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Elaboration and optical properties of $GaFeO_3$ thin films

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Abstract

$GaFeO_3$ thin films were prepared on MgO(001), Al_2O_3(0001) and fused quartz substrates by the pulsed laser deposition technique. The lattice match mechanisms between $GaFeO_3$ thin films and substrates have been analyzed. Results of optical properties analysis show that the thin films have the different band gaps and optical properties. These differences can be ascribed to the different lattice strains induced by the different lattice mismatch and thermal expansion coefficients between the $GaFeO_3$ thin films and the substrates.

Keywords: $GaFeO_3$; Thin films; Optical properties; Pulsed-laser deposition

1. Introduction

Magnetoelectric multiferroics, which show spontaneous magnetic and electric ordering in the same phase, are intensively studied in the past few years, due to their potential application in future information technology [1–3]. $GaFeO_3$, a polar ferrimagnet, was firstly reported by Remeika [4], and has been intensively studied recently for its potential application as a magnetoelectric ferrimagnet [5–11]. However, the reports on the preparation and properties of $GaFeO_3$ thin films are sporadic. This is probably due to the large lattice mismatch between $GaFeO_3$ and currently used substrates. As we know, $GaFeO_3$ has an orthorhombic unit cell, whereas the substrates usually used in preparation of thin films, such as Si, $SrTiO_3$, MgO, Al_2O_3 etc., have the cubic or the hexagonal crystal structure. Recently, Kundaliya et al. [10] reported the magnetization and large second-harmonic Kerr rotation of the $GaFeO_3$ thin films prepared on Yttrium stabilized zirconia buffered (001) silicon substrates by the pulsed laser deposition method (PLD). The crystal growth and optical properties of the $GaFeO_3$ thin films have not been reported till now.

Usually, enormous strains can exist in thin films when one material is deposited on another, due to the difference in crystal lattice parameters and thermal expansion behavior between the film and the underlying substrates or the defects formed during films deposition. Moreover, the existed strain can take great effect on the properties of the thin films, such as ferroelectricity, magnetism, etc [12]. In this paper, we report on the preparation of $GaFeO_3$ thin films (GFO) on three kinds of substrates, that is fused quartz, MgO(001) and Al_2O_3(0001) (AlO), and study the effects of the strain induced during deposition of the thin films on the optical properties.

2. Experiments

The fabrication of $GaFeO_3$ ceramic target has been described in detail elsewhere [13]. The PLD technique was employed to prepare the oriented $GaFeO_3$ films on the MgO(001), Al_2O_3 (0001) and quartz substrates. During the deposition process, a XeCl excimer laser (308 nm, 17 ns full width at half maximum, 3 Hz repetition rate, ~1.5 J/cm^2) was focused on the $GaFeO_3$ ceramic target, 45 mm from the substrates. The deposition atmosphere was pure oxygen with gas pressure maintained at 10 Pa and the deposition temperature was about 700–750 °C. The crystalline and orientation of the thin films were evaluated by the X-ray diffraction (XRD) pattern in θ–2θ scan mode which were carried out on the Rigaku D/Max-2400 V diffractometer equipped

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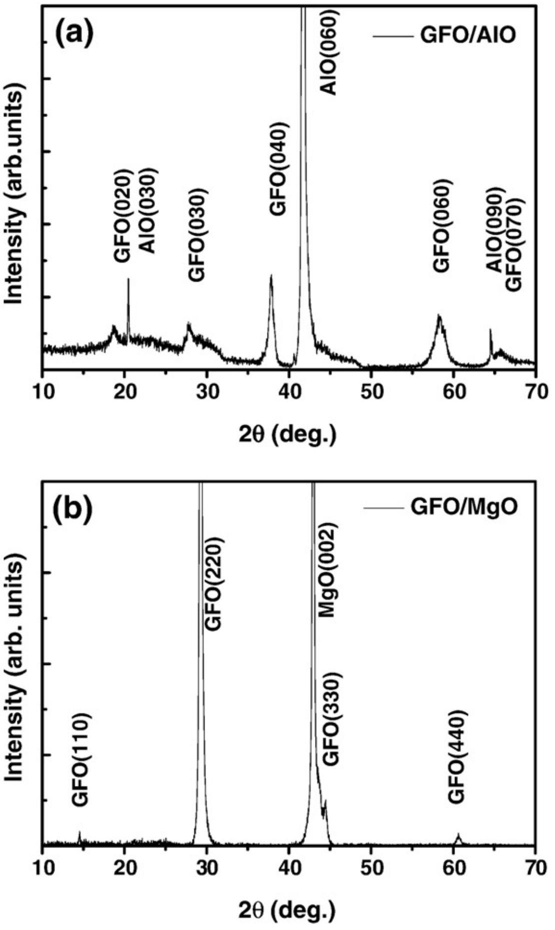

