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Growth and characterization of ZnMgSrO thin films lattice-matched to ZnO and with deep-UV energy band gap

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ABSTRACT

Quaternary $Zn_{1-x-y}Mg_xSr_yO$ films were grown and characterized in detail, which were observed to be lattice matched to the ZnO by the X-ray diffraction (XRD). Cathodoluminescence measurement showed that near-band UV emission peaks of the samples move toward higher energy as concentration of Mg and Sr increases, to 3.67 eV for the $Zn_{0.87}Mg_{0.08}Sr_{0.05}O$ and to 4.02 eV for the $Zn_{0.72}Mg_{0.17}Sr_{0.11}O$. It was also observed by the scanning electron microscopy and the XRD that the films are single crystalline. It is believed that the ZnMgSrO films would be one of the important candidate materials for the high quality deep-UV optoelectronic devices.

1. Introduction

Zinc oxide (ZnO) has been widely studied as the potential substrate material for the UV optoelectronics devices, with wide direct energy band-gap (E_g) and high exciton binding energy.[1,2] One of the important requirements to fabricate high performance UV devices is the energy band-gap engineering to obtain large enough E_g and to realize hetero-junction and/or multi-quantum-well devices.[3,4]

Ternary $Zn_{1-x}Mg_xO$ alloys have been mainly investigated as the active material for the UV emission.[5,6] Wurzite ZnMgO films with energy band gap as high as ~4.55 eV have been demonstrated, by adding about 55 mol% of MgO.[7] Lattice constant of the ZnMgO also decreases with the addition of MgO to ZnO, however, which results in residual strains and/or dislocations within the films.[7]

In fact, more serious problems exist in the case of the AlGaN/GaN system, which are the most intensively studied materials for the UV optoelectronics. It is well known that residual strains and/or high density of misfit dislocations exist within the AlGaN/GaN layers, which act as the non-radiative recombination center and deteriorate performance of the optoelectronic devices.[8]

It would be therefore important and beneficial to develop a UV range material system, with no or very low mismatch strain when grown on ZnO and/or GaN substrates. In this work, quaternary $Zn_{1-x-y}Mg_xSr_yO$ films were fabricated by simultaneously alloying ZnO with MgO and SrO and characterized in detail. It is shown that this material system possesses large enough E_g to achieve the UV devices and has the lattice constant matched with that of ZnO and GaN. Structural properties and emission spectra of the ZnMgSrO films were characterized in detail, mainly utilizing the X-ray diffraction (XRD) and the cathodoluminescence (CL) measurement.

2. Experimental details

The ZnMgSrO films investigated in this study were grown on (001) Al_2O_3 substrates using an RF magnetron sputtering system, at the growth temperature of 600 °C and the RF power of 120 W. The chamber pressure was maintained at 1.3 Pa during the sputtering process by flowing oxygen at a constant rate of 40 sccm. Before the film growth, targets were pre-sputtered for 10 min to remove possible surface contamination. About 500 nm thick films were obtained after 2 h sputtering, except that thickness of the $Zn_{0.68}Mg_{0.20}Sr_{0.12}O$ film was ~200 nm.

Cathodoluminescence (CL, Shimadzu AT-100AP) spectra were obtained at room temperature (RT) using a spectrometer with wavelength range of 100~800 nm. A Philips X′Pert PRO-MRD high-resolution 4-crystal triple axis X-ray diffractometer (XRD) was employed to study crystallinity and crystallographic orientation of the prepared ZnMgSrO films, using the CuKα radiation. A Hitachi S-4700 field emission scanning electron microscopes (SEM), operating at 15 kV, and a Digital Instruments MultiMode atomic force microscope (AFM),

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operating at the tapping mode using the phosphorous-doped Si tip, were also used to observe microstructure of the samples. Quantitative chemical analysis of the films was performed using a Shimadzu EPMA-1610 electron probe microanalysis system.

