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Various Donors in n-ZnSb and the Influence of Sample Treatment

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Various donor doping of ZnSb is investigated. Te-doping yields the most stable n-type crystals at room temperature; the samples show p-type behaviour at low temperatures. The influence of surface effects is demonstrated. It was possible to prepare n-type ZnSb for the whole temperature range.

For a long time only p-ZnSb was available. In 1969 n-ZnSb, by doping with In, could be prepared for the first time[1]. In this paper we report on the possibility of obtaining n-ZnSb with doping materials of the third and sixth group of the periodic table. We were able to prepare ZnSb with n-type characteristics in the whole temperature range from 4.2 K up to the temperature region of intrinsic conduction. Up to now, the n-type samples showed always the peculiarity of becoming p-type at low temperatures a behaviour known also for n-type CdSb and CdSb-ZnSb-alloys[2]. When stored, these n-type samples sometimes convert to p-type for the whole temperature range. We have investigated the influence of the sample surface on these properties.

Care was taken of reducing the influence of oxygen: Both the starting materials (Zn and Sb of 99.9999% purity) and the ZnSb-melt were submitted to repeated reducing processes in hydrogen atmosphere. Oxide coatings of the starting materials were removed by filtering through capillaries in high vacuum. Melting and purifying of the materials was done in carefully cleaned and baked quartz ampoules, which were mostly coated with a carbon film inside. Production of single crystals was done by zone melting, usually with an Sb-rich molten zone. Before zone melting the material was treated with hydrogen once again in a quartz ampoule, which was then filled with argon of 400 mm Hg and sealed off. After annealing, zone melting begun with a zone temperature of 575 °C and a zone velocity of 2 mm/h. Variation of the preparation procedure showed that omitting individual cleaning and reduction processes reduces the long time stability of the n-type samples against conversion to p-type at room temperature.

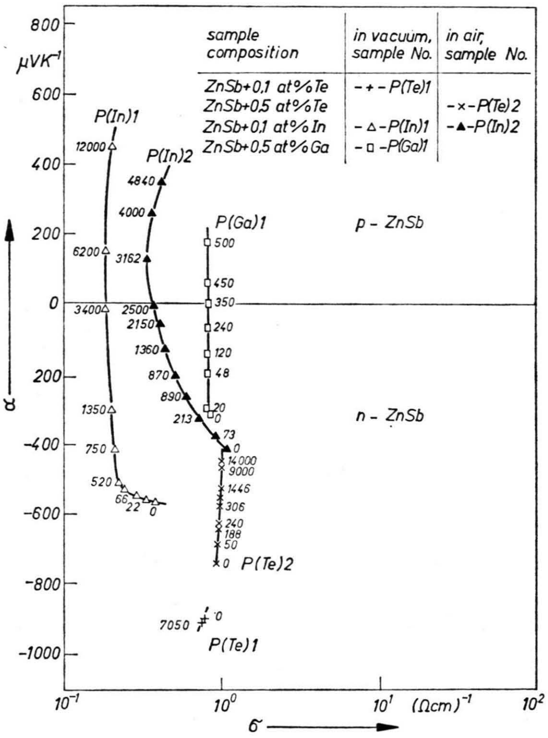

Fig. 1. α, log σ-diagram at room temperature.

This instability is illustrated for differently doped samples in the α, log σ-diagram of Fig. 1 where the variation of the thermoelectric power α and the electrical conductivity σ with time (numbers: time in hours) is shown. The first finding is that, besides the dopant In, also Ga as a further element of the third group of the periodic table can produce n-ZnSb. Doping experiments with Te and Se (sixth group) yielded n-type ZnSb with Te-doping, but p-type ZnSb with Se-doping. This agrees with investigations on CdSb-ZnSb mixed crystals, where only CdSb-rich crystals can be inverted to n-type by Se-doping. Production of n-conducting polycrystalline ZnSb was not possible; this suggested the influence of surfaces such as inner crystallite interfaces and chemisorption processes. Figure 1 shows that zone molten n-type crystals change to the p-region. Specially in air chemisorption of oxygen on the surfaces favors the p-type. At the same time a diffusion of donors out of donor sites cannot be excluded, for n-type samples with different donors convert to p-type within different time. Thus In-doped samples show somewhat quicker conversion in air, but in vacuum the rate of conversion is considerable too [samples P(In)1 and P(In)2]. The Te-doped sample [P(Te)2] in air shows a slower conversion, and Te-doped material [P(Te)1] in vacuum turns out to be approximately stable. Ga-doped n-type samples are most instable even in vacuum [P(Ga)1]. These results suggest a superposition of the two aforesaid processes, which are the reason for the difficult production of n-type material. The possibility of formation of InSb and excess Zn or ZnTe and excess Sb by doping ZnSb with In or Te, respectively[3], and a resulting different behaviour of differently doped samples should also be discussed in relation to chemisorption processes. Comparison of ionic radii shows that Te should be well incorporated into Sb sites, but not so well In into Zn sites. But in this way the instability of Ga-doped material is difficult to interprete, because Ga should be more easily incorporated than In.

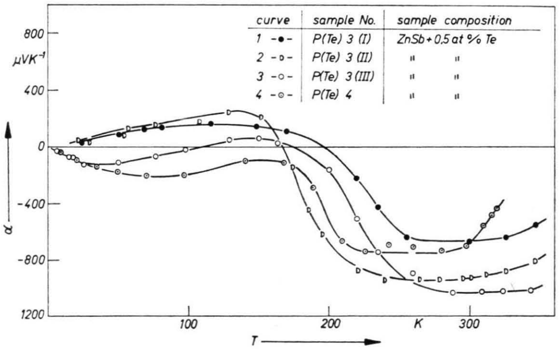

Fig. 2. Thermoelectric power vs. temperature.

Figure 2 shows the influence of surface treatment on the thermoelectric power α for two samples P(Te)3 and P(Te)4 doped with 0.5 at% Te. Curve 1 concerns an untreated zone molten sample; there is the above mentioned behavior of negative thermoelectric power at room temperature, but positive values in the low temperature region. Grinding the surface results in an enlargement of the negative thermoelectric power range to lower temperatures (curve 2). Subsequent etching and annealing of the sample in vacuum shifts the thermoelectric power curve towards the n-type region yielding even negative values at the lowest temperatures (curve 3). After surface treatment the sample was always soldered again to the cryostat before taking curves 1 till 3. The sample P(Te)4 was cemented to the cryostat with Stycast without increased temperature after grinding the surface. This handling yields a further displacement of the curve into the n-type region; now the Te-doped ZnSb sample shows negative thermoelectric power in the whole temperature range (curve 4). In this way it could be demonstrated for the first time that ZnSb is not only available as n-type at room temperature by incorporation of various doping materials into Zn or Sb sites, but the n-type can be produced in the whole temperature range too. The investigations suggest that besides the purity of the starting materials, influences of surface and temperature handling are important and should be taken into account during ZnSb sample preparation. Measurements on further samples confirmed these results. In this connection it is interesting that the Hall coefficient, e. g. for sample P(Te)4, can show a sign reversal. An explanation seems possible in connexion with remaining p-conducting surface areas and should be discussed in another paper.

Investigations on n-conducting samples above room temperature yielded a sign reversal to the p-type range in the intrinsic region. The determination of the mobility ratio $b = \mu_p/\mu_n$ yields $b = 1.56$ showing a lower electron mobility, which is 350 cm^2/Vs at 250 K. The calculation of the effective mass from thermoelectric power and Hall coefficient data gives a value of $m_n = 0.82\ m_0$ for electrons and $m_p = 0.56\ m_0$ for holes.

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