species. The vapor-phase reaction of MCl_4 and NH_3 at low temperature (<200 °C) are reported to produce $MCl_4 \cdot xNH_3$ adducts.[55,87-89] These adducts are undoubtedly less reactive than the putative NH_2-substituted compounds. Our system is therefore also kinetically more labile than the MCl_4/NH_3 system.

Conclusion

We have prepared high-quality TiN, Zr_3N_4, and Hf_3N_4 thin films from tetrakis(dialkylamido)metal(IV) complexes and ammonia precursors with high growth rates at low temperatures (200-450 °C). The TiN and Hf_3N_4 were slightly nitrogen rich. The TiN films displayed metallic properties and were crystalline as deposited. The Zr_3N_4 and Hf_3N_4 films were crystalline, yellow, transparent, and insulating. Periodic trends can be used to rationalize the contrasting result that Ti(III) films deposited from Ti(IV) precursors whereas Zr(IV) and Hf(IV) films deposited from Zr(IV) and Hf(IV) precursors.

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Registry No. TiN, 25583-20-4; Hf_3N_4, 104382-33-4; Zr_3N_4, 12033-93-1.

(87) Fowles, G. W. A.; Pollard, F. H. *J. Chem. Soc.* **1953**, 2588.
(88) Antler, M.; Laubengayer, A. W. *J. Am. Chem. Soc.* **1955**, *77*, 5250.
(89) Hojo, J.; Kato, A. *Yogyo-Kyokai-Shi* **1981**, *89*, 277.

Amorphous Alloy Thin Films from Molecular Precursors. Evidence of Structure and Stoichiometry from Crystallization and Effects of Precursor Ligand Structure on Stoichiometry

B. H. S. Thimmappa and Thomas P. Fehlner*

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

Gary J. Long* and O. Allan Pringle

Departments of Chemistry and Physics, University of Missouri—Rolla, Rolla, Missouri 65401

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The crystallization at 400 °C of amorphous thin films formed by the thermal decomposition of $HFe_3(CO)_9BH_4$ at low low pressure has been studied by using the techniques of X-ray diffraction and Mössbauer spectroscopy. The results unambiguously show that the films are iron rich in terms of the ideal stoichiometry of Fe/B = 3, signifying some loss of boron during film formation. The iron-main group atom phase that crystallizes from the amorphous film is orthorhombic $Fe_3B_{1-x}C_x$, with x for the specific film examined lying between 0.3 and 0.4. The cleavage of CO is postulated to account for the overall Fe/B ratio of 3, formation of the mixed boride/carbide phase and the presence of B_2O_3 in the film. That is, the boron sequesters the oxygen atom as B_2O_3, whereas the carbon atom replaces boron so lost in Fe_3B to form the $Fe_3B_{1-x}C_x$ phase. Deposition of films from a closely related precursor, $HFe_3(CO)_{10}BH_2$, have also been examined. Most of the boron is lost during deposition even at the lowest substrate temperature. Crystallization of these amorphous films requires higher temperatures and yields α-Fe and a phase indistinguishable from orthorhombic Fe_3C. Decomposition during sublimation with the production of $Fe(CO)_5$ accounts for the qualitatively different behavior of $HFe_3(CO)_{10}BH_2$.

