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$Zn_{1-x}Cu_xO$ Films Grown by Remote-plasma-enhanced Metalorganic Chemical Vapor Deposition with $Cu(dibm)_2$

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1. Introduction

ZnO has some typical features of a wide bandgap energy (Eg) of 3.28 eV and a large excitonic binding energy of 60 meV at room temperature, which suggests potential applications for novel optical devices. We have already demonstrated ZnO-based alloy film systems utilizing remote plasma enhanced metalorganic chemical vapor deposition (RPE-MOCVD), exhibiting a bandgap energy lineup from 1.9 eV to 3.7 eV with cadmium and magnesium[1]. In addition, RGB electroluminescence emissions have been successfully achieved by current injection using ZnO-based heterojunctions[2], which clearly indicates a feasibility of ZnO-based oxide semiconductor material systems for photonic application. The research into high-quality ZnO-based alloy systems and efficient p-type doping method is becoming increasingly important.

While $Zn_{1-x}Cu_xO$ system grown by laser molecular beam epitaxy, have been recently reported as a candidate with p-type conductivity control[3] and a small bandgap narrowing[4] from the viewpoint of ferromagnetic semiconductor, the details are controversial. In this paper, we describe $Zn_{1-x}Cu_xO$ film growth by RPE-MOCVD with $Cu(dibm)_2$: Copper bis(diisobutyrylmethanate) and the optical properties.

2. Experimental

$Zn_{1-x}Cu_xO$ films were grown on a-plane sapphire substrates by RPE-MOCVD, using DEZn: diethyl zinc, $Cu(DIBM)_2$: copper bis(diisobutyrylmethanate) and oxygen radical generated by a radio frequency (RF) of 13.56MHz as material sources. Growth conditions for $Zn_{1-x}Cu_xO$ are shown in Table I. We have both nitrogen and hydrogen as a carrier gas. We have characterized the crystallinity using x-ray diffraction (XRD). The bandgap energies and optical properties were characterized by optical transmission measurements and photoluminescence measurements. The contents of the films were analyzed by atomic absorption spectroscopy. The electrical specification of the films was done by Van der Pauw method.

3. Results and discussion

Figure 1 (a) shows the XRD patterns on $Zn_{1-x}Cu_xO$ films. Here, samples used for this study were grown at 400 ° C with N_2 carrier gas. The XRD results show that the (0002) diffraction angles are becoming larger with increasing Cu content. Figure 1(b) summarizes that the c-axis length becomes gradually smaller with increasing Cu content, indicating the substitution of Zn^{2+} by smaller Cu^{2+} ion. This tendency coincides with the previous result[4]. Typically, $Zn_{1-x}Cu_xO$ with the Cu content x of 2.9% has the smaller c-axis lattice parameter by 0.38% comparing with that of ZnO film.

Optical transmission spectra of $Zn_{1-x}Cu_xO$ films showing a change of absorption edge in Fig. 2(a), and the corresponding optical band edges are summarized In Fig. 2(b). The optical bandgap energies were determined from a plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$). It is found that the optical band edges are becoming larger, typically 3.30 eV at x= 0.0026 with increasing Cu content. However, it is known that copper oxide (CuO) exhibits a broad violet luminescence band around 403nm (3.08eV) with a broad tail in the green spectral region, while it has a narrow band gap of 1.2 eV[5] and, on the contrary, cuprous oxide (Cu_2O) has a direct bandgap of 2.17eV at 6K with four different excitonic states[6]. Accordingly, it seems that the blue shift tendency of the band gaps of $Zn_{1-x}Cu_xO$ films with relatively small content x in Fig. 2 (b) does not coincide with the tendency of the above oxide systems. The further experiments on $Zn_{1-x}Cu_xO$ films with larger Cu content are necessary.

Figure 3 shows the preliminary photoluminescence spectrum of the ZnO:Cu film at 20K. The sample used here was grown at 300 ℃ with H_2 carrier gas. We can find the 3.27 eV peak associated with the DAP of the film indicating p-type nature, which corresponds to hole concentration of 1×10^{19} cm^{-3}.

4. Conclusions

We have successfully grown $Zn_{1-x}Cu_xO$ films utilizing RPE-MOCVD with $Cu(dibm)_2$. It was found that the c-axis lattice parameter gradually decreased with increasing the Cu content and the typical corresponding bandgap of 3.30 eV at x=0.019. We have also confirmed Cu doped ZnO film shows p-type conduction nature.

