

Formation of the Atomically Ordered $L1_0$ Structure with the [001] Orientation during the Solid-State Reaction in Fe/Pd Bilayer Thin Films

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Abstract—The formation of the atomically ordered $L1_0$ -FePd structure during the solid-state reaction in Fe/Pd bilayer thin films is in situ investigated by electron microscopy and electron diffraction analysis. The initial iron and palladium layers were mainly coherently oriented crystallites with the orientation relationship α -Fe (001)[110] || Pd(001)[100]. It is established that the solid-state reaction between the iron and palladium layers upon heating at a rate of 4–8°C/min starts with the formation of the FePd solid solution at 390°C; at 430°C, the formation of the atomically ordered $L1_0$ -FePd structure is observed. It is shown that at the low heating rate (4–8°C/min), the $L1_0$ -FePd structure with the [001] orientation relative to the film plane forms, while at the high heating rate (50°C/min) it forms with the [100], [010], and [001] orientations.

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1. INTRODUCTION

Nanomaterials based on atomically ordered structures of the $L1_0$ type in the Fe–Pd and Fe–Pt systems have unique magnetic properties, including high coercivity ($H_c \sim 10$ kOe) and large uniaxial magnetic anisotropy ($K_u \sim 10^7$ – 10^8 erg/cm³) [1] caused by tetragonal crystal lattice symmetry, which make these materials promising for application in magnetic recording technologies, such as magnetoresistive random access memory (MRAM) [2] and heat assisted magnetic recording (HAMR) [3, 4]. At present, researchers intensively seek an optimal method for forming nanomaterials based on atomically ordered $L1_0$ structures with perpendicular magnetic anisotropy occurring during the formation of the structure with the [001] orientation relative to the substrate plane. It is well-known that when the Fe–Pd and Fe–Pt systems undergo the phase transition from the face-centered cubic (fcc) to atomically ordered $L1_0$ structure, the latter can form with three mutually perpendicular orientations (the $L1_0$ [001] direction is parallel to one of the [100], [010], and [001] fcc directions) [5], which is caused by the trend to minimizing internal stresses [6]. For instance, Halley et al. [7] showed that the atomically ordered $L1_0$ -FePd structure with three orientations, [100], [010], and [001], is formed upon annealing of the FePd thin films, which represent an atomically disordered solid solution. Similar results

were obtained for the $L1_0$ -FePd structure formed during the solid-state reaction upon annealing of Fe/Pd bilayer thin films [8]. Several methods for forming the atomically ordered $L1_0$ -FePd structure with the [001] orientation were proposed, including simultaneous sputtering of iron and palladium by electron beam epitaxy onto the Pd(001) epitaxial layer grown on the MgO(001) substrate [9], cooling of the single-crystal atomically disordered FePd solid solution from 750 to 600°C at a rate of 0.1–1°C/min at a pressure of 40 MPa [10], and annealing of the single-crystal atomically disordered FePd solid solution at temperatures of 520–540°C in magnetic field [11]. For the Fe–Pt system, the following techniques for obtaining the atomically ordered $L1_0$ -FePt structure with a specified orientation were proposed: annealing of polycrystalline Fe/Pt multilayers with a single layer thickness of 0.4 nm on glass substrates [12], fast heating of the 40-nm-thick Fe–Pt solid solution films on glass substrates from room temperature to 800°C at a rate of 40°C/min [13], and annealing of the Fe/FePt/Pt multilayer films at 478°C in external magnetic field [14, 15]. Thus, the atomically ordered $L1_0$ structures in the Fe–Pd and Fe–Pt films are formed mainly from the atomically disordered state by annealing. On the other hand, one of the methods for forming the atomically ordered structures in thin films is the solid-state reaction, which, in contrast to other

methods, allows forming the atomically ordered structures with the exactly specified atomic ratio between elements at relatively low temperatures. As was shown in [16], the solid-state reaction between the palladium and iron layers in the Pd/ α -Fe(001) bilayer thin films starts at a temperature of 400°C with the formation of the disordered Fe–Pd solid solution and, at a temperature of 480°C, the atomically ordered $L1_0$ -FePd structure starts forming.

In this study, we present the results of in situ electron microscopy and electron diffraction investigations of the formation of the atomically ordered $L1_0$ structure during the solid-state reaction in coherently oriented Fe/Pd bilayer thin films. The solid-state reaction is initiated by heating the Fe/Pd bilayers at rates from 4 to 50°C/min. In addition, the formation of the atomically ordered $L1_0$ -FePd structure from the atomically disordered state upon annealing is studied.

