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Temperature-dependent photoluminescence properties of $ZnO/Zn_{1-x}Mg_xO$ multilayers grown by pulsed laser deposition

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ABSTRACT

$ZnO/Zn_{0.9}Mg_{0.1}O$ multilayer thin films were deposited on p-Si(1 0 0) substrates using pulsed laser deposition technique at varying substrate temperatures ranging from 300 °C to 700 °C. X-ray diffraction (XRD) studies reveal that the films possess a preferred (0 0 0 2) growth orientation with the intensity gradually increasing with substrate temperature. Temperature-dependent photoluminescence properties were studied in details to investigate the origin of near band edge emission and the quenching mechanism. The band gap at 10 K shows a blue-shift with the increase of substrate temperature, but is found to be higher for the sample grown at 500 °C than that of the 600 °C and 700 °C grown samples at all temperatures above 25 K. It appears that the dominant recombination mechanism changes from donor-bound to localized excitons with the increase in substrate temperature.

1. Introduction

ZnO is an attractive material for application in optoelectronic devices like laser, LEDs, UV detector [1–4], due to its wide band gap (3.37 eV at room temperature) and large excitonic energy (60 meV). The wavelength for emission or detection can be tuned by using either ZnO quantum well or by alloying ZnO with a higher band gap material. MgO has a band gap of about 6.7 eV. Though the equilibrium solid solubility of MgO in ZnO in the bulk form is limited (less than 4 mol. %), but the ionic radii of Mg^{2+} (0.057 nm) is similar to that of Zn^{2+} (0.060 nm) [5]. Since physical vapor deposition is a non-equilibrium processing route, solid solubility of MgO in ZnO can be significantly enhanced (say upto 33 mol%) [6] in the metastable state after thin film deposition. Thus, when ZnO is alloyed with MgO, the band gap can be tuned and can be increased to above 4 eV [6]. When the higher band gap ternary $Zn_{1-x}Mg_xO$ alloy is grown in combination with a lower energy gap ZnO, they can provide a barrier/well heterostructure required for developing resonant tunneling diode (RTD) [7]. Double barrier resonant tunneling devices (DBRTD) are much attractive for ultra-high frequency mixing and microwave–millimeter wave oscillation circuits, alternating to direct current converters, multi-valued logic, etc. It has been found that much higher optical efficiencies at room temperature can be obtained from core-shell ZnO/ZnMgO multi-quantum well heterostructures [8]. Tuning of optical band gap can also be done by varying the ZnO sublayer thickness in ZnO/MgO multilayers [9]. Besides band gap tuning, MgZnO thin film shows much higher sensor response to hydrogen than the undoped ZnO films [10].

There are several techniques for growing ZnO thin films, such as chemical vapor deposition [11], molecular beam epitaxy (MBE) [12], sputtering [13], pulsed laser deposition [14], and sol–gel technique [15]. Of these, pulsed laser deposition [16] and laser-induced MBE [17] have been successfully used to deposit high quality epitaxial layers of ZnO on sapphire and other substrates. These films are highly suitable for electronic and optoelectronic devices. In this paper, we report the growth of ZnO/ZnMgO multilayer thin films of same barrier and well thickness on p-Si(1 0 0) substrates at varying substrate temperatures using pulsed laser deposition technique. The effect of substrate temperature on the structural and optical properties of the films has been studied. Temperature-dependent photoluminescence properties of these films are also reported.

2. Experimental details

ZnO/ZnMgO multilayer thin films were deposited on p-Si(1 0 0) substrates at varying substrate temperatures (T_s) by the pulsed laser deposition (PLD) technique. Two ceramic targets of ZnO and $Zn_{0.9}Mg_{0.1}O$ (both of purity 99.999%) were used for this purpose.

