Cobalt−Palladium and Cobalt−Platinum Bilayer Films Formed by Chemical Vapor Deposition

Sam W.-K. Choi and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

Received November 7, 1996. Revised Manuscript Received February 17, 1997[⊗]

The complexes $[Co_3(CO)_9CCl]$, $[Co_3(CO)_9CH]$, $[Co_2(CO)_6(HC{\equiv}CPh)]$ and $[Co_2(CO)_6(HC{\equiv}C^t\text{-}Bu)]$ are shown to be excellent precursors for CVD of pure cobalt films, when using hydrogen as carrier gas. These compounds all possess good air and moisture stability, have high volatility, and are easy to prepare, store, and handle. Using these precursors and the known palladium and platinum precursors $[Pd(hfac)_2]$ and $[PtMe_2(COD)]$, it has been shown that bilayer films glass/Co/Pd, glass/Pd/Co, glass/Co/Pt, and glass/Pt/Co can be grown easily. There is a sharp boundary and good adhesion between the two metal layers, suggesting that this method may be suitable for the formation of bilayer films for magnetooptical applications.

Introduction

A number of magnetic materials have been suggested in recent years for use in magnetooptical (MO) memory for the storage of digital information.[1] Among them, amorphous rare-earth transition metal alloys have drawn much attention. However, such alloys suffer from several deficiencies, most notably from the easy oxidation of the rare-earth metal components with consequent loss of the magnetic properties required in recording.[2] Recently, perpendicular magnetic anisotropy in Co/Pd and Co/Pt multilayer films has been revealed and studied extensively.[1b,d,e] Cobalt, palladium, and platinum are much more resistant to oxidation by air and unprotected metal bilayered structures stored under ambient conditions for several months undergo neither oxidation nor corrosion, and the magnetic and MO data remain unchanged.[3] This is a clear advantage over the rare-earth transition-metal alloys. Traditionally, the metal bilayers have been prepared by physical vapor deposition (PVD), such as rf sputtering,[4] magnetron sputtering,[5] or electron beam evaporation.[3] Chemical vapor deposition (CVD) has advantages over the physical deposition methods mentioned above in terms of conformal coverage and low-cost operation,[6] and so it is surprising that there has been no research reported on the synthesis of these metal bilayer structures by CVD. Since CVD routes to platinum and palladium films were available in this group,[7] the challenges were to choose an appropriate precursor and develop a procedure for CVD of pure cobalt and then to prepare and characterize the Co/Pd and Co/Pt bilayers by a sequential CVD technique.

There have been previous studies by others on the CVD of cobalt thin films, particularly using organometallic precursors (OMCVD). Examples include $[Co_2(CO)_8]$,[8a,b] $[Co(CF_3)(CO)_4]$,[8b] $[Co(NO)(CO)_3]$,[8c] $[Co(Cp)(CO)_2]$,[8b,d] and $[Co(Cp)_2]$ (Cp = cyclopentadienyl).[8b,e] However, many of these precursors are not ideal for CVD of cobalt because of, for example, the air instability of precursors[8a,d,e] and the presence of carbon and oxygen impurities in the resulting cobalt films.[8d] In this work, the cobalt carbonyl complexes, $[Co_3(CO)_9CCl]$[9a] **(1)**, $[Co_3(CO)_9CH]$[9a] **(2)**, $[Co_2(CO)_6(HC{\equiv}CPh)]$[9b] **(3)**, and $[Co_2(CO)_6(HC{\equiv}C^tBu)]$[9b] **(4)**, are used as CVD precursors (Chart 1). These compounds all possess good air and moisture stability, have high volatility and are easy to prepare.

