To link to this article: doi.org/10.1149/1.3207589
URL: http://dx.doi.org/10.1149/1.3207589

Iron amidinates as precursors for the MOCVD of iron-containing thin films

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Within the framework of an ongoing project, we are currently investigating the co-deposition of bimetallic and trimetallic films by MOCVD within the Al-Cu-Fe system. This intermetallic system can be a base for preparing complex metallic alloys (CMA) having unique combinations of properties.[1] The component metals of the Al-Cu-Fe system have differing chemical properties and the choice of the right precursors is not just finding metal complexes with similar volatilities and similar decomposition temperatures. First of all, the highly electropositive character of aluminium excludes the presence of highly electronegative elements such as oxygen and halogens. The present report deals with non oxygenated iron precursors. A wide range of precursors has already been tested for MOCVD of iron, but an optimal iron compound for practical MOCVD of pure iron films is missing. Besides, the affinity of iron for carbon facilitates the formation of carbides. This is the first reported study of iron amidinates tentatively used as precursors for MOCVD of iron. Iron amidinates were chosen because they contain no oxygen atoms and no Fe-C bonds. We report here on the investigation of two iron amidinates: dinuclear[2] iron bis(*N,N'*-diisopropylacetamidinate) ($Fe_2(\mu\text{-}^i Pr\text{-}MeAMD)_2(\eta^2\text{-}^i Pr\text{-}MeAMD)_2$) (**1**), and mononuclear[2] iron bis(*N,N'*-di-*tert*-butylacetamidinate) ($Fe(^t Bu\text{-}MeAMD)_2$) (**2**). Mass spectrometry showed them to be mononuclear in the gas phase. Depositions were made on polycrystalline copper discs in the temperature ranges of 350-450°C with **1** and 280-350°C with **2**. Deposited films were analyzed and characterized by electron probe microanalysis (EPMA), X-ray photoelectron spectroscopy (XPS), grazing incidence X-ray diffraction (GIXRD) and scanning electron microscopy (SEM). They contain Fe and/or Fe_3C. The films prepared from **1** contain Fe_4C also. Those prepared from **2** contain Fe_4C or Fe_4N, depending on the temperature and the ratio between precursor and H_2 flows. The isopropyl derivative proved to release more carboneous deposits (Table 1). The mechanism of Fe_4N formation from **2** was deduced from mass spectrometry analysis. The films deposited on well polished copper present a grey, mirror-like metallic surface. This morphology is more pronounced for films processed from precursor **2**. When deposited at temperature below 300°C, the films are made of densely packed nanocrystallites (size < 100 nm), independently of the precursor. The film prepared from **2** at 350°C (Fig. 1) is well crystallized and shows the <111> texture of Fe_4N evidenced by the XRD pattern.

This work may be considered as a screening approach for the use of iron amidinates as precursors for preparing iron-based materials by the MOCVD technique. Further studies should investigate the influence of reactive atmospheres. Besides Fe, the two isomeric compounds Fe_4N and Fe_4C are interesting materials for numerous applications, provided appropriate operating conditions are identified in dedicated CVD processes to produce them in the pure state. Fe_4N presents chemically inert and mechanically hard surfaces and interesting magnetic properties. Moreover, for the purpose of the present work, Fe_4N is thermally unstable and decomposes producing pure iron.

References

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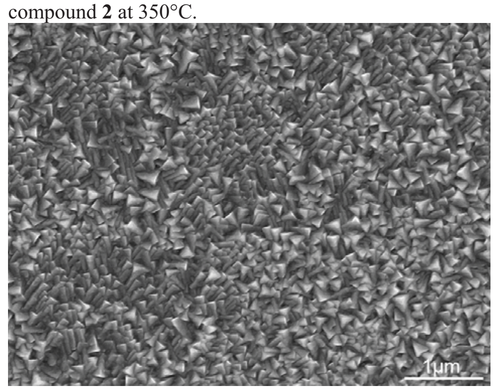
Table 1. Carbon and nitrogen contents, and identified phases of the films, determined by EPMA and XRD, respectively. Parentheses correspond to phases, which have not been unambiguously identified. The sample code shows the precursor (1 or 2), the reactor (A or B) and the temperature of deposition in °C.

Code	Precursor	$T_{deposition}$ (°C)	% at C	% at N	Identified phases
1A350	1	350	24	0	(Fe), Fe_3C
1A400	1	400	28	0	Fe, Fe_3C, Fe_4C
1A450	1	450	33	0	(Fe), Fe_3C, Fe_4C
2A280	2	280	18	0	(Fe, Fe_3C), Fe_4C
2A300	2	300	18	0	(Fe, Fe_3C), Fe_4C
2A320	2	320	15	7	(Fe), Fe_3C, Fe_4N
2A350	2	350	17	7	(Fe), Fe_3C, Fe_4N
2B280	2	280	12	9	(Fe, Fe_3C), Fe_4N
2B300	2	300	19	7	(Fe), Fe_3C, Fe_4N

Fig. 1. SEM-FEG micrograph of the film deposited from compound **2** at 350°C.



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