2. EXPERIMENTAL

The Fe/Pd bilayer thin films were formed by electron beam evaporation in high vacuum (a base residual pressure of 4×10^{-5} Pa) using successive sputtering of Pd and Fe layers onto a substrate. High-purity (99.95% for palladium and 99.9% for iron) initial materials were used. The substrates were fresh-cleaved NaCl(001) single crystals. The substrate temperature during deposition was 120–130°C. The ratio between the individual Fe and Pd layer thicknesses was chosen such that the Pd content corresponded to the stability region of the $L1_0$ -FePd phase, i.e., 50.0–60.5 at % of Pd, according to the phase equilibrium diagram [17]. The total Fe/Pd bilayer thickness was 40–50 nm. The microstructure and phase and elemental compositions of the Fe/Pd films were studied by transmission electron microscopy, electron diffraction, and energy-dispersive X-ray spectroscopy on a JEOL JEM-2100 electron microscope equipped with an Oxford Inca X-sight energy-dispersive spectrometer. Elemental analysis showed that the Fe : Pd atomic ratio in the samples under study is ~46 : 54 at %. Heating of the Fe/Pd films was performed directly in the column of the JEOL JEM-2100 transmission electron microscope (TEM) using a Gatan Model 652 double tilt heating holder, which allows controlled heating from room temperature to +1000°C. For this purpose, the Fe/Pd films were separated from the substrate and set on molybdenum TEM support grids. Electron diffraction patterns were detected and a sample temperature was measured during heating. Electron diffraction patterns were interpreted using Gatan DigitalMicrograph software and the PDF 4+ crystal structure database of the International Center for Diffraction Data [18].

3. RESULTS AND DISCUSSION

Analysis of electron microscopy images (Fig. 1a) and electron diffraction patterns (Fig. 1b) of the initial Fe/Pd films showed that they consist mainly of the coherently oriented α -Fe crystallites (body-centered cubic lattice, sp. gr. $Im\bar{3}m$, the lattice parameter is $a = 2.87$ Å, card no. 00-006-0696 of the PDF 4+ crystal structure database [18]) and Pd crystallites (fcc, sp. gr. $Fm\bar{3}m$, the lattice parameter is $a = 3.89$ Å, card no. 04-001-0111 of the PDF 4+ crystal structure database [18]) 10–20 nm in size. The orientation of α -Fe and Pd crystallites is due to the effect of the single-crystal NaCl(001) substrate upon film sputtering: the orientation relationship α -Fe(001)[110] \parallel Pd(001)[100]. The presence of textured Pd reflections (e.g., $d(111) = 2.25$ Å, Fig. 1b) in the electron diffraction pattern is caused by a small amount of the misoriented Pd and Fe crystalline phase at the crystallite boundaries.

To study the formation of the atomically ordered $L1_0$ -FePd structure during the solid-state reaction, the obtained films were heated from room temperature to 850°C at a rate of 4°C/min. When a temperature of 390°C was reached, the interdiffusion of iron and palladium with the formation of the disordered Fe–Pd solid solution (fcc, sp. gr. $Fm\bar{3}m$, the lattice parameter is $a = 3.81$ Å, card no. 04-003-5130 of the PDF 4+ crystal structure database [18]) started, which was accompanied by broadening of the Pd(200) diffraction reflections. Previously, analogous results were obtained on Pd/ α -Fe(001) thin films [14]. At a temperature of 430°C, the electron diffraction patterns contained the low-intensity reflections corresponding to the superstructural reflections $d(110) = 2.72$ Å of the atomically ordered $L1_0$ -FePd structure (sp. gr. $P4/mmm$, the lattice parameters are $a = b = 3.85$ Å and $c = 3.72$ Å, card no. 03-065-9971 of the PDF 4+ crystal structure database [18]), which is indicative of the onset of formation of the atomically ordered $L1_0$ -FePd structure in the Fe–Pd solid solution layer. At a temperature of 440°C, the superstructural $L1_0$ -FePd reflection with $d(100) = 3.85$ Å were observed in the electron diffraction patterns.

Upon further heating to 600°C, the atomically ordered $L1_0$ -FePd structure grew, which was accompanied by a continuous increase in the intensity of (110) and (100) superstructural reflections. The electron diffraction pattern shown in Fig. 2a contains the (100) and (010) reflections of the atomically ordered $L1_0$ -FePd structure and no (001) reflections. This allows us to conclude that the atomically ordered $L1_0$ -FePd structure forms with the [001] orientation relative to the film plane. The geometry of diffraction reflections in Fig. 2a corresponds to the orientation relationship α -Fe (001)[110] \parallel $L1_0$ -FePd(001)[100] \parallel Pd(001)[100].

