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## Epitaxial growth and magnetic properties of ultraviolet transparent $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$ multilayer thin films

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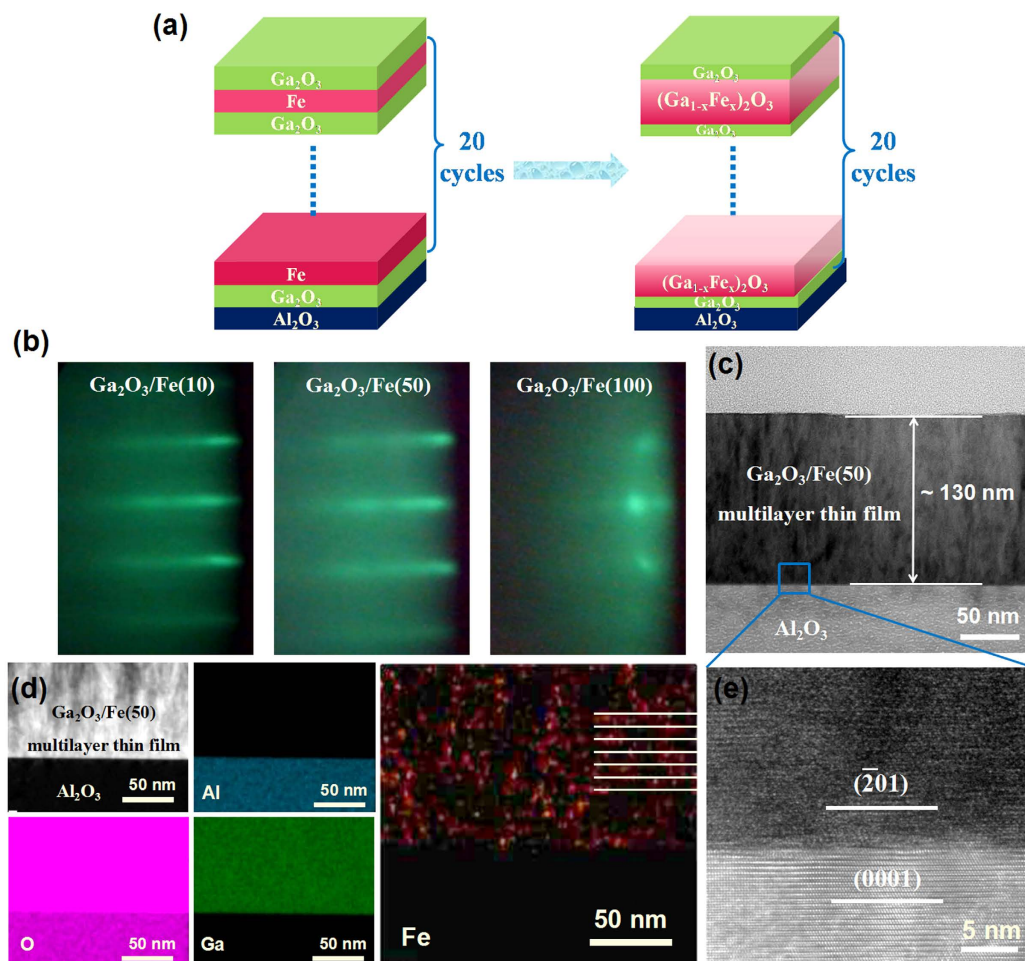
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Multilayer thin films based on the ferromagnetic and ultraviolet transparent semiconductors may be interesting because their magnetic/electronic/photonics properties can be manipulated by the high energy photons. Herein, the  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer epitaxial thin films were obtained by alternating depositing of wide band gap  $\text{Ga}_2\text{O}_3$  layer and Fe ultrathin layer due to inter diffusion between two layers at high temperature using the laser molecular beam epitaxy technique. The multilayer films exhibits a preferred growth orientation of  $(\bar{2}01)$  crystal plane, and the crystal lattice expands as Fe replaces Ga site. Fe ions with a mixed valence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are stratified distributed in the film and exhibit obvious agglomerated areas. The multilayer films only show a sharp absorption edge at about 250 nm, indicating a high transparency for ultraviolet light. What's more, the  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer epitaxial thin films also exhibits room temperature ferromagnetism deriving from the Fe doping  $\text{Ga}_2\text{O}_3$ .

