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Thermally induced conduction type conversion in *n*-type InP

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n-type semiconducting InP is changed into *p*-type semiconducting by short time annealing at 700 °C. Further annealing for a longer time leads to a second conduction-type conversion changing the material back to *n* type again but with a much higher resistivity. These conduction conversions indicate the formation of both acceptor and donor defects and the progressive variation of their relative concentrations during annealing. © *1999 American Institute of Physics.* [S0021-8979(99)07616-1]

In recent years, the electrical property of annealed InP has been investigated with a view to understanding the compensation mechanism in this material.[1–5] Generally, thermally induced defects in the annealed material can be detected by different spectroscopy methods.[6–8] However, most of the reports so far[4–8] (including our previous work),[9] have been carried out in a single annealing run with high temperature and long duration. The defects in the material can only be detected in their final thermodynamic equilibrium states after long time annealing. It is also difficult to understand the final compensation mechanisms in which these defects are involved. Besides, the formation and interaction processes of defects in these samples can not be clearly observed in these cases.

Compared to GaAs, whose conduction type can readily be changed from *n* type to *p* type by heat treatment,[10–14] there has been no report of thermally induced conduction conversion for InP.[15] Thermally induced conduction-type conversion of GaAs has been found to arise from the formation of gallium vacancy related defects.[10–12] It is anticipated that a similar process may occur in InP if thermal acceptor defects can be formed upon high temperature annealing.

In this article, we report annealing results of InP for different heat treatment durations. It is found that *n*-type semiconducting samples change to *p*-type conduction upon short time annealing. Further annealing of the samples for a longer time will see a second conversion which gradually reconverts the material back to *n*-type conduction but at a much higher resistivity. This observation indicates that thermally induced acceptor defects, other than acceptor impurities, are most likely to be responsible for the first conduction-type conversion from *n* type to *p* type. We think that these thermally induced acceptor defects causing the first conversion may well be the precursors of some donor defects giving rise to the second conversion to *n*-type high resistivity.

InP wafer samples with a thickness of 1 mm were cut perpendicularly to the axis of a single crystal liquid encapsulated Czochralski (LEC) ingot grown along the (100) direction by the phosphorus *in situ* injection technique. Previous work has shown that unintentional hydrogen contamination in these samples can be high ($\sim 10^{16}\,\mathrm{cm}^{-3}$),[16] and this may well come from the high water content in B_2O_3.[17] The electron concentration and mobility of these samples are around $3\times10^{15}\,\mathrm{cm}^{-3}$ and 3000 $\mathrm{cm}^2/\mathrm{v\,s}$, respectively. The annealing of these wafers was carried out in a sealed quartz tube which had been cleaned and evacuated. These wafers were chemically cleaned before loading into the quartz tube. A quantity of 6N/s red phosphorus, was placed in the quartz tube in order to supply the requisite phosphorus ambient of 60 mbar. This is to prevent the InP samples from dissociation. After annealing the samples were cooled slowly to room temperature. Before the electrical measurements, the samples were thinned to the thickness of 0.4, 0.6, and 0.8 mm, respectively, by removing a layer on both sides of the annealed wafers.

The carrier concentration, mobility, and resistivity of the samples were measured by van der Pauw technique using a Bio-Rad HL5500 Hall measurement system. All the samples are square wafers with dimensions of about $6\times8\,\mathrm{mm}^2$. Ohmic contacts were prepared by indium alloying at 450 °C in flowing pure hydrogen gas for 10 min. The temperature dependent Hall measurement (TDH) was carried out between 300 and 430 K to obtain the carrier activation energy of the annealed samples.

The carrier concentration and mobility of five annealed samples with three different thicknesses are shown in Fig. 1. It can be seen from the results that this *n*-type semiconducting sample has changed to *p*-type semiconducting by annealing at 700 °C for 5 and 10 h. We see that the results are pretty well consistent for all three thickness indicating reasonable uniformity in this material. In fact, the Hall coefficient of the two short time (5 and 10 h) annealed samples are positive and their low mobilities are indicative of typical *p*-type conduction in bulk materials. The decreasing hole concentration and mobility of the 10 h annealed sample also shows an increase of donor concentration and conversion of conduction to *n* type. For longer time annealing of 20, 40, and 80 h, the samples are *n* type again. Gradually, the mo-

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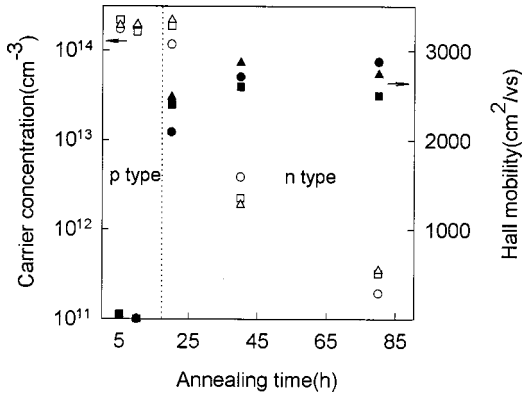

FIG. 1. Change of carrier concentration (open symbols) and mobility (close symbols) of *n*-type InP after annealing of different durations. The data of triangle, square, and circle are from samples of 0.4, 0.6, and 0.8 mm, respectively.

