Reactive Deposition of Conformal Palladium Films from Supercritical Carbon Dioxide Solution

Jason M. Blackburn, David P. Long, and James J. Watkins*

Department of Chemical Engineering, The University of Massachusetts, Amherst, Massachusetts 01003

Received February 14, 2000. Revised Manuscript Received May 4, 2000

High-purity palladium films were deposited onto Si wafers and polyimide by the reduction of organopalladium compounds in supercritical CO_2 solution using a batch process at temperatures between 40 and 80 °C and pressures between 100 and 140 bar. Hydrogenolysis of π-2-methylallyl(cyclopentadienyl)palladium(II) in CO_2 at 60 °C is complete in less than 2 min, yielding continuous, 100−200 nm thick, reflective films and the benign, fully hydrogenated ligand decomposition products, cyclopentane and isobutane. Analysis of the deposited films by X-ray photoelectron spectroscopy indicates that they are free of ligand-derived contamination. Deposition of thin films on patterned silicon wafers having feature sizes as small as 0.1 μm wide by 1.0 μm deep is strictly conformal, including uniform coverage of the lower corners and bottoms of the trenches. Deposition by hydrogenolysis of palladium(II) hexafluoroacetylacetonate also yields high-quality films while deposition using π-allyl-(2,4-pentanedionato)palladium(II) is sensitive to fluid-phase decomposition of the precursor and yields nonuniform deposits.

Introduction

Thin films of palladium and its alloys are used in a variety of technologically important applications including catalysis, gas sensors, and H_2 permselective membranes.[1−3] Moreover, Pd is the most common noble metal in microelectronics where it is used as a contact material in integrated circuits and as a seed layer for the electroless deposition of other interconnect metals.[4−6] Presently, Pd films are prepared by vacuum sputtering and electroplating. Although effective for planar surfaces, these techniques are problematic when applied to substrates with complex topographies.[7] This constraint is particularly severe for applications in microelectronics where shrinking device dimensions require efficient filling of sub-quarter-micrometer, high-aspect ratio features.

The potential for chemical vapor deposition (CVD) to deliver high purity and conformal coverage[8,9] has motivated recent studies of its application to the preparation of palladium thin films.[7,10−12] High-purity Pd can be deposited using a variety of organopalladium compounds as precursors, but temperatures above 200 °C are usually required to maintain acceptable purity and deposition rates.[13] Moreover, depositions under these conditions are typically mass-transport limited, which precludes uniform surface coverage. Consequently, the preparation of Pd films using CVD is not yet a commercial process.

Current research in palladium CVD is directed primarily toward two objectives. The first is reducing deposition temperature while maintaining film purity. Low deposition temperatures are desirable for applications in microelectronics to suppress the development of thermal-mechanical stress during device fabrication, minimize interdiffusion and reaction between adjacent layers, and for compatibility with polymer-based dielectrics. One approach is the use of reactive carrier gases such as H_2 or O_2 to facilitate deposition. For example, substantial improvements in Pd film purity upon the addition of H_2 arise via catalytic hydrogenation of the ligand decomposition products at the incipient metal surface. Kodas and co-workers reported the deposition of contaminant-free films from the fluorinated precursor palladium(II) hexafluoroacetylacetonate, $Pd(hfac)_2$, using hydrogen-assisted CVD at temperatures as low as 80 °C,[11] although similar success has not been reported

* To whom correspondence should be addressed. E-mail: watkins@ecs.umass.edu.

(1) Hsieh, H. P. *Inorganic Membranes for Separation and Reaction*; Elsevier: New York, 1996.
(2) Shu, J.; Granjean, B. P. A.; Neste, A. V.; Kaliaguine, S. *Can. J. Chem. Eng.* **1991**, *69*, 1036.
(3) Hughes, R. C.; Schubert, W. K.; Buss, R. J. *J. Electrochem. Soc.* **1995**, *142*, 249.
(4) Mak, C. Y.; Miller, B.; Feldman, L. C.; Weir, B. E.; Higashi, G. S.; Fitzgerald, E. A.; Boone, T.; Doherty, C. J.; van Dover, R. B. *Appl. Phys. Lett.* **1991**, *59*, 3449.
(5) Potochnik, S. J.; Pehrsoon, P. E.; Hsu, D. S. Y.; Calvert, J. M. *Langmuir* **1995**, *11*, 1841.
(6) Dubin, V. M.; Lopatin, S. D.; Sokolov, V. G. *Thin Solid Films* **1993**, *226*, 94.
(7) Zhang, Y.; Yuan, Z.; Puddephatt, R. J. *Chem. Mater.* **1998**, *10*, 2293.
(8) Hitchman, M. L.; Jensen, K. F. *Chemical Vapor Deposition Principles and Applications*; Hitchman, M. L., Jensen, K. F., Ed.; Academic Press: London, 1993.
(9) Kodas, T. T.; Hampden-Smith, M. J. In *The Chemistry of Metal CVD*; Kodas, T. T., Hampden-Smith, M. J., Ed.; VCH: New York, 1994.
(10) Bhaskaran, V.; Atanasova, P.; Hampden-Smith, M. J.; Kodas, T. T. *Chem. Mater.* **1997**, *9*, 2822.
(11) Bhaskaran, V.; Hampden-Smith, M. J.; Kodas, T. T. *Chem. Vap. Deposition* **1997**, *3*, 85.
(12) Hierso, J.-C.; Satto, C.; Feurer, R.; Kalck, P. *Chem. Mater.* **1996**, *8*, 2481.
(13) Hampden-Smith, M. J.; Kodas, T. T. *Chem. Vap. Deposition* **1995**, *1*, 8.