Introduction

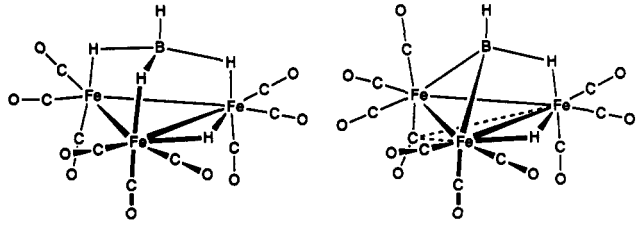
We have previously described the thermal decomposition of $HFe_3(CO)_9BH_4$ at 175-200 °C and low pressures at the surface of various substrates. The result was the deposition of uniform, thin, amorphous alloy films of approximate composition $Fe_{75}B_{25}$.[1] Apparently the ligands of $HFe_3(CO)_9BH_4$ are lost as CO and H_2, and the Fe_3B core of the cluster is left as a solid deposit. The Mössbauer spectra of these films show that the local structure of the film is similar to that observed for films prepared by rapid quenching techniques but that the magnetically ordered films formed exhibit magnetic moments with a preferential orientation normal to rather than parallel with the film plane. This orientation is independent of the temperature. The films are stable in air, and the carbon and oxygen impurities found are known to be incorporated in the film during the deposition procedure. The oxygen appears to be present principally as B_2O_3, and as a result the Mössbauer spectra indicate that the films contain no ordered iron oxides.

Our earlier work raised a number of fundamental questions that required more experimental work and are answered herein. First, the spectroscopic analysis did not define the film composition with sufficient accuracy to prove that the ferraborane cluster core was deposited intact. Indeed there was an indication that the films had a Fe/B ratio somewhat higher than 3. Second, although oxygen impurities at low levels appeared to be tied up with

(1) Amini, M. M.; Fehlner, T. P.; Long, G. J.; Politowski, M. *Chem. Mater.* **1990**, *2*, 432.

0897-4756/91/2803-1148$02.50/0

Chart I



(a) (b)

boron rather than iron, the chemical state of the carbon impurity was unknown. Finally, the internal structural details of the solid films were unknown. That is, although the films were amorphous by XRD, the local structure or microstructure is not necessarily the same as that in the material prepared by rapid quenching methodology. Earlier work has demonstrated that the crystallization behavior of Fe_xB_{1-x} amorphous materials is sensitive to both the composition and local structure in the amorphous form.[2] Hence, we have investigated the crystallization of our films in order to address these questions.

An additional question was generated by the comparison of the deposition behavior of the ferraborane clusters relative to an isoelectronic cluster containing nitrogen rather than boron.[3] In the latter case nitrogen was lost, partly as NH_3, even at the threshold temperature for deposition such that α-Fe was a major product. It is not known whether this behavior is a result of thermodynamic or kinetic factors, i.e., does the precursor structure play any role in solid formation or is cluster core composition the only important factor? Hence, we have compared the deposition behavior of $HFe_3(CO)_9BH_4$ (Chart Ia)[4] with that of $HFe_3(CO)_{10}BH_2$ (Chart Ib). The second compound has an additional CO ligand and two fewer bridging hydrogen atoms.[5]

Results and Discussion

The general crystallization behavior observed for systems with an iron to boron ratio Fe/B $\geq$ 3 is expressed in eq 1.[6] On initial heating the metastable crystalline Fe_3B

$$Fe_{3+x}B \rightarrow Fe_3B + x\alpha\text{-Fe} \rightarrow Fe_2B + (1 + x)\alpha\text{-Fe} \quad (1)$$

phase and, for iron contents greater than 75%, α-Fe are produced. Further heating leads to the stable crystalline Fe_2B phase and additional α-Fe. Heating of compositions with less than 75% iron, i.e., x less than zero, leads directly to Fe_2B. Hence, crystallization of our films provides a means of determining whether the films formed from $HFe_3(CO)_9BH_4$ are iron rich, iron poor, or precisely $Fe_{75}B_{25}$. In addition, the crystalline form of the first formed phase or phases provides information on the local structure in the amorphous film. There are two known crystalline forms of Fe_3B, tetragonal and orthorhombic, and it has been suggested that the latter is stabilized by carbon impurities.[7] Information about the local structure in the amorphous material can be obtained under the hypothesis that the first-formed modification will be that most closely reflecting the atom arrangement existing in the amorphous material.[8] In this way it has been shown that amorphous $Fe_{75}B_{25}$ behaves differently from amorphous $Fe_{86}B_{14}$.[9] The former yields a pure body-centered-tetragonal Fe_3B phase when annealed at 400 °C, whereas the latter gives much more complex behavior and yields an orthorhombic Fe_3B phase.

