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Preparation and evaluation of Mn-Doped ZnO films

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Mn-doped ZnO ($Zn_{1-x}Mn_xO$) thin films were grown on ZnO epitaxial layer by pulsed laser deposition method. A ZnO epitaxial layer with x-ray rocking curve line width of 190[arcsec] was grown on sapphire (0001) substrates and was used as the template for $Zn_{1-x}Mn_xO$ growth. High quality epitaxial $Zn_{1-x}Mn_xO$ thin film was obtained with x=0.17. With increasing Mn content, c-axis lattice constant of $Zn_{1-x}Mn_xO$ films was increased and full-width at half maximum (FWHM) of the (0002) diffraction in $2\theta/\theta$ scan was also increased. The optical transmittance was degraded with increasing Mn content and the color of film became yellowish brown. The surface of $Zn_{0.83}Mn_{0.17}O$ films was very smooth and the root mean square (RMS) value of surface roughness was about 1nm. RHEED pattern of the $Zn_{0.983}Mn_{0.017}O$ films exhibited elongated spotty diffraction patterns.
Key words: $Zn_{1-x}Mn_xO$, Transition metals, pulsed laser deposition

1. INTRODUCTION

Zinc oxide (ZnO) is one of wide band-gap oxide semiconductors. For industrial applications, this material has many advantages such as its low cost, abundance of raw materials and environmental friendliness. ZnO has also been attracted considerable attention as an optoelectronic material because of its direct band-gap energy of about 3.37eV at room temperature and a very large free exciton binding energy of 60meV[1-5].

Since the discovery of magnetic properties controlled by changing carrier density in InMnAs[6,8] and GaMnAs[7,8], diluted magnetic semiconductors (DMS) have been of much interest because of their potentiality as a new functional material. The Curie temperature (T_c) of the DMS based on III-V compounds is as low as 100K, and the low solubility of Mn in them prevents us from realizing a large magnetization. Recently, ZnO-based magnetic semiconductor[9-12] has been paid much attention due to the theoretical prediction[13,14] of the possibility of ferromagnetic ordering above room temperature. In case of ZnO, high spin state realized with Mn^{2+} and high solubility of Mn in ZnO are expected. Fukumura et al.[15] reported that Mn atom could be doped in ZnO up to about 35%. However, magnetic properties of Mn doped ZnO were not observed clearly and crystallinity of film was not reported in detail. Therefore, further investigation on the feasibility of ZnO-based DMS is required.

In this report, we deposited $Zn_{1-x}Mn_xO$ films on high quality ZnO epitaxial template fabricated on sapphire substrates by pulsed laser deposition (PLD), and investigate the structural, optical and electrical properties of $Zn_{1-x}Mn_xO$ films.

2. EXPERIMENT

In order to achieve high quality films, a 0.25um-thick epitaxial layer ZnO film was grown on c-plane sapphire substrates by PLD method, and was used as the template for $Zn_{1-x}Mn_xO$ growth. Fig.1 shows the growth system in the present work. The deposition chamber was evacuated with turbo molecular pumps and the base pressure of the growth chamber was lower than 2.5×10^{-4}Pa. Oxygen gas was introduced to the chamber during the deposition (1.2×10^{-2}Pa). The target was fabricated with ZnO (99.999% purity) and MnO (99.9% purity) and was sintered in oxygen atmosphere. Target was placed on a rotational holder located at the bottom of the chamber. The distance between target and substrate was 70mm. The substrate temperature was held constant at 773K. A XeCl laser (wavelength; 308nm) was used and the laser beam was introduced into the reaction chamber through a focusing lens. The laser repetition rate was 5Hz and the energy density of focused laser beam was roughly estimated to be $4J/cm^2$ at the target surface.

The film thickness was measured with a step analyzer and the surface morphology was observed using an optical microscope and atomic force microscopy (AFM) in a contact mode. The crystalline qualities of the deposited films were characterized by X-ray diffraction (XRD) measurements with Cu K_α radiation and reflection high-energy electron diffraction (RHEED).