References

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Table Ⅰ. Growth conditions of $Zn_{1-x}Cu_xO$.

Growth temperature	300~400 °C
RF power	20~40 W
Growth pressure	0.1 Torr
Carrier gas	N_2 or H_2
Substrate	a-plane sapphire

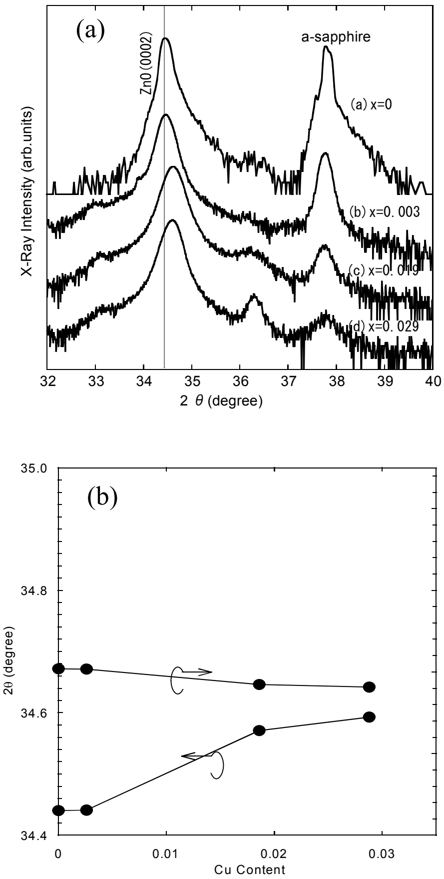

Fig. 1 (a)X-ray diffraction of $Zn_{1-x}Cu_xO$ (x=0,0.003,0.019,0.029)

(b)C-axis length versus Cu content of $ZnC_{1-x}u_xO$ alloy films.

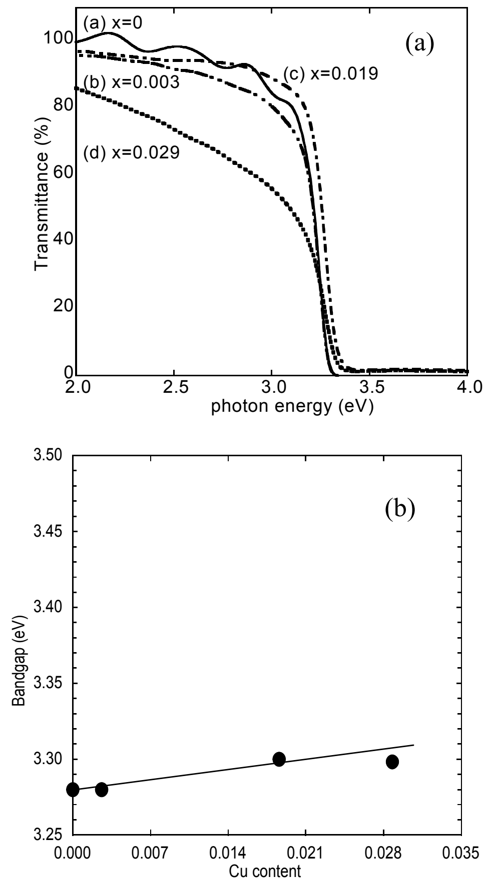

Fig. 2 (a) Optical transmission spectra of $Z_{1-x}nCu_xO$ (x=0.003, 0.019, 0.029)

(b) Band gap energy of $Zn_{1-x}Cu_xO$ alloy films versus Cu content.

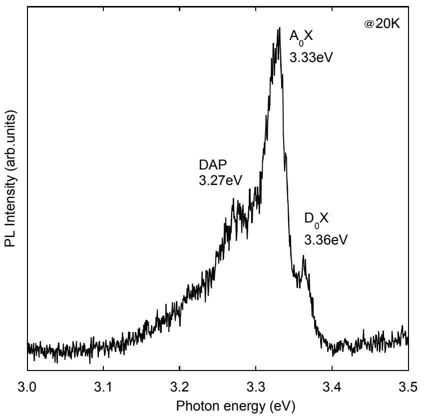

Fig. 3 PL spectra (at 20K) of as-grown ZnCuO at 300℃.