Fig. 1. X-ray diffraction patterns for $GaFeO_3$ thin films deposited on (a) Al_2O_3 and (b) MgO substrates.

with Cu Kα. The surface morphologies and roughness of the films were measured by atomic force microscopy (AFM) in contact mode. A randomly chosen area of 5×5 μm^2 on each film was surveyed. The layer thickness of the films was measured using surface profilometry (Dektak-8, Veeco Metrology Group, USA). The stoichiometry of the thin films was analyzed by the quantitative energy dispersive X-ray spectroscopy in a high resolution scanning electron microscopy (XL30S-FEG, FEI Company, American).The films quantitative compositional data were generated by a built-in software program (PGT-IMIX PTS), which uses In and Se single-crystal standards, did the background correction and gave the percentage of the elements. The main signals for the individual elements are derived from In Lα and Se Lα radiations. The measurements were carried out with accelerating potentials in the range 7–20 kV and an electron beam current between 1 and 2 nA The X-ray yield was collected for a fixed time interval of 100 s. An X-ray photoelectron spectroscopy (XPS) study of the films was carried out using a VG electronic spectrometer equipped with a twin anode (Mg and Al). Fe 2p core-level spectrum was collected using Al Kα as the X-ray source. The surfaces of all samples were cleaned by Ar^+ ion bombardment before they were measured, and all the spectra were referenced to the adventitious C1s peak at 285.0 eV. The optical absorption properties of the thin films were investigated at room temperature with a Spectrapro500i spectrophotometer (Acton research Corporation).

3. Results and discussion

Fig. 1(a) and (b) shows the XRD patterns for the thin films grown on the MgO(001), Al_2O_3(0001) substrates. As revealed from the XRD patterns, (ll0) oriented peaks are observed for the films on the MgO(001) substrate, while (0l0) oriented peaks on Al_2O_3(0001). The film deposited on quartz substrate displays (0l0) orientation but with poor crystalline (not shown here). According to Wood et al., [14] the single crystal of gallium iron oxide always took on two types, needles shown in {110} faces and pseudohexagonal plates shown in {010} faces. Thus can interpret the different orientation of $GaFeO_3$ thin films deposited on different substrates.

Fig. 2 shows the AFM images of the $GaFeO_3$ thin films. The surface RMS roughness is 0.542 nm and 1.886 nm, for the films on MgO and Al_2O_3 substrates respectively. In order to verify the stoichiometry of the prepared $GaFeO_3$ thin films, the quantitative energy dispersive X-ray spectroscopy is used and the Ga: Fe ratios are found to be approximately 1:1. Besides, the Fe oxidation state is investigated using the X-ray photoelectron spectroscopy. All samples behave similarly; a representative scan of the Fe 2p line is shown in Fig. 3. The position of this line is expected to be 711 eV for Fe^{3+} and 709.5 eV for Fe^{2+}. From Fig. 3, we infer that the oxidation state of Fe in our $GaFeO_3$ thin films is Fe^{3+}.

