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The effect of linear and non-linear diffusion on exciton energies in quantum wells

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This paper considers the technique of investigating diffusion processes via monitoring spectroscopically the ground state energy of an exciton confined in a quantum well. It is shown that the change in the exciton energy $E-E_0$ during linear diffusion, can be described by an empirical relationship $E-E_0=(E_g^b-E_0)(1-\exp\{-\gamma\sqrt{Dt}/l_w\})$, where E_g^b is the band gap of the initial barrier material, D the diffusion constant and t the time. Detailed calculations accounting for the changes in the exciton binding energy have shown that the parameter $\gamma\sim 1.5$ for *all* wells of width $l_w>40$ Å regardless of the material system. It is proposed that this relationship could be used to determine the linear diffusion coefficient D. Once D has been determined the relationship could then be utilized as a predictive tool, e.g., to determine the annealing time necessary to produce a given energy shift for a particular quantum well width. The paper goes on to discuss the effects non-linear diffusion processes could have on exciton energies in quantum wells. In particular, it is shown how detailed spectroscopy and annealing experiments when coupled with accurate modelling could be used to distinguish between constant and concentration dependent diffusion coefficients.
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I. INTRODUCTION

The opto-electronic characteristics of devices based on semiconductor quantum well structures are dependent on the confining potentials associated with the conduction and valence band, which in turn are a reflection of the structural parameters of the device. Quantum wells formed from a binary compound AC and its ternary alloy $A_{1-x}B_xC$ are susceptible to diffusion under real operating conditions due to the rapid change in the concentration of the alloy component B at the heterojunction. Hence diffusion could significantly affect the operational lifetime of a device.

This work constitutes a study of the temporal evolution of the ground state heavy-hole exciton energy in a quantum well during diffusion. It differs from other work, for example, Ref. 1, in that it looks at materials in which the exciton binding energy cannot be ignored, for example the II–VI semiconductor CdTe/Cd$_{1-x}$Mn$_x$Te. Furthermore both linear and non-linear diffusion processes are investigated and their effects contrasted.

II. THEORETICAL MODEL

The one-dimensional diffusion equation for a diffusant distribution represented by $x(z)$ is[2,3]

$$\frac{\partial x}{\partial t}=\frac{\partial}{\partial z}\left(\mathscr{D}\frac{\partial x}{\partial z}\right), \tag{1}$$

where t is the time. The diffusion coefficient $\mathscr{D}$ will, in general have a temporal t, spatial z and concentration x dependence. Equation 1 can be expanded in terms of finite differences to give

$$\begin{aligned}\frac{x(z,t+\delta t)-x(z,t)}{\delta t}&=\left(\frac{\mathscr{D}(x,z+\delta z,t)-\mathscr{D}(x,z-\delta z,t)}{2\,\delta z}\right)\\&\quad\times\left(\frac{x(z+\delta z,t)-x(z-\delta z,t)}{2\,\delta z}\right)+\mathscr{D}(x,z,t)\\&\quad\times\left(\frac{x(z+\delta z,t)-2x(z,t)+x(z-\delta z,t)}{(\delta z)^2}\right).\end{aligned} \tag{2}$$

It is obvious that the function $x(z,t)$ is known when $t=0$, it is simply the initial profile of the diffusant. In order to proceed with the calculation the entity $\mathscr{D}$ must be prescribed, i.e., its functional dependence on the variables x, z and t must be known. Given this, it is apparent from Eq. 2 that the concentration x at any point z can be calculated a short time interval δt into the future, provided the concentration x is known at small spatial steps δz on either side of z.

Although the concentration x dependence has been much discussed in the literature we note that a spatial dependence can arise from the lattice damage accompanying ion implantation and that a temporal t dependence can arise from the annealing out of this damage.