Table I. XRD Data on the Annealed Film Formed by the Deposition of $HFe_3(CO)_9BH_4$

d(obsd), Å	rel int	hkl	d(calcd),[a] Å
3.06	2	111	3.05
2.40	49	121	2.40
2.34	5	201	2.30
2.25	15	002	2.24
2.15 (br)	20	211, 012	2.18, 2.13
2.07	100	130, 102	2.07, 2.07
2.03	140	α-Fe	
2.00	62	031	2.00
1.98	62	112	1.98
1.87 (br)	46	131, 022	1.88, 1.86
1.76	20	122	1.76
1.70	13	202	1.72
1.63	5	212, 310	1.66
1.43	30	α-Fe	
1.32	2	203	1.31
1.22	5	340	1.22
1.17	25	α-Fe	

[a] Calculated for an orthorhombic cell with a = 5.371, b = 6.715, c = 4.481 Å.

Table II. Cell Constants for Orthorhombic $Fe_3B_{1-x}C_x$ (Å)

x	a	b	c
0.0[a]	5.43	6.66	4.45
0.1[b]	5.40	6.66	4.45
0.2[b]	5.38	6.66	4.45
0.3[b]	5.37	6.67	4.46
0.4[b]	5.34	6.67	4.47
1.0[a]	5.08	6.73	4.51
c	5.37	6.71	4.48

[a] Reference 8. [b] Estimated from Figure 1 in ref 8. [c] This work.

A 10000-Å-thick film formed from $HFe_3(CO)_9BH_4$ that had already been characterized by Auger and X-ray diffraction (XRD) spectroscopies and that was similar to a film characterized by Mössbauer spectroscopy was selected for crystallization. The film was annealed under vacuum at 400 °C for three separate 1-h periods. After each heating the sample was examined by XRD. The very broad XRD pattern characteristic of an amorphous material disappeared and was replaced with a normal powder diffraction pattern after the first heating. No change in this powder pattern was observed after the second and second and third heating, although these data alone do not define the extent of crystallinity of the film. The XRD data are given in Table I. The presence of a crystalline α-Fe phase demonstrates that the films are iron rich relative to the $Fe_{75}B_{25}$ composition of the precursor core, a result in agreement with the Auger composition.[1] The X-ray d spacings and intensities correspond to no known phase; however, the spectrum was successfully indexed in terms of an orthorhombic unit cell with cell constants intermediate between those of orthorhombic Fe_3B and Fe_3C. By assuming that this crystalline material is $Fe_3B_{1-x}C_x$, we have used the reported lattice parameters for crystalline $Fe_3B_{1-x}C_x$, x = 0.0–0.4 (Table II) to estimate x = 0.3–0.4 for our material.[8]

(2) Chien, C. L.; Musser, D.; Gyorgy, E. M.; Sherwood, R. C.; Chen, H. S.; Luborsky, F. E.; Walter, J. L. *Phys. Rev. B* **1979**, *20*, 283.
(3) Fehlner, T. P.; Amini, M. M.; Stickle, W. F.; Pringle, O. A.; Long, G. J.; Fehlner, F. P. *Chem. Mater.* **1990**, *2*, 263.
(4) Vites, J. C.; Eigenbrot, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4633.
(5) Vites, J. C.; Housecroft, C. E.; Eigenbrot, C.; Buhl, M. L.; Long, G. J.; Fehlner, T. P. *J. Am. Chem. Soc.* **1986**, *108*, 3304.
(6) Kemeny, T.; Vincze, I.; Fogarassy, B.; Arajs, S. *Phys. Rev. B* **1979**, *20*, 476.
(7) Zhang, Y. D.; Budnick, J. I.; Sanchez, F. H.; Hines, W. A.; Yang, D. P. *J. Appl. Phys.* **1987**, *61*, 4358.
(8) Zhang, Y. D.; Budnick, J. I.; Ford, J. C.; Hines, W. A.; Sanchez, F. H.; Hasegawa, R. *J. Appl. Phys.* **1987**, *61*, 3231.
(9) Sanchez, F. H.; Zhang, Y. D.; Budnick, J. I.; Hasegawa, R. *J. Appl. Phys.* **1989**, *66*, 1671.

