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Low-Temperature Diffusion of Lithium in CdTe

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The diffusion of lithium at 300°C has been studied in CdTe samples in which the native defect concentration was fixed by preliminary heat treatments in Cd and Te vapors. It has been found that at low temperatures lithium diffuses in two forms characterized by two different diffusion mechanisms. The high-concentration, slowly diffusing form depends on the cadmium vacancy concentration (via the nature of heat treatment) whereas the low-concentration, fast-diffusing form is independent of it. The experimental results were analyzed in terms of Kucher's phenomenological theory. This theory supposes the simultaneous diffusion of the diffusing species in two different forms with exchange interaction between them. Whereas the rapid form is likely to be interstitial lithium, the slowly diffusing one is lithium interacting with cadmium vacancies, probably in a nonsimple configuration.

Introduction

Lithium is a common residual acceptor impurity in most of the II–VI compounds (*1*). Thanks to its small atomic size it enters very easily and penetrates very deeply into crystals. Besides, the interest of lithium as a doping impurity has to be stressed as it introduces the shallowest acceptor state in II–VI compounds. As a matter of fact lithium is an amphoteric impurity and the acceptor states, attributed to metal-substituted lithium, are very often compensated by donor states which are put in relation with interstitial Li (*1*, *2*). The balance between Li-related donor and acceptor states is a problem of major importance in the field of compensation phenomena and conductivity-type conversion of this class of materials. This balance is intimately connected with the concentration of point defects in crystals and especially metal vacancies.

All these considerations prompted us to undertake a study of the incorporation of lithium from the microscopic point of view. We decided to investigate the atomic diffusion of lithium with the defect concentration as a parameter.

CdTe was chosen as the material because of its availability in large crystals of both *n*- and *p*-type conductivity. To begin with, a low temperature range was considered where the generation of native defects can be considered as frozen in the time intervals used for the diffusions.

Experimental

The procedure employed involved the use of samples cut from Bridgman-grown CdTe ingots prepared in our laboratory. The samples, about 1 mm thick, were monocrystalline, nonoriented, not intentionally doped. (The residual impurity concentration was around 10^{16} cm^{-3}.) Before any heat treatment the samples were etched in a bromine methanol mixture and carefully rinsed in methanol and deionized water.

In order to obtain different vacancy concentrations, before the diffusion of lithium each sample was equilibrated in the vapors of either cadmium or tellurium by heating at

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300°C in a closed evacuated quartz vessel in the presence of a small amount of Cd or Te. There were therefore two different kinds of samples differing from each other through vacancy concentration. Because of the relatively low temperature used, the Cd equilibrium pressure over CdTe can be identified with that over pure Cd, whereas in the presence of tellurium the Cd-equilibrium pressure was assumed to be given by $k(T)(p^0\mathrm{Te}_2)^{1/2}$, where $k(T)$ is the CdTe dissociation constant (*3*). These points correspond to the existence range limits in the pressure–temperature diagram of CdTe at 300°C. The average duration of this treatment was ~50 days. The diffusion depths in our experiments have generally not exceeded 50 μm. Taking into account the fact that the chemical diffusion controlling the equilibration is very fast it can be verified that equilibrium was established in the regions of diffusion.

After this equilibration, one face of the samples was optically polished (necessary for further ion-probe analysis). The most difficult problem was to find a suitable lithium source. It was absolutely necessary that the original surface remain undamaged after the diffusion, because any deterioration of the surface could make determination of the penetration profile seriously imprecise if not impossible. The best lithium source corresponding to these conditions was found to be lithium hydride. The alcoholic solution of lithium hydride was deposited on the polished surface of the sample (after slight etching) and dried by evaporation of the alcohol just before the diffusion. The diffusion anneal was then performed under precisely the same conditions of temperature and partial pressure as the prediffusion anneal.

