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Room temperature ferromagnetism in (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ epitaxial thin films

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Mn-doped monoclinic $\beta$-(Ga$_{1-x}$Mn$_x$)$_2$O$_3$ thin films were epitaxially grown on $\alpha$-Al$_2$O$_3$ (0001) substrates by alternately depositing Ga$_2$O$_3$ and Mn layers using the laser molecular beam epitaxy technique. The crystal lattice expands and the energy band gap shrinks with the increase of Mn content for Mn ion incorporated into Ga site. Ferromagnetism appears even above room temperature when $x \geq 0.11$ and can be remarkably enhanced with the continuous increase of Mn indicated by the increased magnetization and coercivity. The study presents a promising candidate for use in spintronics devices that are capable of working at room temperature.
Introduction

Magnetic semiconductors have attracted considerable attentions for their potential applications in spintronics devices,\textsuperscript{1-5} such as fast nonvolatile semiconductor memories and integrated magnetic/electronic/photonic devices. According to the theoretical prediction by Dietl,\textsuperscript{6} high Curie temperature ($T_c$) even exceeding room temperature could be achieved in some wide band gap semiconductors when they are doped with transition metals, especially Mn. The thus-far doping work has been carried out mainly in some conventional II-VI and III-V compounds,\textsuperscript{7-12} such as (Ga,Mn)As, (In,Mn)As, (Ga,Mn)N and (Zn,Mn)O, etc., while mechanism for the appearance of ferromagnetism remains rather elusive. The discovery of more ferromagnetic semiconductors is always desired not only because they can provide complementary knowledge helpful for clarifying the fundamental issue but also due to their potential practical applications.

Gallium oxide (Ga$_2$O$_3$), a wide direct band gap semiconductor with a gap size of $\sim$ 4.9 eV,\textsuperscript{13-15} is a good place for such exploration. High photon energy and high transparency in the visible and ultraviolet region ($> 280$ nm) enable the easy manipulation of the spins by photons, and thus make Ga$_2$O$_3$ attractive for use in spintronics devices.

Ga$_2$O$_3$ can crystalize in five different phases (known as $\alpha$, $\beta$, $\gamma$, $\delta$, and $\varepsilon$-phases).\textsuperscript{16} Among these, 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 $\beta = 103.7^\circ$ has been recognized as the most stable phase suitable for various characterizations and more intensively studied.\textsuperscript{16-18} Ferromagnetism was observed in Mn-doped $\gamma$-Ga$_2$O$_3$ at room temperature as well as in highly crystalline corundum-structured $\alpha$-(Ga$_{1-x}$Fe$_x$)$_2$O$_3$ ($x=0.58$) thin film.\textsuperscript{19-21} However,
magnetic properties of Mn-doped $\beta$-Ga$_2$O$_3$ have not been studied yet. In this work, we report on the observation of ferromagnetism even above room temperature in epitaxially grown Mn-doped $\beta$-Ga$_2$O$_3$ thin films with high Mn concentrations.

**Experimental**

The film growth of Mn-doped $\beta$-Ga$_2$O$_3$ was performed by using the laser molecular beam epitaxy technique with a pulse energy density of $\sim 5$ J/cm$^2$ on $\alpha$-Al$_2$O$_3$ (0001) substrates at 900 $^\circ$C. The Ga$_2$O$_3$ and Mn layers were alternately deposited and both depositions were repeated for 20 times. The Mn concentrations were controlled by solely changing the laser pulse numbers during each run of depositing the Mn layers (defined as N, N=10, 20, 30, 40, 50) while those for depositing Ga$_2$O$_3$ layers in each run were fixed at 100. The alternating deposition enabled the realization of (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ thin films with different compositions due to inter diffusion between Mn and Ga$_2$O$_3$ layers at high temperature. The Mn concentrations in (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ films were determined as 6.06 at.% 10.97 at.% 17.64 at.% 31.17 at.% and 53.10 at.% respectively by the X-ray energy dispersive spectroscopy (EDS). The orientation and crystallinity of the as-grown films were investigated by X-ray diffraction (XRD) at 0-20 scan and *in-situ* reflection high-energy electron diffraction (RHEED). The valences of Mn ions and elements distribution were analyzed by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). Magnetic properties of the films were measured in a commercial superconducting quantum interference device (SQUID), Quantum design.
Results and discussion

