Reactive Deposition of Cobalt and Nickel Films from Their Metallocenes in Supercritical Carbon Dioxide Solution

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High-purity Co and Ni thin films were deposited directly onto the native oxide of Si wafers and onto TaN and TiN films supported on Si wafers by the hydrogen reduction of their respective metallocenes in supercritical CO_2 solution using a batch, cold-wall chemical fluid deposition (CFD) reactor. For Co deposition from bis(cyclopentadienyl)cobalt, substrate temperatures ranged between 285 and 320 °C and reactor pressures were 220−260 bar. For Ni deposition from bis(cyclopentadienyl)nickel, substrate temperatures were 175−200 °C and reactor pressures were 190−230 bar. In all cases, the reactor wall temperatures were maintained between 90 and 120 °C, restricting the depositions to the heated substrates only. The deposited films were characterized by SEM, XRD, and XPS. The films were found to be essentially free from ligand-derived contamination.

Introduction

Co and Ni thin films and deposits are technologically important for applications ranging from microelectronic and magnetic devices to protective coatings deposited by plating operations. For example, Co and Ni are employed in giant magnetoresistance (GMR) devices and other memory and data storage elements. Device structures for these applications include multilayer, granular, and heterogeneous alloy thin films and arrays of isolated Co wires in high aspect ratio features.[1−8] In microelectronics, $CoSi_2$, prepared by annealing Co films deposited on Si, is employed in silicide gate technology.[9,10] Recently, the potential for Co deposits to improve the performance of Cu interconnect structures in integrated circuits has received considerable attention. Co can serve as a capping layer to mitigate electromigration and oxidation of Cu.[11] Moreover, Co films doped with other elements including P, B, or W are reported to arrest the diffusion of Cu into adjacent dielectrics and could serve as conductive Cu diffusion barriers.[12,13] Finally, Co is reported to improve Cu adhesion to adjacent device layers. The development of a versatile Co deposition method thus provides the attractive possibility of a single technique solution for a number of issues.

To date Co and Ni thin films have been deposited using a variety of techniques including sputtering,[1,3,14] evaporation,[9,15] electrodeposition,[16,17] and chemical vapor deposition.[11,18−28] CVD is attractive for the most

