The Effects of Processing Parameters in the Chemical Vapor Deposition of Cobalt from Cobalt Tricarbonyl Nitrosyl

Ana R. Ivanova,^a Guillermo Nuesca,^a Xiaomeng Chen,^a Cindy Goldberg,^a Alain E. Kaloyeros,^Z Barry Arkles,^b and John J. Sullivan^c,*

^aNew York State Center for Advanced Thin Film Technology and Department of Physics, The State University of New York at Albany, Albany, New York 12222, USA

^bGelest Incorporated, Tullytown, Pennsylvania 19007, USA

^cMKS Instruments, Andover Massachusetts 01810, USA

This paper reports the development of a thermal chemical vapor deposition process for pure cobalt from the source precursor cobalt tricarbonyl nitrosyl for incorporation in integrated circuit silicide applications. Studies were carried out to examine the underlying mechanisms that control Co nucleation and growth kinetics, including the effects of key process parameters on film purity, texture, morphology, and electrical properties. For this purpose, systematic variations were implemented for substrate temperature, precursor flow, hydrogen reactant flow, and deposition time (thickness). Resulting films were analyzed by Rutherford backscattering spectrometry, X-ray photoelectron spectroscopy, X-ray diffraction, fourpoint resistivity probe, scanning electron microscopy, and atomic force microscopy. These investigations identified an optimized process window for the growth of pure Co with resistivity of $9 + 2 \mu\Omega$ cm, smooth surface morphology, and root-mean-square surface roughness at or below 10% of film thickness.

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Continued enhancement in integrated circuitry (IC) speed and performance through scaling down of the minimum feature size below 0.25 μ m requires the implementation of innovative material and process solutions.¹ A case in point is cobalt silicide (CoSi₂), which is emerging as a viable silicide replacement for titanium silicide (TiSi₂) in future self-aligned silicide (salicide) technology.² The key advantages of CoSi₂, in comparison with TiSi₂, are wider silicidation window, and easier scalability to finer line geometries.² Additionally, epitaxial CoSi₂ exhibiting superior material integrity and thermal stability can be formed on Si(100) in a fashion which is highly com-patible with current Microelectronics technology.³⁻⁵

In a typical salicide process, the blanket metal is deposited first, followed by annealing to form a silicide phase on the device regions with exposed Si, and the unreacted metal is subsequently etched.⁶ Sputtering^{4,7,8} or evaporation^{9–11} techniques are commonly employed for Co deposition. Sputtering is typically preferred over evaporation due to the higher purity of sputterdeposited films³ and superior control of the sputter-deposition process.⁶ However, the highly energetic ions in the sputtering process can potentially induce substrate damage. This is particularly undesirable in salicide processing, since the metal is deposited directly over the active source and drain device regions which are formed in single-crystal Si.

Alternatively, chemical vapor deposition (CVD) can be employed to grow pure metal films without ion-induced substrate damage.¹² Other attractive features of CVD include the ability to uniformly coat aggressive substrate topographies and compatibility with emerging microelectronics fabrication flows.¹³ Furthermore, the substrate surface could be actively involved in the CVD reaction pathways, thereby allowing tight control of film texture and grain size, including the formation of metastable phases and epitaxial growth.¹⁴ These features can possibly lead to silicide formation with superior performance as compared to conventional physical deposition methods, especially given the strong dependence of the silicide on the metal/Si interfacial conditions.

A key component in the development of a viable Co CVD process is the identification of a suitable precursor source with the chemical characteristics required for growth of pure Co films at acceptable delivery and process temperature windows. The majority of CVD Co work has focused on fabrication of Co layers for magneto-optic applications,^{15,16} magnetic Co-containing alloys,^{17,18} or in situ doping with Co.^{19–21} There are also some recent reports on CVD CoSi₂ formation by codeposition.^{22,23} In these applications, metallorganic compounds are typically employed, since cobalt halides are not suitable due to low volatility and high decomposition temperatures.^{24,25}