The crystal structures of the as-grown films were characterized from θ-2θ scans of XRD, the results are shown in Fig. 1(a). Except diffraction peaks of the Al₂O₃ substrate, only diffraction peaks located at around 19°, 38°, and 59° were observed, all of them belongs to (Ga₁₋₃Mnx)₂O₃. No peaks from Mn metal clusters, Mn oxide, MnₓGaᵧ or MnGa₂O₄ phases were exist. As seen from the enlarged view of θ-2θ XRD patterns around 38° (Fig. 1(b)), the peaks are located at 38.34°, 38.12°, 37.94°, 37.77°, 37.60°, and 37.15° for x= 0, 0.06, 0.11, 0.18, 0.31, and 0.53, respectively, indicating that the peak gradually shifts to smaller 2θ with the increase of x. Meanwhile, no abrupt shift or half height width changing of diffraction peak were observed with the increase of x (the relative large shift for x=0.53 may be attributed to the relative much increase of Mn content from 0.31 to 0.53). Thus, the possibility of phase transformation would be excluded. According to relevant references, the (2 0 1) diffraction peak of β-Ga₂O₃ (PDF#43-1012) and the (2 2 2) diffraction peak of γ-Ga₂O₃ (References 19 and 20) should be located at 38.40° and 37.28°, respectively. For x=0.06, if γ-phase appears, the diffraction peak around 38° should present an abrupt shift to near, even lower than 37.28° due to Mn doping. Actually, the peak locates at 38.12° which is closer to the 38.40° of β-phase. Thus, we believe that β-Ga₂O₃ is obtained by Mn-doping. The diffraction peaks located at around 19°, 38°, and 59° are correspond to (2 0 1) and higher order peaks of monoclinic β-phase Ga₂O₃ respectively, indicating a preferred (2 0 1) plane orientation of the thin films. The x dependence of (2 0 1) plane distance is depicted in Fig. 1(c), showing that the d spacing increases almost linearly
with the increase of $x$. With the increase of $x$, the peak shift of $(201)$ plane to smaller
20 indicates a gradual increase of the lattice constants because the radii of Mn ions are
larger than that of Ga ion ($\text{Mn}^{2+}$, $\text{Mn}^{3+}$ and $\text{Ga}^{3+}$ ionic radii are 0.83, 0.64 and 0.62 Å,
respectively). These facts, along with the EDS results, demonstrate the successful
incorporation of Mn ions into the lattice of $\text{Ga}_2\text{O}_3$. The clear and streaky RHEED
patterns shown by Fig. 1(d) suggest that the $(\text{Ga}_{1-x}\text{Mn}_x)_2\text{O}_3$ films are of single phase
with very smooth surfaces.

Hayashi et al. reported that Mn-doped $\text{Ga}_2\text{O}_3$ (7 cation % of Mn) thin film grown at
500° exhibits spinel structure of $\gamma$-phase. According to the temperature dependent
phases transformation by Roy, $\gamma$-phase is metastable and would transfer to the stable
monoclinic $\beta$-phase above 650°C. It is reasonable for Mn-doped $\text{Ga}_2\text{O}_3$ thin film
exhibiting $\gamma$-phase when the films deposited at 500°C. When the deposition temperature
is above 600°C, $\beta$-$\text{Ga}_2\text{O}_3$ will appear in Mn-doped $\text{Ga}_2\text{O}_3$ films, indicating that the
transformation of $\gamma$-phase to $\beta$-phase has began at 600°C. Herein, the $(\text{Ga}_{1-x}\text{Mn}_x)_2\text{O}_3$ thin
films were growth with a substrate temperature of 900°C, all the metastable phases
would be transfer to $\beta$ phases. We have characterized the $(\text{Ga}_{1-x}\text{Mn}_x)_2\text{O}_3$ thin film with
$x=0.06$ using selected-area electron diffraction patterns in an orientation parallel to the
$(10\overline{1}0)$ of $\text{Al}_2\text{O}_3$ substrate, and the results confirmed the obtained film was
$\beta$-$\text{Ga}_2\text{O}_3$. More sophisticated research is under way.

Compositions as a function of film thickness were also characterized by using the
SIMS depth profiling. The results for the representative $(\text{Ga}_{0.47}\text{Mn}_{0.53})_2\text{O}_3$ film were
summarized in Fig. 2 by showing intensities of the Mn and Ga ion currents as a function
of sputter depth of the film. Intensities of both Mn and Ga ion currents remain almost constant indicating that Mn is actually uniformly distributed in the film without any detectable enrichment or segregation. Meanwhile, the streak lines of RHEED patterns always keep sharp during the growth processes, indicating that Mn ions are uniformly distributed in-plane. These results thus evidently excludes the possibility of formation of Mn-rich layers in (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ thin films.

