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Ferromagnetism and *p*-type Conductivity in Laser-deposited (Zn,Mn)O Thin Films Codoped by Mg and P

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We report on the observation of *p*-type conductivity and ferromagnetism in diluted magnetic semiconductor $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films grown on SiO_2/Si substrates by pulsed laser deposition. The *p*-type conduction with hole concentration over 10^{18} cm^{-3} is obtained by codoping of Mg and P followed by rapid thermal annealing in an O_2 atmosphere. Structural and compositional analyses for the *p*-type $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films annealed at 800 °C indicates that highly *c*-axis oriented homogeneous films were grown without any detectable formation of secondary phases. The films were found to be transparent in the visible range. The magnetic measurements clearly revealed an enhancement of room temperature ferromagnetism by *p*-type doping.

Keywords : diluted magnetic semiconductors, Zinc oxide, ferromagnetism, spintronics

1. Introduction

Oxide-based diluted magnetic semiconductors (DMS) have recently attracted a great deal of attention because of their promising potential for spintronic devices and, in particular, some reports of appearance of room temperature ferromagnetism in several oxide DMS [1-3]. Among these systems, ZnO- and TiO_2-based DMS have been intensively studied to realize ferromagnetic semiconductors operating at room temperature. While values of the Curie temperature above room temperature have been reported in Co-doped TiO_2 [4], ZnO [5] and Mn-doped ZnO [6], we cannot clearly rule out the possibility of an extrinsic origin of ferromagnetism, such as ferromagnetic clustering, in these materials. Recently, both theoretical and experimental works suggested that wide bandgap oxide semiconductors with high carrier density are one of the most favorable host materials to ferromagnetic DMS with higher Curie temperature [1-3].

ZnO is well known as a wide bandgap (E_g = 3.437 eV at 2 K [7]) semiconductors with a high transmittance (≈ 90%) in the visible range. Among ZnO-based DMS, Mn-doped ZnO [(Zn,Mn)O] has been intensively studied due to the high solubility of Mn larger than 10 mol% [8] and some theoretical predictions of the possibility of room temperature ferromagnetism in *p*-type (Zn,Mn)O [9, 10]. Meanwhile, most experimental works have been conducted on *n*-type (Zn,Mn)O because of much difficulty on fabricating *p*-type (Zn,Mn)O. There have been a few recent works reporting realization of *p*-type ZnO [11, 12] and (Zn,Mn)O [13] via doping P as acceptors and thermal annealing treatment. The addition of Mg into ZnO is known to shift the conduction band edge to higher energy [14], leading to reduction of the electron concentration. It is important to control both the electrical properties and magnetic properties of (Zn,Mn)O for practical spintronic applications.

In this article, we report on the appearance of the *p*-type conduction and room temperature ferromagnetism in laser-deposited (Zn,Mn)O thin films codoped by Mg and P. The effects of rapid thermal annealing on the structural, electrical, optical and magnetic properties of the films have been systematically examined.

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2. Experiments

$(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films were deposited on SiO_2 (200 nm)/Si (100) substrates by using pulsed laser deposition (PLD) method from ceramic targets. The films for optical measurements were separately grown on sapphire substrates. The targets with a P doping level of 2 mol% were fabricated by standard solid-state reaction method. Prescribed amount of ZnO, MgO, MnO and P_2O_5 powders were mixed and pressed disks with a diameter of 1 inch, which were fired 1200°C during 6 hr and cooled to room temperature during 24 hr in an air atmosphere. The sintered targets were ablated by KrF excimer laser pulses ($\lambda = 248$ nm, 10 Hz) with a fluence of 5 J/cm^2. The target-to-substrate distance was 4.5 cm. The substrate temperature was in the range from 300 to 600°C and the oxygen pressure were fixed at 5×10^{-5} Torr during growth. We employed rapid thermal annealing (RTA) at temperatures in the range of 600-900 °C under O_2 ambient to control the carrier concentration and conduction type in as-deposited films. The thicknesses of the grown films were around 2000 Å.

