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Immersion Deposition of Metal Films on Silicon and Germanium Substrates in Supercritical Carbon Dioxide

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A low-temperature CO_2-based technology, supercritical fluid immersion deposition (SFID), has been developed for producing Pd, Cu, Ag, or other metal films on Si-based substrates in supercritical CO_2 solutions. The reaction is most likely initiated by oxidation of elemental silicon to SiF_4 or H_2SiF_6 with HF, causing the reduction of a metal chelate precursor to the metallic form on silicon surface in CO_2. Using this method, only the substrate surfaces exposed to CO_2 solutions are coated with metals, and the metal films (Pd, Cu, and Ag) exhibit good coverage, smooth and dense texture, and high purity. Preliminary experiment indicates that palladium films deposited on silicon by SFID can be converted to palladium silicide by annealing treatment. Metal films can also be deposited onto germanium substrates using SFID. The gaslike properties and high pressure of the supercritical fluids, combined with the low reaction temperature, make this SFID method potentially useful for fabricating thin films of metal or metal silicide in small features, which is difficult to accomplish by conventional metal deposition methods.

Introduction

The manufacture of thin films has been an area of significant importance in the microelectronics industry and related fields. A number of techniques have been established for depositing metal films on semiconductor substrates including electroless deposition,[1−4] electrodeposition,[5−8] immersion deposition,[9−10] sputtering,[11−14] chemical vapor deposition (CVD),[15−20] and evaporation.[21−24] Since the past decade, supercritical fluid deposition techniques have been extensively studied.[25−27] Supercritical fluids exhibit a unique combination of gaslike and liquidlike properties. They can dissolve solid compounds as liquids do, and they provide low viscosity and high diffusivity as gases do. The low viscosity, high diffusivity, and the ability to tune solvation power continuously with pressure and temperature enable supercritical fluid deposition techniques to attain high

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uniformity and to reach small areas. Byproducts and contaminants can be easily removed from the system and thin films of high purity can be obtained. In addition, supercritical CO_2 is considered a green solvent because it is environmentally benign and does not create a liquid waste problem for large-scale industrial applications.

Rapid expansion of supercritical solution is the first technique developed for physical deposition of thin films on solid surfaces.[28−32] In the physical rapid expansion process, a metal precursor or polymer is first dissolved in a supercritical fluid, and then the supercritical solution is suddenly expanded through a nozzle at a very high velocity. This abrupt reduction of the medium's solvent capacity leads to the precipitation of solutes onto an exposed substrate as a thin film. One major limitation of the physical rapid expansion process is that most metallic species of interest are not soluble in supercritical fluids. Rapid expansion of supercritical solution can be coupled with CVD for chemical deposition. The supercritical fluid transport−chemical deposition technique expands a CO_2 solution of metal precursor through a restrictor into a conventional CVD deposition chamber where the rapid expansion of the supercritical fluid causes vaporization of the solute(s).[33−37] The vaporized precursor compounds are then induced to decompose in the vicinity of the substrate to form a thin film.

A challenge in today's semiconductor materials processing is filling metals via holes and trenches. In this case, supercritical fluid chemical deposition and chemical fluid deposition techniques show great promise because of their simplicity and via-hole filling ability.[38−47] In a supercritical fluid chemical deposition process, a precursor is transported to a heated substrate in a supercritical fluid reactor where it undergoes thermolysis to yield a thin solid film.[38,39] In chemical fluid deposition, after transporting a metal precursor to a heated substrate in a supercritical fluid reaction vessel, a reducing agent is introduced into the fluid phase initiating a reaction with the precursor causing deposition of metals onto the substrate surface.[40−45] High-quality films of Cu, Pt, Pd, Au, and Rh have been fabricated on inorganic and polymer substrates by H_2 reduction of the corresponding metal precursors in supercritical CO_2.[35,39−42] The gaslike properties and high pressure of the supercritical fluids facilitate the delivery of precursors to small holes or narrow tubing, thus producing thin films in small features. However, deposition of metals on the walls of the reaction vessel also occurs in supercritical fluid chemical deposition and chemical fluid deposition processes.

Recently, we developed a supercritical fluid immersion deposition (SFID) process for producing thin metal films on substrates or into porous solids of elemental semiconductor silicon and germanium. This method involves a redox reaction between a metal chelate precursor and an elemental semiconductor in supercritical carbon dioxide using HF as a reagent. For silicon substrate, the deposition reaction is initiated by oxidation of elemental silicon to a fluoride, causing the reduction of an oxidized metal in a precursor to its metallic form. A unique feature of this method is that the metal films will form only on the semiconductor substrate surface, and other parts of the high-pressure system including the container walls will not be coated. A variety of precursors, even those with low volatilities, can be used as starting materials if they are soluble in CO_2. Furthermore, HF is miscible with CO_2, and the fluorine-containing byproducts from the deposition process are usually soluble in CO_2. The deposition can be carried out at temperatures above the critical temperature of CO_2 (31.3 °C) in supercritical CO_2 or at room temperature in liquid CO_2. Heating of the supercritical CO_2 system at modest temperatures (80−100 °C) leads to the formation of high quality metal films on silicon. In this paper, the fundamental aspects of the SFID method for depositing metal films (palladium, copper, and silver) on silicon or germanium surfaces are discussed. A method of delivering HF into a supercritical CO_2 system using a HF−pyridine complex supported on polymer is described. Possible mechanisms of the metal deposition reaction on silicon are also discussed based on spectroscopic measurements of the byproducts and surface analysis of SFID-deposited films. The SFID of palladium film is used as an example because palladium is important in integrated circuits that require creation of Pd−silicide as an initial layer in bilayer/trilayer metal contacts.[48] Palladium also serves as a seed layer for the electroless deposition of other interconnecting metals.[49] A preliminary experiment was carried out to test the possibility of fabricating palladium−silicide by annealing the SFID-deposited palladium films on silicon. The mechanism of developing a copper film on a silicon surface by dipping a silicon wafer into a diluted aqueous solution containing HF and copper ions is known in the literature.[50,51] The SFID of copper is used as an example