Experimental Section

Materials and Procedures. All the Co precursors were prepared by published methods.[9] The precursor complexes $[Pd(hfac)_2]$[10] and $[Pt(COD)Me_2]$[11] were prepared by the literature methods (hfac = $CF_3COCHCOCF_3$, COD = 1,5-cyclooctadiene),

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

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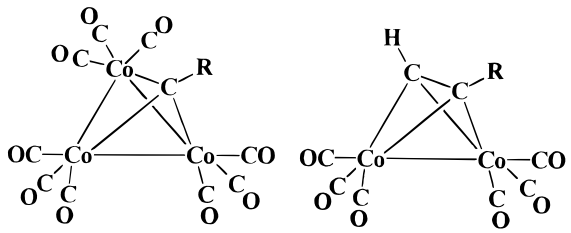
S0897-4756(96)00577-7 CCC: $14.00

Table 1. CVD Conditions and XPS Analysis of Cobalt Films

				XPS analysis/atomic %		
precursor	precursor temp/°C	substrate temp/°C	H_2 mL/min	Co	C	O
$[Co_3(CO)_9CCl]$	30	250−280	250	76	4	20
	30	250−280	900	98	2	0
$[Co_3(CO)_9CH]$	30	250	900	100	0	0
$[Co_2(CO)_6(HC{\equiv}CPh)]$	15	250	900	67	33	0
$[Co_2(CO)_6(HC{\equiv}C^tBu)]$	15	200−250	900	100	0	0

Chart 1



1, R = Cl
2, R = H
3, R = Ph
4, R = ^{t}Bu

and details of their use in CVD can be found elsewhere.[7b,12] Pure cobalt metal (99.95%) for XPS standard was purchased from Aldrich. Thermal CVD experiments were conducted by using a Pyrex vertical cold-wall reactor at reduced pressure with dynamic pumping. A sidearm was present to enable introduction of H_2 as reactive carrier gas. The glass substrate was heated by a temperature-controlled heating rod. As the Pd and Pt precursors are unstable under the H_2 atmosphere, they were loaded into the reaction zone by using a stream of N_2 from one sidearm, while H_2 was introduced close to the reaction surface via another sidearm. The Co precursors are stable under H_2 atmosphere and the precursors were carried by a H_2 stream directly to the substrate. The conditions used for the CVD of cobalt are summarized in Table 1.

For the CVD of Pd films using $[Pd(hfac)_2]$, the precursor reservoir and all connecting tubing were maintained at ca. 60 °C. N_2 was used to carry the precursor from the reservoir to the substrate and Pd metal was deposited on the glass substrate in the presence of H_2 gas. The deposition experiments were carried out using a substrate temperature of about 200 °C. The CVD of Pt films was carried out at 250 °C, with the precursor $[PtMe_2(COD)]$ warmed to 50 °C so as to give a reasonably fast rate of deposition. Again, the temperature of the connecting tubing was maintained at 50 °C to prevent any condensation of the precursor.

Co/Pd and Co/Pt bilayer films were prepared by sequential CVD of each metal. In a typical experimental approach, a Pd thin film was first prepared by the procedures and conditions described above. Then the cobalt precursor was introduced and cobalt was deposited on the Pd-coated glass substrate using the CVD conditions (H_2 flow rate, substrate temperature and precursor reservoir temperature) listed in Table 1. The Co/Pt, Pd/Co, and Pt/Co bilayer films were grown by analogous sequential CVD procedures.

The thermogravimetric analyses (TGA) were carried out using a Perkin-Elmer TGA7 thermogravimetric analyzer. The films prepared by CVD were analyzed by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). XPS spectra were obtained by using a SSL SSX-100 small-spot XPS surface-analysis instrument with a monochromatized Mg Kα X-ray source (1253.6 eV). All the films were cleaned extensively by Ar-sputtering at 4 keV before data collection. Analytical data are given in units of atom percent in Table 1. Metal composition depth profiles of metal bilayers were performed by XPS by continuous Ar sputtering of the metal surfaces. Top and cross-sectional view of SEM micrographs were taken from a Hitachi S-4500 scanning electron microscope.