10.1021/cm000118e CCC: $19.00 © 2000 American Chemical Society
Published on Web 08/17/2000

with other precursors. Deposition from π-allylpalladium hexafluoroacetylacetonate, (π-C_3H_5)Pd(hfac), in the presence of hydrogen at 140 °C, for example, yields films contaminated with 15 atomic % (atom %) carbon,[14] while the nonfluorinated precursor, allyl(cyclopentadienyl)-palladium(II), CpPd(π-C_3H_5), yields films containing in excess of 20 atom % carbon in the presence of H_2 at 45 °C.[12]

A second research objective is the alleviation of mass-transfer limitations by optimizing ligand structure to achieve high precursor volatility. One strategy is the use of fluorinated ligands. For example, $Pd(hfac)_2$ exhibits markedly higher vapor pressure than its hydrogenated analogue, palladium(II)acetylacetonate, and its use as a Pd precursor for CVD has been studied extensively.[11,15,16] Despite its high volatility, depositions using $Pd(hfac)_2$ at 120 °C in the presence of H_2 are feed rate limited, which precludes uniform trench filling.[11] A promising series of fluorinated allyl(β-diketonato)-palladium complexes, including some liquid precursors has recently been prepared by Puddephatt.[7] CVD using these compounds in the presence of H_2 or O_2 can be conducted at temperatures between 170 and 315 °C, but high purity depositions (<1% carbon) require temperatures above 230 °C. A major drawback to the use of fluorinated ligands is the generation of objectionable effluent streams. Moreover, conformal coverage of complex topographies using these precursors has not been reported.

Continued development may gradually erode the limitations of Pd CVD, but the fundamental conflict between the process requirements of CVD and rapid, conformal deposition of high purity films at low temperatures suggest alternative strategies may be required. Chemical fluid deposition (CFD) is a fundamentally new approach to metal deposition that involves the chemical reduction of soluble organometallic compounds in supercritical carbon dioxide at low temperature (40−80 °C).[17,18] This method has multiple advantages. First, since CO_2 is a good solvent for a broad range of organometallic compounds[19,20] and their organic decomposition products, the process can be carried out using a variety of precursors at fluid-phase concentrations that are several orders of magnitude greater than those used in CVD.[18] Moreover, supercritical CO_2 is completely miscible with gaseous reducing agents such as H_2. High reagent concentrations in CFD will mitigate mass-transfer limitations and promote conformal film growth. Second, the elimination of the volatility requirement removes severe constraints to precursor development and enables the use of nonfluorinated precursors containing environmentally benign ligands. Third, high solubility of the ligand decomposition products in CO_2 enhances film purity at low temperature by facilitating desorption of potential contaminants from the surface of the incipient film. In contrast, desorption of the decomposition products is thermally activated in CVD such that reductions in process temperatures can generally be expected to increase contamination of the deposited film. Fourth, carbon dioxide adsorbs only weakly to metal surfaces and is unlikely to cause contamination or compete with precursor for active sites. Finally, while CFD is solution-based, the advantageous transport and interfacial properties of SCF solutions alleviate issues of poor mass transfer typically associated with liquid-phase reductions. SCFs exhibit low viscosity and high diffusivity relative to liquids[21] the absence of surface tension inherent to supercritical solutions ensures complete wetting of tortuous surfaces. In summary, CFD may be viewed as a hybrid of CVD and liquid-phase deposition techniques such as electroless plating that preserves the attributes while minimizing the disadvantages of each.

In this paper, we apply CFD to the deposition of high-purity palladium metal onto polyimide, the native oxide surface of Si wafers, and patterned Si test wafers from CO_2 solutions of palladium(II) hexafluoroacetylacetonate, π-allyl(2,4-pentanedionato)palladium(II), and π-2-methylallyl(cyclopentadienyl)palladium, CpPd(π-C_4H_7), using a batch process.

Experimental Section

Allylpalladium chloride dimer, palladium(II) chloride, and cyclopentadienylthallium (99% sublimed) were purchased from Strem Chemicals. Sodium acetylacetonate monohydrate, 3-chloro-2-methylpropene (2-methylallyl chloride), and palladium-(II) hexafluoroacetylacetonate were purchased from Aldrich Chemical Co. Each was used as received.

Precursor synthesis was carried out under inert atmospheres of purified argon using standard Schlenk techniques. Transfer of air-sensitive reagents during synthesis and loading of high-pressure reaction vessels with palladium precursors was conducted inside a glovebox that had been purged for 30 min with prepurified nitrogen. All solvents used for air or moisture sensitive reactions were dried over sodium and benzophenone ketyl and then distilled under an atmosphere of purified argon.

π-Allyl(2,4-pentanedionato)palladium(II) was synthesized using literature procedures immediately prior to use.[22] The compound was found to be pure by proton NMR. ^{1}H NMR: 200 MHz in $CDCl_3$, 2.01 ppm (s, 6H, CH_3 acac), 2.90 ppm (d, J_{H-H} = 11.9 Hz, 2H, *anti*-H of CH_2), 3.88 ppm (d, J_{H-H} = 6.8 Hz, 2H, *syn*-H of CH_2), 5.39 ppm (s, 1H, C−H acac), 5.57 ppm (triplet of triplets, 1H, C−H allyl). 2-Methylallyl palladium chloride dimer, [(π-C_4H_7)PdCl]$_2$, was prepared according to standard literature procedures[23] and found to be pure by proton NMR. ^{1}H NMR: 200 MHz in $CDCl_3$, 2.15 ppm (s, 3H, CH_3), 2.89 ppm (s, 2H, *anti*-H of CH_2), 3.87 ppm (s, 2H, *syn*-H of CH_2).