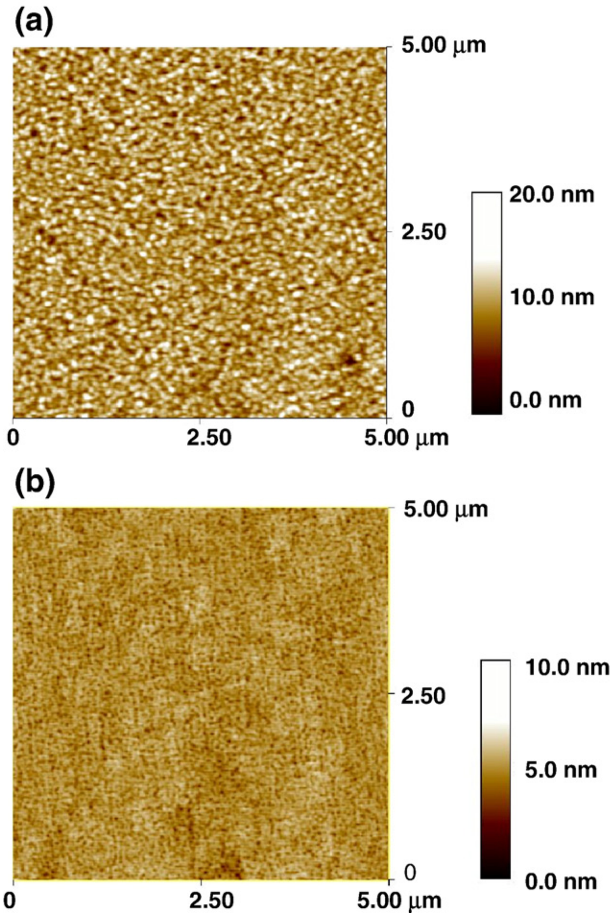

Fig. 2. AFM images of the $GaFeO_3$ thin films on (a) Al_2O_3 and (b) MgO substrates.

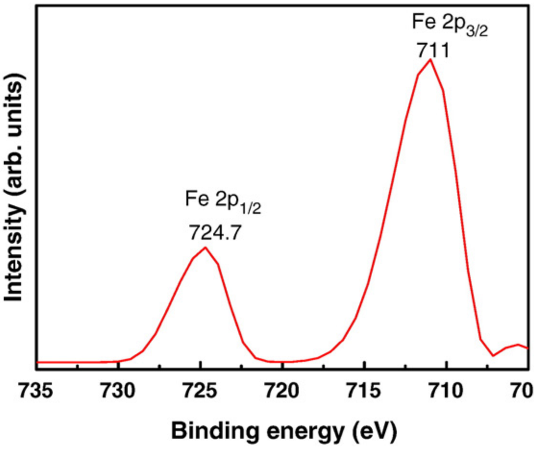

Fig. 3. X-ray photoelectron spectrum of Fe 2p lines for GFO/MgO.

Considering the in-plane lattice parameter of MgO(001) and Al_2O_3(0001), the lattice mismatch f_m between $GaFeO_3$ and MgO(001) and Al_2O_3(0001) substrates can be calculated using the relation

$$f_m = [(a_l - a_s)/a_s] \times 100\%, \tag{1}$$

where a_l is the epilayer and a_s is the substrate lattice constant.

Firstly, for the (110) oriented thin films grown on MgO(001) substrate, although the crystal structure and the lattice constant of MgO are different from that of $GaFeO_3$, the atomic arrangement of the (110) plane of $GaFeO_3$ is similar to the Mg(001), just as shown in Fig. 4. In the structural model, $GaFeO_3$(110) and MgO(001) are parallel, and $GaFeO_3$[001] is parallel to MgO[110] and $GaFeO_3$[$1\bar{1}0$] is parallel to MgO[$1\bar{1}0$]. Thus, according to Eq. (1), the f_m along [110] and [$1\bar{1}0$] of MgO are about 7.8% and −14.7% respectively.

Secondly, for the (010) oriented $GaFeO_3$ thin films on the Al_2O_3(0001) plane, it is worth noting that $GaFeO_3$ might crystallize in the pseudohexagonal structure with lattice constants $a' = \sqrt{a^2 + c^2} = 10.11575$ Å and $c' = b = 9.394$ Å, [14] although the $GaFeO_3$ has a orthorhombic structure with lattice constant of $a = 8.747$ Å, $b = 9.394$ Å and $c = 5.082$ Å.[13] Then, the lattice mismatch f_m of $GaFeO_3/Al_2O_3$ (GFO/AlO) can be calculated using the Eq. (1) to be about 6.3%.