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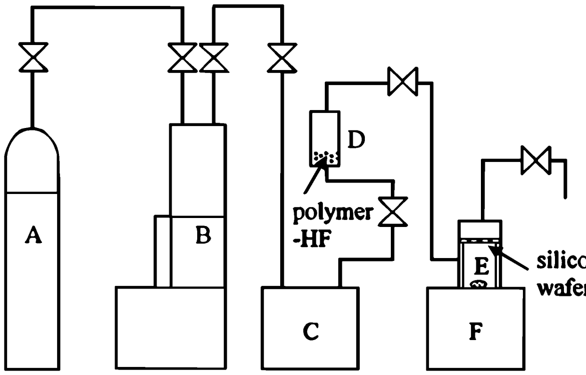

Figure 1. Experimental setup for immersion deposition process in supercritical CO_2: (a) CO_2 tank, (b) syringe pump, (c) supercritical CO_2 solution of precursor, (d) mix chamber, (e) deposition chamber, and (f) electromagnetic stirring.

for comparison of reaction mechanisms between the two different solvent systems.

Experimental Section

Metal chelate precursors, $M(hfa)_2 \cdot xH_2O$ (M = Pd or Cu; hfa = hexafluoroacetylacetonate) and AgFOD (FOD = 6,6,7,7,8,8,8-heptafluoro-2,2-demethyl-3,5-octanedionato) were purchased from Aldrich Chemical Co., and HF−pyridine complex supported on polymer, poly[4-vinylpyridinium poly(hydrogen fluoride)] (PVPD-HF, ~35−40% HF and ~60 mesh) was obtained from Fluka. Unless otherwise stated, all chemicals were used as received. Semiconductor substrates used were P-type silicon ⟨100⟩ wafers (100 mm diam., 10−20 Ω·cm resistivity) and pure germanium disks (15 mm diam. and 5 mm thick). The silicon specimens used for the experiments were 1.5 cm × 1.5 cm square pieces cleaved from the wafer and cleaned according to the standard RCA process.[52] Ge disks were polished with a 600 grit sandpaper, ultrasonicated in distilled water and acetone sequentially for 15 min, and then etched with 5% HF solution for 5 min.

The experimental setup for SFID metal coating is outlined in Figure 1. A metal chelate precursor was dissolved in a reservoir by supercritical or liquid CO_2. The CO_2 solution was pumped into a vessel where PVPD-HF was loaded. The HF bound to the polymer was released almost completely into the CO_2 solution after 5 min of interaction, and the PVPD solid was left behind in the vessel. In this process, PVPD acts as a HF carrier, fixing HF first and releasing it later. This is a safe and convenient way of introducing HF into the supercritical fluid system. Thereafter, the solution was passed into a reactor where the silicon or germanium substrate was mounted on a substrate holder. The entire reactor was put inside an oven that controlled the temperature, and the CO_2 solution was stirred rapidly with a magnetic stirrer. After a period of time, a metal film was deposited on the substrate surface and the reactor was depressurized. These experiments involve the use of high pressures and HF, both of which require special safety precautions. The experiments were performed in a hood to prevent possible leakage of the gases. In addition, the exhausted gas from the reactor was trapped with a sodium hydroxide solution to neutralize HF. The postdeposition cleaning of the metal film was undertaken by rinsing with distilled water and acetone alternatively. After that, some silicon specimens deposited with palladium were annealed at 320 °C for 5 min in a furnace using He ambient for silicide formation.

A tape peel test was used to assess the adhesion of the resulting metal films on semiconductor substrates. The surface morphology of the film was examined by AMRAY 1830 scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Physical Electronics Quantum-2000 scanning electron spectroscopy for chemical analysis (ESCA) microprobe using a focused monochromatic Mg Kα (1253.6 eV) or Al Kα (1486.7 eV) X-ray for excitation and a spherical section analyzer. The instrument has a 16-element multichannel detection system. The X-ray beam used was 100 μm in diameter and rastered over a 1.4 mm × 0.2 mm rectangle on the sample. The X-ray beam was incident normal to the sample and the X-ray detector was at 45° away from the normal. The pressure of the analyzer chamber was maintained at $1.0-1.2 \times 10^{-8}$ Torr during the measurement. Survey and high-resolution spectra were obtained with the analyzer pass energy set at 117.4 and 23.5 eV, respectively. The collected data were referenced to an energy scale with binding energies for $Cu_{2p3/2}$ at 932.67 ± 0.05 eV and $Au_{4f7/2}$ at 84.0 ± 0.05 eV. The resolution of binding energy value was 1.6 and 0.75 eV in survey and high-resolution XPS spectra, respectively.

^1H and ^{19}F nuclear magnetic resonance (NMR) spectra of the byproducts from the deposition reaction were obtained using a Bruker 300 MHz spectrometer. NMR samples were prepared by venting the reactor and trapping the effluent into deuterated chloroform. Mass spectroscopic (MS) analysis of byproduct species was carried out on a JEOL JMS AX-505HA spectrometer.