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(1) Parkin, S. S. P.; Li, Z. G.; Smith, D. J. *Appl. Phys. Lett.* **1991**, *58*, 2710−2712.
(2) Xiao, J. Q.; Jiang, J. S.; Chien, C. L. *Phys. Rev. Lett.* **1992**, *68*, 3749−3752.
(3) Berkowitz, A. E.; Mitchell, J. R.; Carey, M. J.; Young, A. P.; Rao, D.; Starr, A.; Zhang, S.; Spada, F. E.; Parker, F. T.; Hutten, A.; Thomas, G. *J. Appl. Phys.* **1993**, *73*, 5320−5325.
(4) McGuire, T. R.; Plaskett, T. S. *J. Appl. Phys.* **1994**, *75*, 6537−6539.
(5) Li, X. G.; Murai, T.; Chiba, A.; Takahashi, S. *J. Appl. Phys.* **1999**, *86*, 1867−1773.
(6) Bal, M.; Ursache, A.; Tuominen, M. T.; Goldbach, J. T.; Russell, T. P. *Appl. Phys. Lett.* **2002**, *81*, 3479−3481.
(7) Zhang, Z.; Dai, S.; Blom, D. A.; Shen, J. *Chem. Mater.* **2002**, *14*, 965−968.
(8) Mattei, G.; Fernandez, C. d. J.; Mazzoldi, P.; Sada, C. *Chem. Mater.* **2002**, *14*, 3440−3447.
(9) Takahashi, F.; Irie, T.; Shi, J.; Hashimoto, M. *Appl. Surf. Sci.* **2001**, *169*−*170*, 315−319.
(10) Lee, S.-Y.; Cao, W.; Lee, E.; Lo, P.; Lee, S. K. *Thin Solid Films* **2002**, *405*, 73−76.
(11) Gu, S.; Atanasova, P.; Hampden-Smith, M. J.; Kodas, T. T. *Thin Solid Films* **1999**, *340*, 45−52.
(12) Shacham-Diamand, Y.; Zylberman, A.; Petrov, N.; Sverdlov, Y. *Microelectron. Eng.* **2002**, *64*, 315−320.
(13) Segawa, Y.; Horikoshi, H.; Ohtorii, H.; Tai, K.; Komai, N.; Sato, S.; Takahashi, S.; Ohoka, Y.; Yasuda, Z.; Ishihara, M.; Yoshio, A.; Nogami, T. In *ULSI XVII*; Materials Research Society: Montreal, PQ, 2001; pp 567−572.
(14) Childress, J. R.; Chien, C. L. *J. Appl. Phys.* **1991**, *70*, 5885−5887.
(15) Colgan, E. G.; Cabral, C. J.; Kotecki, D. E. *J. Appl. Phys.* **1995**, *77*, 614−619.
(16) Li, J.; Moskovits, M.; Haslett, T. L. *Chem. Mater.* **1998**, *10*, 1963−1967.
(17) Lee, C.-C.; Chou, T.-C. *Ind. Eng. Chem. Res.* **1998**, *37*, 1815−1820.
(18) Gross, M. E.; Kranz, K. S.; Brasen, D.; Luftman, H. *J. Vac. Sci. Technol. B* **1988**, *6*, 1548−1552.
(19) Dormans, G. J. M. *J. Cryst. Growth* **1991**, *108*, 806−816.
(20) Dormans, G. J. M.; Meekes, G. J. B. M.; Staring, E. G. J. *J. Cryst. Growth* **1991**, *114*, 364−372.
(21) Maruyama, T.; Nakai, T. *Appl. Phys. Lett.* **1991**, *59*, 1433−1434.
(22) Dickson, R. S.; Yin, P.; Ke, M.; Johnson, J.; Deacon, G. B. *Polyhedron* **1996**, *15*, 2237−2245.
(23) Choi, S. W. K.; Puddephatt, R. J. *Chem. Mater.* **1997**, *9*, 1191−1195.
(24) Gu, S.; Yao, X.; Hampden-Smith, M. J.; Kodas, T. T. *Chem. Mater.* **1998**, *10*, 2145−2151.
(25) Ivanova, A. R.; Nuesca, G.; Chen, X.; Goldberg, C.; Kaloyeros, A. E.; Arkles, B.; Sullivan, J. J. *J. Electrochem. Soc.* **1999**, *146*, 2139−2145.
(26) Brissonneau, L.; de Caro, D.; Boursier, D.; Madar, R.; Vahlas, C. *Chem. Vap. Deposition* **1999**, *5*, 143−149.

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demanding applications as it offers the potential for conformal coverage in confined geometries and high film purity. Options for Co CVD are limited, however, because useful precursors exhibit limited volatility, and deposition temperatures are often high. For example, deposition of Co via thermal CVD onto the native oxide of Si requires deposition temperatures up to 700 °C using cobaltocene and up to 600 °C using $(C_5H_5)Co(CO)_2$ as precursors.[19,20] Hydrogen-assisted CVD can reduce deposition temperature appreciably. For example, hydrogen-assisted reduction of cobaltocene via CVD can be conducted at 300 °C.[19] However, CVD depositions at these conditions are mass-transport limited, precluding conformal depositions in complex features.[19,20] A few other precursors have also been investigated for Co CVD. Some examples are $Co(acac)_2$,[11] $Co_2(CO)_8$,[18,20,24] $Co(CO)_3NO$,[25] and other carbonyl-based precursors.[20,22] Ni CVD also presents a number of challenges. $Ni(CO)_4$ is a useful precursor, but it is extremely toxic. The use of nickelocene often results in significant carbon contamination.[26,28]

We have developed an alternative approach to metal deposition that involves the reduction of soluble organometallic compounds dissolved in supercritical carbon dioxide (SC CO_2). The technique, called chemical fluid deposition (CFD), is essentially a hybrid approach that combines the advantages of solution-based processes, namely high precursor concentration and the elimination of precursor volatility constraints, with those of vapor phase techniques, namely favorable transport properties and an absence of surface tension. CFD has been used previously to deposit a number of high-quality metal films including Cu on various substrates.[29−33] In the case of Cu, CFD yields defect-free filling of sub-100 nm, high-aspect features on unseeded supports in a single step.[31,34] We also reported the preparation of conformal Ni films from $NiCp_2$ via CFD at 60 °C, but deposition at this temperature required substrate seeding with a catalytic seed layer such as Pd.[31]

