Chemical Fluid Deposition: Reactive Deposition of Platinum Metal from Carbon Dioxide Solution

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Chemical vapor deposition (CVD) is an established, versatile technique for the preparation of high-quality metal and semiconductor thin films on solid surfaces.[1,2] Despite its utility, constraints inherent to the process, including the requirement of high precursor vapor pressure and thermally coupled transport and deposition steps, generally preclude its use at low temperature and for non-line-of-sight applications such as the metallization of microporous and mesoporous supports. In this report, we describe chemical fluid deposition, a fundamentally new approach to metal deposition that involves the chemical reduction of soluble organometallic compounds in supercritical carbon dioxide at low temperature.[3] The process circumvents the limitations described above and yields CVD-quality deposits on polymer and inorganic solid surfaces and within porous inorganic supports at modest temperature (80 °C).

In thermal CVD, a volatile precursor is transported into a deposition chamber by means of a carrier gas. The precursor adsorbs to a heated surface and reacts to yield a metal atom and surface-bound ligand decomposition products, which subsequently desorb from the nascent surface and are removed from the reactor. Inorganic precursors such as metal halides produce pure metal films, but deposition temperatures are prohibitively high, often in excess of 600 °C. Organometallic or metal−organic compounds can yield metal films at less severe conditions, but temperatures above 250 °C are usually required to maintain acceptable purity and deposition rates. Under these conditions, film purity and precursor decomposition rates are often enhanced by the addition of a reducing agent such as hydrogen gas.

Current research in metal CVD is directed at achieving still lower deposition temperatures through precursor design.[4] Reduced temperatures would suppress the development of thermal−mechanical stress during device fabrication,[5] minimize interdiffusion and reaction between adjacent layers, and accelerate the development of polymer-based dielectrics. Unfortunately, since desorption of the ligand decomposition products is thermally activated, reducing CVD deposition temperature typically increases contamination of the film. Moreover, low-temperatures exacerbate precursor volatility constraints: low concentrations of precursor in the vapor can result in mass-transfer limitations to film deposition, position dependent growth rates, and thus nonuniform films. Therefore, at low temperature, the combination of low precursor volatility, unfavorable adsorption equilibrium constants for ligand desorption, and sluggish decomposition kinetics are at odds with the nature of the thermal CVD.

Table 1. Comparison of Reduction Media for the Deposition of Metal Films

	liquid	SCF	gas (CVD)
density (g/cm^3)	1	0.1−1	10^{-3}
viscosity (Pa s)	10^{-3}	10^{-4}−10^{-5}	10^{-5}
diffusivity (cm^2/s)	10^{-5}	10^{-3}	10^{-1}
precursor concn (M/cm^3)[a]	10^{-5}	10^{-5}	10^{-8}
hydrogen concn (M/cm^3)	10^{-4}	10^{-2}	10^{-4}

[a] The precursor concentrations cited are for CODPtMe$_2$ in liquid heptane[7] and CO$_2$ (this work).

Chemical fluid deposition (CFD) offers a flexible alternative to CVD. The key to CFD is the physicochemical properties of the solvent, which lie intermediate to those of liquids and gases. Table 1 compares process parameters for metal deposition from vapor, liquid, and supercritical fluid (SCF) media. The density of supercritical CO$_2$ can approach or exceed that of liquids, and thus it can be a good solvent for organometallic compounds and their organic decomposition products. Consequently, precursor transport occurs in solution and reduction occurs at the solution/solid interface at significantly lower temperatures and higher reagent concentrations than those of vapor-phase techniques such as CVD. Moreover, while the presence of SCF CO$_2$ as solvent facilitates desorption of ligand decomposition products, it adsorbs only weakly to metal surfaces and is unlikely to cause contamination or compete with precursor for active sites. Finally, although CFD is solution-based, the transport properties of the SCF[5] (low viscosity and high diffusivity relative to liquids), the absence of surface tension, and its miscibility with gaseous reducing agents, such as H$_2$, render the process unencumbered by issues of poor mass transfer and poor deposition rates associated with liquid phase reductions. Thus, CFD uniquely combines the advantages of CVD and liquid-phase epitaxy while minimizing the disadvantages of each.