Within the scarce literature on cobalt CVD, considerable attention has been given to the deposition of Co by thermal decomposition of cobalt carbonyl $Co_2(CO)_8$.^{19,22,23,26} The most serious drawback associated with its use

* Electrochemical Society Active Member

^z E-mail: ak127@csc.albany.edu

is the existence of undesirable, but thermodynamically favorable, precursor reaction pathways which compete with the deposition of pure Co. These pathways include polymerization reaction in the gas phase and reaction of the precursor with H₂ to form a highly volatile and extremely unstable hydrocobalt tetracarbonyl HCo(CO)₄.²⁷ Furthermore, Co₂(CO)₈ decomposes during storage even under vacuum or inert atmosphere.²¹

Other candidate precursors for Co CVD included cobaltocene $Co(C_5H_5)_2$, cyclopentadienylcobalt dicarbonyl $C_5H_5Co(CO)_2$, and cobalt acetylacetonate $Co(C_5H_7O_2)_3$. ^{22,28,29} All three sources require H₂ reduction and have been typically employed in atmospheric pressure CVD (APCVD), yielding Co films with an unacceptably rough surface morphology. At reduced reactor pressure, deposition from cobaltocene does not occur on any substrate,²⁸ while use of $C_5H_5Co(CO)_2$ results in Co films containing up to 50 atom carbon.²²

It is thus apparent that the cobalt precursors discussed do not exhibit the desired properties for applications in a CVD-based salicide process. Accordingly, we have identified cobalt tricarbonyl nitrosyl, $Co(CO)_3NO$, as a more suitable precursor for such applications. This assessment is based on its favorable chemical and physical properties, which include high volatility (vapor pressure 26 Torr at 0°C and 100 Torr at 25°C), availability in liquid form, and relatively good stability (decomposition temperature >66°C). ^{25,30} Furthermore, Co is in an oxidation state of zero in this compound, which implies that metal-ligand bonds are easily cleaved to yield pure metal films according to³¹

$$Co(CO)^{3}NO(g) \rightarrow Co(s) + 3CO(g) + NO(g)$$
 [1]

In this respect, Co(CO)_3NO has not been studied to the same extent as other metal carbonyls, and most of the research has focused on photolysis reactions. 15,16

Accordingly, we sought to develop a co CVD-based route to the formation of CoSi₂ for applications in sub-0.25 μ m microelectronics technology. In this respect, the present paper focuses on the development and optimization of CVD processing conditions, leading to the deposition of pure Co films with viable properties and performance. The incorporation of the CVD Co process in the formation of device-quality CoSi₂ is the subject of a subsequent report by the present authors.

Experimental

Process development was performed in a standard custom-designed, stainless steel alpha-type CVD reactor.

The precursor was delivered to the reactor chamber using an MKS type 1150C vapor source mass flow controller (MFC) to ensure reliable and reproducible delivery. The unit was calibrated to a maximum flow of 5 sccm of $Co(CO)_3NO$. During actual processing, the 1150C MFC was maintained at 50°C, while the upstream and downstream delivery lines were kept at 40 and 55°C, respectively, in order to prevent precursor recondensation.

The precursor was maintained in a specialized glass reservoir, which was immersed in an ice bath to ensure that the precursor temperature was constantly maintained at 0°C. This source temperature was mandated by the need to maintain a highly controllable precursor vapor pressure, given that the performance of the MKS 1150 MFC is dependent on the inlet (upstream) and outlet (downstream) pressures. From this standpoint, the vapor pressure of the source, as driven primarily by its temperature in this case, plays a significant role in the MFC's delivery profile.

In the reactor geometry employed, the precursor delivery lines and gas sidelines were connected to a cone-type showerhead, which was mounted on the top of the reactor chamber and designed to provide uniform gas flow over the entire substrate surface. In this geometry, reactants were flowed downward with pumping being carried out from the bottom of the reactor. The CVD system was equipped with two separate gas delivery lines for Ar and H₂, whose flow was controlled using MKS type 1259C electronic MFCs. The process chamber walls were maintained at $60 \pm 10^{\circ}$ C.

