Research News

Chemical Fluid Deposition: A Hybrid Technique for Low-Temperature Metallization**

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Chemical fluid deposition (CFD) is a novel approach to metal deposition that involves the chemical reduction of organometallic compounds in supercritical carbon dioxide to yield high purity films at low temperature. Since supercritical CO_2 can exhibit densities that approach those of a liquid solvent while retaining the transport properties of a gas, CFD is essentially a hybrid technique that uniquely blends the advantages of chemical vapor deposition (CVD) and electroless plating. Here, we describe the deposition of high-purity films of Pt, Pd, Au, and Rh onto inorganic and polymer substrates by the reduction of appropriate precursors in CO_2 at 60 °C.

1. Introduction

Chemical vapor deposition (CVD) and aqueous electrolytic and electroless plating are currently employed for the reactive deposition of metal films with each technique offering distinct advantages and limitations.[1,2] CVD provides high purity and the promise of conformal coverage of complex surface topographies. In practice, however, it is often limited by precursor vapor pressure requirements and mass-transfer-limited kinetics that preclude uniform filling of high aspect-ratio features. In addition, high deposition temperatures inherent to CVD can lead to the generation of thermal–mechanical stress during device fabrication, and are incompatible with thermally labile substrates such as polymers.[1] Moreover, the requirement of high precursor volatility often dictates the use of fluorinated ligands or toxic carbonyl compounds that can generate undesirable effluents.

Aqueous plating techniques such as electroless deposition offer low temperature operation and a wide-range of suitable, inexpensive precursors. Mass transfer within the liquid phase however is sluggish, and can lead to poor control over the deposition process. Moreover, surface tension prevents uniform deposition in tortuous environments, and poor miscibility with hydrogen and other gas phase reduc-

ing agents necessitates the use of toxic liquid reductants such as formaldehyde and sodium hypophosphite. Finally, electroless deposition generates large volumes of wastewater derived from plating and rinse baths that are subject to strict environmental regulations.

2. A New Approach to Metal Deposition

It is conceptually simple to envision a deposition scheme that would embody the desirable attributes of CVD and aqueous plating techniques while minimizing the disadvantages of each. Such a process would be solution based, eliminating the precursor volatility constraints and elevated deposition temperatures associated with CVD, but retain conformal coverage and desirable transport properties associated with the vapor phase. Evidently, what is required is a medium that is essentially a gas–liquid hybrid. Fortunately supercritical fluids (SCFs) are such media[3] and can be adapted for the reactive deposition of metal films.

At temperatures above the critical point of a pure fluid, the distinction between the vapor and liquid phases is lost. Increasing pressure leads only to an increase in fluid density, without the possibility of encountering a vapor–liquid transition. Since fluid densities can approach or even exceed those of liquids, various supercritical fluids including carbon dioxide, are good solvents for many organic and organometallic compounds.[3,4] Despite near-liquid densities, the transport properties of SCFs are more akin to those of gases than liquids: in SCFs viscosities are orders of magnitude lower and diffusivities orders of magnitude higher than in liquids. Moreover SCFs do not exhibit surface tension and are fully miscible with gas phase reagents such as H_2. Thus SCFs appear to be ideal media for metal deposition.

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ADVANCED MATERIALS

We have validated the utility of SCFs for reactive metallization through the development of chemical fluid deposition (CFD), a fundamentally new technique that fully exploits the physiochemical properties of SCFs.[5–7] The method involves the chemical or thermal reduction of organometallic compounds in supercritical carbon dioxide solution to yield CVD-quality metal films. We choose carbon dioxide as the SCF for a number of reasons. It is inexpensive, widely available, environmentally benign and exhibits convenient critical properties (T_c = 31 °C, P_c = 73.8 bar). Moreover liquid and supercritical CO_2 have been employed as inert media for catalytic and radical chemistry including hydrogenations, hydroformylations, oxidations, and polymerizations.[8–13] Finally CO_2 adsorbs only weakly to metal surfaces and is unlikely to cause contamination or compete with precursor for active sites. The primary restriction for CFD is that the reduction chemistry must proceed readily at the relatively low temperatures employed in the process.