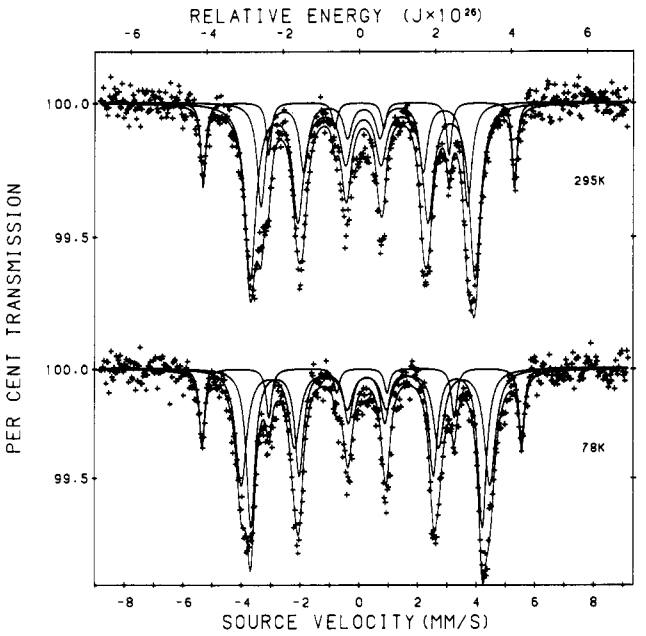


Figure 1. Mössbauer spectra of an iron boride film formed by the deposition of $HFe_3(CO)_9BH_4$ on Pyrex glass and annealed at 400 °C for a total of 3 h.

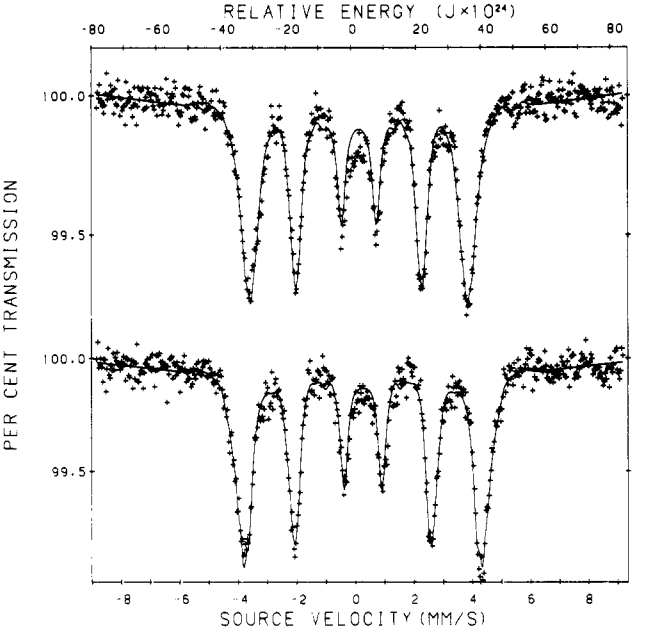


Figure 2. Distribution fit of the Mössbauer spectrum at 295 (top) and 78 K (bottom) of the iron boride film described in Figure 1 and the text with the α-Fe component removed.