In a typical CVD experiment, the samples were placed on a resistive heater positioned directly under the showerhead. The reactor was pumped down to a base pressure of 10^{-6} Torr using a Seiko-Seiki model STP-300 turbomolecular pump. The substrates were then heated to the desired processing temperature and the reactants introduced into the reactor chamber. A mechanical pump was used for process pumping, and the pumping speed was controlled with a manual throttle valve.

The silicon substrates used in this study were cleaned ex situ by rinsing with acetone and methanol, and then dried using compressed high-purity argon gas. The native oxide was subsequently removed with a 1 min dip in a 10% hydrofluoric acid solution followed by a deionized water rinse. Finally, the samples were again dried in a high-purity argon atmosphere. Additional substrates used were blanket silicon dioxide (SiO₂) and silicon nitride (Si₃N₄) on Si, and Sematech produced patterned structures with nominal 0.25 μ m, 4:1 aspect ratio (AR) features. These samples were subjected to acetone and methanol rinse only.

As mentioned earlier, the effects of four key process parameters on resulting film characteristics were investigated. These were substrate temperature, deposition time, precursor flow, and H₂ reactant gas flow. The process regime investigated is given in Table I. It should be noted that subsequent analyses showed that the resulting film characteristics were not dependent on the type of substrate used (i.e., n-or p-type Si, SiO₂, or Si₃N₄). Thus, the results reported herein are primarily from the analyses of films deposited on Si substrates.

Analytical Techniques Employed

The compositional, structural, and electrical properties of the deposited Co films were thoroughly analyzed by Rutherford back-scattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), four-point resistivity probe, scanning electron microscopy (SEM), and atomic force microscopy (AFM). The resultant findings are presented in terms of the properties of the Co films produced under the process regime given in Table I.

Film thickness was measured by RBS and cross-sectional SEM. RBS analyses were carried out on a 4.5 MeV Dynamitron model P.E.E. 3.0 linear accelerator. RBS spectra were taken using a 2 MeV He⁺ beam. SEM investigations employed a Zeiss DSM 940 microscope using a 20 keV primary electron-beam.

Deposition rates were defined as T/t, where T is film thickness and t deposition time. Deposition time was measured as the period of time during which the precursor was delivered to the reactor. Four-point probe measurements were performed to determine the sheet resistance on the blanket samples. The film resistivity was then calculated using the thickness values measured with RBS, since thickness measurements by RBS and SEM were in excellent agreement.

Film composition and associated elemental chemical states were investigated using XPS. The XPS measurements were carried out on a Perkin-Elmer PHI 5500 multitechnique system with spherical capacitor analyzer. The gold $f_{7/2}$ line was used as a reference and the analyzer calibrated accordingly. The primary X-ray beam was generated with a Mg K α X-ray source at operating power of 300 W and 15 keV applied to the anode. The results were standardized using a sputtered Co sample.

XRD analysis were done on a Scintag XDS 2000 X-ray diffractometer equipped with a Cu K α X-ray source and a horizontal wide-angle four-axis goniometer with stepping motors which allowed independent or coupled theta/2 theta axes motion. XRD spectra were collected in the low-angle incidence geometry, with an angle of incidence of 5° being used (angle as measured between the incident beam and the sample surface). In this mode, data collection is performed by fixing the incidence angle at 5°, and the XRD Table I. Process regime investigated for CVD Co. For all experiments, the precursor source temperature was kept at 0° C.

