Thin Solid Films 518 (2010) 1883–1891

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Structural characterization of sputtered single-phase γ‴ iron nitride coatings

I. Jouanny [a], P. Weisbecker [b], V. Demange [a,c,*], M. Grafouté [d], O. Peña [c], E. Bauer-Grosse [a]

[a] Institut Jean Lamour UMR CNRS 7198, Nancy-Université, Ecole des Mines de Nancy, Parc de Saurupt, CS 14234, 54042 Nancy Cedex, France
[b] Laboratoire des Composites Thermostructuraux UMR-CNRS 5801, 3 Allée de La Boétie, 33600 Pessac, France
[c] Université de Rennes 1, Sciences Chimiques de Rennes UMR-CNRS 6226, Campus de Beaulieu, Avenue du Général Leclerc, CS 74205, 35042 Rennes Cedex, France
[d] Institut FEMTO-ST, Département MN2S, UMR-CNRS 6174, Pole Universitaire, BP 71427, 25211 Montbeliard cedex, France

ARTICLE INFO

Article history:
Received 18 September 2008
Received in revised form 2 July 2009
Accepted 2 July 2009
Available online 10 July 2009

Keywords:
Iron nitride
Sputtering
Crystal structure
X-ray diffraction
Transmission electron microscopy

ABSTRACT

Single-phase γ‴-FeN films were deposited by d.c. magnetron sputtering in a reactive Ar/N_2 atmosphere. The films were characterized by X-ray diffraction, scanning and transmission electron microscopies, electron energy-loss and Mössbauer spectroscopy. The average lattice parameter of the γ‴ cubic cell is 0.455 nm. Microstructure studies by electron microscopies revealed nanostructured columnar films with no preferential orientation. Diffraction peak intensities (X-ray and electron diffraction) are close to the theoretical values for a ZnS-type structure while profile analysis of the X-ray diffraction pattern using Rietveld refinement method demonstrated that the γ‴-phase is of ZnS-type. The energy-loss near-edge structures of N K-edge of the γ‴-phase is similar to those of the ZnS-type γ″-phase suggesting an identical local atomic environment for N atoms. On the contrary, Mössbauer spectra of both structures are different, which is understood as a consequence of numerous vacancies in the γ‴ structure. Investigations of magnetic properties showed that the γ‴-FeN compound is paramagnetic from room temperature to 2 K. The main conclusion of this work is that the γ‴-FeN phase is of ZnS-type, and not of NaCl-type as it is usually reported.

1. Introduction

Research on iron nitrides is mainly focused on compounds with nitrogen content lower than about 35 at.%. These nitrides present noticeable magnetic and mechanical properties, and are extensively studied for applications in magnetic storage, coating and steel industries. A recent interest was developed on nitrides with richer amounts of nitrogen, in particular on the mononitride γ″-FeN (zinc blend structure), because of its ability to grow on the semiconductor GaN (wurtzite structure, structurally related to zinc blend structure). Indeed, there is a strong interest in the field of spintronic to grow transition metals nitride materials, which are potentially ferromagnetic, on semiconductors [1,2]. A second potential application of iron nitrides is the formation of an interlayer between the semiconductor and a ferromagnetic material as α-Fe or γ′-Fe_4N. Another promising application is the recently observed catalytic properties of iron nitrides, these properties being improved by the increase of the nitrogen amount in the compound [3].

Three phases (all face-centered-cubic (fcc)) with about 50 at.% of nitrogen were discovered in the Fe–N system, namely γ″ ($a = 0.433$ nm) [4], γ‴ ($a = 0.450$ nm) [5] and γ_4 ($a = 0.866$ nm) [6]. These compounds were obtained with physical vapour deposition techniques, mainly by reactive sputtering of a metallic target. Structure of the γ″-phase was determined to be of ZnS-type (zinc blend, space group F 43m; N°216) [4,7–9]. γ_4 is a derivative structure of γ″, its formation being induced by diffusion of nitrogen atoms under beam irradiation of a γ″ single-phase film in a transmission electron microscope (TEM) [6]. By similarity with the known CrN nitride, the γ‴ phase was first presented as being of NaCl-type structure (rocksalt, space group Fmm; N°225) by assuming an ionic character of Fe–N bondings [5], although the large value of the experimental ratio $I_{\{111\}}/I_{\{200\}}$ observed in X-ray pattern of the γ‴ single-phase film was in favour of the ZnS-type. It was concluded that if the structure was really of the NaCl-type, then the γ‴ film should be {111} textured [10]. In the last two decades, controversial observations on the actual structure of γ‴ have been reported by different research groups [11–13]. Among the experimental studies, the major part deals with samples being mixtures of γ‴-FeN with other nitrides like γ″-FeN or ε-$Fe_{2-3}N$. Therefore, the difficulty to produce this nitride as pure phase prevented the accurate characterization of its structural and physical properties. In addition, preparation of this compound is so far only possible under the form of thin films, which limits the range of structural studies. Moreover, all theoretical studies on the equiatomic iron nitrides predict that the NaCl form should have a lattice parameter lying between 0.39 and 0.42 nm [14–21], which is considerably lower than the experimentally reported 0.450 nm value (Table 1). Up to now, there is no experimental report of the FeN–NaCl phase with $a \leq 0.42$ nm.

