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The diffusion of Cl into CdTe

E D Jones†, J Malzbender†, J B Mullin‡ and N Shaw§

† School of Natural and Environmental Sciences, Coventry University, Coventry CV1 5FB, UK

‡ Electronic Materials Consultant, The Hoo, Brockhill Road, West Malvern, Worcester WR14 4DL, UK

§ *DRA Electronics Division, RSRE, St Andrews Road, Great Malvern, Worcester WR14 3PS, UK*

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Abstract. Results on the diffusion of Cl into CdTe are described. Diffusion anneals were carried out at selected temperatures in the range between 200 °C and 700 °C in evacuated SiO_2 ampoules using a diffusion source of $CdCl_2$ under saturated vapour pressure conditions. The concentration profiles were measured using a radiotracer sectioning technique. The profiles were found to be composed of four parts, to which a computer package consisting of the sum of four complementary error functions (erfc) gave satisfactory fits to the data. The fastest-diffusing component gave values of the diffusivity that agreed with previously published results. Proposals explaining how this type of diffusion may occur are given.

1. Introduction

Despite recent advances in materials technology, it remains a difficult task to control the conductivity and to maintain a stable junction in p–n junction devices manufactured from II–VI semiconducting materials. Consequently it is vital that the rates of diffusion of appropriate dopants through the host material are known so that the most suitable one can be selected for a particular device [1].

In has been the most widely used n-type dopant in CdTe and $(Hg_xCd_{1-x})Te$, but as it has proved to be a fairly fast diffusant [2] attention has been directed to the halogens, which are expected to reside on anion sites. I has been used on a regular basis as an n-type dopant in devices grown epitaxially [1], but recent measurements have shown that I is a fairly fast diffusant if diffused from an external source [3], producing diffusivities of 10^{-14} cm^{-2} s^{-1} at room temperature [4]. Such measurements have produced complex diffusion profiles, which could be fitted by a function composed of the sum of four complementary error functions. The reasons for this are still not fully explained.

Watson and Shaw [2] measured the rate of diffusion of Cl into CdTe in the temperature range 520–800 °C. They used a radiotracer sectioning technique employing radioactive Cl in the form of $CdCl_2$ as a diffusion source and obtained diffusion profiles fitted by a single erfc function. Near to saturated Cd overpressure the diffusivity was expressed by the following Arrhenius relationship:

$$D = (0.071 \overset{\times}{\div} 2.4) \exp[-(1.60 \pm 0.07 \text{ eV})/kT] \text{ cm}^2 \text{ s}^{-1}.$$

It was concluded that Cl diffuses via the neutral defect pair, $(V_{Cd}V_{Te})^*$. However, on close inspection of the profiles (e.g. figure 4(a)) the presence of a fast diffusing tail can be seen. Watson and Shaw [2] attributed this to an irregular behaviour. Advances in sectioning techniques have now made it possible to make a more detailed study of such profiles, which is the subject of this paper.

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2. Experimental techniques

Wafers of bulk grown CdTe, supplied by GEC Marconi Infrared Limited, Southampton, which had been cut with a diamond saw from large boules, containing a few grains, were used in this investigation. Single-crystal slices (about 8 mm $\times$ 8 mm) were cleaved out and chemically polished with 1% Br_2 in methanol to remove cutting damage. In this process a total thickness of between 100 and 200 μm was removed from the surface of each slice.

Each CdTe slice was sealed in an evacuated SiO_2 capsule (volume 10 cm^3) with sufficient $CdCl_2$ containing radioactive Cl to maintain a saturated vapour pressure over the slice throughout each anneal. The radioactive Cl contained the isotope ^{36}Cl, which has a half life of 3.01×10^5 years [5] and the $CdCl_2$ was produced using the process described by Watson and Shaw [2].

The anneals were carried out under isothermal conditions in an electric furnace in the temperature range 200–700 °C. The Cl concentration profiles were measured by radiotracer sectioning techniques [6] and the radioactivity was measured with a liquid scintillation counter.

During the diffusions the $CdCl_2$ diffusion source was not allowed to come into direct contact with the CdTe slice and so only molecules from the gas phase could enter the slice. At the end of each diffusion no weight change in the CdTe slice was detected and it was not possible to observe any change in its physical appearance.

3. Results

The shape of each of the profiles can be divided up empirically into four distinct regions and each profile can be described mathematically by a function consisting of the sum of four erfc expressions giving four values for the diffusivity, one for each part of the profile. A typical profile is shown in figure 1 and the four parts to each profile can be distinguished clearly; the three slowest-diffusing components are shown under high depth resolution in (a) and (b), D_1 and D_2 in (a) and D_1–D_3 in (b), whereas the whole concentration profile is shown in (c).