π-2-Methylallyl(cyclopentadienyl)palladium(II) was synthesized from [(π-C_4H_7)PdCl]$_2$ and cyclopentadienythallium. In a standard preparation, 2.63 g (6.676 mmol) of [(π-C_4H_7)PdCl]$_2$ and 2 equiv (3.60 g, 13.35 mmol) of cyclopentadienythallium were sealed together in a Schlenk flask under an atmosphere of purified argon. The flask was cooled to −78 °C, and 70 mL of tetrahydrofuran, previously dried from sodium and benzophenone ketyl, was condensed onto the reagents. With

(14) Yuan, Z.; Puddephatt, R. J. *Adv. Mater.* **1994**, *6*, 51.
(15) Jeon, N. L.; Lin, W. B.; Erhardt, M. E.; Girolami, G. S.; Nuzzo, R. G. *Langmuir* **1997**, *13*, 3833.
(16) Lin, W. B.; Warren, T. H.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 11644.
(17) Watkins, J. J.; McCarthy, T. J. Method of Chemically Depositing Material on a Substrate. U.S. Patent 5,789,025, 1998.
(18) Watkins, J. J.; Blackburn, J. M.; McCarthy, T. J. *Chem. Mater.* **1999**, *11*, 213.
(19) Smart, N. G.; Carleson, T.; Kast, T.; Clifford, A. A.; Burford, M. D.; Wai, C. M. *Talanta* **1997**, *44*, 137.
(20) Lagalante, A. F.; Hansen, B. M.; Bruno, T. J.; Sievers, R. E. *Inorg. Chem.* **1995**, *34*, 5781.
(21) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*; Butterworth: Boston, 1986.
(22) Imamura, S.; Kajimoto, T.; Kitano, Y.; Tsuji, J. *Bull. Chem. Soc. Jpn.* **1968**, *42*, 805.
(23) Sakakibara, M.; Takahashi, Y.; Sakai, S.; Ishii, Y. *Chem. Commun.* **1969**, 1969.

Table 1. Representative Conditions for Pd Film Deposition

complex	T (°C)	P (bar)	OM wt %[a]	substrate	comments[b]
$Pd(hfac)_2$	60	124	0.28	polyimide	bright, reflective film; fair adhesion
$Pd(hfac)_2$	80	138	0.29	polyimide	bright, reflective film; poor adhesion
$Pd(hfac)_2$	60	124	0.30	Ti/W−Si[c]	reflective film; poor adhesion
$(\pi^3\text{-}C_3H_5)Pd(acac)$	40	103	0.38	Si wafer	bright, nonuniform film; poor adhesion
$(\pi^3\text{-}C_3H_5)Pd(acac)$	40	103	0.25	polyimide	bright, nonuniform film
$(\pi^3\text{-}C_3H_5)Pd(acac)$	60	103	0.24	polyimide	bright, nonuniform film
$(\pi^3\text{-}C_3H_5)Pd(acac)$[d]	40	138	0.36	polyimide	thermolysis, dull gray film, carbon contamination
$CpPd(\pi^3\text{-}C_4H_7)$	60	103	0.21	polyimide	bright, reflective film; good adhesion
$CpPd(\pi^3\text{-}C_4H_7)$	60	138	0.21	polyimide	bright, reflective film; good adhesion
$CpPd(\pi^3\text{-}C_4H_7)$	60	138	0.26	patterned Si wafer	bright, reflective film, conformal coverage

[a] Concentration of organometallic compound in CO_2 solution. [b] See text for explanation of adhesion terms. [c] Si wafer sputtered with ~7 nm of 88% Ti/12% W. [d] Depositions performed thermally without hydrogen addition (see text for details).

constant stirring, the reaction was warmed overnight to room temperature and then filtered under a stream of argon to remove precipitated thallium chloride. A crude product was recovered from the filtrate by vacuum evaporation. This material was easily sublimed (60 °C at 0.2 Torr) yielding pure long dark-red needles of $CpPd(\pi\text{-}C_4H_7)$ in 70% yield. ^1H NMR: 200 MHz in benzene-d_6, 1.69 ppm (s, 3H, CH_3), 2.12 ppm (s, 2H, *anti*-H of CH_2), 3.39 ppm (s, 2H, *syn*-H of CH_2), 5.86 ppm (s, 5H, C_5H_5).

Boron-doped, P-type silicon test wafers with a <100> orientation were obtained from International Wafer Service. All wafers were cleaned by immersion in boiling deionized water, followed by rinsing and sonication in acetone or methyl alcohol for 20 min. The wafers were then dried overnight in air at 100 °C. Sheets of Kapton polyimide of 50 μm thickness were cleaned using a similar procedure. Carbon dioxide (Coleman grade) and hydrogen (high-purity grade) were obtained from Merriam-Graves and used as received.

All depositions from CO_2 were conducted in 17-mL high-pressure stainless steel reactors (High-Pressure Equipment Company) sealed with a plug at one end and a high-pressure needle valve at the other. A single substrate (~1 × 4 cm samples of silicon wafer or ~1 × 7 cm samples of polyimide) and a known amount (10−40 mg) of precursor were added to the vessel. $Pd(hfac)_2$ was loaded at ambient conditions. The precursor $(\pi\text{-}C_3H_5)Pd(acac)$ decomposes slowly in air at room temperature[14] and was therefore loaded under a stream of argon or inside the nitrogen glovebox. $CpPd(\pi\text{-}C_4H_7)$ is stable for short periods of time in the atmosphere, but was loaded in the drybox as a precaution. The vessels were purged with CO_2, weighed, placed in a circulating constant-temperature bath (40−80 °C), and allowed to equilibrate to the desired temperature. Carbon dioxide was then added to the desired pressure via a high-pressure manifold described previously[24] or a high-pressure syringe pump (Isco, Inc. Model 260D) that was maintained at the desired temperature using a water jacket. The vessels were mixed, weighed to determine the mass of CO_2 added, and then returned to the constant-temperature bath for 1 h for depositions using $Pd(hfac)_2$ or $CpPd(\pi\text{-}C_4H_7)$ or 15 min for depositions using $(\pi\text{-}C_3H_5)Pd(acac)$. Solubility of the precursors in CO_2 at the deposition conditions was verified optically using a variable volume view cell and the method described by McHugh.[21] Film deposition was initiated by reduction of the precursor either thermally or upon reaction with hydrogen. For hydrogenolysis, a 60−100 fold molar excess of H_2 was transferred to the reaction vessel via a small pressurized manifold (3.6 mL), consisting of a section of high pressure tubing capped at both ends with needle valves and equipped with a pressure gauge. The quantity of hydrogen admitted into the vessel was calculated from the pressure-drop measured in the manifold. The rate of hydrogen addition was regulated using a needle valve at ~200 μmols per minute. After hydrogen addition, the reactions were allowed to stand for a period of 1−2 h, although kinetic experiments (see below) indicate that the reaction is complete in less than 2 mins for $CpPd(\pi\text{-}C_4H_7)$. A detailed study of the reduction kinetics of Pd-(hfac)$_2$ was not conducted, but experiments in a high-pressure view cell indicate that deposition occurs readily upon the addition of H_2 to $CO_2/Pd(hfac)_2$ solutions. For depositions by thermolysis of $(\pi\text{-}C_3H_5)Pd(acac)$, the solutions were loaded and maintained at the conditions of interest for the desired reaction period (2−14 h). The vessels were then depressurized and the effluent was directed through an activated charcoal bed. In some cases, the reaction byproducts contained in the CO_2 mixture were first collected for NMR analysis by venting the vessel through a bubbler containing an appropriate solvent prior to directing the effluent to the carbon bed.