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For the preparation of $Zn_{1-x}Mg_xO$ target ($x=0.1$), the desired amount of MgO powder was mixed homogeneously with ZnO powder, and disk-shaped specimens of 20 mm in diameter and 5 mm in thickness were obtained by the uniaxial pressing at 6×10^6 kg/m^2. The specimens were sintered at 800 °C for 2 h and at 1200 °C for 4 h to obtain high density targets. Before loading into the growth chamber, the substrates were degreased in acetone and ethanol followed by etching in 1% HF solution for 2 min to remove the native oxide layer from the surface of the substrate, and then rinsed in de-ionized water. A KrF excimer laser ($\lambda=248$ nm, $\tau=25$ ns) at an energy density of ~2 J/cm^2 was used for the ablation of the targets. The substrate was placed at a distance of 4 cm from the target. The growth chamber was evacuated to a base pressure of 1×10^{-6} mbar using a combination of rotary and turbo pumps before deposition. To reduce the lattice mismatch-induced strain effect, a ZnO buffer layer of about 145 nm thick was grown on the p-Si(1 0 0) substrate at 100 °C in vacuum. Then, a series of 3 period ZnO/ZnMgO multilayers were grown at different substrate temperatures varying from 300 °C to 700 °C. During the multilayer film deposition, the oxygen pressure inside the chamber was kept at 1×10^{-1} mbar and the pulse repetition rate was maintained at 10 Hz. The ZnMgO barrier and ZnO well layer thickness were kept fixed at 100 nm and 10 nm, respectively, for all the samples.

The cross-section of the deposited films were studied using a field emission scanning electron microscope (ZEISS SUPRA 40) equipped with energy-dispersive X-ray analyzer. The phase aggregate of the multilayer was characterized by X-ray diffraction (XRD) (Philips X-Pert MRD) pattern using CuKα radiation (45 kV, 40 mA) of wavelength 0.15418 nm in grazing incidence mode. Photoluminescence (PL) measurements in the temperature ranging from 10 to 300 K were carried out using a He–Cd laser as an excitation source which is operating at 325 nm with an output power of 45 mW, and a TRIAX 320 monochromator which is fitted with a cooled Hamamatsu R928 photomultiplier detector.

3. Results and discussion

Fig. 1 shows the cross-sectional field emission scanning electron microscopy (FESEM) of the multilayer grown at 500 °C. The bottom layer i.e. layer 1 is ZnO buffer layer. Layers 2, 4, 6, and 8 as denoted by arrows, are that of ZnMgO. The thin layers in between them, i.e. 3, 5, and 7 are that of ZnO.

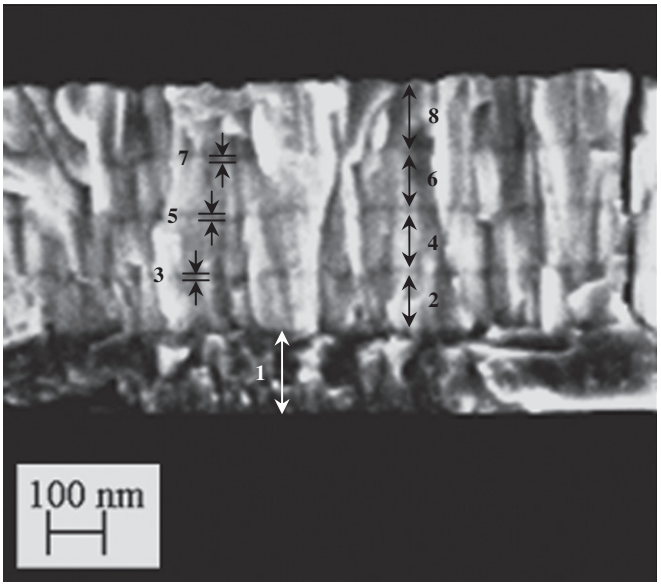

Fig. 1. Cross-sectional FESEM micrograph of the multilayers grown at 500 °C. Bottom layer is ZnO buffer layer, followed by 3 periods of ZnO (thin layer)/ZnMgO layers, i.e. layer 1 is ZnO buffer layer, layers 2, 4, 6, and 8 are that of ZnMgO, and layers 3, 5, and 7 are that of ZnO.