The four values of the diffusivities D_1–D_4 obtained for each concentration profile are shown on Arrhenius graphs in figure 2. The diffusivities are best described by an equation of the form $D = D_0 \exp(-Q/kT)$ and a fit through each set of points resulted in the following Arrhenius parameters:

$$Q_1 = (1.32 \pm 0.10)\ \text{eV} \qquad D_{01} = (3.3 \pm 1.0) \times 10^{-2}\ \text{cm}^2\ \text{s}^{-1}$$

$$Q_2 = (1.14 \pm 0.10)\ \text{eV} \qquad D_{02} = (4.5 \pm 1) \times 10^{-6}\ \text{cm}^2\ \text{s}^{-1}$$

$$Q_3 = (0.89 \pm 0.10)\ \text{eV} \qquad D_{03} = (3 \pm 1) \times 10^{-10}\ \text{cm}^2\ \text{s}^{-1}$$

$$Q_4 = (0.63 \pm 0.10)\ \text{eV} \qquad D_{04} = (2.5 \pm 1.6) \times 10^{-13}\ \text{cm}^2\ \text{s}^{-1}.$$

The corresponding values of the surface concentrations C_{01}–C_{04} obtained from the computer fitting are plotted on Arrhenius graphs in figure 3.

4. Discussion

The results reported here show some features that are similar to those reported for the I diffusion into CdTe [3] and some that are different.

The similar features are that four component diffusion profiles were obtained in both cases and satisfactory computer fits were obtained using a fitting package consisting of

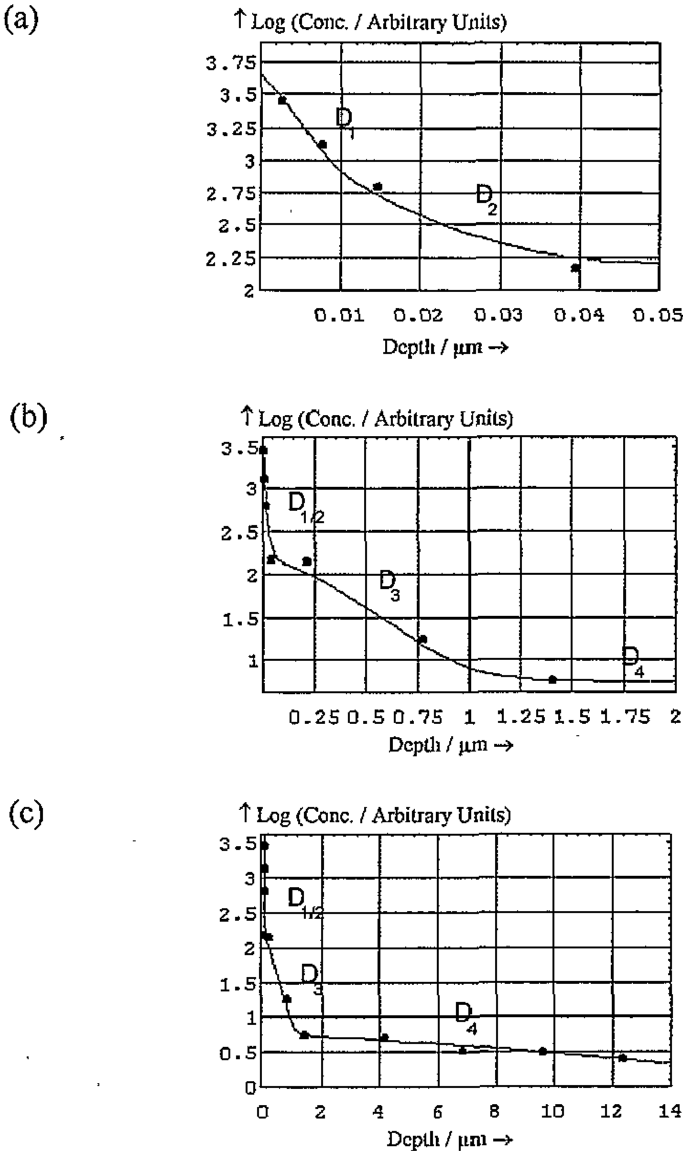

Figure 1. A typical concentration profile for the diffusion of Cl into CdTe. Diffusion details: temperature = 400 °C, duration = 24 h. The four parts of the profile can be distinguished clearly; the slowest components D_1–D_3 are shown in (a) and (b), D_1 and D_2 in (a) and D_1–D_3 in (b), whereas the whole profile is shown in (c).

the sum of four erfc functions. As with the I diffusion the values of C_0 increased with decreasing temperature (T) and, in the case of C_{04}, exceptionally high values, approaching 10^{23} cm^{-3}, were obtained.