Substrate temperature (°C)	Precursor flow (sccm)	H ₂ reactant flow (sccm)	Reactor pressure (Torr)	Deposition time (min)				
Substrate temperature series								
210	0.5	750	1.5	15				
240	0.5	750	1.5	15				
270	0.5	750	1.5	15				
300	0.5	750	1.5	15				
330	0.5	750	1.5	15				
360	0.5	750	1.5	15				
390	0.5	750	1.5	15				
420	0.5	750	1.5	15				
450	0.5	750	1.5	15				
480	0.5	750	1.5	15				
Deposition time series								
390	0.5	750	1.5	3				
390	0.5	750	1.5	5				
390	0.5	750	1.5	10				
390	0.5	750	1.5	15				
390	0.5	750	1.5	20				
390	0.5	750	1.5	30				
Precursor flow series								
390	0.25	750	1.5	20				
390	0.5	750	1.5	10				
390	1	750	1.5	7				
390	1.5	750	1.5	5				
Hydrogen reactant flow series								
390	0.5	500	1	10				
390	0.5	600	1.28	10				
390	0.5	750	1.5	10				
390	0.5	850	1.67	10				
390	0.5	1000	2	10				

pattern is collected for 2q ranging 25-65°. The advantages of this approach include increased sensitivity due to the longer X-ray transmission path through the thin film and elimination/minimization of the high-intensity peak from the Si substrate. The collected XRD patterns were compared to the Co reference patterns from the standard Joint Committee for Powder Diffraction Standards (JCPDS) powder diffraction file (PDF).

AFM was performed on a Digital Instruments Nanoscope III multimode scanning probe microscope. Data was collected in tapping mode AFM with Si cantilevers at resonance frequencies in the range 200-300 kHz. Surface roughness was calculated as the standard deviation of the mean height of surface structures. Multiple surface locations were probed for each sample using a variety of scan sizes ranging from 500 x 500 nm to 10 x 10 μ m. The average surface grain size was determined using standard statistical averaging techniques.

Hydrogen incorporation in representative samples was analyzed on the Dynamitron linear accelerator using a ^{15}N beam. The nuclear reaction $^{15}N(p, \alpha, \gamma)^{12}C$ with resonance energy of 6.385 \pm 0.005 MeV was employed.

Results and Discussion

Study of reaction kinetics. Figure 1 displays an Arrhenius plot of the ln (growth rate) vs. the reciprocal absolute temperature for thermal CVD Co from $Co(CO)_3NO$. As can be seen in Fig. 1, no film deposition was observed below 150°C. Between 150 and 200°C, the films were a cobalt oxide phase which was heavily contaminated with carbon and nitrogen, as supported by the XPS and XRD data shown in Fig. 2 and 3, respectively, and listed in Table II, and were typically electrically insulating.

The observation of the CoO phase is supported by the work of Roustan et al., 32 which indicated the existence of Co(CO)₃NO reaction pathways which



Figure 1. Arrhenius plot for CVD Co from $Co(CO)_3NO$ as a function of substrate temperature.



Figure 2. XPS compositional trends for CVD Co films as a function of substrate temperature.

are thermodynamically favorable to the growth of CoO. Roustan et al. performed time-resolved Fourier transform infrared (FTIR) and massspectrometry studies of the adsorption and reaction of $Co(CO)_3NO$ on a catalytic surface, namely, activated alu-mina $(Al_2O_3)^{.32}$ The latter was maintained at room temperature. Under such experimental conditions, Roustan et al. observed the adsorption of CoNOCO radicals to the alumina surface. Further-more, they found that surface isocyanates (NCO) were readily formed from NO and CO ligands, with the Co atom being the most likely candidate to act as acceptor for the extra oxygen atom. The net result was the formation of a CoO phase which was contaminated with C and N.

Between 200 and 250°C, no carbon was detected in the CoO phase, even though the films were still contaminated with N, as documented by the XPS and XRD data shown in Fig. 2 and 4a. This finding is supported by the energetics of chemical bonding configurations in Co(CO)₃NO. In particular, it is known that the Co-NO bond in Co(CO)₃NO is a three-electron π -type bond, which is shorter than the Co-CO bond.³¹ These characteristics indicate that the Co-NO bond is thus stronger, and is thus expected to require even higher energy to cleave, than the Co-CO bond. It is suggested that in the temperature



Figure 3. Typical low angle incidence XRD pattern of Co film deposited at 180°C.

regime 200-250°C, the thermal budget available is conducive to complete dissociation of the Co-CO but not the Co-NO bond. This results in the presence of Co-NO radicals on the Si surface. As proposed by Roustan et al.,³² these radicals subse-quently react to produce a nitrogen-contaminated CoO phase.