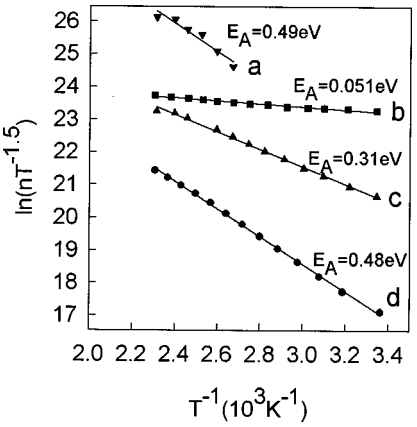

FIG. 2. Carrier activation energy of annealed InP obtained by TDH measurements in the range of 300–430 K. Before annealing, this sample is *n*-type semiconducting with an electron concentration of $3\times10^{15}\,\mathrm{cm}^{-3}$ and mobility of 3000 $\mathrm{cm}^2/\mathrm{v\,s}$. Curve a is for the 5 h annealed sample which changes to *p* type. Curves b, c, and d are for the 20, 40, and 80 h annealed samples, respectively, which change to *n*-type again.

bility of this sample increases while its electron concentration decreases rendering the material highly resistive.

In principle, impurity contamination and thermally induced defects can cause the conduction type conversion as found in heat treated GaAs.[18] However, impurity contamination can be excluded in this study because we have obtained bulk *p*-type conversion after only a short annealing process. The concentration and diffusion coefficient of most acceptor impurities are not large enough to cause *p*-type conduction in such a short annealing time.[2,19] Moreover, from long duration annealing results, the fact that these samples again change towards *n* type can definitely exclude acceptor impurity contamination. Thus, one only reasonable explanation for these conduction conversion phenomena is that acceptor defect are formed at the beginning of the annealing process and this is followed by the formation of donor defects. Conduction-type conversion of this annealed InP material is largely caused by the formation of these native defects. This kind of process has been found in annealed *n*-type semiconducting GaAs in which a large quantity of gallium vacancy related acceptor defects are formed.[12,20]

To investigate the origin of the dominant defects in the annealed high resistivity materials, TDH measurements have been carried out and the results are shown in Fig. 2. The slopes of these curves give one dominant defect level from which the Fermi level is pinned. Four slopes have been found from four samples with different carrier concentrations. Although the activation energy of carrier is not exactly the same as that of the dominant defect level, it can be considered to be the defect level if this level measured by other spectroscopy is around the activation level position in the gap,[14] as in the case of GaAs materials.[21] In annealed InP, defect levels around 0.3, 0.43, and 0.49 eV have been found by deep level transient spectroscopy and photoinduced current transient spectroscopy in annealed InP materials.[21–24] These level positions are basically the same as the activation energy obtained from TDH measurements of our annealed InP samples. Thus, it is very likely that three native donor defects dominate in InP annealed at different durations. It also follows that the concentration of every defect is a function of annealing time. It seems that the concentration of the deeper defect level gradually increases while that of shallow level decreases as the annealing time lengthens.

It is interesting to note that, after an annealing time of 5 h, the sample with an activation energy of 0.49 eV is a *p*-type material. An acceptor level around 0.49 eV should exist in this material in high concentration. For those three *n*-type samples obtained by long time annealing, the earlier mentioned conversion process indicates that the dominant levels are donors. Here, the shallowest donor level is at 51 meV.

The formation process of the defects in annealed InP has not been clearly understood so far. However, a previously proposed model may shed some light on the actual mechanism giving rise to the observed conduction-type conversion.[9] In another work, the hydrogen indium vacancy complex $V_{\mathrm{In}}H_4$ has been found to be a common defect in high concentration in as-grown LEC InP.[16] The thermal decomposition of the hydrogen complex $V_{\mathrm{In}}H_4$ supplies indium vacancy related acceptor defects in annealed InP material and tends to convert it into *p*-type semiconducting. This picture is certainly consistent with our experimental results of InP upon a short time annealing. Some acceptor impurity hydrogen complexes have also been found in as-grown LEC InP.[17] These can also increase the acceptor concentration by thermal decomposition. However, the second conversion into *n* type for our samples indicates that donor defects have been formed most likely by phosphorus atoms occupying indium vacancies. It implies that a significant portion of the defects in the material may well be the indium vacancy related defects.

In summary, *n*-type semiconducting LEC InP has been found to convert into *p*-type semiconducting upon high temperature annealing for a few hours. Further annealing for a few tens of hours results in a second conversion changing the material back to *n* type again but with high resistivity. These conduction conversions indicate the formation of native defects and the progressive variation of their relative concentration during annealing.

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