



Optical study of interdiffusion in CdTe and ZnSe based quantum wells

D. Tönnies ^{*,a}, G. Bacher ^a, A. Forchel ^a, A. Waag ^b, Th. Litz ^b, D. Hommel ^b,
Ch. Becker ^b, G. Landwehr ^b, M. Heuken ^c, M. Scholl ^c

^a Technische Physik, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

^b Experimentelle Physik III, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

^c Institut für Halbleitertechnik-Lehrstuhl I, RWTH Aachen, Templergraben 55, D-52062 Aachen, Germany

Abstract

The interdiffusion in single quantum well structures was studied for a variety of II–VI semiconductor materials based on CdTe and ZnSe. In particular we have investigated CdTe/CdMnTe, CdTe/CdMgTe, $\text{Hg}_x\text{Cd}_{1-x}\text{Te}/\text{Hg}_y\text{Cd}_{1-y}\text{Te}$ and ZnSe/CdZnSe structures in which an intermixing of column II elements can be induced as well as ZnSe/ZnSSe allowing an interdiffusion within the column VI sublattice. The diffusion was induced by rapid thermal annealing (RTA) for 1 min at different temperatures. The resulting blue shift of the characteristic emission spectrum was analyzed using photoluminescence spectroscopy. We observed a significant difference of the diffusion behavior between both groups of materials. While in all three CdTe based material systems an almost complete interdiffusion within the column II sublattice could be obtained at a high optical quality of the structures, both ZnSe based quantum wells show only remarkably small diffusion lengths. For all three CdTe based quantum wells we derived an activation energy of the interdiffusion process from a simple Fickian diffusion model applied to our measurements. We obtained a value of 2.8 eV for CdTe/CdMnTe and CdTe/CdMgTe and a value 2.1 eV for $\text{Hg}_x\text{Cd}_{1-x}\text{Te}/\text{Hg}_y\text{Cd}_{1-y}\text{Te}$.

Due to the fundamental role of diffusion for the production of semiconductor devices, the study of diffusion in semiconductor crystals has been of large interest in the last years. Self-diffusion or impurity diffusion in III–V and II–VI bulk materials was studied, e.g. by secondary ion mass spectroscopy (SIMS), a technique that allows a direct scanning of the diffusion profile [1]. In recent years, diffusion has also been investigated in thin heterostructures which offer an

interesting source of concentration gradients. The interdiffusion of the materials in the well and barrier layers results in a blue shift of the emission spectrum [2]. The technological interest on this effect arises from the possibility to tune the wavelength of an optical emitter by simply annealing the device. On the other hand, it has been shown in III–V quantum wells that the selective implantation of ions in a semiconductor heterostructure offers the possibility to define a lateral confinement [3,4]. Up to now the investigation of diffusion in heterostructures has been restricted mainly to III–V materials. Only few

* Corresponding author.

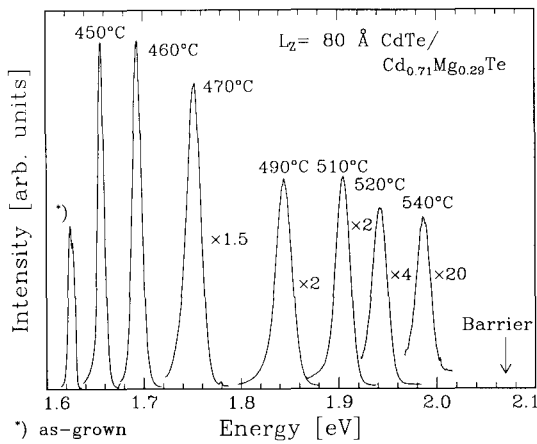


Fig. 1. PL spectra of the excitonic recombination of a 80 Å CdTe/Cd_{0.71}Mg_{0.29}Te quantum well before and after annealing for 1 min at temperatures between 450 and 540°C. The energy of the barrier is indicated by an arrow.

results have been reported on interdiffusion in II–VI heterostructures [5,6].

