Reactive Deposition of Conformal Palladium Films from Supercritical Carbon Dioxide Solution

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High-purity palladium films were deposited onto Si wafers and polyimide by the reduction of organopalladium compounds in supercritical CO₂ solution using a batch process at temperatures between 40 and 80 °C and pressures between 100 and 140 bar. Hydrogenolysis of \( \pi \)-2-methylallyl(cyclopentadienyl)palladium(II) in CO₂ 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 \( \mu \text{m} \) wide by 1.0 \( \mu \text{m} \) deep is strictly conformal, including uniform coverage of the lower corners and bottoms of the trenches. Deposition by hydrogenolysis of palladium(II) hexafluoropropionate also yields high-quality films while deposition using \( \pi \)-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 H₂ 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 electrodeless 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 coverage⁸⁻⁹ 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 H₂ or O₂ to facilitate deposition. For example, substantial improvements in Pd film purity upon the addition of H₂ 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) hexafluoropropionate, Pd(hfac)₂, using hydrogen-assisted CVD at temperatures as low as 80 °C,¹¹ although similar success has not been reported.

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with other precursors. Deposition from \( \tau \)-allylpalladium hexafluoroacetylacetonate, \( (\tau-C_3H_5)Pd(hfac) \), in the presence of hydrogen at 140 °C, for example, yields films contaminated with 15 atomic % (atom %) carbon,\(^\text{14}\) while the nonfluorinated precursor, \( \text{allyl}(\text{cyclcopentadienyl}) \)-palladium(II), \( \text{CpPd}(\tau-C_3H_5) \), yields films containing less than 20 atom % carbon in the presence of \( \text{H}_2 \) at 45 °C.\(^\text{12}\)

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, \( \text{Pd}(hfac)_2 \) 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.\(^\text{11,15,16}\) Despite its high volatility, depositions from \( \text{Pd}(hfac)_2 \) at 120 °C in the presence of \( \text{H}_2 \) are feed rate limited, which precludes uniform trench filling.\(^\text{11}\)

A promising series of fluorinated \( \text{allyl}(\beta\text{-diketonato}) \)-palladium complexes, including some liquid precursors has recently been prepared by Puddephatt.\(^\text{7}\) CVD using these compounds in the presence of \( \text{H}_2 \) or \( \text{O}_2 \) 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).\(^\text{17,18}\) This method has multiple advantages. First, since \( \text{CO}_2 \) is a good solvent for a broad range of organometallic compounds\(^\text{19,20}\) 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.\(^\text{18}\) Moreover, supercritical \( \text{CO}_2 \) is completely miscible with gaseous reducing agents such as \( \text{H}_2 \). High reagent concentrations in CFD will mitigate mass-transfer limitations and promote conformal film growth. Second, the elimination of the volatility requirements 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 \( \text{CO}_2 \) 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 adsors 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\(^\text{21}\) 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 \( \text{Co}_2 \) solutions of palladium(II) hexafluoroacetylacetonate, \( \tau\text{-allyl}(2,4\text{-pentanedionato})\text{palladium(II)} \), and \( \tau\text{-2-methylallyl(cyclcopentadienyl)palladium, \text{CpPd}(\tau-C_3H_5) \), using a batch process.

**Experimental Section**

Allylpalladium chloride dimer, \( \text{palladium(II)} \), and cyclopentadienythallium (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 for air or moisture sensitive reactions were dried over sodium and benzophenone ketyl and then distilled under an atmosphere of purified argon.

\( \tau\text{-Allyl}(2,4\text{-pentanedionato})\text{palladium(II)} \) was synthesized using literature procedures immediately prior to use.\(^\text{22}\) The compound was found to be pure by proton NMR. \( ^1H \) NMR: 200 MHz in CDC\(_3\), 2.01 ppm (s, 6H, CH\(_3\) acac), 2.90 ppm (d, J\(_{\text{H-H}} = 11.9 \text{ Hz}, 2 \text{H}, \text{anti-H of CH}_2\)), 3.88 ppm (d, J\(_{\text{H-H}} = 6.8 \text{ Hz}, 2 \text{H}, \text{syn-H of CH}_2\)), 5.39 ppm (s, 1H, CH\(_3\) allyl), 5.57 ppm (triplet of triplets, 1H, C–H allyl). 2-Methylallylpalladium chloride dimer, \( (\tau\text{-C}_3\text{H}_5)\text{PdCl}_2 \), was prepared according to standard literature procedures\(^\text{23}\) and found to be pure by proton NMR. \( ^1H \) NMR: 200 MHz in CDC\(_3\), 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\(_2\)).