3. Results and discussion

To prepare the ZnMgSrO films, lattice constants of the films were estimated using the Vegard's rule. According to the rule, the lattice constants linearly vary with concentration of the component elements, ZnO, MgO, and SrO in this case [9]. It is therefore expected that the $Zn_{1-x-y}Mg_xSr_yO$ film will have a lattice constant equal to the ZnO materials when the x/y ratio is about 1.5, as ZnO has a hexagonal close-packed (hcp) structure with d(100) = 0.325 nm, the face-centered cubic (fcc) SrO has a lattice constant d(110) of 0.365 nm, and the fcc MgO has a d(110) of 0.298 nm. It is reminded that the (110) plane of fcc structure corresponds to the (100) plane of the hcp structure.

Fig. 1 shows (a) high resolution (HR) XRD patterns and (b) CL spectra of the $Zn_{1-x-y}Mg_xSr_yO$ films sputter grown on Al_2O_3 with the x/y ratio of 1.55~1.6. The XRD spectrum from a ZnO/Al_2O_3 film is also shown in Fig. 1a, for the purpose of the comparison. It is shown from the HR-XRD (Fig. 1a) that the (002) peaks of all of the films appear at the same position, ~34.42°, except for the $Zn_{0.68}Mg_{0.20}Sr_{0.12}O$ film, indicating that the lattice matched films were indeed obtained. In Fig. 1b, CL near-band emissions from the quaternary films move toward higher energy with addition of MgO and SrO, appearing at 337 nm (3.67 eV) for the $Zn_{0.87}Mg_{0.08}Sr_{0.05}O$ film and at 308 nm (4.02 eV) for the $Zn_{0.72}Mg_{0.17}Sr_{0.11}O$ film.

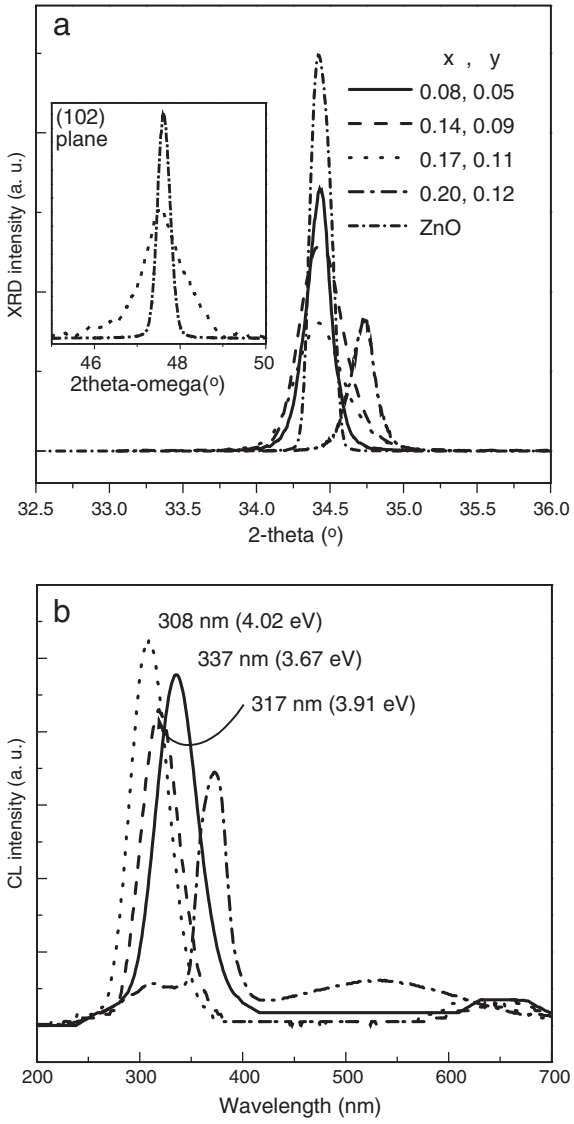

Fig. 1. Characterization results of the $Zn_{1-x-y}Mg_xSr_yO$ films sputter grown on Al_2O_3 with the x/y ratio of ~1.5, (a) HR-XRD spectra and (b) CL spectra. The XRD spectrum from a ZnO/Al_2O_3 film is also shown in (a), for the purpose of the comparison.

