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Surface-Selective Deposition of Palladium and Silver Films from Metal–Organic Precursors: A Novel Metal–Organic Chemical Vapor Deposition Redox Transmetalation Process

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The deposition of metals by chemical vapor deposition (CVD) routes is a topic of great current interest and is particularly relevant to the metalization of microelectronic devices.[1–3] *Surface-selective* depositions, i.e., those in which deposition takes place only on certain surfaces but not on others, are especially interesting.[4–11] Here we report the first surface-selective depositions of Pd and Ag films from metal–organic precursors. We also describe mechanistic studies of this process by in situ kinetic and spectroscopic studies conducted in ultrahigh vacuum.

Few metal–organic precursors for the deposition of Pd and Ag thin films have previously been described, none of which deposits films selectively.[12–15] We have studied three precursors containing the hexafluoroacetylacetonato (hfac) ligand: $Pd(hfac)_2$ (**1**), Ag(hfac)(PMe_3) (**2**), and $Ag(hfac)(PMe_3)_2$ (**3**). Compound **1** was prepared by a literature route,[16,17] and the two new silver compounds were prepared by addition of the corresponding amount of PMe_3 to Ag(hfac).[18] Single-crystal X-ray diffraction studies show that **2** has a trigonal planar structure while **3** adopts a distorted tetrahedral structure.[19] These compounds (especially **1**) are reasonably volatile and sublime readily in vacuo at temperatures of 20–50 °C.

Chemical vapor depositions from these precursors have been conducted at 200–425 °C both under vacuum (10^{-4} Torr) and in the presence of H_2. In the presence of H_2, $Pd(hfac)_2$ readily gives micron-thick films of pure palladium metal on glass, silicon, copper, tungsten, aluminum, and nickel at temperatures as low as 200 °C.[20] Mass spectrometric analysis of the byproducts suggests that deposition of Pd involves the reaction of $Pd(hfac)_2$ with H_2 to form hexafluoroacetylacetone (hfacH). Similar surface-independent depositions of Ag films are observed for the silver precursors under an H_2 atmosphere.

In contrast to the results above, under vacuum no deposition of Pd or Ag occurs at 200–425 °C on glass, silicon, aluminum, tungsten, nickel, cobalt, or silver; instead, the precursor passes through the hot zone intact. However, on copper substrates, $Pd(hfac)_2$, Ag(hfac)(PMe_3), and $Ag(hfac)(PMe_3)_2$ readily give bright, silvery deposits. Auger electron spectroscopy establishes that the interiors of the films contain less than 1% C, O, and F contaminants.[21] Auger depth-profile studies of films deposited from **1** reveal that a binary Pd/Cu phase[22,23] several microns in thickness is formed and that the Pd concentration is dependent on the reaction temperature, precursor exposure, and depth below the surface of the film; the maximum Pd concentration is 80 atom %. Evidently, grain boundary interdiffusion[24] is relatively rapid under the reaction conditions. In contrast, due presumably to a lower interdiffusion rate, passage of the silver-containing precursors **2** and **3** over copper substrates at 250–425 °C yields pure silver films about 0.5 μm thick as shown by Auger depth-profile studies.

As deposition of Pd on Cu takes place from the palladium precursor $Pd(hfac)_2$, a green material condenses on the cool walls of the reaction apparatus downstream of the deposition zone; this material was identified by mass spectrometry and EPR spectroscopy as the copper(II) hexafluoroacetylacetonate complex $Cu(hfac)_2$.[25] This result suggests that the precursor undergoes a redox reaction with the copper surface in which deposition of metal is accompanied by production of the $Cu(hfac)_2$:

$$Pd(hfac)_2 + Cu \rightarrow Pd + Cu(hfac)_2 \tag{1}$$

The mass spectra of the volatile byproducts formed from the deposition from **2** and **3** are also consistent with the formation of copper hfac byproducts.[26]

Confirmation that eq 1 best describes the net reaction was obtained by directing a continuous molecular beam of $Pd(hfac)_2$ toward a copper surface and analyzing the molecules scattered from the surface by mass spectrometry. The composition of the desorbing flux was determined as a function of the temperature of the copper surface. At temperatures between 300 and 400 K, desorption features for both $Cu(hfac)_x$ and $Pd(hfac)_x$ species are

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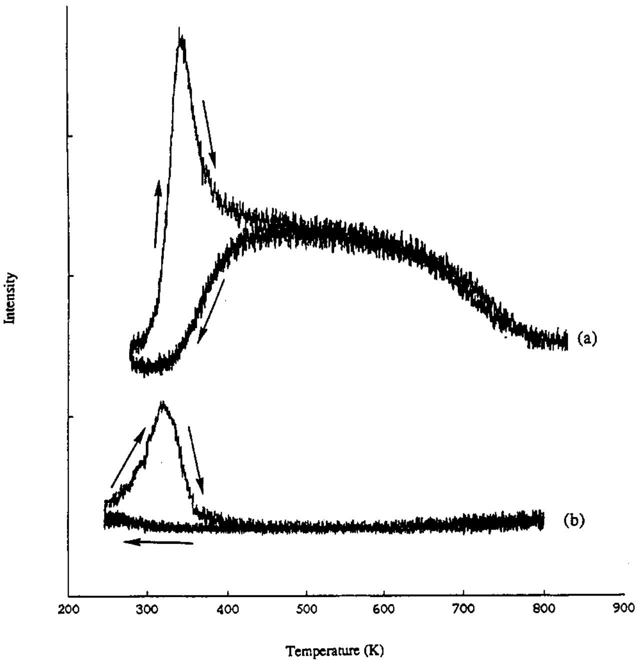