According to the analysis above, the large lattice mismatches are induced when the $GaFeO_3$ thin films were deposited on the MgO(001) and Al_2O_3(0001) substrates. Along with the difference of thermal expansion coefficients between GFO and substrates (shown in Table 1), the lattice strains can be induced accordingly. As follows, we investigate the out-plane lattice

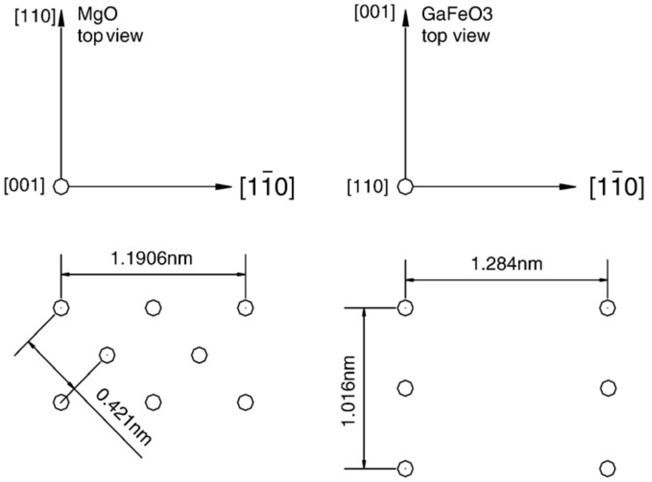

Fig. 4. Scheme depicting the top view of the arrangement of the atoms in the $GaFeO_3$ thin film and MgO substrate.

Table 1
Parameters of the strain and the absorption of the $GaFeO_3$ thin films

Sample	Strain	Thermal expansion coefficient of substrate	E_g (eV)	a1 (eV)	a2 (eV)	a3 (eV)
GFO/MgO	−4.8%	12.8×10^{-6} / K	2.92	1.5	2.13	2.6
GFO/AlO	1.3%	7.5×10^{-6} / K	3.0	1.5	1.8	2.46
GFO/Quartz	0	0.54×10^{-6} / K	2.76	1.5	2.18	