Alternatively, in the process temperature range 250-350°C, the films were mostly a Co phase, which included a small concentration of the CoO oxide phase. Finally, in the temperature range above 350°C, the films were Co metal, as documented by the XPS and XRD data shown in Fig. 2 and 4b. The observed trend in the dependence of growth rate on substrate temperature indicates that the CVD Co process is in the mass-transport-limited regime. Our results seem to indicate that the deposition of pure cobalt occurs upon the availability of sufficient thermal energy for complete precursor dissociation and complete desorption of reaction by-products from the substrate surface prior to the occurrence of the undesirable reactions discussed.

Effects of substrate temperature on film properties. The dependence of film composition on substrate temperature has already been discussed in the first section and summarized in Table II. Therefore, only relevant data is presented herein for the sake of clarity and completion.

Compositional uniformity across the bulk of the films was determined by XPS depth profiling and found to be consistently uniform throughout the entire process window investigated. This is illustrated in Fig. 5 for pure Co films grown at 390°C. Additionally, accurate chemical phase determination was achieved by examining the location (E) of the high-resolution XPS Co 2p_{3/2} core peak as well as the difference in binding energies (δ) between the Co XPS 2p_{3/2} and 2p_{1/2} core peaks. For example, a determination of the chemical phase present in samples deposited at 390°C was performed by comparing associated XPS data, with E = 785.5 eV, δ = 15.08 eV, to those of a Co reference standard, with E = 778.5 eV, $\delta = 15.08$ eV. The XPS data thus showed that the films were a pure Co metal phase. Similarly, the detection of Co²⁺ XPS shake-up peaks in the samples deposited at 210°C, along with the observation of E = 778.96 eV, $\delta = 15.20$ eV, indicate that the films were primarily a CoO phase, for CoO standard, E = 780.4 eV, $\delta = 15.5 \text{ eV}$. The overall dependence of film composition on substrate temperature is displayed in Fig. 2.

Hydrogen profiling indicated that hydrogen content in the films was inversely proportional to substrate temperature, with 10 atom % hydrogen incorporated in samples deposited at 210°C, while the samples grown at 390°C were hydrogen-free.

The dependence of film texture on substrate temperature was also investigated by low angle incidence XRD, as shown in Fig. 4a and 4b. All films were polycrystalline, regardless of the chemical phase present or substrate temperature used. Below a substrate temperature of 250°C, the XRD

Table II. Summary of film compositional characteristics as a function of substrate temperature.

Temperature range	150-200°C	210-250°C	250-350°C	350-480°C	
Oxygen, atom % (XPS)	15-25	15-20	2.5-10	<1 atom %	
Nitrogen, atom % (XPS)	5-7	4-5	<1	<1 atom %	
Carbon, atom % (XPS)	4	<1	<1	<1 atom %	
Resistivity, $\mu\Omega$ cm (four-point probe)	>1000	>1000	15-40	8.5-11 μΩ cm	
Structure (XRD)	CoO	CoO	hcp Co	fee Co	
rms surface roughness, nm (AFM)	~10	6-7	20-30	12-18 (up to 450°C)	
				110 (above 450°C)	
Average surface grain size, nm (AFM)	~70	63	135	75-112 (up to 450°C)	
				500-3000 (above 450°C)	

spectra corresponded primarily to a CoO face-centered-cubic (fcc) phase, as documented by the presence of the CoO (111), (200), and (220) reflection peaks. No Co metal reflection peaks were detected within the detection limits of XRD. However, all peak positions were shifted from the reference CoO XRD pattern, as obtained from the Powder Diffraction File (JCPDS PDF no. 9-402). This shift was attributed to the existence of a nonstoichiometric oxide phase. In addition, lattice constant measurements, as derived from the (111) peak positions, yielded values of 4.44 and 4.48 Å for samples deposited at 210 and 240°C, respectively. Alternatively, the lattice constant for the reference CoO phase is 4.26 Å. As a result, it is suggested that the higher lattice constant observed for the CoO samples could be attributed to the presence of a significant concentration of defects in the CoO matrix. In particular, oxygen concentrations were only about 15-20 atom % in the CVD CoO films grown between 200 and 250°C, vs. 50 atom % in the reference CoO sample.

