Use of $\text{Ga}_2\text{O}_3[1\ 0\ 0]$ monocrystals as substrates for the synthesis of GaFeO_3 thin films

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ABSTRACT

The aim of this work is to explore the use of thermal oxidation for the synthesis of GaFeO_3 (GFO) thin films, by employing *ex-situ* annealed samples comprised of sputtered $\text{Fe}_{72}\text{Ga}_{28}$ layers deposited on top of $\text{Ga}_2\text{O}_3[1\ 0\ 0]$ monocrystals. To avoid Ga evaporation, $\text{Fe}_{72}\text{Ga}_{28}$ were capped with 60 nm-thick Mo. No surface damaged was observed when annealed between 200 °C and 400 °C. Indications of GFO formation have been obtained by X-ray diffractometry in samples with a FeGa thickness of 560 nm annealed at 300 °C and 400 °C. The hysteresis loops exhibit a coercive field close to the reported value for GFO when annealed at 400 °C. All the experimental results encourage the application of this growth routine to synthesize high quality GFO thin films.

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Magnetoelectricity can be exploited in multiferroic devices thanks to the manipulation of the magnetic properties by an electric field, and vice versa [1]. This is important since electric-field control of magnetism requires less energy than the use of magnetic fields [1]. GFO exhibit magnetoelectric properties [2–7] and high quality films can be deposited by pulsed laser deposition [8–13]. In a recent work, laser molecular beam epitaxy growth protocol was reported and based on the sequential deposition of Ga_2O_3 and Fe layers followed by a thermal treatment [14]. However, *ex-situ* oxidation in oxygen atmosphere using uncapped sputtered FeGa layers was unsuccessful [15]. The main complications observed in our previous work were: i) annealing promoted the evaporation of Ga after the formation of Ga_2O_3 oxides whereas Fe mainly remained in its metallic state, and ii) large surface damages [15]. Therefore, capped FeGa layers to reduce damage, and using Ga_2O_3 as a substrate to enhance the Ga content in the oxidized layers might be a better strategy to obtain GFO films. Here, we propose to grow FeGa layers capped with Mo on top of Ga_2O_3 monocrystals that are subsequently *ex-situ* annealed to eventually synthesize GFO.

The samples studied in this work are: $\text{Ga}_2\text{O}_3[1\ 0\ 0]/\text{Fe}_{72}\text{Ga}_{28}(x\text{ nm})/\text{Mo}(60\text{ nm})$ in which the FeGa thickness (x) has been modified

between 560 nm and 250 nm (samples scheme in Fig. 1). $\text{Ga}_2\text{O}_3[1\ 0\ 0]$ monocrystals were obtained by mechanical exfoliation following the procedure presented in reference [16]. $\text{Fe}_{72}\text{Ga}_{28}$ and Mo were sputtered with a DC power of 90 W and an Ar pressure of 0.3 Pa. Samples were *ex-situ* annealed at temperatures ranging from 200 °C to 700 °C in air atmosphere during 1 h. X-ray diffractometry (XRD) in the Bragg-Brentano configuration was performed in a Philips X'Pert MPD using the $\text{Cu K}\alpha$ wavelength (1.5406 Å). Surface morphology was imaged by an Olympus BX60M microscope, and with a JEOL JSM-IT300 scanning electron microscope (SEM) working at 20 keV. The in-plane hysteresis loops were measured at room temperature in a vibrating sample magnetometer (VSM) from LakeShore.

After thermal treatments, the surface morphology was routinely checked to determine the optimum temperature range to minimize surface damage. For annealing temperatures between 500 °C and 700 °C we observed a surface full of craters, in contrast to the pristine surface observed for thermal treatments between 200 °C and 400 °C (Fig. 1).

The XRD diffraction patterns taken from the samples are rather complex to analyze since the peaks related to the Ga_2O_3 monocrystals are very intense and can hide the substantially lower peaks of the other phases. However, small misalignments during XRD measurements enable to avoid the substrate peaks. The proximity between diffractions peaks makes also challenging to determine the evolution of the different phases with the annealing tempera-

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Fig. 1. Optical image of the sample $\text{Ga}_2\text{O}_3[1\ 0\ 0]/\text{Fe}_{72}\text{Ga}_{28}(560\text{ nm})/\text{Mo}(60\text{ nm})$ annealed at $400\text{ }^\circ\text{C}$. Right upper corner: scheme of the samples. Left upper corner: detail of the surface obtained by SEM microscopy.

