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Morphological, electrical and optical properties of highly oriented undoped and doped zinc oxide and cadmium oxide films grown by atmospheric-pressure chemical vapor deposition

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ABSTRACT

Morphological, electrical and optical properties of undoped and Ga-doped ZnO and undoped CdO films grown on sapphire (Al_2O_3) substrates by the atmospheric-pressure CVD method using Zn, Cd, H_2O and $GaCl_3$ as source materials were investigated. The influences of the deviation from the stoichiometric composition were clearly observed on photoluminescence (PL), photoluminescence excitation (PLE) and photoacoustic (PA) spectra of the undoped ZnO films. The carrier concentration n in the undoped ZnO film was found to be dominated by the hydrogen related donors rather than native defects. The Ga doping in ZnO film led to the degradation of surface flatness, the increase in carrier concentration n and the decrease in Hall mobility μ. With increasing carrier concentration n, the Ga-related neutral donor bound exciton line of the Ga-doped ZnO film shifted towards shorter wavelengths, accompanied by asymmetric broadening. This is probably due to the screening of the Coulomb potential by heavily introduced donors and free-electrons. Highly oriented CdO films with smooth surfaces were successfully grown on r-Al_2O_3 substrates. Transmittance values for the CdO/r-Al_2O_3 films were higher than 70% in the range of 700–2500 nm. Under the assumption that the reflectance is neglected, the direct and indirect optical gap energies of the CdO films determined from the transmittance spectra were 2.34–2.38 eV and 1.98–2.06 eV, respectively. PA measurements for the CdO films revealed that the tail states associated with the residual impurities and/or the structural defects reduce the direct optical gap energy. A maximum Hall mobility μ of 178 cm^2/Vs was achieved on the CdO/r-Al_2O_3 film with the carrier concentration n of 4.2×10^{19} cm^{-3}.

1. Introduction

Zinc oxide (ZnO) with a wurtzite structure is one of the promising materials for ultraviolet-light-emitting devices because of its wide band gap energy of 3.37 eV at room temperature (RT) and its large exciton binding energy of ~60 meV [1]. Cadmium oxide (CdO) with a rock salt structure has a wide direct band gap of ~2.6 eV and exhibits an n-type conduction. Recently, CdO films have attracted much attention because of their high Hall mobility values. Hall mobility of ~460 cm^2/Vs was obtained in the undoped CdO film with carrier concentration of 3.4×10^{18} cm^{-3} grown by rf-magnetron sputtering [2]. A maximum Hall mobility of 609 cm^2/Vs was achieved on the epitaxial CdO film doped with 2.5% Sn prepared by pulse laser deposition (PLD) [3].

Moreover, solid solutions of ZnO and CdO, namely (Cd,Zn)O alloys, are expected to be a good candidate for the active layers of ZnO based light emitting diodes (LEDs) [4] and laser diodes (LDs) driven in the wide visible region. Usually ZnO films and ZnO based quantum wells have been grown on c- and a-plane sapphire substrates, where they have <001> growth direction, i.e. c-axis oriented growth. However, electrons and holes confined in the active layers of (Zn,Mg)O/ZnO and ZnO/(Cd,Zn)O quantum wells grown in the <001> orientation will be spatially separated by spontaneous internal electric fields along the c-axis resulting in the decrease in internal quantum efficiency [5]. One of the possible solutions to avoid this problem is growth of the non-polar films, i.e. a-axis oriented growth.

Chemical vapor deposition (CVD) methods are effective in obtaining high-quality films at low cost. We believe that the key to establish the conductivity control involving conduction type control is the impurity doping under the accurate stoichiometry control. Complete separation of the source material for zinc (Zn) and that for oxygen (O) is one of the important factors for adjusting the supply ratio of O to Zn. In the previous papers, we have reported the successful growth of epitaxial ZnO films on r-plane sapphire (denoted by "r-Al_2O_3") substrates by atmospheric-pressure CVD (AP-CVD) method using Zn and H_2O as source materials [6]. Moreover, preliminary to the film growth, CdO nanostructures with various shapes were successfully grown on Au nanocolloid coated

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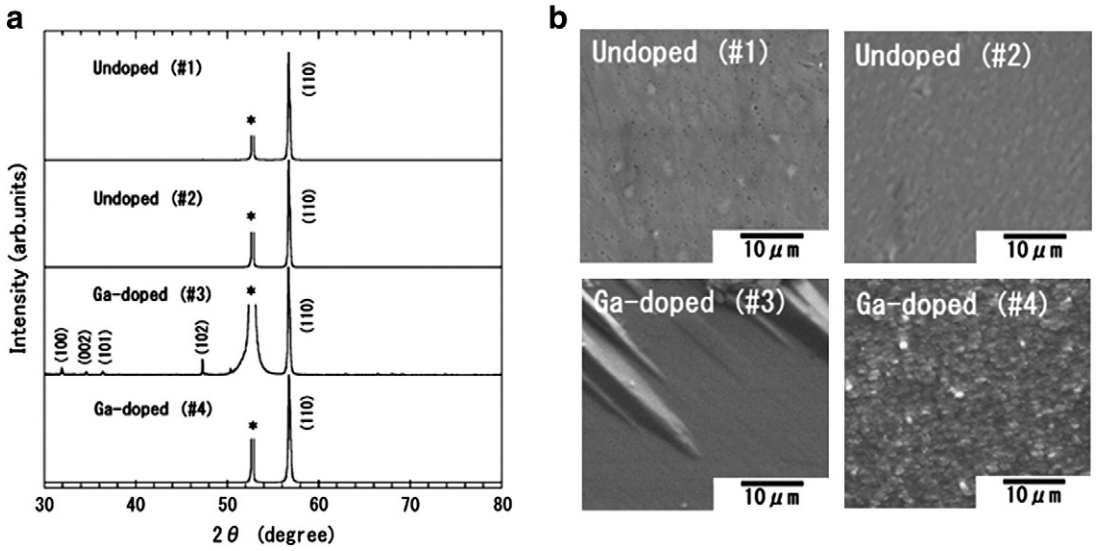

Fig. 1. (a) XRD patterns and (b) surface SEM images of the undoped and Ga-doped ZnO films grown on *r*-Al_2O_3 substrates grown at substrate temperatures (T_S) of 700 °C (sample numbers 1 and 2: undoped films and sample numbers 3 and 4: Ga-doped films). Growth conditions of these films are listed in Table. 1.

c-plane sapphire (denoted by "*c*-Al_2O_3") substrates by AP-CVD using Cd powder and H_2O as source materials [7].