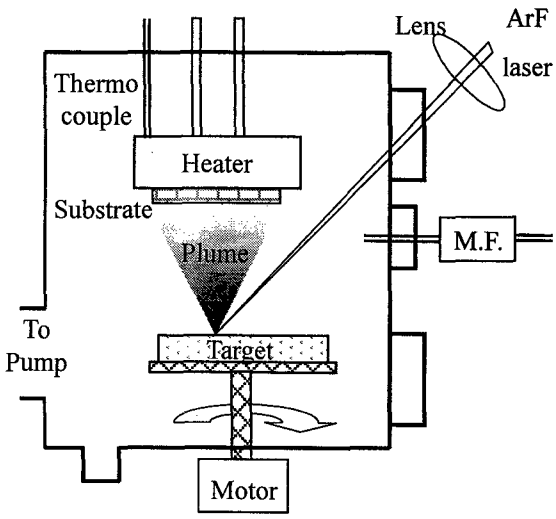

Fig. 1. PLD system for growth of $Zn_{1-x}Mn_xO$ films.

Mn content in the film was measured with electron probe microanalysis (EPMA). A double beam spectrometer was used to obtain transmission spectra. Electrical contact was made using indium-evaporated electrode. The electrical properties of $Zn_{1-x}Mn_xO$ film on high quality ZnO epitaxial template were measured by using Van der Pauw technique in the Hall effect measurements at room temperature.

3. RESULTS AND DISCUSSION

3.1 ZnO template

Fig. 2 shows the typical XRD patterns observed from ZnO film. The rocking curve line width of (0002) peak of ZnO film was $\Delta\omega \approx 190$ [arcsec]. The RHEED pattern of ZnO film showed sharp streak patterns, implying that the film is epitaxially grown on sapphire substrates with smooth surface morphology. From the AFM observation, the root mean square (RMS) value of surface roughness of 1×1um scans of ZnO film was about 0.59nm, consistent with the result of RHEED. Transmission spectra of ZnO film were measured at room temperature.

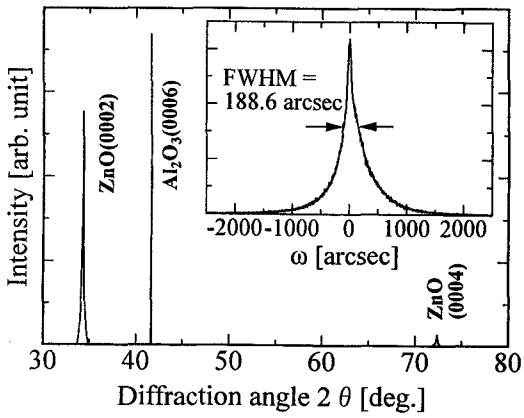

Fig. 2. XRD pattern of ZnO template grown on sapphire substrates. (Inset: XRC spectrum)

ZnO film showed high transparency (over 75%) in the visible region of 380~800nm. Electrical properties of ZnO film were examined using 4-point probe instrument, but resistivity of ZnO film was very high. Due to high resistivity of ZnO film, the mobility and carrier concentration could not be measured precisely.

3.2 Mn-doped ZnO films on ZnO template

Fig. 3 shows XRD patterns of $Zn_{1-x}Mn_xO$ thin films grown on ZnO template with various Mn contents. Below x=0.17, only (000n) peaks were observed. From the XRD results of $Zn_{1-x}Mn_xO$ film, diffraction peaks related to $Zn_{1-x}Mn_xO$ films were overlapped to the (0002) diffraction peak of ZnO template. With increasing Mn content, $Zn_{1-x}Mn_xO$ (000n) diffraction peak move to lower diffraction angle and clearly separate from ZnO peak. For the $Zn_{0.66}Mn_{0.34}O$ film, another peak was observed near ZnMnO (0002) peak, which was assigned as Mn (211) meaning that segregation of Mn occurs. In order to estimate the c-axis lattice constant and the crystalline quality, the (0002) peak of $Zn_{1-x}Mn_xO$ films was separated from the (0002) diffraction peak of ZnO assuming Gaussian fitting. As