In this paper we report on a comparative investigation of diffusion in II–VI single quantum wells from five different material systems grown by molecular beam epitaxy (MBE) or metalorganic vapor phase epitaxy (MOVPE). Three of these, namely CdTe/CdMgTe, CdTe/CdMnTe and Hg_xCd_{1-x}Te/Hg_yCd_{1-y}Te, are based on CdTe while the other two, ZnSe/CdZnSe and ZnSe/ZnSSe, are based on ZnSe. In all three CdTe-based material systems and in ZnSe/CdZnSe, the interdiffusion takes place within the column II sublattice, while in ZnSe/ZnSSe the column VI elements are intermixing. We annealed single quantum well structures grown of

these materials and characterized the processed samples by photoluminescence (PL) spectroscopy. From the observed blue shifts we found a different diffusion behavior for CdTe and ZnSe-based materials. While CdTe-based materials show a blue shift up to the barrier energy, in ZnSe-based quantum wells no blue shift larger than a few meV could be induced.

In Table 1 an overview of the investigated samples is given. Listed for each material system are the growth technique, the growth temperature, the substrate material and the quantum well thickness. The interdiffusion was induced by rapid thermal annealing (RTA) at different temperatures with an annealing time chosen to be 1 min. During the annealing process, the samples were exposed to a continuous flux of N₂ to avoid surface oxidation and covered with a silicon wafer to reduce material evaporation. Due to the interdiffusion, the composition profile of the structures is altered in such a way that the bottom of the conduction band (top of the valence band) is shifted to higher (lower) energies resulting in a blue shift of the excitonic recombination. We used photoluminescence spectroscopy (PL) to characterize the annealed samples. The CdTe based structures were excited by the 514.5 nm line of an Ar⁺ laser, while the 363 nm line was used to excite both ZnSe based systems. The photoluminescence signal was dispersed by a 0.3 m monochromator and detected by a CCD camera. For HgCdTe a cooled germanium detector was used.

Fig. 1 displays some photoluminescence spectra of the excitonic recombination of an 80 Å CdTe/CdMgTe quantum well annealed at differ-

Table 1

Structural properties of the single quantum wells investigated in this work; listed are the technique of epitaxial growth, the growth temperature, the substrate material and the quantum well thickness L_z

Material	Growth technique	Growth temperature (°C)	Substrate	L_z (Å)
CdTe/Cd _{0.71} Mg _{0.29} Te	MBE	230	CdZnTe	80
CdTe/Cd _{0.86} Mn _{0.14} Te	MBE	230	CdTe	40
Hg _{0.53} Cd _{0.47} Te/Hg _{0.29} Cd _{0.71} Te	MBE	180	CdZnTe	40
Cd _{0.2} Zn _{0.8} Se/ZnSe	MBE	300	GaAs	33
ZnSe/ZnS _{0.68} Se _{0.32}	MOVPE	480	GaAs	10

ent temperatures. The leftmost spectrum was taken from the as-grown structure. The other spectra are those of the annealed samples and exhibit the blue shift of the photoluminescence signal. For an annealing time of 1 min increasing the annealing temperatures from 450 to 540°C leads to an increasing blue shift of the photoluminescence spectra. For the highest annealing temperatures of 540°C the photoluminescence signal is blue-shifted almost to the energy of the barrier, i.e. nearly through the entire spectral region possible, indicating an almost complete intermixing of the well and barrier materials.

For quantum wells annealed at temperatures higher than 460°C, the halfwidth of the photoluminescence spectra increases from about 10 to 15 meV for CdTe/CdMgTe. This is probably due to a slightly inhomogeneous diffusion process leading to non-uniform shapes of the composition profile throughout the samples. Nevertheless the broadening of the photoluminescence signal is relatively small and indicates a good optical quality of the processed structures. In conjunction with the increase of the linewidth, the intensities of the PL signals decrease for the strongly intermixed quantum wells. We attribute this to the creation of defects during the diffusion process.