During the past ten years, multilayer thin films based on magnetic and nonmagnetic layers have great deal of scientific and industrial attention due to their anomalous spin dependent effects and potential applications in magnetic sensors, information storage media, thermoelectric devices and high frequency devices<sup>1-3</sup>. Particularly, the ferromagnetic and transparent semiconductors multilayer thin films are interesting because where the ferromagnetic properties can be controlled by light<sup>4-6</sup>. It integrates magnetism into optoelectronics devices, appealing materials for magneto-optical devices<sup>7,8</sup>. So far, there have been a few reports on transparent ferromagnetic multilayer thin films. For example,  $\text{ZnO}/\text{Fe}_3\text{O}_4$  and  $\text{In}_2\text{O}_3/\text{Fe}_3\text{O}_4$  multilayer structure films were fabricated and their optoelectrical and magnetic properties were studied<sup>9-11</sup>. As a typical wide band gap semiconductor material,  $\beta\text{-Ga}_2\text{O}_3$ , with a band gap of 4.5~5.3 eV and a high transparency for the visible and wide range of ultraviolet down to 280 nm<sup>12-14</sup>, is considered as one of ideal candidates to fabricate transparent multilayer magnetic-optic-electronic devices<sup>15,16</sup>.  $\text{Ga}_2\text{O}_3$  can crystallize in five different phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$ )<sup>17,18</sup>. Amongst them, the monoclinic  $\beta\text{-Ga}_2\text{O}_3$  (space group: C2/m) with the lattice parameters of  $a = 12.23 \text{ \AA}$ ,  $b = 3.04 \text{ \AA}$ ,  $c = 5.80 \text{ \AA}$ , and  $\beta = 103.7^\circ$  is considered to be the most stable thermally in the range from room temperature up to the melting point of about 1800 °C what determines also the possibility of working at high temperatures<sup>19</sup>. Additionally,  $\beta\text{-Ga}_2\text{O}_3$  has great chemical stability, being unaffected even by concentrated acids such as hydrofluoric acid<sup>20</sup>. More importantly,  $\beta\text{-Ga}_2\text{O}_3$  is known to exhibit a strong dynamic nuclear polarization upon saturation of the magnetic resonance of conduction electrons, which is at the origin of a free electron memory referred to as bistable conduction electron spin resonance<sup>21-22</sup>. On the other hand,  $\beta\text{-Ga}_2\text{O}_3$  is also the host material for magnetic semiconductors, and room temperature ferromagnetism was observed in Mn-doped  $\beta\text{-Ga}_2\text{O}_3$  by our group<sup>15</sup>.

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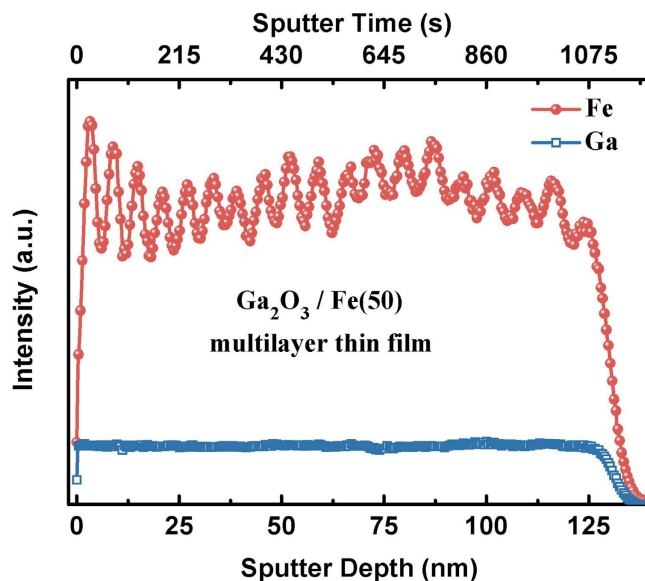