Table III. Mössbauer Spectral Parameters from the Distribution Fits for the $Fe_3B_{1-x}C_x$ Component

T, K	$\langle H_{int} \rangle$, kOe	δ,[a] mm/s	QS, mm/s	$\langle \Gamma \rangle$, mm/s	% area[b]	abs area (%ϵ), mm/s
295	234	0.014	0.00	0.31	88.2	0.82
78	259	0.026	0.00	0.28	86.7	1.86

[a] Relative to room-temperature natural α-iron foil. [b] The remaining area was α-iron.

A confirmation of the above composition was obtained in a Mössbauer spectral examination of the identical sample of annealed material. For this purpose the now brittle and cracked film was removed from the Pyrex glass substrate, and the Mössbauer spectrum was obtained on a dispersion of the resulting fragments in vasalene. The spectra at 295 and 78 K are shown in Figure 1 with a fit to three sextets. The sharpness of the spectral absorption lines and goodness of fit strongly suggests that the thin film is now completely crystalline. The sextet with a hyperfine field of 329 kOe at 295 K and 338 kOe at 78 K is due to α-Fe. This signal constitutes 11.8 and 13.3% of the total spectral absorption area at 295 and 78 K, respectively. The remaining absorption lines are clearly due to a superposition of two or more sextets. The interpretation of the XRD spectrum in terms of an orthorhombic $Fe_3B_{1-x}C_x$ phase requires a distribution of iron sites in which the three main-group nearest-neighbor atoms vary from 3C to 3B atoms. Thus, we have chosen to fit the spectrum with a distribution of hyperfine fields and have assumed there is a single average type of iron site in Fe_3E rather than two distinct ones. To do such a distribution fit, we found it was necessary to subtract the sharp α-Fe sextet from the spectral data. The final fits and the distribution of internal hyperfine fields are shown in Figures 2 and 3. The resulting Mössbauer spectral parameters are given in Table III. The rather narrow spectral line widths suggest that the fit is reasonable. The average 295 K hyperfine field of 234 kOe lies between the 208 ± 2 kOe value found in pure orthorhombic Fe_3C[10] and the 250 ± 5 kOe value found

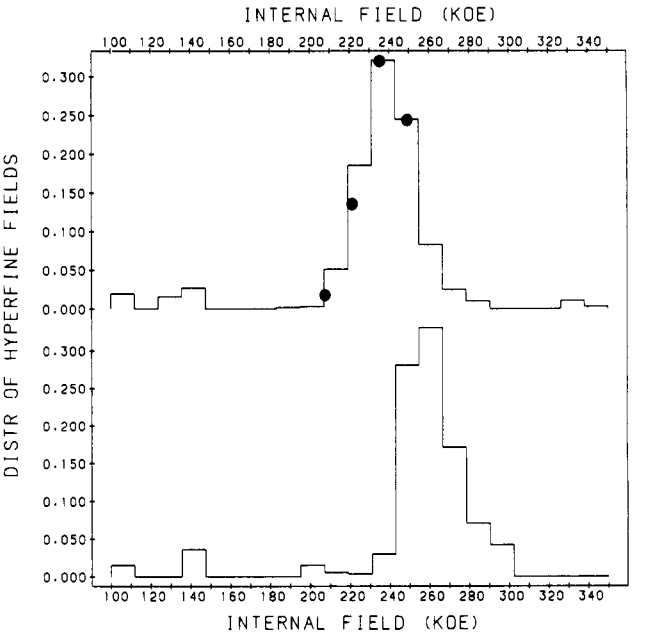


Figure 3. Distribution of hyperfine fields vs internal filed corresponding to the fit shown in Figure 2. The closed circles correspond to the expected binomial distribution for $Fe_3B_{1-x}C_x$ for $x = 0.3$.

in pure orthorhombic Fe_3B,[11] as would be expected for a $Fe_3B_{1-x}C_x$ phase. Hence it follows that the low average hyperfine field observed for the amorphous film is due to carbon incorporation. The Mössbauer spectrum of the annealed film is entirely consistent with the interpretation of the XRD data on the annealed film, i.e., the material consists of two crystalline phases, α-Fe and orthorhombic $Fe_3B_{1-x}C_x$.

