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Fabricating magnetic Co-Ni-C thin-film alloys by organometallic chemical vapor deposition

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We have deposited $\text{Co}_x\text{Ni}_y\text{-C}$ films with a variety of compositions to verify dependence of the saturation magnetization on the composition. These experiments suggest that we can produce $\text{Co}_x\text{Ni}_y\text{-C}$ films with a variety of magnetic properties. The $\text{Co}_x\text{Ni}_y\text{-C}$ films were fabricated by ultraviolet decomposition of cobaltocene and nickelocene. We demonstrated that the photolytic decomposition of these metallocenes produces cyclopentadienyl (C_5H_5) species, consistent with recent studies of the energetics of the ligand metal bonds.

Over the past several years films with a multilayered structure have been studied extensively for the high storage magnetic recording media.¹⁻⁵ In a compositionally modulated structure, the composition is varied in a controlled manner, providing materials, crystal structures, and magnetic properties not found with uniform bulk materials.⁶

For Co_xNi_y films, the saturation magnetization is approximately the sum of the magnetization expected for hcp Co and fcc Ni.⁷ Addition of carbon to the alloy acts to reduce coercivity and the saturation magnetization.^{8,9} The magnetic properties of Co-Ni alloys can be adjusted to be compatible with existing recording systems by changing the nickel content in the range of 10 to 30 wt%.^{10,11} In this paper we show that stable $\text{Co}_x\text{Ni}_y\text{-C}$ films with a variety of compositions and varying saturation magnetization can be deposited by photolysis.

Films were fabricated from cobaltocene and nickelocene onto gold coated quartz crystal by photolysis in the glass vacuum system as described in detail elsewhere.¹²⁻¹⁴ Photolytic decomposition of $\text{Co}(\text{Cp})_2$ and $\text{Ni}(\text{Cp})_2$ was done by a commercial (Moletron) pulsed nitrogen laser (337 nm).

The torque magnetometer was used to measure the saturation magnetic moments of $\text{Co}_x\text{Ni}_y\text{-C}$ films in the vacuum system as described elsewhere.^{15,16}

$\text{Co}_x\text{Ni}_y\text{-C}$ films with periodicity and thickness ratios (4:1 to 1:4) were deposited in alternating multilayers by photolysis with the individual layered pairs about 800 Å thick. After the Co-C (or Ni-C) coating was made, the glass vacuum system was evacuated to the background pressure. Then next layer of Ni-C (or Co-C) was deposited to the desired thickness. These processes were repeated 5 times. The total film thickness was about 4000 Å.

Based on thermodynamic cycle (Fig. 1) as described elsewhere,¹² we postulate that single photon process using the N_2 laser, could cause decomposition of these molecules at the surface. The energies needed to go from the absorbed metallocene to the absorbed metal atom [$\text{M}(\text{Cp})_2(\text{ads}) \rightarrow \text{M}(\text{ads}) + 2(\text{Cp})(\text{gas})$] are less than that needed to drive the same reaction in the gas phase. Multiphoton processes (for photon energies of 3.68 eV) would be necessary in the gas phase. The successful decomposi-

tion of cobaltocene and nickelocene indicates that the photoassisted deposition of cobalt and nickel from their metallocenes is energetically feasible.¹² The thermodynamic cycles (Fig. 1) of cobaltocene and nickelocene indicate that once the first Cp ligand is stripped away, the second one is removed much more easily. Both the energetics (Fig. 1) and photolytic deposition studies suggest that the photolysis of metallocenes can be used to limit the deposition reaction to the illuminated surface region and to form the pattern coatings.^{13,14}

Studies of the residual gas mixture by the quadrupole mass spectrometer during deposition clearly show that UV photolysis of cobaltocene results in the production of gaseous C_5H_5 species, as seen in Fig. 2. This result, suggesting the clean dissociation of metal ligand bonds to form vola-

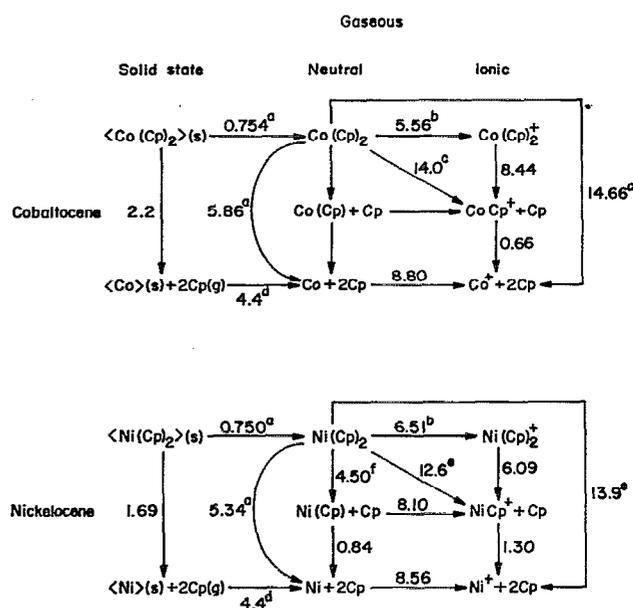


FIG. 1. The energetics of decomposition of cobaltocene and nickelocene. All numbers are in unit of eV. The data was obtained from literature, according to: a, Ref. 24; b, Ref. 25; c, Ref. 26; d, Ref. 27; e, Ref. 28; f, Ref. 29.

