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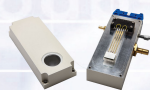
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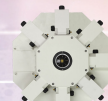
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## Thermal stability of CdZnO/ZnO multi-quantum-wells

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The thermal stability of CdZnO/ZnO multi-quantum-well (MQW) structures was studied using rapid thermal annealing in nitrogen from 300 to 750 °C. Photoluminescence (PL) emission from the MQWs was studied while varying the annealing temperature and time. For 15 min annealings, the PL center wavelength showed a 7 nm reduction for temperatures up to 650 °C. Above 650 °C, the wavelength changed rapidly, with a 50 nm reduction at 750 °C. Annealing at 700 °C for up to 20 min produced a systematic reduction in PL wavelength up to 39 nm. The data suggest that CdZnO/ZnO MQWs are relatively stable for nitrogen annealing below 650 °C for times up to 15 min. © 2007 American Institute of Physics. [DOI: 10.1063/1.2812544]

Recently, ZnO has attracted considerable attention as a candidate for high temperature blue and ultraviolet (UV) light emitters. ZnO has a much higher free-exciton binding energy, 60 meV,<sup>1,2</sup> as compared with other wide band gap materials such as GaN and SiC. This has been shown to ensure efficient excitonic optical emission at elevated temperatures up to even 650 K.<sup>3</sup> Additional advantages of ZnO include higher quantum efficiency, greater resistance to high-energy radiation, and better compatibility with wet chemical etching.<sup>1,4-6</sup> A critical element for the development of ZnO-based optical devices is the ability to tune its band gap through alloying, leading to the formation of both energy barriers and quantum wells that unlock the route toward more effective quantum confinement and increased internal quantum efficiency. Moreover, the ability to tune the ZnO band gap would enable light emission over a broad spectrum, i.e., from the deep UV to the visible regime, which greatly increases the perspective applications for this material system. Mg<sub>x</sub>Zn<sub>1-x</sub>O compounds with band gaps of over 6 eV (Refs. 7 and 8) have already been developed by alloying with the dielectric MgO which has a RT band gap of 7.9 eV.<sup>8</sup> Among possible narrow band gap materials, CdZnO is the most promising based on two observations: (i) CdO has a room temperature (RT) band gap of 2.3 eV (Ref. 9) and (ii) Zn and Cd atoms have a similar ionic radius.<sup>10</sup> Experimentally, a number of techniques have already been used to deposit CdZnO films.<sup>10-13</sup> At high Cd concentrations, however, the quality of the Cd<sub>x</sub>Zn<sub>1-x</sub>O films is often compromised by phase segregation<sup>12</sup> and severe Cd concentration fluctuations.<sup>11</sup> Previously, we reported on the growth of CdZnO epilayers using plasma-assisted molecular beam epitaxy (MBE),<sup>14</sup> demonstrating the ability to tune the energy gap of CdZnO through the visible range ( $\lambda=380-620$  nm) for Cd concentrations up to 30%.<sup>15</sup>

Here, we report on the thermal stability of CdZnO multi-quantum-well (MQW) heterostructures that emit in the visible region. It has been found that typical growth tempera-

tures for high quality CdZnO lie below 500 °C in order to suppress phase segregation.<sup>16</sup> Despite the high quality of CdZnO epilayers achieved,<sup>15</sup> there remains a need to understand their thermal stability and expected behavior when subjected to postgrowth thermal processing during the fabrication process for useful light emitters. Typical processing temperatures for optical devices include annealing of contact metallizations in the 400–600 °C range in order to achieve high quality Ohmic behavior. In this letter, we report on the thermal stability of CdZnO MQW structures when subjected to annealing for temperatures up to 750 °C.

The CdZnO/ZnO MQW structure was grown by plasma-assisted MBE on a *c*-plane sapphire (Al<sub>2</sub>O<sub>3</sub>) substrate. The MQW structure consisted of five periods of CdZnO (2.5 nm)/ZnO (6.0 nm), with a cadmium concentration of roughly 12% in the quantum well region as verified by secondary ion mass spectrometry and Rutherford backscattering spectroscopy. A ZnO buffer layer was grown prior to the MQW region to form a high quality template on top of the sapphire substrate. Annealing of the samples was done in a Modular Process Technology Corporation RTP 600S rapid thermal annealer at temperatures between 350 and 750 °C in a nitrogen ambient, delivered at a rate of 3.0 SCCM (SCCM denotes cubic centimeter per minute at STP). Prior to annealing, back side wafer polishing was required to remove the back side metal from the substrate since it was found that the spectral characteristics of the metal were affected by annealing at these temperatures. Room temperature photoluminescence (PL) was excited using the 325 nm line of a Kimmon IK3501 He–Cd cw laser using a power of 45 mW. A band-pass filter was used to remove the 442 nm line from the laser output. Luminescence from the samples was collected with standard optics and directed into a Newport M257 spectrometer with an attached TE cooled charge coupled device camera.