In Fig. 2, the corresponding blue shifts of the photoluminescence from the annealed structures are plotted versus the annealing temperature for all three CdTe-based materials. For CdTe/CdMgTe we observed energy shifts up to 360 meV. This value is larger than any interdiffusion induced energy gap change achieved in III–V materials so far. The proper temperature regions for 1 min annealing are roughly the same for CdTe/CdMnTe and CdTe/CdMgTe and lies between 400 and 540°C, while annealing temperatures between 280 and 330°C are sufficient to induce interdiffusion in $\text{Hg}_x\text{Cd}_{1-x}\text{Te}/\text{Hg}_y\text{Cd}_{1-y}\text{Te}$ quantum wells. For all three materials the photoluminescence signal shifts close to the energy of the barrier. Thus, within all three CdTe-based materials, it is possible to intermix the well and barrier material almost completely without destroying the high quality of the epitaxy.

From the measured energy shifts we derived diffusion coefficients for each annealing tempera-

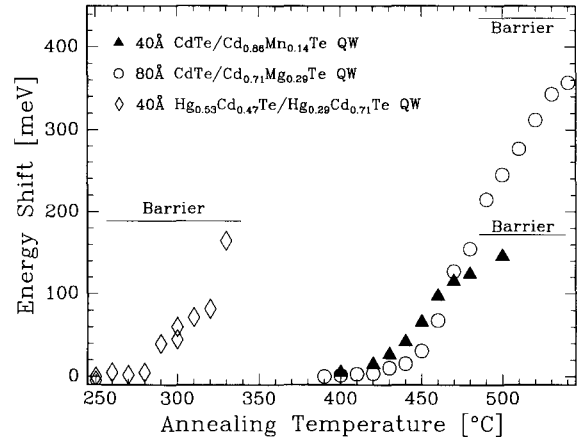


Fig. 2. Energy shifts of the PL signal of annealed $\text{Hg}_{0.53}\text{Cd}_{0.47}\text{Te}/\text{Hg}_{0.29}\text{Cd}_{0.71}\text{Te}$, $\text{CdTe}/\text{Cd}_{0.71}\text{Mg}_{0.29}\text{Te}$ and $\text{CdTe}/\text{Cd}_{0.86}\text{Mn}_{0.14}\text{Te}$ quantum well structures. The largest energy shifts of each material corresponds to the energy of the barrier in the as-grown samples.

ture. The profile of the interdiffused quantum well was determined from the composition profile depending on the diffusion length L_D . We solved the one-dimensional Schrödinger equation numerically [7] and obtained thereby a correlation between the measured blue shift and the diffusion length. Finally, the diffusion coefficient was calculated from $D = L_D^2/\tau$, where τ is the annealing time. The results are displayed in Fig. 3. The diffusion coefficients D are plotted versus the reciprocal temperature $1/kT$. The approximately linear dependence of $\ln D$ and $1/kT$ allows one to model the temperature dependence of the diffusion coefficient by an Arrhenius law,

$$D(T) = D_\infty \exp(-E_a/kT),$$

where E_a is the activation energy necessary for a single diffusion process of a particle within the crystal lattice. The activation energy can be derived from the slope of the linearly fitted curves. We obtained a value of 2.8 eV for both the CdTe/CdMnTe and the CdTe/CdMgTe quantum well and a value of 2.1 eV for $\text{Hg}_x\text{Cd}_{1-x}\text{Te}/\text{Hg}_y\text{Cd}_{1-y}\text{Te}$. In our calculations we neglected for simplicity the concentration dependence of the diffusion in HgCdTe, which is reported by several authors [6,8]. In consequence our value of

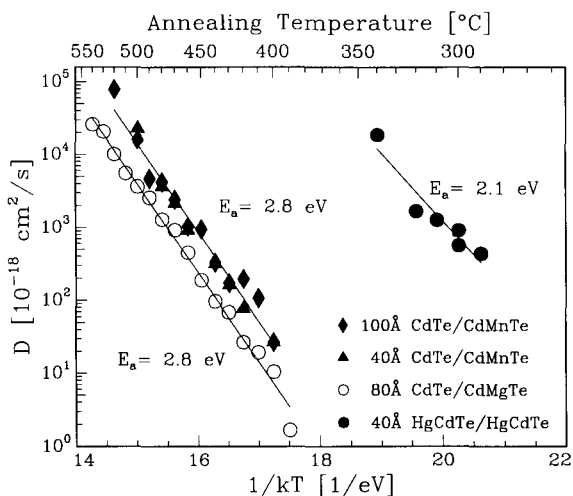


Fig. 3. Diffusion coefficients D versus the reciprocal temperature for CdTe/CdMnTe, CdTe/CdMgTe and Hg_{1-x}Cd_xTe/Hg_{1-y}Cd_yTe. The activation energies are estimated from the slope of the curves.

