Synthesis of textured films of hexagonal barium ferrite on Al₂O₃/Si₃N₄ amorphous structure

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Abstract. In this work structural studies of BaFe₁₂O₁₉/Al₂O₃/Si₃N₄ thin films with different thicknesses of aluminum oxide and silicon nitride are represented. It is shown that barium hexaferrite crystallizes on the amorphous surface of aluminum oxide with spontaneously formed (00l) uniaxial texture. Microstructural differences in BaFe₁₂O₁₀ films were observed with varying of the thickness of amorphous sublayers, which is explained by the effect of mechanical stress.

1. Introduction

BaFe₁₂O₁₉ hexagonal barium ferrite (BaM) is well-known essential material in microwave technology and radio electronics. At present, an intensive search and study of materials based on BaM are underway for new generation microwave devices, in particular, integrated with semiconductor planar technology. Technologies for producing anisotropic BaM films are being actively developed in this area. However, due to the peculiarities of the material, the synthesis of such films is associated with certain difficulties [1].

Usually, to obtain anisotropic films, the principle of epitaxial growth is used and single-crystal substrates are required. In this context, the possibility of obtaining such films on amorphous substrates is advantageous and eliminates the need for single crystals. Spontaneous textured growth is based on the principle of selective formation of film nuclei with an orientation that provides a minimum of surface and interfacial energies [2]. In materials with a close-packed structure, energy is minimized by orienting the packing direction perpendicular to the film surface. Thus, the (111) texture is observed for metals with a face-centered cubic unit cell, and for materials with a hexagonal close packing, such as hexaferrites, the texture type is (001).

After deposition, the films do not have sufficient crystallinity and, as a consequence, have no magnetic ordering. For the formation of the crystalline barium hexaferrite from such an amorphous precursor, annealing at temperatures above 800 °C is required. This raises a problem of a different kind. During annealing, the material crystallizes throughout the entire volume of the film, i.e. in energetically nonequivalent positions: on the surface, at the film-substrate interface, and in the bulk. In these positions, the most favorable crystallite orientation may differ. Thus, near the film / substrate interface, crystallites are formed with an orientation inherited from the substrate. On the surface grains with minimal surface energy crystallize. In the volume, the orientation of the grains can either be random or determined by the minimization of mechanical stresses. In the case of hexaferrite on an amorphous substrate, the largest contribution to the deterioration of the (00l) texture is expected from bulk crystallites. However, their formation can be avoided. As shown in [3, 4], in hexaferrite films
with thickness less than 100 nm crystallization of randomly oriented grains does not occur. Thus, to avoid crystallization of non-oriented grains in the bulk of the film, in this work, the hexaferrite thickness also did not exceed 100 nm.

Obtaining a textured BaFe$_{12}$O$_{19}$ film on amorphous substrates, texture perfection assessment and investigation of the effect of the thickness of amorphous underlayers are the objectives of this work.

2. Experimental

Silicon nitride films were synthesized on single-crystal silicon wafers by plasma enhanced chemical vapor deposition method (Corial D250) with the following process parameters: substrate temperature 250 °C, operating pressure 2 Torr, RF generator power 90 W, gas flow rate 50, 180, 1500, and 100 sccm for SiH$_4$, NH$_4$, N$_2$, and Ar, respectively. Films of aluminum oxide and barium hexaferrite were deposited by ion-beam sputtering. A polycrystalline plate of Al$_2$O$_3$ and a BaFe$_{12}$O$_{19}$ disk prepared by standard ceramic technology were used as targets. The deposition was proceeded in a UVN-71 apparatus with a following parameters: the discharge current of the ion source was 40 mA, the discharge voltage was 2 kV, the working gas (Ar) pressure was 0.3 mTorr, and the substrate temperature was 300–330 °C. After deposition, the BaM films were annealed for 1 hour at 900 °C with 5 °/min heating rate and natural cooling.