Figure 1. The profiles for the molecular beam surface reactive scattering of Pd(hfac)$_2$ on a copper surface: (a) $m/e = 201$ (Cu(hfac) − CF$_3$) profile; (b) $m/e = 244$ (Pd(hfac) − CF$_3$) profile. The flux used was $\sim 1 \times 10^{14}$ molecules cm^{-2} s^{-1}, and the heating rate was 7.5 K/s. The sample was held initially at low temperature and then was cycled over the temperature range shown.

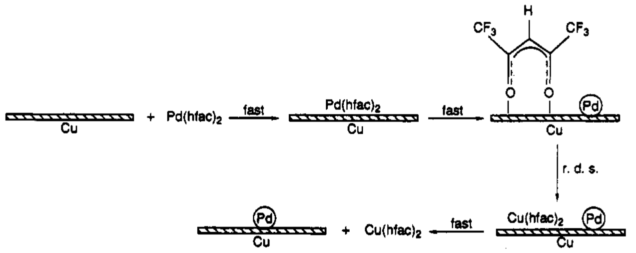
seen (Figure 1).[27,28] As the temperature of the surface is increased, however, the Pd(hfac)$_x$ species quickly disappear from the scattered products and are replaced by Cu(hfac)$_x$ species. Integrated desorption mass spectra (IDMS) taken during the scattering experiment in the flux limited regime between 450 and 500 K indicate that the predominant desorbing species is Cu(hfac)$_2$.

During the temperature ramp, the amount of Cu(hfac)$_2$ desorbing from the surface first crests due to reaction-limited desorption, and then reaches a steady-state limit due to the flux-limited conversion of the starting material. Taken together, the data reveal that, above $\sim$400 K, the Pd complex reacts completely to give, at least in part, Cu(hfac)$_2$ that desorbs from the surface. Above 600 K, the amount of Cu(hfac)$_2$ desorbing begins to decrease and eventually falls to zero at temperatures higher than 750 K. This fall-off is due to the irreversible thermolytic decomposition of hfac ligands on copper surfaces at these temperatures.[27]

The cooling profiles closely track the heating profiles except that they lack the low-temperature features ascribed to the reaction-limited desorption of Pd(hfac)$_x$ and Cu(hfac)$_x$ species. This behavior is expected: at the beginning of the heating cycles, the steady flux of material to the surface and the slow desorption rates lead to an accumulation of hfac-containing species on the surface; subsequent heating to the multilayer desorption temperature then results in a large desorbing flux. In contrast, no such accumulation of hfac-containing materials occurs in the cooling cycles until the temperature is low enough that desorption stops.

In situ X-ray photoelectron spectroscopic studies at submonolayer coverages ($\theta < 0.2$ L) show that, even at 120 K, chemisorption of Pd(hfac)$_2$ on copper surfaces results in a large shift in the Pd (3d$_{5/2}$) core level binding energy from 339.1 eV to 335.5 eV; this shift is consistent with the reduction[29] of the Pd^{II} center of Pd(hfac)$_2$ to metallic Pd^0 as the result of migration of hfac ligands from Pd(hfac)$_2$ to the copper surface.[30] The C, O, and F binding energies[31,32] at 120 K are also consistent with the presence of surface-bound hfac ligands; the low temperature at which the hfac ligands migrate to the Cu surface show that this step cannot be rate-limiting. No features consistent with the formation of a Cu^{II} center are seen in the Cu 2p core level spectra even at higher temperatures, and thus desorption of Cu(hfac)$_2$ cannot be rate-limiting. Therefore, the XPS and TPD studies strongly suggest that the rate limiting step for the reactive scattering experiments is the formation of Cu(hfac)$_2$ from surface-bound hfac groups. The overall mechanism for the conversion of Pd(hfac)$_2$ to Cu(hfac)$_2$ is summarized in Scheme I. The XPS studies also confirm that diffusion of Pd atoms into polycrystalline Cu is facile at temperatures above 400 K.

Scheme I. Mechanism of the Redox Transmetalation Reaction under Steady-State Conditions at 400 K



The observation that passage of Cu(hfac)$_2$ over Pd surfaces only results in the deposition of Cu at temperatures where fragmentation of the hfac ligands begins to occur suggests that the primary driving force for eq 1 is not mass action but rather a favorable redox potential.[33]

This redox transmetalation route may be generally applicable provided that the redox potentials are favorable and that the surface atoms can be carried away as a volatile hfac complex. Further studies of these novel surface-selective depositions are in progress.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, and bond distances and angles for Ag(hfac)(PMe$_3$), **2**, and Ag(hfac)(PMe$_3$)$_2$, **3** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(30) By assuming that this process is unimolecular and taking a typical value of $\sim 1 \times 10^{13}$ for the preexponential factor, an upper limit of $\sim$7 kcal/mol can be deduced for the activation energy of this reduction/dissociation reaction.

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