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Citation: *Appl. Phys. Lett.* **99**, 111903 (2011); doi: 10.1063/1.3639129

View online: <http://dx.doi.org/10.1063/1.3639129>

View Table of Contents: <http://aip.scitation.org/toc/apl/99/11>

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## Cd diffusion and thermal stability of CdZnO/ZnO heterostructures

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(Received 19 July 2011; accepted 26 August 2011; published online 13 September 2011)

Structural properties and thermal stability of CdZnO/ZnO heterostructures grown on sapphire substrate by metal-organic vapor phase epitaxy (MOVPE) have been studied. Zn/Cd interdiffusion and Cd evaporation appear as key factors limiting the thermal stability of CdZnO/ZnO heterostructures. Cd diffusion in MOVPE ZnO is found to start already at 600 °C with an activation energy of  $\sim 2.2$  eV and yields a saturation in the Cd concentration at 0.1-1 at. %. The actual Cd content remaining in the samples upon annealing is determined by a competition between Cd evaporation via the surface and diffusion/segregation in the bulk. © 2011 American Institute of Physics. [doi:10.1063/1.3639129]

Understanding of ZnO-based materials attracts steadily growing interest due to potential applications in optoelectronics.<sup>1,2</sup> Pure ZnO is a wide and direct band gap semiconductor ( $E_g \approx 3.4$  eV) exhibiting significantly higher free-exciton binding energy ( $\sim 60$  meV) as compared to other wide band gap materials like GaN or SiC. Alloying of ZnO with CdO ( $E_g \approx 2.3$  eV) results in a gradual reduction of the band gap<sup>3</sup> and applications can be extended toward the use of heterostructures, quantum wells/dots, etc.<sup>1,4</sup> Enhancing the thermal stability or at least understanding the processing window is a fundamental challenge in the utilization of complex heterostructures in optoelectronic applications. Surprisingly, there are only a few reports in the literature regarding the effect of annealing on the properties of CdZnO and CdZnO/ZnO heterostructures.<sup>5-10</sup> Nevertheless, it is well understood that phase separation might have a profound influence on the thermal stability of CdZnO (Refs. 5 and 8) because of different equilibrium phases of the binary components. Indeed, ZnO crystallizes in a wurtzite (w) structure under normal conditions while CdO adopts rock salt (rs) symmetry leading to a metastable state in, e.g., w-CdZnO, as long as the Cd concentration exceeds the solubility limit in the w-matrix. Note that there is no reliable binary CdO-ZnO phase diagram reported in literature and, in particular, solubility values reported for Cd in equilibrium with w-ZnO are contradictory (see, for example, Ref. 11 and references therein). Moreover, interdiffusion must be taken into account when considering thermal stability of CdZnO/ZnO heterostructures. For instance, Thompson *et al.*<sup>6</sup> have reported a significant reduction in photoluminescence (PL) wavelength for CdZnO/ZnO multi-quantum wells annealed at temperatures above 650 °C and suggested that this degradation may be attributed to Cd redistribution. However, the literature data documenting Cd diffusion in ZnO are limited. Very recently, Lange *et al.*<sup>9</sup> have shown that pulsed laser deposited ZnO/CdZnO/ZnO heterostructures may be stable up to 720 °C and estimated the activation energy of Cd diffusion to be in the range of 2.1-3.5 eV based on the fitting of PL data with simulated Cd profiles. Another attempt to characterize Cd redistribution upon rapid thermal annealing has been performed using secondary ion mass spectrometry (SIMS).<sup>7</sup>

However, the interpretation of SIMS results in terms of alloy element redistribution is complicated by so-called “matrix” effects on ionization probabilities and sputtering yields in samples with variable Cd content. In the present work, we study Cd diffusion in w-ZnO using a combination of SIMS (because of its high sensitivity) and Rutherford backscattering spectrometry (RBS) (because of its excellent sensitivity to heavy elements like Cd and lack of “matrix” effects). As a result, Cd/Zn inter-diffusion and Cd evaporation via the surface are found to be critical factors limiting the thermal stability of CdZnO/ZnO heterostructures.