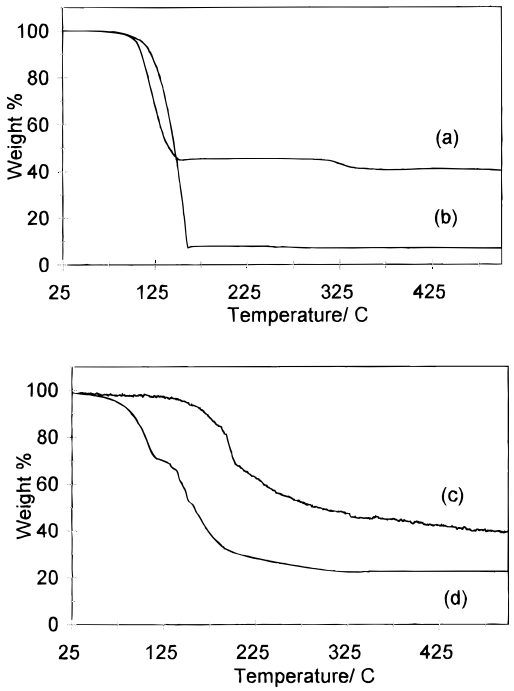


Figure 1. TGA traces of (above) (a) $[Co_3(\mu_3\text{-}CCl)(CO)_9]$ and (b) $[Co_3(\mu_3\text{-}CH)(CO)_9]$; (below) (c) $[Co_2(CO)_6(HC{\equiv}CPh)]$ and (d) $[Co_2(CO)_6(HC{\equiv}C^tBu)]$.

Results and Discussion

Cobalt CVD. One of the reasons of choosing the precursors **1**−**4** for CVD of cobalt is because of their good volatility. The purple crystals of **1** and **2** can be sublimed easily at room temperature. Moreover, **3** and **4** are red liquids at room temperature and also have reasonably high vapor pressures. The liquid state has an additional advantage over solid precursors that the vapor pressure is unrelated to the surface area and the grain size of the precursors. Thermogravimetric analysis (TGA) was used to monitor the thermal properties of **1**−**4**, and the results are shown in Figure 1. From the diagram, both **1** and **2** showed a sharp decrease of weight at about 100 °C, and **2** gave less residue than **1**. Clearly, **2** underwent almost quantitative sublimation. The residue for **1** and **2**, which is believed to be a mixture of cobalt metal and cobalt oxide, are 40.7% and 8.0%, respectively, of the original weight of the complexes. On the other hand, from Figure 1, it is noticed that the TGA of **3** and **4** are very similar, with a simple one-step decrease in weight which is then followed by a slow and complex decomposition. The measured weight loss for the first step for **3** is 29−31% and for **4** is 27−29%, compared to the theoretical value of 26.3% and 22.3% if thermolysis leads to initial loss of the alkyne ligand. From the TGA results, it can be concluded that

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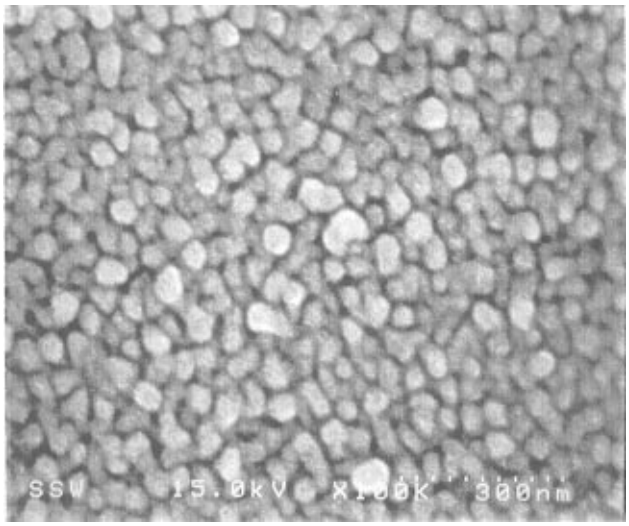

Figure 2. Scanning electron microscope image (top view) of a typical cobalt film.

these precursors are suitable only for low-pressure CVD, since decomposition occurs prior to evaporation at atmospheric pressure. The black residues obtained after pyrolysis indicate formation of oxide or carbide rather than metallic cobalt under these conditions and so suggest that a reducing gas (H_2) should be used to remove carbonaceous and oxide impurities in the CVD experiment.

In the CVD experiments, **1** and **2** were warmed slightly to 30 °C to provide sufficient vapor pressure for CVD, whereas a water-cooled bath (15 °C) was used for **3** and **4** to lower their evaporation rate. The precursor temperatures are much lower than that of the inorganic cobalt precursors[13] and similar to that of other reported organometallic CVD precursors, such as $[Co_2(CO)_8]$[8a,b] and $[Co(Cp)(CO)_2]$.[8b,d] Deposition conditions for different experiments are given in Table 1. From the table, the substrate temperatures ranged from 200 to 280 °C, which were much lower than that of $[Co(Cp)_2]$ (300−700 °C).[8b,e] Also, it is shown that a high H_2 gas flow rate of about 900 mL/min is necessary to obtain pure cobalt films. The high H_2 flow rate is not unusual in other reported Co CVD experiments.[8] If the flow rate was lowered, as in the case of **1** shown in Table 1, cobalt films contaminated by oxygen and carbon were obtained. The role of the hydrogen is probably to hydrogenate surface carbide, oxide, or unsaturated CHO-containing groups to volatile hydrocarbons and water, and the high flow rate is probably needed to ensure that the byproducts are flushed from the system as they are formed.