(24) Watkins, J. J.; McCarthy, T. J. *Macromolecules* **1995**, *28*, 4067.

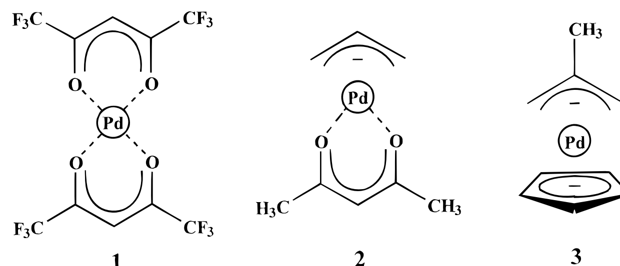


Figure 1. Precursors used in this study: (1) $Pd(hfac)_2$, (2) $(\pi\text{-}C_3H_5)Pd(acac)$, and (3) $CpPd(\pi\text{-}C_4H_7)$.

X-ray photoelectron spectroscopy (XPS) was conducted using a Perkin-Elmer Physical Electronics 5100 spectrometer with Mg Kα excitation (400 W, 15.0 kV). To ensure representative analysis, a sampling area of 4 × 10 mm was employed. The films were cleaned by Ar^+ sputtering to remove atmospheric contaminants until the measured atomic concentrations in consecutive analysis were invariant. Field emission scanning electron microscopy (FE-SEM) was performed using a JEOL 6400 FXV SEM and an accelerating voltage of 5−10 kV. Analysis of cross sections of Pd films on polyimide was conducted after embedding in epoxy and subsequent cyromicrotomy. Wide-angle X-ray diffraction (WAXD) was performed on a Phillips X'Pert PW 3040 using Cu Kα radiation.

Results and Discussion

Palladium was deposited onto Si wafers or polyimide by hydrogenolysis of each of the precursors (Figure 1) or by thermal decomposition of $(\pi\text{-}C_3H_5)Pd(acac)$ at 40−80 °C, pressures being between 100 and 140 bar and precursor concentrations in CO_2 ranging from 0.2 to 0.6 wt % (Table 1). A 60−100 fold molar excess of H_2 was used for each hydrogenation. The resulting films were analyzed by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and wide-angle X-ray diffraction (WAXD). Figure 2 shows an XPS survey of a palladium film deposited from a 0.21 wt % solution of $CpPd(\pi\text{-}C_4H_7)$ in CO_2 at 60 °C and 138 bar acquired after Ar^+ sputtering. Prior to sputtering, the analysis revealed the expected $Pd3d_{5/2}$ and $Pd3d_{3/2}$ peaks at binding energies of 334.6 and 339.9 eV

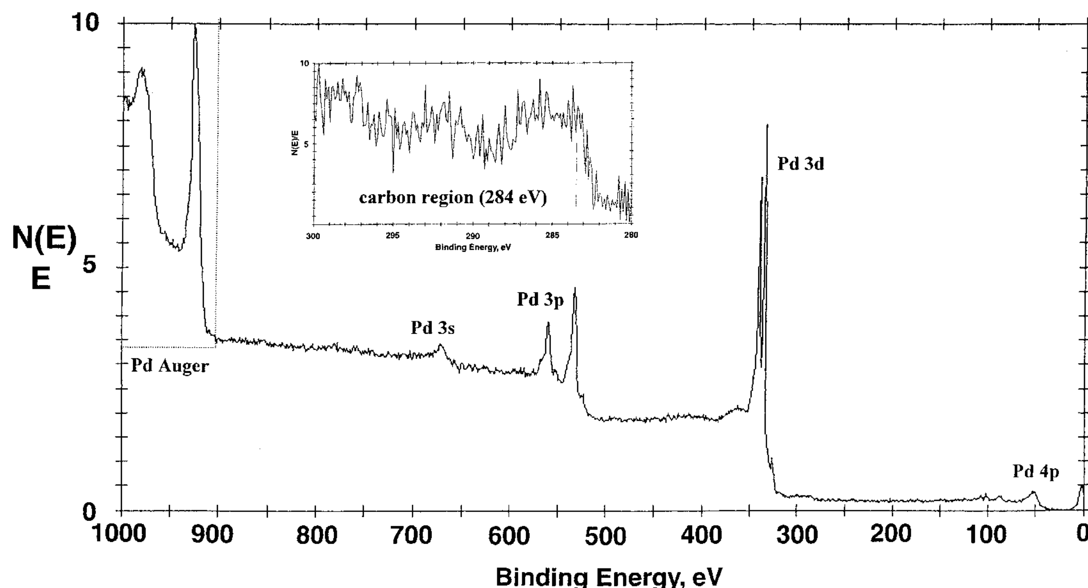


Figure 2. XPS survey of a Pd film deposited onto polyimide by reduction of a 0.2 wt % solution of $CpPd(\pi\text{-}C_4H_7)$ in CO_2 at 138 bar and 60 °C. The spectrum was collected after Ar^+ sputtering to remove atmospheric contaminants. The inset is the multiplex scan of the carbon 1s (284 eV) region showing no measurable levels of contamination.

