An optical study of interdiffusion in ZnSe/ZnCdSe

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This letter presents a study of intermixing in ZnSe/ZnCdSe quantum well structures, using repetitive thermal annealing with photoluminescence measurements. An improvement in the optical quality of the samples was found for anneals at temperatures (~500 °C) for which macroscopic intermixing is not observed. The interdiffusion process of this system was found to be Fickian with no dependence on alloy composition or strain. An activation energy of 2.3±0.2 eV was obtained for the interdiffusion process over a 250 K temperature range and four decades of interdiffusion coefficient.
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The wide gap II–VI semiconductors have become of increasing technological importance, in particular for the development of lasers operating in the visible to ultraviolet region. Such devices contain heterojunctions and quantum well layers and so, because of the large concentration gradients present, interdiffusion of the matrix components during growth and processing is of inevitable concern. Such interdiffusion can, during the growth or subsequent processing, lead to composition changes of the interface and well profiles and the strain distribution, modifying the band gap configuration and consequently the device parameters. A quantitative knowledge of the interdiffusion parameters is, therefore, essential.

In this letter, we present the results of a photoluminescence study of the intermixing in ZnSe/$Zn_{(1-x)}Cd_{(x)}Se$ strained quantum well structures. In our experiments, we have measured the interdiffusion for different compositions, $x=0.11$ and $x=0.21$, over a 250 K temperature range of 500–750 °C. Using repetitive annealing and photoluminescence, coupled with a simple diffusion model developed for this material, we have been able to determine the interdiffusion parameters.

The samples studied in this letter were grown using an ASM OMR 12 low-pressure metal organic vapor phase epitaxy (MOVPE) equipment with a classical horizontal reactor. The substrates were semi-insulating epiready (100) GaAs provided by MCP, Ltd. These substrates exhibit low dislocation densities revealed by the etch pit density (EPD) technique (EPD~10^4 cm^{-2}). The samples were grown using hydrogen selenide 25% in hydrogen (H_2Se) dmethyl-cadmium (DMCd) and triethylamine:dimethyl-zinc adduct (TEA:DMZn) as precursors. The metal–organic precursors were supplied by Epichem Ltd. Prior to growth, the substrates were loaded into the growth chamber without any previous chemical treatment and were deoxidized by heat treatment at 580 °C for 10 min in an H_2 ambient. The samples consist of a 10 nm ZnSe/$Zn_{(1-x)}Cd_{(x)}Se$ quantum well, with x either 0.11 or 0.21, embedded between a 300 nm thick ZnSe buffer layer and a 200 nm thick ZnSe cap layer. The samples were grown at a temperature of 300 °C with a molar VI/II ratio of 5/1 under an overall reactor pressure of 40 Torr. The growth rates were 0.35 μm/h for ZnSe and 0.5 μm/h for ZnCdSe. In order to improve the interface abruptness, a growth interruption of 20 s was introduced at each interface.

Prior to the annealing experiments the samples were capped with silicon nitride in a plasma enhanced chemical vapor deposition system to avoid any surface degradation during the subsequent processing. The capping temperature was ~300 °C. A 30 nm thick nitride layer was deposited on the front and back surface of the sample. Sequential anneals and photoluminescence (PL) measurements were used to quantify intermixing in these materials. For the anneals, a rapid thermal annealer system was used. This consisted of two resistively heated graphite strips with the sample in a space between them. Temperature measurement was performed using an optical lightpipe sensor and controlled via an ''Accufiber Model 10'' pyrometer. In this system, a constant ramp up time of 15 s is obtained and the plateau anneal temperature held to an accuracy of ±1.0 °C. A photoluminescence measurement was performed on each of the samples prior to any anneal. A series of isothermal anneals were performed for an individual sample with the photoluminescence recorded between each anneal so that we could follow the evolution of the diffusion with anneal time. The PL measurements were made on a standard dispersive system consisting of a 1 m spectrometer (Spex 1702) with a silicon avalanche photodetector. The laser beam was chopped at ~330 Hz and conventional lock-in detection employed. The samples were excited using the 351 nm line from a Spectra Physics 2025 argon ion laser. The samples were cooled to 77 K for the PL measurements in an Oxford Instruments CF1204 dynamic continuous flow cryostat.