For the purpose of illustration we will base our work on the CdTe–Cd$_{1-x}$Mn$_x$Te system. This II–VI material is also interesting, compared with a typical III–V material, such as GaAs–Ga$_{1-x}$Al$_x$As, in that changes in the exciton binding energy resulting from the diffusion process cannot be ignored.[1] It will be assumed that the spectroscopic technique to be considered is photoluminescence excitation (PLE). This has the advantage that the Stokes shift due to interface disorder relaxation of the excitons[4] can be ignored, as can

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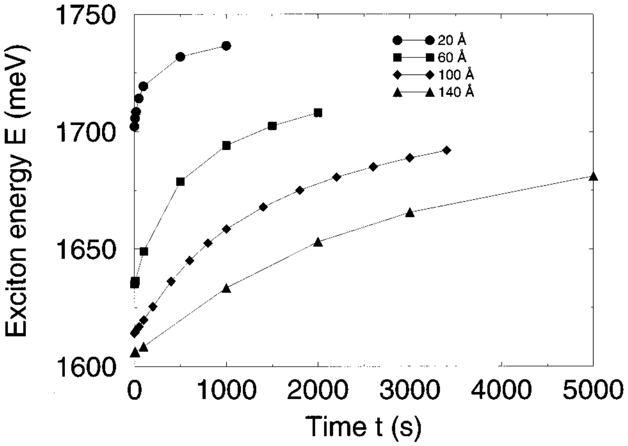

FIG. 1. Temporal evolution of the calculated e1–hh1 exciton energy for a constant diffusion coefficient $D=1$ Å^{2}s^{-1} for various quantum well widths.

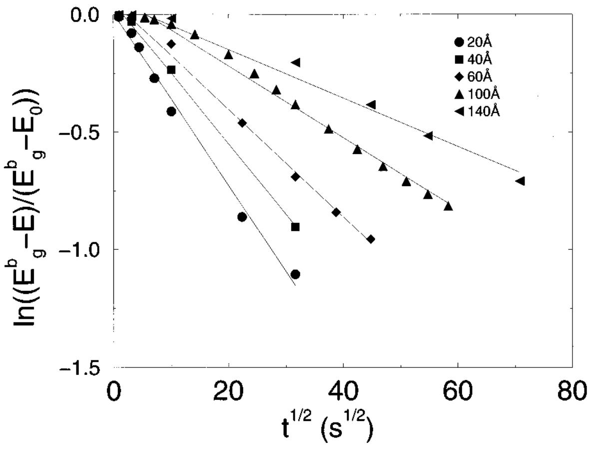

FIG. 2. Temporal evolution of the calculated e1–hh1 exciton energy for a constant diffusion coefficient $D=1$ Å^{2}s^{-1} for various quantum well widths.

any complicating features due to magnetic polaron formation.[5] The band gap of the well material CdTe was taken as $E_g^w=1606$ meV and the band gap of the barrier Cd$_{1-x}$Mn$_x$Te was taken as $E_g^b=E_g^w+x1587$ meV. Unless otherwise stated, 40% of the total band discontinuity κ, was taken to lie in the valence band,[6] the alloy concentration x of the undiffused barrier material was taken to be 0.1 (10%) and the electron and heavy-hole effective masses used were 0.096 and 0.6 m_0 respectively.

The exciton energies were calculated using a numerical solution to the one-dimensional Schrödinger equation appropriate to a diffused quantum well profile,[7] evaluated using the technique outlined above. The exciton binding energies were calculated with a two parameter variational calculation, see for example Ref. 7. Recent work[8] has shown that this exciton model allows self-consistent effects to be neglected in the calculation of exciton energies in the type I single quantum wells considered here.

III. LINEAR DIFFUSION

Figure 1 shows the effect of diffusion characterized by a constant coefficient $\mathscr{D}=D_0=1$ Å^{2}s^{-1} on the ground state heavy-hole exciton energies E in a series of quantum wells of widths $l_w=$ 20, 60, 100 and 140 Å . These curves are typical and differing forms of $\mathscr{D}$ are qualitatively similar.

