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Effects of zinc anneals in the (400-550 °C) range on the acceptor concentration in ZnTe

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Résumé. — Les recuits thermiques à (400-550 °C) sous vapeur de zinc dans le ZnTe ont deux effets : dans le cœur des échantillons, on libère les impuretés cuivre et lithium qui passent en site accepteur CuZn et LiZn. La surface des échantillons exposée aux vapeurs de zinc devient compensée. Le raccord entre les deux effets est traduit dans des recuits de courte durée par l'existence d'une bosse d'accepteurs située sous la surface exposée aux vapeurs de zinc.

Abstract. — Annealing ZnTe in Zinc vapour at 400-550 °C gives two effects : within the bulk of the samples, impurities (copper and lithium) are released from the Te excess and act as CuZn and LiZn. On the surface, an electrically compensated zone is created. The result of these effects is the appearance of an acceptor bump located below the surface exposed to a short time anneal under zinc pressure.

1. Introduction. — The p-type II-VI compound ZnTe has two dominant acceptor levels which are now attributed to impurities [1]. A small part of these impurities is present in the lattice at zinc sites (∼ 10^{15} \text{At/cm}^3) and controls the electrical and optical properties : Cu_{Zn} is the acceptor « a » at 149 meV [2] and Li_{Zn} is the acceptor « b » at 61 meV [3]. The major part of the impurities is trapped in the excess tellurium contained in the sample (Te-rich inclusions trapped during growth and Te precipitates due to the retrograde Te solidus line). The as-grown sample is then in a metastable equilibrium and every anneal will simultaneously modify the stoichiometry of ZnTe and the impurity concentrations. Whilst annealing allows some of the impurities to be extracted from the samples (lithium for instance), the others (copper, but also silver since it can also be released from the inclusions) remain quite homogeneously distributed throughout the crystal, with a residual concentration of (2-4) × 10^{16} \text{At/cm}^3, whatever the annealing atmosphere [4]. We have studied these effects especially after Te anneals, since in this case, we have roughly the same stoichiometry for the surface and the bulk of the sample. By contrast, anneals under zinc atmosphere lead to stoichiometric differences from the surface to the bulk since all the Te excess cannot be dissolved, even at high temperature (950 °C) [5].

The residual impurity concentration is then interpreted as the limit of purity accessible due to the equilibrium between impurities in ZnTe and the external conditions (molten Te or Zn which provides the annealing atmosphere, purity of the quartz tubes...). So, we conclude that, unless more severe precautions are taken, we will not be able to get a sample free of acceptors by thermal anneals, and since impurity segregation occurs during the growth process, the as-grown samples finally appear as the purest samples we can obtain, from the point of view of the electrical or optical properties (ZnTe lattice properties).

Another way is to lower the acceptor concentration only in a small region under the surface (≤ 10 \text{μ}) by a low temperature anneal, as we discuss in this work. The production of such zones may be a necessary condition if we want to introduce a donor in good site, without forming complexes with the acceptors. Self compensation is indeed explained by the fact that copper which always exists in excess, is a fast diffusing species and possesses a high association tendency, and thus can, during a thermal anneal, either occupy the zinc site before the donor, or associate with it, giving a complex (Al in ZnTe for instance [6]) and so prevent the donor from being active in the zinc site and giving at best a highly resistive zone.

2. Experimental. — The samples are grown by a Bridgman method, in Te solution. They are mechanically and chemically polished with Br-methanol.
The anneals are made in a two-zone furnace under a zinc pressure in an open quartz tube [7]: the sample is at the annealing temperature $T_r$. At one of the ends of the tube, a piece of zinc (6 $N$ purity) at $T > T_r$ provides a Zn atmosphere, which flows over the samples and condenses at the other, colder, end of the tube. Although the zinc pressure above the samples is less well defined than in the case of a zinc pump [8], we assume that, in the range of temperatures studied (400-550 °C) the $P_{Zn}$ variations are weak ($P_{Zn} \approx$ 5 torr at 550 °C). But this system allows a steady state of zinc vapor always renewed and presumably purer than a zinc atmosphere in an anneal in a zinc pump where the same zinc is recirculated. Electrical measurements are made on Schottky diodes made on the samples. From capacitance versus reverse voltage ($C(V)$) measurements, we obtain the doping profile ($Na^-\cdotNd^+$) on a few microns. To study the samples throughout their entire thickness, we can either lap mechanically and chemically the samples after each measurement, or better bevel the samples and make Schottky diodes on the bevels. By capacitance versus temperature ($C(T)$) measurements, we can obtain [9] the relative concentrations of the various acceptors present. Finally, photoluminescence studies (PL) at low temperature (5 K) give sharp qualitative spectroscopic information on the acceptor levels involved.