The chemical compositions and chemical states of Mn ions in the films were characterized by using XPS, presented in Fig. 3. The elements present in the (Ga$_{0.47}$Mn$_{0.53}$)$_2$O$_3$ film are Mn, Ga, O, and C (not shown). The charge-shift spectrum was calibrated using the fortuitous C 1s peak at 284.8 eV. The spectrum of Mn 2p shows a spin-orbit doublet ($j = 3/2, 1/2$). The Mn 2p$_{3/2}$ main peak has a satellite structure on the higher binding-energy side separated by $\sim 6$ eV, which indicates a strong Coulomb interaction between the Mn 3d electrons and hybridization between the Mn 3d and other valence orbitals.$^{25}$ No Mn 2p$_{3/2}$ peaks for metallic Mn (located at 639 eV) are visible in Fig. 3, indicating no Mn metallic clusters present in the films.$^{26}$ It is also noted that Mn 2p$_{3/2}$ main peak contains two peaks corresponding to 640.59 and 641.74 eV, respectively, implying the presence of two possible valence states (Mn$^{2+}$/Mn$^{3+}$) with a ratio of about 19:81. The neutral configuration of Mn in Ga$_2$O$_3$ should be Mn$^{3+}$ when viewed as replacing Ga$^{3+}$ in the lattice. However, there are many oxygen vacancies as donor-type defects in $\beta$-Ga$_2$O$_3$ thin films, which would lead to the valence of Mn change from $+3$ to $+2$.$^{14}$ In addition, seen from the XPS spectrum of Ga 3d core-level in the inset of Fig. 3, there is only one peak at 20.4 eV, which comes from the Ga ions in the (Ga$_{1-x}$Mn$_x$)$_2$O$_3$
films. And another peak at ~ 18.4 eV for decomposed Ga atoms cannot be found, suggesting that the metallic Ga or Mn$_x$Ga$_y$ are not present in our samples.

The band gap of (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ thin films can be modified by changing the Mn content, indicated by the ultraviolet-visible (UV-Vis) absorbance measurements. Shown by the absorbance spectra of (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ (x=0, 0.11, 0.31) thin films in Fig. 4, the spectrum of the host exhibits a sharp intrinsic absorption edge at ~ 250 nm, whilst those of Mn-doped samples display clear red-shift. The gap sizes can be derived by fitting the linear region of the $(\alpha h\nu)^2$ versus $h\nu$ plot, shown by the inset to Fig. 4. The gap size decreases from 4.92 eV for x = 0 to 4.87 eV and 4.72 eV for x = 0.11 and x=0.31, respectively.

Figure 5 shows the magnetization versus magnetic field ($M$-$H$) curves of (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ films at room temperature measured with the applied magnetic field parallel to the films. The diamagnetic contribution from the sapphire substrate was subtracted from the data. The (Ga$_{0.94}$Mn$_{0.06}$)$_2$O$_3$ film displays typical paramagnetic behavior while (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ thin films with $x \geq 0.11$ show hysteresis loops indicative of ferromagnetism. However, for $\gamma$-phase Mn-doped Ga$_2$O$_3$, the film with Mn concentration even of 7% has shown room temperature ferromagnetism with a magnetization of 2.8 emu/cm$^3$ at 2 kOe, which may be attributed to different phase type of (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ thin films. Magnetic parameters for (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ films with respect to x are listed in Table 1. The saturation magnetizations ($M_s$) increase monotonically from 5.5 emu/cm$^3$ to the maximum value of 33.1 emu/cm$^3$ at 2 kOe with the increase of x and the coercivity and magnetic remanence ($M_r$) increase as well,
revealing apparent enhancement of ferromagnetism with the increase of Mn content. For 
\((Ga_{0.47}Mn_{0.53})_2O_3\) film, the coercivity and \(M_r\) reach \(~109\) Oe and \(7.6\) emu/cm³, respectively. The temperature dependent magnetization \((M-T)\) of \((Ga_{0.47}Mn_{0.53})_2O_3\) film was measured at \(2\) kOe using field-cooling mode. Seen from the \(M-T\) curve shown in the inset of Fig. 5, \(M\) is seen to be fairly constant in the measurement temperature range of \(15 \sim 400\) K.

The above XRD, SIMS, XPS, UV-Vis absorption, and magnetic properties characterizations on \((Ga_{1-x}Mn_x)_2O_3\) films are sufficient to confirm the successful substitution of Mn for Ga. Meanwhile, according to the XRD and XPS analyses, we did not found any room ferromagnetic second phase, such as Mn₄Ga₂ clusters. Nevertheless, for the possible secondary phases of Mn metal and Mn-based oxides, only Mn₃O₄ is ferromagnetic with a small \(T_c\) of \(43\) K while others are all antiferromagnetic.\(^{10,29}\) It is reasonably to conclude that the room temperature ferromagnetism in the \((Ga_{1-x}Mn_x)_2O_3\) thin films with high Mn concentrations is intrinsic.