the activation energy in this material lies a little above those published in these works.

The investigation of the ZnSe-based material systems reveals a significantly different diffusion behavior. In Fig. 4, the PL spectrum of the as-grown 33 Å ZnSe/CdZnSe quantum well and of the same structure annealed at 600°C is displayed. The annealed sample exhibits an energy shift of 20 meV in conjunction with a decrease of

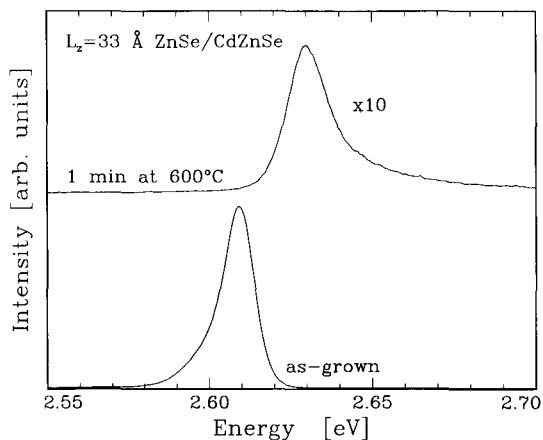


Fig. 4. PL spectra of the excitonic recombination of a 33 Å ZnSe/Cd_{0.20}Zn_{0.80}Se quantum well before and after annealing.

the PL intensity by more than one order of magnitude. Annealing at higher temperatures leads to no further energy shift but to a complete vanishing of the characteristic photoluminescence signal, although from the total confinement of the quantum well blue shifts up to 200 meV should be possible. The 10 Å ZnSe/ZnSSe samples were annealed at 580, 660 and 700°C, and reveal energy shifts smaller than 40 meV, which are lower than the band discontinuity of this quantum well structure of about 400 meV. A further increase of the annealing temperature quenches the PL intensity completely. For both material systems, a variation of the annealing time did not improve the quality of the annealed structures. This diffusion behavior is in strong contrast to that of CdTe based quantum wells, where a almost complete intermixing is possible without quenching the luminescence signal. The explanation of this effect is not clear yet. Although an explanation is probably difficult due to a lack of information on the crystal lattice, it is worth noting that CdTe, HgTe, MnTe and MgTe have noticeable larger lattice constants than the other materials (see Table 2), which might have an influence on the stability of these crystals against annealing.

Another interesting point are the temperature regions necessary to induce interdiffusion in the investigated quantum well structures. The smallest temperatures are necessary for Hg_xCd_{1-x}Te/Hg_yCd_{1-y}Te which show interdiffusion effects

Table 2

Properties of several II–VI semiconductor materials; listed are the lattice constant a , the Debye temperature Θ_D at 0 K and the melting point T_m

Material	a (Å)	Θ_D at 0 K (K)	T_m (°C)
HgTe	6.5 ^a	147 ^b	670 ^a
CdTe	6.5 ^a	150, 160 ^a	1092 ^a
MnTe	6.3 ^c	–	–
MgTe	6.4 ^d	–	–
CdSe	6.1 ^a	230, 315 ^b	1241 ^a
ZnSe	5.7 ^a	~ 270 ^b	1520 ^a
ZnS	5.4 ^a	334 ^b	1830 ^a

^a Ref. [9].

^b Ref. [10].

^c Ref. [11].