A point of interest is whether there is a way of characterizing the curves representing the temporal evolution of the exciton energy during annealing, so as to be able to distinguish between linear and non-linear diffusion processes.

Examination of the curves in Fig. 1 shows that they have the appearance of growing exponentials and it is obvious that the increase in the exciton energy with diffusion must saturate when $E=E_g^b$, i.e., when the well has completely diffused and the band gap around the former well region is just that of the barrier. Hence it is tempting to postulate that the change in exciton energy $E-E_0$ might be

$$E-E_0=(E_g^b-E_0)\left(1-\exp\left(-\frac{\gamma\sqrt{Dt}}{l_w}\right)\right), \tag{3}$$

where γ is some (as yet) unknown parameter. Note that here E_g^b must include the bulk exciton binding energy. Hence

$$\ln\left(\frac{E_g^b-E}{E_g^b-E_0}\right)=-\frac{\gamma\sqrt{Dt}}{l_w}. \tag{4}$$

Thus a plot of $\ln((E_g^b-E)/(E_g^b-E_0))$ versus $\sqrt{t}$ should be a straight line through the origin with a slope of $-\gamma\sqrt{D}/l_w$.

Figure 2 displays the data of Fig. 1 in this format. From the slopes the unknown parameter γ was calculated as 0.73, 1.20, 1.37, 1.52 and 1.44 for the 20, 40, 60, 100 and 140 Å quantum wells respectively. It appears from these values that γ could, within certain parameter domains, be taken as a constant centered around 1.5. To investigate this further, calculations were performed for the 100 Å single quantum well for three different values of the diffusion coefficient, i.e., $D_0=1$, 2, and 3 Å s^{-1}. The results of the calculations are plotted in Fig. 3.

Analysis of the slopes gives values of γ as 1.52, 1.44 and 1.49 for $D_0=1$, 2, and 3 Å s^{-1} respectively. Further calculations with differing initial barrier heights, i.e., $x=0.2$ and 0.3, and different band alignments, i.e., $\kappa=0.2$, also gave $\gamma\sim 1.5$. In a further set of calculations the electron and hole

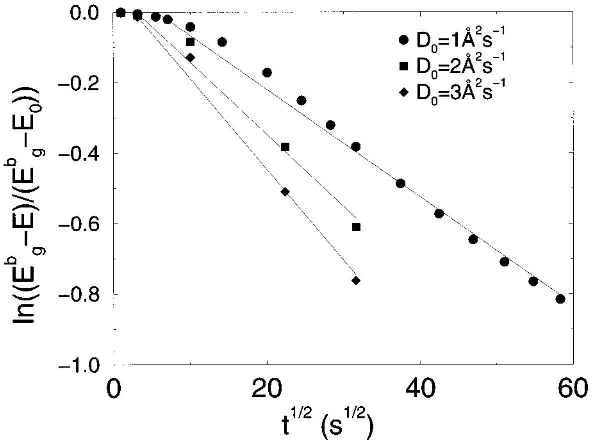

FIG. 3. Temporal evolution of the calculated e1–hh1 exciton energy in a 100 Å quantum well with $\mathscr{D}=D_0=1$, 2 and 3 Å^{2}s^{-1}.

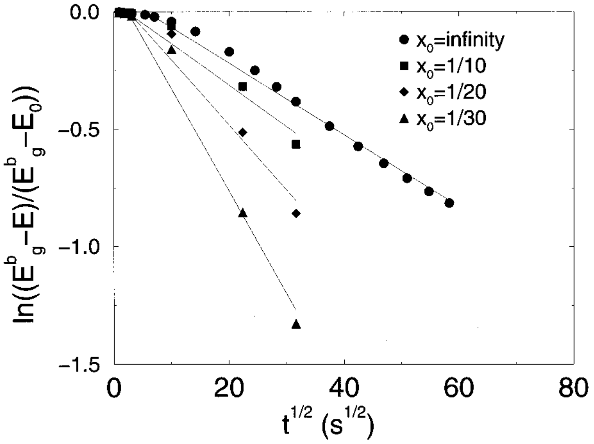

FIG. 4. Temporal evolution of the calculated e1–hh1 exciton energy in a 100 Å quantum well with the diffusion coefficients given by $\mathscr{D}=1$ Å^{2}s^{-1}exp(x/x_0).