In this paper, we will discuss morphological, optical and electrical properties of undoped and Ga-doped ZnO/*r*-Al_2O_3 films and undoped CdO/*c*- or *r*-Al_2O_3 films grown by AP-CVD in terms of growth condition and temperature dependence.

2. Experiments

2.1. CVD growth

2.1.1. Undoped and Ga-doped ZnO

Undoped and Ga-doped ZnO films were grown on *r*-Al_2O_3 substrates by the AP-CVD apparatus with a horizontal furnace and vaporizers for H_2O and $GaCl_3$ [8]. The horizontal furnace had two temperature zones; one was for heating the substrate and the other for vaporizing high purity Zn powder (Sigma Aldrich, purity 99.995%). The growth reactor was a quartz tube (1000 mm in length and 35 mm in diameter). Substrate temperature (T_S) was chosen between 550 and 750 °C. Source temperature of Zn (T_{Zn}) was varied in the range from 550 to 700 °C. Temperatures of vaporizers for H_2O (T_{H_2O}) and $GaCl_3$ (T_{GaCl_3}) were 45–75 °C and 50–80 °C, respectively. Both the H_2O and $GaCl_3$ vapors were transported from their vaporizer to the growth reactor by N_2 carrier gas. Flow rate of the carrier gas for Zn (F_{Zn}) and that for H_2O (F_{H_2O}) were 120 and 320 sccm, respectively. Flow rate of the carrier gas for $GaCl_3$ (F_{GaCl_3}) was the same as F_{Zn} because both the sources were introduced to the substrate through the common path. The source supply ratio of H_2O to Zn, denoted hereafter by "H_2O/Zn ratio", was changed by T_{Zn} and T_{H_2O}. Growth time (t_g) was 2 h. Thicknesses of the undoped and Ga-doped films were distributed in the range from 0.36 to 12 μm, depending on growth condition. Regardless of such large layer thicknesses, no crack was observed.

Table 1
Growth conditions of undoped and Ga-doped ZnO films.

Sample number	Substrate	T_S (°C)	T_{Zn} (°C)	T_{H_2O} (°C)	T_{GaCl3} (°C)	F_{Zn} (=F_{GaCl_3}) (sccm)	F_{H_2O} (sccm)	Growth time (h)
#1	*r*-Al_2O_3	700	700	54	–	120	320	2
#2	*r*-Al_2O_3	700	700	65	–	120	320	2
#5	*r*-Al_2O_3	700	700	45	–	120	320	2
#3	*r*-Al_2O_3	700	700	54	80	120	320	2
#4	*r*-Al_2O_3	700	675	65	60	120	320	2
#6	*r*-Al_2O_3	700	675	54	60	120	320	2

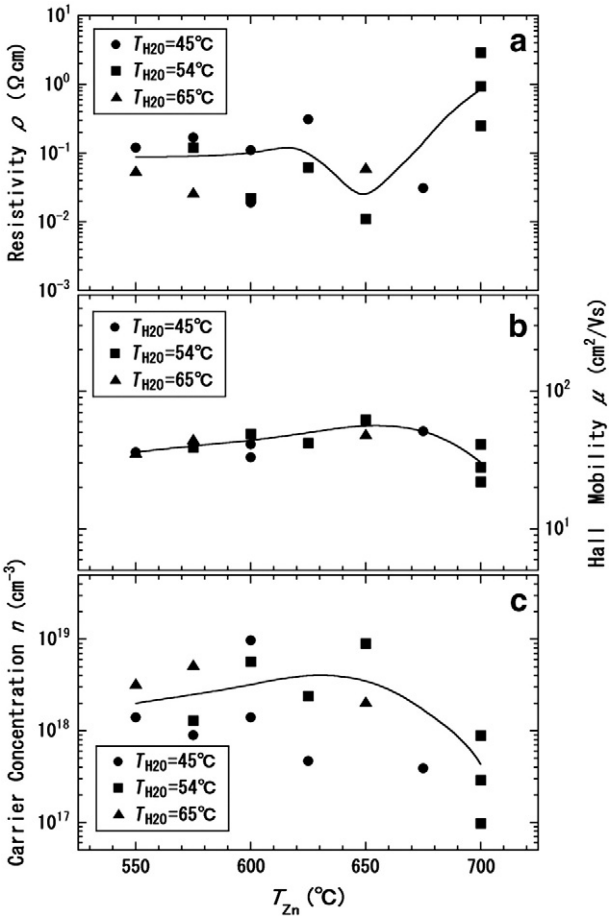

Fig. 2. Variations of (a) resistivity ρ, (b) Hall mobility μ and (c) carrier concentration n as a function of Zn source temperature (T_{Zn}) for the undoped ZnO films grown at different H_2O vaporizer temperatures (T_{H_2O}) of 45, 54 and 65 °C. Values of T_S, F_{Zn} and F_{H_2O} are kept at 700 °C, 120 sccm and 320 sccm, respectively.