All cobalt films prepared from **1**, **2**, and **4** are shiny and mirrorlike, while that of **3** are darker in color. They gave good adhesion to glass substrates as tested by scratch or adhesive tape tests. The thickness of the Co film was investigated by the cross-sectional scanning electron microscope (SEM). It is found that the rate of film growth increased along with the substrate temperature. The liquid precursor complex **4** gave the fastest growth rate of 100 Å/min, consistent with it having the greatest volatility (Figure 2). **1** and **2** gave a lower growth rate, because of their lower volatility as compared with **4**. The resistivities of the cobalt films were investigated by using a four-point probe method. The resistivities varied from 9.0×10^{-5} to 1.4×10^{-4} Ω cm (thickness 0.15 mm). For comparison, bulk cobalt has a resistivity of 9.8×10^{-6} Ω cm, so the film resistivities were 9−14 times greater than for pure bulk cobalt. This may be attributed in part to the presence of thin layers of cobalt oxide on the surface of the films and in part to the film morphology. The presence of oxide film is expected to occur on exposure of the films to air and was confirmed by the detection of extensive amount of oxygen impurities by XPS studies on nonsputtered cobalt films.

XPS was used to analysis the films and the results are tabulated in Table 1. The binding energy of the Co $2p_{3/2}$ peak at 778.2 eV and the energy split of 14.7 eV between the two $2p_{3/2}$ and $2p_{1/2}$ doublet all agreed well with the reported data for pure cobalt metal.[14] Also the absence of a peak at ca. 780 eV excluded the possibility that the Co exists in the form of cobalt oxide.[14] From the XPS results, all films prepared from **2** and **4** were free from C and O impurities within the detection limits (∼1 at. %) after extensive argon sputtering. The absence of carbon contamination may be due to the ability of the cobalt to convert surface carbon into volatile hydrocarbons in the presence of H_2. On the other hand, it is surprising that the cobalt films were free from oxygen contamination, as this is common in cobalt films obtained by CVD.[8] Basically, the oxygen contamination arises from a heterogeneous decomposition of the carbonyl groups of the carbonyl-containing precursors. Clearly, with these precursors and a rapid hydrogen flow, either the cleavage of the carbonyl ligands is prevented or the oxide is hydrogenated to water as it forms. The high carbon impurities in cobalt films obtained from **3** may be due to the presence of the phenyl ring, which often introduces carbon impurities in OMCVD of other metals.[6] In the absence of H_2 gas, all films were dull and black in color and contained significant amounts of carbon and oxygen contamination. The same observation was obtained if water-saturated H_2 was used instead of dry H_2. The morphology of the cobalt films was examined by SEM measurements. A typical SEM micrograph, showing a top view of the cobalt film, is shown in Figure 2. The film, which was grown at 250 °C from the precursor **2**, was uneven with particle sizes ranging from 30 to 90 nm. The clear edges indicate that the particles were crystalline.

Bimetallic Bilayer Films. The Co/Pd and Co/Pt bilayer films were prepared by sequential CVD, that is, by deposition of a thin film of the first metal followed by deposition of a thin film of the second metal. In all experiments, a glass substrate was chosen since glass is the usual substrate for magnetooptical studies of metal bilayers.[4] Precursor **4** was used for the preparation of cobalt films, while $[Pd(hfac)_2]$ and $[Pt(COD)Me_2]$ were used in deposition of the palladium and platinum films, respectively. The palladium precursor [Pd(allyl)(hfac)], which is an excellent precursor for palladium films when oxygen is used as carrier gas,[7f] is less suitable for bilayer formation since cobalt metal has a high affinity toward oxygen gas.[15] All combinations glass/Co/Pd, glass/Pd/Co, glass/Co/Pt, and glass/Pt/Co were studied by these methods.

