Journal of the European Ceramic Society 21 (2001) 1925–1929

www.elsevier.com/locate/jeurceramsoc

The study of barium ferrite thick films prepared by electron beam evaporation

M. Vérité *, A. Bessaudou, E. Briney, A. Célérier, F. Cosset, J.C. Vareille

IRCOM Laboratory (UMR 6615)/Equipe Capteur Microélectronique et microoptiques, 123, Avenue Albert Thomas, 87060 Limoges Cedex, France

Received 4 September 2000; received in revised form 14 December 2000; accepted 21 December 2000

Abstract

In this paper, we present the results obtained on thick layers (≈ 12 μm) of barium ferrite. Those are prepared by electron beam evaporation, under oxygen and at a substrate temperature of 700°C. We then looked at the influence of the deposition rate and post deposition annealing on the magnetic, crystallographic and morphologic properties of the layers. Before annealing the layers are crystallized according to the phase of the bulk ferrite and present good magnetic properties. Moreover starting from one certain deposition rate ($V_d \approx 10$ μm/h) the annealing modifies the composition of the layers and increases the value of the coercive field.

Keywords: Electron microscopy; Ferrites; Films; Magnetic properties; X-ray methods

1. Introduction

To reduce the size and the cost of microwave circulators, it would be necessary to use one permanent magnet deposited in thick films, avoiding the need for an external magnet.[1] Moreover, films may provide enhanced compatibility with planar circuit designs such as monolithic microwave integrated circuits (MMIC).[2] Barium hexaferrite ($BaFe_{12}O_{19}$) is well adapted because of its strong coercive field (H_c) and its high saturation magnetization ($4\pi M_s$). The ferrite deposits are carried out by electron beam evaporation because we must deposit 100 μm to reduce insertion losses in the circulator circuit.[3] The films are realized on various underlayers (≈ 1 μm): gold, gold on titanium, copper and copper on titanium. These metallic layers are used as the ground plane in the circulator circuit and have been grown by dc cathodic magnetron sputtering on silicon (100) substrates. The metallic layers increase adhesion and minimize the cracks on the film surface.

The effects of the deposition rate and post deposition annealing on crystallographic structure, magnetic properties, morphology and stoichiometric ratio of the ferrite have been investigated.

2. Experimental procedure

Before each deposit we prepared a new ingot having a Fe/Ba ratio closed to 11.5. Prior to the deposition, the substrates (underlayers on silicon substrate) are cleaned by Ar^+ bombardment using an RF generator in the following conditions: argon pressure: 0.33 Pa, RF incident power: 200 W, cleaning time: 5 min.

Then the ferrite ($BaFe_{12}O_{19}$) is evaporated under 100% oxygen atmosphere. The total deposition pressure is kept constant and equal to 0.46 Pa using oxygen pressure regulation. The substrate temperature is 700°C and the thickness of all the films, determined with a profilometer, is equal to 12 μm. All the films are post-annealed at the following conditions: annealing temperature: 850°C, oxygen pressure: 5.10^4 Pa, annealing time: 2 h, rise rate: 10°C/min.

During this study, the deposition rate has varied between 6 and 37 μm/h and the others deposition parameters have been kept constant.

Then the films obtained are characterized. The crystallographic structure is analyzed by XRD with a SIEMENS generator equipped with a goniometer. The saturation magnetization ($4\pi M_s$) and coercive field (H_c) are measured using an hysteresismeter M2100 with alternative magnetic field (50 Hz) applied in the film plane. We use a scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analysis system, to

* Corresponding author. Tel.: +33-5-55-45-74-48; fax: +33-5-55-45-74-50.

E-mail address: marc.verite@unilim.fr (M. Vérité).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00144-3

characterize morphology and to determine stoichiometric ratio. The EDX analysis are realized on different parts of the films surface to make sure that they are homogeneous.

3. Experimental results

3.1. Structural properties

The structural analysis is made during 1 h 30 min. We observed that at a substrate (underlayers on silicon substrate) temperature of 700°C, the not-annealed layers are crystallized mainly according to the phase of the bulk ferrite for all the deposition rates (Fig. 1). The results show that the films present a preferential orientation in the plane (h,k,0). The most important peaks corresponding to under-layer titanium gold are also visible on the spectra of X-rays diffraction. According to the figure, it is not possible to deduce an unspecified influence of the deposition rate on the crystallization of the layers. After the phase of annealing at high temperature (850°C), new peaks corresponding to bulk ferrite appear in addition to those which were already present before annealing (Fig. 2). Moreover it would seem that those peaks appear only starting from one certain deposition rate. This rate is ranging between 17 and 30 μm/h. We can conclude that after annealing when the deposition rate is higher than 30 μm/h, the crystallization of the films is better than before annealing.