Cd<sub>0.07</sub>Zn<sub>0.93</sub>O/ZnO and CdO/ZnO heterostructures were grown by metal organic vapor-phase epitaxy (MOVPE) on c-axis oriented sapphire substrates. The thickness of the top CdZnO (or CdO) layers was varied between 50 nm and 100 nm, while the ZnO layers had a thickness in the range of 80-1500 nm. More details on the MOVPE growth can be found elsewhere.<sup>12</sup> Annealing of the samples was done in air at 600–900 °C. In addition, hydrothermally (HT) grown w-ZnO single crystals were implanted at room temperature with 300 keV <sup>114</sup>Cd<sup>+</sup> ions to a dose of  $5 \times 10^{15}$  cm<sup>-2</sup> and annealed at temperatures up to 1000 °C in air. The samples were analyzed by SIMS, RBS, and x-ray diffraction (XRD). The RBS measurements were done with 2 MeV <sup>4</sup>He<sup>+</sup> ions backscattered into a detector at 170° relative to the incident beam direction followed by standard procedure for the extraction of Zn/Cd depth profiles.<sup>13</sup> Cd depth profiles were also measured by SIMS (Cameca IMS7f microanalyzer) using 10 keV O<sub>2</sub><sup>+</sup> primary ions and RBS data for calibration of the SIMS intensity signals. Depth conversion of the SIMS profiles was performed by the measurement of crater depth using a surface stylus profilometer and assuming a constant erosion rate. XRD analysis was undertaken using a D8 Bruker setup to unveil possible phase evolution in the films.

Fig. 1(a) shows RBS spectra of the as-grown and annealed (90 nm Cd<sub>0.07</sub>Zn<sub>0.93</sub>O)/(80-100 nm ZnO) samples. Surface positions of Cd, O, and Zn atoms as well as the Al position at the film/substrate interface are indicated by the arrows. RBS resolves the entire heterostructure and Cd redistribution into ZnO is readily observed. Note the results also reveal a congruent Zn redistribution into the space originally corresponding to the CdZnO layers (see the spectral range around channel numbers of 400 in Fig. 1(a)) confirming a correlation in the transport of these two species.<sup>14</sup> Fig. 1(b)

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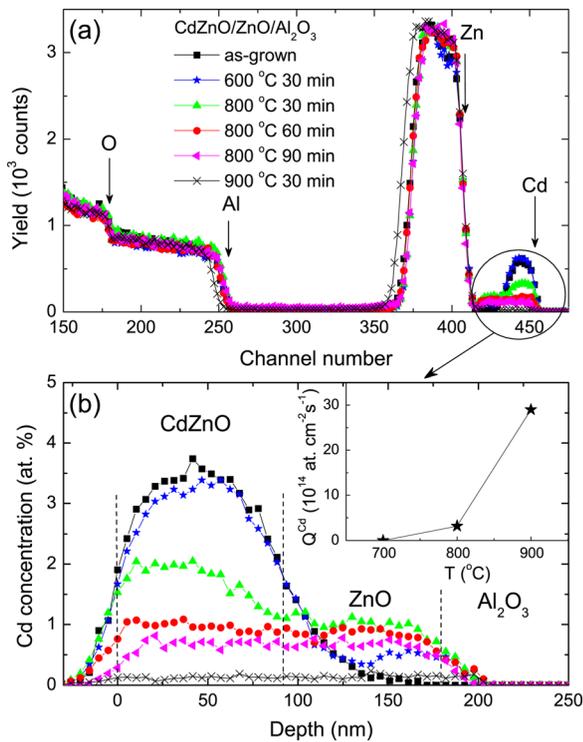


FIG. 1. (Color online) (a) RBS spectra of  $\text{Cd}_{0.07}\text{Zn}_{0.93}\text{O}/\text{ZnO}/\text{Al}_2\text{O}_3$  heterostructures grown on sapphire substrate for various annealing conditions indicated in the legend. Corresponding Cd depth profiles are shown in panel (b). The inset in panel (b) shows average Cd evaporation rate ( $Q^{\text{Cd}}$ ) as a function of annealing temperature.

