

Room Temperature Ferromagnetic ZnO Films Prepared by Solution Chemical Reactions

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Fe introduced ZnO film with characteristic wurtzite structure has been prepared by simple chemical processes composed of chemical deposition of ZnO film and chemical introduction of Fe impurity into the ZnO film in aqueous solutions. The Fe incorporated ZnO film showed ferromagnetism at room temperature and high optical transparency at wavelengths in visible light region as well as n-type semiconducting feature.

Keywords: zinc oxide, iron, transparency, ferromagnetism, chemical reaction

1. Introduction

Zinc oxide (ZnO) is a realistic candidate of the host semiconductor for room temperature ferromagnetic material and transition metals such as Fe, Co, and Ni are appropriate to realize room temperature ferromagnetism.¹⁻³ Supplying room temperature ferromagnetism to ZnO film opens new doors to fabricate smart devices with correlations between the optical, electrical, and magnetic characteristics, because of its high optical transparency, ease to control electrical properties, and possibility for employing to ultra-violet laser emitting device. Many research works were performed by using gas-phase deposition techniques such as radio-frequency magnetron sputtering, molecular beam epitaxy, and laser ablation,^{4,5} the preparation of room temperature ferromagnetic ZnO was not realized at present.

Izaki proposed low temperature chemical processes for preparing wurtzite ZnO film directly from an aqueous solution^{6,7} and for introducing impurity elements into the ZnO film.⁸ Chemical processes are carried out only by simple immersion in aqueous solutions at low temperature of around 333K. Preparation of oxide films from aqueous solutions has several

advantages over gas-phase deposition techniques, and is less hazardous and environmentally friendly. Also, the chemical processes are suited to mass production, because the preparation equipment is not expensive. In this paper, we report a transparent room temperature ferromagnetic zinc oxide incorporated Fe impurity and the low temperature preparation with chemical reactions.

2. Experimental procedure

The ZnO film was deposited chemically on a glass substrate by a simple immersion for 1h in an aqueous solution containing 0.1 mol/L zinc nitrate hydrate and 0.03 mol/L dimethylamineborane (DMAB) at 333K. And then, the introduction of Fe impurity into the ZnO film was carried out by immersion in an aqueous solution containing iron(III) nitrate hydrate at 323K. Prior to the preparation, glass substrates were rinsed in acetone, and then catalyzed by an industrial activation process (C. Uyemura & Co. Ltd., S-10X, MSA-27, and A-10X). The solutions were prepared with reagent grade chemicals and distilled water purified using a Milli RX12 Plus system (Millipore Corporation).

3. Results and discussion

Transparent film with yellow color could be obtained on the glass substrate by our chemical process. From the ICP analysis and film weight, the film composition was estimated to be 33mol%Zn, 17mol%Fe, and 50mol%O. Figure 1 shows depth profiles of Fe, Zn, and O for the $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ film. The depth profiles were recorded with ULVAC-PHI SIMS model 6650 with Cs^+ primary ion source. The depth of sputtered crater formed after the SIMS analysis was determined by using a surface roughness analyzer. $^{64}\text{Zn}^+$, $^{56}\text{Fe}^+$, and $^{16}\text{O}^+$ ions were detected for recording depth profiles. The $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ film was composed of aggregates of hexagonal columnar grains grown to the direction normal to the substrate surface and had smooth surface of 2.4nm in root mean square roughness (Rms) calculated from the atomic force microscopic image. Any defects such as pores could not be located through the film thickness. The surface morphology and structure were almost the same as those for ZnO film. It was confirmed with a SEM-EDX that the Zn and Fe elements were distributed homogeneously on the surface of the film. Also, from the depth profiles, Fe, Zn, and O elements were distributed homogeneously throughout the film thickness and

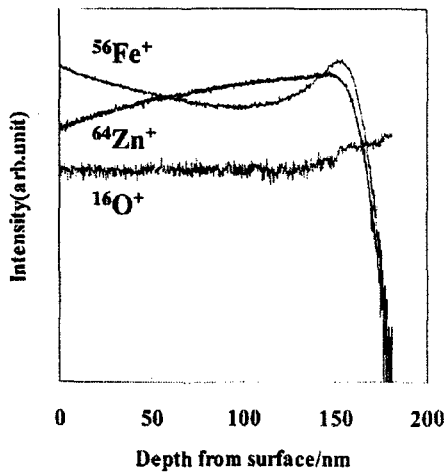


Fig. 1 Depth profiles of Fe, Zn, and O taken with a SIMS for $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ film.

at a interface between the film and glass substrate Fe and Zn signals began to fall and O signal increased slightly because of exposing the glass substrate.

