

Comment on "Binding and formation energies of native defect pairs in GaAs"

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Some aspects of the model of Baraff and Schlüter [Phys. Rev. B **33**, 7346 (1986)] predicting native point-defect autocompensation in gallium arsenide are shown to be contrary to experimental data.

Recently, Baraff and Schlüter¹ have calculated the free-energy changes for the following vacancy-antisite defect reactions:

$$V_{\text{Ga}} = V_{\text{As}} - \text{As}_{\text{Ga}}, \quad (1)$$

$$V_{\text{As}} = V_{\text{Ga}} - \text{Ga}_{\text{As}}, \quad (2)$$

as a function of Fermi-energy position. Their calculations predicted that, because of the Fermi-energy (E_F) dependence of the formation energy of the vacancy-antisite nearest-neighbor defect, the free energies of both of the above reactions change sign as E_F is swept across the forbidden gap. Thus, with E_F near the conduction band, they predicted that reaction 1 was driven to the left, forming V_{Ga}^{3-} , while reaction (2) was driven to the right, with V_{Ga}^{3-} bonded to $\text{Ga}_{\text{As}}^{2-}$ in nearest-neighbor position. Conversely, with E_F close to the valence band, the reactions were predicted to proceed in the opposite direction with the formation of V_{As}^{2+} with $\text{As}_{\text{Ga}}^{2+}$ in nearest-neighbor positions [reaction (1)] and V_{As}^{2+} [reaction (2)]. This model has been used by Walukiewicz² to construct a new mechanism for Schottky barrier formation in GaAs.

The purpose of this Comment is to point out that these results of Baraff and Schlüter cannot be entirely valid at melt and epitaxial growth temperatures since they imply donor compensation in a way which is contrary to experimentally observed behavior. (Baraff and Schlüter¹ ignored any temperature dependence of their reactions by dismissing as small, compared to other uncertainties, the entropy term in the reaction energy.)

Reactions (1) and (2) are presumed to occur as the crystal cools and the number of antisites generated will depend on the number of arsenic and gallium vacancies grown into the crystal, as well as on the Fermi energy. The "grown-in" nonstoichiometry (δ) is dominated by the arsenic Frenkel defects, viz., $\delta = [\text{As}_i] - [V_{\text{As}}]$ (Refs. 3 and 4) in the concentration range up to $\sim \pm 3 \times 10^{18}$

cm^{-3} as the arsenic composition of the melt from which the crystal is grown is varied. By contrast, the grown-in number of gallium Frenkel defects (V_{Ga} and Ga_i) is around 2 orders of magnitude smaller.⁴ It is believed that these defects are annihilated during cool-down of the crystals to room temperature to form the *EL2* donor and the "A" acceptor centers.^{4,5} In any event, free gallium vacancies are not present in any significant concentration in GaAs at room temperature.⁶ On the other hand, positron-annihilation results⁶ show that arsenic vacancies are preserved down to room temperature in *n*-type "as-grown" material at a concentration of 10^{17} – 10^{18} cm^{-3} . (These have to be in a neutral charge state at room temperature since electrical effects at this level are not seen.)

We now return to reactions (1) and (2). We see that, because of the low concentration of grown-in V_{Ga} , the number of compensating native donors (V_{As}^{2+} and $\text{As}_{\text{Ga}}^{2+}$) which can be formed by reaction (1) in *p*-type material is also very small and is unlikely to be discernable from effects due to residual background donor impurities. However, the high concentration of grown-in V_{As} , particularly in material grown from a gallium-rich melt as in liquid-phase epitaxy (LPE), would result in the formation of a large concentration ($\sim 10^{18} \text{ cm}^{-3}$) of compensating $\text{Ga}_{\text{As}}^{2-}$ acceptors in donor-doped material. Thus, if the Baraff and Schlüter model was correct and operative at LPE-growth temperatures, then attempts to donor-dope such material should lead to autocompensation up to donor-doping levels of the order of 10^{17} – 10^{18} cm^{-3} . In fact, this is contrary to experimental observation where donor doping from quite low up to very high levels occurs normally. (See, for example, Goodwin *et al.*⁷).

Hence we must conclude that for reaction (2), either (a) the calculated reaction energies are significantly different from the true values, or (b) some other competing reaction which leaves the dominant native point defects in an uncharged state occurs preferentially.

¹G. A. Baraff and M. Schlüter, Phys. Rev. B **33**, 7346 (1986).

²W. Walukiewicz, J. Vac. Sci. Technol. B **5**, 1062 (1987).

³A. N. Morozov and V. T. Bublik, J. Cryst. Growth **75**, 491 (1986).

⁴D. T. J. Hurler, in *Proceedings of the 5th Meeting on Semiconducting III-V Materials, Malmö, 1988*, edited by G. Grossmann and L. Ledebö (Hilger, Bristol, 1988), p. 11.

⁵J. Lagowski, H. C. Gatos, J. N. Parsey, K. Wada, M. Kaminska, and W. Walukiewicz, Appl. Phys. Lett. **40**, 342 (1982).

⁶V. Hautojarvi, in *Characterization of Defects in Materials*, Vol. 82 of *Materials Research Society Symposium Proceedings*, edited by R. W. Siegel, J. R. Weertman, and R. Sinclair (MRS, Pittsburgh, 1987), p. 3.

⁷A. R. Goodwin, C. D. Dobson, and J. Franks, in *Gallium Arsenide—Proceedings of the 2nd International Symposium*, IOP Conf. Ser. No. 7, edited by C. I. Pederson (IOP, Bristol, 1968), p. 36.