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

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Multilayer thin films based on the ferromagnetic and ultraviolet transparent semiconductors may be interesting because their magnetic/electronic/photonic properties can be manipulated by the high energy photons. Herein, the Ga$_2$O$_3/(\text{Ga}_{1-x}\text{Fe}_x)_2$O$_3$ multilayer epitaxial thin films were obtained by alternating depositing of wide band gap Ga$_2$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 exhibit a preferred growth orientation of (201) crystal plane, and the crystal lattice expands as Fe replaces Ga site. Fe ions with a mixed valence of Fe$^{2+}$ and 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 Ga$_2$O$_3/(\text{Ga}_{1-x}\text{Fe}_x)_2$O$_3$ multilayer epitaxial thin films also exhibit room temperature ferromagnetism deriving from the Fe doping Ga$_2$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$^{1-3}$. Particularly, the ferromagnetic and transparent semiconductors multilayer thin films are interesting because where the ferromagnetic properties can be controlled by light$^{4-6}$. It integrates magnetism into optoelectronics devices, appealing materials for magnetooptical devices$^{7,8}$. So far, there have been a few reports on transparent ferromagnetic multilayer thin films. For example, ZnO/Fe$_3$O$_4$ and In$_2$O$_3$/Fe$_3$O$_4$ multilayer structure films were fabricated and their optoelectrical and magnetic properties were studied$^{9-11}$. As a typical wide band gap semiconductor material, \(\beta\)-Ga$_2$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$^{12-14}$, is considered as one of ideal candidates to fabricate transparent multilayer magnetic-optic-electronic devices$^{15,16}$. Ga$_2$O$_3$ can crystallize in five different phases (\(\alpha\), \(\beta\), \(\gamma\), \(\delta\), and \(\varepsilon\))$^{17,18}$. Amongst them, the monoclinic \(\beta\)-Ga$_2$O$_3$ (space group: C2/m) with the lattice parameters of \(a = 12.23\) Å, \(b = 3.04\) Å, \(c = 5.80\) Å, and \(\beta = 103.7°\) 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$^{19}$. Additionally, \(\beta\)-Ga$_2$O$_3$ has great chemical stability, being unaffected even by concentrated acids such as hydrofluoric acid$^{20}$. More importantly, \(\beta\)-Ga$_2$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$^{21-22}$. On the other hand, \(\beta\)-Ga$_2$O$_3$ is also the host material for magnetic semiconductors, and room temperature ferromagnetism was observed in Mn-doped \(\beta\)-Ga$_2$O$_3$ by our group$^{15}$.

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The $\beta$-Ga$_2$O$_3$ and $\beta$-Ga$_2$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 Ga$_2$O$_3$/(Ga$_{1-x}$Fe$_x$)$_2$O$_3$ multilayer epitaxial thin films and investigated their structural, optical, and magnetic properties.

Results and Discussion

The Ga$_2$O$_3$/(Ga$_{1-x}$Fe$_x$)$_2$O$_3$ and Ga$_2$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 Ga$_2$O$_3$/(Ga$_{1-x}$Fe$_x$)$_2$O$_3$ multilayer epitaxial thin films and investigated their structural, optical, and magnetic properties.

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TEM image of the interface between the Ga2O3/Fe(50) multilayer film and Al2O3 substrate as marked by a blue small pane in Fig. 1(c), which clearly indicates the orientation relationship of (201) β-Ga2O3//(0001) Al2O3. 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 (Fe2+^+, Fe3+^+, and Ga3+^+ ionic are 0.74, 0.64, and 0.62 Å, respectively23–25), and the lattice parameters of Ga2O3 change rarely with the Fe doping; (2) The Fe doping concentration of the Ga2O3/Fe(N) multilayer thin film is low (it is 2.44 at.% for N = 50). To investigate the composition distributions in the Ga2O3/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 Ga2O3/Fe(50) and Al2O3 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 Ga2O3/Fe(50) film. However, Fe element exhibits clear agglomerated areas and obvious stratified phenomenon. Al metal is derived from the Al2O3 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 Ga2O3/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 (Ga1−xFex)2O3 thin film in our scheming Ga2O3/(Ga1−xFex)2O3 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 Ga2O3 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 Ga2O3/(Ga1−xFex)2O3 multilayer thin films were determined from 0–2θ scans of XRD, as is shown in Fig. 3(a). In order to facilitate compared with the others, the diffraction intensities of the Ga2O3/Fe(0) and Ga2O3/Fe(100) films were multiplied by 3 and 10 times respectively. Except Ga2O3/Fe(100) film, only (201) and higher order peaks of Ga2O3 monoclinic β phase appear for the other as-grown Ga2O3/(Ga1−xFex)2O3 multilayer films besides those from the substrate, indicating single phase and a preferred (201) plane orientation of the films. Furthermore, as shown in Fig. 3(b) with the enlarged view of 0–2θ XRD patterns around 38°, the peaks of (402) are located at 38.36°, 38.31°, 38.29°, 38.26°, 38.24°, and 38.19° for N = 0, 10, 20, 30, 40, and 50, respectively, indicating that the peak gradually shifts to smaller 2θ with the increase of Fe layer thickness. The lower angles shift of (201) 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 Ga2O3/Fe(100) film, extra diffraction peaks of (110) and (113) of β phase Ga2O3 appear and the diffraction intensity of the family of (201) crystal planes decreases, featuring a polycrystalline nature. No impurity peaks related to Fe metal clusters and Fe oxides were observed.