3. Deposition of Pt, Pd, Au, and Rh Films from Supercritical CO_2 Solution

Recently we reported the deposition of pure, reflective platinum and palladium thin films onto inorganic and polymer substrates by the reduction of appropriate metal precursors, including dimethyl(1,5-cyclooctadiene)platinum(II) [CODPtMe$_2$] and 2-methylallyl(cyclopentadienyl)palladium(II) [CpPd(π-C$_4$H$_7$)] (where COD = cyclooctadiene) (Fig. 1), with hydrogen in CO_2 solution at temperatures between 60 and 80 °C and pressures between 100 and 155 bar.[5–7] The films were free of ligand-derived contamination and exhibited excellent conformity on patterned surfaces including etched Si wafers. Note that the precursors chosen for these depositions yield only environmentally benign, saturated hydrocarbon decomposition products. For example hydrogenolysis of CpPd(π-C$_4$H$_7$) in CO_2 at 60 °C yields only the continuous metal films, cyclopentane, and isobutane. Consequently our method avoids the environmental liabilities associated with aqueous plating techniques that include heavy metal contamination of wastewater streams.

We have since expanded the scope of CFD to include the depositions of other metals: here we report the preparation of gold and rhodium films. High purity gold can be deposited from solutions of dimethyl(acetylacetonate)gold(III) [(acac)Au(CH$_3$)$_2$] in supercritical carbon dioxide by reduction of the precursor with hydrogen. The deposition is highly selective for metals over glass and polymeric substrates such as polyimide. Deposition on these non-growth surfaces, however, can be induced by first depositing an ultra-thin seed layer of Pd or Pt using the chemistry described above. This selectivity is beneficial in two respects. First, the generation of patterned surfaces is possible by localizing the seed layer. Second, it mitigates parasitic depletion of the precursor solution by deposition onto vessel walls and fixtures.

Gold films deposited onto Pd-seeded polyimide, glass, Si wafers, and bare nickel foil are bright and highly reflective. Figure 2a shows a scanning electron microscopy (SEM) micrograph of a gold film deposited onto a Pd-seeded silicon wafer by the reduction of an 0.36 wt.-% solution of (acac)Au(CH$_3$)$_2$ in CO_2 with an 80-fold molar excess of hydrogen at 60 °C and 140 bar. X-ray photoelectron spectroscopy (XPS) indicates the films are free of ligand-derived contamination. Figure 2b shows an XPS survey spectra for gold deposited onto nickel foil using CFD. The analysis was conducted after Ar+ sputtering to remove atmospheric contaminants. X-ray diffraction (XRD) revealed reflections from the $\langle 111 \rangle$, $\langle 200 \rangle$, $\langle 220 \rangle$, and $\langle 311 \rangle$ crystallographic planes at the expected locations. Adhesion of the gold films to Pd-seeded polyimide is excellent, application and removal of a pressure sensitive adhesive does not damage the coating.

Rhodium can be deposited via CFD by the reduction of (1,5-cyclooctadiene)(2,4-pentanedionato)rhodium(I) [(acac)Rh(1,5-COD)] with H$_2$. A 180 nm thick rhodium film was deposited onto Pd-seeded polyimide using an 0.23 % solution (acac)Rh(1,5-COD) in supercritical CO_2 and a forty-fold molar excess of hydrogen at 60 °C and 165 bar. SEM indicates the film is polycrystalline (Fig. 3a) and analysis by XPS indicates the film is free of carbon contamination (Fig. 3b).
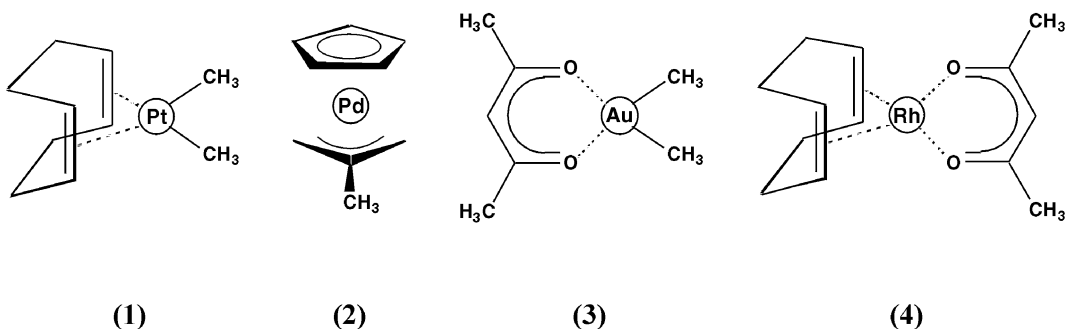