Results and Discussion

Factors Influencing Metal Deposition by SFID. In the SFID process, the deposition rate, morphology, thickness, and adhesion of the metal film depend on several factors, including concentrations of the precursor and HF, and deposition temperature, time, and pressure. Table 1 summarizes the conditions derived from this study for depositing Pd, Ag, and Cu films on silicon substrate by SFID in CO_2. The concentrations of the metal chelate precursors and HF can greatly influence the quality of the metal film deposited. Similar to the immersion deposition process in aqueous solution, a CO_2 solution with high concentrations of a precursor and HF will deposit metal very quickly, resulting in rough metal films with poor uniformity and adhesion. Therefore, the concentrations of the precursor and HF should be moderate. However, too low a concentration will result in poor coverage and discontinuity of the film. Uniform, smooth, continuous, and adhesive films can be produced only in an appropriate concentration range. The optimized concentration range, according to our experiments, is 1.4×10^{-2} to 5.0×10^{-4} mol/L of $Pd(hfa)_2$ and 1.2×10^{-1} to 6.0×10^{-3} mol/L of HF (corresponding to 7.0−0.35 g/L of PVPD-HF) in SFID of palladium films on silicon. For developing copper films on silicon through SFID, the optimum concentration range of $Cu(hfa)_2$ is from 8.1×10^{-3} to 5.0×10^{-4} mol/L. If AgFOD is used as a precursor for making silver films on silicon, the concentration range should be 2.0×10^{-3} to 5.0×10^{-4} mol/L. This concentration range was achieved by using tributyl phosphate as a CO_2 modifier (1.0×10^{-2} mol/L) because AgFOD has solubility less than 5.0×10^{-4} mol/L in CO_2.

Temperature is an important parameter that determines the deposition rate and the quality of the film produced. The deposition can occur at room temperature in liquid CO_2, and the rate will increase with temperature in supercritical CO_2. Figure 2a−d shows the SEM pictures of palladium films deposited on silicon wafers at different temperatures with the following parameters fixed: $Pd(hfa)_2$ 1.0×10^{-3} mol/L, HF 1.5×10^{-2} mol/L, deposition time 1 min, pressure 80 atm. Foggy metal film, cloudy and rough, with poor adhesion and unifor-

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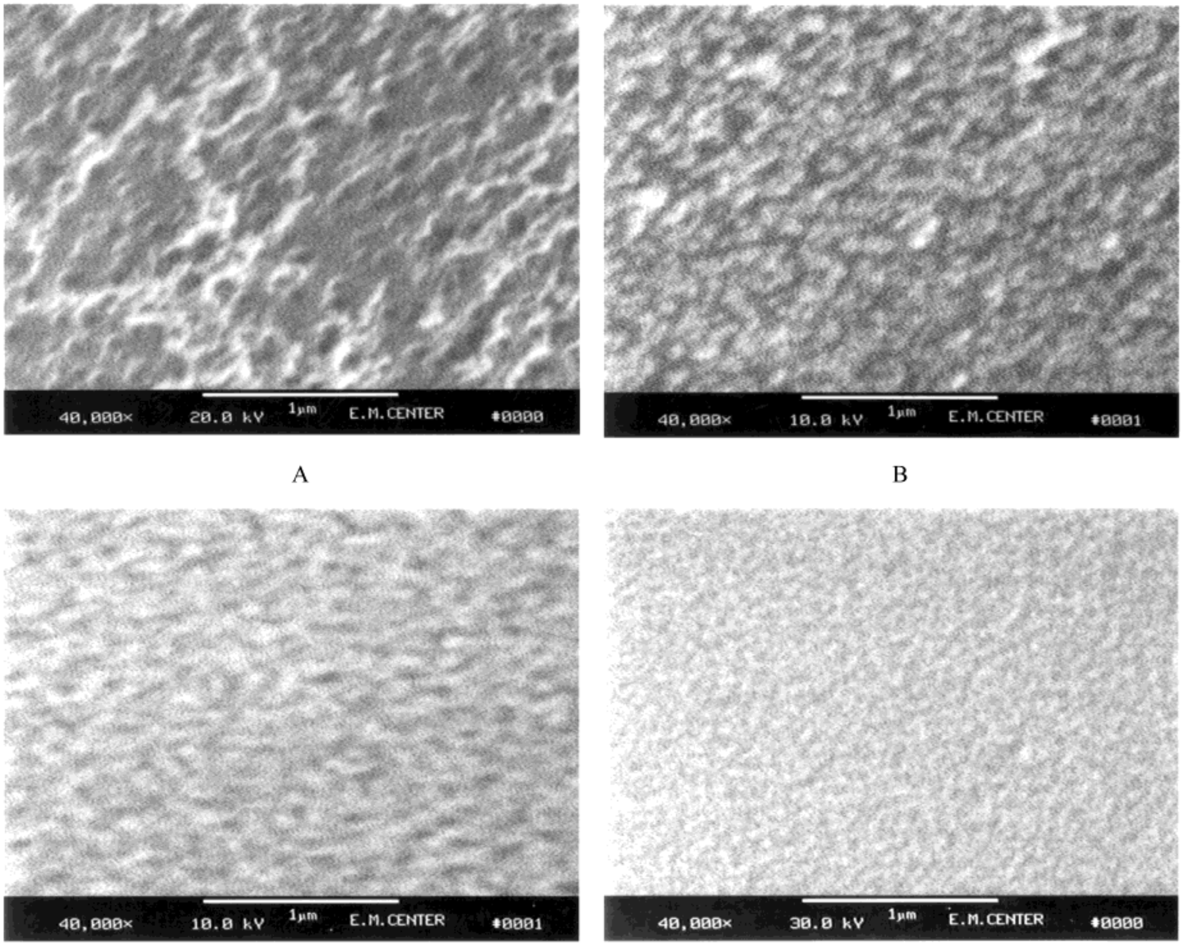
Table 1. Optimized Conditions for Deposition of Palladium, Silver, and Copper Films on Silicon in CO_2