The structure analysis and phase identification of the films were carried out by using a two-circle X-ray diffractometer (XRD). Electrical conductivity, conduction type, carrier concentration and mobility were determined at room temperature from Hall measurement using a van der Pauw configuration. Optical spectra were measured at room temperature in the wavelength range of 200-3200 nm using an ultraviolet-visible-near infrared spectrometer. Magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 5-350 K with the magnetic field applied parallel to the film surface.

3. Results and Discussion

We first discuss the influence of the rapid thermal annealing treatment under O_2 ambient on the electrical properties of the laser-deposited $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films. Figure 1 shows the Hall measurement results of the carrier concentration and conduction type for the films deposited at three substrate temperatures (400, 500 and 600°C) and subsequently annealed at several temperatures in the range of 600-900°C. We found that the as-deposited films exhibit *n*-type conduction, whereas the annealed films display *p*-type conduction depending on the annealing temperature. We note here that the conduction type of the films annealed under O_2 ambient changes from *n*-type to *p*-type with increasing annealing temperature. This result indicates that phosphorus as a *p*-type dopant in (Zn,Mn)O

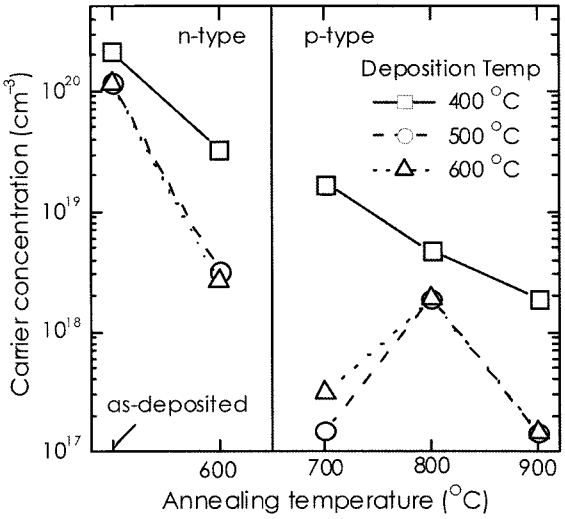

Fig. 1. Carrier concentration and conduction type in $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films as-deposited at several deposition temperatures and post-annealed under O_2 ambient at various temperatures.

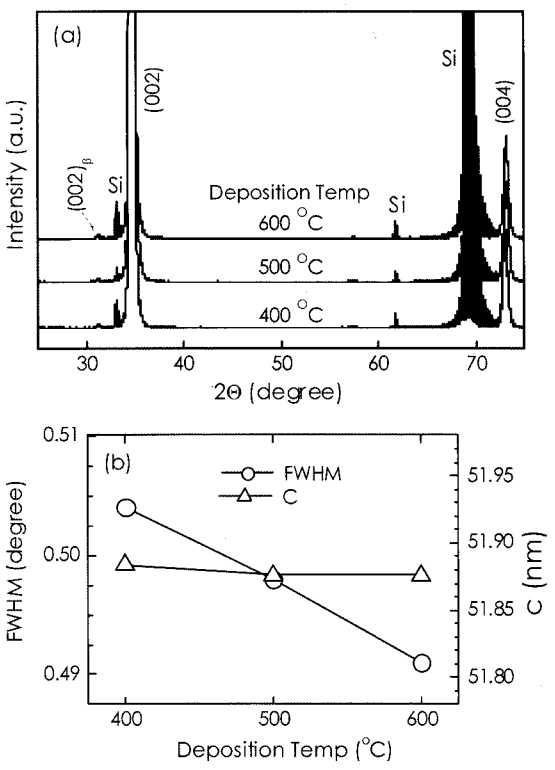

Fig. 2. (a) X-ray diffraction patterns of the laser-deposited $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films annealed at 800°C under O_2 ambient for several deposition temperatures. (b) Variations of the full width at half maximum (FWHM) and the *c*-axis lattice parameters, estimated from the (004) peak, with the deposition temperature.

is more active at high thermal energy to suppress substantially oxygen vacancies and generate free holes. Similar

behavior of the change in the conduction type via post-annealing treatment has been observed in sputtered $Zn_{0.99}Mn_{0.01}O$:P films [13]. The hole concentrations for the $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films annealed at 800°C were estimated to be above 10^{18} cm^{-3}.