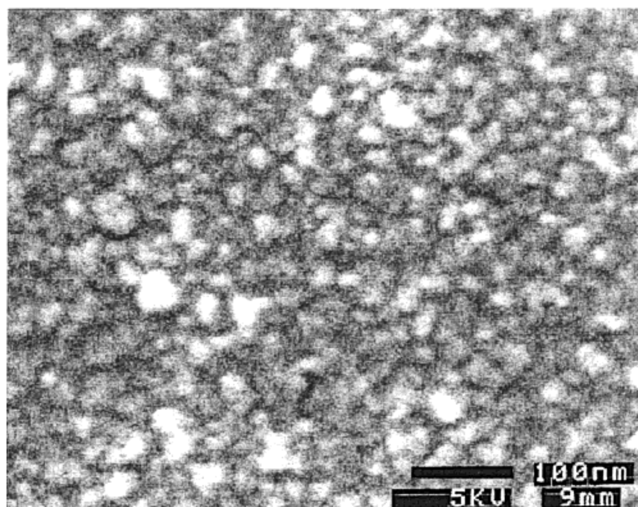
respectively, and the presence of considerable carbon contamination as evident by the C 1s peak 284.5 eV. After Ar^+ sputtering to remove the atmospheric contaminants, the carbon peak receded to below the limit of detection of the instrument and could not be meaningfully quantified by multiplex analysis (see inset). These results are in sharp contrast to the extensive carbon contamination observed in CVD studies using cyclopentadienyl precursors.[12,25] XPS survey spectra for palladium films deposited by hydrogen-assisted CVD from $CpPd(\pi\text{-}C_3H_5)$ at 45 °C published by Hierso et al. exhibit clearly resolved C 1s peaks after sputtering, indicating carbon contamination in excess of 26 atom % (3 wt %).[12] Increasing temperature reduces, but does not eliminate the residual carbon. Films prepared at 250 °C by CVD using $CpPd(\pi\text{-}C_3H_5)$ by Gozum et al. contain ~5% carbon.[25] Two factors may explain the marked decrease in contamination upon deposition from CO_2 relative to CVD. First, hydrogenolysis of $CpPd(\pi\text{-}C_4H_7)$ in CO_2 yields only the fully reduced byproducts (cyclopentane and isobutane, vide infra) that adsorb weakly to the incipient metal surface relative to unsaturated byproducts of hydrogen-assisted CVD of $CpPd(\pi\text{-}C_3H_5)$, which include cyclopentadiene and cyclopentene. Second, the solubility of isobutane and cyclopentane in CO_2 facilitates desorption of these potential contaminates from the film surface.

Hydrogenolysis of $Pd(hfac)_2$ in CO_2 yields high-purity Pd films. XPS analysis indicated films deposited from 0.2 wt % and 0.6 wt % $Pd(hfac)_2$ precursor solutions in CO_2 were free of carbon impurities within the detection limits of the instrument. Moreover, fluorine was not detected in any of the films deposited from $Pd(hfac)_2$, which further suggests that ligand-derived contamination does not occur. These results are consistent with recent low-temperature CVD studies.[11]

The morphology of palladium films deposited onto polyimide using $CpPd(\pi\text{-}C_3H_5)$ and $Pd(hfac)_2$ was studied using SEM (Figure 3). The film deposited from $Pd(hfac)_2$ contains grains of ~10 nm in size while deposition from $CpPd(\pi\text{-}C_4H_7)$ yielded well-defined grains between ~30 and ~70 nm in diameter. The larger grain size observed using $CpPd(\pi\text{-}C_4H_7)$ as the precursor relative to films deposited from $Pd(hfac)_2$ was typical under the deposition conditions studied. SEM analysis of the polymer/Pd film cross sections revealed Pd was not deposited within the substrate. This is an expected result as polyimide exhibits excellent barrier properties. WAXD of the deposited film revealed characteristic reflections from the (111), (200), and (220) Pd crystal planes. Film thickness in these batch experiments is dictated by the initial loading of the precursor. At the conditions studied, films deposited onto polyimide from $Pd(hfac)_2$ and $CpPd(\pi\text{-}C_4H_7)$ were 100 to 200 nm thick, as calculated by mass gain and confirmed by analysis of film cross sections by SEM. Thicker films can be grown by sequential batch deposition cycles or by the use of a continuous flow reactor, but simply increasing precursor concentration in the batch process yields poor results. From variable volume view cell experiments, it was found that the solubility of both precursors readily exceeds 1 wt % at 60 °C and 138 bar. However, operation at concentrations above 1 wt % leads to gas-phase nucleation and deposition of Pd particulates, which degrades film quality. Gas-phase nucleation is also observed upon rapid addition of excess H_2 at all precursor concentrations. This problem is mitigated by limiting the rate of H_2 addition to less than 200 μmols/min using a needle valve. The appearance of Pd clusters upon rapid H_2 addition is consistent with observations of gas-phase nucleation in CVD processes using $Pd(hfac)_2$ at high hydrogen partial pressures.[11]

Adhesion of the Pd films to the substrates was assessed qualitatively by the application and removal of adhesive tape. Adhesion of films deposited onto polyimide using $CpPd(\pi\text{-}C_4H_7)$ is good: the continuous metal coating is not damaged by the test and no metal is observed on the adhesive tape after its removal. The

(25) Gozum, J. E.; Pollina, D. M.; Jensen, J. A.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 2688.