We investigated the formation of the atomically ordered $L1_0$ -FePd structure from the atomically disor-

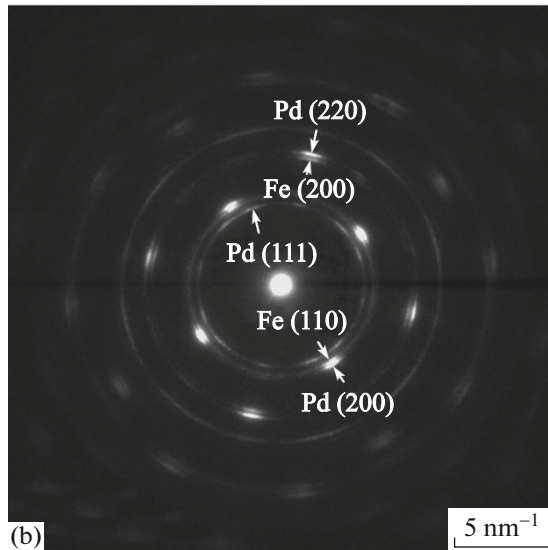
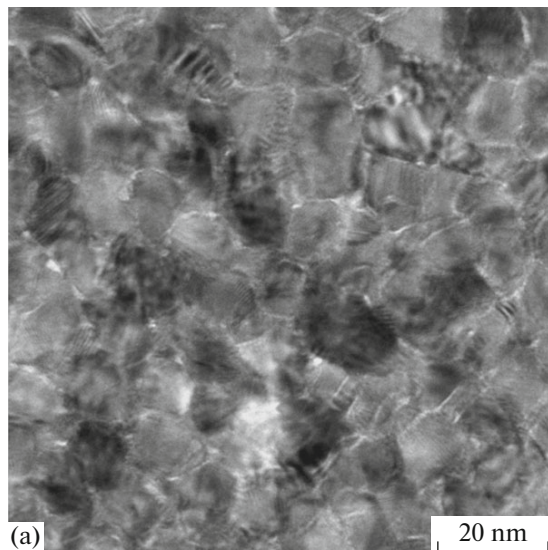


Fig. 1. (a) Electron microscopy image and (b) electron diffraction pattern of the initial Fe/Pd thin films.

dered FePd solid solution upon annealing. The atomically disordered solid solution was obtained by annealing of the samples preheated to 850°C at a temperature of 1000°C for an hour. Analysis of the electron diffraction patterns (Fig. 2b) obtained after annealing at 1000°C showed that the samples consist of coherently oriented FePd crystallites with the $[001]$ orientation. Then, the samples were cooled to 600°C at a rate of $\sim 200^\circ\text{C}/\text{min}$ and annealed at this temperature for 90 min. The formation of the atomically ordered $L1_0$ -FePd structure was observed right after sample cooling to 600°C . The low-intensity $L1_0$ -FePd reflections occurred in the electron diffraction patterns. Upon annealing at 600°C for 30 min, the growth of an atomically ordered structure was observed, which was accompanied by an increase in the intensity

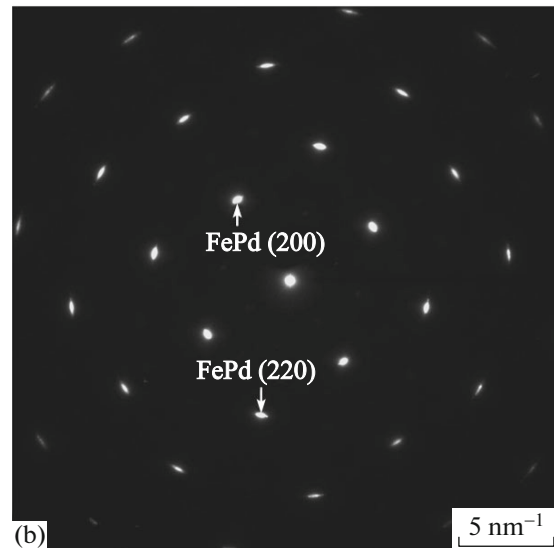
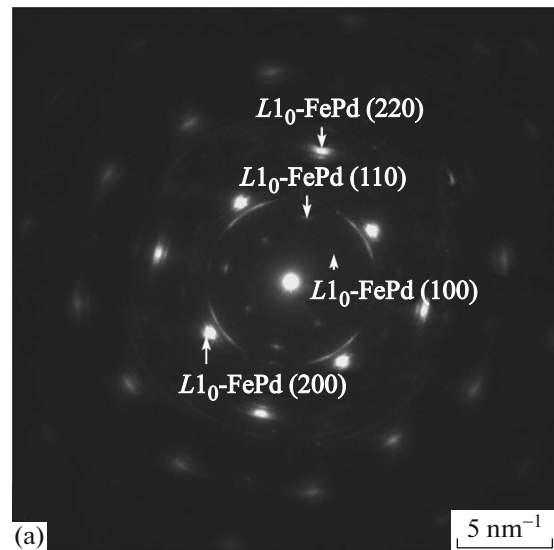