After rapid thermal annealing treatment at 800°C during 10 min, we observed no significant change in the crystalline structure of the $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films. Figure 2(a) shows the XRD patterns of the films annealed at 800°C for several deposition temperatures. Only (002) and (004) peaks of the wurtzite phase as pure ZnO were observed with no detectable impurity peaks, indicating a *c*-axis preferred-orientation growth. Secondary ion mass spectrometer (SIMS) analysis for a film deposited at 500 °C revealed that rapid thermal annealing at 800°C causes little change in the SIMS spectra, displaying a homogeneous distribution of Mn ion with the film depth without any surface or interface segregation of Mn ions. In Fig. 2(b) are shown the variations of the values of FWHM (full width at half maximum) and the *c*-axis lattice parameter, estimated from the (004) peak, with the deposition temperature. The FWHM value reduces linearly with increasing deposition temperature, signifying an improvement of crystallization. On the other hand, the *c*-axis lattice parameter exhibit no considerable change with the deposition temperature.

Now we discuss the effect of rapid thermal annealing under O_2 ambient on the optical properties of the $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films. For the optical measurements, the films were deposited on double-polished Al_2O_3 substrates at a substrate temperature of 500°C. Fig. 3(a) shows the optical transmission spectra obtained before and after annealing at 800°C. Although they were as thick as ~1100 nm, both as-deposited and annealed films still displayed a transmittance of more than 80% in the wavelength range of 500-2500 nm and furthermore the annealed film exhibited a high transmittance of ~90% for the wavelength above 2500 nm. In the inset of Fig. 3(a) are shown the pictures of both samples, demonstrating both films are transparent in the visible range. The color of the films changed from light yellow to light orange after annealing. For evaluating the optical bandgap energy E_g, we used the formula $\alpha \propto (E-E_g)^{1/2}$ and the data were replotted in Fig. 3(b) in the form of the curve of α^2 versus E, where α is the absorption coefficient and $E = h\nu$ is the photon energy. The value of the bandgap E_g, defined from the intersection of the dotted extrapolation lines in Fig. 3(b), was found to decrease from 3.35 to 3.27 eV after annealing. Given that the carrier concentration of the as-deposited film is higher than that of the annealed one, the observed reduction in the energy gap after annealing may be attributed to the Moss-Burstein effect (saying that the band gap increases with carrier density) [15], as commonly observed in ZnO films [16, 17].

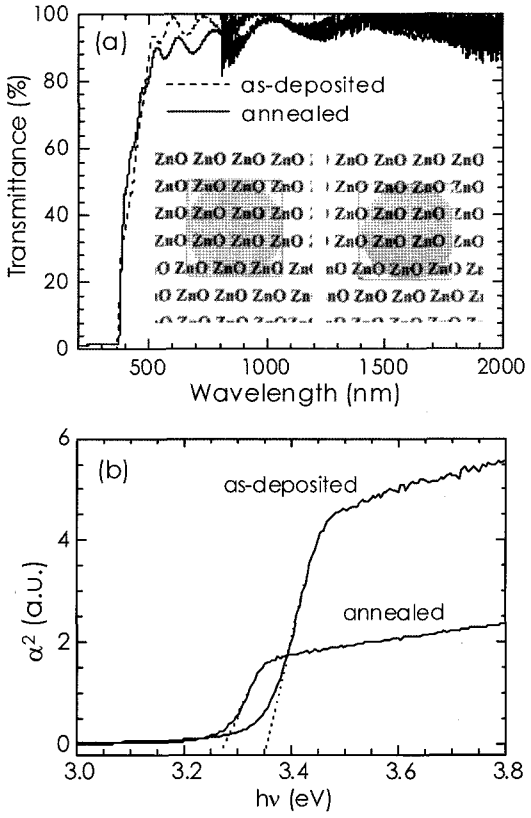

Fig. 3. (a) Optical transmission spectra of the laser-deposited $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films as-deposited and annealed at 800 °C. The pictures in the inset demonstrate that the films are transparent in the visible range. (b) Photon energy dependence of α^2 for deducing bandgap from the intersection of the extrapolated dotted lines.