metal film	precursor, mol/L	HF, mol/L	temp, °C	pressure, atm	time, min
palladium	$Pd(hfa)_2$, $1.4 \times 10^{-2} - 5.0 \times 10^{-4}$	$1.2 \times 10^{-1} - 6.0 \times 10^{-3}$	70−150	75−200	0.5−10
silver	AgFOD, $2.0 \times 10^{-3} - 5.0 \times 10^{-4}$	$1.2 \times 10^{-1} - 6.0 \times 10^{-3}$	70−150	75−200	0.5−5
copper	$Cu(hfa)_2$, $8.1 \times 10^{-3} - 5.0 \times 10^{-4}$	$1.2 \times 10^{-1} - 6.0 \times 10^{-3}$	70−100	75−200	0.5−5



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C D

Figure 2. SEM pictures of palladium films deposited on silicon wafers from CO_2 solution at (a) room temperature, (b) 40 °C, (c) 60 °C, and (d) 80 °C. The following factors were fixed for deposition: $Pd(hfa)_2$ 1.0×10^{-3} mol/L, HF 1.5×10^{-2} mol/L, deposition time 1 min, and deposition pressure 80 atm.

mity, was obtained at room temperature from liquid CO_2. Under scanning electron microscope, scattered white spots and bands were observed sticking or inlaying on the surface of the film. These white spots and bands were probably caused by impurities or byproducts from the deposition reaction, and could not be removed completely by postdeposition cleaning. The film produced at 40 °C from supercritical CO_2 was still foggy, with the presence of some white spots in the SEM image, although the number of spots was less. For the film deposited at 60 °C, the surface was almost clean but rough and loose, and the average particle size was around 150 nm. However, at a deposition temperature of 80 °C, the film produced was quite clean, with no visible white spots or bands in the SEM image. The film exhibited good coverage and continuity along with a smooth and dense texture with fine grain sizes of about 50 nm. The tape peel test showed that good adhesion was achieved, as there was no removal of palladium coatings. Further increase in temperature did not seem to change the quality of the film; e.g., the quality of palladium films formed at 100 °C resembles that of those deposited at 80 °C. A similar temperature effect was observed in SFID of silver and copper films. Compared with the temperatures required by traditional CVD processes, the required temperature for SFID is quite modest. The temperature effect observed in the SFID process is different from that reported for immersion deposition processes in aqueous solutions which were usually done at room temperature or approximately 20−25 °C. In aqueous immersion deposition, the brightness of the films deposited from the aqueous solution changes little with temperature. This is obviously due to the different solvent properties between CO_2 and water, which will be discussed later in this paper.

The thickness of the metal film deposited on the substrate surface is determined by the time of immersion. An insufficient immersion time will result in an incomplete coating of the substrates. An excessive immersion time will cause cracking, flaking, blistering, or peeling of the metal deposited on the semiconductor surface, and is probably due to the increased stress with the deposition of a thick film.[48,53−54] According to our