effective masses were chosen to be double their accepted values and γ was found to be ~ 1.1. Hence it appears that for typical well widths (i.e., >40 Å) Eq. 3 can be used to describe the expected PLE data for annealed samples and that the resulting curves are characterized by a parameter γ whose value lies typically in the range of 1 to 1.5.

IV. NON-LINEAR DIFFUSION

As discussed previously there are many functional dependencies of the diffusion coefficient $\mathscr{D}$ that could be considered, the purpose of this work however is to demonstrate a method of utilizing optical data from diffusion experiments within quantum well structures, to determine whether non-linear diffusion processes are occurring or not. With this aim the particular case of a concentration dependent diffusion coefficient $\mathscr{D}=D(x)$ will be used and as an example

$$\mathscr{D}=D_0\exp\left(\frac{x}{x_0}\right), \tag{5}$$

where the constant D_0 was chosen to have the value of 1 Å^{2}s^{-1} and x_0 is a constant describing the strength of the dependence of the diffusion coefficient on the concentration x.

Two series of calculations were performed with the dependency of Eq. 5—one for the 100 Å quantum well with $x_0=\infty$, 1/10, 1/20 and 1/30. The first of these, $x_0=\infty$ just reproduces the constant (or linear) D_0 situation. Remembering that the maximum value of x is 0.1 then, $x_0=1/10$, 1/20 and 1/30 implies that $\mathscr{D}$ varies by factors of e, e^2, and e^3, respectively, between $x=0$ and $x=0.1$. In the second series of calculations, x_0 was kept constant at 1/10 for the four quantum wells of width 20, 60, 100, and 140 Å .

The data from both sets of calculations are qualitatively similar to the linear case, when plotted in the format of both Fig. 1 and Fig. 2. This is illustrated in Fig. 4 for the first series of calculations, i.e., the 100 Å quantum well with varying values of x_0. Although straight lines could be fitted to the curves as suggested by Eq. 4, strictly speaking a value for γ should not be quoted since D is no longer a constant. However one can obtain a value for the product $\gamma\sqrt{D}$, and by choosing for D the value of D_0 (corresponding to $x_0=\infty$, which in experimental terms can also be realized by choosing low concentrations) one can deduce a value of γ. Figure 4 shows that if the system diffuses non-linearly then this value is very different from the linear ($x_0=\infty$) value of 1.52. For the data of Fig. 4, γ=1.76, 2.77 and 4.36 for x_0=1/10, 1/20 and 1/30 respectively. Note that the stronger the non-linearity, the greater the γ. The second series of calculations which involved a constant x_0 and varying well width lead to similar conclusions.

TABLE I. The heavy-hole exciton data as a function of annealing temperature as measured by Tönnies *et al.*

T (°C)	E (meV)
as grown	1646
400	1649
430	1672
450	1712
460	1743
480	1772
500	1794

A similar discrepancy from $\gamma\sim 1.5$ will be obtained for a diffusion coefficient which decreases with increasing concentration, as suggested by Fleming *et al.*,[9] for the GaAs–AlAs system. In contrast, this will lead to smaller values of γ. Hence this is a simple characteristic of the temporal evolution of the exciton energy during annealing which could be an indication of non-linear diffusion.

V. ANALYSIS OF EXPERIMENTAL DATA

Tönnies *et al.*[10] performed photoluminescence experiments on CdTe/Cd$_{1-x}$Mn$_x$Te quantum well samples that had undergone rapid thermal annealing for the set time of 1 minute, but at a variety of temperatures. The samples, all cleaved from the same wafer, consisted of a single 40 Å wide CdTe quantum well surrounded by Cd$_{0.86}$Mn$_{0.14}$Te barriers. The observed ground state heavy-hole exciton energy E as a function of the annealing temperature T is given in Table I.

