

Cd Diffusion into PbTe

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Cadmium diffusion into p-type PbTe wafers and out of n-type Cd-diffused PbTe wafers was studied. The electrical properties and Cd content of the wafers showed that only about 150 ppm of the diffused Cd affect the electrical properties of PbTe. The fact that most of the diffused Cd has no effect on the electrical properties of the material is explained on the basis of two different processes of Cd incorporation into the PbTe crystal.

Introduction

Cadmium is known to reduce the carrier concentration and change the conductivity type when diffused into p-type PbTe or $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ (1). Application of this property to electrooptical device fabrication (2) has led to the study of the diffusion process and the electrical properties of Cd-diffused PbTe and $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ (3, 4). It has been shown that only a minor percentage of the diffused Cd atoms are electrically active, compensating the metal vacancy acceptor sites in the crystal. Most of the Cd atoms in the diffused material behave as an electrically inactive impurity, the nature and location of which is unclear (3-5). The present study is concerned with the incorporation of Cd into PbTe by diffusion. By assuming different processes for the incorporation of the electrically active and inactive Cd atoms, the behavior of

the diffused Cd in PbTe may be better understood.

Experimental

p-Type PbTe wafers were cut from ingots grown in our laboratory by the non-seeded vapor growth method (6). The material was of 6N purity. The (100)-oriented slices were cut from the crystal with a wire saw, and the surface damaged by cutting was removed by mechanochemical polishing with $\text{HBr} + 10\% \text{Br}_2$ solution. The wafers, about $400 \mu\text{m}$ thick, were sealed in an evacuated quartz ampoule together with etched Cd granules. The ampoule was loaded in a two-zone furnace, the PbTe wafer was at 400°C , while the Cd source was held at 300°C , giving a Cd vapor pressure of about 0.1 Torr. The diffusion time t_d varied between 0.5 hr and 1 month. Cooling to room temperature took about 15 min.

Out-diffusion experiments (3) were carried out with Cd-diffused PbTe wafers of $t_d = 7$ days, for another 7 days. The wa-

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fers were carefully polished and their *n*-type conductivity determined before loading the ampoule. The furnace had a 400–100°C temperature profile, giving a Cd vapor pressure of $<10^{-6}$ Torr. The wafers were characterized metallographically, by electron probe microanalysis (EPMA), X-ray diffraction (XRD), atomic absorption analysis (AA), and electrical measurements.

Results

The PbTe wafer removed from the ampoule after the Cd-diffusion process had a gray, rough, mat surface instead of its original, polished, mirrorlike surface. The change in surface characteristics occurred even after half an hour of diffusion, which was the minimum t_d studied in the present work. Metallographic studies revealed that the surface was covered with microspheres, between which a polycrystalline phase could be detected (Fig. 1). The microspheres were of various sizes, reaching a diameter of about 50 μm for the prolonged diffusion experiments. XRD patterns of the surface showed a number of characteristic lines of CdTe reflected from various crystallographic planes, some of which were not parallel to the (*h*00) plane. Other lines were identified as

belonging to elemental lead. Polishing away the CdTe layer of the Cd-diffused PbTe wafer, regardless of the t_d , resulted in a surface similar to the one before the diffusion process took place. XRD showed only the (*h*00) orientation of the PbTe single crystal. No shift in the Bragg angle reflection of the (800) plane could be detected. Metallographic examination and SEM analysis of a cross section of a Cd-diffused PbTe wafer showed three distinct formations (Fig. 2), the outermost being metallic microspheres. EPMA (sensitivity ≥ 1 mole%) showed that the wafer itself remained unchanged, i.e., pure PbTe, even to a distance of 1–2 μm from the interface. The PbTe wafer was completely covered (even in the case of $t_d = 0.5$ hr) with a polycrystalline, pure CdTe phase, on top of which were pure Pb drops. No elemental Cd could be detected on the surface by any analytical method.