4. EDX analysis

As Fig. 3 indicates, before annealing, the Fe/Ba ratio on the layers increases when the deposition rate increases. Indeed, this ratio varies between 7.4 (±0.5) and 14.2 for rates going from 6 to 37 μm/h. We found the composition of bulk material (11.5) for a deposition rate closed to 30 μm/h. For lower deposition rates, there is a barium excess which tends to increase when the rate decreases. Moreover, we note that annealing does not modify the Fe/Ba ratio at the low deposition rates (< 11 μm/h). At the more significant rates, we observe a difference between

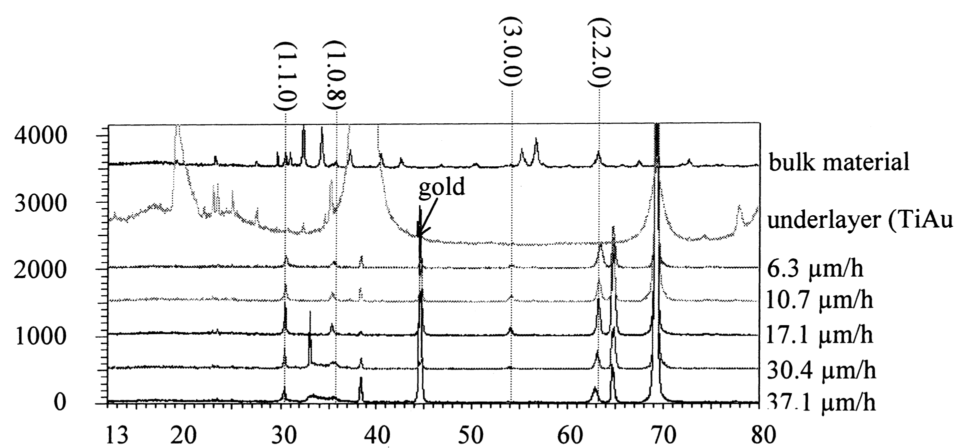

Fig. 1. XRD patterns of films prepared at different deposition rates on titanium-gold underlayers before annealing.

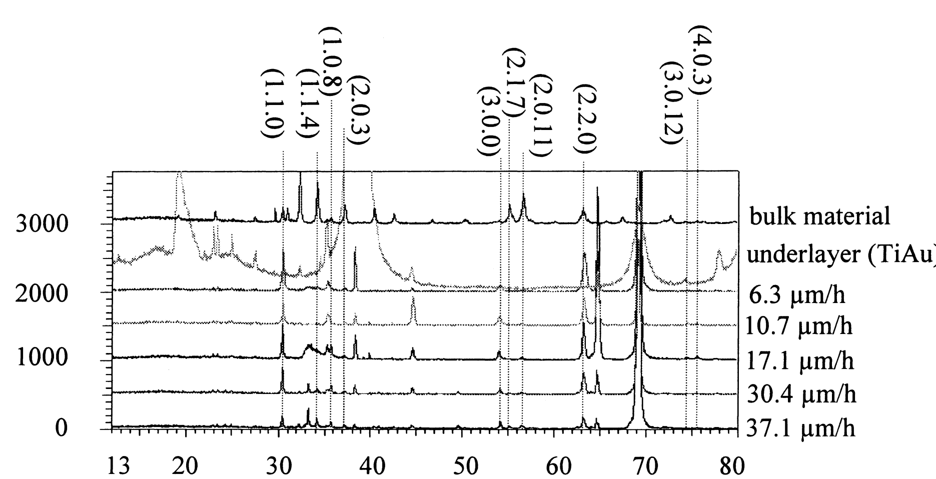

Fig. 2. XRD patterns of annealed films prepared at different deposition rates on titanium-gold underlayers.

the values of Fe/Ba measured before and after annealing. This variation tends to increase when the deposition rate increases. The values of the Fe/Ba ratio thus vary between 7.5 and 31.2 on the annealed samples. To explain this phenomenon, we have studied the evolution of the Fe/Ba ratio against the depth of analysis before and after annealing for deposits realized at 10.71, 30.39 and 37.1 µm/h. The depth on which we realized this analysis varied between 0.65 and 4.6 µm. The results are plotted in Fig. 4. Starting from a depth of analysis equal to 1.5 µm, the results obtained show that, before annealing, the composition of the layers is the same for all the depths of analysis. Indeed, the Fe/Ba ratio is constant. It is the same thing after annealing when the deposition rate is lower than 10 µm/h. At more important rates, we have observed an increase of the barium quantity when the depth of analysis increases. In conclusion, the increase in the Fe/Ba ratio after annealing is probably due to the diffusion of barium in the layers during the phase of annealing.