Here we validate CFD for the deposition of CVD-quality platinum metal films on silicon wafers and polymer substrates via hydrogenolysis of dimethyl(cyclooctadiene)platinum(II) (CODPtMe$_2$) at 80 °C. Pt films have a number of uses, such as corrosion resistant contacts for microelectronic devices. We also demonstrate that independent control of the transport (via solution) and deposition mechanisms (via chemical reducing agent) renders CFD effective for the metallization of porous solids. This deposition scheme is particularly well-suited for the preparation of nonacidic supported Pt catalysts. We choose CODPtMe$_2$ as the

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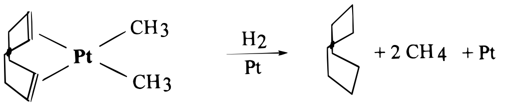
precursor for several reasons. First, although the low volatility of $CODPtMe_2$ is a significant handicap, high-purity Pt films have been obtained from the precursor via CVD in the presence of H_2 with temperatures in excess of 250 °C.[6] Second, unlike most CVD precursors, detailed information regarding the thermal decomposition and reduction of $CODPtMe_2$ with H_2 is available. The heterogeneous reduction of $CODPtMe_2$ with H_2 over platinum black in *n*-heptane proceeds readily at room temperature and has been shown to be autocatalytic (eq 1). The reaction, however, is mass-transport-limited at



(1)

temperatures above −20 °C by transport of hydrogen across the heptane/H_2 interface.[7] Finally, $CODPtMe_2$ is attractive due to its high platinum content (58.5 wt %), low toxicity of the ligands, and heptane solubility, which is a good indicator of solubility in CO_2.[8]

All depositions were conducted in high-pressure stainless steel reactors using variants of the following procedure. A single substrate (~1 × 4 cm section of a polished Si wafer, poly(tetrafluoroethylene), Kapton polyimide, or Anopore aluminum oxide membrane) and a known mass of precursor were placed in ~1.2 cm (i.d.) by 10 cm sections of $^1/_2$ in. schedule 160 seamless pipe sealed with a plug at one end and a high-pressure needle valve at the other. The vessel was purged with CO_2, weighed, and immersed in a circulating controlled-temperature bath equilibrated at 80 °C. Compressed CO_2 was transferred using a high-pressure manifold, as described previously.[9] The contents of the reactor were mixed using a vortex mixer, reequilibrated to 80 °C, and repressurized to the desired pressure; the mass of CO_2 transferred was determined gravimetrically. The vessel was maintained under these conditions (which are nonreducing for the precursor) for a period of at least 1 h to ensure complete dissolution of the precursor and even heating. Hydrogen gas was then transferred from a small manifold (3.2 mL) consisting of a section of high-pressure tubing capped at either end with $^1/_8$ in. high-pressure valves and equipped with a pressure gauge. The mass of H_2 transferred (usually a 15-fold molar excess) was metered into the vessel by controlling the pressure drop in the manifold during the transfer. The reduction was carried out for at least 1 h. The complete miscibility of H_2 with SCFs[10,11] obviates concerns regarding H_2 solubility and mass transfer that are often limiting in liquid-phase reductions. Experiments performed in an optical cell confirmed the solubility and stability of the precursor in the absence of H_2 under all conditions used.[12]

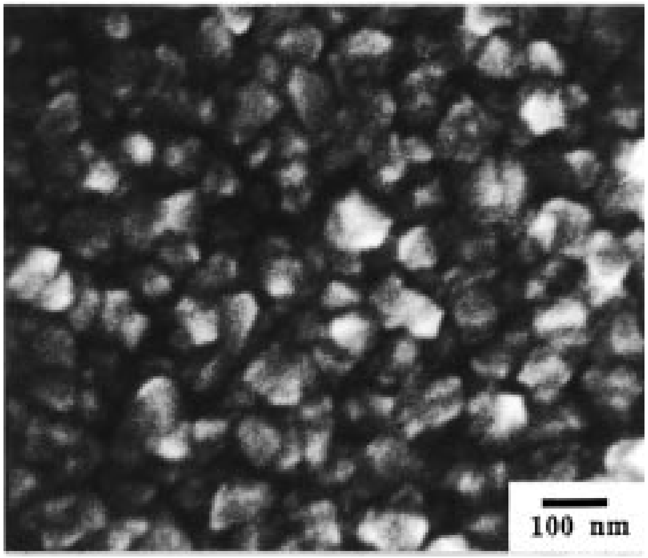


Figure 1. SEM micrograph of a Pt film deposited onto a silicon wafer by hydrogenolysis of a 0.6 wt % solution of $CODPtMe_2$ in CO_2 at 80 °C and 155 bar.

