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Epitaxial films of an alternative multiferroic material, $GaFeO_3$ (GFO), were grown by pulsed laser deposition on yttrium-stabilized zirconia (001) and on conducting buffer layers of indium tin oxide (001). They present a perfect epitaxial growth along the GFO [010] axis and six crystallographic variants in the film's plane. Their magnetic properties are close to those of the bulk with an out-of-plane [010] hard direction and a Curie temperature of ~200 K. The films did exhibit ferroelectric properties when characterized by electrostatic force microscopy. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2813020]

Multiferroic materials receive a considerable renewal of interest because of the increased possibilities their properties offer to electronic devices.[1–3] Recently, the multifunctional character of multiferroics has been exploited to design magnetic tunnel junctions.[4] Such junctions, presenting both magneto- and electroresistance effects, define a four-resistance-state system and constitute a major progress in spintronics. However, few materials simultaneously present magnetic and electric orderings.[5] Among these materials, those presenting ferri—or ferromagnetic properties are extremely rare, the vast majority being antiferromagnets.[6] $BiMnO_3$ (BMO), which is one of the very few ferromagnetic multiferroic materials, has been until now the favorite candidate for the fabrication of tunnel junctions.[7] However, its Curie temperature of 105 K is far from room temperature and the stabilization of a pure BMO phase is rather difficult. There is a need for alternative materials. $GaFeO_3$ (GFO) is a very promising one. It is ferroelectric and ferrimagnetic.[8] Its Curie temperature is of about 200 K and may be increased to values above room temperature by increasing the Fe content x of the $Ga_{2-x}Fe_xO_3$ cell ($T_{Curie}=350$ K for $x=1.4$).[9] The physical properties of GFO are well documented in the bulk form since the 1960s. It was discovered by Remeika in 1960.[10] Its crystallographic structure (orthorhombic unit cell in the space group $Pc2_1n$ with $a=0.875\,12\pm0.000\,08$ nm, $b=0.939\,93\pm0.000\,03$ nm, and $c=0.508\,06\pm0.000\,02$ nm) was described by Abrahams *et al.*[11] a few years later on the basis of a proposition made by Wood.[12] According to Levine *et al.*,[13] its magnetic ordering temperature is 240 K and the low temperature spontaneous moment is of $0.76\mu_B$ per Fe atom. Another extremely interesting property of this material is the magnetoelectric effect observed by Rado[14] in the bulk.

However, applications of the multiferroic properties of this very promising material in electronic devices require the fabrication of thin films. Up to now, only one paper deals with this fabrication.[15] While the crystallographic properties of the films are the key point on which the physical properties depend, no particular focus was made in that paper on the crystallographic properties of the films, especially in plane. Another crucial point that needed to be addressed is the existence of a crystallographically compatible material suitable to be used as a conducting electrode. It has indeed been predicted[16] and experimentally proven for (100) oriented CoFe/MgO/CoFe junctions[17] that fully epitaxial tunnel barriers can give rise to higher tunneling spin polarization than amorphous ones because of highly spin dependent evanescent decay of certain wave functions. In this letter, we report the fully epitaxial growth of GFO on conducting indium tin oxide (ITO) buffered yttrium-stabilized zirconia (YSZ) (001) by pulsed laser deposition (PLD) and present the crystallographic relationships between the films and the substrate. The implications of these relationships on the magnetic properties will also be given. The ferroelectric proper-

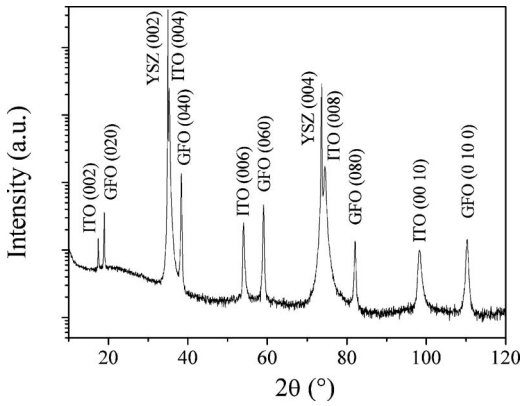

FIG. 1. XRD pattern of a GFO film grown at 900 °C under 100 Pa O_2:N_2, on an epitaxially ITO buffered YSZ (001) substrate.

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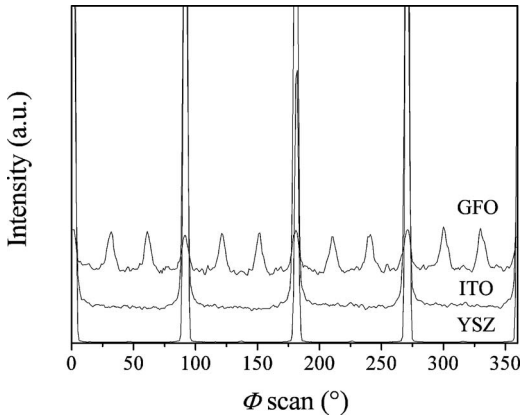

FIG. 2. φ scans of the GFO {062}, ITO {408}, and YSZ {204} planes showing a 30° periodicity for multivariant GFO and 90° periodicities for both cubic monovariant ITO and YSZ.

ties of the deposited GFO films were demonstrated through polarization–electric field (*P-E*) hysteresis loops measured by electrostatic force microscopy (EFM).