Up to now, there is no a perfect model that can well describe the origin of the room-temperature ferromagnetism of Mn-doped Ga₂O₃. Hayashi et al.\(^{19}\) suggested that the room temperature ferromagnetism of \(\gamma-(Ga_{1-x}Mn_x)_2O_3\) can be explained by a carriers-mediated double exchange model that had been used to explain room temperature ferromagnetism in Mn-doped GaN. Pei et al.\(^{30}\) also used the model to propose the ferromagnetic coupling in their theoretical study on magnetic properties of Mn-doped \(\beta\)-Ga₂O₃ and pointed out that the ferromagnetic ground state could be established even at a small Mn concentration of \(12.5\) at.%. For the carrier-mediated
double exchange model, a large quantity of mobile carriers are desired to induce ferromagnetism.\textsuperscript{4,31} However, in our system, the charge carriers should be highly localized due to the high intrinsic properties of $\beta$-Ga$_2$O$_3$ hosts, as a result, we failed to measure the carrier type and carrier concentration in $(\text{Ga}_{1-x}\text{Mn}_x)_2\text{O}_3$ thin films using Hall Effect measurement. So the framework of bound magnetic polaron (BMP) model should be more suitable. In the BMP model, ferromagnetic exchange is mediated through localized donor electrons in the impurity band.\textsuperscript{32} The interactions of BMPs in an insulator follow essentially from the Loss and DiVincenzo\textsuperscript{33} proposal for spin-based solid-state quantum computing electrons localized in electrostatically defined quantum dots, with coupling between electron spins via the exchange interaction. Base on doping level, the ferromagnetism coupling could be classified to three main processes in BMP model.\textsuperscript{34-35} In miner-doped, the remote impurities produce low magnetic moments for weak interaction. In appropriate-doped, a sufficiently large number of bound magnetic polarons long-range ferromagnetic order would be established. While in heavy-doped, the increase of dopant concentration will strengthens dopant-dopant associations and leads to progressive orbital moment quenching, causing the decrease of the ferromagnetism. The BMP model seems to be more suitable for our experiment results, but it does not mean that the BMP is a satisfied model to explain room-temperature ferromagnetism in $(\text{Ga}_{1-x}\text{Mn}_x)_2\text{O}_3$. In order to deeper understand the mechanism, more experimental and theoretical works should be done to improve the current models or propose a better model.
Conclusions

In conclusion, monoclinic $\text{(Ga}_{1-x}\text{Mn}_x\text{)}_2\text{O}_3$ thin films with a preferable $(201)$ orientation on $\alpha$-$\text{Al}_2\text{O}_3$ (0001) substrates were epitaxially grown by using laser molecular beam epitaxy technique. The systematic characterizations by XRD, SIMS, XPS and UV-Vis absorbance spectrum confirmed the incorporation of Mn into the lattice of $\beta$-$\text{Ga}_2\text{O}_3$ and revealed its effects on the crystal and electronic structures. Magnetic properties measurements revealed that the $(\text{Ga}_{1-x}\text{Mn}_x\text{)}_2\text{O}_3$ thin films are ferromagnetic even above room temperature, and the ferromagnetism can be enhanced with increasing the Mn content.
Acknowledgements

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References


Figure and Table Captions

**Fig. 1** (a) 0-20 XRD patterns, (b) enlarged view of 0-20 XRD patterns around 38°, (c) the Mn doping concentration dependence of (20 1) lattice plane distance, and (d) RHEED patterns of (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ thin films (x=0.06, 0.31).

**Fig. 2** Mn and Ga SIMS depth profiles for (Ga$_{0.47}$Mn$_{0.53}$)$_2$O$_3$ thin film.

**Fig. 3** XPS spectra of Mn 2p and Ga 3d (inset) core level for (Ga$_{0.47}$Mn$_{0.53}$)$_2$O$_3$ thin film.

**Fig. 4** Absorption spectra of (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ (x= 0.11, 0.31) thin films compared with that of pure β-Ga$_2$O$_3$ thin film and the plot of ($αhν)^2$ versus hν in inset.

**Fig. 5** M-H curves of (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ thin films at room temperature and temperature dependence magnetization of (Ga$_{0.47}$Mn$_{0.53}$)$_2$O$_3$ thin film at 2 kOe (inset).

**Table 1.** Magnetic parameters for (Ga$_{1-x}$Mn$_x$)$_2$O$_3$ thin films with different Mn content. The given $M_s$ are at the magnetic field of 2 kOe.
FIG. 1
FIG. 2
FIG. 3
FIG. 4
FIG. 5
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<th>Coercivity (Oe)</th>
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