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Optical and morphological properties of MBE grown wurtzite $Cd_xZn_{1-x}O$ thin films

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Abstract

Wurtzite $Cd_xZn_{1-x}O$ epilayers with cadmium concentrations ranging from $x = 0.02$ to 0.30 were investigated using photoluminescence, transmission/reflection spectroscopy, and atomic force microscopy. The $Cd_xZn_{1-x}O$ photoluminescence peak was found to shift through the visible region from 421 (2.95 eV) to 619 nm (2.0 eV) as the cadmium concentration was increased from 2% to 30%. An additional broad photoluminescence peak was observed and is attributed to deep levels – the center of the broad peak was found to shift from 675 to 750 nm as the cadmium concentration was increased. RMS roughness of the epilayers increased from 1.5 nm ($x = 0.02$) to 9.2 nm ($x = 0.30$), as determined from atomic force microscopy. The demonstrated visible wavelength tunability throughout the visible range verifies the viability of using wurtzite $Cd_xZn_{1-x}O$ compounds for visible light emission in future optoelectronic devices.

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Keywords: Zinc oxide; Cadmium zinc oxide; Wide band gap; Wurtzite oxides

1. Introduction

The use of ZnO-based compounds in optoelectronic devices has advanced substantially in recent years [1–6]. As a wide band gap semiconductor ($E_{g,RT} = 3.37$ eV), ZnO is a suitable material for ultraviolet light emitting devices. Much of the current interest in wurtzite ZnO is a result of its strikingly similar properties to the much more mature wurtzite GaN system used in commercially available LEDs and other electronic devices. This interest has been further strengthened by several potential advantages of ZnO over GaN. First, ZnO substrates have become commercially available with relatively low dislocation densities of 10^4–10^5 cm^{-2} [7], enabling homoepitaxial growth that may result in a considerable reduction of interface dislocations. Additionally, high quality ZnO epilayers can be grown on Al_2O_3 substrates, mediated by low temperature MgO buffer layers, allowing one to avoid the relatively larger expense of ZnO substrates. Perhaps one of the more attractive properties of ZnO is its compatibility with wet etch chemistries – its GaN counterpart is generally limited to dry etching methods with low selectivities between the epilayer and photoresist mask [8]. In fact, selective wet etching has recently been demonstrated for the ZnO/$Cd_xZn_{1-x}O$ system [9]. This should enable inexpensive device processing and engender new optical structures and devices based on ZnO ternary heterostructures. Lastly, the exceptional exciton binding energy of ZnO (60 meV) enables efficient photoluminescence at room temperature and has allowed researchers to realize high temperature UV lasing with epitaxially grown ZnO films [10–12].

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While bulk ZnO itself offers many potential benefits, advanced heterostructures require the ability to tune the bang gap and confinement energies of the individual layers. This has recently been achieved through alloying with cadmium or magnesium, shifting the band gap to longer or shorter wavelengths, respectively [5,13–15]. Despite issues with solid solubility [16], incorporation of Mg and Cd has improved dramatically using techniques such as pulsed laser deposition (PLD), laser assisted molecular beam epitaxy (LMBE) and, in particular, remote plasma enhanced metalorganic chemical vapor deposition (RPE-MOCVD). Current data holds that the band gap energy of wurtzite ternary ZnO compounds can successfully be tuned from ~1.7 eV to 4 eV by appropriate Cd or Mg integration [5,6,17].

In order to effectively engineer sophisticated heterostructure devices, ternary $Cd_xZn_{1-x}O$ and $Mg_xZn_{1-x}O$ alloys must be well characterized in terms of optical properties as well as surface quality. In this study, $Cd_xZn_{1-x}O$ thin films were investigated as candidates for achieving optical devices in the UV and visible range. Epilayers of various Cd concentrations were grown by RF plasma-assisted molecular beam epitaxy and characterized using spectrophotometry, power-dependent photoluminescence, and atomic force microscopy.