**Figure 1.** (a) Schematic diagram of alternating deposition of  $\text{Ga}_2\text{O}_3$  and Fe ultrathin layers for fabricating the  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer thin films; (b) RHEED patterns of the  $\text{Ga}_2\text{O}_3/\text{Fe}(10)$ ,  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  and  $\text{Ga}_2\text{O}_3/\text{Fe}(100)$  multilayer thin films; (c) Cross-sectional low-magnification TEM bright-field image of the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer thin film; (d) TEM-EDX measurement of cross-sectional observation image of the interface between  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer thin film and  $\text{Al}_2\text{O}_3$  substrate, and the composition distributions of Al, O, Ga and Fe elements drawn by different colors; (e) Cross-sectional high-resolution TEM image of the interface between the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer film and  $\text{Al}_2\text{O}_3$  substrate as marked by a blue small pane in (c).

The  $\beta\text{-Ga}_2\text{O}_3$  and  $\beta\text{-Ga}_2\text{O}_3$  based magnetic semiconductors multilayer thin films with a high ultraviolet transparency may exhibit some special magnetic/electronic/photonic properties through the manipulation of high energy photons. Generally, epitaxial growth is very essential for the properties of these multilayer thin films. Recent improvements in deposition technology enable an alternative approach in the manipulation of ultrathin layer for growing multilayer thin films. Herein, we fabricated the  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer epitaxial thin films and investigated their structural, optical, and magnetic properties.

## Results and Discussion

The  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer thin films were fabricated by alternating depositing of  $\text{Ga}_2\text{O}_3$  layer and Fe ultrathin layer due to inter diffusion between two layers at high temperature using the laser molecular beam epitaxy (LMBE) technique, as is shown in Fig. 1(a). The thickness and composition of  $(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  thin layer can be controlled by solely changing the laser pulse numbers during each run for depositing the Fe layer (defined as N, N = 0, 10, 20, 30, 40, 50, 100) while those for depositing  $\text{Ga}_2\text{O}_3$  layers in each run were fixed at 100. Herein, samples were abbreviated as  $\text{Ga}_2\text{O}_3/\text{Fe}(N)$  multilayer thin films for the laser pulse numbers N of depositing Fe layer. The sharp and streaky reflection high-energy electron diffraction (RHEED) patterns indicate the achievement of an atomically flat surface of  $\text{Ga}_2\text{O}_3/\text{Fe}(10)$  and  $\text{Ga}_2\text{O}_3/\text{Fe}(40)$  multilayer thin films [Fig. 1(b)]. While the RHEED patterns of  $\text{Ga}_2\text{O}_3/\text{Fe}(100)$  film are fuzzy and punctiform, meaning a rough surface. Cross-section low-magnification transmission electron microscope (TEM) investigations were carried out to identify the microstructure of the thin film. The  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer thin film shows a thickness of about 130 nm estimated by the cross-sectional TEM bright-field image of Fig. 1(c). The average thickness of the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  single thin layer is about 6.5 nm due to the layer number of 20. Figure 1(e) shows the cross-sectional high-resolution