The diffusion was made in quartz vessels cleaned in a mixture of hydrofluoric and nitric acids and rinsed with deionized water. The ampules containing the samples were then sealed under a residual argon pressure of about 10^{-4} Torr. The diffusion time varied between 2 and 48 hr. After diffusion each sample was quenched to room temperature and cleaned in boiling deionized water. To avoid the eventual changes in the profile at room temperature, the time between diffusion and analysis was reduced to a minimum, about 2 hr.[1]

The penetration profile of lithium was measured by means of an ion microprobe (SIMS) using the crater method. The primary ion beam was formed by oxygen ions. The oxygen was found to be better than argon because of the higher sensitivity and better stability of the probe. Moreover the surface charging in the case of highly compensated samples is always lower especially with O^-. Each penetration profile is composed of 100 or a multiple of 100 "experimental points" measured automatically by the microprobe. For the sake of convenience they are replaced on the figures by a continuous line. The depth of the crater was measured either by a Talystep (up to ~10 μm) or under a microscope (more than ~10 μm).

The part of the concentration profiles close to the surface shows an enhancement due to oxygen supersaturation of the surface. It has to be deducted before normalizing the concentration to the surface value.

Results

Typical penetration profiles are shown in Fig. 1. Two facts become apparent by a simple examination of the experimental profiles. First, the profiles cannot be approximated by any function corresponding to a simple diffusion process. Most of them are clearly divisible into two parts. Second, the penetration depth of lithium depends strongly on the previous heat treatment.

The first phenomenon has been observed already by authors who studied diffusion of some impurities in II–VI compounds (*5*, *6*). It has been interpreted as diffusion through an interstitial-substitutional mechanism. In this process the impurity diffuses simultaneously in two forms with two different diffusion coefficients. The first form, dominant at high concentrations and slowly diffusing, is considered to be substitutional, whereas the form

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[1] We have not studied the behavior of Li at room temperature, but the relatively high values of the effective diffusion coefficient of Li in CdTe at 60°C (*6*) show that changes due to the diffusion at room temperature are possible.

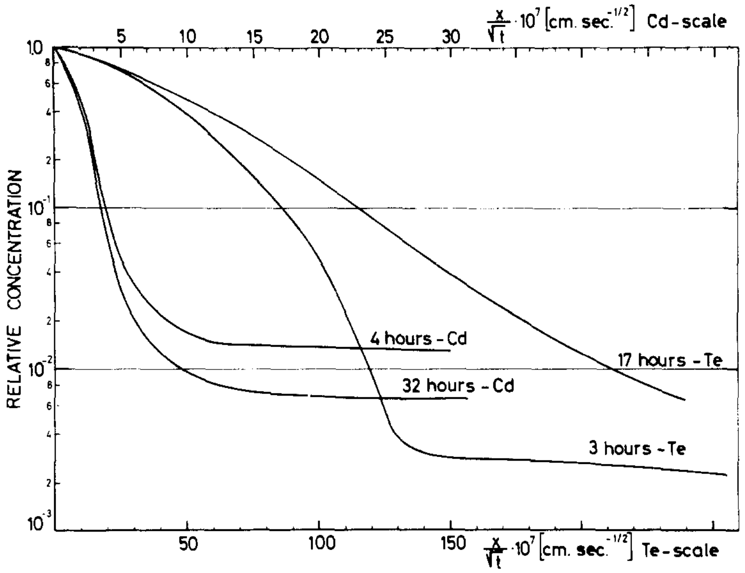

FIG. 1. Comparison between lithium diffusion profiles in CdTe measured on Cd-saturated and Te-saturated samples.

dominant at low concentrations which diffuses rapidly is considered to be interstitial. This behavior is also expected for the diffusion of the amphoteric impurity Li, but for reasons discussed later we prefer not to specify the nature of the diffusing components in this paper.