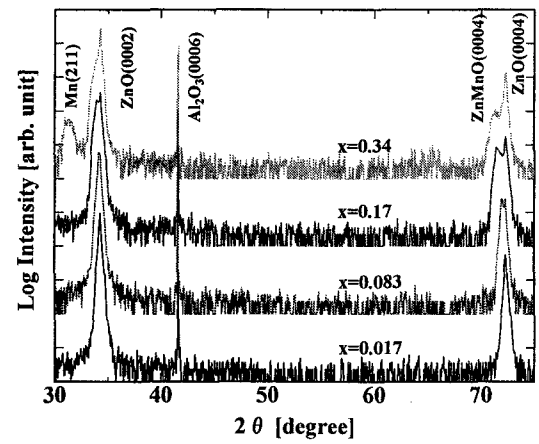

Fig. 3. XRD patterns of $Zn_{1-x}Mn_xO$ films grown on ZnO epitaxial layer.

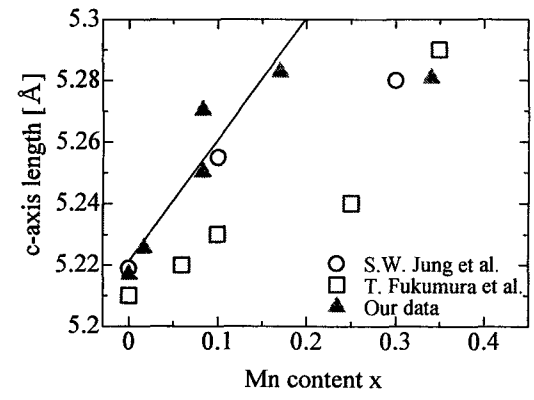

Fig. 4. Mn content dependence of c-axis length of $Zn_{1-x}Mn_xO$ films grown on ZnO epitaxial layer.

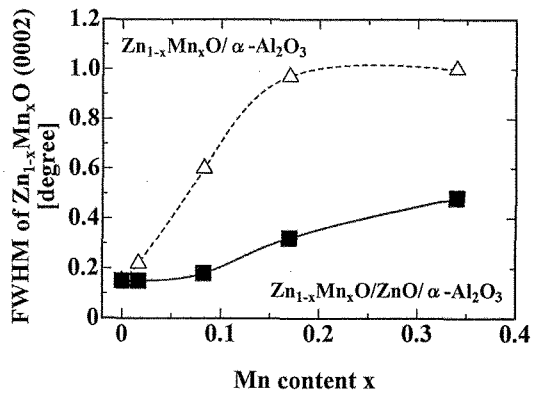

Fig. 5. XRD FWHM of $Zn_{1-x}Mn_xO$ (0002) peaks on ZnO epitaxial layer compared with those of directly grown on sapphire substrates.

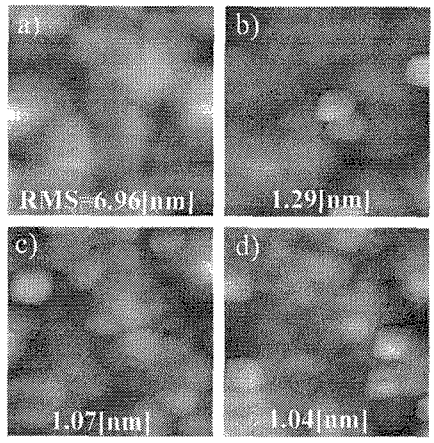

Fig. 6. AFM images of $Zn_{1-x}Mn_xO$ films grown on ZnO epitaxial layer a) x=0.017, b) x=0.083, c) x=0.17, d) x=0.34. The scan area is 1μm×1μm.