The Cl results are different from the I results in two respects. The first is that with the I diffusions, the activation energies for all four components were similar (0.25 ± 0.05 eV), suggesting that similar transport mechanisms are operating, whereas for Ce diffusions the activation energies are much higher (0.63–1.32 eV) and the values vary monotonically with the diffusivity. This implies that there are differences between the diffusion of the two

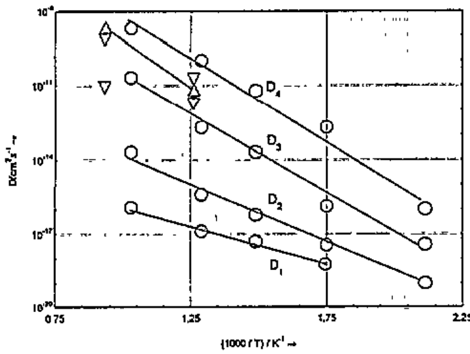

Figure 2. An Arrhenius graph of the diffusivities of the four components of each diffusion profile obtained by fitting a function composed of the sum of four erfc functions to each of the profiles. The Arrhenius fit quoted by Watson and Shaw [2] is also shown (Δ). Two of the profiles given by Watson and Shaw were refitted by a double erfc function and the corresponding diffusivities are also plotted on the graph (∇).

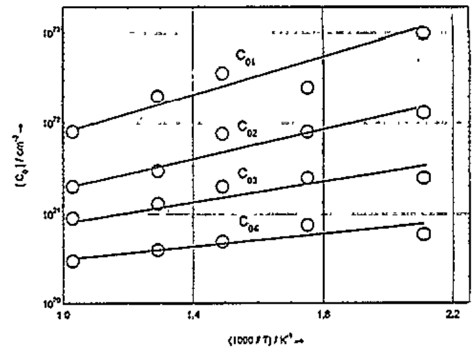

Figure 3. An Arrhenius graph of the corresponding values of C_0 obtained from the computer fitting.

elements. The mechanisms are either similar to those of I, but influenced by the ionic radii or the electronegativities of the Cl ion, or they are completely different. The second difference is that in the case of the I diffusions, because of the low activation energy, the fastest-diffusing component gives a significant value of D at normal ambient temperature ($D_4 \simeq 10^{-14}$ cm^{-2} s^{-1} [4]), whereas in the case of the Cl diffusions the corresponding value is 6×10^{-25} cm^{-2} s^{-1}. This implies that, in contrast to I, Cl is suitable as a long-term stable dopant in devices where sharp junctions are required.

The results obtained by Watson and Shaw [2], represented by the Arrhenius expression quoted in their paper, are shown in figure 2. Their measurement covered the temperature range 520–800 °C, whereas the measurements reported here were more extensive, covering the range 200–700 °C. Watson and Shaw [2] fitted a single erfc function to their results and, as can be seen from figure 2, their results gave reasonable agreement with the results reported here for D_4.

One reason why Watson and Shaw [2] observed single-component profiles only is that they did not use a sectioning technique with such a good depth resolution as was used for the work reported here [6]. The average section thickness removed by Watson and Shaw was ~ 2 μm, compared with ~ 0.03 μm in the depth range 0–1 μm and ~ 2 μm for the remainder of the profiles reported in this work. In their measurements, it is possible that Watson and Shaw [2] only observed a limited region of each diffusion profile. A refit of some of their profiles was carried out using software consisting of the sum of two erfc functions. An example of such a fit is shown in figure 4 and the corresponding diffusivities are shown in the Arrhenius graph, figure 2. It can be seen that the profiles of Watson and Shaw give results not inconsistent with the results that are presented here for the deeper parts of the profiles. The main difference between the two sets of results is that Watson and Shaw did not observe the slowest-diffusing components, D_1 and D_2, that are reported here.