Fig. 2. Electron diffraction patterns of Fe/Pd thin films (a) during heating at a rate of $4\text{--}8^\circ\text{C}/\text{min}$ at $T = 600^\circ\text{C}$ and (b) after annealing at 1000°C for an hour.

of $L1_0$ -FePd superstructural reflections. Further, the intensity of these reflections remained invariable, which indicates that upon annealing at 600°C for 30 min the atomically ordered structure formed over the entire film volume.

The electron microscopy image (Fig. 3a) obtained from the sample annealed at 600°C is typical of $L1_0$ -FePd with the twin structure [19]. The areas of different contrasts in the electron microscopy image correspond to crystallites of the atomically ordered $L1_0$ -FePd structure with different orientations. The electron diffraction pattern (Fig. 3b) of the sample obtained during annealing (the diffraction region is $\sim 1\ \mu\text{m}$) contains the reflections corresponding to the

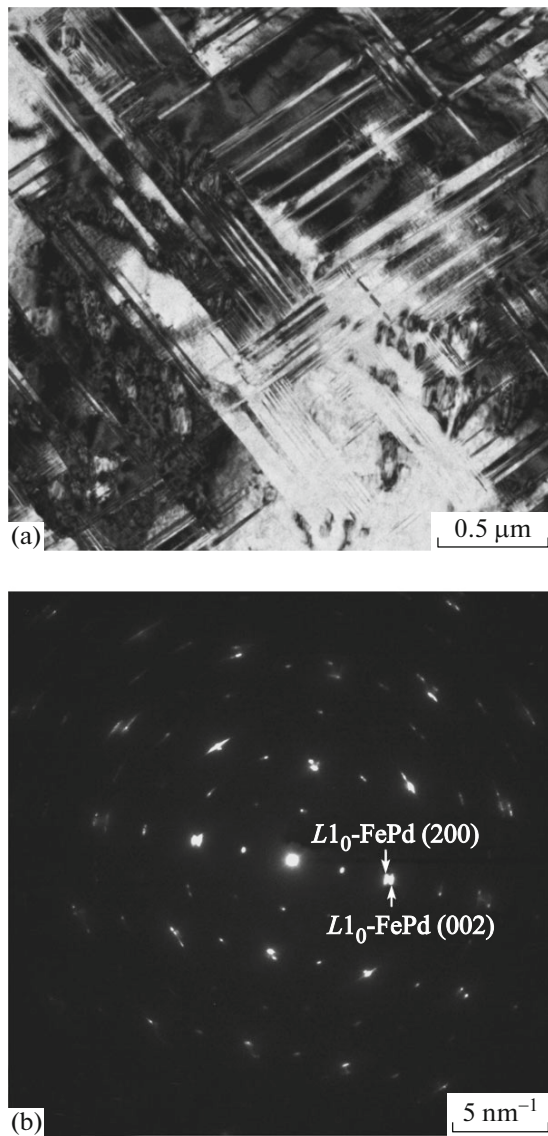


Fig. 3. (a) Electron microscopy image and (b) electron diffraction pattern of the FePd thin film annealed at 600°C for 90 min.

interplanar spacings of $d(200) = 1.92 \text{ \AA}$ and $d(002) = 1.86 \text{ \AA}$ of the atomically ordered $L1_0$ -FePd structure. This is indicative of the formation of $L1_0$ -FePd with mutually perpendicular [001], [010], and [100] orientations, which is consistent with the results reported in [7].

To study the formation of the atomically ordered $L1_0$ -FePd structure during the solid-state reaction initiated by fast heating, the Fe/Pd bilayers were heated to 550°C at a rate of 50°C/min and annealed at this temperature for 3 h. The formation of the atomically ordered $L1_0$ -FePd structure with three different orientations was noticed already at the initial stages of the solid-state reaction at 520°C upon heating, which is confirmed by the (200) and (002) reflections in the electron diffraction patterns. As was shown in [8], the

solid-state reaction results in the formation of the atomically ordered $L1_0$ -FePd structure with three orientations in the Fe(001)/Pd(001) bilayer thin films upon annealing. However, the results reported in [8] were obtained using ex situ techniques, which did not allow the authors to determine the $L1_0$ -FePd orientation at the initial stages of the solid-state reaction. In this study, we showed that the atomically ordered $L1_0$ -FePd structure with three orientations forms already at the initial stages of the solid-state reaction.