Tönnies *et al.* deduced that the temperature dependence of the diffusion coefficient could be described by an Arrhenius type relation, i.e.,

$$\mathscr{D}=D_\infty\exp\left(-\frac{E_a}{kT}\right). \tag{6}$$

Substituting this form of $\mathscr{D}$ into Eq. 4 gives

$$\ln\left(\frac{E_g^b-E}{E_g^b-E_0}\right)=-\frac{\gamma\sqrt{D_\infty t}}{l_w}\exp\left(-\frac{E_a}{2kT}\right) \tag{7}$$

which is of the form of a straight line through the origin. Figure 5 displays the experimental data of Tönnies *et al.* in the straight line form suggested by Eq. 7, using the activation energy E_a of 2.8 eV.[10]

It is clear from Fig. 5 that the data indeed follow a straight line through the origin which helps validate the proposed empirical relationship of Eq. (3). Taking the nominal

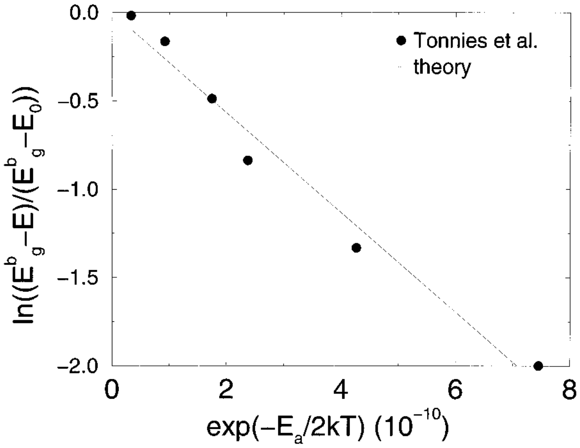

FIG. 5. The experimental data of Tönnies *et al.* (solid circles) in comparison with the theoretical fit.

well width, together with the diffusion time as $t=60$ s and $D_\infty=3.7$ m^{2}s^{-1} as in Ref. 10, allows γ to be determined as $\sim$0.8, which is similar to the value of 1.2 deduced theoretically above for the same well width. The difference can easily be accounted for in terms of uncertainties in the structural parameters which would lead to large discrepancies in D_∞.[11]

Kossacki *et al.*[12] annealed a sample which contained several CdTe quantum wells of differing width, separated by $Cd_{0.525}Mn_{0.475}Te$ barriers for 15 s at 450 °C. The reported heavy-hole exciton energies before E_0 and after E the anneal are given in Table II.

Figure 6 displays the data of Kossacki *et al.* in the form suggested by Eq. 4. As above, a theoretical fit can be made which is a straight line passing through the origin although there is some scatter in the data points. Taking $\gamma=1.5$ from the theoretical calculations earlier, then the diffusion length $l_d=\sqrt{Dt}$ can be deduced from the slope of Fig. 6, thus giving $l_d \sim 2$ Å. Taking the scatter in the experimental data as representative of the uncertainty, then this translates to an uncertainty in the diffusion length l_d of the order of 0.5 Å. This value of l_d is smaller than that deduced by Kossacki *et al.* However the difference could be accounted for by the fact that Kossacki *et al.* deduced the value of l_d from measurements on the Zeeman splittings of the reflectivity spectra. In their analysis these authors ignored enhancements in the paramagnetic response at interfaces between magnetic and non-magnetic semiconductors,[13,14] arising from the presence of the magnetic Mn^{2+} ion. Such enhancements lead to an increase in the Zeeman splitting of excitons in a magnetic field. Hence ignoring the effect will lead to an overestimation of the manganese concentration in the well and therefore an overestimation of the diffusion length.