For substrate temperatures between 250 and 300°C, the XRD spectra corresponded primarily to a Co hexagonal-close-packed (hcp) phase, as documented by the presence of the hcp Co (100), (002), and (101) reflection peaks. The locations of these peaks are in agreement with the reference hcp Co XRD pattern, as obtained from the JCPDS PDF no. 5-727. Corresponding lattice constants for the hexagonal structure were a = 2.16 Å and c = 4.06 Å. Alternatively, in the substrate temperature range 300-350°C, XRD signaled the presence of a mixture of the hcp and fcc phases, as documented by the detection of the additional Co(111) and (200) fcc reflection peaks. The intensity of the Co fcc peaks increased gradually with higher substrate temperature, while the height of their hcp counterparts decreased in a similar fashion. This behavior indicated that the fcc phase was becoming the dominant phase with increased thermal budget. Finally, all films grown above 450°C consisted entirely of a Co fcc phase. The corresponding lattice constant for the cubic structure was a = 3.54 Å, in excellent agreement with the reference Co XRD pattern, as obtained from the JCPDS PDF no. 15-806.



Figure 4. Low angle incidence XRD patterns of Co films deposited at substrate temperature in the range (a, top) 200-350°C and (b, bottom) 360-500 °C.



Figure 5. Ttypical XPS depth profile of a pure, 140 nm thick, Co film deposited at 390°C.

Film resistivity values were consistent with the observed compositional trends across the entire process window investigated, as summarized in Table II and plotted in Fig. 6. As expected, film resistivity was elevated in the oxide phase, with the resistivity increasing with higher contamination. Alternatively, resistivity decreased from values in the range 15-40 $\mu\Omega$ cm for substrate temperatures of 250-350°C, to values in the range 8.5-10.0 $\mu\Omega$ cm for substrate temperatures of 350-450°C. In this respect, the increase in intensity and associated decrease in full-width-at-half-maximum (fwhm) of the XRD (111) reflection of the Co metal fcc phase, as shown by Fig. 4b, indicates a more textured Co phase with increased thermal budget.

Surface grain morphology and associated roughness were also highly dependent on substrate temperature. In particular, films grown in the temperature window 200-250°C exhibited a dense surface grain morphology, with average grain size around 63 nm (Fig. 7a). Corresponding rms surface roughness ranged between 6 and 7 nm for ~45 nm thick films, or ~1.5% of total film thickness. Conversely, films deposited between 250 and 350°C showed a markedly different surface grain morphology, with frequently well-separated, irregularly shaped grains, as shown in Fig. 7b. Average surface grain size was ~135 nm.

For films grown at processing temperatures in the range $350-450^{\circ}$ C, the films exhibited smooth and dense surface morphology. For example, the rms surface roughness and average grain size were 12.5 and 75 nm, respectively, for a 140 nm thick film grown at 390° C (Fig. 7c). Above 450° C, films exhibited significant increase in surface roughness, from an rms value of 37 nm for films grown at 450° C, up to 110 nm for their 480° C counterparts. Corresponding surface morphology consisted primarily of an underlying layer of large grains, with sizes ranging from ~0.5 to ~3.0 μ m, covered with a matrix of smaller grains, approximately 10 nm diameter, as shown in Fig. 7d.

Evolution of film characteristics as a function of deposition time. — The evolution of film structure and morphology as a function of processing time was examined by performing deposition runs for 3, 5, 10, 15, 20, and 30 min, and examining the structural and compositional characteristics of the resulting films by XPS, XRD, AFM, SEM, RBS, and four-point resistivity probe. For these runs, substrate temperature, precursor flow, hydrogen reactant flow, and reactor pressure were maintained at 390°C, 0.5 sccm, 750 sccm, and 1.5 Torr, respectively.