The interface between the PbTe and CdTe phases could be clearly observed by metallography. The CdTe layer thickness varied along the wafer irregularly, leading to a “ripple”-like interface. This is probably due to irregular defects in the PbTe crystal, permitting easier permeation of Cd atoms in these regions. An average CdTe layer thickness d was mea-

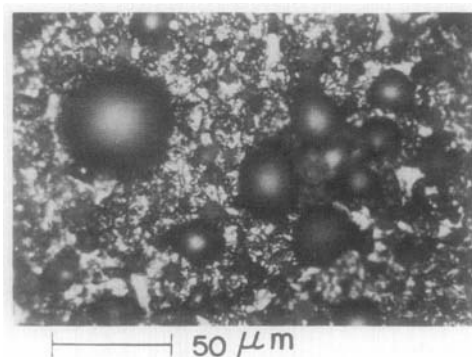


FIG. 1. Photomicrograph of the surface of a PbTe wafer after Cd diffusion at 400–300°C for 7 days.

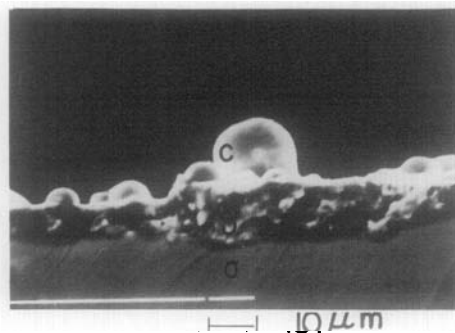


FIG. 2. Photomicrograph of a cross section of the wafer shown in Fig. 1: (a) PbTe; (b) CdTe; (c) Pb drops.

sured as a function of t_d and found to increase with t_d , as shown in Fig. 3. It should be noted that in some regions the CdTe layer thickness reached as much as twice its measured average d values.

The electrical properties of the Cd-diffused PbTe as a function of t_d were determined by thermal probe or Hall effect measurements. After diffusion for about an hour, a PbTe wafer of hole concentration $p = 3 \times 10^{18}/\text{cm}^3$ was converted into n-type material. For $t_d \sim 3$ hr the carrier concentration reached the value of $n = 1.2 \times 10^{18}/\text{cm}^3$, which is the saturation value of electron concentration achieved by Cd diffusion into PbTe (3). The Cd content of PbTe wafers of various t_d , after careful removal of any CdTe traces by polishing, was determined by the AA technique. The Cd content of the diffused PbTe was found to increase with t_d , as shown in Fig. 3. When the saturation value of n is reached the Cd content of the PbTe is less than 200 ppm. After $t_d = 7$ days, the Cd content of the material is 2–3 times as much, reaching several hundred parts per million Cd. Hence, the Cd content of the PbTe continues to increase many hours after the saturation value of carrier concentration has been reached.

After the out-diffusion process, there is no apparent change in the surface characteristics of the PbTe wafers. Electrical

measurements showed the material regained its p-type conductivity, as expected (3). Determination of the Cd content of the out-diffused PbTe wafers revealed several hundred parts per million Cd still present in the PbTe, in spite of its p-type conductivity. This electrically inactive Cd impurity did not diffuse out of the PbTe although the Cd partial pressure in the ampoule was changed from 0.1 to $<10^{-6}$ Torr. Hence, once the electrically inactive Cd is incorporated into the PbTe crystal its concentration does not depend on the Cd vapor pressure. The Cd content of the out-diffused PbTe was lower than in the case of Cd-diffused PbTe by 100–150 ppm. For example, a Cd-diffused wafer cut in two, only half of which was subjected to an out-diffusion process, showed Cd concentrations of 516 and 403 ppm, respectively (AA determination accuracy $\sim 4\%$).

Discussion

Three processes occur during Cd-diffusion into PbTe at 400–300°C: (a) a surface reaction of Cd with PbTe to produce CdTe and Pb; (b) diffusion of Cd into PbTe which affects the electrical properties of PbTe, Cd_a , the concentration of which is Cd vapor pressure dependent (3, 4); (c) diffusion of Cd into PbTe which has no effect on the electrical properties of PbTe, i.e., electrically inactive Cd_{in} ; once incorporated into the crystal, Cd_{in} concentration is independent of the vapor pressure of Cd.