In this work, we established that during the solid-state reaction initiated by heating at a rate of 4–8°C/min, the atomically ordered $L1_0$ -FePd structure in the atomically disordered solid solution layer forms with the [001] orientation. The $L1_0$ -FePd growth with the [001] orientation is apparently caused by the following reasons: (i) the initial iron and palladium layers consist mainly of the coherently oriented [001] crystallites and (ii) the interdiffusion direction is perpendicular to the film plane. Due to the low rate of the growth of crystallites of the atomically ordered $L1_0$ -FePd structure upon slow heating (at a rate of 4–8°C/min), the conditions for the occurrence of internal stresses sufficient for the formation of other orientations are not provided in the film. Since the film consists of separate crystallites, a great number of intergrain boundaries can facilitate the compensation of internal stresses induced by the growth of the atomically ordered $L1_0$ -FePd structure from the atomically disordered solid solution.

In this work, we established that when the solid-state reaction is initiated by fast heating at a rate of 50°C/min, the atomically ordered $L1_0$ -FePd structure forms with three orientations: [100], [010], and [001]. In this case, due to the high heating rate and fast growth of crystallites of the atomically ordered $L1_0$ -FePd structure, the only mechanism of compensation of internal stresses in the film is the formation of crystallites of the atomically ordered $L1_0$ -FePd structure with three orientations relative to the film plane: [100], [010], and [001].

We estimated the order parameter η of the atomically ordered $L1_0$ -FePd structure formed during the solid-state reaction in the Fe/Pd bilayers upon heating at a rate of 4–8°C/min. The estimation technique is analogous to that used in [20], where the authors estimated the order parameter of atomically ordered $L1_0$ -FePd nanoparticles by analyzing the intensity of superstructural and structural $L1_0$ -FePd reflections in electron diffraction patterns. Here, we estimated the order parameter from the ratios between the intensities of (110) and (220) diffraction reflections of the atomically ordered $L1_0$ -FePd structure in the electron diffraction patterns of the samples obtained during heating. It was found that the long-range order parameter of the atomically ordered $L1_0$ -FePd structure formed with the [001] orientation during the solid-state reac-

tion upon heating at a rate of 4–8°C/min attains $\eta = 0.7 \pm 0.1$ at a temperature of ~600°C. The maximum calculated value of the $L1_0$ -FePd order parameter for the atomic ratio Fe : Pd = 46 : 54 at % typical of the films investigated here is $\eta = 0.96$. However, due to the great number of crystal lattice defects, including grain boundaries, the obtained order parameter of the investigated samples does not attain its maximum value. The similar order parameters were obtained for the atomically ordered $L1_0$ -FePd structure formed by annealing of the Fe/Pd bilayer thin films at 500°C ($\eta = 0.8$) [8] and epitaxial thin films of the atomically disordered Fe–Pd solid solution at 600°C ($\eta = 0.6$ –0.7) [21].

4. CONCLUSIONS

Thus, we demonstrated that the solid-state reaction initiated by slow heating at a rate of 4–8°C/min in the coherently oriented Fe/Pd bilayer thin films leads to the formation of the atomically ordered $L1_0$ -FePd structure with the [001] orientation relative to the film plane. The estimation of the order parameter of the $L1_0$ -FePd structure formed during the solid-state reaction showed that the atomically ordered structure has a fairly high degree of ordering ($\eta = 0.7 \pm 0.1$). In the case of fast heating at a rate of 50°C/min with subsequent annealing at 550°C and at 600°C from the atomically disordered state, the atomically ordered $L1_0$ -FePd structure with the [100], [010], and [001] orientations forms already at the initial stages. It was assumed that the formation of the atomically ordered $L1_0$ -FePd structure with the [001] orientation upon slow heating at a rate of 4–8°C/min is caused by the low rate of $L1_0$ -FePd crystallite growth and compensation of internal stresses induced by grain boundaries during the crystallite growth. Upon fast heating at a rate of 50°C/min with subsequent annealing and annealing from the atomically disordered state, due to the high growth rate of $L1_0$ -FePd crystallites, the compensation of internal stresses induced during the growth occurs via the formation of crystallites with different orientations: [100], [010], and [001].

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