Here we report the deposition of Co and Ni films directly onto a native oxide of Si wafers and onto TaN and TiN films supported on Si wafers, without the need for a catalytic layer, by H_2 reduction of cobaltocene ($CoCp_2$) or nickelocene ($NiCp_2$) in carbon dioxide solution. The Co films were deposited at a substrate temperature of 285−320 °C. Despite a low deposition temperature relative to CVD, high-purity Co films essentially free of C and O contaminations were obtained. In a related study, we have found that Co films can be doped with P at controlled levels via CFD, which broadens the utility of Co depositions via CFD in interconnect applications.[35] High-purity Ni films were deposited on the substrates at temperatures between 175 and 200 °C.

(27) Brissonneau, L.; Vahlas, C. *Chem. Vap. Deposition* **1999**, *5*, 135−142.
(28) Kang, J.-K.; Rhee, S.-W. *J. Mater. Res.* **2000**, *15*, 1828−1833.
(29) Watkins, J. J.; Blackburn, J. M.; McCarthy, T. J. *Chem. Mater.* **1999**, *11*, 213−215.
(30) Blackburn, J. M.; Long, D. P.; Watkins, J. J. *Chem. Mater.* **2000**, *12*, 2625−2631.
(31) Blackburn, J. M.; Long, D. P.; Cabanas, A.; Watkins, J. J. *Science* **2001**, *294*, 141−145.
(32) Long, D. P.; Blackburn, J. M.; Watkins, J. *J. Adv. Mater.* **2000**, *12*, 913−915.
(33) Kondoh, E.; Kato, H. *Microelectron. Eng.* **2002**, *64*, 495−499.
(34) Cabanas, A.; Blackburn, J. M.; Watkins, J. J. *Microelectron. Eng.* **2002**, *64*, 53−61.
(35) Hunde, E. T.; Blackburn, J. M.; Drewery, J.; Gaynor, J.; Watkins, J. J. manuscript in preparation.

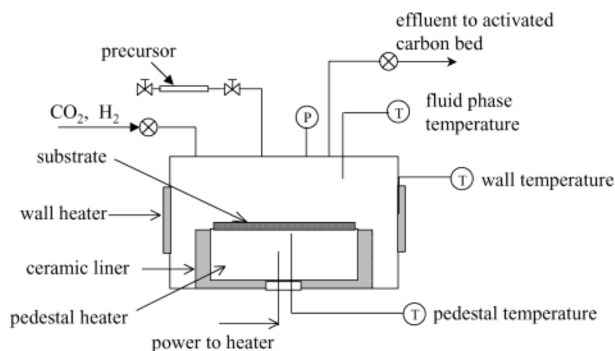


Figure 1. Schematic of the high-pressure cold-wall deposition system.

Experimental Section

$CoCp_2$ (min. 98%) and $NiCp_2$ (99%) were obtained from Strem Chemicals, Inc.,[36] and used as received. Coleman grade CO_2 (99.99%) and ultrahigh purity H_2 (99.999%) were obtained from Merriam-Graves Industries. The precursors were crushed to fine particle sizes to facilitate their dissolution in SC CO_2 and weighed inside a N_2 filled glovebox. The weighed precursor was then transferred to the reactor using a precursor delivery unit consisting of a section of 4.6-mm i.d. tubing isolated by ball valves at each end.

All deposition reactions were carried out in a cold-wall stainless steel reactor (Figure 1). The cold-wall reactor was equipped with a band heater to heat the reactor wall and a resistively heated pedestal heater to heat the substrate to the desired reaction temperature. Separate temperature controllers were used for the band heater and the pedestal heater allowing the selective heating of the substrate during the deposition reactions while keeping the reactor wall at a lower temperature. In all cases deposition proceeded selectively on the heated substrate with no reaction in the gas phase or on the reactor walls except as noted in the text.