* Corresponding author. Université de Rennes 1, Sciences Chimiques de Rennes UMR-CNRS 6226, Campus de Beaulieu, Avenue du Général Leclerc, 35042 Rennes Cedex, France. Tel.: +33 2 23 23 67 88; fax: +33 2 23 23 67 99.
E-mail address: valerie.demange@univ-rennes1.fr (V. Demange).

0040-6090/$ – see front matter
doi:10.1016/j.tsf.2009.07.039

Table 1
Lattice parameters, magnetic properties of ZnS-type and NaCl-type structure in FeN, according to several theoretical studies.

FeN phase with ZnS-type structure	FeN phase with NaCl-type structure	Refs.
	Stable structure $a=0.4$ nm Ferromagnetic	[14,15]
Stable structure $a=0.421$ nm	$a=0.389$–398 nm	[16]
	$a=0.397$–0.399 nm Ferromagnetic	[17]
$a=0.436$ nm Paramagnetic	$a=0.420$ nm Antiferromagnetic	[18]
Stable structure 0.4169–0.4215 nm Paramagnetic	$a=0.3937$–0.402 nm Ferromagnetic	[19]
Stable structure $a=0.425$ nm	$a=0.395$ nm Ferromagnetic	[20]
$a=0.435$ nm Paramagnetic	Stable structure $a=0.411$ nm Ferromagnetic	[21]

Actually, the equilibrium lattice constant of any of the transition metal (M_T) nitrides with the zinc blend structure should be always significantly larger than that with the NaCl-type [20]. In addition, among the theoretical studies, there exists a controversy about the stable form of the fcc AB compound in FeN, being either NaCl according to [14,15,18,21] or ZnS according to [16,19,20] (see Table 1). In particular, Miao et al. have shown that the early transition metals nitrides (ScN, TiN, VN, CrN) prefer the NaCl structure while the later ones (MnN, FeN, CoN) are predicted to be of ZnS-type [20].

It is well-known that NaCl and ZnS-types can be distinguished by calculations of their respective structure factors (F), and by measurement of the ratio of the experimental diffraction intensities in X-ray and electron diffraction patterns [22]. In the ZnS-type structure, the half-filling of the nitrogen atoms in tetrahedral sites of the fcc iron lattice makes each Fe fourfold coordinated with N atoms (Fig. 1a). Accordingly, the structure being non-centrosymmetric, tetrahedra are not in a symmetrical array (Fig. 1c). In the NaCl-type structure, all the octahedral sites are filled by the nitrogen atoms (Fig. 1b) and each Fe has 6 N neighbors (Fig. 1d). Calculations of the structure factors (F) show that the diffraction intensity ($I \propto |F|^2$) of the same family of planes is different for each structure. For ZnS-type, the structure factor is equal to $F=4[f_{Fe}+f_N \exp i\pi/2(h+k+l)]$ with f_{Fe} and f_N, the atomic scattering factors of iron and nitrogen, respectively. Thus, the diffraction intensities are $|F|^2=16(f_{Fe}-f_N)^2$ if $h+k+l=2n$, $16(f_{Fe}+f_N)^2$ if $h+k+l=4n$ and $16(f_{Fe}^2-f_N^2)$ if $h+k+l=2n+1$. By taking in account that f_{Fe} and f_N are functions of $\sin\theta/\lambda$, relations between intensities of the first three diffraction peaks are: $I\{111\}>I\{220\}>I\{200\}$, with a $I\{111\}/I\{200\}$ ratio about 3.8. For NaCl-type structure, the structure factor is equal to $F=4[f_{Fe}+f_N \cos\pi(h+k+l)]$. Thus, the diffraction intensity is equal to $|F|^2=16(f_{Fe}+f_N)^2$ if $h+k+l=2n$ or $16(f_{Fe}-f_N)^2$ if $h+k+l=2n+1$. Consequently, the relative intensities are: $I\{200\}>I\{111\}>I\{220\}$ with a $I\{111\}/I\{200\}$ ratio about 0.6. Fig. 1e, f shows the simulated X-ray diffraction patterns of the γ‴-phase ($a=0.450$ nm) with both structures, obtained by using the Powder-Cell software [23], with $K\alpha_{Co}$ radiation. Comparison between these two calculated patterns demonstrated that the structure of γ‴ can be deduced from X-ray (or electron diffraction) experiments, if no preferential orientation is present in the γ‴ film.