summarizes the corresponding Cd depth profiles confirming a dramatic redistribution of Cd into the ZnO layer, which starts already at 600 °C. Note that our results do not reveal any substantial Cd diffusion into the sapphire substrate.<sup>15</sup> Therefore, the overall decrease in the Cd content may be attributed to its evaporation via the surface. The Cd concentration in ZnO increases with temperature and appears to saturate at  $\sim 1$  at. % after 30 min at 800 °C. In its turn, the Cd concentration in CdZnO is reduced during the course of the 800 °C, anneals, and reaches the same level as that in the ZnO part of the sample after 60 min. Further annealing at 800 °C (90 min) leads to a uniform decrease of the Cd concentration throughout the heterostructure with a noticeable loss near the surface. Annealing at 900 °C results in dramatic out-diffusion (evaporation) of Cd, and the average Cd evaporation rate as a function of annealing temperature is depicted in the inset of Fig. 1(b). The Cd evaporation rate exhibits a nonlinear behavior with temperature yielding  $\sim 3 \times 10^{14}$  Cd/( $\text{cm}^2 \text{ s}$ ) at 800 °C and approximately an order of magnitude higher value at 900 °C.

Figure 2 shows typical  $2\theta$  XRD scans of the as-grown and annealed  $\text{CdZnO}/\text{ZnO}$  samples (as selected from the samples investigated in Fig. 1). The as-grown film displays two overlapping peaks at  $\approx 34.3^\circ$  and  $\approx 34.5^\circ$  which are attributed to the (002) diffractions in w-CdZnO and w-ZnO, respectively, and one peak at  $41.7^\circ$  related to the sapphire substrate. After the 800 °C annealing for 90 min, only the pure w-ZnO related peak remains (somewhat broaden towards the low  $2\theta$  angles) consistent with RBS data in Fig. 1. Here, it may be emphasized that no rs-related signatures are observed neither before nor after annealing.

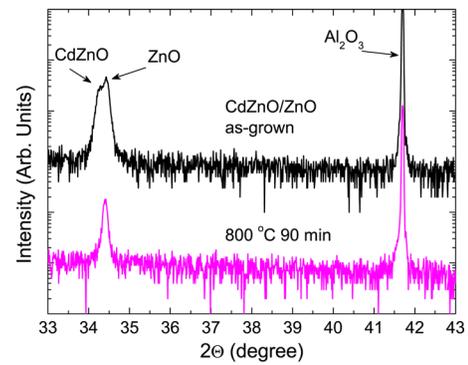


FIG. 2. (Color online) XRD  $2\theta$ -scans of  $\text{Cd}_{0.07}\text{Zn}_{0.93}\text{O}/\text{ZnO}/\text{Al}_2\text{O}_3$  heterostructure before and after annealing at 800 °C for 90 min.

In order to elucidate the Cd diffusion mechanisms, CdO/ZnO structures with thicker ZnO spacers ( $\sim 1.5 \mu\text{m}$ ) have been investigated, and Fig. 3(a) shows Cd depth profiles in CdO/ZnO samples as measured by SIMS.<sup>16</sup> Strong Cd diffusion occurs already at 600 °C but saturates at higher temperatures, consistent with the data for thinner films (Fig. 1). The Cd diffusion coefficients were extracted by fitting of the experimental data with a solution of the one dimensional Fick's equation, assuming an unlimited Cd source and fully reflective boundary conditions at the film/substrate interface. Fig. 3(b) shows an Arrhenius plot for the Cd diffusivities extracted from the data in Fig. 3(a). Employing a conventional relationship between the diffusivity and temperature,  $D_{\text{eff}} = D_0 \exp(-E_a/kT)$ , the activation energy ( $E_a$ ) and pre-exponential factor ( $D_0$ ) for Cd diffusion are found to be  $2.2 \pm 0.2$  eV and  $0.6 \text{ cm}^2/\text{s}$ , respectively.

