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Migration and luminescence enhancement effects of deuterium in ZnO/ZnCdO quantum wells

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ZnO/ZnCdO/ZnO multiple quantum well samples grown on sapphire substrates by molecular beam epitaxy and annealed *in situ* were exposed to D₂ plasmas at 150 °C. The deuterium showed migration depths of $\sim 0.8 \mu\text{m}$ for 30 min plasma exposures, with accumulation of ²H in the ZnCdO wells. The photoluminescence (PL) intensity from the samples was increased by factors of 5 at 5 K and ~ 20 at 300 K as a result of the deuteration, most likely due to passivation of competing nonradiative centers. Annealing up to 300 °C led to increased migration of ²H toward the substrate but no loss of deuterium from the sample and little change in the PL intensity. The initial PL intensities were restored by annealing at ≥ 400 °C as ²H was evolved from the sample ($\sim 90\%$ loss by 500 °C). By contrast, samples without *in situ* annealing showed a decrease in PL intensity with deuteration. This suggests that even moderate annealing temperatures lead to degradation of ZnCdO quantum wells. © 2008 American Institute of Physics. [DOI: [10.1063/1.2836946](https://doi.org/10.1063/1.2836946)]

There is an extensive current interest in developing the ZnMgCdO system for blue and ultraviolet optoelectronic devices.^{1,2} ZnO is attractive for optoelectronic applications due to its large exciton binding energy (60 meV),³ which allows excitonic recombination above room temperature. In addition, ZnO substrates are commercially available and ZnO films of excellent optical quality can be grown at relatively low temperatures. ZnO-based alloys, such as Zn_{1-x}Mg_xO and Zn_{1-x}Cd_xO, add tunability in the alloy bandgap for bandgap engineering. The larger gap ZnMgO can be used as cladding layers in double heterostructures and with active layers of ZnCdO, the bandgap energy can be tuned as desired within the blue-yellow spectral range for light-emitting diodes.⁴⁻⁹ There is great interest in the fundamental optical properties and associated recombination processes in ZnCdO. In ZnCdO/MgZnO quantum wells with very low Cd content of 0.4%, the low temperature emission is attributed to recombination of excitons localized by potential fluctuations due to alloy disorder and well width variations.¹⁰ The role of hydrogen on ZnCdO quantum wells is unclear. Hydrogen is a common impurity in ZnO and related alloys and produces a donor state in pure ZnO.¹¹⁻²⁵ It has a high diffusivity in the binary¹⁴ and is thought to be responsible for part of the commonly observed *n*-type background in most ZnO.¹⁵⁻¹⁸ Hydrogen may passivate nitrogen acceptors in vapor phase grown ZnO (Ref. 16) and also form a variety of complexes with O.^{12,13,17-25}

In this letter, we report on the incorporation of deuterium into ZnCdO/ZnO quantum wells by exposure to a ²H plasma, its migration during annealing, and its effect on enhancing the luminescence intensity from the quantum wells.

The samples investigated consisted of wurtzite 2 nm ZnCdO multiple quantum wells with 6 nm ZnO barriers on a 1.0 μm ZnO:Ga buffer layer grown on (0001) sapphire substrates by molecular-beam epitaxy at 500 °C and annealed *in situ* at 550 °C under O₂ to improve crystalline quality.^{26,27} This type of annealing has been shown to enhance the optical properties of ZnCdO multiple quantum wells.²⁸ The Cd composition in the wells was ~ 12 at. %. The photoluminescence (PL) peak from the ZnCdO quantum wells (QWs) was centered at ~ 2.9 eV at 300 K. Based on transmission electron microscopy and selected area diffraction pattern measurements, the alloy has excellent crystalline quality with no evidence of second phase formation. The samples were exposed to a ²H plasma for 30 min at 150 °C with a chamber pressure of 800 mtorr and a rf power (13.56 MHz) of 30 mW cm⁻². Some samples were annealed at temperatures up to 500 °C for 5 min under O₂ ambient following the deuteration treatment. The ²H depth profile was obtained by secondary ion mass spectrometry (SIMS) using a 14.5 keV Cs⁺ ion beam and detecting negative secondary ions. The concentrations were quantified using ion implanted standards. A Verdi/MBD-266 laser system ($\lambda=266$ nm) was used as an excitation source during PL measurements. Optical signals during PL measurements were dispersed by a grating monochromator and detected by a charge-coupled detector. An oscillating pattern seen in the PL spectra is likely a result of interference within the multilayer structure.

