_{\mathrm{h}} A \mathrm{e}^{-E_{\mathrm{a}}/RT} \tag{A2}$$

$$R_{\mathrm{trans}}(\mathrm{hfac}) = 2{\theta_{\mathrm{h}}}^2 {n_{\mathrm{h}}}^2 \theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' \mathrm{e}^{-E_{\mathrm{a}}'/RT} \tag{A3}$$

where the parameters are defined as in the text.

Conservation of hfac groups demands that $R_{\mathrm{trans}} + R_{\mathrm{decomp}} - R_{\mathrm{adsorp}} = 0$. Thus:

$$2{\theta_{\mathrm{h}}}^2 {n_{\mathrm{h}}}^2 \theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' \mathrm{e}^{-E_{\mathrm{a}}'/RT} + \theta_{\mathrm{h}} n_{\mathrm{h}} A \mathrm{e}^{-E_{\mathrm{a}}/RT} - 2\sigma = 0 \tag{A4}$$

Solving this quadratic equation for the quantity ($\theta_{\mathrm{h}} n_{\mathrm{h}}$), we find (taking the positive root):

$$\theta_{\mathrm{h}} n_{\mathrm{h}} = \{-A\mathrm{e}^{-E_{\mathrm{a}}/RT} + (A^2 e^{-2E_{\mathrm{a}}/RT} + 16\sigma\theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' \mathrm{e}^{-E_{\mathrm{a}}'/RT})^{1/2}\}/4\theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' \mathrm{e}^{-E_{\mathrm{a}}'/RT} \tag{A5}$$

Substituting eq A5 into eq A3 gives the transmetalation rate (i.e., the rate of hfac desorption in the form of Cu(hfac)$_2$ molecules); the resulting expression below reflects the partitioning of hfac groups along the transmetalation and decomposition channels:

$$\Phi = \frac{\mathrm{Cu(hfac)_2\ flux\ out}}{\mathrm{Pd(hfac)_2\ flux\ in}} = \{-\mathrm{Ae}^{-\mathrm{E_a}/\mathrm{RT}} + (A^2 \mathrm{e}^{-2E_{\mathrm{a}}/RT} + 16\sigma\theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' \mathrm{e}^{-E_{\mathrm{a}}'/RT})^{1/2}\}^2/16\sigma\theta_{\mathrm{Cu}} n_{\mathrm{Cu}} A' \mathrm{e}^{-E_{\mathrm{a}}'/RT} \tag{A6}$$

Equation A6 contains two unknowns, the activation parameters for the transmetalation process, A′ and E$_{\mathrm{a}}$′. Most of the other parameters in eq A6 are known accurately, as discussed in the main body of this paper. Because σ and A' always appear together as a product in eq 6, any systematic error in the estimation of σ will affect the best-fit value of A', but will *not* affect the calculated activation energy E_{a}'.

Least-squares fits of the reactive scattering data corresponding to the curve in Figure 1b carried out with eq A6 gave fits that were as good as those carried out by assuming that the assembly of Cu(hfac)$_2$ molecules is first order in hfac coverage (eq 6); the preexponential factor and the activation energy derived from the least-squares fit are $A' = 3 \times 10^{-16}$ molecules^{-1} cm^2 s^{-1} and $E_{\mathrm{a}}' = 35.8$ kcal mol^{-1}. The preexponential factor, however, is four orders of magnitude too large compared with those characteristic of third-order reactions,[24] and thus the assumption that the assembly of Cu(hfac)$_2$ molecules on the surface is second order in hfac coverage leads to physically unreasonable activation parameters.

The assumption that the assembly of Cu(hfac)$_2$ on the surface is second order in hfac coverage (rather than first order) makes one important qualitative difference: the shape of the curve above 600 K should be flux dependent. Even at a constant temperature, the partitioning of hfac groups between the decomposition and transmetalation channels will depend on the hfac coverage because these processes are first order and second order in this parameter, respectively. If the flux of Pd(hfac)$_2$ to the surface is higher, the surface hfac coverage is high as a result, and the associative reaction of two hfac groups and a copper atom becomes more likely statistically. Under normal MOCVD conditions, therefore, where the precursor fluxes are many orders of magnitude higher than those used in the reactive scattering experiments and where the surface hfac concentrations are also high, the transmetalation reaction should be much faster, sufficiently so as to remain competitive with hfac fragmentation even at high temperatures (up to ∼800 K). This prediction is in conflict with the experimental results, which show that even at high Pd(hfac)$_2$ fluxes, the decomposition of hfac groups is kinetically dominant at 800 K. Thus, we conclude that the rate of assembly and desorption of Cu(hfac)$_2$ is not second order in hfac coverage.

Acknowledgment. We thank the Department of Energy under Contract No. DEFG02-91ER45439 for support of this work. Partial support from the National Science Foundation (CHE 9300995) is also gratefully acknowledged. We also thank Professor Nate Lewis for a helpful suggestion. W.L. is the recipient of a University of Illinois Department of Chemistry Fellowship, and G.S.G. is the recipient of an A. P. Sloan Foundation Research Fellowship and a Henry and Camille Dreyfus Teacher-Scholar Award.

JA944131+

---

(24) Preexponential factors for other third-order reactions are typically ∼10^{-19} molecules^{-2} cm^4 s^{-1}. See: Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, New York, 1981; Chapter 7, pp 361−366.