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Stability and phase changes in thin layers of rare-earth metals/iron and other binary compounds

V. Prysyazhnyuk *, O. Mykolaychuk

Ivan Franko National University of Lviv, Chair of Physics of Metals, Kyrylo and Mephodiy Street, 8, 79005, Lviv, Ukraine

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ABSTRACT

The structure, thermal stability and phase transformations in thin Gd–Fe films have been studied. The films were obtained by means of thermal evaporation in vacuum. At room temperature of substrates (T_s) amorphous films were formed, at $T_s = 300–500$ K – amorphous–crystal condensates, and at $T_s > 500$K – polycrystalline films. The crystal structure of condensates was determined at various temperatures and crystallization of amorphous films was found to have a heterogeneous character. During crystallization of Gd_2Fe_{17} amorphous films, formation of two phases, viz. Gd_6Fe_{23} and a-Fe was observed. In the films obtained at substrates temperature > 500K, the presence of three phases was established: a hexagonal phase Gd_2Fe_{17} of the Th_2Ni_{17}-type structure, a rhombohedral phase Gd_2Fe_{17} of the Th_2Zn_{17}-type structure and a hexagonal phase $GdFe_5$ of the $CaCu_5$-type structure. $GdFe_2$ films had a face-centered cubic structure, expected in bulk $GdFe_2$.

1. Introduction

The interest in GdFe films structure and structural stability is due to their unique electrophysical [1] and magnetic properties. It is known that structural, substructural and nanostructural features of films essentially influence other physical properties [2]. The aim of this paper is to investigate stability and phase changes during thermal annealing and to establish the relation between the structure of the formed films and the temperature of substrates as a technological parameter.

2. Experimental procedures

Films of Gd_2Fe_{17}, $GdFe_5$ and $GdFe_2$ compounds were obtained by techniques of thermal evaporation of a polycrystalline mixture of a respective composition in vacuum [5]. For structural investigations, 500–600 A thick films were precipitated on chips of alkali-haloid monocrystals NaCl. The thickness of films was measured with an optical interferometer. The substrate temperature was chosen to be within the 300–600 K range. The structural investigations were carried out by a UEMV-100 K electron microscope. The thermal stability and phase changes in thin layers of rare-earth metals/iron were investigated by means of direct heating inside the microscope's column (at a heating rate of 5–30 K/min).

* Corresponding author. Tel.: +380 322 964 594.
E-mail address: prysyazhnyuk@physics.wups.lviv.ua (V. Prysyazhnyuk).

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3. Results and discussion

Amorphous films. Electron diffraction patterns of films of all the studied compounds obtained at $T_s = 300$K reveal a diffuse halo [1,4] identifying their amorphous structure. The high resolution of the diffuse halo is evidence of some regularity in an amorphous state with predominance of a uniform type of short range ordering. The distances to the nearest neighbors in amorphous condensates are estimated to be: for $GdFe_2$ – 0.339 nm, for $GdFe_5$ – 0.355 nm and for Gd_2Fe_{17} – 0.332 nm. Electron diffraction studies have demonstrated films to be continuous, with no pores and no apparent infringements of a substructure, and very finely dispersed (Fig. 1). The diameters of nuclei are 7–9 nm. Decoration of alkali-haloid monocrystals is not revealed what suggests low surface mobility of the adsorbed atoms in the precipitation process.

Stability of amorphous films. Crystallization of $GdFe_2$ films starts at the temperature of 720 K (see Figs. 2 and 3). At this temperature a sharp diffraction peak appears on the diffuse halo background in the electron diffraction patterns (at $S = 2.89$ A^{-1}) which corresponds to the inter-planar distance of $d = 2.17$ A (Fig. 3). At the temperature of 770 K in the electron diffraction patterns additional diffraction peaks appear at $S = 3.37$ A^{-1} and $S = 4.33$ A^{-1}, corresponding to inter-planar distances of $d = 1.86$ A and $d = 1.45$ A, respectively (Fig. 4). All the diffraction peaks correspond to distances between (3 1 1), (4 0 0), (5 1 1) planes in a face-centered cubic lattice of $GdFe_2$ (Fig. 5).

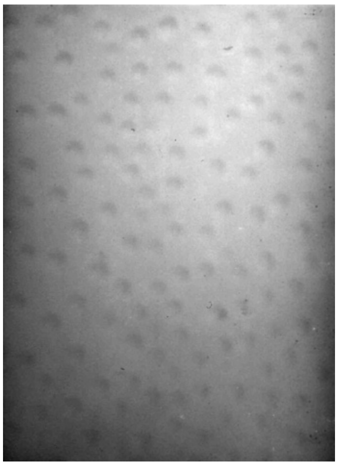

Fig. 1. Microphotography of $GdFe_5$ amorphous film.