shown in Fig. 4, the c-axis lattice constant of $Zn_{1-x}Mn_xO$ thin films was linearly increased with increasing the Mn content, and the estimated lattice constant seems be well agree with that reported by Jung et al. The lattice constant of $Zn_{0.66}Mn_{0.34}O$ was far from the trend. Since the segregation of Mn was observed in $Zn_{0.66}Mn_{0.34}O$, Mn concentration occupying lattice site would be lower that that of measured by EPMA. $Zn_{0.83}Mn_{0.17}O$ film showed an increase in the lattice constant by 1.26%. Fig. 5 shows FWHM of $Zn_{1-x}Mn_xO$ (0002) peaks on ZnO epitaxial layer compared with those of directly grown on sapphire substrates. The FWHM value was increased with increasing Mn content. In $Zn_{0.9}Mn_{0.1}O$ thin film on ZnO template, FWHM was decreased to a half of that from the sample grown directly on the sapphire substrates. The crystallinity of $Zn_{1-x}Mn_xO$ film was improved by the ZnO template, and the $Zn_{0.983}Mn_{0.017}O$ films revealed sharp (0002) peak and the FWHM of the peak was about $\Delta 2\theta \approx 0.18°$.

The RHEED pattern of the $Zn_{0.983}Mn_{0.017}O$ films exhibited elongated spotty diffraction patterns. With increasing Mn doping, RHEED patterns of $Zn_{1-x}Mn_xO$ films were changed from spotty to halo pattern. Epitaxial $Zn_{1-x}Mn_xO$ film was deposited below x=0.17.

AFM images of $Zn_{1-x}Mn_xO$ films were shown in Fig. 6. The root mean square (RMS) roughness on $Zn_{0.983}Mn_{0.017}O$ film was about 7nm, and was decreased in $Zn_{0.917}Mn_{0.083}O$ films, with increasing Mn content. The grain size was also decreased as shown in Fig. 6.

The transmission spectra of $Zn_{1-x}Mn_xO$ films were measured at room temperature and shown in Fig.7. The entire sample was highly transparent in the visible region from 550 to 800nm. Increasing Mn content, absorption was observed below 500nm and the color of $Zn_{1-x}Mn_xO$ film was changed yellowish brown. In case

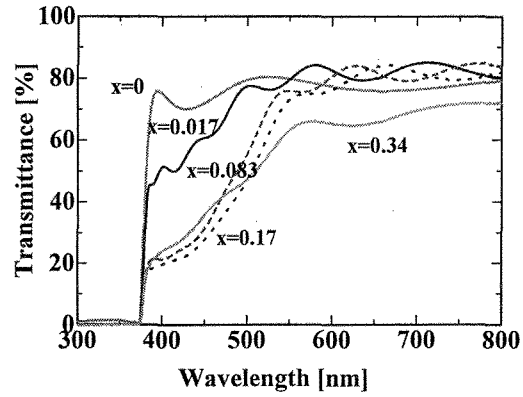

Fig. 7. Transmittance spectra of $Zn_{1-x}Mn_xO$ films on ZnO epitaxial layer at room temperature.

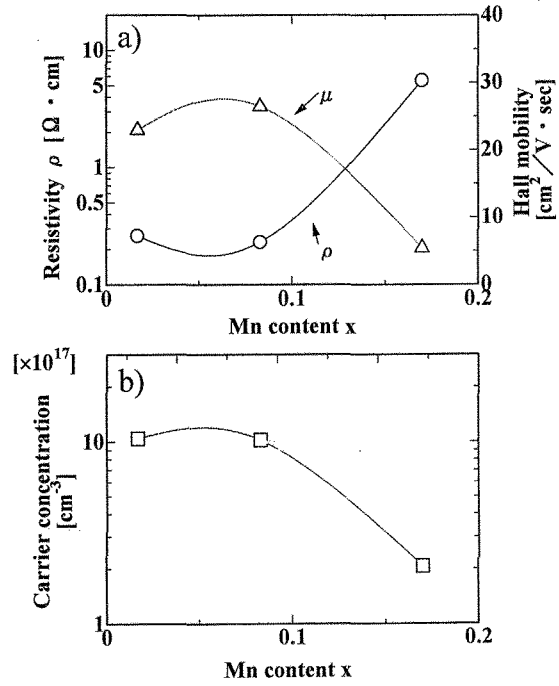

Fig. 8. Hall measurement results of $Zn_{1-x}Mn_xO$ films grown on sapphire substrates a) resistivity and mobility b) carrier concentration.

of the $Zn_{1-x}Mn_xO$ film directly grown on sapphire substrates, the slope of the absorption edge was broadened and shifted to short wavelength with increasing Mn content.