So called "surface alloying" during Cd diffusion in PbTe crystals has been reported (1, 4, 7); however, no detailed study of its origin and character had been carried out. This "surface alloying" is probably the same surface reaction observed in the present case: Cd vapor, at a pressure of ~ 0.1 Torr, at 400°C, reacts

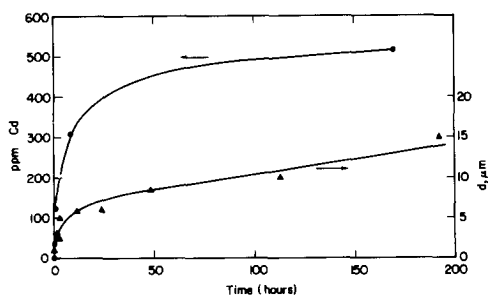


FIG. 3. Cd content and CdTe layer thickness, d , of PbTe wafers as a function of Cd diffusion time t_d (400–300°C).

with PbTe according to:



The reaction yields three separate phases: the original PbTe, CdTe and Pb. Since Pb is liquid at 400°C, Pb droplets are formed as the reaction proceeds. The drops solidify on cooling, as seen in the photomicrographs (Figs. 1 and 2). The absence of elemental Cd, either dissolved in the Pb drops or as a separate phase means that any excess Cd present on the crystal surface reacts immediately with PbTe. CdTe is formed from the very beginning of the Cd diffusion process (Fig. 3). The decrease in growth rate of the CdTe layer with t_d is probably due to the CdTe layer buildup. This reaction might be diffusion controlled: Cd has to diffuse in, and Pb has to diffuse out, through the CdTe layer.

The difference in the behavior of Cd_a and Cd_{in} in PbTe, as shown in the present study, suggests that the mechanism of Cd incorporation into the PbTe crystal in the two cases is not the same. Most probably, Cd_a atoms reach the PbTe crystalline phase as Cd^0 atoms, thus able to serve as electrical donors in PbTe. The metal vacancy sites in the PbTe crystal are compensated by these Cd_a , as described previously (4). When the metal vacancy sites become fully compensated by Cd_a , saturation in electron concentration is reached (3, 4). However, Cd_{in} is assumed to be incorporated into the PbTe crystalline phase via a PbTe–CdTe interdiffusion process, the CdTe formed by reaction (1). Since the Te sublattice is identical in the two compounds, the interdiffusion process involves Pb–Cd only. In this case, Cd replaces Pb in metal sites of the PbTe crystal, $\text{Cd}_{in} \equiv \text{Cd}_{pb}$ (using Kröger–Vink symbols) the Cd and Pb species being in the same ionization state, +2 (8). Hence, Cd_{in} reaches the PbTe crystalline phase

as Cd^{+2} ions. These are unable to serve as electrical donors and their concentration should be independent of the Cd vapor pressure.

Since CdTe and PbTe have different crystalline structures, the PbTe–CdTe interdiffusion reaction seemed questionable. Therefore, an experiment to confirm this reaction was carried out. A PbTe wafer, after $t_d = 7$ days, having a CdTe layer of $d \sim 15 \mu\text{m}$, was sealed in an evacuated quartz ampoule of minimum volume. The ampoule was annealed for 24 hr at 700°C. This temperature is much below the melting temperature of PbTe or CdTe and a solid solution of up to $y = 0.09$ is known to exist at this temperature (8). After the experiment the wafer was found to have a different type of surface (Fig. 4), mirror-bright but not flat. A cross section showed one phase only. XRD of the surface showed (100) oriented PbTe with the Bragg angle reflection of the (800) plane shifted, indicating a different lattice constant. According to Rosenberg *et al.* (8), the material was $\text{Pb}_{1-y}\text{Cd}_y\text{Te}$ with $y = 0.063$. Hence, the interdiffusion process in the PbTe–CdTe system was confirmed.

It is reasonable to assume that the same reaction occurs at 400°C. The PbTe–CdTe interdiffusion at 400°C probably yields $\text{Pb}_{1-y}\text{Cd}_y\text{Te}$ with $y \leq 0.01$.