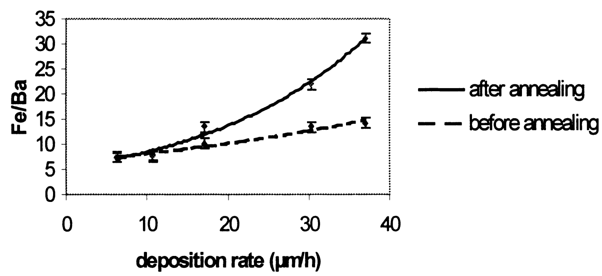

Fig. 3. Variation in Fe/Ba ratio as function of deposition rate.

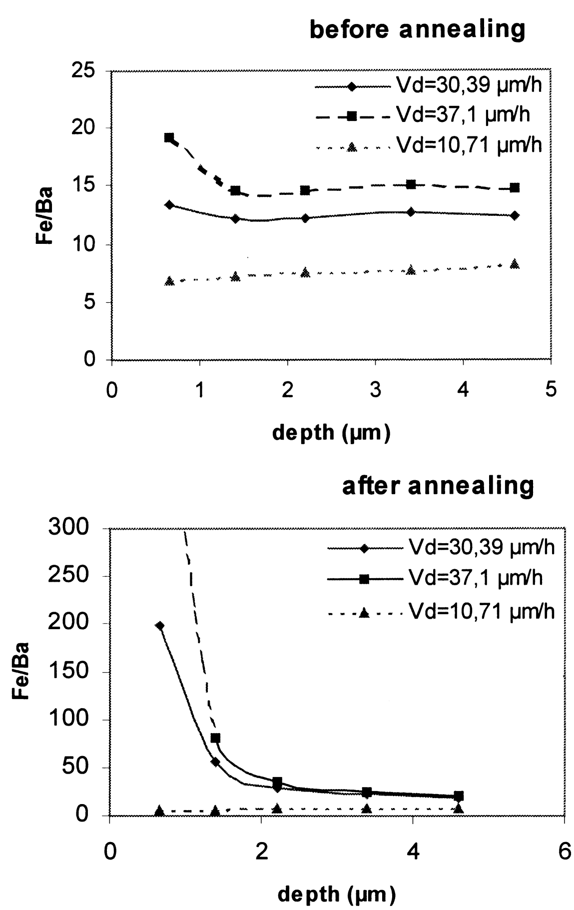

Fig. 4. Evolution of Fe/Ba against the depth of analysis.

5. SEM characteristics

We can see that the layers are adherent and present few cracks (Fig. 5). After annealing, the deposits are always adherent but have a more cracked surface. For rates lower than 11 µm/h the grains present a lengthened form before and after annealing. The length of these grains varies between 1 and 3 µm (Fig. 6). For higher deposition rates, the layers present grains whose dimensions vary between 500 nm and 2 µm. At this rates, the pictures of samples annealed gave the results

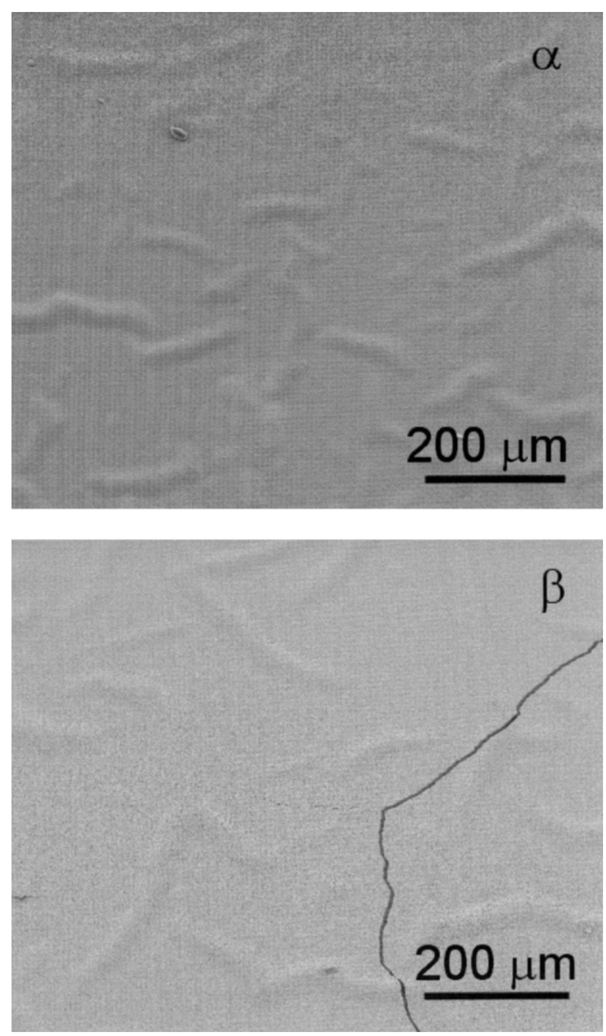

Fig. 5. SEM pictures of ferrite films on gold (α) before annealing and (β) after annealing.

