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Annealing and structural properties of composite films

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Abstract. The composite films were investigated by AFM methods before and after annealing. Topographic and phase-contrast AFM images of the composite films at different annealing temperature were obtained. The separate metal granules and larger-scale labyrinth-like formations were described. These formations appear by the process of the film growth, also by film annealing. Strong changes of the structural properties of the films are observed after the percolation transition. The significant changes of the structural properties are connected with nanostructural transformations in the metal granules topology and presence of metal crystal phase.

Introduction

The investigation of thin composite films is a dynamically developing branch of condensed matter physics. The composite films can distinguish nanoscale systems that have significant nonlinear phenomena and quantum effects. Such effects as giant magnetoresistance, quantum Hall effect, strong magneto-optical response are characterized the films [1, 2]. Giant values of the magnetic permeability in the microwave range have been obtained for the composite films [3]. New information of processes occurring in the composite films by nanoscale systems allow to produce materials with specified or controllable magnetic properties, and makes possible to create new high-density magnetic storages and magnetic RAM. At the same time, the relationship of topology structure and the physical properties of the composite films were not studied enough. The structure of the metal-dielectric composite thin films described in article is very inhomogeneous and strongly depends on metal/dielectric concentration ratio. The analysis of the atomic force microscope (AFM) topographic images makes possible to reduce the relationship between the average size of the surface nanoparticles and the metal concentration. Areas of metal (granules) of the films can be in superparamagnetic or ferromagnetic condition depending on film thickness, which complicates the analysis of microwave magnetic properties. In the paper the separate metal granules and larger-scale labyrinth-like formations are described. These formations appear by the process of the film growth, also by film annealing and partial fusion of small granules.

Upon annealing, the structure of the films is significantly modified. Electric and magnetic properties of the composite films also changes with the structure changing [2]. In particular, this leads to a shift of the percolation threshold. The microwave magnetic characteristics (the line width of ferromagnetic resonance (FMR) and the position of the resonance) are changed [3, 5].

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Object and investigation methods

This work investigates the structure of composite films, which have a composition of $(Co_{45}Fe_{45}Zr_{10})_x(Al_2O_3)_{1-x}$, where 0.25<x<0.65 (A series). The percolation threshold of these films is about x=0.45 [1]. All samples were prepared by ion-beam sputtering and vacuum deposition of the target material on the polycrystalline glass substrate [3]. The target was composed of a slab (270×70×14 mm^3) of Co-Fe-Zr alloy and was perpendicular to the longitudinal axis dielectric plates (70×9×2 mm^3). It was possible to vary the dielectric width, and consequently to form the dielectric concentration gradient on the substrate. The deposition was performed in the argon atmosphere at pressure P(Ar) = 4×10^{-2} Pa. The deposited layer thickness was determined by the deposition time. Chemical composition and thickness of the films were obtained by scanning electron microscope JSM-6400. The surface topographic and the phase-contrast structure were investigated by atomic force microscope (AFM) ARIS-3500 (Burleigh Instrument Co, USA) with scanning field 70×70 um^2. Surface scanning was carried out using NC10 (NT-MDT) cantilevers. The radius of tip curvature was about 10 nm. The investigations were performed at room temperature. In order to obtain exact metric data the scale calibration was performed using certified test samples.

The films samples were annealed at various temperatures to determine the influence of annealing on the films structure [3,5]. Temperature control was carried out using a chrome-alumel thermocouple. The temperature changed from 530 K to 830 K with the step 50 K, the error was about 2%.

Annealing influence and structure of composite films

Topographic and phase-contrast images of unannealed composite films $(Co_{0.3}Fe_{0.3}Zr_{0.1})_x(Al_2O_3)_y$, where 0.25<x<0.65 were obtained (Fig. 1). The images of films with different ratio of the metal-dielectric are shown on figure. It can be seen that the films are highly heterogeneous structure in which the individual granules cannot be selected. It is also observed for both low and high metal concentration. However, in the case of high concentration of the metal the relief film is less heterogeneous, and it is possible to separate relatively large pores and a hills. A more uniform growth of the film beyond percolation takes place. White spots in the images correspond to the surface pores of the film. Phase-contrast AFM images of the films shows that at low concentration of the metal there is strong mixing of metal and dielectric and there is no separated particles. In contrast, if the metal concentration is high, particles during film deposition growth are combined into labyrinth-like structures with multiple particles (width size and bridges between them up to 0.7 μm).