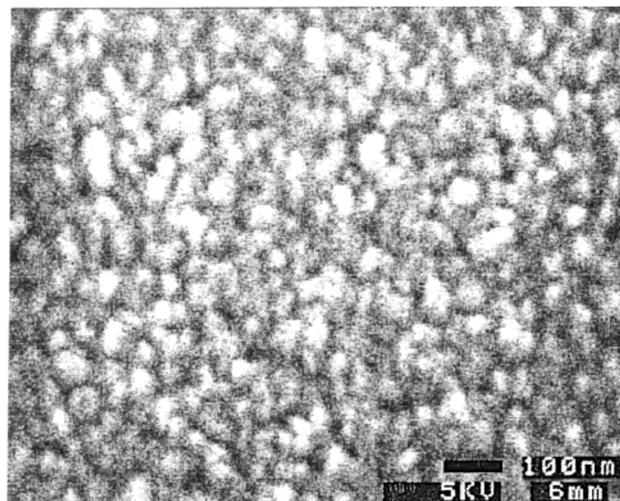


Figure 3. SEM micrographs of palladium films deposited onto polyimide from (a) a 0.2 wt % solution of $Pd(hfac)_2$ in CO_2 at 124 bar and 60 °C and (b) a 0.2 wt % solution of $CpPd(\pi\text{-}C_4H_7)$ in CO_2 at 138 bar and 60 °C.

adhesion of the Pd films deposited via $Pd(hfac)_2$ onto virgin polyimide is fair: removal of the pressure-sensitive adhesive results in partial failure at the metal polymer interface. Surface modification of the polymer substrate eliminates this problem. For example, deposition of Pd films onto polyimide pretreated by acid hydrolysis yields tenaciously adherent films.[26] Adhesion of all films deposited by hydrogenolysis of all precursors onto native Si wafers was relatively poor and films could easily be removed by the tape or by abrasion. Adhesion of films deposited by thermal decomposition onto all substrates was good.

The efficacy of deposition via thermolytic reduction was investigated using the labile precursor, $(\pi\text{-}C_3H_5)$-Pd(acac), which decomposes slowly at room temperature. Thermolysis of $(\pi\text{-}C_3H_5)$Pd(acac) in neat CO_2 at 40 °C for 14 h, yielded dark, poorly reflective films. XPS analysis confirmed extensive carbon contamination (~8 atom %). Film purity can be substantially improved by the addition of hydrogen immediately following dissolution of the precursor; however, XPS analysis revealed that films deposited in this manner contain traces of carbon. Moreover this procedure yielded discontinuous, nonuniform films. NMR analysis of the decomposition products (see below) suggests thermolysis and hydrogenolysis can occur competitively under the conditions studied. The thermal stability of this class of precursors can be improved by altering the ligand structure. For example, unlike $(\pi\text{-}C_3H_5)$Pd(acac), $(\pi\text{-}C_4H_7)$Pd(acac) is reportedly stable at room temperature[14] and may prove to be a better Pd precursor for film formation via hydrogenolysis. Given the excellent results obtained with $CpPd(\pi\text{-}C_4H_7)$, however, we did not further pursue additional depositions using (allyl)Pd(acac) precursors.

Organic Byproducts and Mechanistic Considerations. Hydrogenolysis of organoplatinum and organopalladium compounds is autocatalytic in both organic solution and the vapor phase.[27,28] We expect a similar mechanism for reactive depositions from CO_2. Reduction of deep red solutions of $CpPd(\pi\text{-}C_4H_7)$ in supercritical CO_2 within a variable volume view cell proceeds immediately upon addition of H_2 as evidenced by the immediate loss of all color in the cell and the formation of a metallic film on the quartz window. Nuclear magnetic resonance spectroscopy (NMR) was used to analyze the products of $CpPd(\pi\text{-}C_4H_7)$ hydrogenolysis

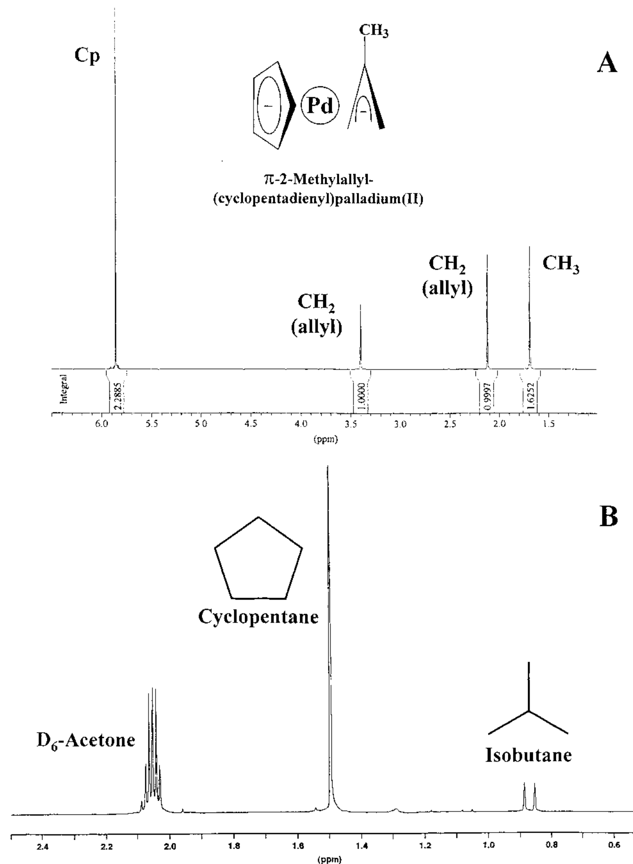


Figure 4. ^1H NMR (200 MHz) of $CpPd(\pi\text{-}C_4H_7)$ before (a) and after (b) reduction with H_2 in CO_2 (138 bar/40 °C). Part b confirms that the reduction products from $CpPd(\pi\text{-}C_4H_7)$ are entirely cyclopentane and isobutane by the presence of a singlet at 1.5 ppm and a doublet at 0.87 ppm. ^1H NMR spectra are referenced to residual protons in $CDCl_3$ at 7.27 ppm (a) and acetone-d_6 at 2.05 ppm (b).