To obtain the interdiffusion parameters from the PL measurements the change of the well profile with time has to be modeled, the band diagram calculated, and Schrödinger's

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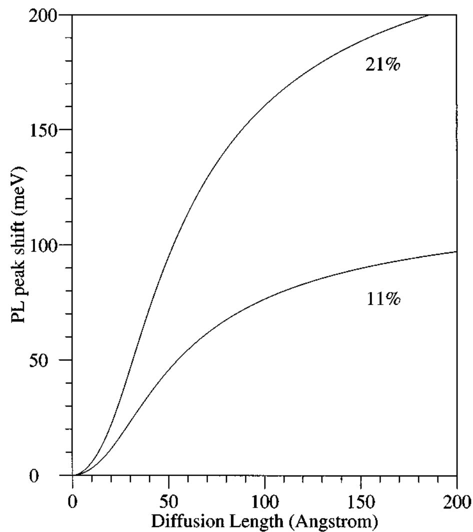

FIG. 1. The calibration curves, of the PL peak energy shifts against diffusion length, for the 11% Cd and 21% Cd content wells, calculated by solving the Schrödinger equation for the diffused wells.

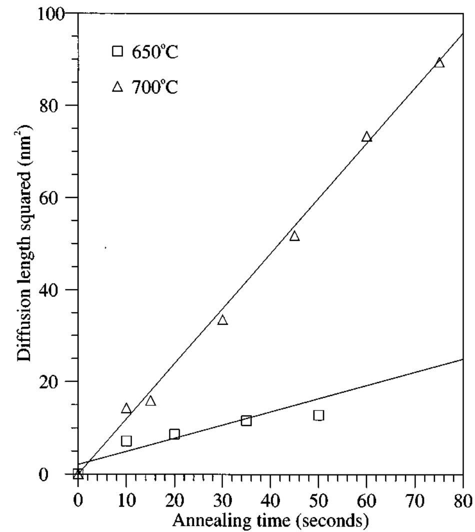

FIG. 3. A plot of diffusion length squared against anneal time for various anneal temperatures. The solid lines are least-squares fits to the data.

equation solved for the diffused well as a function of diffusion. This leads to the production of a calibration curve, of diffusion length against the shift of the peak PL energy for the sample of interest. The curves calculated for the 11% and 21% Cd content samples are shown in Fig. 1. The diffusion model assumed Fick's Law is being obeyed with a constant diffusion coefficient and this behavior is subsequently verified. This method has been used by the authors frequently in the study of interdiffusion in a range of III–V systems and a fuller description of it can be found in Ref. 1. The material parameters used in this calculations were: the strained band gap $[=2820-1530x+510x^2$ (meV)]; the strained electron and heavy hole potentials, $925x$(meV) and $435x$(meV), respectively, the electron effective mass (=0.2026) and the heavy hole effective mass (=0.49).[2]

In Fig. 2, we show a photoluminescence spectrum measured before and after annealing. It can be seen that the intensity of the unannealed sample initially increases after annealing. We have observed this phenomenon for even low temperature (500 °C) anneals and is evidence that the optical quality of ZnSe/ZnCdSe has been improved. However, at these low temperatures there is no significant shift in the PL peak energy so little interdiffusion can have occurred in the growth direction. From Fig. 1 it can be seen that ~1 nm of diffusion could have occurred before PL emission would be expected to shift measurably. This phenomenon has been observed previously in the III–Vs (Ref. 3) and has been attributed to interface smoothing as a result of small scale local lateral diffusion. This phenomenon is not pursued further in this letter but we note that it may be of considerable technological interest in itself.