Figure 1 presents the time-normalized penetration curves corresponding to different diffusion times in samples treated in Cd and Te vapor. It can be seen that whereas the first part of the profiles in Cd-saturated samples follows a simple $t^{1/2}$ law, the second part of the penetration curve does not obey this law. The same general trend can be seen for the samples preannealed in tellurium vapor. It can be stated that the deviations from the simple $t^{1/2}$ law are much more important in this case than in the preceding one. The dependence of the penetration profile on the diffusion time suggests that there is an interaction between the slow- and fast-diffusing species. This interaction is much more important for samples annealed in tellurium vapor.

It is also obvious that the slow-component part of the penetration profile depends very strongly on the nature of the heat treatment. The diffusion profile in the Te-saturated samples is more than 10 times more extended than that in Cd-saturated samples. This indicates that the diffusion coefficient of the slowly diffusing form depends on the concentration of native defects. On the other hand the diffusion coefficient associated to the fast-diffusing part of the profile is not influenced by the heat treatment, as can be stated from the comparison of the slopes of the penetration curves.

Analysis of the Results

The simultaneous diffusion of an impurity in a crystal in two different forms has been discussed and theories have been given with different approximations. Mathematically these theories are based on the solution of the system of differential equations:

$$\begin{aligned} \frac{\delta C_1}{\delta t} &= D_1 \frac{\delta^2 C_1}{\delta x^2} - AC_1 + BC_2, \\ \frac{\delta C_2}{\delta t} &= D_2 \frac{\delta^2 C_2}{\delta x^2} + AC_1 - BC_2, \end{aligned} \tag{1}$$

where C_1, C_2 are concentrations of slow and fast impurity atoms, D_1, D_2, are slow and fast-diffusion components, A is the impurity atom transition probability per unit time from a site

1 to a site 2, and B is the impurity atom transition probability per unit time from a site 2 to a site 1. The impurity is considered to diffuse simultaneously under both forms from a constant source at the surface into a semi-infinite homogenous crystal along with transitions between both forms with probabilities A and B.

A simplified solution has been given by Wei (*7*). A detailed discussion of this problem is given by Kucher (*8*). The results of his discussion will be used throughout this work for the interpretation of experimental results.

The initial and boundary conditions are

$$\begin{array}{lll} t=0: & C_1(x,0)=C_1^0 & \text{for } x=0, \\ & \qquad\quad =0 & \text{for } x>0; \\ x=0: & C_1(0,t)=C_1^0 & \\ & C_2(0,t)=C_2^0 & \text{for } t\geqslant 0. \end{array} \qquad (2)$$

The complete solutions can be found in Kucher's paper and will not be reproduced here. It is assumed that $D_2 \gg D_1$ and $A \ll B$ and that these probabilities do not vary with time.

Because of the exchange between the fast and the slow forms, the penetration curve is generally not a simple superposition of two Fickian profiles. During the diffusion the concentration of the fast component decreases ($A \ll B$) while the concentration of the slowly diffusing component increases. This process leads to a deformation of the penetration profile (compared to a simple superposition) which increases with increasing diffusion time. True experimental values of diffusion coefficients D_1 and D_2 therefore have to be determined from short diffusion time profiles where the deformation caused by exchange can be neglected.

At the surface the ratio of the two surface concentrations is given by $C_2^0/C_1^0 = A/B$. This ratio can be determined from experimental curves for short-diffusion times by extrapolating to the zero distance the rapid-form profile. To determine separately the transition probabilities A, B we have calculated the series of theoretical curves corresponding to the experimentally determined values of D_s and D_i, A/B, a given value of t, and different B. Comparing the experimental curve with this set of calculated curves an approximate value of B was deduced. Then a closer fit between theory and experiments was sought to give a more accurate value.

In what follows we discuss the penetration profiles of Li corresponding to different diffusion times. In each figure the experimental profile (bold lines) is compared to the best corresponding calculated curve (dashed lines). The discussion is divided into two sections according to the nature of the heat treatment.