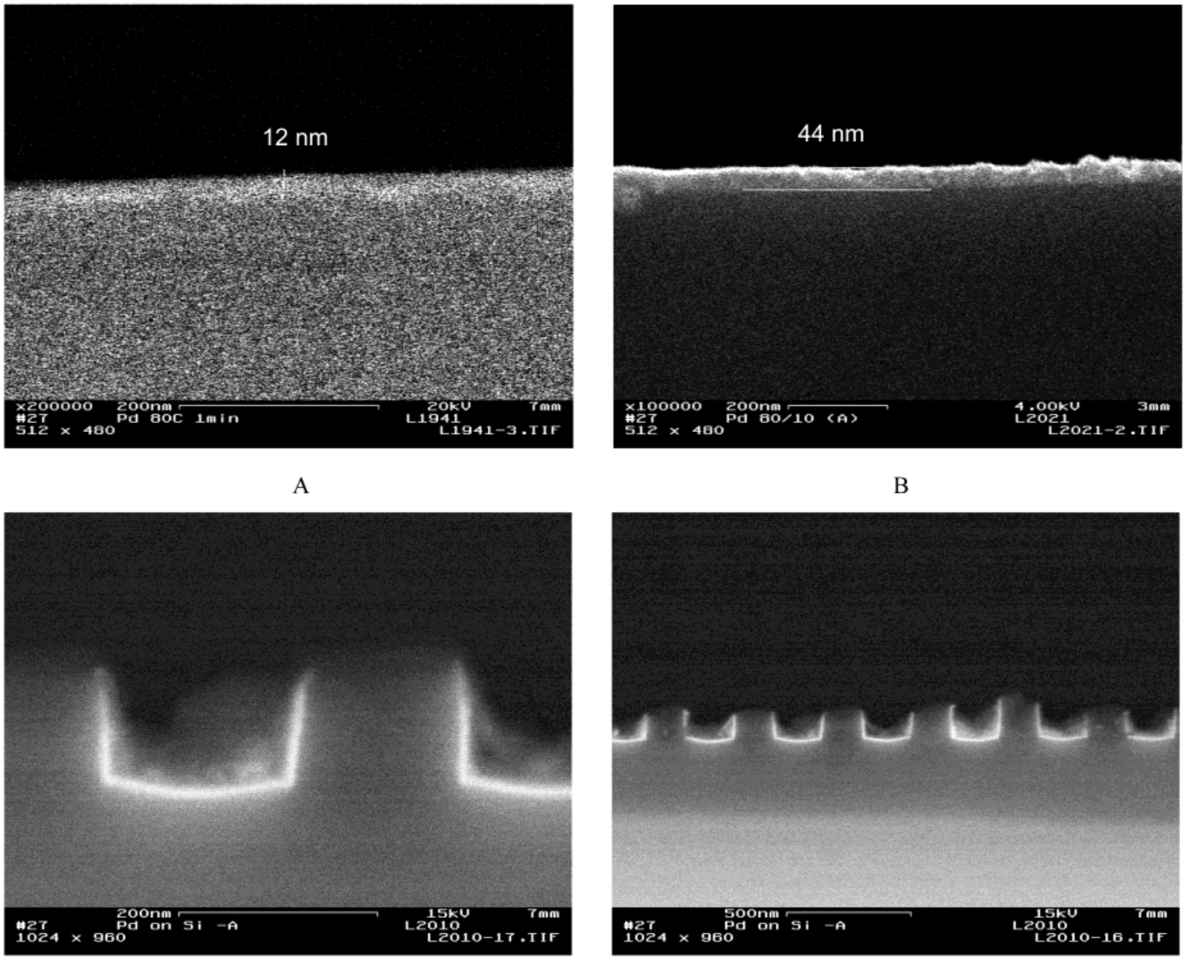

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Figure 3. Cross-sectional SEM images of palladium films deposited on (a)−(b) silicon, or (c)−(d) featured Si/Ta_2O_5/Si substrates from CO_2 solution with Pd(hfa)$_2$ 1.0 × 10^{-3} mol/L and HF 1.5 × 10^{-2} mol/L at 80 atm and 80 °C. Deposition times: 1 min for (a) and 10 min for (b).

experimental conditions, 0.5 to 10 min of immersion time is preferred for palladium deposition. The film thickness so-produced was approximately 10−50 nm based on our SEM analysis of the silicon/Pd film cross section. For SFID of copper and silver, the preferred immersion times are both between 0.5 and 5 min. Figure 3 shows SEM images of silicon/Pd film cross sections. The metal films are continuous, and the film thickness is 12 nm for film 3(a) and 44 nm for film 3(b). The SFID method obviously is able to deposit thin metal films on silicon substrates. Because of its ability to produce nanometer-level metal films, this technique may provide a method for coating small channels and pores in semiconductor devices. Figure 3c,d shows thin Pd films deposited into small features on a Si/Ta_2O_5/Si substrate. Pressure does not seem to show a measurable effect for deposition of metal films on Si surfaces. For example, increasing deposition pressure from 80 to 150 atm showed virtually no difference in the quality of the palladium films formed on silicon under the specified conditions: Pd(hfa)$_2$ 1.0 × 10^{-3} mol/L, HF 1.5 × 10^{-2} mol/L, temperature 80 °C, and deposition time 1 min.

Germanium can also be used as a substrate in SFID, and the conditions and results are similar to those of silicon described above. A SEM picture of a palladium film deposited on a germanium substrate is given in the Supporting Information.

Composition of SFID-Deposited Thin Metal Films on Silicon and Silicide Formation. The compositions of the films were analyzed by XPS combined with Ar^+ beam etching. Figure 4a,b illustrates the XPS survey spectra (Mg Kα as excitation) of a palladium film deposited on silicon from a CO_2 solution of 1.0 × 10^{-3} mol/L Pd(hfa)$_2$ and 1.5 × 10^{-2} mol/L HF at 80 °C and 80 atm for 1 min. For as-deposited film, the Pd_{3p}, Pd_{3d}, Pd_{4p}, and Pd_{MNN} peaks were all observed. The C_{1s} signal could be attributed to contamination and adsorption. The absence of the O_{1s} and O_{KLL} signals indicates no oxidation of the palladium film surface during exposure to air. Additionally, the spectrum is free of the N_{1s} and F_{1s} bands, revealing that no impurities from precursor or PVPD-HF were detectable on the film surface. After etching the film with Ar^+ beam for 4 min, the carbon contaminant peak became barely detectable and the Pd bands remained. The small carbon peak observed at 284.6 eV may be caused by the trace impurity in the matrix of pure palladium film. The absence of silicon peaks (Si_{2s} peak at 153 eV, Si_{2p} peaks at 102 and 103

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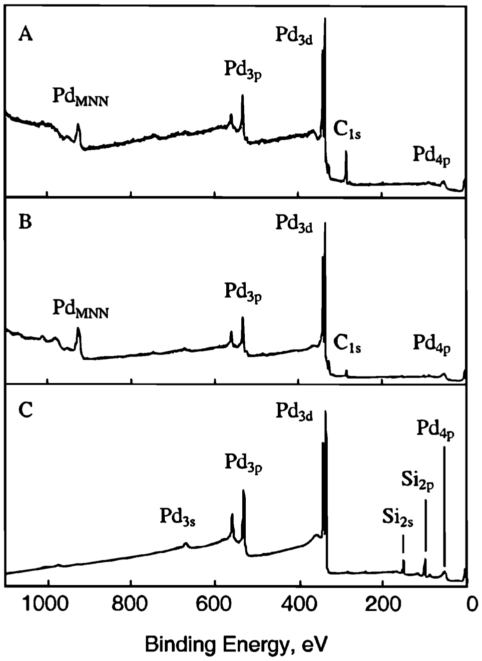