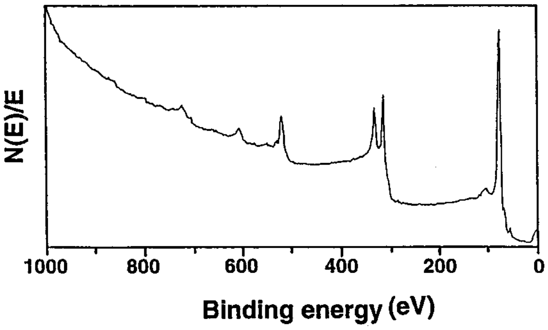


Figure 2. XPS survey spectrum of a Pt film deposited onto a silicon wafer by hydrogenolysis of a 0.6 wt % solution of $CODPtMe_2$ in CO_2 at 80 °C and 155 bar.

Platinum metal was deposited onto Si wafers from 0.6 wt % $CODPtMe_2/CO_2$ solutions at 80 °C and 155 bar upon addition of a ~15× molar excess of H_2 gas, yielding adherent, continuous, and reflective films. Scanning electron microscopy (SEM) analysis of the uncoated metal film using a JEOL 35 microscope revealed well-defined ~80−100 nm platinum crystals (Figure 1). The platinum film was approximately 1.3 μm thick and uniform, as determined by SEM analysis of fracture cross sections of the metallized wafer. X-ray photoelectron spectroscopy (XPS) using a Perkin-Elmer Physical Electronics 5100 spectrometer with Mg Kα excitation (400 W, 15.0 kV) indicated that the film was free of ligand-derived contamination. Figure 2 shows an XPS survey spectrum of the film taken after sputter cleaning (Ar^+ ions) to remove atmospheric contaminates. The small C_{1s} carbon peak (284 eV) observed in the spectrum is at the detection limit of the instrument and could not be meaningfully quantified by multiplex analysis. The continuity of the film is confirmed by the absence of Si_{2s}

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peaks at 153 eV. (Si_{2p} peaks at 102 and 103 eV, if present, would be obscured by the Pt_{5s} photoelectron line.) Pt photoelectron lines are observed at the following energies: $4f_{7/2} = 73$ eV, $4f_{5/2} = 76$ eV, $4d_5 = 316$ eV, $4d_3 = 333$ eV, $4p_3 = 521$ eV, $4p_1 = 610$ eV, $4s = 726$ eV. The sampling area of the detector is approximately 4 × 10 mm. By comparison, XPS analysis of Pt films prepared by CVD in the presence of H_2 contained 4% carbon and 2% oxygen.[6]

Platinum metal was deposited on a section of 0.9 mm thick PTFE sheet by the reduction of $CODPtMe_2$ in CO_2. A 1.2 wt % solution of $CODPtMe_2$ in CO_2 was equilibrated with the PTFE sample at 80 °C and 155 bar for 4 h. The precursor was then reduced by the addition of a 15× molar excess of H_2 gas. The sample was recovered following depressurization and exhibited a bright reflective coating. SEM analysis of the polymer/metal composites was performed using a JEOL 6400 FXV field emission SEM. Secondary electron images (1 kV) of the uncoated composite surface revealed ~100 nm Pt clusters. The composite cross section was analyzed by transmission electron microscopy (TEM) performed using a JEOL 100 CX electron microscope. Sections for analysis were obtained by embedding the composite in epoxy and subsequent cryogenic microtomy. Small Pt clusters (~30 nm) were found to be distributed throughout the substrate.[13] Deposition within the substrate is a consequence of permeation of the precursor/CO_2 solution within the polymer, a result that can be avoided by shortening or eliminating the equilibration time prior to reduction.