Films have been realized using a KrF excimer laser ($\lambda=248$ nm) with a 10 Hz repetition rate and a fluence of 1 J/cm^2. The ITO and $GaFeO_3$ targets were made from sintering the relevant powders at 1400 °C for 24 h [In_2O_3 doped with 10 wt. % SnO_2 (Aldrich) for ITO and a stoichiometric mixture of high purity Ga_2O_3 (99.99%, Fluka A.G.) and Fe_2O_3 (99%, Prolabo) for $GaFeO_3$]. A 60 nm thick ITO conducting layer was first deposited under 7×10^{-3} Pa O_2:N_2 at 600 °C on YSZ (001) substrate. A 180 nm thick $GaFeO_3$ layer was then deposited under a wide range of deposition substrate temperatures (600–900 °C) and reactive gas partial pressures (50–100 and 20–100 Pa for O_2 and O_2:N_2, respectively). After the deposition, the samples were cooled down to room temperature under the gas deposition pressure. The sample crystallographic structure was characterized by x-ray diffraction. θ-2θ scans were collected with a D500 Siemens diffractometer equipped with cobalt radiation ($K\alpha=0.178\,901$ nm). φ scans and reciprocal lattice mappings were made using a D8 Siemens diffractometer equipped with copper radiation ($K\alpha=0.154\,059$ nm). The magnetic properties were studied using a superconducting quantum interference device magnetometer (Quantum Design). The ferroelectric characterization of the samples was performed at room temperature with a commercial atomic force microscope (Nanofocus, Inc.), modified to a dynamic contact mode EFM, operating with a lock-in modulation frequency of 19 kHz and controlled through the WSXM software.[18] Details on the experimental setup and ideas of the dynamic contact mode were published earlier.[19,20] In our experiments, the cantilever is in heavily doped Si and has a spring constant of 0.5 N/m and a tip apex radius of 20 nm. Local polarization–electric field (*P-E*) hysteresis loop measurements were performed on single polarization domains with a dc voltage swept between +10 and −10 V.[21]

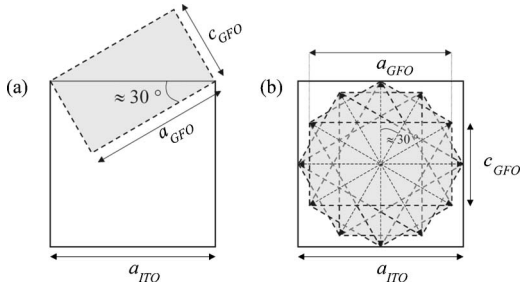

FIG. 3. (a) Illustration of the consequence of the $\sqrt{a_{GFO}^2+c_{GFO}^2}\approx a_{ITO}$ relationship. (b) The six resultant in-plane possible orientations of a GFO (0k0) cell (gray) on ITO (001).

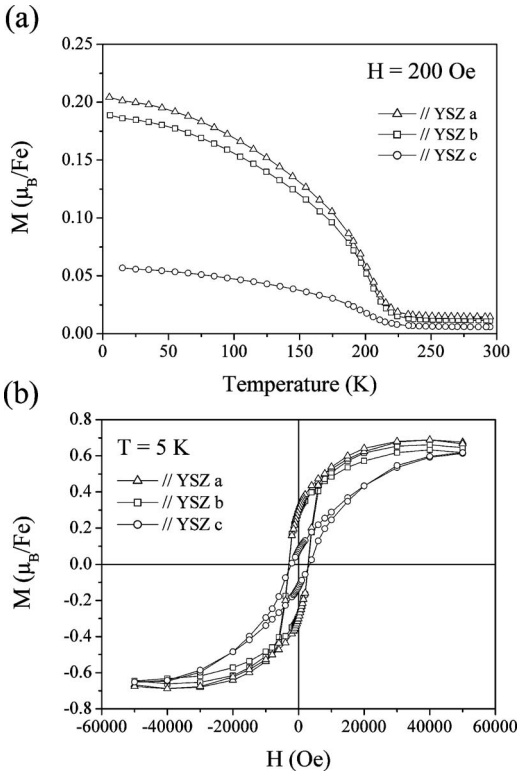

FIG. 4. Variation of the (a) magnetization with temperature under a 200 Oe applied field and (b) hysteresis loops at 5 K (b) along the three YSZ substrate crystallographic directions (*a* and *b* are in plane and *c* is out of plane).