presented in Fig. 7. In this case, it is very difficult to evaluate the grains size.

6. Magnetic properties

Before annealing, the value of the coercive field grows moderately when the deposition rate is lower than 11 μm/h then it decreases dramatically (Fig. 8). H_c varies between 112 and 50 kA/m. Moreover, beyond 18 μm/h the values of H_c measured on the layers are lower than that of the bulk barium ferrite (94 kA/m). After annealing the evolution of the coercive field is the same one up to 18 μm/h. Beyond this rate the values of H_c are higher than those measured on the not annealed layers. Indeed, H_c varies then between 123 and 93 kA/m. This phenomenon can be explained by the SEM characteristics. Indeed, it's well known that lower is the grains size and higher is the coercive field.[4] It is verified when the deposition rate is important.

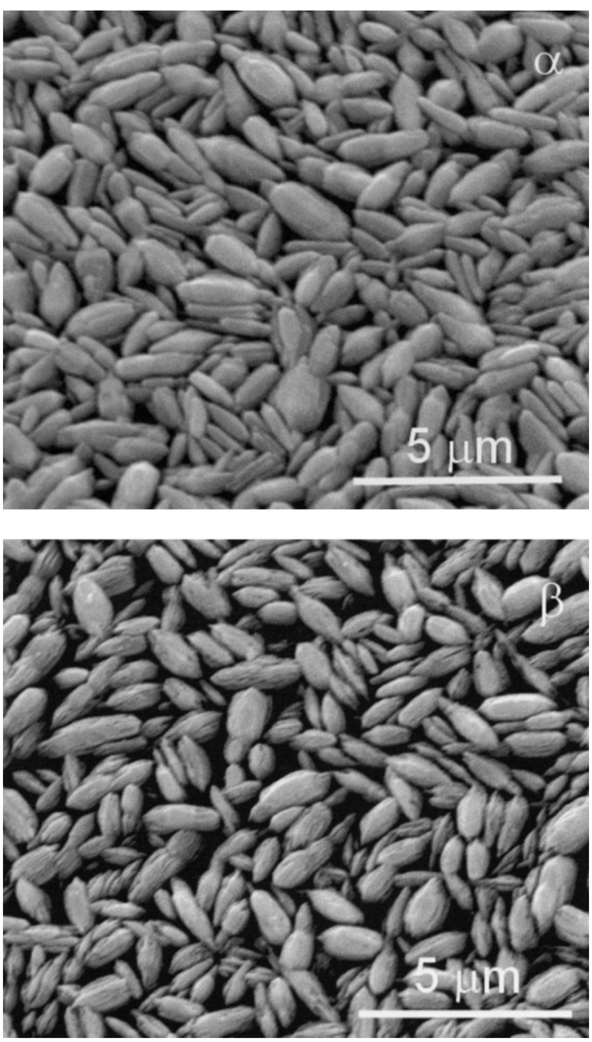

Fig. 6. SEM pictures of ferrite films prepared at 11 μm/h before (α) and after (β) annealing.

Up to 30 μm/h, the magnetization saturation measured on the layers increases when the deposition rate increases (Fig. 9). Indeed, it varies between 0.17 and 0.26 Tesla. Beyond this rate we observe a decrease of magnetization. After annealing, the values of $4\pi M_s$ are almost identical except at the low rates (<17 μm/h) where they are slightly higher. In all the cases, the measured values are lower than those of bulk ferrite ($4\pi M_s = 0.39$ Tesla). This is with the fact that during the procedure of deposition at 700°C, elements of underlayer diffuse in ferrite