1. *Diffusion in Cd-Saturated Samples*

Figure 2 shows the time-normalized penetration profiles of lithium for a short diffusion time of 4 hr. The slow- and fast-diffusing components are well separated. By the method described above we found $D_1 = 2 \times 10^{-14}$ cm^2 sec^{-1}, $D_2 = 1 \times 10^{-10}$ cm^2 sec^{-1}, and $A/B = 0.017$.

The analysis of the profile corresponding to the diffusion time $t = 7$ hr leads to the same result as the preceding one. This result confirms the assumption that in this time interval both parts of the penetration curves are nearly independent.

Figure 3 applies to $t = 16$ hr. The deformation due to the exchange between both species is no longer negligible, as can be seen from the difference between the profiles calculated with the assumption of independence (–.–.–.) and the experimental curve. The analysis of

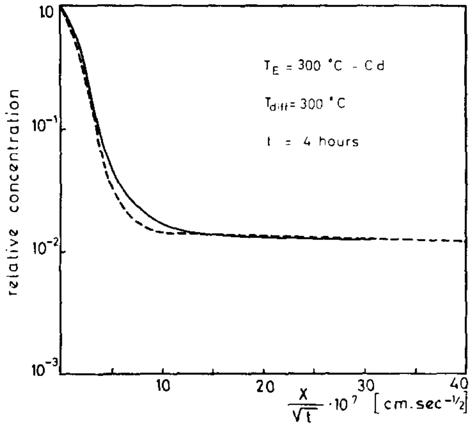

FIG. 2. Comparison of the experimental diffusion profile corresponding to $t = 4$ hr in a Cd-saturated CdTe sample (bold line) with the calculated curve.

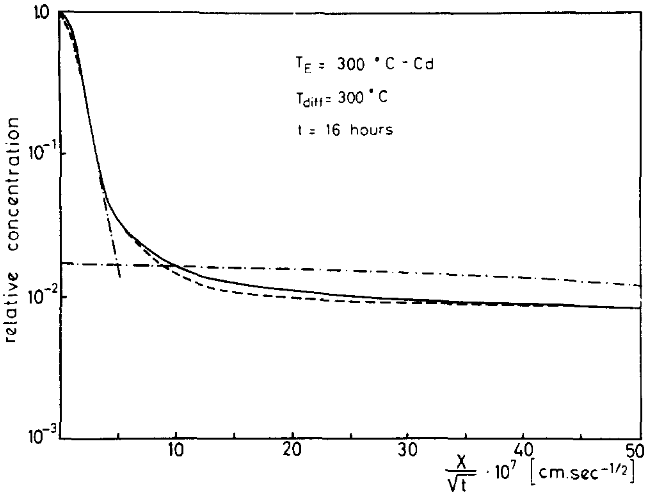

FIG. 3. Comparison of the experimental diffusion profile corresponding to $t = 16$ hr in a Cd-saturated CdTe sample with the calculated curve.

the actual profile by the method described gives $A = 1.4 \times 10^{-7}$ sec^{-7} and $B = 8 \times 10^{-6}$ sec^{-1}.

The $t = 48$ hr profile presented in Fig. 4 shows no clear separation between two processes. In this case we have obtained a better fit with the experimental curve increasing slightly the slow component diffusion to $D_1 = 5.10^{-14}$ cm^2 sec^{-1}. This variation could be due to experimental error.

2. *Diffusion in Te-Saturated Samples*

Annealing in Te vapor increases the Cd-vacancy concentration and should increase the diffusion coefficient D_1 and the probability of the transition from the rapid to the slow form.

Figure 5 shows that the general form of the penetration curve corresponding to the short diffusion time ($t = 2$ hr) is conserved. The slow-diffusion part and the rapid-diffusion part of the penetration profile are well distinguished so that it is possible to determine the experimental values of substitutional and interstitial diffusion coefficients. We found $D_s = 5 \times 10^{-11}$ cm^2 sec^{-1}; $D_i = 5 \times 10^{-10}$ cm^2 sec^{-1}, and $A/B = 0.003$.