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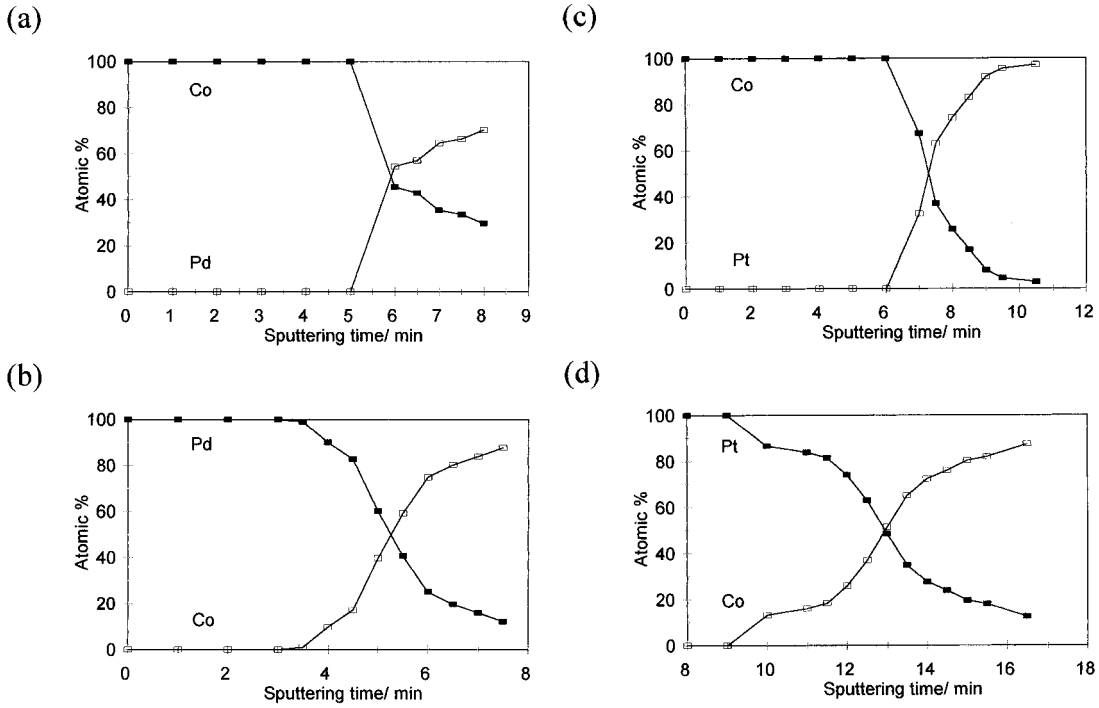

Figure 3. XPS argon-sputtering depth profile of bilayer films: (a) Co/Pd; (b) Pd/Co; (c) Co/Pt; (d) Pt/Co, showing the distinct interface.

The resulting bilayer films showed good adhesion between the cobalt and palladium or platinum layers. For most film characterization, films of thickness 100−200 nm in each metal were grown, and the film purity was then checked by XPS analysis and the morphology and film thickness by SEM. Continuous argon sputtering and XPS studies of the bilayer films could reveal the purity and the depth profile of the films. From the XPS result, carbon and oxygen contamination was absent in all metal films when grown under optimum conditions. The depth profiles of the bilayer films Co/Pd, Co/Pt, Pd/Co, and Pt/Co are shown in Figure 3. It is clearly shown that there was clear and sharp interface between the two metal layers, with minimal diffusion between the two layers. This conclusion is supported by the cross-sectional SEM images. Figure 4 shows the images of the bilayers deposited at a glass substrate at a temperature of 250 °C. All of them show clearly the presence of a distinct boundary between the two metal layers. In the bilayer films, adhesion between the two metal layers was much stronger than the adhesion to the glass substrate, which commonly failed the tape test.

