ANOMALOUS BEHAVIOUR OF DOPANTS IN GaAs DURING GROWTH PROCESS

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The concentration dependence of effective distribution coefficients for electrically active and isoelectronic impurities in GaAs have been studied. GaAs single crystals were grown in (111) and (100) by the LEC technique.

An impurity concentration range has been found in the melt, where the effect of an anomalous incorporation of dopants and intrinsic point defects into the crystal was observed. This range is (at/cm³): Te-(1 - 13)·10¹⁸; Sn-(1 - 13)·10¹⁸; Zn-(1 - 20)·10¹⁹; Sb-(2 - 20)·10¹⁹.

Several studies on GaAs crystals weakly doped with other impurities (Ge, Se, In) allow us to suggest that the observed effect is of a general character.

The doping of semiconductor crystals not only gives rise to changes in equilibrium intrinsic point defect concentrations but under certain conditions promotes the incorporation of non-equilibrium point defects into a growing crystal in accordance with the model proposed by Voronkov [1]. A probable mechanism for nonlinear kinetic effects at the growth interface resides in the fact that the vacancies play an important role during impurity capture; the vacancy concentration can show a considerable deviation from the equilibrium value on doping. The impurity distribution coefficient $K$ (ratio of impurity concentration in the crystal to that in the melt) in its turn will depend on the impurity concentration [1]. Consequently, the analysis of concentration dependences of distribution coefficients will allow to elucidate the dopant concentration ranges where nonlinear effects can be observed at the growth interface accompanied by the concentration change of intrinsic point defects.

We have investigated the concentration dependences for effective distribution coefficients of electrically active and isoelectronic impurities in gallium arsenide. GaAs single crystals were grown in {111} and {100} direction by LEC-technique. The structural perfection and homogeneity of single crystals were evaluated by preferential chemical etching patterns ("conventional", "projection" and photoetching). Electrophysical parameters were measured by the Hall method, the impurity content by mass-spectrum and X-ray spectrum analysis.

A concentration range was found in the melt, where the effect of an anomalous incorporation of dopants and intrinsic point defects into the crystal bulk could be observed. This range is (at/cm³): for Te-doping: (1 - 10)·10¹⁸, for Sn doping: (1 - 30)·10¹⁸, for Zn doping: (1 - 20)·10¹⁹, for Sb doping: (2 - 20)·10¹⁹.
Let us examine the results obtained for GaAs, doped with donor impurities, as an example. As it follows from Figs 1 and 2, on Te and Sn doping of GaAs a scattering and increase of impurity coefficient values is observed in a low concentration range \((C < (2 - 3) \times 10^{17} \text{ at/cm}^3)\) in the crystal) the impurity content exceeds charge carrier concentration \([2]\), resulting in a non-reproducibility of single crystals with given (preset) electrophysical parameters.

During the metallographic study on crystals an appropriate change in the etching pattern character with the dopant concentration change has been observed. During a "conventional" doping of GaAs, doped with donor impurities, etch pits of a non-dislocation type, inherent to undoped GaAs single crystal grown in the same conditions could be evidenced at the impurity concentration level \((2 - 3) \times 10^{17} \text{ cm}^{-3}\). The authors \([3]\) believe that such a matrix etching is caused by microdefects resulting from the decay of a supersaturated gallium solid solution on GaAs matrix.

At higher impurity content \((C_{\text{Te}} \sim (2 - 8) \times 10^{17}, C_{\text{Sn}} \sim (2 - 10) \times 10^{17} \text{ at/cm}^3)\), e.g. in a concentration range where the effective distribution coefficient is stable, the crystal matrix remained smooth on etching patterns. At \(C_{\text{Sn}} \sim (2 - 3) \times 10^{17} \text{ at/cm}^3\) the morphology change of dislocation traces occurs on "projection" etching patterns obtained in an Abrahams–Buiochi etchant.

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