TABLE II. The heavy-hole exciton data as a function of well width, both before (E_0) and after (E) anneal as measured by Kossacki *et al.*

l_w (Å)	E_0 (meV)	E (meV)
39	1739.5	1763.1
49	1697.4	1713.5
58	1675.0	1682.5
68	1656.4	1662.6
78	1636.6	1644.0

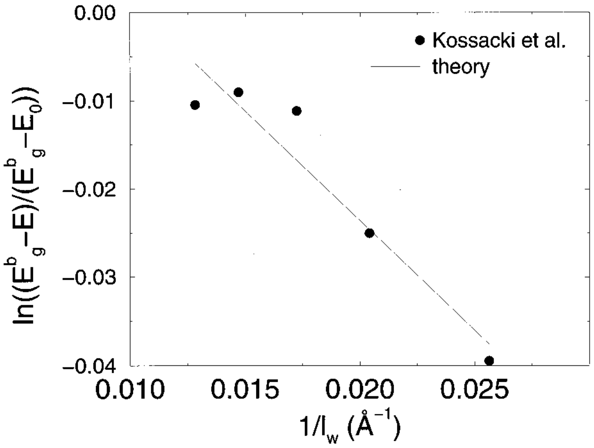

FIG. 6. The experimental data of Kossacki *et al.* (solid circles) in comparison with the theoretical fit.

VI. CONCLUSION

It has been shown that exciton energies as a function of annealing time in diffused quantum wells can be described by a simple empirical relationship. Such a relationship can be used as a predictive tool in order to determine required annealing times for particular quantum well structures, in order to achieve desired exciton energy changes. The validity of the empirical relationship has been substantiated by comparison with experimental data.

Furthermore it has been shown that detailed annealing/spectroscopy experiments coupled with accurate modelling could be used to distinguish between constant and concentration dependent diffusion coefficients.

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[1] M. T. Furtado and M. S. S. Loural, Superlatt. Microstruct. **14**, 21 (1993).
[2] A. Fick, Ann. Phys. Lpz. **170**, 59 (1855).
[3] J. Crank, *The Mathematics of Diffusion* (Oxford University Press, London, 1956).
[4] T. Stirner, P. Harrison, W. E. Hagston, and J. P. Goodwin, Surf. Sci. **313**, 417 (1994).
[5] D. R. Yakovlev, in *Festkörperprobleme/Advances in Solid State Physics*, edited by U. Rössler (Vieweg, Braunschweig, 1992), Vol. 32, p. 251.
[6] S. R. Jackson, J. E. Nicholls, W. E. Hagston, P. Harrison, T. Stirner, J. H. C. Hogg, B. Lunn, and D. E. Ashenford, Phys. Rev. B **50**, 5392 (1994).
[7] P. Harrison, W. E. Hagston, and T. Stirner, Phys. Rev. B **47**, 16404 (1993).
[8] T. Piorek, P. Harrison, and W. E. Hagston, Phys. Rev. B **52**, 14111 (1995).
[9] R. M. Fleming, D. B. McWhan, A. C. Gossard, W. Weigmann, and R. A. Logan, J. Appl. Phys. **51**, 357 (1980).

[10] D. Tönnies, G. Bacher, A. Forchel, A. Waag, and G. Landwehr, Appl. Phys. Lett. **64**, 766 (1994).

[11] T. Stirner, P. Harrison, and W. E. Hagston, J. Appl. Phys. **77**, 1314 (1995).

[12] P. Kossacki, N. T. Khoi, J. A. Gaj, G. Karczewski, T. Wojtowicz, E. Janik, A, Zakrzewski, M. Kutrowski, and J. Kossut, Superlatt. Microstruct. **16**, 63 (1994).

[13] W. J. Ossau and B. Kuhn-Heinrich, Physica B **184**, 422 (1993).

[14] T. Stirner, J. M. Fatah, R. G. Roberts, T. Piorek, W. E. Hagston, and P. Harrison, Superlatt. Microstruct. **16**, 11 (1994).