Figure 6. CVD Co film resistivity as a function of substrate temperature.

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Figure 7. AFM images of Co films deposited at substrate temperature of (a, top left) 210, (b, top right) 330, (c, bottom left) 390, and (d, bottom right) 480°C. The scale in (d) was magnified 10 times in order to provide a better illustration of associated film morphology.

RBS and SEM findings indicated that film thickness was a linear function of deposition time, as shown in Fig. 8. The resulting line could be extrapolated directly through the origin of the x-y axes, which indicated the absence of an incubation period and the occurrence of Co growth immediately upon exposure of the substrate to precursor flux. The corresponding slope yielded an average growth rate of ~ 10 nm/min.

XRD analyses showed the presence of a Co hcp phase for films grown within the first 5 min of substrate exposure to precursor flux, or film thickness below ~50 nm. The intensity of the Co fcc peaks increased gradually with longer run times, while the height of their hcp counterparts decreased in a similar fashion. This behavior resulted in the detection of mixed hcp and fcc Co phases for film thickness between 50 and 300 nm. Finally, only the Co fcc phase could be seen for run times above 30 min, or film thickness above 300 nm.



Figure 8. CVD Co film thickness as a function of deposition time.

As expected, all films were pure Co, within the detection limits of XPS and RBS. Corresponding resistivity was ~15.0 \pm 1.5 $\mu\Omega$ cm for ultrathin films with thickness below 50 nm. This value decreased to ~9.0 \pm 1.0 $\mu\Omega$ cm for films with thickness in the range 50-200 nm and ~7.0 \pm 0.5 $\mu\Omega$ cm for thicker films. All films exhibited smooth and continuous surface morphology, with rms surface roughness being consistently below 10.0 \pm 2.0% of film thickness and average surface grain size ~70.0 \pm 3.0 nm.

Effects of precursor flow on film properties. For this study, precursor flow was varied between 0.25 and 1.5 sccm, which corresponded to precursor partial pressures in the range 0.5-3 mTorr. For these runs, substrate temperature, hydrogen reactant flow, and reactor pressure were maintained at 390°C, 750 sccm, and 1.5 Torr, respectively. Based on an initial set of screening



Figure 9. CVD Co film growth as a function of CO(CO)3NO flow.



Figure 10. CVD Co film growth rate as a function of hydrogen reactant flow.

studies, deposition times were adjusted to obtain a constant film thickness of \sim 100 nm for the various precursor flows used. The purpose was to eliminate any thickness-induced variations in film properties.

In this respect, Fig. 9 plots film growth rates as a function of precursor flow. As can be seen in the figure, growth rates exhibited a linear dependence on precursor flow, with growth rates increasing nearly 80% in response to a 100% rise in precursor flow. This behavior could indicate that virtually all the precursor is being consumed in the CVD decomposition reaction within the process window investigated. Alternatively, the linear dependence on flow rate can possibly be attributed to first-order kinetic dependence on precursor pressure, since this variable appears to change linearly with precursor flow rate.

For precursor flows below 1.5 sccm, all films were pure Co, within the detection limits of XPS and RBS. Corresponding resistivity increased from 9.0 to $11.0 \pm 1.0 \,\mu\Omega$ cm as a function of precursor flow. At 1.5 sccm, however, XPS indicated the presence of ~ 1.5 atom % oxygen. This contamination is attributed to oxygen inclusion upon film exposure to air, as supported by XPS and AFM. In particular, the high-resolution Co $2p_{3/2}$ core peak position, as well as the difference in binding energies (8) between the co $2p_{3/2}$ and $2p_{1/2}$ XPS core peaks, corresponded to a pure Co phase. Additionally, AFM micrographs of the surface morphology of the Co film showed the presence of frequently well-separated, irregularly shaped grains. These findings seem to suggest that diffusion from air through intergranular gaps might have led to the incorporation of oxygen at Co grain boundaries. Corresponding resistivity was ~ 15.0 ± 1.5 $\mu\Omega$ cm.