The distribution of internal fields, shown in Figure 3, provides an independent means for determining the value of x in $Fe_3B_{1-x}C_x$, a value that may then be compared with that obtained from the XRD data. There are two iron sites in orthorhombic Fe_3E, E = B, C, with differing nearest-

(10) Bernas, H.; Campbell, I. A.; Fruchart, R. *J. Phys. Chem. Solids* **1967**, *28*, 17.

(11) Choo, W. K.; Kaplow, R. *Metall. Trans. A* **1977**, *8A*, 417.

neighbor E arrangements and, indeed, the Mössbauer spectrum of orthorhombic Fe_3B actually consists of two sextets with hyperfine fields of 264 and 235 kOe.[11] However, for the purposes of this analysis we assume that there is a single type of iron surrounded by 3 E atoms, where the occupancy of E with C or B is random. Thus, the relative probability of C_3 to C_2B to CB_2 to B_3 is related to x by the binomial distribution. By using the hyperfine fields of 208, 222, 236, and 250 kOe for iron sites with C_3, C_2B, CB_2, or B_3 near neighbors, we obtain a binomial distribution consistent with the experimental one found in Figure 3. The calculations indicate that x is between 0.3 and 0.4 for the 295 K distribution and, with an appropriate increase in the hyperfine fields, the same range of x fits the 78 K distribution. This range of x values agrees well with the XRD result.

The above analysis raises the questions of where the boron went (the amorphous and crystalline films have Fe/B ratios of ≈3) and where the carbon came from. The answer can be found in the Auger compositions. In our earlier work[1] we noted that these films contained 5–10% carbon and oxygen impurities under the best vacuum conditions. Further, it was demonstrated by direct measurement of oxidized boron as a function of oxygen content that B_2O_3 was the product of the oxidation process. These observations along with the XRD and Mössbauer results on the crystallized material can now be reconciled in the following manner.

The specific film crystallized had an Auger atomic composition of 63.1% Fe, 18.6% B, 8.6% C, and 9.8% O. If one assumes that the oxygen is present completely as B_2O_3, that the excess iron over that required for Fe_3E, E = C, B, is given by the Mössbauer spectra, and that the film contains only α-Fe, $Fe_3B_xC_{1-x}$, and B_2O_3, then x is calculated to be 0.34. This implies a carbon content of 6.3% based on $Fe_3B_xC_{1-x}$ or 9.8% based on formation of B_2O_3 from CO. The observed value is 8.6%. Considering the uncertainties in the Auger measurements, this must be considered excellent agreement with the values of x obtained from the XRD and Mössbauer spectra.

Thus, the fact that the Fe/B ratio of the amorphous film formed from $HFe_3(CO)_9BH_4$ is close to the expected value of 3 is deceptive, and the 5-10% carbon and oxygen present in the films are found in unexpected forms. The boron combines with oxygen, whereas the available carbon replaces boron in the alloy phase. This suggests that under the best of conditions employed in the deposition experiments to date not all the CO ligands escape and that $Fe_3B(CO)_x$ is actually deposited and the overall reaction is (3) rather than (2). The highly reactive boron atom

$$HFe_3(CO)_9BH_4 \rightarrow Fe_3B + {}^5/_2H_2 + 9CO \qquad (2)$$

$$HFe_3(CO)_9BH_4 \rightarrow Fe_3B_{1-x}C_x + {}^5/_2H_2 + (9 - 3x/2)CO + x/2B_2O_3 + 1/2x[C] \qquad (3)$$

splits the CO molecule forming B_2O_3 and the resulting carbon replaces boron in the Fe–E, E = C, B, alloy phase. Finally, the formation of α-Fe on crystallization suggests that some of the boron of $HFe_3(CO)_9BH_4$ is lost to the gas phase, probably as B_2H_6. However, see below.

