# Photochemical Vapor Deposition of Iron–Cobalt Thin Films: Wavelength and Temperature Control of Film Compositions

David K. Liu,* Roger J. Chin, and Angela L. Lai

*Lawrence Berkeley Laboratory*
*University of California*
*Berkeley, California 94720*

*Received September 25, 1990*
*Revised Manuscript Received November 28, 1990*

It is well known that films of alloys such as Fe–Co and Fe–Ni possess unique magnetic properties and are of interest in memory storage applications.[1,2] The most commonly used techniques for the growth of these magnetic thin films include sputtering, molecular beam epitaxy, and vacuum evaporation.[1,2] Recently, the use of chemical vapor deposition (CVD) to prepare Fe–Co films by thermally decomposing organometallic clusters at 300–350 °C was reported.[3] Since then, we have demonstrated that using ultraviolet irradiation, magnetic thin films of Fe–Co and Fe–Ni can be prepared at ambient temperature using organometallic precursors containing heteronuclear metal–metal bonds.[4] A major advantage of this photochemical vapor deposition (PCVD) technique is the low temperature employed, allowing the preparation of amorphous materials as well as the use of a wide variety of substrates. Furthermore, problems associated with thermal CVD, such as the diffusion of impurities from the reactor or substrate into the growing film, may be avoided. In this communication, we describe an extension of this PCVD technique that allows the systematic control of film compositions with the excitation wavelength and the vaporization temperatures of simple metal carbonyl precursors.

The precursors for Fe–Co thin films in this study were $Fe(CO)_5$ for Fe and $Co(CO)_3NO$ or $Co_2(CO)_8$ for Co. All metal carbonyls were purchased commercially and used as received. Alternately, $Co(CO)_3NO$ was synthesized according to published procedure.[5] The apparatus used for the growth of thin films by PCVD has been depicted, and the instruments used for film characterization have been described in detail previously.[4] In a typical experiment using $Fe(CO)_5$ and $Co(CO)_3NO$ precursors, 3.0 mL of each compound was placed in separate 100-mL round-bottom flasks, and the metal carbonyl vapors were carried into the PCVD cell by using CO with a flow rate of 20 $cm^3/min$. The vaporization temperatures for each precursor can be independently lowered by using cooling baths, if desired. In the case where $Co_2(CO)_8$ was used as the Co source, the flask containing the precursor was placed in an oven maintained at 45 °C. The Pyrex PCVD cell (25-mm diameter × 105 mm) was equipped with a quartz window and a stainless steel substrate holder at each end. The inside surface of the quartz window was purged with CO at 50 $cm^3/min$ during photolysis to prevent deposition on it. A precleaned[6] Al or Si(111) substrate was mounted on the holder, which was air-cooled to 25 °C during photolysis. The temperature of the substrate surface during photolysis was measured to be ~50 °C by using a thermocouple. The flasks containing the metal carbonyl precursors and PCVD cell were evacuated to 5–10 Torr throughout the experiment by using a liquid nitrogen trapped roughing pump. The emission from a 200-W mercury arc lamp was directed normally at the substrate with a power density of about 3.0 $W/cm^2$. A color filter glass was placed between the light source and the quartz window of the PCVD cell when selective excitation experiments were performed. The photolysis time was generally 10 min.

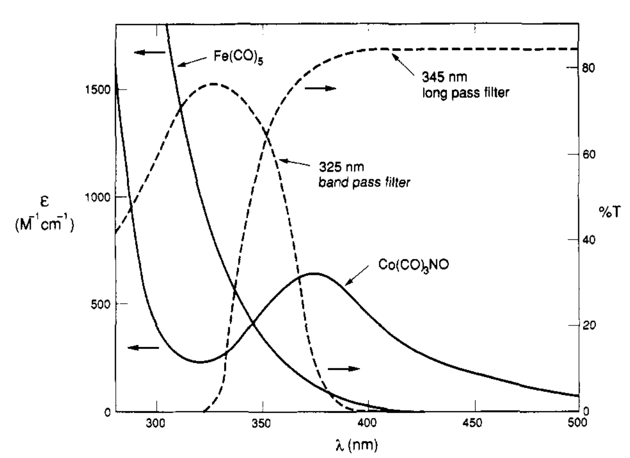

**Figure 1.** Electronic absorption spectra of $Fe(CO)_5$ and $Co(CO)_3NO$ in alkane solutions at 25 °C (from refs 7 and 8).

**Table I. Fe/Co Ratio of Thin Films Prepared by Wavelength-Selective PCVD Using $Fe(CO)_5$ and $Co(CO)_3NO$ Precursors at 20 °C[a]**

| photolysis condition | Fe/Co ratio |
|---|---|
| with 325-nm bandpass filter | 1.31 |
| with no filter | 1.00 |
| with 345-nm long-pass filter | 0.52 |

[a] These results represent the average values of at least two different films, and the margin of error was ±10%.