A cleaned substrate was mounted and secured on top of the pedestal heater. The reactor was then flushed with N_2 while the wall was heated to a temperature of 90 °C using the band heater. The pedestal heater remained turned off until the end of the dissolution period. When the pedestal temperature reached 60 °C, carbon dioxide was added to the reactor up to the desired pressure (∼110 bar) from a high-pressure syringe pump (Isco, Inc. model 260D) maintained at 60 °C using a heating water jacket. CO_2 addition was conducted in 2 steps. First, the reactor was charged with CO_2 up to ∼60 bar. During this time the precursor remained in the delivery unit isolated from the reactor by the ball valves. Next, the CO_2 line was connected to the precursor delivery line and the remaining amount of CO_2 was charged, flushing the precursor into the reactor. Typically precursor concentrations between 0.2 and 0.5 wt % were used in the experiments.

After the addition of CO_2 and precursor, the reactor was maintained at ∼70 °C for about an hour to ensure complete dissolution of the precursor. The pedestal heater was then turned on to heat the substrate to the desired reaction temperature (285−320 °C in the case of Co CFD and 175−200 °C in the case of Ni CFD). The wall heater was turned off during pedestal heating. Once the pedestal temperature equilibrated to the desired value, H_2 was added to the reactor from a 26-mL high-pressure manifold at room temperature. The amount of H_2 added was calculated from the measured pressure drop in the H_2 manifold. A molar ratio of H_2 to precursor of 60−100 was used for the reduction of $CoCp_2$ and $NiCp_2$. The reactor pressures were typically 190−230 bar for Ni CFD and 220−260 bar for Co CFD during the deposition

(36) Strem Chemicals, Inc.: Newburyport, MA; www.strem.com.

Table 1. Representative Conditions for Co and Ni Film Depositions[a]

precursor	substrate	*T* (°C)	*P* (bar)	OM wt %	thickness (nm)	comments
$CoCp_2$	Si wafer	285	260	0.29	160	bright, reflective film
$CoCp_2$	Si wafer	300	224	0.20	680	mirror-like, reflective
$CoCp_2$	Si wafer	300	238	0.13	330	slightly dark and dull
$CoCp_2$	Si wafer	300	238	0.23	680	slightly dark and dull
$CoCp_2$	TaN/Si	300	224	0.20	720	bright, not reflective
$CoCp_2$	TaN/Si	300	220	0.31	340	slightly dark, dull
$CoCp_2$	TaN/Si	300	255	0.30	420	bright, not reflective
$CoCp_2$	TiN/Si	300	224	0.20	720	mirror-like, reflective
$CoCp_2$	TiN/Si	300	220	0.34	640	reflective
$CoCp_2$	TiN/Si	320	260	0.28	830	dark, nonuniform
$NiCp_2$	Si wafer	175	230	0.14	100	highly reflective
$NiCp_2$	Si wafer	175	200	0.20	170	reflective
$NiCp_2$	Si wafer	200	197	0.42	280	highly reflective
$NiCp_2$	Si wafer	200	197	0.31	230	reflective
$NiCp_2$	TaN/Si	175	230	0.14	170	highly reflective
$NiCp_2$	TaN/Si	175	204	0.49	240	reflective
$NiCp_2$	TaN/Si	200	208	0.29	300	reflective
$NiCp_2$	TaN/Si	200	210	0.34	290	reflective
$NiCp_2$	TiN/Si	175	190	0.27	110	bright, not reflective
$NiCp_2$	TiN/Si	175	200	0.20	130	reflective
$NiCp_2$	TiN/Si	200	200	0.25	190	bright, not reflective
$NiCp_2$	TiN/Si	200	197	0.42	210	reflective

[a] The deposition time was 30 min in all cases.

reaction depending on the deposition temperature, the loading of CO_2, and the amount of H_2 added. The reaction was allowed to run for 30−45 min. At the end of the reaction time, the pedestal heater was turned off and the reactor effluent was vented through an activated carbon bed. The reactor was then flushed dynamically with CO_2 to remove ligand decomposition products and residual precursor and to clean the reactor. Typical results of the deposition experiments are summarized in Table 1. Each deposition was conducted for 30 min. Because the depositions were conducted in batch mode, the deposition time does not reflect the growth rate, but rather was chosen for convenience.

The pedestal temperature and the wall temperature were measured as shown in the experimental set up in Figure 1. The substrate surface temperature was determined using a calibration of surface temperature versus pedestal temperature. The calibration curve was obtained by measurement of substrate temperature using a washer-type thermocouple affixed to the surface over a range of pedestal temperatures. The deposition temperatures reported refer to the substrate temperature.