Prior to annealing, the PL uniformity across the sample was investigated. The variation in the center wavelength across the 2 in. sample was found to be ~7 nm. In order to eliminate the intrinsic PL wavelength variation, all samples were characterized by PL both before and after annealing to

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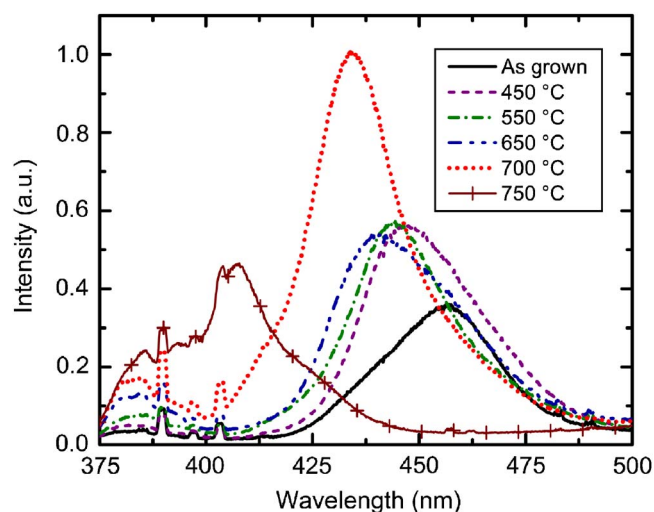


FIG. 1. (Color online) Photoluminescence spectra for CdZnO MQW samples annealed for 15 min in nitrogen at temperatures ranging from 450 to 750 °C.

ensure that any peak shift observed was only a direct result of the thermal process. Figure 1 provides the PL data for CdZnO MQW samples annealed for 15 min at temperatures between 450 and 750 °C. Inspection of the PL data from the as-grown sample shows the MQW luminescence to be centered around a wavelength of 457.2 nm, with a full width of half maximum (FWHM) of  $\sim 34$  nm. The smaller broad peak at 380 nm is attributed to the ZnO buffer layer below the CdZnO MQW region. As annealing temperature is increased, a clear trend of reduced center wavelength is observed. This is quantitatively provided in Fig. 2, showing the center wavelength position of the PL peaks as a function of annealing temperature. For annealing at temperatures below 450 °C, no discernible wavelength shift was observed in the PL emission. For annealing temperatures above 450 °C, the PL peak is found to blueshift up to 50 nm as annealing temperature is increased to 750 °C. Comparison of the FWHM values shows no clear trend, with values randomly ranging from  $\sim 26$  to 37 nm. Measurement from multiple positions on the as-grown wafer indicated that intrinsic variations in the

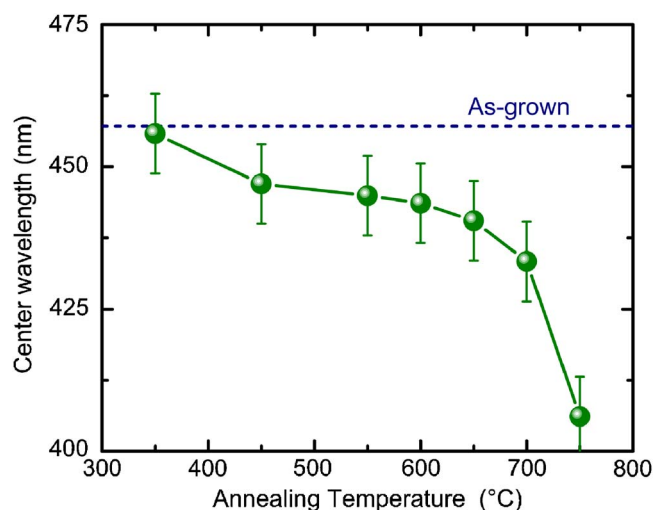


FIG. 2. (Color online) The center wavelength of the photoluminescence emission peaks as a function of annealing temperature.

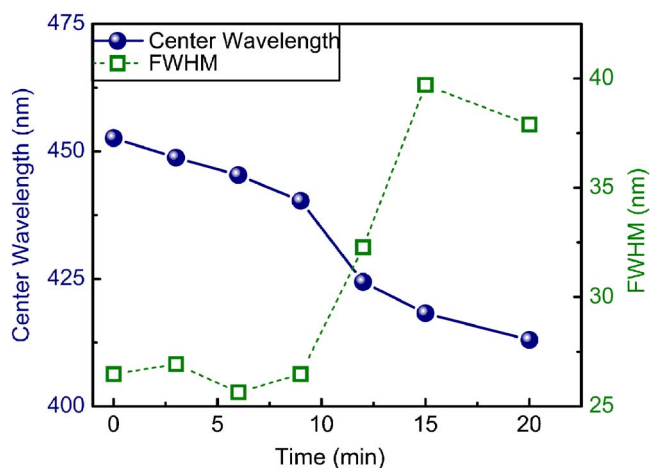


FIG. 3. (Color online) The center wavelength (solid line) and full width at half maximum (dashed line) of the MQW photoluminescence peaks for CdZnO samples annealed at 700 °C for times ranging from 0 to 20 min.

sample could account for this despite the center wavelength variation being limited to  $\sim 7$  nm.