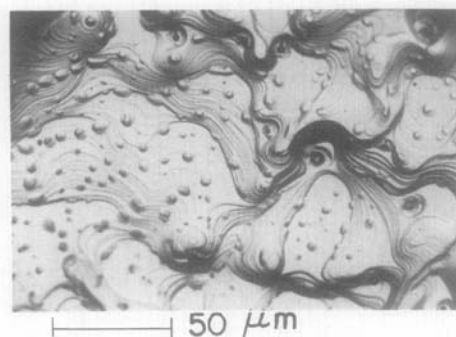


FIG. 4. Photomicrograph of the wafer shown in Fig. 1, after 24 hr at 700°C.

From the change in Cd content with t_d , a limiting y value which is less than 0.01 was calculated for this ternary system at 400°C. This result is in agreement with Rosenberg *et al.* (8) when extrapolating their results to 400°C, but contradicts others (9). A Cd mole fraction of ≤ 0.01 is too low to be detected by XRD or EPMA.

The physical chemistry of the $Pb_{1-y}Cd_yTe$ crystalline solution has been studied (5, 8-11) and thus Cd_{in} characteristics are well known. The $Pb_{1-y}Cd_yTe$ crystal is of the rocksalt structure, like the PbTe system, although CdTe has the zinc blende structure. Cd is uniformly distributed in the crystal at metal sites, in an almost completely ionized state. This agrees well with reported results (4, 12), namely that the Cd impurity in the diffused PbTe is not aggregated along dislocations and grain boundaries but is uniformly distributed in the diffused PbTe crystal. The Cd_{in} concentration in PbTe at 400°C can be considered an inert impurity, which does not affect the PbTe properties. It is believed that once Cd ions have reached the metal sites, there is no way to distinguish between Cd_a and Cd_{in} species. However, when the Cd vapor pressure decreases (or increases), a certain concentration of Cd atoms diffuses out (or in) of the PbTe as Cd^0 , adjusting the PbTe electrical properties to the new conditions of the system (3, 4). However, Cd_{in} is an integral part of the crystal. A reversible PbTe-CdTe interdiffusion process is not possible.

The composition profile of Cd^{+2} in PbTe during interdiffusion should be of the type given for similar systems, e.g., Ref. (13). Thus, the Cd concentration in the PbTe is the highest near the PbTe-CdTe interface, decreasing with distance from the interface. The interdiffused-Cd front proceeds into the crystal with increasing t_d . Polishing the wafer after dif-

fusion to remove any CdTe traces removes also $Pb_{1-y}Cd_yTe$ with the highest y . Hence, the actual Cd content of the diffused PbTe wafers should be higher than determined. This explains the discrepancies between the present results and others (3) concerning the Cd content of the diffused PbTe. Since CdTe is formed from the very beginning of the diffusion process at 400-300°C, the interdiffusion reaction probably starts from the very beginning as well. It is reasonable to assume that both Cd^0 diffusion and PbTe-CdTe interdiffusion occur simultaneously, probably independent of each other because of the high Cd vapor pressure in the system.

Experiments carried out with $Pb_{1-x}Sn_xTe$ ($x = 0.20$) wafers showed the same phenomenon, however; Cd is incorporated into $Pb_{0.8}Sn_{0.2}Te$ in smaller amounts than in the PbTe case, for the same diffusion time. After 1 week of diffusion the Cd content of a $Pb_{0.8}Sn_{0.2}Te$ wafer was 232 ppm and after 1 month it was 602 ppm. The interdiffusion experiment at 700°C for 24 hr showed a smaller shift in the reflection of the (800) plane, indicating a lower Cd content in the $Pb_{1-x-y}Sn_xCd_yTe$ than in the PbTe case, in spite of the fact that the buildup of the CdTe layer with t_d was about the same for both cases.

In conclusion, when Cd diffuses into PbTe, at 400-300°C, two phenomena occur: (a) Cd diffuses into the material and affects the electrical properties, its concentration in PbTe being Cd vapor pressure dependent. Since this Cd reaches the PbTe crystals as Cd^0 , it is able to serve as an electrical donor; (b) Cd is incorporated into PbTe by a PbTe-CdTe interdiffusion process, reaching the PbTe as Cd^{+2} ions which are unable to serve as electrical donors and yielding $Pb_{1-y}Cd_yTe$ with $y < 0.01$. This interdiffusion process results from CdTe formation on the crys-

tal surface during the Cd-diffusion process.

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