The deposited films were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) techniques. X-ray diffraction was performed on the films using a Phillips X'Pert PW 3040 with a Cu Kα radiation. Field emission scanning electron microscopy (FE-SEM) was performed using a JEOL JSM 6320 FXV SEM. A Physical Quantum 2000 scanning ESCA microprobe was used for XPS analyses. Resistivity of the films was measured using a four point probe from Jandel.

Results and Discussion

Co Deposition. High-purity Co films were deposited onto the native oxide of Si wafers and films of tantalum nitride and titanium nitride supported on Si wafers (TaN/Si and TiN/Si, respectively) by the hydrogen reduction of $CoCp_2$ at temperatures between 285 and 320 °C and reactor pressures between 220 and 260 bar (Table 1). The concentration of $CoCp_2$ in CO_2 was 0.2−0.5 wt %. A molar ratio of H_2 to $CoCp_2$ of 60−100 was used for the reduction of $CoCp_2$.

The Co films deposited on the substrates ranged from highly specular and reflective to dull in appearance, depending on deposition temperature. Co films deposited onto the native oxide surface of Si at 285 °C were reflective, whereas films deposited at 300 °C were often darker and dull. On TiN/Si, reflective films were deposited at 300 °C whereas films deposited at higher temperature (320 °C) were darker and nonuniform. Co films deposited onto TaN/Si at 300 °C varied from somewhat reflective to nonreflective.

The thickness of the deposited Co films ranged 150−1000 nm. The adhesion of the Co films was good on TaN/Si surface as evidenced by the results of a simple tape test. The films did not peel off of the TaN/Si substrate and neither was any metal observed on the tape when an adhesive tape was stuck to the films and removed subsequently. The adhesion of the Co films on the native oxide surface of Si and on TiN/Si substrate was less tenacious: some of the deposited metal transferred to the tape and a few of the films delaminated from the substrates during the tape test. No attempts were made to optimize adhesion.

Although we did not attempt to measure deposition kinetics in the batch reactor, a dramatic increase in film thickness and mass gain on the substrate was observed when the deposition temperature was increased from 285 to 300 °C during depositions onto the native oxide surface of Si, indicating that the deposition rate was much faster at 300 °C. For example, when a precursor concentration of 0.23 wt % and $H_2/CoCp_2$ of 80:1 was used, the film thickness obtained at 300 °C (680 nm) was more than 4 times that obtained at 285 °C (150 nm) for the same reaction time. There was no apparent difference in the morphology or resistivity of the films deposited at 285 and 300 °C. At these deposition conditions, reducing the precursor concentration by half resulted in the reduction of the weight of the deposited film by almost half.

No significant deposition was observed below 280 °C on any of the 3 substrates. In fact, Co CFD from $CoCp_2$ is selective for catalytic and metallic surfaces versus the native oxide and barrier layers below 280 °C.[37] The

(37) Hunde, E. T.; Blackburn, J. M.; Drewery, J.; Gaynor, J.; Watkins, J. J. manuscript in preparation.

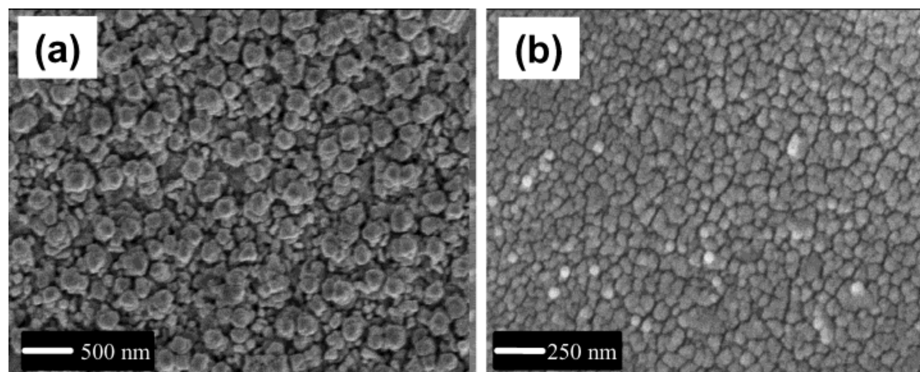


Figure 2. SEM images of Co films deposited onto: (a) native oxide of Si at 300 °C and 260 bar from $CoCp_2$ (0.23 wt %) in CO_2 solution, and (b) TiN/Si at 300 °C and 258 bar from $CoCp_2$ (0.25 wt %) in CO_2 solution.