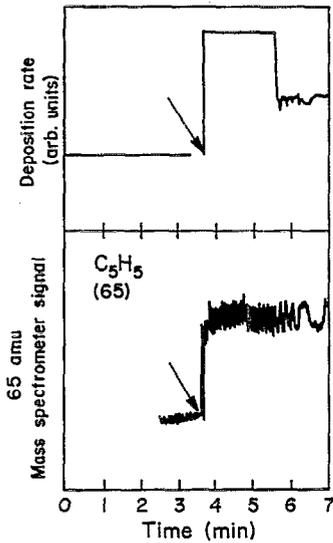


FIG. 2. Dependence of the 65 amu (C_5H_5) signal and the deposition rate of Co-C film on UV light. The arrows indicate the onset of incident radiation (nitrogen laser on).

tile cyclopentadienyl species, is consistent with the thermodynamic cycle of cobaltocene (Fig. 1). The deposition rate of Co film and the 65 amu (C_5H_5) signal increased abruptly with advent of the nitrogen laser light (Fig. 2).

Faster deposition rates, as noted in other studies,¹⁷ will lead to ligand incorporation into the growing film. By employing very fast deposition rates ($\sim 100 \text{ \AA}/\text{min}$) in our system we were able to incorporate carbon as indicated in Table I.

The SEM analysis of the films provided that the morphologies of the films are fairly smooth. The XES analysis provided cobalt, nickel, and gold XES lines in the spectra. The gold XES lines were from the substrate. The atomic percentage of metals in the films provided by XES are summarized in Table I. XES could not detect hydrogen, carbon, and oxygen.

Co_xNi_y -C films were composed of ten alternating multilayers from Co-C (first layer) to Ni-C (last layer) except $Co_{80}Ni_{20}$ -C film. $Co_{80}Ni_{20}$ -C film has a reverse sequence. The XES data was reflected this multilayer features in Table I especially for $Co_{80}Ni_{20}$ -C film. Composition analysis always exhibits a composition weighted toward the metal of the terminal film. Such an effect would not be observed if the material was isotropic. From these results we confirmed that the films have the modulated composition.

Auger electron spectroscopy depth profiling was undertaken using Auger electron spectroscopy with Ar ion sputtering. No correction has been made for ion mixing or preferential sputtering.¹⁸ There is considerable amount of carbon incorporation in the film as indicated by the AES results in Table I, which is the result of the incomplete dissociation of the metallocenes due to the rapid deposition rate. The Auger electron spectroscopy depth profile after removing carbon contribution to the film also suggested there is a modulated composition with film thickness.

The saturation magnetization of the films was also used to determine the atomic percentage of Co and Ni. This was obtained by considering Co-C and Ni-C saturation magnetizations and inferring the composition of Co-Ni-C films from the data summarized in Table I.

Magnetic properties of Co_xNi_y -C films were measured by torque magnetometer using the methodology of Gradmann.¹⁹ The magnetic energy of a film in a field H is

$$E(\theta, \phi) = -M_s V H \cos \theta + 2\pi M_s^2 V \cos^2(\theta - \phi) + KV \cos^2(\theta - \phi), \quad (1)$$

where M_s is the saturation magnetization moment, V is the volume of the magnetic film, θ is the angle between M_s and H , K is the crystal anisotropy constant, and ϕ is the angle between H and the normal to the film. The first term is magnetostatic energy, the second is a shape anisotropy term, and the third is a crystal anisotropy term.

The equation governing the oscillation of the plate is

$$I\phi = -k(\pi/2 + \phi) - (\pi + 2\phi) \frac{M_s H L V}{M_s H + 2L}, \quad (2)$$

where k is the wire torque constant ($I\omega_0^2$), I is the moment of inertia of the substrate, and ω_0 is the frequency of oscillation of the substrate without the film and where $L = 2\pi M_s^2 + K$.

To yield the saturation magnetic moments of Co_xNi_y -C films, we get

$$\frac{1}{R} = \frac{1}{I(1/\omega_i^2 - 1/\omega_0^2)} = \frac{1}{M_s V_i H} + \frac{1}{2L V_i}, \quad (3)$$

where ω_i is the frequency of oscillation of the substrate with the film and V_i is the volume of the film. We have

TABLE I. The ratio of the film thickness measured by a thickness monitor, the calculated atomic percentage from XES data, the saturation magnetization characterized by a torque magnetometer, and the atomic composition inferred from the saturation magnetization and AES depth profile data. The rate of the film growth was approximately $100 \text{ \AA}/\text{min}$. The atomic percentage in the parentheses indicates the corrected composition of Co and Ni after removing carbon.