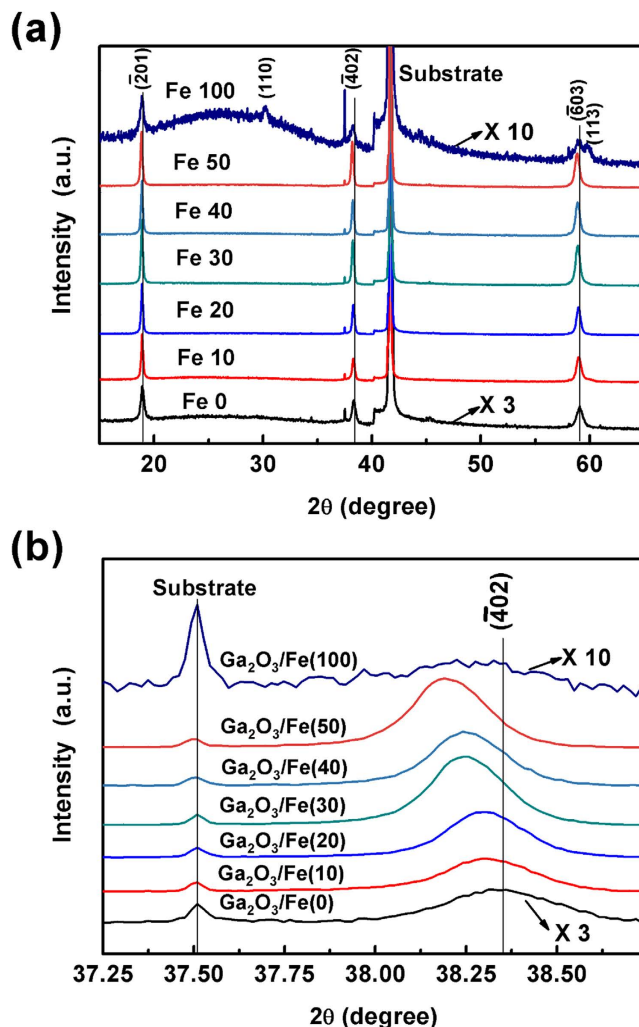
**Figure 2.** Fe and Ga SIMS depth profiles for the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer thin film.

TEM image of the interface between the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer film and  $\text{Al}_2\text{O}_3$  substrate as marked by a blue small pane in Fig. 1(c), which clearly indicates the orientation relationship of  $(\bar{2}01)$   $\beta$ - $\text{Ga}_2\text{O}_3//(\text{0001})$   $\text{Al}_2\text{O}_3$ . However, it does not found obvious multilayer structure, which can be attributed to the following two factors: (1) The radii of Fe and Ga cations are close ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ga}^{3+}$  ionic are 0.74, 0.64, and 0.62 Å, respectively<sup>23–25</sup>), and the lattice parameters of  $\text{Ga}_2\text{O}_3$  change rarely with the Fe doping; (2) The Fe doping concentration of the  $\text{Ga}_2\text{O}_3/\text{Fe}(N)$  multilayer thin film is low (it is 2.44 at.% for  $N = 50$ ). To investigate the composition distributions in the  $\text{Ga}_2\text{O}_3/\text{Fe}$  multilayer thin films, the elemental composition mapping of cross-sectional observation was obtained by the energy dispersive X-ray (EDX) measurement in TEM. The elements of Ga, Fe, Al, and O which compose  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  and  $\text{Al}_2\text{O}_3$  were chose as the target elements, as is shown in Fig. 1(d). From the analysis results, Ga and O elements are distributed uniformly and there are no remarkable phase separating area in the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  film. However, Fe element exhibits clear agglomerated areas and obvious stratified phenomenon. Al metal is derived from the  $\text{Al}_2\text{O}_3$  substrate and O is from thin film and substrate.

In order to further confirm the multilayer structure of the as-grown thin films, the compositions as a function of film thickness were characterized by using the secondary ion mass spectrometry (SIMS) depth profiling. The results for the representative  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  film were given in Fig. 2 by showing intensities of the Fe and Ga ion currents as a function of sputter depth of the film. The intensity of Ga ion remains almost constant as the sputter depth of the film. However, the intensity of Fe ion exhibits evident wavy shape with 19 peaks, corresponding to the 19 layers of  $(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  thin film in our scheming  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer structure. Notably, the difference value between peaks and troughs of few layers near-surface is larger than that near-substrate, which is attributed to the inter diffusion between Fe ultrathin layer and  $\text{Ga}_2\text{O}_3$  layer at high temperature for much more time. As a result, both the TEM-EDX and SIMS results indicate that Fe ion is uneven and stratified distributed in the film.