Our PCVD procedure consistently gave thin Fe–Co films that were metallic in appearance and were coherent and adherent in nature, as shown by scotch tape tests. Control experiments without photochemical excitation gave no observable deposits. Film thickness and deposition rates were 0.03–0.06 μm and 0.2–0.4 μm/h, respectively, as measured by stylus profilometry. The absence of observable lines except for those of the substrates in X-ray powder diffraction (XRD) spectra suggested that the deposited films are amorphous. Scanning electron microscopy (SEM) analysis of the deposited films revealed granular surfaces with particle sizes of 0.2–0.4 μm. X-ray fluorescence (XRF) spectroscopy established uniform Fe/Co distributions throughout the entire area of the deposited films. There was no substantial difference in deposition rate, morphology, or composition of thin films deposited on Al and Si substrates.

Interestingly, we found that the Fe/Co ratio in these films can be manipulated by the excitation wavelength. The electronic absorption spectra of $Fe(CO)_5$ and $Co(CO)_3NO$ are shown in Figure 1. Besides the intense $M \rightarrow \pi^*CO$ transitions at <300 nm for both compounds,[7,8] $Co(CO)_3NO$ also has an absorption maximum at 374 nm ($\epsilon = 640\ M^{-1}\ cm^{-1}$) attributed to a $M \rightarrow \pi^*NO$ transition.[8,9]

---

(1) Maissel, L. I.; Francombe, M. H. *An Introduction to Thin Films*; Gordon and Breach: New York, 1973.

(2) Falicov, L. M.; Pierce, D. T.; Bader, S. D.; Gronsky, R.; Hathaway, K. B.; Hopster, H. J.; Lambeth, D. N.; Parkin, S. S. P.; Prinz, G.; Salamon, M.; Schuller, I. K.; Victora, R. H. *J. Mater. Res.* **1990**, *5*, 1299.

(3) Czekaj, C. L.; Geoffroy, G. L. *Inorg. Chem.* **1988**, *27*, 8.

(4) Liu, D. K.; Lai, A. L.; Chin, R. J. *Mater. Lett.*, in press.

(5) Job, R.; Rovang, J. *Synth. React. Inorg. Metal-Org. Chem.* **1976**, *6*, 367.

(6) Hue, Z.; Strouse, M. J.; Shuh, D. K.; Knobler, C. B.; Kaesz, H. D.; Hicks, R. F.; Williams, R. S. *J. Am. Chem. Soc.* **1989**, *111*, 8779.

(7) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

(8) Clark, R. J. *Inorg. Chem.* **1967**, *6*, 299.

0897-4756/91/2803-0013$02.50/0

**Table II. Fe/Co Ratio of Thin Films Prepared by PCVD Using $Fe(CO)_5/Co(CO)_3NO$ and $Fe(CO)_5/Co_2(CO)_8$ Precursors at Different Vaporization Temperatures**[a]

| *T*, °C | | | |
|---|---|---|---|
| $Fe(CO)_5$ (°C) | $Co(CO)_3NO$ (°C) | $Co_2(CO)_8$ (°C) | Fe/Co ratio |
| 20 | -1 | | 1.40 |
| 20 | 4 | | 1.25 |
| 20 | 20 | | 1.00 |
| 2 | 20 | | 0.78 |
| 20 | | 45 | 0.66 |
| 5 | | 45 | 0.21 |
| 0 | | 45 | 0.13 |

[a] These results represent the average values of at least two different films, and the margin of error was ±10%.

Therefore, PCVD experiments using a 345-nm long-pass filter to selectively excite this M → $\pi^*$NO absorption band of $Co(CO)_3NO$ should yield Co-rich films relative to control experiments using no filter. On the contrary, if a 325-nm bandpass filter is used such that the percent transmittance at 374 nm is reduced to ~0.1, Fe-rich films should be obtained. The results in Table I demonstrate that the relative proportions of Fe and Co in alloy thin films, as determined by XRF, can be manipulated in a predictable fashion using this selective excitation approach. The only published report on wavelength control of film composition was by Armstrong et al.,[10] in which two different Fe/Ni ratios were obtained by using metallocene precursors and two different lasers as irradiation source. Under their experimental conditions, "significant carbon content" was found in the resulting films,[10] compared with the <1% C found in our Fe–Co films (see below).

The Fe/Co ration in the deposited films can also be controlled in a systematic manner by the vaporization temperatures and hence the vapor pressures of the metal carbonyl precursors. By simply varying the vaporization temperatures of the precursors, both Fe- and Co-rich films can be prepared, as shown in Table II. Therefore, this PCVD technique allows the fine control of film compositions and could lead to thin films with interesting electrical or magnetic properties.