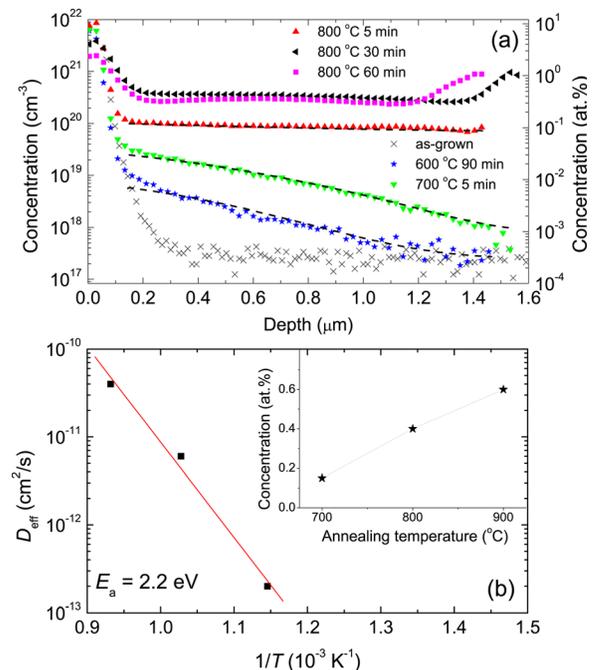


FIG. 3. (Color online) (a) Cd concentration vs depth profiles in MOVPE grown CdO/ZnO for various annealing conditions indicated in the legend and corresponding diffusion equation solutions (dashed lines) and (b) an Arrhenius plot of the effective diffusion constant ( $D_{\text{eff}}$ ) vs the reciprocal temperature. The inset in panel (b) shows Cd saturation level in MOVPE ZnO as a function of annealing temperature.

In contrast, HT ZnO demonstrates considerably lower Cd diffusion as compared to that in MOVPE ZnO and annealing of Cd implanted HT ZnO samples did not reveal any measurable Cd diffusion into the bulk for temperatures up to 1000 °C (not shown). The pronounced difference of Cd diffusion in MOVPE and HT ZnO may be attributed to the sample's microstructure. Indeed, the growth rate anisotropy associated with the hexagonal symmetry typically results in the formation of a dense columnar structure of ZnO during MOVPE synthesis.<sup>17,18</sup> Such a columnar structure exhibits an enhanced density of dislocations at grain boundaries promoting the Cd redistribution, consistently with that observed for impurity diffusion at grain boundaries in ionic crystals.<sup>19</sup> In its turn, the trend of saturation in Cd concentration indicates segregation at the grain boundaries,<sup>20</sup> which increases with temperature, as illustrated by the inset in Fig. 3(b) showing the Cd saturation level as a function of annealing temperature.

Concurrently, the relatively high value of  $E_a$  obtained in our study may also suggest that a vacancy assisted mechanism<sup>21</sup> contributes to the Cd diffusion in MOVPE ZnO too. Thus, the lower Cd diffusivity in HT ZnO may be due to an insufficient concentration of vacancy-related defects mediating the migration of Cd. Furthermore, HT ZnO typically contains significant amount of impurities, specifically Li, unintentionally introduced during the synthesis, which was recently shown to “consume” a large fraction of open volume defects.<sup>22</sup> It should be mentioned that samples with different ZnO layer thickness have shown some variations in the Cd saturation level suggesting fluctuations in the concentrations of dislocations and/or grain sizes in samples with different thickness. In its turn, the actual Cd content remaining in the samples upon high temperature annealing is determined by a competition between Cd evaporation via the surface and its diffusion and/or segregation in the bulk. Finally, the Cd concentration in MOVPE ZnO is slightly enhanced in the vicinity of the film/substrate interface (see Fig. 3(a)), which is attributed to an enhanced concentration of structural defects, acting as traps for Cd atoms, assisted by strain accommodation at the interface.<sup>23</sup>

In summary, the Cd diffusion in MOVPE ZnO is found to be considerably higher than that in HT ZnO. It starts already at 600 °C and exhibits an activation energy of  $\sim 2.2$  eV. The redistribution saturates at 0.1-1 at. % Cd for anneals at  $\leq 800$  °C while higher temperature anneals lead to significant Cd evaporation via the surface. The actual Cd content remaining in the samples is determined by a competition between evaporation via the surface and diffusion/segregation in the bulk of the films.

Financial support from the Norwegian Research Council via FRINAT and RENERGI programs is gratefully acknowledged. The authors acknowledge the Ion Technology Center at Uppsala University for assistance with the Cd implantation.