High concentrations of both I and Cl have been observed by the present authors in their studies of the diffusion in CdTe. This could possibly be due to such atoms being attracted to the CdTe surface by physisorption or chemisorption processes and then forming a ternary compound involving the halogen and CdTe on the surface of the slice during the diffusion. Watson and Shaw [2] reported that they observed alloying at the sample surface at 800 °C,

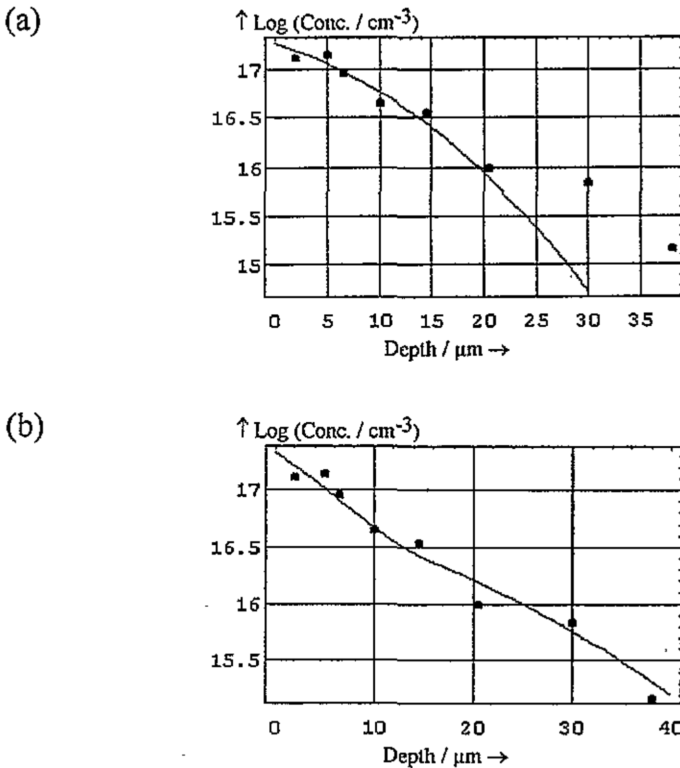

Figure 4. A comparison of a profile obtained by Watson and Shaw [2] as fitted by them (a) and refitted here by a double erfc function (b).

which was not observed in this investigation, possibly due to the higher temperatures used by Watson and Shaw [2]. In addition they observed much lower C_0 values ($< 10^{18}$ cm^{-3}), which was possibly due to the smaller amount of $CdCl_2$ used in their experiments.

The way in which the value of C_0 for both I and Cl diffusions increases with decreasing temperature is another unusual phenomenon in these diffusion studies. It may be possible to explain this in terms of the net flux of atoms competing for sites on the CdTe surface and their relative sticking coefficients. Initially, on heating the CdTe, there will be a net flux of Cd and Te from the surface to create an atmosphere that eventually enables an equilibrium to be established between the fluxes leaving and arriving at the surface. The loss of Te provides a high concentration of anion sites for occupation by incoming halogen atoms. At higher temperatures the loss of Cd and Te from the surface will increase as will the incident flux of Cd, Te and the halogen atoms. The observed decrease in C_0 with increasing temperature might be caused by either

(i) the relative fluxes of Cd and Te being such as to decrease the number of available anion sites or

(ii) the bonding of the halogen being sufficiently weak as to result in a flux from the surface that reduces the net flux.

In our studies of the diffusion of I into CdTe localized areas of high concentrations of I atoms have been observed just under the surface using secondary ion mass spectroscopy (SIMS) in the imaging mode [7]. It has been proposed that these atoms have been trapped at defect sites and it is plausible to assume that a similar effect occurred in the Cl diffused

CdTe slices. The existence of Cl clusters has been reported in Cl doped CdTe grown from the melt [8].

It is difficult at this stage of the investigation to describe a model that will explain the four-component profiles that occur in both the I and Cl diffusions but the two observations described above may possibly exert a considerable influence. The first is that the high concentration of Cl in the surface layers of the slice, formed by physisorption and chemisorption, will act as a subsidiary diffusion source, which will result in the components D_1 and D_2. The second is that the localized areas observed just under the surface using SIMS in the imaging mode for the diffusion of I into CdTe [7] and the melt growth of Cl doped CdTe [8] will act as a further diffusion source and can give rise to the components D_3 and D_4. Further profiling measurements using exceedingly high depth resolution will be required to explain this fully.

5. Conclusions

It is possible to draw the following conclusions from the work reported in this paper.

(i) The diffusion of Cl into CdTe produces four-component profiles, which can be described by an expression consisting of the sum of four erfc functions.

(ii) In contrast to I the four components of the profiles for Cl diffusions give different activation energies.

(iii) Surface concentrations of up to 10^{23} cm^{-3} were measured, suggesting that a layer of Cl or a Cl compound forms on the surface of the CdTe slice during the diffusion.

(iv) Clusters of Cl can be expected just under the surface of the CdTe.

(v) The projected room temperature diffusivity for the fastest part of Cl diffusion profiles (6×10^{-25} cm^{-2} s^{-1}) is much lower than the corresponding value for the I profiles (10^{-14} cm^{-2} s^{-1}).

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