Only few reports deal with magnetic properties of the γ‴-FeN structure which was found to show no magnetic order and is paramagnetic at 4.5 K [5,24]. On the contrary, the theory predicted that the iron nitride with the NaCl structure ($a \approx 0.4$ nm) should be ferromagnetic [14,15,17,19–21] or antiferromagnetic [18]. The γ″-FeN phase is also known to be paramagnetic from room temperature to 4.5 K [7,25–27], which is in agreement with theoretical studies [18,19,21] (Table 1).

In this paper, we report the deposition of single-phased fcc γ‴-FeN coatings by reactive sputtering of an iron target in an Ar/N_2 atmosphere. In view of the above-mentioned controversies, structure of the γ‴ phase was investigated experimentally by X-ray diffraction (XRD) and TEM in order to compare experimental diffraction intensities to above-presented simulations, decoupled from orientation effects. In addition, atomic environments of both nitrogen and iron atoms in the nitride were studied by electron energy-loss spectroscopy (EELS) and Mössbauer spectroscopy, respectively. Finally, the susceptibility and magnetization properties of the γ‴-FeN compound were investigated in order to determine its magnetic properties.

2. Experimental section

Experimental conditions needed to obtain monophased γ‴-FeN films were previously determined in [28] and will be the subject of a forthcoming paper.

In the present study, single-phase γ‴-FeN films were prepared on two types of substrates, namely on soda–lime glass and on copper substrate. The glass substrate was cleaned with a liquid soap, then with ethanol. The copper substrate was polished and heated in carbon tetrachloride until boiling then cleaned ultrasonically in a bath of ethanol. The experimental sputtering device was a 30-litre chamber equipped with a magnetron target, supplied with an advanced energy d.c. generator which can deliver a maximal power of 1.5 kW. The configuration corresponds to a triode sputtering system, with a supplementary tungsten filament as second cathode and a ring placed between the substrate and the target as second anode [28,29]. A specific iron (purity: 99.5%) target, detailed in a previous work [29], was used for this study. Its thickness and diameter were 0.5 mm and 50 mm, respectively. The substrate-holder was parallel and in front of the target. The substrate-to-target distance was fixed at $D_{S-T}=80$ mm (the substrate–ring anode distance was $D_{S-A}=20$ mm, while anode–target distance was $D_{A-T}=60$ mm). Current of the tungsten filament was $I_W=5$ A and the target current was $I_T=0.2$ A. A base vacuum of about 10^{-4} Pa was ensured by a secondary suction system composed of primary and secondary oil diffusion pumps. The coatings were obtained in argon/dinitrogen (Ar/N_2) atmosphere. The respective gas flow rates (D_{Ar} and D_{N2}) were controlled by digital MKS flowmeters and were regulated at 30 standard cubic centimeters per minute (sccm) for both gases. The working pressure, measured using a MKS Baratron absolute gauge, was fixed at about 0.35 Pa with the help of a throttle valve. During the deposition process, the substrates were maintained at about 373 K during 2 h. With the purpose to discuss particular structural properties of monophased γ‴-FeN, samples were compared to three other compounds, namely γ″-FeN and ε-$Fe_{2-3}N$ nitrides and γ‴-Fe(N,O) oxynitride. Elaboration details of these last ones were described elsewhere [6,28,29].

The films were characterized by XRD using a Siemens D500 diffractometer (Bragg–Brentano geometry) with a cobalt anode ($\lambda_{K\alpha 1Co}=0.1788965$ nm). Silicon powder was scattered on the sample surface to be used as an internal standard to correct the data from the instrumental errors and as a reference for the instrumental broadening. The peaks positions were determined with the help of the DIFFRAC^{plus} EVA software using mid cord positions. The films were also characterized using an INEL diffractometer with a curved detector (CPS120), a germanium monochromator and a cobalt anode under a fixed incidence of 2°. The film on glass was also studied by using a four-circle diffractometer (2θ, ω, χ, φ geometry—$\lambda_{K\alpha Co}$, Kβ filtered) equipped with a rotating sample-order. 10 $\theta/2\theta$ scans were recorded at different χ (ranging from 0 to 45°) with 2θ spanning from 25 to 120° on the four-circle diffractometer, assuring a continuous φ rotation of the sample at 600 rpm. Rietveld [30] refinement of the structure was