The crystal structure and film orientation of the  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer thin films were determined from  $\theta$ - $2\theta$  scans of XRD, as is shown in Fig. 3(a). In order to facilitate compared with the others, the diffraction intensities of the  $\text{Ga}_2\text{O}_3/\text{Fe}(0)$  and  $\text{Ga}_2\text{O}_3/\text{Fe}(100)$  films were multiplied by 3 and 10 times respectively. Except  $\text{Ga}_2\text{O}_3/\text{Fe}(100)$  film, only  $(\bar{2}01)$  and higher order peaks of  $\text{Ga}_2\text{O}_3$  monoclinic  $\beta$  phase appear for the other as-grown  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer films besides those from the substrate, indicating single phase and a preferred  $(\bar{2}01)$  plane orientation of the films. Furthermore, as shown in Fig. 3(b) with the enlarged view of  $\theta$ - $2\theta$  XRD patterns around  $38^\circ$ , the peaks of  $(\bar{4}02)$  are located at  $38.36^\circ$ ,  $38.31^\circ$ ,  $38.29^\circ$ ,  $38.26^\circ$ ,  $38.24^\circ$ , and  $38.19^\circ$  for  $N = 0, 10, 20, 30, 40,$  and  $50$ , respectively, indicating that the peak gradually shifts to smaller  $2\theta$  with the increase of Fe layer thickness. The lower angles shift of  $(\bar{2}01)$  and higher order diffraction peaks indicates an increase of the lattice constants, which means that Fe ion has incorporated into Ga ion site and possesses a larger radius than Ga ion<sup>23–25</sup>. However, for the  $\text{Ga}_2\text{O}_3/\text{Fe}(100)$  film, extra diffraction peaks of  $(110)$  and  $(113)$  of  $\beta$  phase  $\text{Ga}_2\text{O}_3$  appear and the diffraction intensity of the family of  $(\bar{2}01)$  crystal planes decreases, featuring a polycrystalline nature. No impurity peaks related to Fe metal clusters and Fe oxides were observed.

The chemical compositions and chemical states of Fe ions in the as-grown films were characterized by using X-ray photoelectron spectroscopy (XPS), presented in Fig. 4. The elements present in the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer film are Fe, Ga, O, and C (not shown). The reason of C found in the samples was asserted to be due to surface contamination. The charge-shift spectrum was calibrated using the fortuitous C 1s peak at 284.8 eV. The energy peak for Ga 3d is centered at 20.4 eV [Fig. 4(a)], which is attributable to the presence of Ga-O bond<sup>26</sup>. The high-resolution XPS spectrum of Fe 2p core level shows a spin-orbit doublet ( $j = 3/2, 1/2$ ) [Fig. 4(b)]. Of the two peaks Fe  $2p_{3/2}$  peak is narrower and stronger than Fe  $2p_{1/2}$  and the area of Fe  $2p_{3/2}$  peak is greater than that