3. Results and discussion. — After a zinc anneal, we must distinguish two patterns of behaviour in the samples: that of the zinc exposed surface and that of the bulk: these two patterns have to be separated since they correspond to two different stoichiometric equilibria: we have respectively close to the surface and in the bulk a ($Zn-ZnTe$) and a ($Te-ZnTe$) equilibrium, the Te excess coming from the undissolved Te inclusions and precipitates.

- As the precautions taken for the crystal growth were increased, the sample doping decreased from $\sim 6 \times 10^{16}$ At/cm$^3$ to (5-8) $\times 10^{14}$ At/cm$^3$ for our best crystals.

- We have shown elsewhere [10] that, for a given annealing time ($t \sim 30$ min) the extent of the compensated zone increased with the annealing temperature. In the (300-400 °C) range, there is an abrupt rise in the initial doping at the end of the compensated region. On the contrary, in the (500-600 °C) range, the penetration depth shows little variation but the curvature of the profile changes.

- The reproducibility of the results on different samples after an anneal at 410 °C/1 h is shown on figure 1. The integrated loss of acceptors is roughly equivalent for all the samples where $(Na-Nd)$ as-grown $< 10^{15}$ At/cm$^3$ and thus the same defects and reactions exist in the different samples. We remark that for samples with doping $> 10^{16}$ At/cm$^3$ the loss is larger.

- In figure 2, we have the doping profile through the thickness of different samples. The shape of the profile is the same for all the samples with $(Na-Nd) \leq 10^{16}$ At/cm$^3$: 2 humps exist below each surface. In the bulk, we get a doping value slightly higher than the initial doping. The samples have been annealed horizontally, one surface is exposed to the zinc pressure, while the back face lies on a quartz plate.

![Fig. 1. Doping profile obtained by Schottky measurements on samples annealed at 410 °C/1 h. The dashed lines are extrapolated.](image1)

![Fig. 2. Samples annealed at the same time: doping profiles through the sample normalized thickness obtained by coupling Schottky measurements and etching.](image2)
anneals described here. The release of the impurities is thus different on the zinc exposed surface and in the bulk, as we see from the table: the hump is due to Li_{\text{Zn}}, which is also confirmed in PL. As in high temperature anneals [5], the Li_{\text{Zn}} hump is located under the surface for short-time anneals. We show, on figure 3, the evolution of the acceptor profiles when the anneal time increases: the hump has a tendency to disappear, showing a progressive release of lithium contained in the inclusions. The hump obtained after short time anneals is formed when some zinc penetrates into the sample, combines to the Te excess which releases the impurities (especially lithium) as we have verified with a theoretical model [11]. So, there are two differentbehaviours for the lithium release: on the surface, some of the Te excess combines with the in-diffusing zinc and releases its lithium, part of which migrates towards the surface where it is extracted. In the bulk, the impurities are relatively more slowly released since the local equilibrium is dominated by the (ZnTe-Te excess) one. During the anneal, the impurity released from the tellurium diffuses and is equilibrated. In reality, there are two impurities with two different solubility limits. The C(T) results nevertheless show that the [Cu_{\text{Zn}}] concentration changes are small and the important effects come from lithium, as we have already noticed for the high temperature anneals [5].