The thickness of the films was estimated using a contact profilometer (DekTak 150). For all samples, the BaM thickness was approximately 100 nm. The set of thicknesses for Al$_2$O$_3$ and Si$_3$N$_4$ is presented in Table 1.

X-ray diffraction (XRD) patterns were obtained on a BRUKER D8 ADVANCE diffractometer (Cu Kα, λ=0.154 nm, U=40 kV, I=40 mA). The surface morphology of the films was studied by atomic force microscopy (AFM, NT-MDT NTEGRA Prima).

| Sample, № | Al$_2$O$_3$ thickness, nm | Si$_3$N$_4$ thickness, nm |
|-----------|--------------------------|--------------------------|
| 1         | 200                      | 50                       |
| 2         | 200                      | 100                      |
| 3         | 200                      | 200                      |
| 4         | 100                      | 100                      |
| 5         | 50                       | 100                      |

3. Results and discussion

The XRD patterns of the obtained samples do not fundamentally differ from each other and show only the peaks of the BaM (00l) and of the silicon substrate. The only difference is in the ratio of the intensities of reflexes of different order of reflection, which is not essential in the context of this work. Figure 1 demonstrates a typical X-ray pattern of synthesized sample. Thus, X-ray phase analysis confirms the formation of a textured BaM film and amorphous state of underlayers. On the other hand, there is evidence according to which the film surface could be covered with grains of various orientations, which are undetectable by XRD, but significantly affect the anisotropy of the magnetic properties [5].
Nevertheless, AFM measurements showed the absence of non-oriented grains on the films surface. All crystallites have a circular shape, which is characteristic of the (00l) texture [3, 4]. The ratio of the Al₂O₃/Si₃N₄ thicknesses showed the influence on the microstructure of the BaM films. In particular, Figure 2 shows the AFM images of the surface of samples № 1 and № 2. It can be seen that in film № 1 the relief inhomogeneity is small, and the grains are densely adjacent to each other. In the sample № 2, the observed height difference is more noticeable, and voids are clearly visible between the crystallites. Such microstructural differences are caused by the mechanical stresses in the film, the magnitude of which depends on the thickness of the film and its material [6].

In addition to microstructural differences, the magnitude of mechanical stresses affects the presence of macroscopic defects that destruct the film. In Si₃N₄ and Al₂O₃ films, the stresses have opposite signs and can be compensated [7]. Of all the samples synthesized, sufficient stress compensation was observed for sample №2. As can be seen (Figure 3), there are no macroscopic defects on the surface of this film, while the rest of the samples exhibit blistering of various radii and concentrations. In addition, the size and number of blistering increased over time, to the point that they became visible to the naked eye. Thus, only sample №2 can be suitable for practical applications. On the other hand, its microstructure is less favorable for such applications as magnetic memory devices, for which grain uniformity is important. However, microstructure can be changed by

Figure 1. X-ray diffraction pattern of sample № 4

Figure 2. AFM images of samples №1 (a) and №2 (b)
adjusting the temperature of the substrate during film deposition [8], so the obtained material still has a certain potential for practical application.

![Figure 3](image_url)

Figure 3. Optical images of the samples №2 (a) and №4 (b). The scale is equal, the magnification is x20

4. Conclusions
Textured thin films of BaFe$_{12}$O$_{19}$/Al$_2$O$_3$/Si$_3$N$_4$ with different thicknesses of silicon nitride and aluminum oxide were obtained. The high degree of crystallographic texture of the BaM film is confirmed by X-ray diffraction and atomic force microscopy. In such films the crystallographic c axis of hexaferrite is directed perpendicular to the plane of the film in all grains. As the [001] direction is also the easy magnetization axis, it will determine the anisotropy of the magnetic properties. It is shown that the microstructure changes with varying the thickness of Al$_2$O$_3$ and Si$_3$N$_4$. This fact is important since the magnetic parameters (especially the coercive force) depend on the microstructure.

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