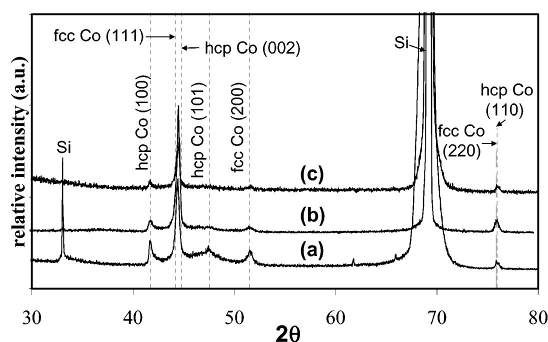
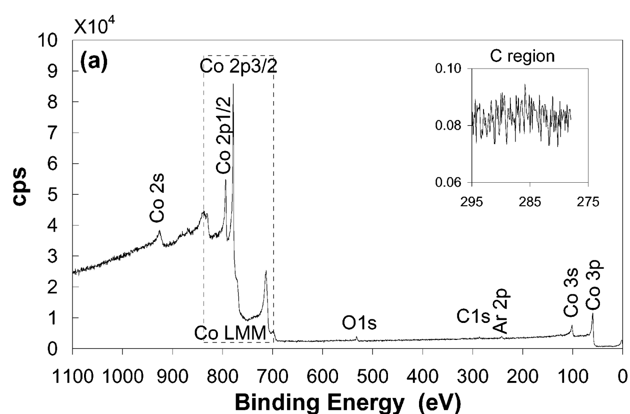


Figure 3. XRD of Co films deposited from $CoCp_2$ at 300 °C onto: (a) native oxide of Si, (b) TaN/Si, and (c) TiN/Si.

morphology of the Co films was studied using SEM. The analysis revealed that Co films exhibited spherical shaped grains with diameters of 50−100 nm on all three substrates (Figure 2). XRD analyses of the films revealed the coexistence of the hcp and fcc Co crystalline structures in the films (Figure 3). Although hcp Co is the stable crystalline structure at temperatures up to about 450 °C, the metastable fcc Co is also commonly observed in Co films deposited at lower temperatures as has been reported by several other groups.[38−40] We have also noted the coexistence of fcc Co and hcp Co structures in Co films we deposited on Cu via CFD at 200−300 °C.[41]

The chemical composition and purity of the films were investigated by XPS. XPS analysis revealed surface contamination of the exposed films as expected. Strong C1s and O1s peaks appeared at ~285 and ~531 eV binding energies, respectively, prior to sputtering of the films with Ar^+. Significant oxygen contamination at the surface is not surprising as the Co films will oxidize upon exposure to the atmosphere. An energy shift of 15 eV was observed between the Co 2p3/2 and Co 2p1/2 peak positions for the films deposited on all three substrates. Figure 4 shows the XPS survey performed on the Co films deposited on the native oxide of Si and TaN/Si, respectively. XPS survey on Co films deposited on TiN/Si showed similar results. In all the cases investigated, the C and O contamination of the films



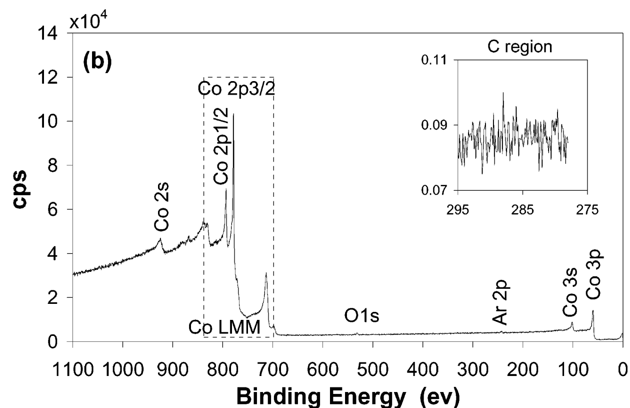


Figure 4. XPS survey on Co films deposited at 300 °C and 224 bar from $CoCp_2$ (0.20 wt %) in CO_2 solution onto: (a) native oxide of Si, and (b) TaN/Si, after sputtering with Ar^+.