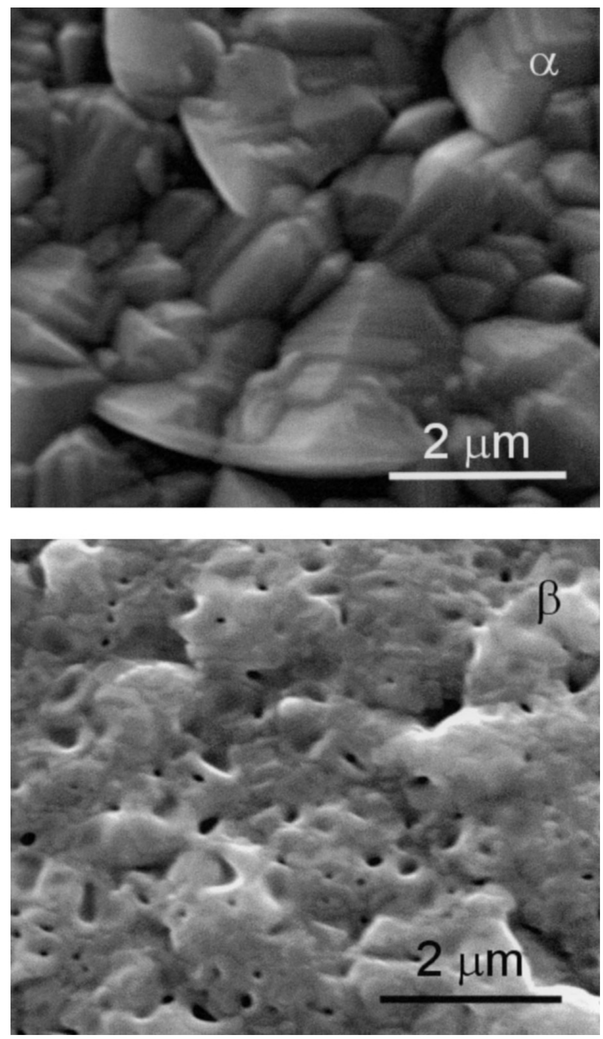

Fig. 7. SEM pictures of ferrite films prepared at 30 μm/h (α) before and (β) after annealing.

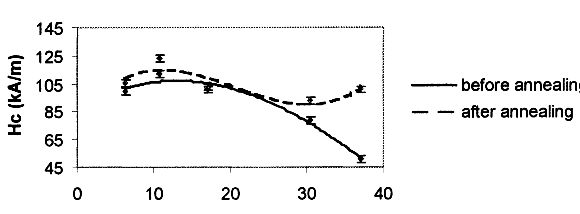

Fig. 8. Variation in coercive field as function of deposition rate.

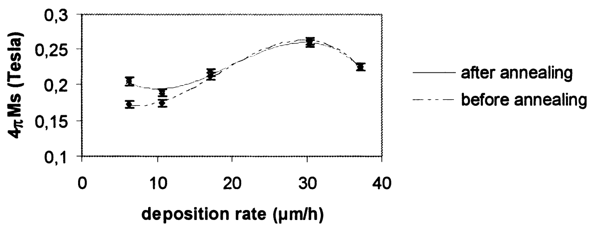

Fig. 9. Variation in saturation magnetisation as function of deposition rate.

and iron and barium diffuse in underlayer. This phenomenon of interdiffusion involves the formation of a nonmagnetic buffer layer to the interface ferrite substrate and thus a reduction of the value of $4\pi M_s$.[5]

7. Conclusion and discussion

During this study, we prepared barium ferrite layers of good quality. Indeed, at the substrate temperature of 700°C the deposits are very adherent and present few cracks for all the deposition rates. Moreover, the magnetic properties ($4\pi M_s$, H_c) obtained are acceptable to realize an integrated circulator functioning at 70 GHz ($4\pi M_{s\,\mathrm{acceptable}} = 0.15 - 0.5$ Tesla).[3] Thereafter it will not be necessary to realize post deposition annealing what still reduces the risk of even appearing cracks. However, in order to still improve the properties of the layers the optimization of the other deposition parameters will be studied.

References

1. Weiss, J. A., Watson, N. G. and Dionne, G. F., New uniaxial-ferrite millimeter-wave junction circulators. *IEEE MTT-S digest*, 1989, 145–148.
2. Glass, H. L., Ferrite films for microwave and millimeter-wave devices. *Proceedings of the IEEE*, 1988, **76**, 151–158.
3. Webb, D. C., *Design and Fabrication of Low-cost Ferrite Circulators*. Naval research Laboratory, Washington, DC, pp. 1191–1200.
4. Herzer, G., Grain size dependence of coercivity and permeability in nanocrystalline ferromagnets. *IEEE Transactions on Magnetics*, 1990, **26**, 1397–1402.
5. Liu, X., Bai, J., Wei, F., Zheng, Y., Morisako, A. and Matsumoto, M., The study of sputtered barium ferrite thin films. *Phys. Stat. Sol.*, 1999, **174**, 389–394.