2. Method

$Cd_xZn_{1-x}O$ epitaxial films were grown by RF plasma-assisted molecular beam epitaxy (MBE) in a SVT Associates growth chamber, as reported elsewhere [1]. Growth was carried out on GaN-buffered, *c*-plane sapphire templates. The GaN epitaxial layer (less than 1 μm in thickness) assists in nucleation of a subsequent ZnO buffer layer, 100–200 nm in thickness. $Cd_xZn_{1-x}O$ epilayers of varying Cd concentration were then grown to a thickness of 200 nm at temperatures below 600 °C using 6 N purity Zn and Cd elemental sources. The resultant wurtzite $Cd_xZn_{1-x}O$ epilayers were investigated by X-ray diffraction, and the Cd composition in each sample was determined by Rutherford backscattering (RBS) and secondary ion mass spectroscopy (SIMS) [1].

Photoluminescence (PL) measurements were carried out using a Spectra Physics BeamLok 2060 krypton ion (Kr^+) gas laser as the pump source, tuned to 350.7 nm (3.535 eV). The output power ranged from 120 to 140 mW, as measured on a Newport 818 optical power meter. The optical power at the sample surface was varied with OD filters from 0.08 mW to 33 mW. The beam was focused with standard optical elements to a spot size of ~1 mm, providing intensities ranging from 0.01 to 4.2 W/cm^2 at the surface of the epitaxial layers. PL from the epilayers was collected with high numerical aperture lens and directed into an Acton 2300i Monochromator and detected using a thermo-electrically cooled Andor CCD array. All PL spectra were corrected to compensate for system response. PL measurements were taken from $Cd_xZn_{1-x}O$ samples ranging in Cd concentration from $x = 0.02$ to $x = 0.30$. Spectrophotometry in the 190–1300 nm range was done using a Cary500 Varian spectrophotometer. Absorption characteristics of the epilayers were determined from reflection and transmission measurements. In order to reduce multiple reflection artifacts in the absorption curves, reflection measurements were first made on the thin films using a single-bounce technique at an incident angle of 24°. Subsequent transmission measurements were made at the same angle, and from these measurements absorption was extracted. Lastly, roughness measurements and surface profiles were conducted using a Veeco Dimension 3100 atomic force microscope (AFM) in tapping mode.

3. Results and discussion

The measured absorption and PL spectra for the $Cd_xZn_{1-x}O$ epilayers as a function of Cd concentration are given in Fig. 1. Prior to measurement, the Cd concentration in each epilayer was determined using RBS and SIMS. As the Cd concentration is increased from 2% to 30%, a systematic shift in the PL peak from the $Cd_xZn_{1-x}O$ epilayers is observed, moving from 421 nm (2.95 eV) to 619 nm (2.0 eV). The peaks are generally Gaussian-like in shape, though interference from multiple internal reflections has a modulating effect on the intensity. The magnitude of the PL for the various samples did not exhibit a clear dependence upon the cadmium concentration, however further investigations are planned to better understand the relation between PL position and magnitude on cadmium concentration. Determination of the PL peak position for the 30% $Cd_xZn_{1-x}O$ sample required peak fitting to separate the excitonic emission from the red defect band PL (discussed later). We anticipate a ±25 nm error associ-

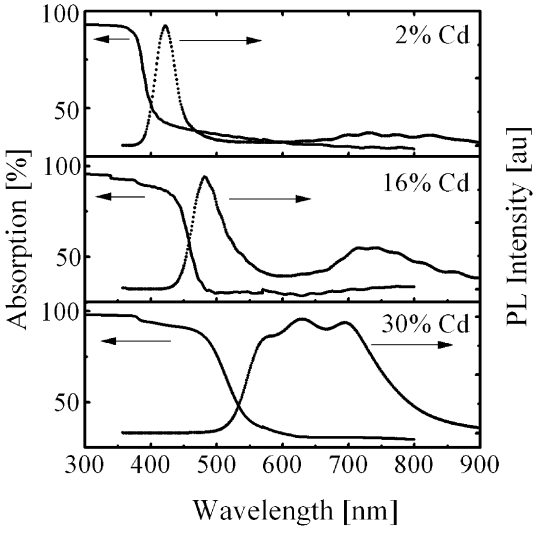

Fig. 1. Room temperature absorption and photoluminescence spectra from $Cd_xZn_{1-x}O$ epilayers with $x = 0.02$, 0.16, and 0.30. A systematic shift of the absorption edge and photoluminescence peak is observed with increasing Cd concentration.