XRD spectra of the multilayers grown at different substrate temperatures are shown in Fig. 2(a). Intensity distribution of characteristic peaks suggests that the multilayer films possess preferred (0 0 0 2) growth orientation for all samples i.e. they are *c*-axis oriented. It is interesting to note that the (0 0 0 2) peak tends to enhance in intensity as the substrate temperature increases from 300 °C to 700 °C. Thus, the intensity ratio of (0 0 0 2) to (1 0 $\bar{1}$ 3) peak also increases gradually with rise of substrate temperature, as shown in Fig. 2(b). This is attributed to the increase of the adatom mobility in the film at higher substrate temperature, resulting in improved crystallinity and preferred growth orientation.

Temperature dependent photoluminescence (PL) measurements were carried out in order to have insight on the emissions related to the variation of the substrate temperature. Fig. 3 shows the normalized PL properties of the samples recorded at 10 K. The broad peak around 2.1–2.5 eV is related to defects, such as oxygen

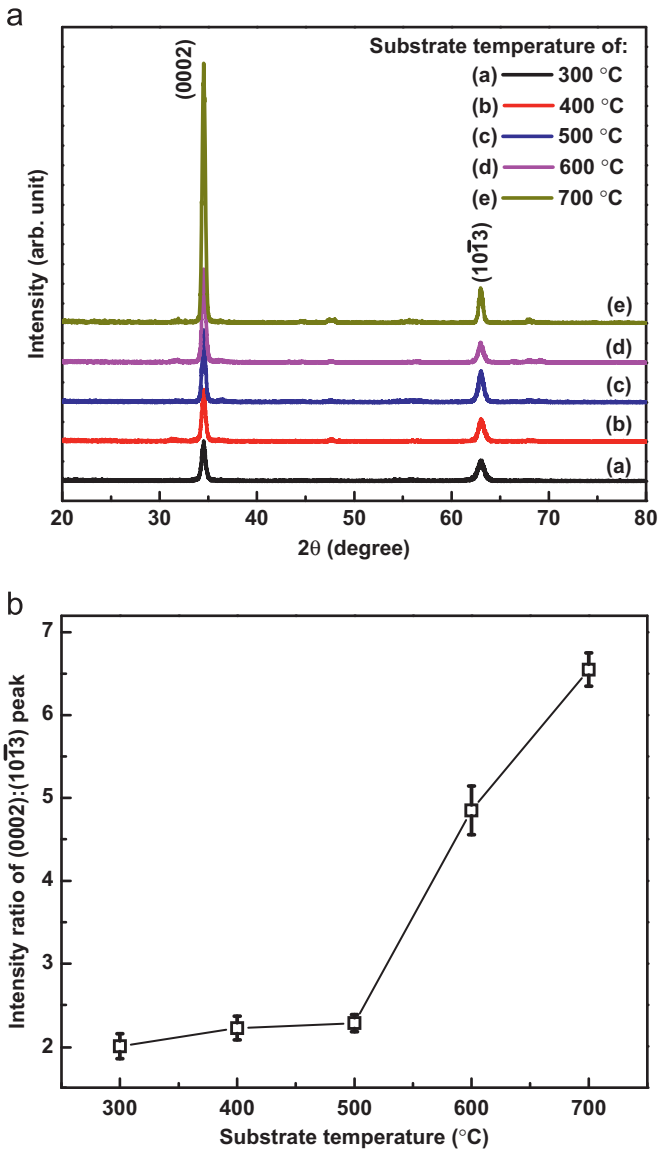

Fig. 2. (a) Grazing incidence X-ray diffraction pattern of the multilayers grown at different substrate temperatures. (b) Variation of peak intensity ratio of (0 0 0 2) to (1 0 $\bar{1}$ 3) planes with substrate temperature.