How do these data compare to the films grown by thermal evaporation and related PVD methods? This has been studied in much greater depth and the degree of alloy formation at the interface has been shown to depend on the order of deposition and, for deposition on single crystals, on the individual crystal face.[16−21]

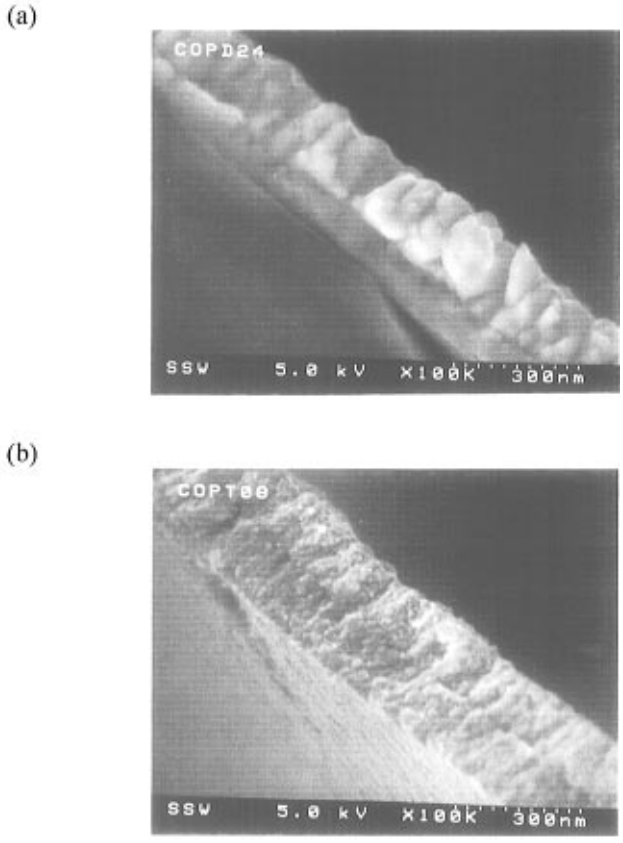

Figure 4. Cross-sectional SEM images of bilayer films: (a) glass/Co/Pd; (b) glass/Co/Pt.

For example, cobalt on platinum(111) gives atomic single-layer growth but diffusion and alloy formation occurs at temperatures of 600 °C or above.[16] For the

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thick CVD films, it is not possible to probe individual layers but it is clear that the deposition conditions are sufficiently mild that long-range diffusion does not occur.

Because the well-characterized CVD films are 200 nm in thickness, it is not possible to comment critically on the magnetooptical properties, for which films an order of magnitude less in thickness (20 nm) are normally used.[19−21] For films in which cobalt is in the top layer (either alone or on Pd or Pt), magnetooptical Kerr effect (MOKE) studies show that good square hysteresis loops are observed for freshly prepared films with no detectable carbon impurity but that the effect is much weaker in aged films or films containing carbon. In Co/Pd or Co/Pt films, grown under conditions where the thickness is expected to be in the required range of 20 nm, hysteresis loops can also be observed, but since the film thickness is not directly determined, these results are preliminary only.

Conclusions

In summary, the cobalt complexes **1**, **2**, and **4** are shown to be excellent precursors for the CVD of thin films of pure cobalt. The precursors are easy to synthesize, store, and handle and have good volatility below or slightly above room temperature. The volatility and thermal stability of the precursors can be modified by changing the substituent on the apical C−X group in the trinuclear cobalt complexes and on the alkyne group in the binuclear cobalt complexes. It is necessary to use a hydrogen carrier gas in order to obtain carbon- and oxygen-free cobalt films.

Once a good method for cobalt CVD was established, it proved straightforward to prepare the desired bilayer Co/Pd and Co/Pt films by sequential OMCVD. From the SEM cross-sectional view and XPS depth sputtering experiment, it is believed that there is a sharp and distinct boundary between the two metal layers. Moreover, the thickness of the films, which is critical for magnetooptical properties, can be controlled readily by adjusting the CVD reaction times, and preliminary MOKE studies indicate that, so long as the films are chemically pure, magnetooptical hysteresis can be observed. In conclusion, CVD is shown to be a useful and potentially applicable low-cost method for the preparation of Co/Pd and Co/Pt bilayers if improved engineering of the CVD process can give greater control and so allow formation of very thin films in a reproducible manner.

Acknowledgment. We thank the Ontario Centre for Material Research (OCMR) and NSERC (Canada) for financial support. S.W.-K.C. acknowledges the receipt of a Croucher Fellowship administered by the Croucher Foundation.

CM9605779