Plotting the data as diffusion length, L_D, squared against

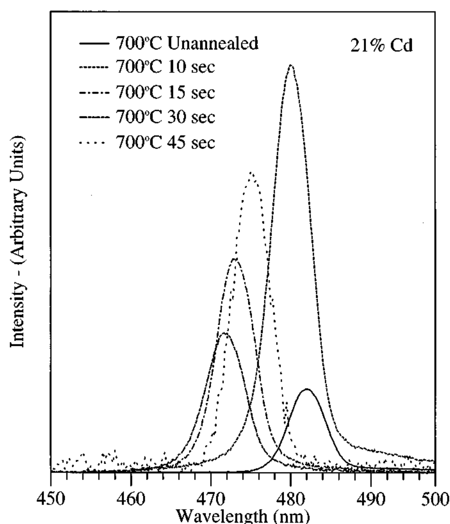

FIG. 2. A plot of PL intensity against wavelength for the 21% Cd sample as a function of annealing time.

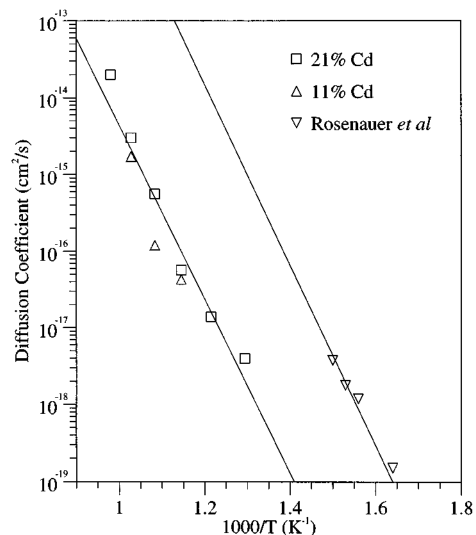

FIG. 4. An Arrhenius plot of diffusion coefficient against inverse temperature for the 11% Cd sample and the 21% sample and for the data of Rosenauer *et al.*[4] for a single monolayer of CdSe in ZnSe. The solid line through our data is the best fit to the 11% and 21% data. The solid line through the Rosenauer data is the best line fit of activation energy 2.3 eV.

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the anneal time, t, as shown in Fig. 3, the diffusion coefficient at a given temperature can be determined directly from the gradient of this plot. The fact that we obtain straight lines on the L_D^2 against t plot confirms that our initial assumption that Fick's Law is being obeyed is correct.[1]

Figure 4 shows the Arrhenius plot of diffusion coefficient against inverse temperature $1000/T$ for both the 11% and 21% samples. From the slope of this plot we obtain an activation energy of 2.4 ± 0.2 eV and a prefactor of 4.6×10^{-3} $cm^2\,s^{-1}$ for the 21% sample and 2.7 ± 0.7 eV and a prefactor of 0.114 $cm^2\,s^{-1}$ for the 11% sample. We note that the activation energies measured for the two different compositions, (11% and 21), of the ZnSe/ZnCdSe materials are identical, within experimental error. Overall the interdiffusion coefficient, D, for the group II sublattice in this system can be described as $D=1.5\times10^{-3}$ $\exp(-2.3$ eV/kT). The other data, shown on Fig. 3, is from a high resolution transmission electron microscopy study of interdiffusion of a molecular beam epitaxy (MBE) grown single CdSe monolayer in ZnSe over a 50 °C range (340–390 °C) of anneal temperature at temperatures near to the growth temperature, due to Rosenauer *et al.*[4] These authors obtain an activation energy of 1.9 eV for the Cd interdiffusion. Within experimental error this activation energy is in agreement with the present study. The prefactor for the MBE grown material, taking the same activation energy of 2.3 eV, is around 2.5 decades higher than our MOVPE material. This could either be the result of different grown in vacancy concentrations on the group II sublattice for the two different growth methods or possibly more likely the result of the different annealing regimes: in our study the samples were capped prior to annealing, in the previous study the samples were annealed uncapped *in situ* in the growth reactor. Finally, we note that the interdiffusion coefficients we obtain for the ZnCdSe system are around 4–5 decades higher than are typically observed for III–V materials.[1] Given that interdiffusion is already found to be a significant factor in the growth and processing of III–V devices,[5] the effects of interdiffusion in the processing of II–VI devices will need to be carefully considered.

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