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A STUDY ON SOLUTION (THM) GROWN Ti DOPED CdTe

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Résumé. — On a étudié les propriétés de cristaux de tellurure de cadmium dopés au thallium. Cette impureté a été introduite au cours de la croissance THM effectuée à 850 °C sous forme de TiTe, Ti₅Te₃ ou sous forme métallique. Des matériaux semi-isolants (\( p = 10^7 \) Ω.cm) ont pu être obtenus, toutefois, des mesures optiques ont mis en évidence une forte densité de précipités.

Abstract. — The properties of cadmium telluride crystals doped with thallium have been investigated. This dopant was introduced during a THM growth process at 850 °C as TiTe, Ti₅Te₃ or even as metallic thallium. Semi-insulating crystals (\( p = 10^7 \) Ω.cm) have been obtained, but optical measurements have shown substantial precipitation.

1. Introduction. — So far, little is known about the behavior of thallium, Ti, in CdTe [1, 2]. Being a group III element, however, it could conceivably act as a useful donor dopant. On the other hand, Ti is often found in the monovalent state in which case and even more importantly, it might serve as an acceptor dopant when substitutionally present on a Cd site.

1.1 Crystal Growth and Dopant Introduction. — We felt that for our particular case, it would be most convenient to introduce the dopant by using Ti or some suitable Ti containing compound as a solvent for the traveling heater method (THM) of growing CdTe [3]. In order to have some indication of possible stoichiometric effects, we used several Ti containing solvents of different compositions. However, we were not successful in growing from liquid metallic Ti, since its solubility for CdTe was apparently too low. Reasonable oligocrystalline materials with the type of crystallinity which is usual for unseeded THM growth were obtained with the two compounds Ti₅Te₃ and TiTe as solvents [4]. Since the former contains excess metal activity relative to CdTe, one might, perhaps, expect somewhat different results.

The growth was carried out by THM [3] with a furnace temperature of 860 °C. The CdTe starting ingots which had previously been THM grown with a Te solvent were 5 to 6 cm long, 1 cm in diameter. The solvent zone was 1 cm long and a growth speed of 4 to 5 mm per 24 hrs was used. The growth proceeded quite smoothly in both cases, indicating reasonable solubility of CdTe in both solvents.

1.2 Results. — 1.2.1 Optical analysis. — An infrared transmission microscope was used to evaluate slices from both ingots. Figures 1 and 2 show the characteristic behavior of both which are quite different.
Whereas the ingot grown from Tl₅Te₃ shows quite regular, large, triangular precipitation (Fig. 1), the growth from TlTe appears like a classical cell structure with all the boundaries decorated by very fine precipitation, most of it scarcely resolvable by the IR microscope which has its maximum sensitivity at 0.8 μm.

Infrared transmission measurements on polished, 2 mm thick slices were also carried out, at room temperature and at liquid nitrogen temperature using Perkin Elmer Model 450 and Model 457 spectrophotometers. The room temperature traces are displayed in figure 3.

![Fig. 3. — Optical transmission of CdTe samples between the electronic band edge and reststrahl band. Tl₅Te₃, and Te were used as solvents.](image)

For comparison the transmission of a slice grown with a Te solvent is also shown. Other than the shift of the band edge characteristic of CdTe, no new features were revealed in the low temperature runs.

1.2.2 Chemical analysis. — Spectrometric analyses of slices from both ingots [5] were carried out. They revealed for the Tl₅Te₃ grown material a Tl content of 0.195 %, and for the TlTe grown material a Tl content of 0.094 %. This is an average analysis and it includes any Tl in precipitates.

1.2.3 Electrical measurements. — Van der Pauw resistivity measurements were made using electroless gold contacts. They revealed resistivities of $6.3 \times 10^6 \, \Omega \cdot cm$ for the Tl₅Te₃ grown material and $1.5 \times 10^7 \, \Omega \cdot cm$ for the TlTe grown material. Useful Hall mobility measurements could not be obtained because of the high resistivity of the samples.

1.2.4 Photoconductivity and nuclear measurements. — Only one ingot grown from the Tl₅Te₃ showed any response to nuclear or optical excitation. A $\mu$ measurement gave a very low value of about $10^{-6} \, cm^2/V$ for electrons with no holes detected. The photoconductive response was also quite small with the maximum signal obtained with the negative contact illuminated with light near the band gap energy. At lower temperatures (below 200 K) even this signal disappeared.

1.3 DISCUSSION. — The optical transmission results show quite clearly the scattering due to the precipitation. Thus, the optical absorption edges are not very steep and well defined and the band edge measurements are therefore probably rather inaccurate. Nevertheless, no drastic changes seem to occur. For material grown from Tl₅Te₃, room temperature values of 1.44 to 1.47 eV (0.84-0.86 μm) were determined by extrapolation. For the slices from the TlTe solvent a value of 1.41 eV (0.88 μm) was found. At liquid nitrogen temperature a value of 1.53 eV (0.81 μm) resulted. No additional absorption peaks were seen throughout the measurement range.

Comparing the infrared microscopy results with material grown from other solvents (such as metallic In) we would have to say that the amount of precipitation found is not enough to justify the conclusion that all the Tl is precipitated. This is, of course, a qualitative finding based solely on our experience, but if amounts like those found chemically are completely precipitated, it has been our observation that virtually opaque material is the usual result.

Hence, we suggest that Tl is in fact present in solid solution in the crystals, and it is compensated in some way which does not greatly affect the optical transmission. It thus does act differently from In [6]. Also, the photosensitivity was quite small compared to CdTe doped with either the halogens, Ga or In.

The short lifetimes along with the lack of significant photosensitivity perhaps suggest that recombination levels for both holes and electrons are introduced by the Tl.

References