The optimal deposition conditions for $GaFeO_3$, determined from direct deposition on YSZ substrates, appear to be at 900 °C under a 100 Pa partial pressure for both reactive gases O_2 and O_2:N_2. For lower reactive gas pressures and temperatures, we observed a parasitic phase corresponding to the cubic magnetite phase. The x-ray diffraction pattern of a GFO film deposited on an ITO buffered YSZ substrate at 900 °C under an O_2 pressure of 100 Pa is shown in Fig. 1. It clearly demonstrates pure *c*- and *b*-axis growths of ITO and GFO, respectively. φ scans of the GFO {062}, ITO {408}, and YSZ {204} planes were carried out (Fig. 2). They present the awaited 90° periodicity for both cubic ITO and YSZ peaks and a 30° periodicity for the GFO one. The ITO layer is perfectly epitaxially grown on YSZ with only one variant. The GFO crystallites, on the other hand, present six variants having in-plane orientations every 30° each. The very small mismatch (1.1%) between the two cubic YSZ and ITO lattice parameters ($a_{YSZ}=0.5139$ nm and $a_{ITO}=1.016$ nm$\approx 2a_{YSZ}$) explains the high crystalline quality and monovariance of the ITO films on YSZ. The different orientations of the GFO crystallites can be explained considering the different matching possibilities between the GFO and ITO lattices: $c_{GFO}=0.5086$ nm and $a_{ITO}=1.016$ nm$\approx 2c_{GFO}$ (0.2% mismatch), on the one hand, and $\sqrt{a_{GFO}^2+c_{GFO}^2}\approx a_{ITO}$ (0.4% mismatch), on the other hand. The angle between *a* and the diagonal of the ac plane of the GFO cell is $\alpha=\cos^{-1}(a_{GFO}/\sqrt{a_{GFO}^2+c_{GFO}^2})\approx 30°$ [Fig. 3(a)]. This allows

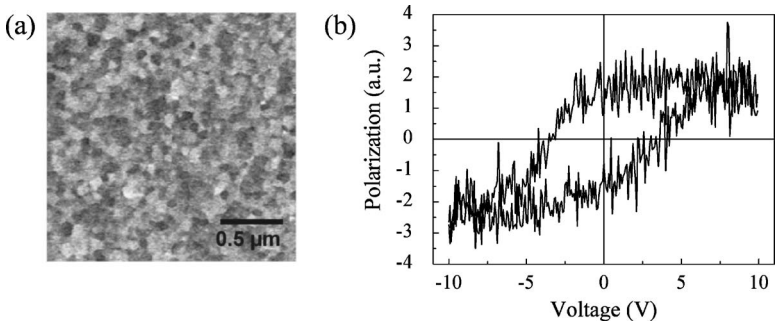

FIG. 5. (a) EFM surface charge image and (b) local *P-E* hysteresis loop measured for voltage sweeping between −10 and +10 V on one particular polarization domain.

the existence of the six variants shown in Fig. 3(b), located every 30°. Magnetization measurements were performed on 3×3 mm^2 samples of GFO/ITO/YSZ films, in two perpendicular in-plane and in the out-of-plane directions. The magnetization versus temperature measurements [Fig. 4(a)], performed in a 200 Oe applied magnetic field, reveal a Curie temperature of about 200 K. The hysteresis cycles (*M-H*) [Fig. 4(b)] were measured at 5 K and show a saturation magnetization of $\sim0.6\mu_B$ per Fe atom. Both magnetic measurements present a strong anisotropy with a hard magnetization direction along the GFO *b* axis (out of plane), but no in-plane anisotropy between the two chosen perpendicular directions. The in-plane coercive field reaches the relatively high value of about 2500 Oe at 5 K. Apart from the in-plane isotropic behavior, all the measured magnetic properties are similar to what are observed in bulk.[13] The absence of in-plane anisotropy is due to the existence of six crystallographic variants, separated by only 30°. Magnetic measurements are in complete agreement with the crystallographic characterization of the GFO layers. EFM imaging of the samples gives a rough polarization domain size of ~0.2 μm [Fig. 5(a)]. Figure 5(b) shows local *P-E* hysteresis measurements obtained by EFM on one particular polarization domain sweeping *E* from −10 to +10 V. Such a polarization loop is a positive evidence of the ferroelectric nature of the elaborated GFO films.

In conclusion, we have shown the possibility to obtain epitaxial thin films of the extremely promising multiferroic material $GaFeO_3$ on perfectly crystallographically matching ITO conducting electrodes. The magnetic properties of the GFO thin films are close to those of the bulk with a relatively high Curie temperature of ~200 K, a hard magnetization direction out of the plane, and a saturation magnetization of $0.6\mu_B$ per Fe atom. The ferroelectric nature of the elaborated GFO films was shown by EFM *P-E* loop measurements.

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