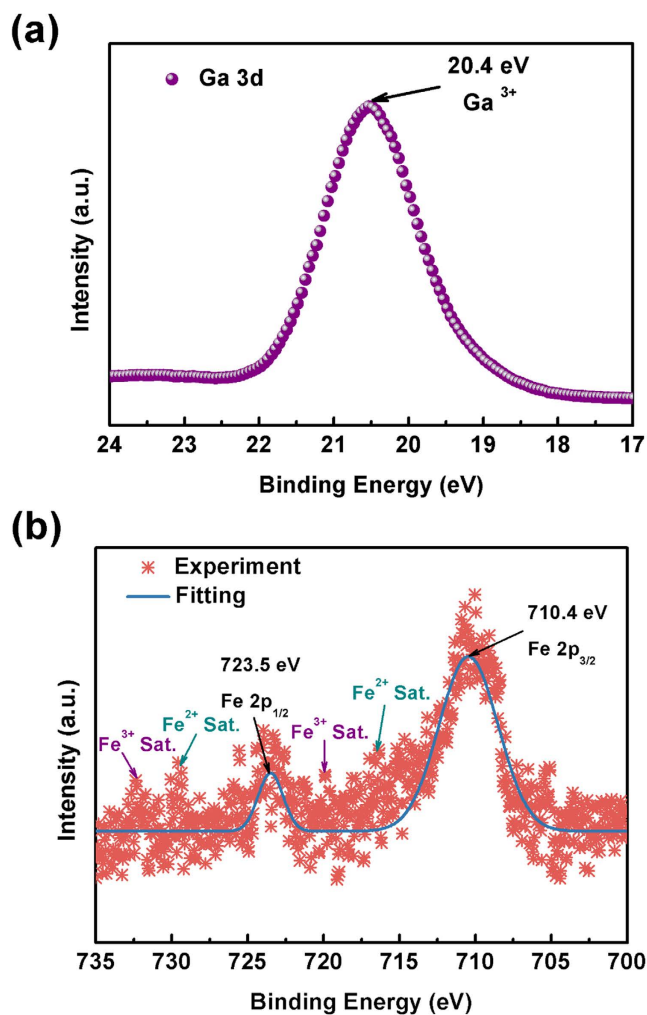


**Figure 3.** (a)  $\theta$ – $2\theta$  XRD patterns of the  $\text{Ga}_2\text{O}_3/\text{Fe}(N)$  multilayer thin film; (b) Enlarged view of  $\theta$ – $2\theta$  XRD patterns around  $38^\circ$ .

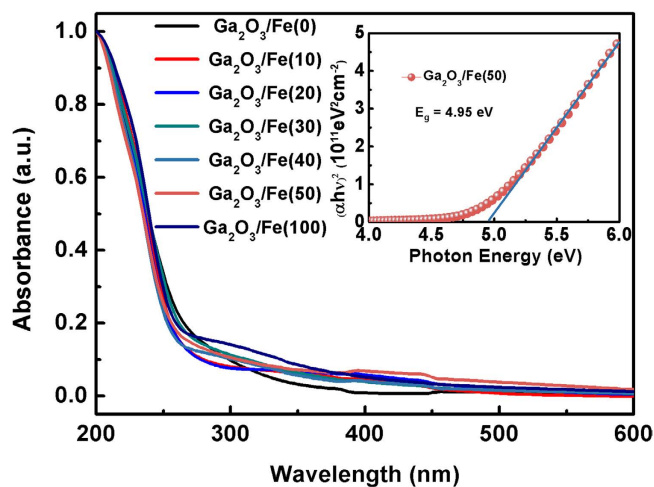
of  $\text{Fe } 2p_{1/2}$  because  $\text{Fe } 2p_{3/2}$  has degeneracy of four states whilst  $\text{Fe } 2p_{1/2}$  has only two. For  $\text{Fe}^{2+}$  cations, the peak position of  $\text{Fe } 2p_{3/2}$  and  $\text{Fe } 2p_{1/2}$  is located at about 709.0 and 722.6 eV, and the satellite peak of  $\text{Fe } 2p_{3/2}$  is located approximately 6 eV higher than the main  $\text{Fe } 2p_{3/2}$  peak; While for  $\text{Fe}^{3+}$  cations, the peak position of  $\text{Fe } 2p_{3/2}$  and  $\text{Fe } 2p_{1/2}$  is located at about 711.0 and 724.6 eV, and the satellite peak of  $\text{Fe } 2p_{3/2}$  is located approximately 8 eV higher than the main  $\text{Fe } 2p_{3/2}$  peak<sup>27,28</sup>. In our  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer thin films, the peak positions of  $\text{Fe } 2p_{3/2}$  and  $\text{Fe } 2p_{1/2}$  are, respectively, 710.4 and 723.5 eV. They are located between the values for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations, which can be deconvoluted into the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  peaks, indicating that both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations are contained. In addition, the satellite peaks at the high binding energy side of the main peaks are further demonstrated the coexistence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .

Figure 5 shows the ultraviolet-visible (UV-Vis) absorbance of the  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer thin films. All the samples exhibit a sharp absorption edge at about 250 nm, corresponding to the intrinsic absorption of  $\beta\text{-Ga}_2\text{O}_3$ <sup>13,14</sup>. The absorption onset shows no obvious shift with the increase of Fe ultrathin layer thickness. The band gap is derived by fitting the linear region of the plot  $(\alpha h\nu)^2$  versus  $h\nu$ . The inset of Fig. 5 shows the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer film has a band gap of about 4.95 eV. On the other hand, it is observed that all the  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer films has no obvious absorbance to the wavelength until 250 nm, indicating a high transparency for ultraviolet light.

Figure 6 shows the magnetization versus magnetic field ( $M$ - $H$ ) curves of the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer thin film at room temperature with that of pure  $\beta\text{-Ga}_2\text{O}_3$  thin film for comparing. The diamagnetic contribution from the  $\alpha\text{-Al}_2\text{O}_3$  substrate was subtracted from the data. The pure  $\beta\text{-Ga}_2\text{O}_3$  thin film [ $\text{Ga}_2\text{O}_3/\text{Fe}(0)$ ] displays paramagnetic behavior while  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  film show hysteresis loops indicative of ferromagnetism when the applied magnetic field is parallel to the films. Furthermore, the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer thin film exhibits a magnetic anisotropy while applying the magnetic field parallel and perpendicular to the film surface. As seen in the enlarged image of  $M$ - $H$  loops in the inset of Fig. 6, the coercivity and magnetic remanence ( $M_r$ ) are  $\sim 73$  Oe and  $4.99 \text{ emu/cm}^3$  for the magnetic field paralleling to the film, while they are  $\sim 91$  Oe and  $3.68 \text{ emu/cm}^3$  respectively for the perpendicular

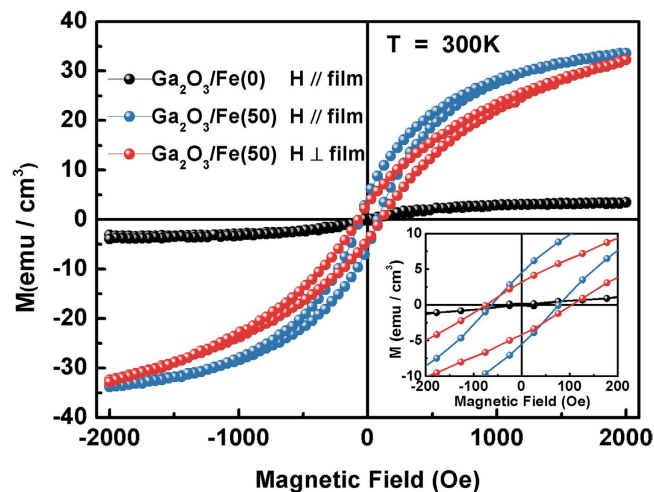


**Figure 4.** XPS spectra of Ga 3d (a) and Mn 2p (b) core level for the Ga<sub>2</sub>O<sub>3</sub>/Fe(50) multilayer thin film.



**Figure 5.** Absorption spectra of the Ga<sub>2</sub>O<sub>3</sub>/Fe(N) multilayer thin films and the plot of  $(\alpha h\nu)^2$  versus  $h\nu$  for the Ga<sub>2</sub>O<sub>3</sub>/Fe(50) film (inset).

one. And the saturation magnetization ( $M_s$ ) of the Ga<sub>2</sub>O<sub>3</sub>/Fe(50) multilayer is similar for parallel and perpendicular which are 33.8 and 32.8 emu/cm<sup>3</sup> respectively at 2 T. The magnetic anisotropy in Ga<sub>2</sub>O<sub>3</sub> with doping other transition metal (such as Mn, Cr) has also been reported<sup>15,16</sup>. Origin of the anisotropic magnetization is not clear