Effects of hydrogen flow on film properties. It is well established that hydrogen plays a key role in the decomposition process of metal carbonyls, leading to the deposition of pure metal.²⁴ In particular, it was reported that hydrogen greatly facilitates the removal of reaction by-products, thereby preventing C and O contamination in Co deposition from carbonyl precursors.²⁷

Our findings are in agreement with these observations, as documented by a study which varied hydrogen flow rates between 500 and 1000 sccm, which corresponded to hydrogen partial pressures in the range ~ 1.0-2 Torr. For these runs, substrate temperature and precursor flow were maintained at 390°C and 0.5 sccm, respectively. In particular, films deposited at the lower hydrogen flow rate of 500 sccm were found to contain up to 2 atom % oxygen and exhibited higher resistivity values in the range 15 to $16 \pm 1.5 \,\mu\Omega$ cm. This is consistent with earlier studies by the present investigators which showed that films grown with hydrogen flows in the range 250-350 sccm were contaminated with up to 50 atom % oxygen, leading to the formation of an insulating CoO phase. Conversely, films grown at hydrogen flows above 500 sccm were pure Co, as documented by XPS, with resistivities in the range 8.0 to $10.0 \pm 1.0 \,\mu\Omega$ cm.

Interestingly, growth rates were found to decrease with higher hydrogen flow at a constant precursor flow, as illustrated in Fig. 10. This trend could be attributed to the role of increased hydrogen flow in reducing precursor residence time in the reaction zone, which decreases the probability for precursor reaction and generates a reduction in growth rates. Another possibility is the saturation of a higher density of substrate surface sites with hydrogen at elevated flow, thus causing a reduction in the availability of surface sites for precursor adsorption and subsequent reaction. The net effect is a reduction in Co growth rates. In this respect, our studies indicated that the rate of rise in pressure was not linear with increased hydrogen flow, a trend



Figure 11. Typical conformality within the process window investigated for CVD Co films in Sematech's nominal 0.25 μ m, 4:1 aspect ratio, trench structures.

that tends to support the reduction in precursor residence time with higher hydrogen flow.

XRD analyses showed the presence of mainly a Co fcc phase, mixed with a small fraction of the Co hcp phase, for flows below 1000 sccm. For the latter, the films consisted solely of the fcc phase.

Co conformality within the process window investigated.—The conformality of co films was investigated in Sematech's nominal 0.25 μ m, 4:1 aspect ratio, trench structures. For these studies, the process window consisted of substrate temperature, hydrogen reactant flow, precursor flow rate, and reactor pressure values of 390°C, 750 sccm, 0.5 sccm, and 1.5 Torr, respectively. It was found that the ratio of film thickness at the bottom of the trench to that in the field was ~55%, as shown in Fig. 11. Alternatively, the ratio of film thickness at the bottom of the trench to that on the sidewalls was ~ 110%. Further studies are underway to establish an understanding of the underlying mechanisms that drive film conformality in aggressive device topographies and derive optimized process parameters for enhanced step coverage in subquarter-micron device structures.

Conclusions

This paper reported the development of a thermal CVD process for the deposition of pure co from the source precursor cobalt tri-carbonyl nitrosyl, Co(CO)₃NO. For this purpose, a study of the reaction kinetics involved in the CVD process indicated that the formation of pure Co occurs in a mass-transport-limited regime above 350°C. Additionally, systematic studies were implemented to establish functionality curves for the dependence of key film properties, namely, purity, texture, resistivity, and morphology on critical process parameters. These parameters were identified as precursor flow, hydrogen reactant flow, substrate temperature, and deposition time (thickness). Subsequent microstructural and microchemical analyses identified an optimized process window for the growth of pure co with resistivity of 9.0 \pm 2.0 $\mu\Theta$ cm, smooth surface morphology, and rms surface roughness at or below 10% thick.

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