drops to trace levels upon sputtering with Ar^+, indicating essentially pure Co deposits in the bulk. ^1H NMR analysis carried out on the effluents of the Co CFD reactions showed peaks corresponding to cyclopentane, cyclopentene, and other trace species that were not identified. In Co CFD, H_2 likely plays a dual role. First, it participates in the reduction of the precursor as evidenced by the ligand decomposition products. Second, because Co oxide is easily reduced by hydrogen, the presence of H_2 mitigates oxidation of the incipient Co film during deposition.[42]

The resistivity of the films was measured using a four-point probe. The values of the resistivity of the Co films on all 3 types of substrates (i.e., native oxide of Si, TaN/

(38) Fauster, T.; Rangelov, G.; Stober, J.; Eisenhut, B. *Phys. Rev. B* **1993**, *48*, 11361−11366.
(39) Rath, C.; Prieto, J. E.; Muller, S.; Miranda, R.; Heintz, K. *Phys. Rev. B* **1997**, *55*, 10791−10799.
(40) Kief, M. T.; Egelhoff, W. F. J. *Phys. Rev. B* **1993**, *47*, 10785−10814.
(41) Hunde, E. T.; Watkins, J. J., manuscript in preparation.
(42) Khodakov, A. Y.; Lynch, J.; Bazin, D.; Rebours, B.; Zanier, N.; Moisson, B.; Chuamette, P. *J. Catal.* **1997**, *168*, 16−25.

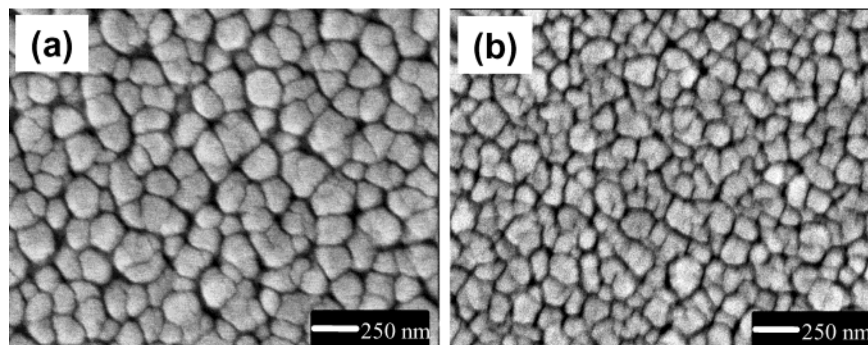


Figure 5. SEM images of Ni films deposited at 175 °C and 218 bar from $NiCp_2$ (0.15 wt %) in CO_2 solution onto: (a) native oxide of Si, and (b) TaN/Si.

Si, and TiN/Si) ranged between 8 and 12 $\mu\Omega$-cm. We note that there is some uncertainty in these values as Co film thickness was estimated from the mass of the deposited films. The measured resistivities are higher than the resistivity of bulk Co (5.6 $\mu\Omega$-cm), but compare favorably to Co films deposited by other means.[25] Because the levels of C and O contamination of the Co films are very small, the higher resistivity values of the films compared to that of bulk Co are most likely due to the morphology of the films.

We attempted to deposit Co on the same substrates from a β-diketonate Co precursor, tris(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(III). Although it was possible to deposit very high purity Co films free of C and O contamination on a Cu/TaN surface from this precursor via CFD in SC CO_2 at temperatures between 200 and 300 °C,[41] no significant deposition was achieved even at 320 °C on the native oxide layer of Si and the barrier layers. We did not pursue the possibility of deposition from this precursor on the substrates used in this study at higher temperatures.