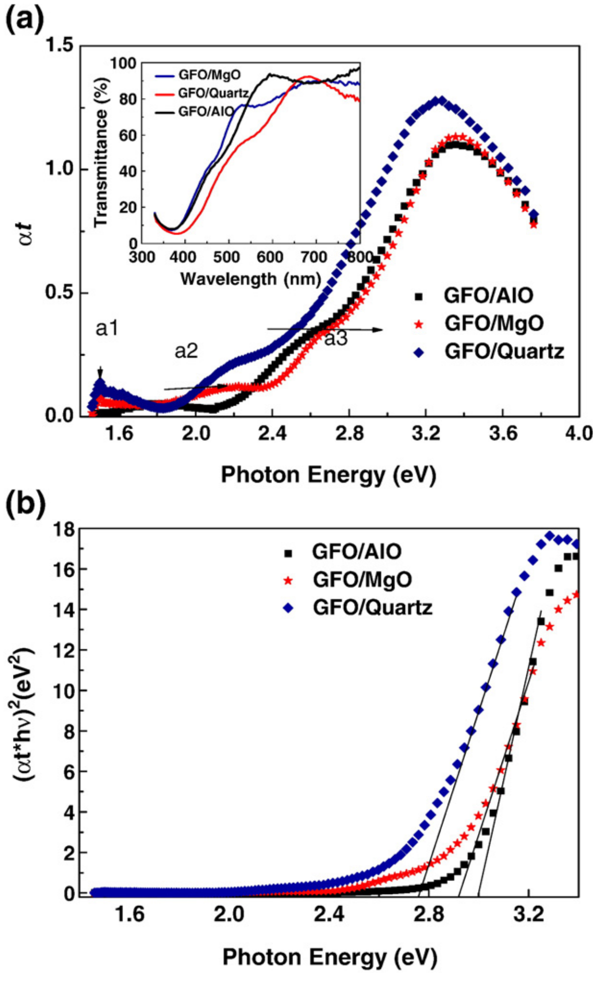

Fig. 5. (a) Absorption spectra, $\alpha(h\nu)t$, and (b) squares of the $\alpha(h\nu)t$ of $GaFeO_3$ thin films deposited on Al_2O_3, MgO and fused quartz. Inset of (a) shows the transmittance spectra of $GaFeO_3$ thin films.

strains of the thin films in accordance with the result of XRD. According to the equation

$$\varepsilon = (d - d_0)/d_0, \tag{2}$$

where d is the lattice spacing calculated from the measured 2θ value of the XRD peaks (Fig. 1) through Bragg equation

$$\lambda = 2d\sin\theta\left(\lambda = 1.5406\,\text{Å}\right), \tag{3}$$

and d_0 is the ideal lattice spacing for the $GaFeO_3$ target [10]. The strain ε existed in the films on MgO and Al_2O_3 is calculated to be about −4.8% and 1.3% respectively, which have been listed in Table 1. The opposite signs indicate the two types of lattice deformation kinetics in the heterointerfaces: the compressive strain is active for the GFO/MgO, while the tensile strain is for GFO/AlO. This result is in accordance with our analysis above about the stress induced in-plane. The lattice strain for the films on amorphous quartz is calculated to be −0.16%.

In order to study the effect of strain on the energy band gap and absorption peaks, we performed optical absorption spectrum studies. Due to the thickness (t) of the thin films on these three substrates are about 200–300 nm, we show $\alpha(hv)t$ rather than absorption coefficient $\alpha(hv)$ (hv is the energy of incident light). Fig. 5(a) presents the optical absorption spectra $\alpha(hv)t$ of the thin films on these three substrates, and the inset shows the optical transmittance spectra. As revealed from Fig. 5(a) and its inset, the films especially for GFO/MgO and GFO/AlO are transparent with the transmittance high than 80% in most of the visible spectrum, and the corresponding absorption edges related with the band gap (E_g) for the thin films shows an apparent redshift. According to the equation $(\alpha * hv)^2 = A(hv - E_g)$, [15,16] the band gaps for GFO/MgO, GFO/AlO and GFO/quartz are obtained to be 2.92 eV, 3.0 eV and 2.76 eV respectively (Fig. 5b). Moreover, in the energy range of 1.4 eV–2.9 eV (shown in Fig. 5a), three characteristic absorption peaks, which are labeled as a1, a2 and a3, are observed. Table 1 gives the energy values corresponding to the absorption peaks a1, a2 and a3. The a1 and a2 peaks are typical for the trivalent iron oxides and can be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$ [11,17]. These two peaks come from the crystal field splitting of FeO_6 octahedron with O_h symmetry as the first approximation. The peak a3 is assigned to the ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^4E_g$ [17]. The reason why the film GFO/Quartz doesn't show the a3 peak can be attributed to the broad transition feature as well as to the contribution from high strong absorption peaks (shown in Fig. 5a).

As shown in Table 1, the thin films deposited on the different substrates show the different energy band gap and absorption peaks, which can be ascribed to the different strain induced in the films we discussed above. Generally, for $GaFeO_3$, the symmetry of FeO_6 octahedra is far from O_h and each Fe ion shifts along the b axis [18]. Due to that the different strain induces the different lattice deformation, the displacement of Fe ions shifting along the b axis changes, thus consequentially affect the crystal fields splitting of FeO_6 octahedron. Therefore, the E_g and absorption peaks change accordingly.

4. Conclusion

In summary, we have prepared the oriented $GaFeO_3$ thin films on three different substrates MgO(001), Al_2O_3(0001) and fused quartz. The corresponding lattice match mechanisms on different structural substrates have been analyzed. In the absorption spectra, these three samples have the different absorption edges and absorption peaks, which can be attributed to the different strain induced in the films.

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