\( \tau\text{-2-Methylallyl(cyclcopentadienyl)palladium(II)} \) was synthesized from \( (\tau\text{-C}_3\text{H}_5)\text{PdCl}_2 \) and cyclopentadienythallium. In a standard preparation, 2.63 g (6.676 mmol) of \( (\tau\text{-C}_3\text{H}_5)\text{PdCl}_2 \) 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

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 was then dried overnight in air at 100 °C. The samples were then dried in a vacuum oven at 100 °C and maintained at this temperature until analysis.

All depositions from CO2 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 (<100)-oriented Si wafer was placed in a circulating constant-temperature bath (40 °C), and allowed to equilibrate to the desired temperature for 1 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 CO2 mixture were first collected for NMR analysis by venting the vessel through a bubbler containing a suitable solvent prior to directing the effluent to the carbon bed.

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 J EOL 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 cryomicrotomy. 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 hydrogenation of each of the precursors (Figure 1) or by thermal decomposition of (Pd(acac)2) in CO2 at 40–80 °C, pressures being between 100 and 140 bar and precursor concentrations in CO2 ranging from 0.2 to 0.6 wt % (Table 1). A 60–100 fold molar excess of H2 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).

Table 1. Representative Conditions for Pd Film Deposition

<table>
<thead>
<tr>
<th>complex</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>OM wt %</th>
<th>substrate</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(hfac)2</td>
<td>60</td>
<td>124</td>
<td>0.28</td>
<td>polyimide</td>
<td>bright, reflective film; good adhesion</td>
</tr>
<tr>
<td>Pd(hfac)2</td>
<td>80</td>
<td>138</td>
<td>0.29</td>
<td>polyimide</td>
<td>bright, reflective film; good adhesion</td>
</tr>
<tr>
<td>Pd(hfac)2</td>
<td>60</td>
<td>124</td>
<td>0.3</td>
<td>Ti/W-Si</td>
<td>reflective film; poor adhesion</td>
</tr>
<tr>
<td>Pd(hfac)2</td>
<td>60</td>
<td>103</td>
<td>0.38</td>
<td>Si wafer</td>
<td>bright, nonuniform film; poor adhesion</td>
</tr>
<tr>
<td>Pd(hfac)2</td>
<td>60</td>
<td>103</td>
<td>0.25</td>
<td>polyimide</td>
<td>bright, nonuniform film</td>
</tr>
<tr>
<td>Pd(hfac)2</td>
<td>60</td>
<td>103</td>
<td>0.24</td>
<td>polyimide</td>
<td>bright, nonuniform film</td>
</tr>
<tr>
<td>CpPd(3-C3H5)Pd(acac)</td>
<td>40</td>
<td>138</td>
<td>0.36</td>
<td>polyimide</td>
<td>thermolysis, dull gray film, carbon contamination</td>
</tr>
<tr>
<td>CpPd(3-C3H5)Pd(acac)</td>
<td>60</td>
<td>103</td>
<td>0.21</td>
<td>polyimide</td>
<td>bright, reflective film; good adhesion</td>
</tr>
<tr>
<td>CpPd(3-C3H5)Pd(acac)</td>
<td>60</td>
<td>103</td>
<td>0.25</td>
<td>polyimide</td>
<td>bright, reflective film; good adhesion</td>
</tr>
<tr>
<td>CpPd(3-C3H5)Pd(acac)</td>
<td>60</td>
<td>138</td>
<td>0.26</td>
<td>patterned Si wafer</td>
<td>bright, reflective film, conformal coverage</td>
</tr>
</tbody>
</table>

Concentration of organometallic compound in CO2 solution. See text for explanation of adhesion terms. Si wafer sputtered with ~7 nm of 80% Ti/12% W. Depositions performed thermally without hydrogen addition (see text for details).