Figure 4. XPS survey spectra of a palladium film deposited on a silicon substrate from a CO_2 solution of 1.0×10^{-3} mol/L $Pd(hfa)_2$ and 1.5×10^{-2} mol/L HF at 80 °C and 80 atm for 1 min: (a) as-deposited, (b) after 4 min of Ar^+ beam etching, and (c) after 5 min of annealing treatment in He ambient at 320 °C and 2 min of Ar^+ beam etching.

eV) indicates that the silicon wafer was coated by a continuous palladium film. Similar conclusions could be drawn for Ag and Cu films. For copper films obtained from SFID, the C_{1s} peak disappeared completely after 3 min of Ar^+ etching cleaning, indicating that high-purity copper films were produced by the SFID process. Furthermore, it has been reported that annealing treatment accelerates the conversion of metals deposited on silicon to silicides.[55,56] As Figure 4c shows, Si_{2s} and Si_{2p} peaks were observed in the survey XPS (Al Kα as excitation) of the same palladium film as in Figure 4a,b after annealing, implying the formation of silicides. Photoelectron lines were unaffected by the use of different excitations. The Pd_{MNN} peak is not shown in Figure 4c, which appears at around 1159 eV in Al Kα excited spectra.

Information about the chemical states of the metal films can be obtained from the high-resolution XPS spectra. Figure 5a shows high-resolution Pd_{3d} spectra of the palladium film after Ar^+ sputtering. The $Pd_{3d5/2}$ and $Pd_{3d3/2}$ peaks at 335.5 and 340.8 eV, as well as the binding energy difference between these two peaks, 5.3 eV, indicate that the film is composed of metallic palladium. High-resolution XPS spectra for silver films yield similar results. For the copper films, Cu_{LMM} line of $Cu_{2p3/2}$ (Mg Kα as excitation) was recorded and is shown in Figure 5b. The Cu_{LMM} line of $Cu_{2p3/2}$ at 337.0 eV and the side peak at 335.0 eV prior to Ar^+ sputtering were identical to those of Cu^+ and Cu^0,[57] respectively, demonstrating that there were two valence states (Cu^+ and Cu^0) on the surface of the copper film. The surface of the film was partially oxidized during exposure to air. After 3 min of sputtering cleaning with Ar^+ ions, the peak at 337.0 eV was reduced to a shoulder peak, while the peak at 335.0 eV grew up to a dominant one. If the sputtering continued for 15 min, the peak at 337.0 eV became insignificant and could be ignored. The peak at 335.0 eV was still evident, revealing that the film was composed of almost pure copper at this depth.

Silicide formation by annealing treatment can also be confirmed by high-resolution XPS spectra. For as-annealed palladium film on silicon, two features can be identified in both $Pd_{3d5/2}$ and $Pd_{3d3/2}$ peaks. $Pd_{3d5/2}$ peak at 336.8 eV and $Pd_{3d3/2}$ peak at 342.1 eV can be assigned to Pd_2Si,[58,59] indicating the conversion of Pd to palladium silicide by annealing at 320 °C. This observation is in agreement with the reported formation temperature of 200−400 °C in conventional furnace annealing.[55,56] $Pd_{3d5/2}$ and $Pd_{3d3/2}$ peaks for palladium also appeared around 335.5 and 340.8 eV. That means the silicification had not been completely finished at the outer layer close to the surface of the film. However, only peaks of Pd_2Si were observed in the spectrum after 10 min of Ar^+ sputtering, demonstrating an entire transformation of Pd to Pd_2Si at the deeper layer. The conversion of the whole palladium film to Pd_2Si should be achieved if higher annealing temperature or longer annealing time is applied.

Mechanism of Metal Film Deposition on Silicon and Germanium by SFID. Immersion deposition of metal films on silicon substrates using aqueous solutions of HF has been shown to be a complicated sequence of equilibriums and reactions,[50−51,60−68] and the general mechanism responsible for such deposition is well defined as a galvanic displacement process. By dipping a ⟨100⟩ silicon wafer into diluted HF aqueous solution containing copper ions, a copper film can be developed on silicon surface according to the reactions as follows:

$$Si^0 + 6\ F^- \rightarrow SiF_6^{\ 2-} + 4\ e^- \text{ (oxidation reaction)} \qquad (1)$$

$$2\ Cu^{2+} + 4\ e^- \rightarrow 2\ Cu^0 \text{ (metal-reduction reaction)} \qquad (2)$$

$$Si^0 + 2\ Cu^{2+} + 6\ F^- \rightarrow SiF_6^{\ 2-} + 2\ Cu^0 \text{ (overall reaction)} \qquad (3)$$