To capture the time evolution of the PL wavelength shift, a single sample was annealed at 700 °C, with PL measurements taken after 0 (as grown), 3, 6, 9, 12, 15, and 20 min of annealing. Figure 3 shows the center wavelength of the PL peaks as a function of time. The FWHM of the peaks is plotted on the right axis. The center wavelength decreases consistently as the sample is annealed for longer times, from 452.6 nm for the as-grown sample to 413.0 nm for a 20 min annealing time, again showing that thermal annealing shifts the PL emission to shorter wavelengths. One possible mechanism for the increased band gap energy is the diffusion of Cd from the quantum wells into the ZnO barriers as the sample is annealed. This makes the MQWs shallower, increasing the band gap energy and causing a blueshift in the PL emission. However, the outdiffusion of Cd also causes the wells to widen, lowering the confinement of the carriers. This decreases the ground state energy of the wells, leading to a redshift of the PL. A one-dimensional Schrödinger equation was used to model the diffusion in a MQW with a gradient in the Cd concentration to study the shift in the energy levels as a function of diffusion length. First order solutions show that there is an increase in the recombination energy for increased diffusion lengths. Assuming that diffusion length increases with higher annealing temperature and longer annealing time, the numerical model confirms that the blueshift due to the decrease in the Cd concentration in the quantum well region is the dominant effect. Such behavior has been observed in many other material systems.<sup>17,18</sup>

Figure 3 also shows a trend of increasing FWHM with longer annealing times, with values ranging from  $\sim 26$  to 40 nm. This is an accurate measurement of the FWHM evolution since only one sample was used in the time-dependent annealing experiment, while several samples taken from different locations on the wafer had to be used for the temperature-dependent experiment. Standard peak fitting methods were used to isolate the PL peak from the CdZnO MQW region from the ZnO luminescence. For annealing times up to 9 min, no measurable change in FWHM is observed despite the continuous reduction in PL wavelength. At 12 min, a sharp change in FWHM occurs, and is maintained for the 15 min annealing. The exact mechanisms for this be-



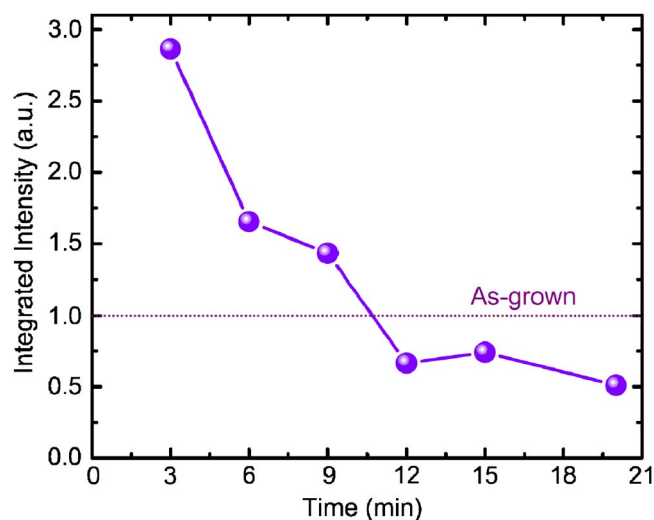


FIG. 4. (Color online) Normalized integrated intensity of the MQW photoluminescence spectra as a function of annealing time for samples annealed at 700 °C.

havior are not yet understood, but it is expected that future studies using cross-sectional transmission electron microscopy will provide the proper insight.

Figure 4 provides the integrated intensity of the PL emission as a function of annealing time. The data show an initial increase in intensity to almost three times the as-grown intensity, followed by a slow decrease as the sample is annealed for longer times. The initial jump in intensity is attributed to annealing out defects, thus reducing the nonradiative recombination, while longer annealing times result in reduced PL emission due to diffusion effects.

PL was used to characterize the thermal stability of CdZnO/ZnO MQW structures annealed in a nitrogen environment. Annealing of the structure in temperatures up to 650 °C for 15 min was found to improve the PL emission from the MQW structure while reducing the as-grown PL center wavelength by only 7 nm. Annealing at temperatures above 650 °C caused more significant reductions in the PL wavelength, with a total shift of ~50 nm at 750 °C. For a sample annealed at 700 °C at different times, the PL wavelength was found to systematically reduce for increasing annealing time up to 20 min. Increases in PL emission intensity were observed for annealing times at 700 °C up to 9 min,

with the FWHM remaining relatively stable. For annealing times above 9 min, the PL emission begins to deteriorate, accompanied by a rapid increase in the FWHM up to 15 nm. This study confirms that CdZnO/ZnO MQW structures are stable for standard contact annealing conditions in nitrogen for temperatures up to 650 °C and times below 15 min.

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