Deposition of Pt metal on a 12.7 μm thick Kapton polyimide sheet by hydrogenolysis of 0.8 wt % $CODPtMe_2$ in CO_2 solution at 80 °C and 185 bar yields adherent, reflective, and continuous films that are approximately 1 μm thick. SEM analysis of the uncoated film revealed a morphology that is similar to that of the film deposited onto the Si wafer. XPS analysis confirmed that the films are free of ligand-derived contamination. There was no indication of cluster deposition within the substrate.

The utility of CFD for the metallization of microporous solids was investigated using Anopore aluminum oxide membranes having 200 nm straight pores (Whatman International Limited). The pores are oriented perpendicular to the surface, are approximately hexagonally packed, and exhibit a narrow pore size distribution. An 11.3 mg sample of the membrane was exposed to a 0.74 wt % solution of $CODPtMe_2$ in CO_2 at 80 °C and 155 bar for 2 h in a small (ca. 3 mL) reaction vessel. $CODPtMe_2$ was then reduced by the addition of H_2 gas, the vessel was depressurized, and a metallic-gray membrane was recovered. A sample of the metallized membrane was cast in epoxy and cross sectioned by cryomicrotomy. TEM analysis of the sections indicated the presence of small Pt clusters (ca. 30 nm) distributed throughout the pores (Figure 3).

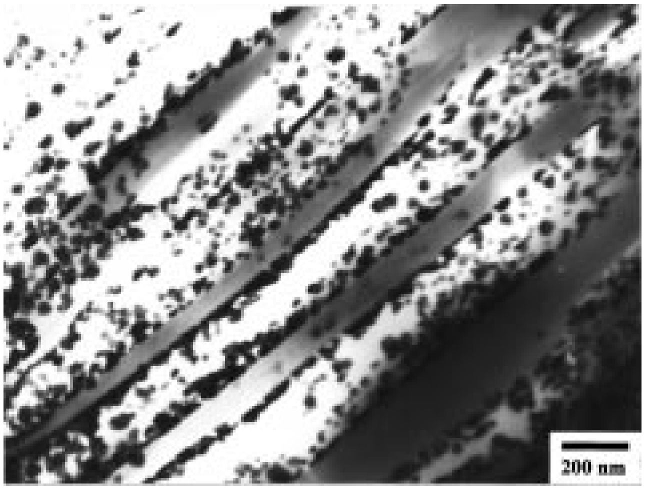

Figure 3. TEM image of Pt clusters deposited within 200 nm pores of an Al_2O_3 membrane by hydrogenolysis of $CODPtMe_2$ in CO_2 at 80 °C and 155 bar.

CFD is ideally suited to the metallization of porous inorganic solids. The transport properties of SCF solutions ensure rapid penetration of the pores. Uniform deposition throughout the pores is further facilitated by independent control of the transport (via solution) and deposition (via chemical reducing agent) mechanisms in CFD. By contrast, these mechanisms are both thermally activated in CVD and are difficult to decouple. In principle, metallization of interstitial cavities by CVD could be conducted at conditions where the deposition is kinetically limited. In practice, however, uniform coatings in tortuous environments, even near the surface, are difficult to achieve using CVD.[14]

In summary, we have developed a simple and effective strategy for the deposition of metals onto and within organic and inorganic substrates by the reduction of organometallic compounds in supercritical carbon dioxide. While others have used SCF solutions to generate aerosols for use in conventional CVD at atmospheric pressure[15,16] and to infuse labile metal precursors into solid polymers which can yield metal clusters by thermolysis after removal of the SCF,[17] we are the first to demonstrate that the reduction of organometallics can proceed readily in SCF solution at low temperature to yield high-purity metal. The requirements of CFD are quite flexible: the precursor must be soluble in CO_2 and the reduction chemistry must proceed rapidly at the deposition temperature of interest. Due to transport in solution at low temperature, precursors that are thermally labile can be employed. A relatively small number of organometallics can bind CO_2. Since CO_2 activation is the exception rather than the rule, this criteria does not exclude a significant number of potential precursors. For transition metal complexes, activation generally requires strong electron-donating ligands, such as phosphines.[18] Finally, while this report is narrowly focused on the deposition of Pt from $CODPtMe_2$, virtually any organometallic compound that is soluble in CO_2 and can be chemically reduced to its base metal is a potential precursor for CFD.[3]

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