These results imply that the mechanism of the decomposition of the precursor $HFe_3(CO)_9BH_4$ on the substrate surface that determines final film structure and composition consists of several parallel pathways. Competitive processes are very sensitive to small changes in reaction barriers. Hence, the deposition behavior of a closely related precursor has been examined. The molecule $HFe_3(CO)_{10}BH_2$ has the same core structure as $HFe_3(CO)_9BH_4$ and, in principle, should yield the same ideal Fe/B ratio of 3. The structures of these molecules are compared in Chart I, where it is noted that the difference in the two compounds is a simple one. Two of the endo hydrogens of $HFe_3(CO)_9BH_4$ are replaced by a bridging CO ligand. Because $HFe_3(CO)_{10}BH_2$ is generally more labile than $HFe_3(CO)_9BH_4$, we surmised that loss of CO might be more rapid, thereby leading to less CO incorporation and consequently a purer film.

Table IV. Comparison of *d* Spacings for Orthorhombic Fe_3C with Those of a Crystalline Phase Produced by the Annealing of a Film Generated from $HFe_3(CO)_{10}BH_2$

d(o-Fe_3C),[a] Å	unknown, Å	intensity	*d*(o-Fe_3C),[a] Å	unknown, Å	intensity
2.01_x	2.014	100	2.20_6	α-Fe	
2.06_7	2.071	80	1.97_6	1.980	70
2.38_7	2.388	60	1.85_4	1.856	60
2.10_6	2.111	70	1.87_3	1.875	50

[a] In order of decreasing intensity.

Deposition of $HFe_3(CO)_{10}BH_2$ at several substrate temperatures was carried out in essentially the same manner as described previously for $HFe_3(CO)_9BH_4$. The film formed at 180 °C had an Auger atomic composition of 85–88% Fe, 4–5% B, 1–2% C, and 7–8% O and films formed at higher substrate temperatures had even lower boron contents. On the basis of Auger line position, the boron was present in the oxidized form, which assuming it to be B_2O_3, agrees with the observed B/O ratio. Analysis by XRD showed that the film was amorphous with some crystalline α-Fe. The latter increased substantially for the films formed at temperatures higher than 180 °C. Clearly there has been substantial boron loss during the deposition process. Proof of this loss came from annealing the films. In contrast to the films formed from $HFe_3(CO)_9BH_4$, no sign of crystallization was observed below 500 °C for the $HFe_3(CO)_{10}BH_2$ derived films. Above this temperature α-Fe and a phase experimentally indistinguishable from orthorhombic Fe_3C were observed in the powder XRD pattern (see Table IV).

Loss of the main group element as a volatile hydride has been observed previously in other systems[12] including our own work on the deposition of iron nitrides from $HFe_4(CO)_{12}N$.[3] However, we could find no direct mass spectrometric evidence for the formation of B_2H_6 during the deposition of $HFe_3(CO)_{10}BH_2$. We did observe substantial formation of a solid residue in the sublimation vessel and the production of $Fe(CO)_5$ during sublimation. Therefore, it appears that a solid-state reaction leading to the production of $Fe(CO)_5$ takes place during the volatilization of this labile molecule. The $Fe(CO)_5$ leads to the formation of the high iron content of the films with the level of boron representative of the relatively low partial pressure of $HFe_3(CO)_{10}BH_2$.

Although changing from $HFe_3(CO)_9BH_4$ to $HFe_3(CO)_{10}BH_2$ led to poorer films in terms of any practical physical properties, the results demonstrate that the sublimation and/or deposition process are very sensitive to the structure and properties of the precursor molecule. It is possible that some decomposition during sublimation also could explain the iron rich films found in the case of the $HFe_3(CO)_9BH_4$ precursor. In all cases the best films are obtained by operating at the lowest practicable sublimination and deposition temperatures.