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FIG. 1. (Color online) SIMS depth profile of deuterium in a ZnCdO/ZnO multiple QW (MQW) sample grown on a thick ZnO buffer and exposed to a D_2 plasma for 30 min at 150 °C and subsequently annealed at different temperatures.

Figure 1 shows the 2H profile in the structure after deuteration and subsequent annealing at different temperatures. Deuterium incorporates to depths of $\sim 0.8 \mu m$ and shows little additional migration until anneals of 300 °C. By 500 °C, the concentration near the surface is lowered as deuterium migrates out of the crystal and its profile extends all the way through the ZnO buffer. Note the higher concentration of deuterium in the region of the ZnCdO quantum wells both after deuteration and all subsequent anneals.

A closeup of deuterium profile in the quantum well region is shown in Fig. 2. The deuterium concentration peaks in the ZnCdO wells, which are regions of strain. Similar accumulation of hydrogen is observed in many similar interfaces or strained regions in multilayered semiconductor structures.²⁹ As the annealing temperature is increased, the deuterium concentration decreases in the first well, and initially increases in the second well as migration into the sample occurs, before decreasing in both wells at the higher temperatures.

Figure 3 shows the areal density of deuterium remaining in the samples as a function of annealing temperature, obtained by integrating the area under the SIMS profiles for each condition. Significant loss of deuterium is only observed above 300 °C, somewhat higher than the temperature of ~ 200 °C reported for bulk ZnO.²⁹ The broad nature of the curve in Fig. 3 is indicative that more than one form of deuterium exists in the samples, since if all the deuterium were present as one configuration, most of it should evolve from the crystal over a narrow temperature range.³⁰ We expect the presence of the various types of oxygen-deuterium centers, deuterium molecules, and deuterium trapped at lat-

FIG. 2. (Color online) Closeup of SIMS depth profile of deuterium in the MQW region.

FIG. 3. (Color online) Areal concentration of deuterium remaining after deuteration and subsequent annealing at different temperatures.

tice defects lead to this broad temperature range for evolution of deuterium from the samples.¹⁷

As shown in Fig. 4, at 5 K, after deuteration we observed a substantial (more than five times) increase of intensities of all recorded emissions and a strong blueshift (~ 70 meV) of the broad emission band peaking at around 3.07 eV. In addition, there was the appearance of a new PL peak at 3.342 eV. At 300 K, there was a strong (~ 20 times) increase of intensities of all recorded emissions. The changes observed in the 5 K PL spectra remain unaffected by annealing performed within the temperature range of 150–300 °C, but were reversed by annealing at ≥ 400 °C.

The observed changes in the PL spectra correlate with the SIMS measurements which imply that they are due to the presence of deuterium. The enhancement of the PL efficiency likely reflects passivation of competing nonradiative recombination centers, as commonly observed in other semiconductors. Assuming that the emission occurs via the tail states, as commonly seen in ZnCdO,³¹ the blueshift of the 3.07 eV line after hydrogenation may reflect passivation of nonradiative recombination centers. This would enhance radiative efficiency of optical transitions via the tail states shallower in energy. The effect of deuteration on samples grown at 500 °C but not given an *in situ* anneal was quite different. In that case, we typically saw a small decrease (of the order of 10%) in the overall PL intensity, probably due to an increase in surface recombination from ion impingement damage during the exposure. This suggests that even an *in situ* annealing at 550 °C of the ZnCdO was sufficient to create nonradiative centers that were passivated by hydrogen and establishes the limit for the onset of thermal degradation. This is consistent

FIG. 4. 5 K PL spectra from ZnCdO/ZnO MQW sample before and after hydrogenation and after subsequent annealing at different temperatures.

with recent data on the effects of *ex situ* annealing on ZnCdO QWs.²⁷

In conclusion, deuteration of ZnCdO/ZnO quantum wells annealed at 550 °C produces a strong enhancement of luminescence intensity that is reversible by annealing at >400 °C. The migration of deuterium is influenced by the presence of the ZnCdO wells and the annealing temperature and correlates with the effect on luminescence.

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