If the impurity behaviour in the bulk is relatively well understood, we do not know the origin of the so-called compensated zone which develops on the zinc exposed surface: is it a compensation by donors or an acceptor depleted zone? Since electrical measurements become inoperative because of the low concentrations (\( \leq 10^{14} \text{ At/cm}^3 \)), we have used optical measurements although these give only a qualitative characterization of the acceptors present. On the surface after a zinc anneal, the total luminescence yield is lower than for an as-grown sample. If the PL lines associated to the Cu_{\text{Zn}} and Li_{\text{Zn}} acceptors have decreased in intensity, by contrast, there is a slight increase of the intrinsic transitions, principally the free exciton lines [12]. This should prove that this compensated zone is due more to a decrease of the acceptor concentration than to a donor compensation. The extent of this zone is different according to whether the Cu_{\text{Zn}} or Li_{\text{Zn}} acceptor dominates. As we can see on figure 4, in the crystals with a small amount of Li_{\text{Zn}}, the depth of the zone is \( \sim (2-2.7) \mu \) at 550 °C. On the other hand, when Li_{\text{Zn}} dominates, the Li has both a higher vapor pressure and a higher chemical reactivity than Cu. The deeper compensated zones in the samples where Li_{\text{Zn}} dominates can also be due to an enhanced diffusion of lithium due to a drift of lithium in the space charge as is well known for lithium doped silicon [13]. The interstitial lithium, a donor species, is ionized and migrates in the electric field of the surface barrier (the intrinsic carrier density is estimated to \( \leq 10^{13} \text{ cm}^{-2} \) at 500 °C so that the band bending may be appreciable). The Li_{\text{i}} is then trapped by a defect and/or a negatively charged acceptor.

\[
\text{Zn}_{n} + I_{\text{Zn}} \rightarrow I_{\text{i}} + \text{Zn}_{\text{Zn}}
\]

where I is the impurity and Zn_{\text{Zn}} is the in-diffusing zinc, for instance, interstitial, then, in the case of the lithium, the Li_{\text{i}} can be extracted at the surface because Li has both a higher vapor pressure and a higher chemical reactivity than Cu. The deeper compensated zones in the samples where Li_{\text{Zn}} dominates can also be due to an enhanced diffusion of lithium due to a drift of lithium in the space charge as is well known for lithium doped silicon [13]. The interstitial lithium, a donor species, is ionized and migrates in the electric field of the surface barrier (the intrinsic carrier density is estimated to \( \leq 10^{13} \text{ cm}^{-2} \) at 500 °C so that the band bending may be appreciable). The Li_{\text{i}} is then trapped by a defect and/or a negatively charged acceptor.
The formation of complexes Li_{1-x}Li_x or Li_{1-y}defects leads to an acceptor loss and to compensation. Anyhow, the result is a lithium extraction as in the high temperature anneals where we can follow the lithium extraction.

- The problem is rather difficult when Cu_{2-x} acceptors dominate in the samples. The copper chemical reactivity is certainly less than that of lithium, and copper seems to be extracted only when annealing in molten zinc is performed [14]. With this hypothesis, the copper released during the dissolution of the Te excess migrates into the bulk contributing to a slight increase of the acceptor concentration (see table), and/or is accumulated on the surface giving complexes which might lower the overall luminescence yield [2, 5].

However if this effect exists, it is too low in the (400-550 °C) zone to be observed in PL, and the best argument for a decrease of acceptors in the compensated zone is the increase in PL of the free exciton lines.

In conclusion, during a zinc anneal, lithium and copper are under two dynamical equilibria: on the surface, Te excess combines with in-diffusing zinc and releases the impurities whose extraction is then a function of their chemical nature. In the bulk, the release of these impurities is less effective. In the area situated below the surface, there is a competition between the impurity extraction and their release from the Te excess. As the anneal temperature increases, the in-diffusion of zinc is increased but so also is the out-diffusion of the acceptor impurities. At T < 500 °C, the zinc in-diffusion dominates. Above this value, the shape of the doping profiles will depend on the acceptor reserve, although we can get, on the zinc exposed surface, an acceptor-depleted zone a few microns thick.

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References