**Figure 6.** Magnetic field dependence of magnetization ( $M$ - $H$  curve) and the corresponding enlarged image (inset) of the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer thin film as the magnetic field is parallel and perpendicular to the film compared with that of pure  $\beta\text{-Ga}_2\text{O}_3$  thin film.

at the moment. The anisotropic behavior cannot be explained by the presence of randomly oriented ferromagnetic particles. In addition, the XRD and XPS measurements have confirmed the successful substitution of Fe for Ga and ruled out the possible secondary phases of Fe metal cluster and Fe-based oxides. It is reasonably to conclude that the room temperature ferromagnetism in the  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer films is intrinsic. The perpendicular & parallel magnetic moments of Fe cation in the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer thin film at 2 T are 3.74 and 3.89  $\mu_B/\text{Fe}$  cation respectively, which are very close to the magnetic moment of Fe cation reported by others<sup>29,30</sup>.

In conclusion, the multilayer epitaxial thin films based on wide band gap of  $\text{Ga}_2\text{O}_3$  and magnetic semiconductor of  $(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  were fabricated by alternating depositing of  $\text{Ga}_2\text{O}_3$  layer and Fe ultrathin layer by LMBE. The systematic characterizations by XRD, TEM-EDX, SIMS, XPS and UV-Vis absorbance spectrum confirmed the incorporation of Fe into the lattice of  $\beta\text{-Ga}_2\text{O}_3$  and the formation of the  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer epitaxial thin films. Optical and magnetic properties measurements revealed that the multilayer films are high ultraviolet transparency and room temperature ferromagnetism.

## Methods

The epitaxial thin films were prepared on  $10 \times 10$  mm  $\alpha\text{-Al}_2\text{O}_3$  (0001) substrates by the LMBE technique at a repetition frequency of 1 Hz and with a fluence of  $\sim 5$  J/cm<sup>2</sup>. The thin film deposition was grown in a vacuum environment of  $1 \times 10^{-6}$  Pa and at a substrate temperature of 900 °C. Alternating depositions of  $\text{Ga}_2\text{O}_3$  layer and Fe ultrathin layer were performed for 20 times to prepare the  $\text{Ga}_2\text{O}_3/(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  multilayer epitaxial thin films. The  $(\text{Ga}_{1-x}\text{Fe}_x)_2\text{O}_3$  layer (that is Fe doping  $\text{Ga}_2\text{O}_3$  layer) was obtained due to inter diffusion between Fe and  $\text{Ga}_2\text{O}_3$  layers at high temperature. The Fe doping concentration of the  $\text{Ga}_2\text{O}_3/\text{Fe}(50)$  multilayer thin film was determined as 2.44 at.% by the X-ray energy dispersive spectroscopy. The targets were kept inside the chamber, so that deposition of all the layers could be done without breaking vacuum. This is essential to avoid any contaminations of interfaces. RHEED was utilized *in-situ* to monitor the whole epitaxial growth process. The orientation and crystallinity of the as-grown thin films were investigated by the XRD at  $\theta$ -2 $\theta$  scan. The thickness and microstructure of thin films were obtained by the TEM. Cross-section TEM specimens were prepared by a standard procedure which includes mechanical grinding, polishing, precision dimpling, and ion milling. The valences of Mn ions and elements distribution were analyzed by XPS and SIMS. Magnetic properties of the films were measured in a commercial superconducting quantum interference device (SQUID), Quantum design.

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## Author Contributions

W.T., P.L. and Z.W. designed this project. D.G. performed the thin film growths, the measurements, analysed the results, and wrote the original manuscript. L.L. and M.L. modified the manuscript. W.C. and X.Z. performed the XRD and EDS measurements respectively. Y.A. and Y.Z. performed the XPS measurements. All authors discussed the results and worked on the manuscript.

## Additional Information

**Competing financial interests:** The authors declare no competing financial interests.

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