ture and the FeGa thickness. In the graphs we have introduced the diffractogram of an as-grown FeGa layer as a reference to facilitate the discussion of the results (Fig. 2). For an annealing temperature of $200\text{ }^\circ\text{C}$, the FeGa(1 1 0) peak disappears in comparison to the as-grown layer but the temperature is too low to promote the formation of GFO as revealed by the absence of the GFO(2 4 0) peak at $2\theta \sim 43.77^\circ$ regardless of the FeGa thickness (Fig. 2a). This is also confirmed by the absence of any secondary peak related to GFO (2 3 1) close to the Mo(1 1 0). For the sample with the lowest thickness, 250 nm, a small diffraction peak related to FeMo is observed. Therefore, this thickness is not considered in the analysis for higher annealing temperatures. In Fig. 2b we present the comparison between samples annealed at $300\text{ }^\circ\text{C}$. For this temperature, the Mo(1 1 0) peak seems to be shifted towards higher angles that can be taken as an indication of the formation of GFO since the GFO(2 3 1) peak appears at $2\theta = 39.6^\circ$. This thermal treatment at $300\text{ }^\circ\text{C}$ also seems to shift the FeGa(1 1 0) peak of the 560 nm-thick FeGa layer to lower diffraction angles, i.e. towards the GFO (2 4 0) reflection, a further indication of the GFO formation

(Fig. 2b). However, the shift of the FeGa(1 1 0) peak is not so evident for the 400 nm-thickness. At $400\text{ }^\circ\text{C}$ and for a FeGa thickness of 560 nm, the measured diffraction pattern is similar to that after annealing at $300\text{ }^\circ\text{C}$, with the same indications for the formation of GFO. From these experimental results we can conclude that the formation of GFO is enhanced for an annealing between $300\text{ }^\circ\text{C}$ and $400\text{ }^\circ\text{C}$ for samples with a 560 nm FeGa thickness. However, the presence of metallic FeGa cannot be ruled out since no clear diffraction peaks but shifts with respect to those present in the as-grown reference FeGa have been observed in the XRD measurements.

The magnetic characterization reveals that the annealing at $300\text{ }^\circ\text{C}$ for the 560 nm-thick FeGa layer does not significantly modify the hysteresis loops (Fig. 3). The magnetic anisotropy present in the FeGa reference layer is almost unaffected by this annealing. However, for $400\text{ }^\circ\text{C}$ it is obtained a larger modification of the magnetic anisotropy. In addition, it has been reported a coercive field (H_C) between 70 and 90 Oe for GFO layers [14]. In the magnetic easy axis (EA) of the sample annealed at $300\text{ }^\circ\text{C}$ we have obtained a H_C of 44 Oe that is close to that of the FeGa reference sample. The same can be said for the magnetic hard axis (HA) of this sample with a H_C of 37 Oe. However, the sample annealed at $400\text{ }^\circ\text{C}$ has a higher H_C in these two axis, 75 in the EA and 72 Oe in the HA. This increase of H_C can be taken as an indication of GFO formation. Therefore, the magnetic results indicate a higher proportion of GFO when annealed at $400\text{ }^\circ\text{C}$ a 560 nm-thick FeGa layer.

In conclusion, the experimental results of this work show the potential of using *ex-situ* annealings to produce GFO thin films when using capped FeGa layers sputtered on top of $\text{Ga}_2\text{O}_3[1\ 0\ 0]$ monocrystals. However, to avoid surface damage it is necessary to restrict the annealing temperature to remain between $200\text{ }^\circ\text{C}$ and $400\text{ }^\circ\text{C}$. XRD has provided indications of GFO formation for an FeGa thickness of 560 nm annealed between $300\text{ }^\circ\text{C}$ and $400\text{ }^\circ\text{C}$. In addition, the sample annealed at $400\text{ }^\circ\text{C}$ exhibits a H_C closer to that reported in GFO.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Fig. 2. XRD diffraction patterns for $\text{Ga}_2\text{O}_3[1\ 0\ 0]/\text{Fe}_{72}\text{Ga}_{28}(x\text{ nm})/\text{Mo}(60\text{ nm})$ with different FeGa thickness annealed at (a) $200\text{ }^\circ\text{C}$ and (b) $300\text{ }^\circ\text{C}$. The diffraction pattern of a FeGa layer (curve in black) has been included as a reference. Peaks related to the Ga_2O_3 monocrystals have been marked with red asterisks. Curves have been shifted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Room temperature hysteresis loops for the as-grown FeGa reference layer (●, ○), and samples with 560 nm-thick FeGa annealed at 300 °C (■, □) and 400 °C (▲, △). HA and EA refers to magnetic hard axis and magnetic easy axis, respectively.

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