- <sup>1</sup>Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, *J. Appl. Phys.* **98**, 041301 (2005).
- <sup>2</sup>A. Janotti and C. G. Van de Walle, *Rep. Prog. Phys.* **72**, 126501 (2009).
- <sup>3</sup>T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, R. Shiroki, K. Tamura, T. Yasuda, and H. Koinuma, *Appl. Phys. Lett.* **78**, 1237 (2001).
- <sup>4</sup>M. Ebihara, I. Suemune, H. Kumano, T. Nakashita, and H. Machida, *Phys. Status Solidi C* **3**, 933 (2006).
- <sup>5</sup>R. Zhang, P. Chen, Y. Zhang, X. Ma, and D. Yang, *J. Cryst. Growth* **312**, 1908 (2010).
- <sup>6</sup>A. V. Thompson, C. Boutwell, J. W. Mares, W. V. Schoenfeld, A. Osinsky, B. Hertog, J. Q. Xie, S. J. Pearton, and D. P. Norton, *Appl. Phys. Lett.* **91**, 201921 (2007).
- <sup>7</sup>L. Li, Z. Yang, Z. Zuo, J. Y. Kong, and J. L. Liu, *J. Vac. Sci. Technol. B* **28**, C3D13 (2010).
- <sup>8</sup>D. W. Ma, Z. Z. Ye, J. Y. Huang, L. P. Zhu, B. H. Zhao, and J. H. He, *Mater. Sci. Eng., B* **111**, 9 (2004).
- <sup>9</sup>M. Lange, C. P. Dietrich, G. Benndorf, M. Lorenz, J. Zúñiga-Pérez, and M. Grundmann, *J. Cryst. Growth* **328**, 13 (2011).
- <sup>10</sup>R. Vinodkumar, K. J. Lethy, P. R. Arunkumar, R. R. Krishnana, N. V. Pillai, V. P. M. Pillai, and R. Philip, *Mater. Chem. Phys.* **121**, 406 (2010).
- <sup>11</sup>V. Venkatachalapathy, A. Galeckas, M. Trunk, T. C. Zhang, A. Azarov, and A. Y. Kuznetsov, *Phys. Rev. B* **83**, 125315 (2011).
- <sup>12</sup>V. Venkatachalapathy, A. Galeckas, R. Sellappan, D. Chakarov, and A. Y. Kuznetsov, *J. Cryst. Growth* **315**, 301 (2011).
- <sup>13</sup>W.-K. Chu, J. W. Mayer, and M.-A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978).
- <sup>14</sup>More detailed Zn redistribution analysis is complicated by the lower scattering cross-section of Zn atoms as compared to that of Cd and a background signal originated from Zn atoms in CdZnO layers. However, note that overall heterostructure thickness remains unchanged in spite of a pronounced Cd evaporation at high temperatures likely on behalf of Zn interdiffusion, while the apparent signal shifts observed in the sample annealed at 900 °C is due to initially slightly thicker ZnO layer.
- <sup>15</sup>An apparent gradient in Cd profiles at the ZnO/Al<sub>2</sub>O<sub>3</sub> interface is a result of the RBS limited depth resolution similar to that at the surface and the CdZnO/ZnO interface.
- <sup>16</sup>It should be mentioned that the calibration of Cd-related SIMS signal is reliable for the depth corresponding to ZnO spacer only, while that in CdO ( $\leq 150$  nm in Fig. 3(a)) may be affected by uncertainties in ionization efficiencies in CdO and in the immediate vicinity of CdO/ZnO interface.
- <sup>17</sup>J. Dai, H. Liu, W. Fang, L. Wang, Y. Pu, Y. Chen, and F. Jiang, *J. Cryst. Growth* **283**, 93 (2005).
- <sup>18</sup>J. Huang, Z. Ye, H. Lu, L. Wang, B. Zhao, and X. Li, *J. Phys. D: Appl. Phys.* **40**, 4882 (2007).
- <sup>19</sup>M. A. N. Nogueira, W. B. Ferraz, and A. C. S. Sabioni, *Mater. Res.* **6**, 167 (2003).
- <sup>20</sup>Y. Sato, F. Oba, M. Yodogawa, T. Yamamoto, and Y. Ikuhara, *J. Appl. Phys.* **95**, 1258 (2004).
- <sup>21</sup>G.-Y. Huang, C.-Y. Wang, and J.-T. Wang, *J. Appl. Phys.* **105**, 073504 (2009).
- <sup>22</sup>K. M. Johansen, A. Zubiaga, I. Makkonen, F. Tuomisto, P. T. Neuvonen, K. E. Knutsen, E. V. Monakhov, A. Y. Kuznetsov, and B. G. Svensson, *Phys. Rev. B* **83**, 245208 (2011).
- <sup>23</sup>C. M. Wang, L. V. Saraf, and Y. Qiang, *Thin Solid Films* **516**, 8337 (2008).