(1)   **(2)**   **(3)**   **(4)**

Fig. 1. Structures of metal precursors used for CFD. 1) CODPtMe$_2$, 2) CpPd(π-C$_4$H$_7$), 3) (acac)Au(CH$_3$)$_2$, 4) (acac)Rh(1,5-COD).
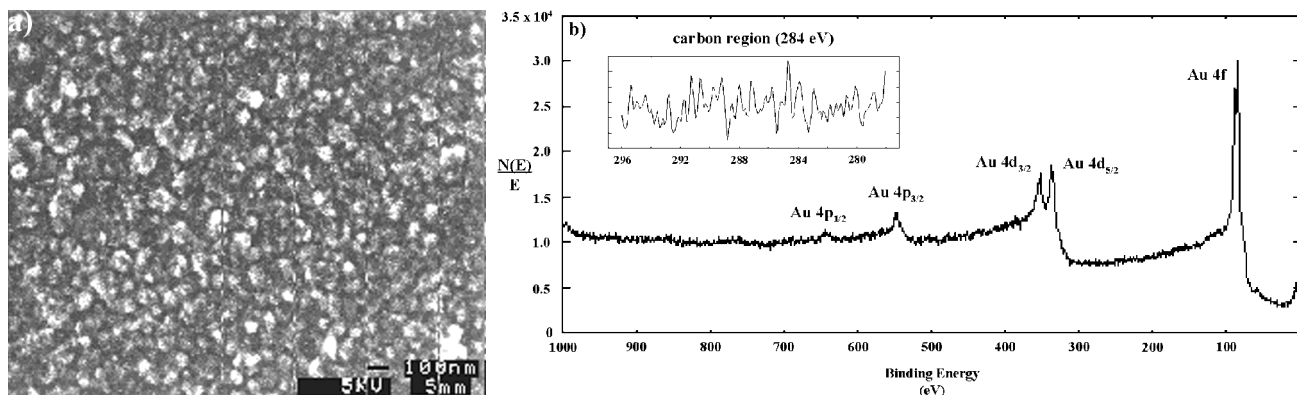
Fig. 2. a) SEM micrograph of an Au film deposited onto a Pd-seeded Si wafer by the reduction of a 0.36 wt.-% solution of $(acac)Au(CH_3)_2$ in CO_2 at 140 bar and 60 °C. b) XPS survey of an Au film deposited onto nickel foil by reduction of a 0.37 wt.-% solution of $(acac)Au(CH_3)_2$ in CO_2 at 140 bar 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.
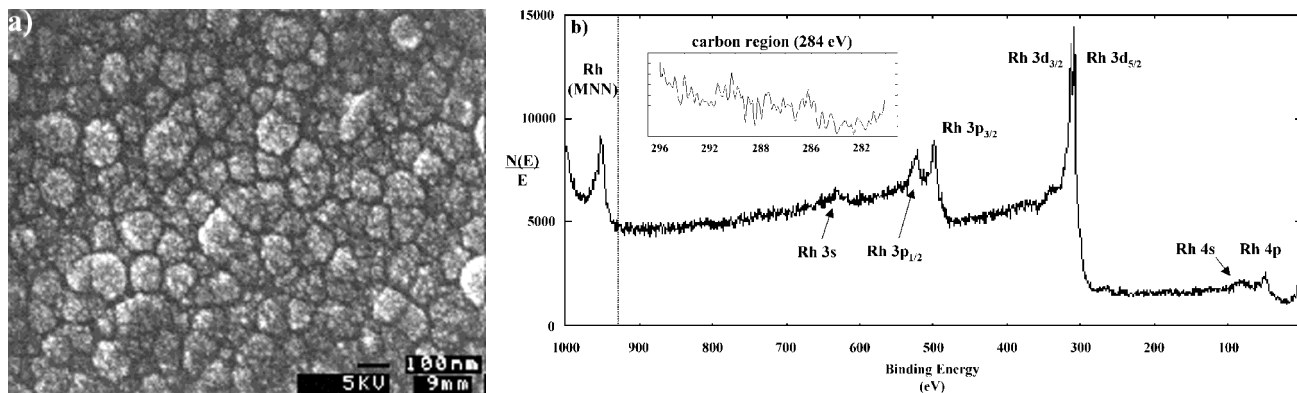

Fig. 3. a) SEM micrograph of a Rh film deposited onto Pd-seeded polyimide by reduction of a 0.23 wt.-% solution of $(acac)Rh(1,5-COD)$ in CO_2 at 165 bar and 60 °C. b) XPS survey of an Rh film deposited as above. The spectrum was collected after Ar^+ sputtering to remove atmospheric contaminants. The inset is the multiplex scan of the carbon 1s (284 eV) region showing no measurable levels of contamination.

4. Conclusions

CFD is a novel, robust approach to low-temperature metal deposition that circumvents many of the technical and environmental constraints associated with CVD and aqueous plating. We expect the technique will become a general approach: to date we have demonstrated the preparation of CVD quality Pt, Pd, Au, and Rh films on inorganic and polymer substrates and are currently expanding the scope of the depositions to include other metals.

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