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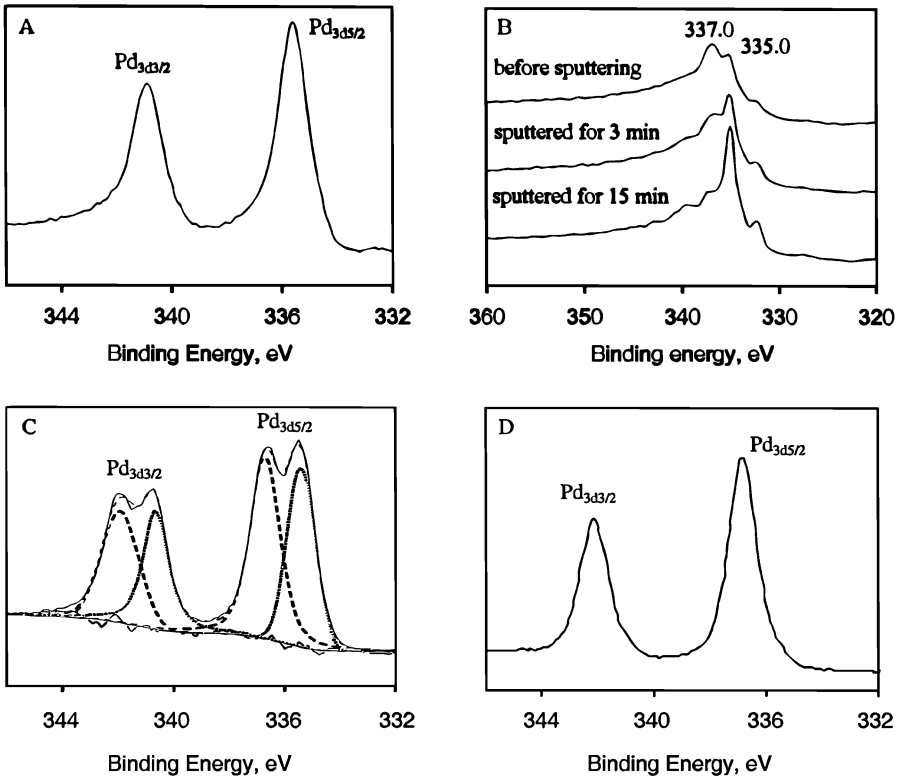

Figure 5. High-resolution XPS spectra of (a) Pd_{3d} line from the palladium film after Ar^+ sputtering, (b) Cu_{LMM} line from the copper film at different sputtering times, (c) Pd_{3d} line from as-annealed palladium film, and (d) Pd_{3d} line from annealed palladium film after 10 min of Ar^+ sputtering.

To evaluate possible mechanisms for SFID of palladium on silicon, we trapped the CO_2 mixture from the deposition reactor into $CDCl_3$ for NMR studies. Both ^1H and ^{19}F NMR spectra of the precursor $Pd(hfa)_2{\cdot}xH_2O$, free ligand Hhfa, and the trapped mixture after palladium deposition from CO_2 at 80 °C and 80 atm were taken. The ^1H NMR spectrum of $Pd(hfa)_2{\cdot}xH_2O$ exhibits two peaks: one singlet at 6.34 ppm and the other one at 1.49 ppm corresponding to the protons from hexafluoroacetylacetonate ion and the coordinated water, respectively. For the ^1H NMR spectrum of free ligand Hhfa, the singlet appearing at 6.32 ppm is attributed to the enol vinyl proton of the ligand.[69,70] As for the ^1H NMR spectrum of trapped mixture, the two singlets at 6.34 and 6.32 ppm indicate the presence of the unreacted precursor $Pd(hfa)_2$ and the free ligand Hhfa produced by deposition reaction, respectively. The additional signals are attributed to $CHCl_3$, or ethanol and acetone used for cleaning the NMR tube. The generation of free ligand from the deposition reaction can be further confirmed by ^{19}F NMR spectra. The spectrum of trapped mixture shows two singlets at −73.49 and −76.90 ppm, which are identical to those of the unreacted precursor and the free ligand, respectively.

The contaminants and impurities on the metal film surfaces were related to the deposition process. Prior to postdeposition cleaning, all palladium films formed at 20−40 °C were masked by a thin layer of white substance, which was probably caused by adsorption of some byproducts from the deposition reaction, or adsorption of byproducts-derived species. After the films were washed with water and acetone, the layer was removed and foggy palladium films were obtained. As shown in Figure 2a and b, some white spots and streaks were observed in SEM images of these films. For the palladium film obtained in supercritical CO_2 at 80 °C, neither the white substance overlayer before post-deposition cleaning, nor the white spots or streaks in the SEM images of the postdeposition treated film was observed. The final films were clear and shining, and a clean surface free of Si and O was manifested by XPS measurement as shown in Figure 4a and b. However, XPS analysis indicated the presence of Si and O elements both in the overlayer of white substance and the foggy film, and most likely, the white spots and streaks were SiO_2. Also, the layer of white substance vanished slowly under electron bombardment and in high vacuum analysis chamber in XPS. It even faded slowly in air. Nevertheless, it did not disappear completely in each case. All these observations suggest that the white substance layer contained some species which can dissociate or volatilize somewhat. We rinsed the white substance layer with methanol in a plastic bottle, and analyzed the methanol solution by MS. The MS results showed that tetramethyl ester of silicic acid $Si(OCH_3)_4$, as characterized by the peaks at 152, 121, 91, and 61, was the principal species in the methanol solution. If deuterated methanol was used to rinse the white substance layer, deuterated tetramethyl ester of silicic acid, $Si(OCD_3)_4$, became the main species, as shown by the corresponding Supporting Information. Evidently, the layer of white substance contains silicon compounds which are reactive to methanol to form tetramethyl ester of silicic acid. Taking the XPS results into account,

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such compounds are probably $Si(OH)_4$. Methoxylation by methanol reacting with surface hydroxyl groups and siloxane bridges of silicates was reported to occur at room temperature.[71,72] The white substance overlayer could be a mixture of $Si(OH)_4$ and small amount of $SiO_2 \cdot xH_2O$.