Finally we discuss the influence of the rapid thermal annealing treatment under O_2 ambient on the magnetic properties of the laser-deposited $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films. Fig. 4(a) shows the temperature dependence of the magnetization (*M-T* curves) during warming in a magnetic field of 2 kOe after cooling without the magnetic field [zero-field cooling (ZFC)] for the as-deposited and annealed films. The diamagnetic contribution due to substrate was substracted from the data. We found that the ZFC and field-cooled (FC) measurements showed no discernable difference in the *M-T* curves, indicating the absence of a spin-glass-like phase in the laser-deposited $(Zn_{0.97}Mg_{0.01}Mn_{0.02})O$:P films. The character of the *M-T* curves shown in Fig. 4(a) can be well understood by the coexistence of ferromagnetic and paramagnetic components, as observed in $Zn_{0.99}Mn_{0.01}O$:P [13], Co-doped Cu_2O [18], Mn-doped GaN [19, 20]. A well-defined magnetic hy-

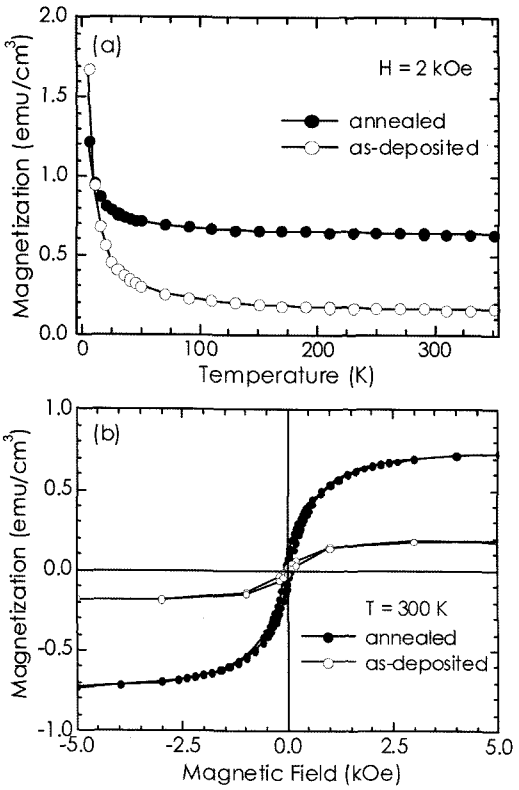

Fig. 4. Magnetic properties of the laser-deposited ($Zn_{0.97}Mg_{0.01}Mn_{0.02}$)O:P films as-deposited and annealed at 800 °C: (a) Temperature dependence of the magnetization measured in a field of 2 kOe, (b) Magnetic field dependence of the magnetization at 300 K.

steresis loop for the annealed film at 300 K is displayed in Fig. 4(b), signifying room temperature ferromagnetism. It is clearly seen from Figs. 4(a) and 4(b) that rapid thermal annealing leads to a remarkable enhancement in the saturation magnetization. We attribute an enhancement of the ferromagnetism in ($Zn_{0.97}Mg_{0.01}Mn_{0.02}$)O:P by rapid thermal annealing to the sufficient generation of the holes by the annealing which results in the *p*-type conduction. Stabilization of the ferromagnetic state by the hole carriers in Mn-doped ZnO was predicted based on *ab initio* band calculations [7]. Here we point out that the observed magnetization of the samples are very small: the value of the magnetic moment per Mn ion is estimated to be 2.6×10^{-2} μ_B and 9.2×10^{-2} μ_B for the *n*-type and *p*-type sample, respectively. A strong intrinsic antiferromagnetic coupling between Mn ions in the insulating (Zn,Mn)O [8] might be among several possible reasons why the observed magnetization is so small.

4. Conclusion

We have successfully grown *p*-type ferromagnetic ($Zn_{0.97}Mg_{0.01}Mn_{0.02}$)O:P thin films using pulsed laser deposition via rapid thermal annealing treatment as well as codoping of Mg and P into Mn-doped ZnO. We experimentally confirmed the key role of the hole carriers for an enhancement of the ferromagnetism in Mn-doped ZnO. The films were observed to be transparent in the visible range. These features suggest that Mn-doped ZnO could be promising for the realization of transparent ferromagnetic semiconductors operating at room temperature by controlling the itinerant carriers.

Acknowledgements

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