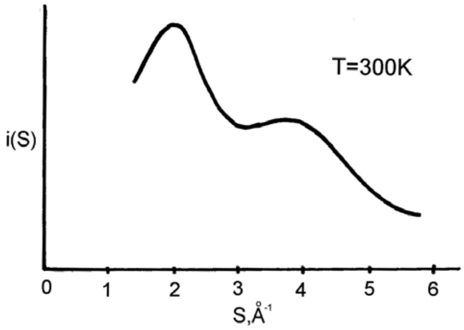

Fig. 2. Curves of electron scattering from $GdFe_2$ amorphous films at different temperatures.

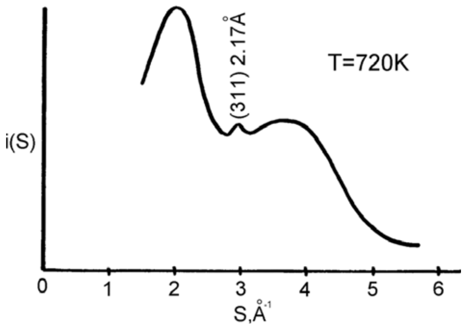

Fig. 3. Curves of electron scattering from $GdFe_2$ amorphous films at different temperatures.

The amorphous structure of $GdFe_5$ film is stable even up to the temperature of 820 K (unfortunately further heating has not been possible due to technological restrictions).

The a-Fe phase is the initial phase of crystallization of Gd_2Fe_{17} amorphous films. Probably, during deposition on cold substrates, fluctuations of chemical composition in Gd_2Fe_{17} condensates appear. Microregions enriched and depleted with Fe are obtained [3]. Chemical composition non-uniformity in an amorphous state promotes the formation of fine dispersed crystallites of a-Fe in an amorphous matrix. The a-Fe phase nuclei density is proportional to the heating rate of an amorphous film. With an increase in temperature the sizes of a-Fe crystallites increase as well. At temperatures exceeding 600 K crystallization of a Gd-enriched amorphous matrix starts with the formation of a Gd_6Fe_{23} compound (Fig. 6). The crystallization process of amorphous films is completed by formation of polycrystalline a-Fe and Gd_6Fe_{23} phases [4].

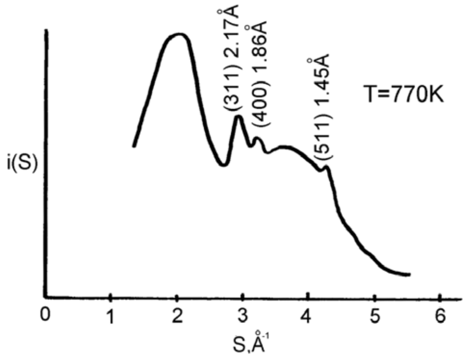

Fig. 4. Curves of electron scattering from $GdFe_2$ amorphous films at different temperatures.

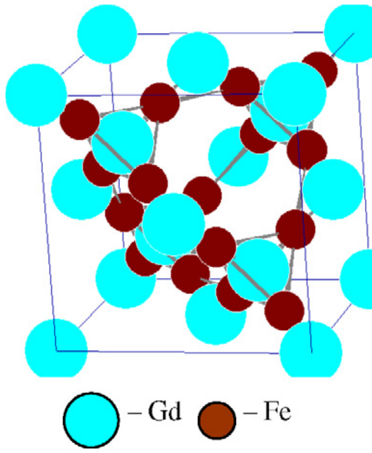

Fig. 5. The structure of $GdFe_2$.

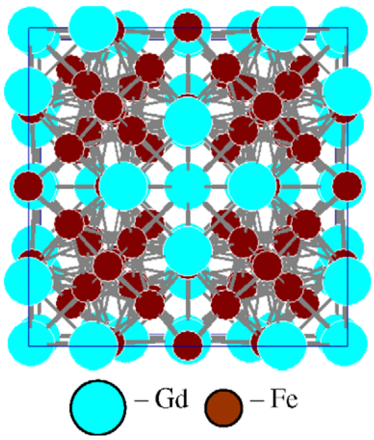

Fig. 6. The structure of Gd_6Fe_{23}.

Polycrystalline films. The $GdFe_2$ films obtained at T_s = 500 K were amorphous–crystalline. About half of a film's volume was amorphous, while the remaining part was polycrystalline with a face-centered cubic structure, appearing also in bulk $GdFe_2$ (Fig. 5). In the case of deposition of $GdFe_2$ films on NaCl monocrystals, epitaxial growth of the (100) plane has been observed. Electron diffraction patterns reveal the (220), (400), (440) reflexes from the

Table 1
Structural parameters of $GdFe_2$ films at T_s = 500 K (T_s – substrate temperature)

$GdFe_2$ in bulk			$GdFe_2$ films (at T_s = 500 K)		
I/I_0	d_n (nm)	(hkl)	I/I_0	d_n (nm)	(hkl)
63	0.2610	(022)	60	0.266	(022)
100	0.2229	(113)	100	0.217	(113)
16	0.2134	(222)	10	0.186	–
3	0.1696	(133)			
20	0.1509	(224)	10	0.164	(224)
19	0.1423	(333)	10	0.145	(333)
18	0.1307	(044)	10	0.132	(044)
7	0.1169	(026)	10	0.114	–
7	0.1128	(335)			
a = 0.7394 nm			a = 0.750 nm		