Ni Deposition. High-purity (>99 at. %) Ni films were deposited onto the native oxide surface of Si, TaN/Si, and TiN/Si substrates at 175–200 °C and 190–230 bar by H_2 reduction of $NiCp_2$ dissolved in SC CO_2 (Table 1). The concentration of $NiCp_2$ in CO_2 was 0.2–0.5 wt %. A molar ratio of H_2 to $NiCp_2$ of 60–100 was used for the reduction of the precursor. Ni films deposited on the substrates were almost always reflective. The thickness of the deposited film ranged between 100 and 300 nm. The adhesion of the films to the substrates was generally good. All the films deposited on TaN/Si and TiN/Si passed the simple tape test. These films also did not fail during a scribed tape test in which a rectangular region of ~1 cm × 1 cm was scored in a crosshatch pattern prior to application and removal of the tape. Most films deposited on Si passed the simple and the scribed tape tests. A few of these films partially failed when the tape was applied at the edge of the substrate during the tape test and some metal was removed on the tape. Although $NiCp_2$ can be used to deposit Ni films on Pd or Pt seeded substrates at 60 °C via CFD, deposition of Ni on the substrates did not occur at temperatures up to 150 °C.

SEM analyses revealed that the Ni films have spherical morphology with grain sizes of 80–190 nm (Figure 5). XRD showed that the Ni films deposited on all three substrates were highly crystalline with strong reflections characteristic of fcc Ni (Figure 6). XPS analyses indicated that the Ni films deposited on all the substrates were essentially free of C and O contamination. Figure 7 shows an XPS survey performed on a Ni film deposited on Si (native oxide surface) at 175 °C. The XPS surveys performed on Ni films deposited on Si, TaN/Si, and TiN/Si at 175 and 200 °C showed similar results.

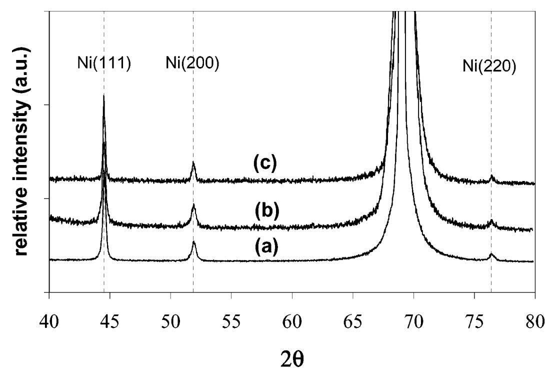


Figure 6. XRD of Ni films deposited from $NiCp_2$ at 175 °C onto: (a) native oxide of Si, (b) TaN/Si, and (c) TiN/Si.

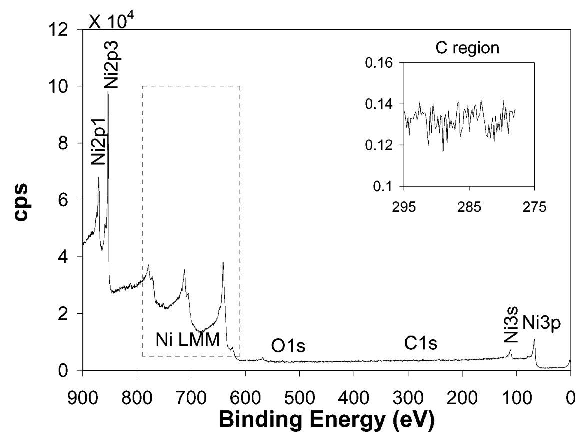


Figure 7. XPS survey on a Ni film deposited onto native oxide of Si at 175 °C and 218 bar from $NiCp_2$ (0.15 wt %) in CO_2 solution after sputtering with Ar^+.

Conclusions

High-purity Co and Ni films (>99 at. %) were deposited directly onto the native oxide of Si, TaN/Si, and TiN/Si substrates by the H_2 reduction of $CoCp_2$ or $NiCp_2$ dissolved in SC CO_2 using CFD without a catalytic seed layer. Deposition of Co did not occur on the substrates up to ~280 °C. At 300 °C, however, high-purity Co films were deposited on all the substrates. Deposition of Ni on the substrates was carried out at 175–200 °C. Our

results demonstrate that CFD is a viable alternative for Co and Ni depositions on a variety of substrates.

Acknowledgment. Support from Novellus Systems, the National Science Foundation (CTS 9811088), and the National Environmental Technology Institute is greatly acknowledged. Facilities supported by the Materials Research Science and Engineering Center at the University of Massachusetts were used for deposit characterization. J.J.W. acknowledges support from the Camille Dreyfus Teacher-Scholar Award and the David and Lucille Packard Foundation.

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