Chemical partial short-range order (SRO) of donor impurity atoms in double-doped GaAs:Te,Ge above the equilibrium doping limit from Hall effect under pressure studies

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We present a detailed interpretation of Hall effect under hydrostatic pressure measurements as a function of high temperature annealings (at 1200ºC and another one done *in-situ* during crystal growth) of single crystal samples of double-doped (co-doped) GaAs:Te,Ge heavily doped exceeding the equilibrium doping limit (EDL) in this n-type material. Experimental EDL equals to ~$4x10^{17}$ cm^{-3} in GaAs:Te,Ge, which surprisingly is one order of magnitude lower than in GaAs:Te [1,2]. The EDL is defined as a maximum *thermally stable* concentration of free carriers in a semiconductor, that is the maximum one which is *insensitive to perturbations e.g. by thermal treatments* (annealing) of samples [2]. EDL's origin remains unclear for over 50 years [1,2] in n-GaAs, and recently a role of impurity molecules (dimers, etc.) has been renewed as DDX centers hypothesis [3], which is a case of chemical short-range order (SRO) that would occur at ultra high doping. The interpretation presented here is based on degenerated electron statistics in the conduction band including pressure-dependent capture of electrons by Ge_{Ga} DX states. The number of Ge_{Ga} DX states in GaAs:Te,Ge is changed by annealing, which we use as a direct argument that the number of isolated Ge_{Ga} impurities, acting as shallow donors, is changed by annealing. We also use electron mobility results versus pressure to argue that a role of Ga vacancy (V_{Ga}^{-3}), often assumed in heavily doped n-GaAs, is irrelevant since it would result in a much lower free electron mobility than we have measured. This argument is based on the electron mobility theory [4], which seems to be the most advanced analytic approach published in literature, as it includes a role of conduction band non-parabolicity within **kp** approximation and it's influence on impurity potential screening.

GaAs:Te,Ge sample was measured in as-grown state and after high temperature annealing at 1200ºC. The 1200ºC annealing had decomposed donor-deactivating defects present in as-grown sample (*in-situ* annealed during crystal growth at lower temperatures than 1200ºC). Hall effect under pressure measurements allowed us to determine the change (increase) of Ge_{Ga} donor concentration $\Delta[Ge_{Ga}]$ caused by 1200ºC annealing in an independent way from a change (increase) of total concentration Δn of free electrons. Estimation of Ge_{Ga} concentration is based on fitting of electron statistics of Ge_{Ga} DX states occupation as a function of pressure, as reported in [5]. The result which we have determined [2]: $\Delta n/\Delta[Ge_{Ga}] = 4.2 \pm 15\%$ is interpreted as a formation/decomposition of Ge-Te_m impurity molecules (*m*- number of Te atoms, *m* = 3÷4 atoms) which deactivates/ /reactivates donor atoms forming such molecules, consistently with DDX defect [3] or Fuller-Wolfstirn [1] impurity molecules hypotheses.

Our results support the notion that structural equilibrium state above the EDL includes the substitutional (also called atomic or chemical in alloyed materials physics) partial SRO, or that above the EDL the dopant atoms distribution at equilibrium is not random.

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