It is known that the reactions of silicon with HF could produce SiF_6^{2-}, H_2SiF_6, or SiF_4. For immersion deposition in aqueous solutions, SiF_6^{2-} ion is produced as a byproduct when F^- reacts with silicon. In SFID, a similar process is expected for the reaction between HF and Si leading to the formation of SiF_4 or H_2SiF_6 as the most possible byproducts. H_2SiF_6 could be formed by the reaction between gaseous HF and SiF_4, a thermodynamic favorable process according to a calculation by Mapstone.[73] In addition, a small amount of water in the system from hydrated metal precursors could also facilitate the formation of H_2SiF_6. On the basis of the analysis and discussion given above, deposition of metal films on silicon surfaces by SFID probably proceeds by the following reactions:

$$Si + 6\ HF + 2\ M(hfa)_2 \rightarrow 2\ M + H_2SiF_6 + 4\ Hhfa \tag{4}$$

$$Si + 4\ HF + 2\ M(hfa)_2 \rightarrow 2\ M + SiF_4 + 4\ Hhfa \tag{5}$$

where M is a divalent metal such as Pd and Cu. For a monovalent metal such as Ag, the reactions can be written as follows:

$$Si + 6\ HF + 4\ AgFOD \rightarrow 4\ Ag + H_2SiF_6 + 4\ HFOD \tag{6}$$

$$Si + 4\ HF + 4\ AgFOD \rightarrow 4\ Ag + SiF_4 + 4\ HFOD \tag{7}$$

The SFID process may involve H_2 as an intermediate. It is possible that true attack of silicon by gaseous HF may lead to the formation of SiF_4, with the evolution of H_2 gas which causes reduction of $M(hfa)_2$:[35,39−45,74−79]

$$Si + 4\ HF \rightarrow SiF_4 + 2\ H_2 \tag{8}$$

$$M(hfa)_2 + H_2 \rightarrow M + 2\ Hhfa \tag{9}$$

The net reaction of this possible mechanism ($Si + 4\ HF + 2\ M(hfa)_2 \rightarrow 2\ M + SiF_4 + 4\ Hhfa$) is identical to reaction 5. Combination of SiF_4 with HF will generate H_2SiF_6, therefore, we can also write a reaction that involves H_2 as an intermediate and H_2SiF_6 as a product. The net reaction will be identical to reaction 4. We cannot distinguish the two reaction paths on the basis of the available experimental data.

The metal precursors, free ligands, HF, and SiF_4 are all soluble in supercritical or liquid CO_2. After the deposition, these fluorinated reactants and products can be easily removed from the surface of metal film. H_2SiF_6 in CO_2 is expected to behave differently from these fluorinated compounds because of its nonvolatile nature. In liquid CO_2 or in supercritical CO_2 at temperature slightly above the critical temperature, H_2SiF_6 can be adsorbed onto the surface and adhere to the texture of the deposited metal film along with trace amount of moisture in CO_2 solution and then react with H_2O to produce $Si(OH)_4$ or $SiO_2 \cdot xH_2O$ which is hard to remove by CO_2, forming the thin layer of white substance, as well as making the film rough and cloudy. Loose texture, low purity, poor adhesion and uniformity thus yield. Postdeposition cleaning can remove $Si(OH)_4$ but not $SiO_2 \cdot xH_2O$. This could be the reason for the observation of white spots and streaks in the SEM pictures of the films deposited from CO_2 solutions at 20−40 °C. In supercritical CO_2 at an elevated temperature (e.g., 80 °C), H_2SiF_6 dissociates and produces HF and SiF_4, both of which are very soluble in CO_2. This is probably the reason that no residue is left on the surface of the metal films obtained from supercritical CO_2 at 80 °C. For immersion deposition process in aqueous solutions, SiF_6^{2-} is soluble in water and is removed as soon as it is produced, therefore a clean film can be obtained at room temperature. It should be noted that the oxidation of Si^0 to Si^{4+} requires F^-; however, HF exists in its molecular form in the nonpolar CO_2, whereas in aqueous solution it dissociates partially and produces enough F^- at room temperature. A trace amount of water, as in the anhydrous etching and cleaning process of silicon,[80,81] should also facilitate the ionization of HF in CO_2. This may be another reason for the different optimum temperature ranges for these two processes. SFID usually proceeds with a reasonable rate at temperatures higher than room temperature.

The mechanism for SFID of metals on Ge could show some similarity to that on Si, and its details remain to be explored. Immersion deposition of metals onto germanium single-crystals from aqueous HF solutions containing metal ions has been manifested to be a typical galvanic displacement process.[82−84] The reduction of metal ions occurred through the electrons transfer from the valence band of the Ge, which was oxidized to Ge^{4+}. Likewise, the oxidation of Ge to Ge^{4+} is also required in SFID of metals on Ge to initiate the metal reduction.

Conclusions

High-purity Pd, Ag, and Cu metal films can be formed on silicon or germanium surfaces using the SFID

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procedure described in this paper. The deposition reactions involve a precursor, HF, and a substrate (silicon or germanium). The reducing agent is the substrate (Si or Ge) itself and metal films will form only on the substrate surfaces. This new metal film deposition process does not require hydrogen gas and high temperature, and HF is introduced by a HF-carrier. The new process is safe, economic in energy consumption, and easy to control. This low temperature process is also less likely to cause decomposition of metal precursors and products compared with other high temperature deposition processes. Preliminary test indicates that SFID deposited palladium films can be converted to palladium silicide by annealing. This environmentally friendly SFID technique in principle can be used to make metal coating on any substrate that reacts with HF and undergoes oxidation. Any metal precursor that is soluble in CO_2 and can be chemically reduced to its base metal by the electrons released from the substrate can be used to make metal films.

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Supporting Information Available: NMR, MS, and SEM pictures of Pd films on Ge. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Posting

Additional information has been added to the Acknowledgment section since the original ASAP posting of this article on 11/16/02. The correct version was posted on 12/03/02.

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