(26) Li, J.; Watkins, J. J. Manuscript in preparation, 1999.
(27) Miller, T. M.; Izumi, A. N.; Shih, Y.-S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3146.
(28) Zinn, A. A.; Brandt, L.; Kaesz, H. D.; Hicks, R. F. In *The Chemistry of Metal CVD*; Kodas, T. T., Hampden-Smith, M. J., Ed.; VCH: New York, 1994.

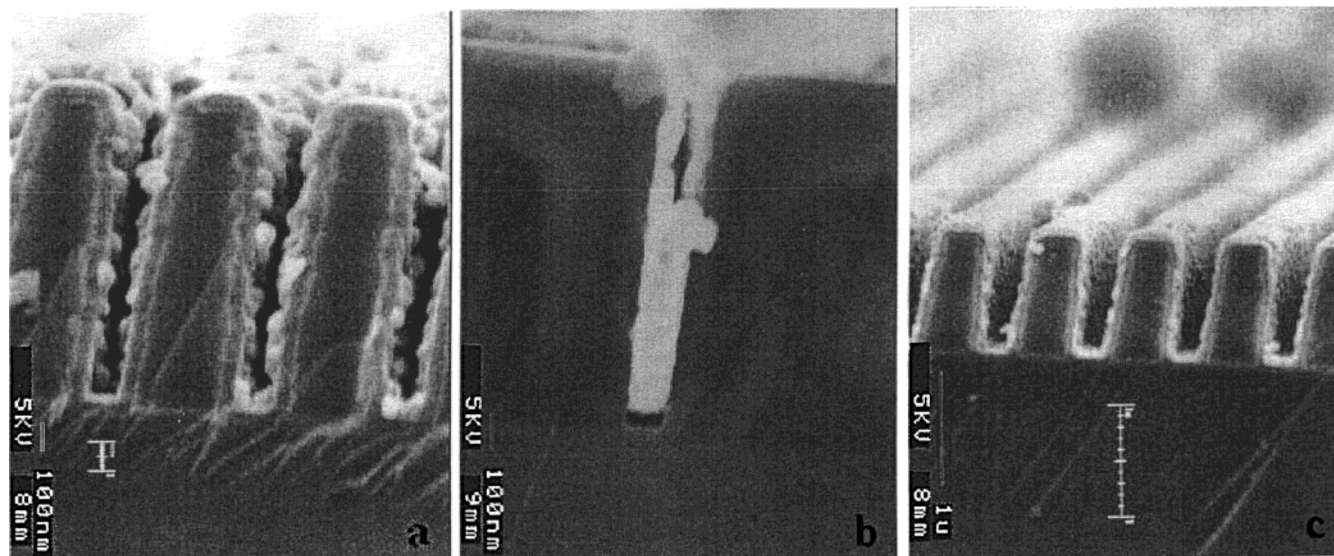
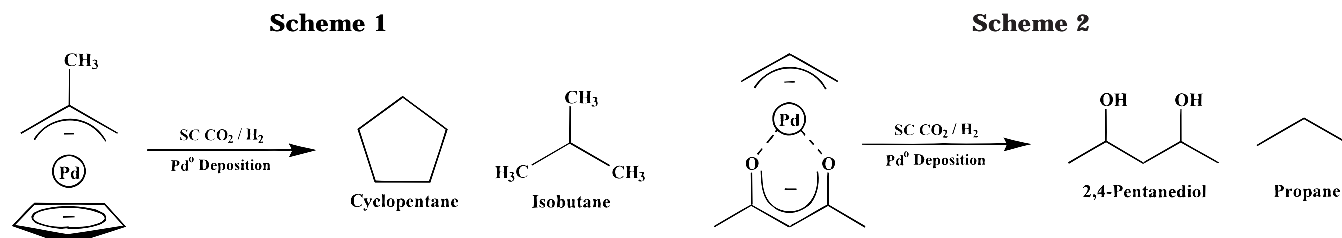


Figure 5. SEM micrographs of palladium films grown on patterned Si wafers using a 0.26 wt % solution of $CpPd(\pi\text{-}C_4H_7)$ in CO_2 at 138 bar and 60 °C. All features are ~1 μm deep with the widths of the etched features as follows: (a, b) 0.12 μm, (c) 0.3 μm (measured at $^1/_2$ the trench height). Separation of the palladium film in b from the bottom of the feature is likely due to adhesive failure during the fracturing process.



in CO_2. Samples for analysis were obtained by passing the effluent gases from the reaction vessel through either deuterated acetone or chloroform. ^{1}H NMR spectra obtained from samples taken before and after deposition of palladium from $CpPd(\pi\text{-}C_4H_7)/CO_2$ solution at 138 bar and 40 °C are shown in Figure 4. Complete reduction of all ligands under these conditions was confirmed by the appearance of a singlet at 1.5 ppm and a doublet at 0.87 ppm corresponding to the protons in cyclopentane and the methyl groups in isobutane, respectively (Figure 4b). The remaining proton of isobutane $[(CH_3)_3-C-H]$ overlaps with a signal attributed to the solvent. An additional signal, appearing as a singlet, is observed at 2.86 ppm and is attributed to dissolved hydrogen. This was confirmed by analysis of H_2-saturated acetone-*d* solutions. No additional proton signals are observed, confirming complete reduction of all double bonds of the cyclopentadienyl and allyl ligands to their expected alkane analogues (Scheme 1). These products are not surprising given the relatively high concentrations of hydrogen in the miscible H_2/CO_2 solution and the presence of Pd, an effective hydrogenation catalyst. By contrast, Hierso et al.[12] examined the organic byproducts from hydrogen-assisted CVD of Pd from $CpPd(\pi\text{-}C_3H_5)$ at 35 °C. GC/MS analysis of the trapped residues revealed the presence of cyclopentadiene, cyclopentene, cyclopentane, and propane, indicating incomplete reduction of the Cp ligand.