The interstitial diffusion coefficient is slightly higher than that found in Cd-saturated samples. The authors attribute this difference to experimental error. In the diffusion profile corresponding to $t = 17$ hr, the general form of the penetration curve consisting of two decreasing functions separated by a plateau is no longer conserved. Comparison with Fig. 3 suggests that the fast-to-slow-form transition process is more important here than in Cd-saturated samples. This confirms the important role of vacancies in the whole process.

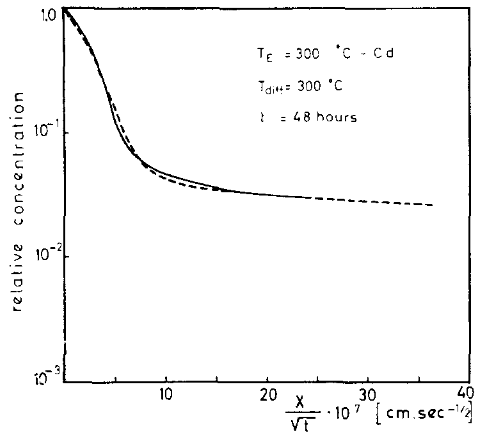

FIG. 4. Comparison of the experimental diffusion profile corresponding to $t = 48$ hr in a Cd-saturated CdTe sample with the calculated curve.

Discussion

The numerical results obtained in this work are collected in Table I.

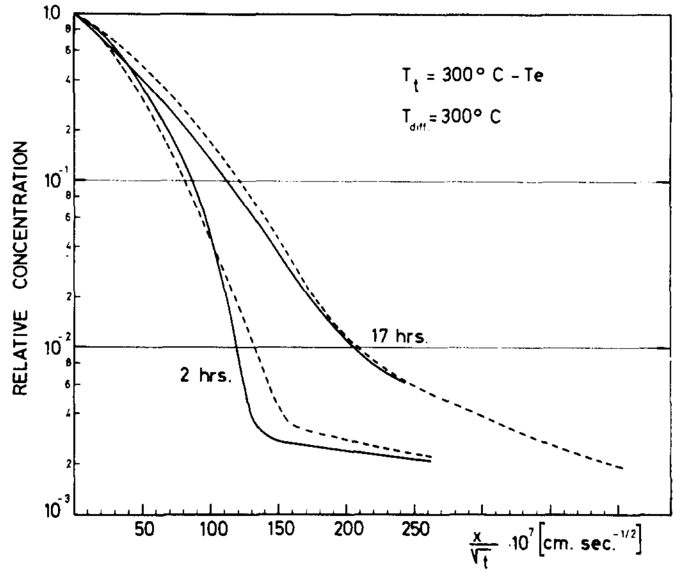

FIG. 5. Penetration curves of lithium in Te-saturated CdTe samples.

TABLE 1

Nature of treatment	D_1 (cm^2 sec^{-1})	D_2 (cm^2 sec^{-1})	$A/B = C_2^0/C_1^0$	A (sec^{-1})	B (sec^{-1})
Cd	2×10^{-14}	1×10^{-10}	0.017	1.4×10^{-7}	8×10^{-6}
Te	1.5×10^{-11}	5×10^{-10}	0.003	1.4×10^{-7}	4.7×10^{-5}

Table I shows that the diffusion coefficient D_1 depends strongly on the nature of the prediffusion anneal. Heating in Te vapors and increasing the Cd-vacancy concentration accelerates the diffusion of the slow component, whereas heating in Cd-vapors reduces the vacancy concentration and slows it down. These results are consistent with the diffusion properties of other amphoteric impurities. For instance, Woodbury (*9*) found that the diffusion of Ag in CdS depend on the nature of firing similarly to ours. He suggests that the faster-diffusing low-solubility component corresponds to interstitial Ag, whereas the slower component corresponds to Ag'_{Cd} or to acceptors composed probably of more than one Ag atom. Akutagava et al. (*10*), studying the properties of Au in CdTe by backscattering, showed that the total Au concentration consists of substitutional Au (50–80%) and of a nonsubstitutional component which is supposed to be interstitial Au. The authors report a dependence of the Au diffusion coefficient on the cadmium and chalcogen pressures similar to Woodbury's results.