The annealing of the films in air atmosphere was carried out. Under such conditions the surface of the film is subjected to partial oxidation, but evaporating of the film components is less than by vacuum annealing. It is seen from the Fig.2 after the weak annealing on the film the surface granular structure appears. It is possible to separate the granules with the size of 0.2 μm at low concentrations. However, their positions are irregular and granules are merged into complex shape forming. The structure is more contrast at the high metal concentration. Phase density image shows that original homogeneous mixture of the components breaks down into Al_2O_3 dielectric matrix with small metal inclusions. The average granule size after the annealing in the case of high metal concentration becomes smaller than mean size of the film separate region before the annealing.

The most significant changes observed after annealing for the films at a high temperature (550°C (Fig. 3)). In this case structural phase transition occurs and AFM images. The clear granular structures for both high and low metal concentrations are shown. The regular arrangement of metal particles in a dielectric matrix is observed at low concentration of metal. Thanks to the fact that the melting of the film material leads to a rearrangement of the film structure and the formation of the ellipsoidal shape particles. It should be noted that annealing the crystallinity of the granules takes place. Before annealing the film was amorphous. After a high temperature annealing at t = 550 C metallic crystalline phase grains appear. The size of crystalline regions increases from 2 nm at x = 0.3 to 8 nm at x = 0.7 [1]. The granulated structure of annealed films is become more competitive.

If the metal concentration is high, the average difference in height of topological irregularities remains big because the individual metal particles have the same size and there is "piling up" to each other.

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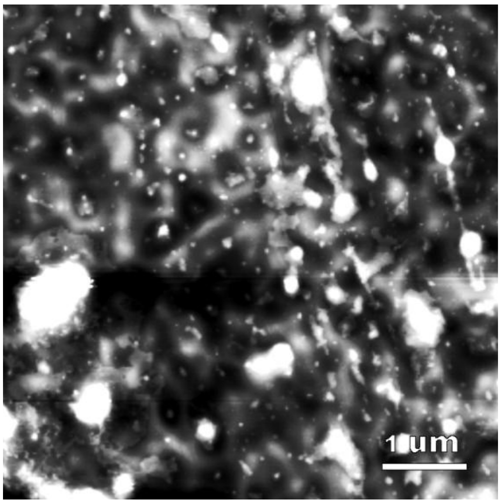
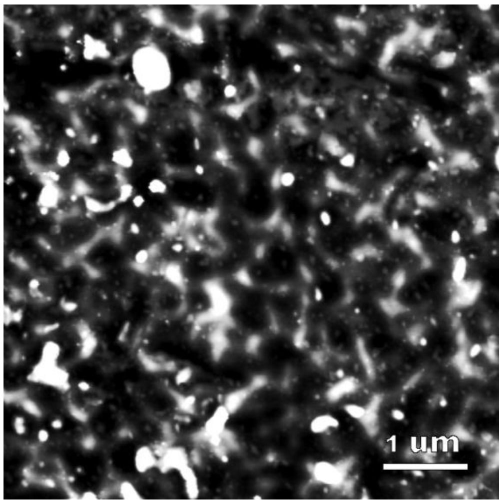
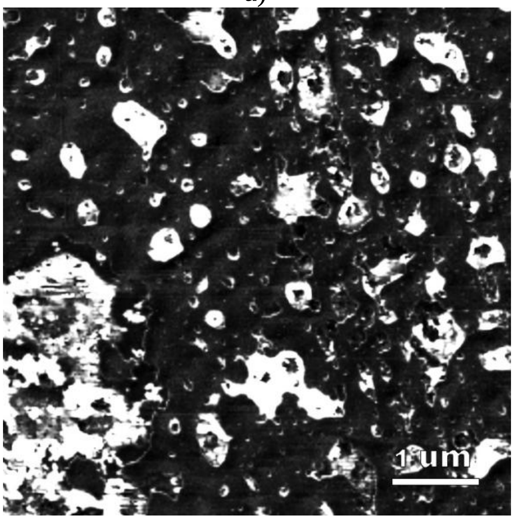


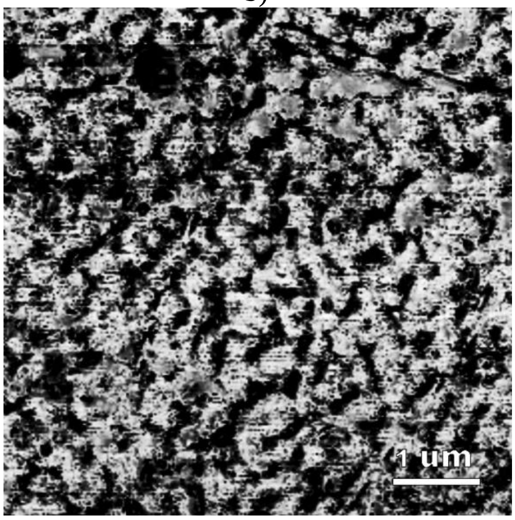
a)



b)



c)



d)