The reduction of $CpPd(\pi\text{-}C_4H_7)$ in CO_2 upon H_2 addition is rapid at the conditions used in these depositions. Hydrogenation was monitored by removing small aliquots of the reaction media at regular time intervals following introduction of H_2 to the solution of $CpPd(\pi\text{-}C_4H_7)$ in CO_2 at 40 °C. NMR analysis of the effluent indicates that the precursor is completely consumed within the first two minutes of the reaction: all resonances assigned to $CpPd(\pi\text{-}C_4H_7)$ are absent and replaced by the signals from cyclopentane, isobutane, hydrogen, and only trace amounts of unidentified, unsaturated species. Analysis of a second aliquot, taken from the reaction 22 min after H_2 addition, indicates complete hydrogenation of the trace, unsaturated products. The third, and all subsequent aliquots taken after 42 min, revealed the peaks are invariant with additional reaction time. These results are consistent with observations in the view cell that suggest there is no significant induction period for the reaction.

The products from the hydrogenolysis of $(\pi\text{-}C_3H_5)Pd(acac)$ at 40 °C and 103 bar and thermolysis at 40 °C and 103 bar were also analyzed. Following hydrogenolysis, the spectra reveal signals at 0.810 and 1.51 ppm that are characteristic of propane (resulting from hydrogenation of the bound allyl group), which appear as the expected triplet and multiplet, respectively. An additional set of resonances was also observed at 1.05 ppm (d), 1.94 ppm (mult), 2.95 ppm (br s), and 4.06 (mult) and match those of 2,4-pentanediol ($C_5H_{12}O_2$) (Scheme 2). A third, unidentified minor product is observed between 1.6 and 1.9 ppm. This species is the only ligand product when deposition was performed thermally and is presumed to be the result of decomposition via reductive elimination prior to the introduction of H_2. The proton resonances corresponding to propane and 2,4-pentanediol evident upon the hydro-

genolysis of (π-C_3H_5)Pd(acac) are not observed when this precursor is decomposed thermally. Finally, unreacted (π-C_3H_5)Pd(acac) or the presence of 2,4-pentanedione ($C_5H_8O_2$) was not detected in either the thermolysis or hydrogenolysis products. Puddephatt and co-workers examined the organic byproducts of (π-C_3H_5)Pd(acac) decomposition under hydrogen-assisted CVD conditions using ^{1}H NMR and GC and identified only propane and 2,4-pentanedione ($C_5H_8O_2$).[7] In congruence with the results from hydrogenolysis of CpPd(π-C_4H_7) discussed above, this indicates that ligand reduction is more complete under the conditions of CFD relative to CVD.

Deposition of Palladium onto Patterned-Silicon Test Wafers. As device dimensions are continually reduced to improve performance, the microelectronics industry faces the formidable challenge of uniformly depositing metal within submicrometer, high-aspect ratio features. The advantageous transport properties of SCF solutions and high precursor concentrations inherent to CFD are ideally suited to these applications. Using this approach we deposited conformal palladium films onto silicon test wafers with features as small as 0.1 μm wide by 1 μm high using the precursor CpPd(π-C_4H_7) via a batch deposition at 138 bar and 60 °C. Cross-sections of the films were prepared for SEM analysis by scoring the reverse of the wafers then fracturing carefully by hand. Images of representative regions are shown in Figure 5. Parts a and b of Figure illustrate deposition within the smallest of these features, which are 100−120 nm in width by 1 μm deep. Figure 5c illustrates results for larger features with dimensions of 0.3 μm wide by 1 μm deep. Palladium deposition was conformal on all surface features forming a thin layer of metal that exactly matched the topography of the wafer, including the corners at the bottom of the etched features. Conformal coverage is maintained in the high-aspect ratio features (0.1 μm wide by 1 μm deep) in which the opposing layers of palladium metal on either side of the feature nearly join. The small space in Figure 5b at the bottom of the feature is likely due to lifting of the metal film from the SiO_2 surface during the wafer fracture. Within the larger features, the thickness of the film is ~100 nm and is uniform along the sides and bottom of each trench. No excess buildup of palladium was observed on the top of the features, which suggests the seams evident in the nearly-filled narrow trenches (Figure 5a,b) could be filled completely by subsequent batch depositions or by deposition in a continuous flow reactor. Thin conformal palladium films could also serve as a seed layer for subsequent electrolytic deposition of other metals, including copper.

The conformal coverage attained by CFD differs markedly from recent reports of Pd CVD.[11] For example, Kodas and co-workers report that Pd CVD using Pd(hfac)$_2$ yields films that vary in thickness from the top to the bottom of 0.5 μm wide by 2 μm deep trench. The asymmetric metal distribution is ascribed to the high surface reaction efficiency of Pd(hfac)$_2$, which when coupled with low vapor phase concentrations inherent to CVD yields feed-rate limited depositions. Such uneven buildup of metal deposits would inevitably lead to bridging of the features.

Conclusions

Chemical fluid deposition provides a flexible route for low-temperature metallization and circumvents precursor volatility constraints associated with CVD. In this report, high-purity Pd films were deposited onto Si wafers and polyimide by hydrogenolysis of organopalladium compounds in CO_2 solution using a batch process at 40−80 °C. Deposition using CpPd(π-C_4H_7) is complete in less than 2 min and yields only pure palladium films and benign, fully hydrogenated ligand decomposition products, cyclopentane and isobutane. Conformal coverage is observed on a patterned Si test wafer with feature sizes of 0.1 μm wide by 1 μm deep. Deposition by hydrogenolysis of Pd(hfac)$_2$ also yielded high-quality films while deposition using (π-C_3H_5)Pd(acac) was sensitive to fluid-phase nucleation and yielded poor-quality films. In all cases, film thickness is dictated by the initial precursor loading. We are presently developing a continuous flow reactor to avoid the limitations of the batch process for the deposition thick films and for the measurement of film growth rate.

Acknowledgment. This work was funded the National Science Foundation (CTS-9734177). Facilities supported by the Materials Research Science and Engineering Center at the University of Massachusetts were used for deposit characterization. J.J.W. gratefully acknowledges additional support from the David and Lucile Packard Foundation.

CM000118E