Ratio of film thickness (%)		Atomic % from XES data		Saturation magnetization M_s (G)	Atomic % from M_s data		Atomic % from Auger depth profile data		
Co	Ni	Co	Ni		Co	Ni	Co	Ni	C
0	100	0.00	100.00	441	0	100	0(0)	37(100)	61
20	80	5.29	94.71	460	17	83	6(13)	40(87)	52
40	60	22.97	77.03						
60	40	69.07	30.93	515	68	32			
80	20	48.89	51.11				24(77)	7(23)	63
100	0	100.00	0.00	550	100	0			

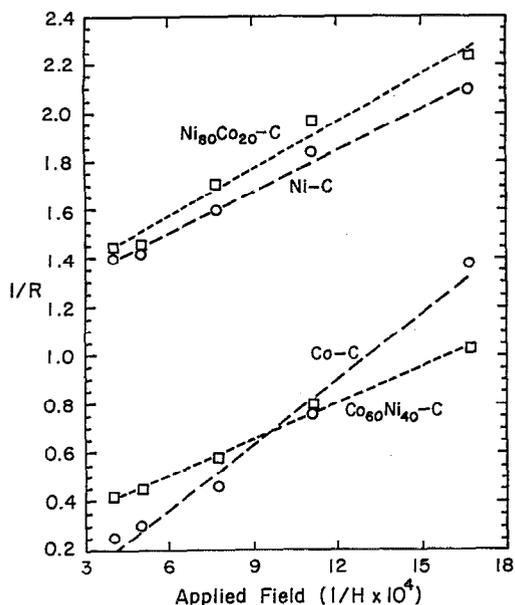


FIG. 3. $1/R$ vs $1/H$ for the frequency measurement of the rotation by torque magnetometer for pure Co film, $\text{Co}_{60}\text{Ni}_{40}$ film, $\text{Co}_{20}\text{Ni}_{80}$ film, and pure Ni film. We employed Eq. (4) for plotting.

plotted $1/R$ vs $1/H$ for the $\text{Co}_x\text{Ni}_y\text{-C}$ films in Fig. 3. The reciprocal of the slope gives the magnetic dipole moment $\mu = M_s V_i$ and yields the saturation magnetic moments of $\text{Co}_x\text{Ni}_y\text{-C}$ films given in Table I. These values increased linearly for Co composition as shown in Fig. 4 and are similar in behavior though much smaller than the saturation magnetic moments of bulk alloys (without carbon).⁷ The differences can be accounted for by the presence of carbon that reduces the net the magnetic moment for Co_xNi_y films as compared to those for pure Co_xNi_y alloys with similar composition. It has been shown that the carbon and oxygen incorporation reduce the saturation magnetization of Co_xNi_y films.^{8,9,20,21} We cannot exclude that the possibility that lattice deformation¹ and defects²² may also lead to a reduction of the saturation magnetization.

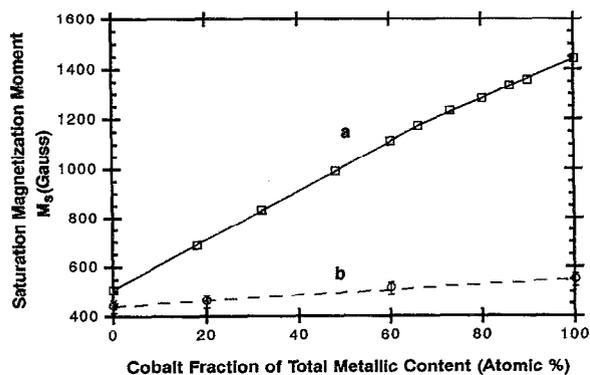


FIG. 4. Dependence of the saturation magnetization on Co composition for (a) Co_xNi_y bulk alloys, extrapolated to 0 K, taken from Ref. 7. (b) $\text{Co}_x\text{Ni}_y\text{-C}$ films at room temperature.

We find that M_s is indeed smaller than that of Co_xNi_y bulk alloys with same compositions since carbon incorporation reduces the saturation magnetization of nickel^{8,9} and cobalt films.

The magnetic properties of the films are consistent with Gradmann's model.¹⁹ The saturation magnetic moments of $\text{Co}_x\text{Ni}_y\text{-C}$ films were dependent upon the effective magnetic volume and increased linearly for Co composition from 440 to 550 G. The results are consistent with Weiss's results if the carbon incorporation is considered.⁷ From these experiments it is clear that we can produce $\text{Co}_x\text{Ni}_y\text{-C}$ films with a variety of magnetic properties, as suggested by other studies.²³

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