Figure 1. Topographic and phase-contrast AFM images of the unannealed films: x = 0.35 (a, c) and x = 0.65 (b, d)

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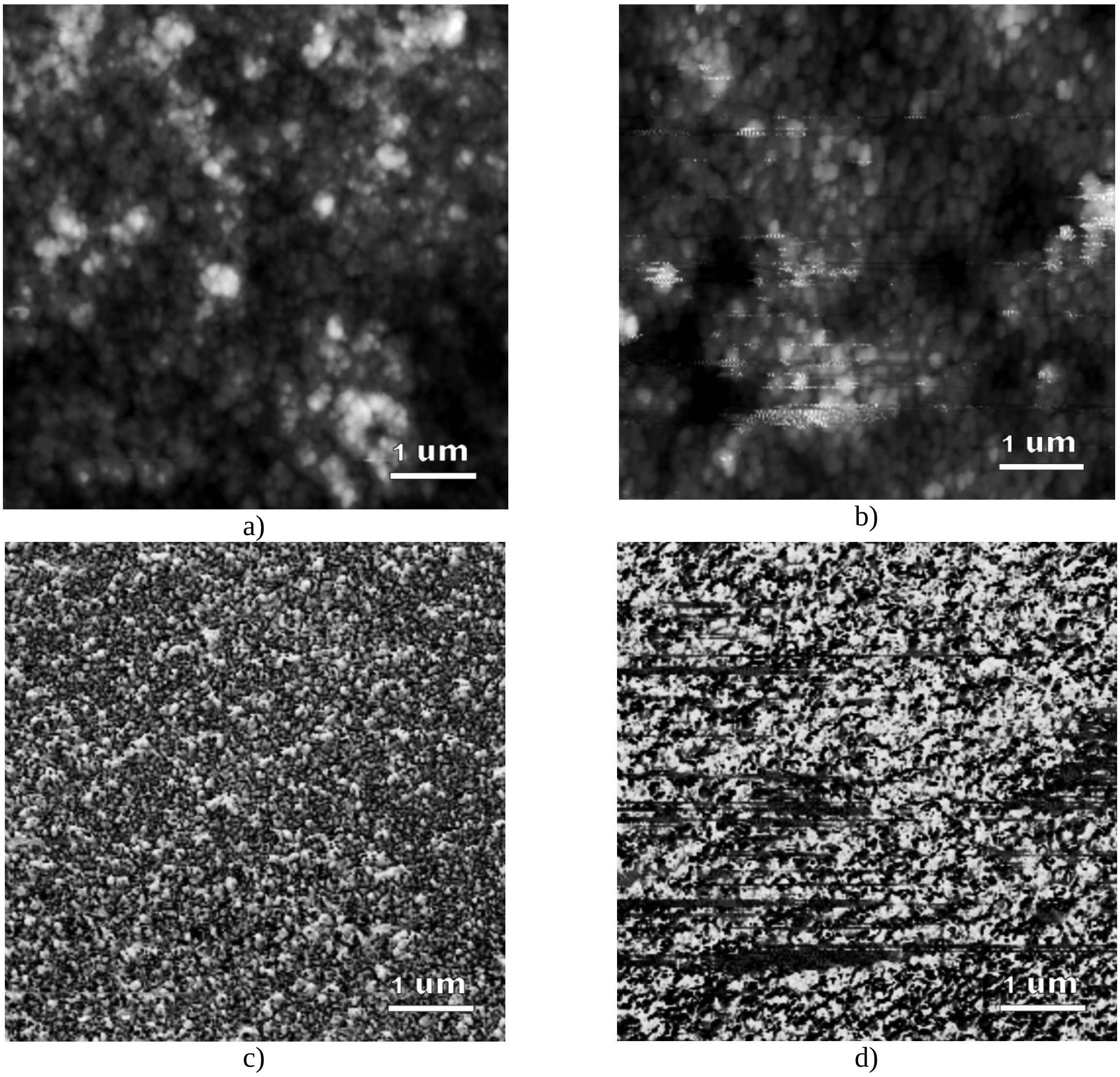
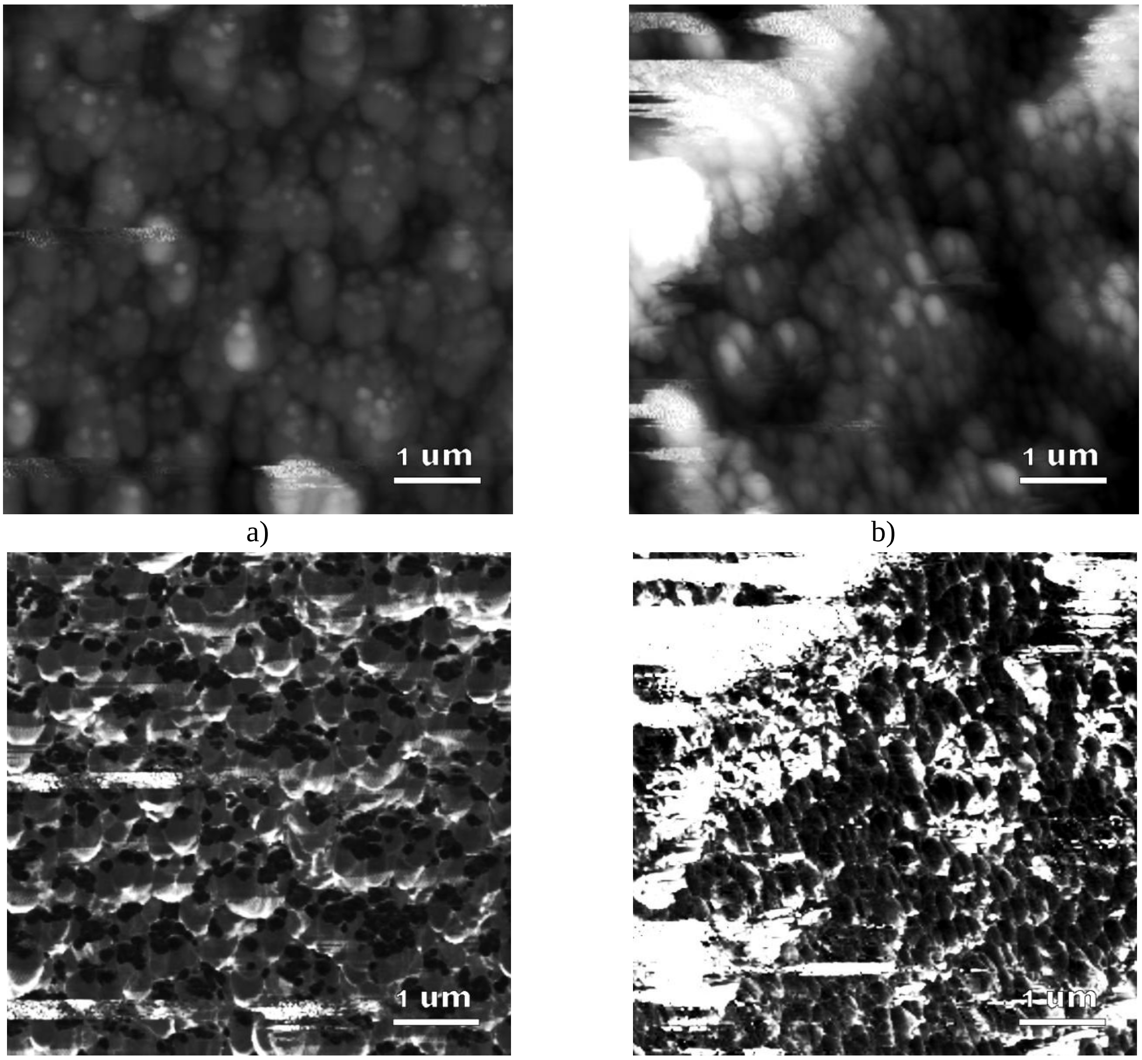


Figure 2. Topographic and phase-contrast AFM images of the annealed films by temperature at 350^{o}C: x = 0.35 (a, c) and x = 0.65 (b, d)



a) b)
c) d)

Figure 3. Topographic and phase-contrast AFM images of the film after annealing by temperature of 550°C: x = 0.35 (a, c) и x = 0.65 (b, d).

Conclusion

Thus the composite films before and after annealing were investigated by AFM methods. Topographic and phase-contrast AFM images of the annealed films at different annealing temperature were obtained. Topology and particle size distribution of composite films were investigated in relation to the annealing. The significant changes of the structural properties are connected with nanostructural transformations in the metal granules topology and presence of metal crystal phase. The mean particles radius increases by increasing of the annealing temperature. The particles anisotropy changes as the result of annealing. Changing of the particle anisotropy can occur due to the increase of the crystal field of metal particles.

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