It is mentioned that d(002) is mainly measured and discussed in Fig. 1a, instead of d(100), as only (002) and (004) planes are measured in the XRD patterns obtained using the standard geometry. Asymmetric XRD measurements were also performed to extract the in-plane parameters. The (102) peak of a $Zn_{0.72}Mg_{0.17}Sr_{0.11}O$ film is observed at ~47.53° as shown in the inset box of Fig. 1a, exactly same position as that of the ZnO films, indicating that the in-plane parameters are also matched to ZnO.

Fig. 2 summarizes results of the CL and the XRD measurements of the $Zn_{1-x-y}Mg_xSr_yO$ films, measured from Fig. 1. It is clearly noticed that the films are indeed lattice matched to the ZnO materials, with d(001) ≈ 0.521 nm, as predicted by the Vegard's rule. There are slight mismatch in the lattice constant between the films and the ZnO, probably because concentration of MgO and SrO was not exactly controlled.

The Vegard's rule was also applied to estimate the band-gap energies of the lattice-matched ZnMgSrO films, and the results are represented by the dotted lines in Fig. 2. The calculation suggested that the band-gap energies would be ~3.67 eV for the $Zn_{0.87}Mg_{0.08}Sr_{0.05}O$ film, ~3.91 eV for the $Zn_{0.77}Mg_{0.14}Sr_{0.09}O$ film, and ~4.02 eV for the $Zn_{0.72}Mg_{0.17}Sr_{0.11}O$ film, as E_g values of MgO, SrO, and ZnO are 7.8 eV, 5.3 eV, and 3.3 eV, respectively.

It is noted that the measured E_g values are 0.1~0.3 eV lower than the calculated values. This is consistent with previous reports that band-edge luminescence peaks appear at a lower energy than the actual E_g in the case of ZnMgO films[10]. In fact, it was also reported that the measured E_g values of ZnMgO alloys are lower than the ones calculated using the Vegard's rule [11]. It is also mentioned that Eg values of cubic MgO and cubic SrO were used to calculate Eg of wurzite ZnMgSrO films, which could be one of the reasons why the measured Eg is different from the calculated one. Another possibility would be the "bowing" of the energy gaps, occurring in many non-ideal compounds.[12] Further investigation is certainly necessary to clarify what would cause this phenomenon.

Fig. 3 shows structural properties of (a, b) $Zn_{0.72}Mg_{0.17}Sr_{0.11}O$ film and (c, d) $Zn_{0.68}Mg_{0.20}Sr_{0.12}O$ film, (a, c) a cross-sectional SEM image

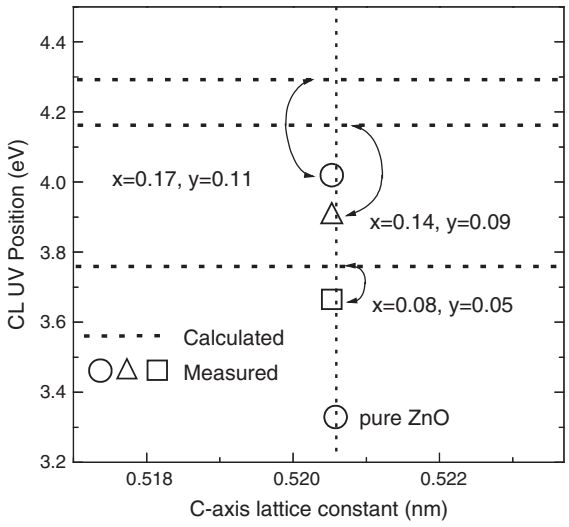

Fig. 2. CL UV peak position and lattice constant of the ZnMgSrO films measured from Fig. 1. Estimated E_g values using the Vegard's rule are also shown.