Figure 2 shows X-ray diffraction spectrum for the $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ film. The diffraction angles were externally referenced to those from a high purity Si powder. Several peaks could be observed on the X-ray diffraction spectrum and were assigned to those for ZnO with wurtzite structure. Unit-cell parameters calculated from peak angles were 0.3255nm in a-axis and 0.5212nm in c-axis, which were larger than those for standard values and were nearly equal to those for chemically deposited ZnO film. Any peaks identified as iron compounds such as iron oxides could not be observed on the X-ray diffraction spectrum, in spite of the large content of Fe impurity.

The resistivity, carrier concentration, and mobility were evaluated at 296K with the van der Pauw method using a hall effects measuring system under 0.5T magnetic field. The ohmic contacts were obtained by evaporating thin gold layer, which were electrically connected with gold wire leads by a small dot of In solder. The resistivity, carrier concentration, and mobility were obtained by averaging five measurements. Chemically deposited ZnO film showed resistivity of $5.6 \times 10^5 \Omega\text{cm}$ with carrier concentration of $2 \times 10^{13} \text{cm}^{-3}$ and mobility of $0.63 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. The $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ film showed increased resistivity of $2 \times 10^6 \Omega\text{cm}$ with decreased carrier concentration of $6.6 \times 10^{12} \text{cm}^{-3}$ and

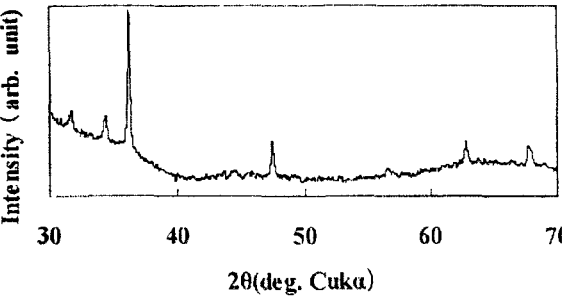


Fig. 2 X-ray diffraction spectrum for $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ film.

decreased mobility of $0.4\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. These facts indicated that the incorporated Fe^{3+} ion did not act as a donor in ZnO film. The decrease in mobility may be due to lattice distortion and increase in ionic defects induced by incorporating Fe impurity, because of no change in morphology and size of ZnO grains.

Figure 3 shows magnetic characterizations for ZnO and $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ films. The magnetization curves were recorded with a vibrating sample magnetometer at room temperature. Chemically deposited ZnO film showed anti-ferromagnetic feature at room temperature. The $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ film showed magnetic hysteresis curve characteristic to ferromagnetic materials and showed about 7emu/cc in saturation magnetization and 85Oe in coercive force.

The $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ film showed high optical transparency at wavelength in visible light region, about 85% at wavelength of 600nm, and showed clear yellow color due to Fe^{3+} ion contained in the film. The optical band gap energy was calculated from the absorption edge on the absorption spectrum recorded with a spectrophotometer and was 3.3eV characteristic value of wurtzite ZnO crystal.

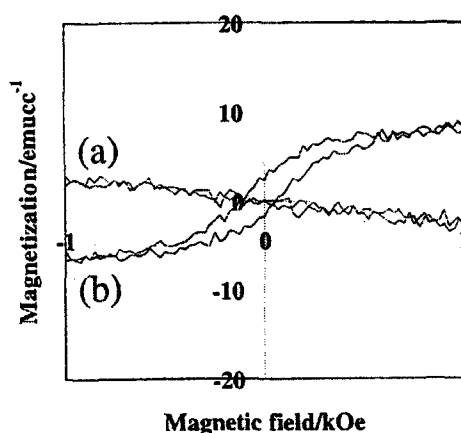


Fig. 3 Magnetization curves for ZnO(a) and $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ films(b).

4. Conclusion

$\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ film has been prepared by a chemical process composed of chemical deposition of ZnO film and chemical introduction of Fe impurity into the ZnO film. The $\text{Fe}_{0.17}\text{Zn}_{0.33}\text{O}_{0.5}$ film showed room temperature ferromagnetism with 7emu/cc in saturation magnetization and 85Oe in coercive force and high optical transparency at wavelengths in visible light region as well as n-type semiconducting feature.

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