None of the inorganometallic precursors we have used to date have given carbon and oxygen free films. However, the presence of carbon in the magnetic phase is not nec-

(12) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643.

essarily detrimental to potential applications. It lowers the maximum hyperfine field somewhat but increases the crystallization temperature. Further the boron precursors have, as it were, a built-in self-cleaning mechanism (a flux) for isolating the oxygen as B_2O_3. As the ligand trapping is apparently a kinetic problem, there may be ways of modifying the deposition process thereby reducing the carbon and oxygen content. Such experiments are in progress.

Experimental Section

The $HFe_3(CO)_9BH_4$ and $HFe_3(CO)_{10}BH_2$ clusters were prepared according to new procedures and were purified by recrystallization from hexanes.[13] The low-pressure CVD reactor has been described previously.[1] Typical deposition times were 15–20 min. The substrates were resistively heated to temperatures ranging from 160 to 300 °C and monitored by a 0.005-in.-diameter iron/constantan thermocouple held in place on the outer face of the substrate surface by the substrate-heater clamp. During deposition, the total pressures were initially $\approx 10^{-4}$ Torr and decreased to 10^{-5} Torr as the solid precursor sublimed away. The depositions were carried out on glass substrates (Corning 7059, 2 × 2.5 cm).

The deposition of the highly air sensitive $HFe_3(CO)_{10}BH_2$ required a sublimation temperature of ≈50 °C, and the solid did not sublime completely leaving a residue in the sublimation cup. To examine the vapor composition including high mass species, a separate experiment was conducted in a Schlenk style vessel with a sidearm connected to the inlet of a Finnigan MAT 8400 mass spectrometer. The vapor components included $Fe(CO)_5$, which was particularly prominent when the sample was warmed to increase the sublimation rate.

The films were annealed in a quartz tube which was heated with a tube furnace under a vacuum of 10^{-6} Torr. Annealing temperatures stated are furnace temperatures, and no attempt was made to measure the temperature thresholds for crystallization. Although the films in the amorphous state adhered well to the glass substrate, after crystallization the surface was cracked and the thicker films pealed away from the substrate. The crystallinity was determined with an Philips 3520 X-ray powder diffraction system.

Auger spectra were obtained on a Perkin-Elmer 590 Auger multiprobe with 3-kV electrons after sputtering with 4 kV Ar^+ (1 mm^2 spot) at 100 Å/m to constant composition (≤200 Å). Beam currents of 3.8 μA were used. Spectra from a foil standard ($Fe_{81}B_{13.5}Si_{3.5}C_2$) were gathered with each unknown sample, and these data were used to calculate sensitivities for Fe, B, and C. The sensitivity for O relative to that of C was the standard instrument value. The variation in atom sensitivities from run to run was small.

The Mössbauer effect spectra were obtained at 296 and 78 K on a constant-acceleration spectrometer which utilized a room-temperature rhodium-matrix ^{57}Co source and was calibrated at room temperature with natural-abundance α-iron foil. The Mössbauer spectra were fit either with three sextets composed of Lorentzian lines as shown in Figure 1 or with a distribution of hyperfine fields[14] as shown in Figure 2. In both cases the intensity of the components of each sextet was constrained to the ratio 3:2:1:1:2:3, as would be expected for the random distribution of the fragments of the foil in the absorber.

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Registry No. $HFe_3(CO)_9BH_4$, 91128-40-4; $HFe_3(CO)_{10}BH_2$, 92055-44-2; $Fe_3B_{0.6-0.7}C_{0.3-0.4}$, 136262-39-0; 63.1% Fe, 18.6% B, 8.6% C, 9.8% O, 136185-05-2.

(13) Meng, X.; Fehlner, T. P. *Inorg. Synth.*, in press.

(14) Wivel, C.; Mørup, S. *J. Phys. E: Sci. Instrum.* **1981**, *14*, 605.