^d Ref. [12].

for temperatures smaller than 300°C. The proper temperature region for annealing CdTe/CdMgTe and CdTe/CdMnTe structures is roughly the same and lies within 390 and 540°C, while for ZnSe/CdZnSe as well as for ZnSe/ZnSSe, a temperature of about 600°C is necessary to obtain small blue shifts. It is interesting to compare the Debye temperature and the melting temperature of these materials, because both the temperature necessary for the activation of lattice vibrations and the destruction of the crystal lattice are expected to be correlated with the temperature necessary to induce interdiffusion. In Table 2, the Debye and melting temperatures are listed for a variety of semiconductor alloys. For HgTe, CdTe and ZnSe, the Debye temperature as well as the melting temperature are growing from HgTe to ZnSe and reveal therefore the same tendency as the characteristic interdiffusion temperatures of the material systems investigated in this paper.

In summary, we have investigated the diffusion in single quantum wells grown of five different II–VI semiconductor materials. We found that all three CdTe-based materials, $\text{Hg}_x\text{Cd}_{1-x}\text{Te}/\text{Hg}_y\text{Cd}_{1-y}\text{Te}$, CdTe/CdMnTe and CdTe/CdMgTe, offer the possibility to completely intermix the quantum well and barrier material without quenching the luminescence signal and as a consequence to shift the photoluminescence signal almost up to the energy of the barrier. This property makes these materials promising candidates for optical emitters with a wavelength that can be tuned by a thermal process. On the other hand, in ZnSe/CdZnSe and ZnSe/ZnSSe quantum wells, energy shifts of only a few meV were achieved without destroying the optical quality of the grown structures. Furthermore, the tempera-

ture necessary to obtain a significant diffusion for 1 min annealing is smallest for the $\text{Hg}_x\text{Cd}_{1-x}\text{Te}/\text{Hg}_y\text{Cd}_{1-y}\text{Te}$ system and increases over CdTe/CdMg(Mn)Te to ZnSe/ZnCd(S)Se.

The work at Würzburg university was financially supported by the Bayerische Forschungsgemeinschaft.

1. References

- [1] D. Shaw, *J. Crystal Growth* 86 (1988) 778.
- [2] M.D. Camras, N. Holonyak, Jr., R.D. Burnham, W. Streifer, D.R. Scifres, T.L. Paoli and C. Lindström, *J. Appl. Phys.* 54 (1983) 5637.
- [3] C. Vieu, M. Schneider, D. Maily, R. Planel, H. Launois, J.Y. Marzin and B. Descouts, *J. Appl. Phys.* 70 (1991) 1444.
- [4] H. Leier, A. Forchel, G. Hörcher, J. Hommel, S. Bayer, H. Rothfrit, G. Weimann and W. Schlapp, *J. Appl. Phys.* 67 (1990) 1805.
- [5] A. Hamoudi, E. Ligeon, K. Saminadayar, J. Cibert, Le Si Dang and S. Tatarenko, *Appl. Phys. Lett.* 60 (1992) 2797.
- [6] A. Tardot, A. Hamoudi, N. Magnea, P. Gentile and J.L. Pautrat, *Semicond. Sci. Technol.* 8 (1993) S276.
- [7] W.W. Lui and M. Fukuma, *J. Appl. Phys.* 60 (1986) 1555.
- [8] J.H.C. Hogg, A. Bairstow, G.W. Matthews, D. Shaw and J.D. Stedman, *Mater. Sci. Eng. B* 16 (1993) 195.
- [9] Landolt–Börnstein, New Series III/22a, Semiconductors: Intrinsic Properties of Group IV Elements and III–V, II–VI and I–VII Compounds, Ed. O. Madelung (Springer, Berlin, 1987).
- [10] Landolt–Börnstein, New Series III/17b, Semiconductors: Physics of II–VI and I–VII Compounds, Semimagnetic Semiconductors, Ed. O. Madelung (Springer, Berlin, 1982).
- [11] R.T. Delves and B. Lewis, *J. Phys. Chem. Solids* 24 (1963) 549.
- [12] A. Waag, H. Heinke, S. Scholl, C.R. Becker and G. Landwehr, *J. Crystal Growth* 131 (1993) 607.