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Fe 2p3/2 and Fe 2p1/2. For Fe2⁺ cations, the peak position of Fe 2p3/2 and Fe 2p1/2 is located at about 709.0 and 722.6 eV, and the satellite peak of Fe 2p3/2 is located approximately 6 eV higher than the main Fe 2p3/2 peak. While for Fe3⁺ cations, the peak position of Fe 2p3/2 and Fe 2p1/2 is located at about 711.0 and 724.6 eV, and the satellite peak of Fe 2p3/2 is located approximately 8 eV higher than the main Fe 2p3/2 peak. In our Ga2O3/(Ga1-xFex)2O3 multilayer thin films, the peak positions of Fe 2p3/2 and Fe 2p1/2 are, respectively, 710.4 and 723.5 eV. They are located between the values for Fe2⁺ and Fe3⁺ cations, which can be deconvoluted into the Fe2⁺ and Fe3⁺ peaks, indicating that both Fe2⁺ and Fe3⁺ cations are contained. In addition, the satellite peaks at the high binding energy side of the main peaks are further demonstrated the coexistence of Fe2⁺ and Fe3⁺.

Figure 5 shows the ultraviolet-visible (UV-Vis) absorbance of the Ga2O3/(Ga1-xFex)2O3 multilayer thin films. All the samples exhibit a sharp absorption edge at about 250 nm, corresponding to the intrinsic absorption of β-Ga2O3. 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 (αhν)^2 versus hν. The inset of Fig. 5 shows the Ga2O3/Fe(50) multilayer film has a band gap of about 4.95 eV. On the other hand, it is observed that all the Ga2O3/(Ga1-xFex)2O3 multilayer films have 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 Ga2O3/Fe(50) multilayer thin film at room temperature with that of pure β-Ga2O3 thin film for comparing. The diamagnetic contribution from the α-Al2O3 substrate was subtracted from the data. The pure β-Ga2O3 thin film [Ga2O3/Fe(0)] displays paramagnetic behavior while Ga2O3/Fe(50) film show hysteresis loops indicative of ferromagnetism when the applied magnetic field is parallel to the films. Furthermore, the Ga2O3/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 ~73 Oe and 4.99 emu/cm³ for the magnetic field paralleling to the film, while they are ~91 Oe and 3.68 emu/cm³ respectively for the perpendicular
one. And the saturation magnetization ($M_s$) of the Ga$_2$O$_3$/Fe(50) multilayer is similar for parallel and perpendicular which are 33.8 and 32.8 emu/cm$^3$ respectively at 2 T. The magnetic anisotropy in Ga$_2$O$_3$ with doping other transition metal (such as Mn, Cr) has also been reported$^{15,16}$. Origin of the anisotropic magnetization is not clear.

Figure 4. XPS spectra of Ga 3d (a) and Mn 2p (b) core level for the Ga$_2$O$_3$/Fe(50) multilayer thin film.

Figure 5. Absorption spectra of the Ga$_2$O$_3$/Fe(N) multilayer thin films and the plot of $(\alpha h\nu)^2$ versus $h\nu$ for the Ga$_2$O$_3$/Fe(50) film (inset).
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 Ga 2O3/(Ga1−xFex)2O3 multilayer films is intrinsic.

The perpendicular & parallel magnetic moments of Fe cation in the Ga2O3/Fe(50) multilayer thin film at 2 T are 3.74 and 3.89 μB/Fe cation respectively, which are very close to the magnetic moment of Fe cation reported by others 29,30.

In conclusion, the multilayer epitaxial thin films based on wide band gap of Ga2O3 and magnetic semiconductor of (Ga1−xFex)2O3 were fabricated by alternating depositing of Ga2O3 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 β-Ga2O3 and the formation of the Ga2O3/(Ga1−xFex)2O3 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 × 10 mm α-Al2O3 (0001) substrates by the LMBE technique at a repetition frequency of 1 Hz and with a fluence of ~5 J/cm². The thin film deposition was grown in a vacuum environment of 1 × 10⁻⁶ Pa and at a substrate temperature of 900°C. Alternating depositions of Ga2O3 layer and Fe ultrathin layer were performed for 20 times to prepare the Ga2O3/(Ga1−xFex)2O3 multilayer epitaxial thin films. The (Ga1−xFex)2O3 layer (that is Fe doping Ga2O3 layer) was obtained due to inter diffusion between Fe and Ga2O3 layers at high temperature. The Fe doping concentration of the Ga2O3/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 θ–2θ 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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