Electrical properties of $Zn_{1-x}Mn_xO$ film on sapphire substrates were measured by Hall effect. The increase of Mn content resulted in an increase of the resistivity. As shown in Fig. 8, carrier concentration and Hall mobility were decreased with increasing Mn content. In $Zn0_{0.917}Mn_{0.083}O$ films, the carrier concentration was about $10^{18}[cm^{-3}]$ and Hall mobility was about $25[cm^2/V \cdot s]$. The lowest resistivity of $Zn_{1-x}Mn_xO$ films in this experiment was about 0.25[Ωcm].

Magnetic characteristics of $Zn_{1-x}Mn_xO$ films were measured using a vibrating sample magnetometer (VSM) at 77K. Ferromagnetic ordering was not clearly observed even at 77K. In order to get ferromagnetic characteristics of $Zn_{1-x}Mn_xO$ DMS film, more detailed research is required.

4. CONCULUSIONS

Epitaxial Mn-doped ZnO thin films have been fabricated on high quality ZnO epitaxial layer by pulsed laser deposition method at 773K. The rocking curve line width of (0002) peak of ZnO epitaxial layer was around 190 [arcsec]. The RHEED pattern of ZnO epitaxial layer showed sharp streak pattern. Crystallinity of $Zn_{1-x}Mn_xO$ films could be improved by using ZnO epitaxial layer. High quality $Zn_{1-x}Mn_xO$ (x=0.017) films revealed sharp (0002) peak and the FWHM of peak was about $\Delta 2\theta \approx 0.18^\circ$. The RMS surface roughness was decreased with increasing Mn content, and RMS value was as low as 1nm. The carrier concentration of $Zn_{1-x}Mn_xO$ films was as high as $10^{18}[cm^{-3}]$.

Reference

1. D. G. Thomas, J. Phys. Chem. Solids **15**, 86 (1960).
2. Y. S. Park, C. W. Litton, T. C. Collins, and D.C. Reynolds, Phys. Rev. **143**, 512 (1966)
3. Z. K. Tang, P. Yu, G. K. L. Wong, M. Kawasaki, A. Ohtomo. H. Koinuma, and Y. Segawa, Solid State Commun. **103**, 459 (1997)
4. Y. Chen, D. M. Bangnail, H. Koh, K. Park, K. Hiraga, Z. Zhu, and T. Yao, J. Appl. Phys. **84**, 3912 (1998).
5. D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, G. Cantwell, and W. C. Harsch, Phys. Rev. B **60**, 2340 (1999)
6. H. Ohno, H. Munekata, T. Penney, S. von Molnar, and L.L.Chang, Phys. Rev. Lett. **68**, 2664 (1992)
7. H. Ohno et al., Appl. Phys. Lett. **69**, 363 (1996)
8. T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science, **287**, 1019 (2000)
9. J. Han, A. M. R. Senos, P. Q. Mantas, J. Eur. Ceram. Soc. **22**, 1653 (2002)
10. X. M. Cheng, and C. L. Chien, J. Appl. Phys. **93**, 7876 (2003)
11. K. Ueda, H. Tabata, and T. Kawai, Appl. Phys. Lett. **79**, 988 (2001)
12. K. Ando, H. saito, Z. Jin, T. Fukumura, M. Kawasaki, Y. Matsumoto, and H. Koinuma, Appl. Phys. Lett. **78**, 2700 (2001)
13. K. Sato, and H. K. Yoshida, Jpn. J. Appl. Phys. **39**, L555 (2000)
14. K. Sato, and H. K. Yoshida, Jpn. J. Appl. Phys. **40**, L334 (2001)
15. T. Fukumura, Z. Jin, A. Ohtomo, H. Koinuma, and M. Kawasaki, Appl. Phys. Lett. **75**, 3366 (1999)
16. S.W. Jung, S.-J. An, Gyu-chul Yi, C.U. Jung, Sung-Ik Lee, and Sunglae Cho, Appl. Phys. Lett. 80, 4561 (2002)

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