Figure 1. Precursors used in this study: (1) Pd(hfac)2, (2) (3-C3H5)Pd(acac), and (3) CpPd(π-C3H5).
respectively, and the presence of considerable carbon contamination as evident by the C 1s peak at 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(\(\pi\)-C\(_3\)H\(_5\)) at 45 °C published by Hirsero et al. exhibit clearly resolved C 1s peaks after sputtering, indicating carbon contamination in excess of 26 atom % ($\sim$3 wt %).$^{12}$ Increasing temperature reduces, but does not eliminate the residual carbon. Films prepared at 250 °C by CVD using CpPd(\(\pi\)-C\(_3\)H\(_5\)) by Gozum et al. contain $\sim$5% carbon.$^{25}$ Two factors may explain the marked decrease in contamination upon deposition from CO\(_2\) relative to CVD. First, hydrogenolysis of CpPd(\(\pi\)-C\(_4\)H\(_7\)) 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(\(\pi\)-C\(_3\)H\(_5\)), which include cyclopentadiene and cyclopentene. Second, the solubility of isobutane and cyclopentane in CO\(_2\) facilitates desorption of these potential contaminants 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(\(\pi\)-C\(_3\)H\(_3\)) and Pd(hfac)\(_2\) was studied using SEM (Figure 3). The film deposited from Pd(hfac)\(_2\) contains grains of $\sim$10 nm in size while deposition from CpPd(\(\pi\)-C\(_3\)H\(_7\)) yielded well-defined grains between $\sim$30 and $\sim$70 nm in diameter. The larger grain size observed using CpPd(\(\pi\)-C\(_4\)H\(_7\)) 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(\(\pi\)-C\(_3\)H\(_3\)) 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 particles, 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 $\mu$mol/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(\(\pi\)-C\(_3\)H\(_7\)) 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

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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, (π-C$_3$H$_5$)Pd(acac), which decomposes slowly at room temperature. Thermolysis of (π-C$_3$H$_5$)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 (π-C$_3$H$_5$)Pd(acac), (π-C$_4$H$_7$)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(π-C$_4$H$_7$), 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

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in CO₂. Samples for analysis were obtained by passing the effluent gases from the reaction vessel through either deuterated acetone or chloroform. "H NMR spectra obtained from samples taken before and after deposition of palladium from CpPd(\(\pi\)-C₄H₇)/CO₂ 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 ([CH₃]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 H₂-saturated acetone–d₆ 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).

The reduction of CpPd(\(\pi\)-C₆H₆) in CO₂ upon H₂ 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 H₂ to the solution of CpPd(\(\pi\)-C₆H₆) in CO₂ 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(\(\pi\)-C₆H₆) 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 H₂ 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 (\(\pi\)-C₃H₅)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 ppm (mult) and match those of 2,4-pentanediol (C₅H₁₀O₂) (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 H₂. The proton resonances corresponding to propane and 2,4-pentanediol evident upon the hydro-
genolysis of (\(\pi\)-C\(_3\)H\(_3\))Pd(acac) are not observed when this precursor is decomposed thermally. Finally, unreacted (\(\pi\)-C\(_3\)H\(_3\))Pd(acac) or the presence of 2,4-pentanedione (C\(_5\)H\(_8\)O\(_2\)) was not detected in either the thermolysis or hydrogenolysis products. Puddephatt and co-workers examined the organic byproducts of (\(\pi\)-C\(_3\)H\(_3\))Pd(acac) decomposition under hydrogen-assisted CVD conditions using \(^1\)H NMR and GC and identified only propane and 2,4-pentanedione (C\(_5\)H\(_8\)O\(_2\)). In congruence with the results from hydrogenolysis of CpPd(\(\pi\)-C\(_3\)H\(_3\)) 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 \(\mu\)m wide by 1 \(\mu\)m high using the precursor CpPd-(\(\pi\)-C\(_4\)H\(_7\)) 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 \(\mu\)m deep. Figure 5c illustrates results for larger features with dimensions of 0.3 \(\mu\)m wide by 1 \(\mu\)m 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 \(\mu\)m wide by 1 \(\mu\)m 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 electrolys deposition of other metals, including copper.

The conformal coverage attained by CFD differs markedly from recent reports of Pd CVD. For example, Kodas and co-workers report that Pd CVD using Pd(hf\(_{\text{ac}}\))\(_2\) yields films that vary in thickness from the top to the bottom of 0.5 \(\mu\)m wide by 2 \(\mu\)m deep trench. The asymmetric metal distribution is ascribed to the high surface reaction efficiency of Pd(hf\(_{\text{ac}}\))\(_2\), 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 in microelectronics. 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(\(\pi\)-C\(_3\)H\(_3\)) is complete in less than 2 min and yields only pure palladium films and benzene, fully hydrogenated ligand decomposition products, cyclopentane and isobutane. Conformal coverage is observed on a patterned Si test wafer with feature sizes of 0.1 \(\mu\)m wide by 1 \(\mu\)m deep. Deposition by hydrogenolysis of Pd(hf\(_{\text{ac}}\))\(_2\) also yielded high-quality films while deposition using (\(\pi\)-C\(_3\)H\(_3\))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.

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