A two-component diffusion profile of Cu in CdTe was also reported by Woodbury (*6*).

On the other hand, Vydyanath and Kroger (*11*) consider Ag_i to be the major migrating species in both parts of the diffusion profile in CdS, the first corresponding to interstitial silver and the second to diffusion along dislocations.

On the basis of the present results the exact mechanisms of Li diffusion cannot be determined. However, it seems probable that the fast lithium component diffuses by an interstitial mechanism which is supported by the independence of the coefficient D_2 on the cadmium vacancy concentration. The identification of the slow lithium component as a form of interstitial Li can be excluded from results of electrical measurements (1), which shows that diffused layers have a *p*-type conductivity. The relative equilibrium concentration of the slow component (B/A) increases when the vacancy concentration increases at the same rate as the exchange probability B: this indicates that this component is lithium interacting in some manner with cadmium vacancies. Generally the diffusion coefficient of impurities diffusing with a given mechanism is not very different from the self-diffusion one. The self-diffusion of Cd via a vacancy mechanism can be estimated from the work of Chern and Kroger (12). Assuming that his formulas can be extrapolated to 300°C one obtains the values $D_{V'_{Cd}} \sim 10^{-26}$ cm^2/sec and $D_{V''_{Cd}} \sim 10^{-29}$ cm^2/sec which are far below our experimental data. Thus it cannot be definitely stated that the slow component is a simple substitutional Li. Identifying the lithium surface concentrations of both species to solubilities, it can be stated that the relative concentration of interstitial lithium at 300°C is approximately 2% in cadmium preannealed samples and approximately 0.3% in tellurium-preannealed samples.

Conclusions

The diffusion coefficient of Li in CdTe at 300°C has been studied for different values of the cadmium vacancy concentration. The results indicate that the diffusion profiles cannot be approximated by a function representing a simple diffusion process, but can be decomposed into two simultaneous processes: one is strongly dependent on previous heat treatments (and therefore on vacancy concentrations), whereas the other is independent of this. The experimental results are interpreted on the basis of Kucher's theory of simultaneous diffusion of one species in two different forms with exchange interaction between them. While the fast-diffusion one is likely to be interstitial lithium, the slow-diffusion one is lithium interacting with cadmium vacancies.

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References

1. C. H. Henry, K. Nassau, and J. W. Shiever, *Phys. Rev. B* **4**, 2453 (1971).
2. F. el Akkad and H. Rodot, *Cryst. Lattice Defects* **6**, 7 (1975).
3. R. F. Brebrick, *J. Electrochem. Soc.* **118**, 2014 (1971).
4. B. M. Vul and V. A. Chapnin, *Sov. Phys. Solid State* **8**, 206 (1966).
5. H. H. Woodbury and R. B. Hall, *Phys. Rev.* **157**, 641 (1967).
6. H. H. Woodbury and M. Aven, *J. Appl. Phys.* **39**, 5485 (1968).
7. L. Y. Wei, *J. Phys. Chem. Solids* **18**, 162 (1961).
8. T. I. Kucher, *Sov. Phys. Solid State* **6**, 162 (1961).
9. H. H. Woodbury, *J. Appl. Phys.* **36**, 2287 (1965).
10. W. Akutagava, D. Turnbull, W. K. Chu, and J. W. Meyer, *J. Phys. Chem. Solids* **36**, 521 (1975).
11. H. R. Vydyanath and F. A. Kroger, *J. Phys. Chem. Solids* **36**, 509 (1975).
12. S. S. Chern and F. A. Kroger, *J. Solid State Chem.* **14**, 44 (1975).