The Fe–Co thin films prepared by PCVD were examined by Auger electron spectroscopy (AES), and a typical depth profile analysis is shown in Figure 2. Our results indicate that Fe and Co are uniformly distributed throughout the thickness of the film and that 5–10% O and <1% C are present. It is believed that most of bulk oxide in the deposited film arises from background gases during deposition and could probably be eliminated by using lower deposition pressures in an improved apparatus. Electrical conductivity measurement of the above Fe–Co film using the four-point probe technique gave a resistivity of 34.4 $\mu\Omega$ cm. The saturation magnetization, $\sigma_{sat}$, of the same Fe–Co film was 24.2 emu/g, as measured by a vibrating sample magnetometer (VSM) operating at 10 kOe. This translates to a saturation moment, $\mu_{sat}$, of 0.50 $\mu_3$/atom, which is substantially lower than the theoretical value of 2.3 $\mu_3$/atom predicted by the Slater–Pauling curves[11] for a 1:1 Fe–Co thin film. The lower saturation moment is probably due to the presence of antiferromagnetic iron and cobalt oxides in these films, as suggested by Auger analysis results. A detailed investigation of the magnetic properties of PCVD-derived Fe–Co thin films as a function of film compositions is underway.

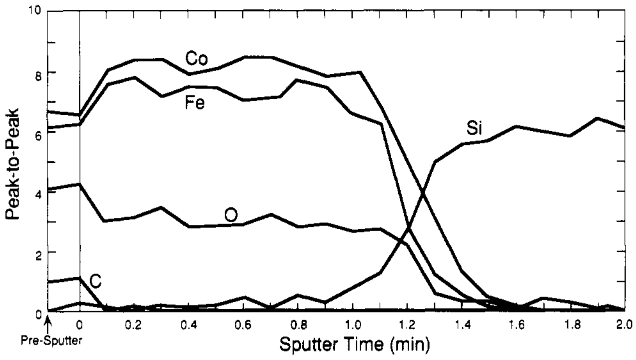

**Figure 2.** Auger depth profile of Fe–Co film deposited on Si substrate by PCVD using $Fe(CO)_5$ and $Co(CO)_3NO$ precursors at 20 °C. The sputtering rate was ~1000 Å/min using $Ar^+$ ions.

The mechanism for the thin film deposition via the photolysis of group VI (Cr, Mo, W) metal carbonyl precursors has been studied by Singmaster et al.[12] It was found that coordinatively unsaturated metal carbonyls formed via gas-phase photolysis can undergo further photochemical and/or thermal CO loss on the surface to form metallic thin films.[12] We believe a similar mechanism is responsible for the deposition of Fe–Co films from Fe and Co metal carbonyls in our experiments.

In summary, we have demonstrated that mixed-metal thin films can be deposited at ambient temperature via the photodecomposition of simple metal carbonyls and that the composition of such films may be controlled systematically by the excitation wavelength as well as the vaporization temperatures of the precursors.

**Acknowledgment.** We thank Mr. R. Giauque, Dr. K.-M. Yu, and Mr. M. Chandramouli for assistance with the XRF, XRD, and VSM measurements, respectively. This work was supported by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

---

(9) Evans, W.; Zink, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 2635.

(10) Armstrong, J. V.; Burk, A. A.; Coey, J. M. D.; Moorjani, K. *Appl. Phys. Lett.* **1987**, *50*, 1231.

(11) Morrish, A. H. *Physical Principles of Magnetism*; Wiley: New York, 1965.

(12) Singmaster, K. A.; Houle, F. A.; Wilson, R. J. *J. Phys. Chem.* **1990**, *94*, 6864.

---

# Synthesis of Layered $Zr(O_3PCH_2CH_2COCl)_2$ from $Zr(O_3PCH_2CH_2COOH)_2$

David A. Burwell and Mark E. Thompson*

*Frick Chemical Laboratory, Princeton University*
*Princeton, New Jersey 08544*

*Received October 10, 1990*
*Revised Manuscript Received November 26, 1990*

Layered metal organophosphonates have received a great deal of attention in recent years due primarily to their use in materials design, ion exchange, and catalysis.[1]

---

(1) (a) Alberti, G. In *Recent Developments in Ion Exchange*; Williams, P. A., Hudson, M. J., Eds.; Elsevier Applied Science: New York, 1987. (b) Alberti, G.; Constantino, U. *J. Mol. Catal.* **1984**, *27*, 235–250. (c) Clearfield, A. In *Design of New Materials*; Cocke, D. L., Clearfield, A., Eds.; Plenum Press: New York, 1988. (d) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125–148. (e) Johnson, J. W.; Brody, J. F.; Alexander, R. M.; Pilarski, B.; Katritzky, A. R. *Chem. Mater.* **1990**, *2*, 198–201. (f) Johnson, J. W.; Jacobson, A. J.; Butler, W. M.; Rosenthal, S. E.; Brody, J. F.; Lewandowski, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 381–383. (g) Lee, H.; Kepley, L. J.; Hong, H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1988**, *110*, 618–620.

0897-4756/91/2803-0014$02.50/0