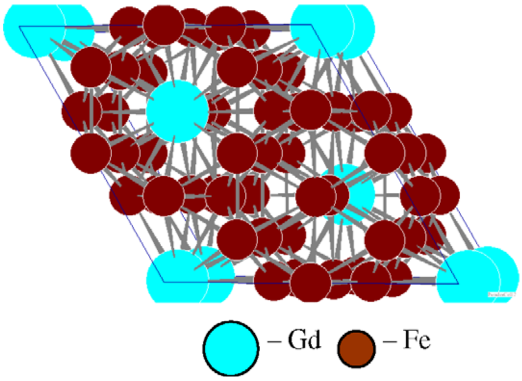

Fig. 7. The structure of Gd_2Fe_{17} of the Th_2Ni_{17} type.

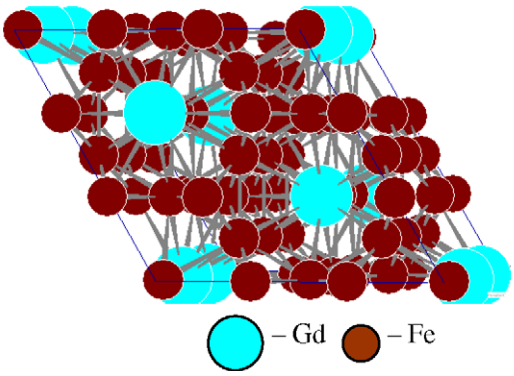

Fig. 8. The structure of Gd_2Fe_{17} of the Th_2Zn_{17} type.

oriented crystal grains 50 nm in diameter. There are also diffraction peaks from the (311), (331), (511), (533) planes of randomly oriented face-centered cubic crystallites (Table 1). The tendency to epitaxial growth of $GdFe_2$ films on NaCl monocrystals may be explained by the proximity of the parameters of their lattices (a_{GdFe2} = 0.739 nm, a_{NaCl} = 0.6639 nm).

A substantially different situation is observed in the kinetics of phase formation during precipitation of Gd_2Fe_{17} films on preheated substrates [4]. Amorphous films are formed in the temperature range from the room temperature up to T_s = 400 K. At T_s = 500 K the films transform into an amorphous–crystalline mixture. With T_s further rising, the polycrystalline phase fraction increases. An analysis of electronograms (Table 1) has shown that the polycrystalline part of films consists of three phases: a hexagonal Gd_2Fe_{17} compound (60%) of the Th_2Ni_{17} structural type (Fig. 7), a rhombohedral Gd_2Fe_{17} compound (30%) of the Th_2Zn_{17} structural type (Fig. 8) and a small amount of a hexagonal $GdFe_5$ compound of the $CaCu_5$ structural type (Fig. 9).

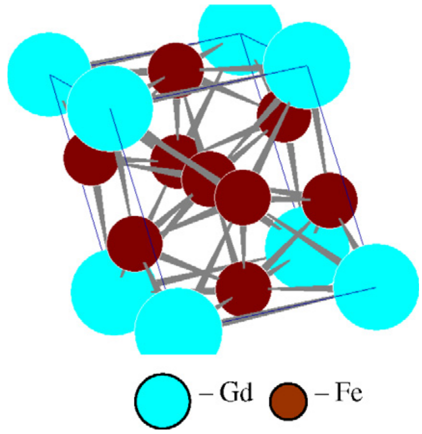

Fig. 9. The structure of $GdFe_5$.

4. Conclusions

The temperature of substrates essentially influences the formation of the structure of the investigated films. At the 300 K substrate temperature amorphous films are formed. Amorphous films are stable enough to temperature. Crystallization processes start at 700–800 K only. It is established that in a precipitation process of films there are microregions enriched and depleted with iron. The process of crystallization of $GdFe_2$ amorphous films is completed by formation of a polycrystalline film with a structure characteristic of the reference bulk $GdFe_2$. The process of crystallization of Gd_2Fe_{17} amorphous films is completed by formation of a polycrystalline a-Fe and Gd_6Fe_{23} phases. The $GdFe_2$ and Gd_2Fe_{17} films obtained at T_s = 500 K have been amorphous–crystalline. GdFe2 films have a face-centered cubic structure, similar to that of bulk $GdFe_2$. The polycrystalline part of Gd_2Fe_{17} films consists of three phases: a hexagonal Gd_2Fe_{17} compound (60%) of the Th_2Ni_{17} structural type, a rhombohedral Gd_2Fe_{17} compound (30%) of the Th_2Zn_{17} structural type and an hexagonal $GdFe_5$ compound of the $CaCu_5$ structural type (10%).

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