

Composition-Dependence of Deep Impurity Levels in Alloys

Recently, Samuelson *et al.*¹ reported the observation of the composition dependence of a few ($m=0, 1, 2, 3,$ and 4) disorder-split Cu impurity levels in $\text{GaAs}_{1-x}\text{P}_x$. Through measurements of the binding energies $E^{(m)}(x)$ relative to the valence-band maximum (VBM), they found a linear behavior with composition $E^{(m)}(x) = E^{(m)}(0) + \alpha^{(m)}x$, and, remarkably, a level-independent slope of $\alpha = 0.43 \pm 0.03$ eV. I wish to point out that this is a consequence of a recently proposed universality rule² which also predicted quantitatively the impurity-independent slope.

Caldas, Fazzio, and Zunger have recently pointed out² (see also Refs. 6, 11, and 12 therein for previous work) that, whereas levels of shallow impurities track closely the host-band edges (e.g., dashed line³ in Fig. 1 showing data for $\text{GaAs}_{1-x}\text{P}_x:\text{Te}$), the *antibonding character* of deep cationic impurities leads, in different materials and alloys, to a constant separation of their binding energies from the *vacuum level* [$\tilde{E}^{(m)}(x)$ in Fig. 1]. This predicted impurity-independent universality, $\tilde{E}^{(m)}(x) = \text{const}$ for deep, antibonding, cation-site impurities, implies that the apparent variations with the host crystal of VBM-referred binding energies [$E^{(m)}(x)$ in Fig. 1] measured by Samuelson *et al.* are merely a consequence of variations $\Phi(x)$ in the position of the VBM with respect to vacuum, not an impurity or disorder (i.e., m dependent) effect. Hence, the conventional VBM-related binding energy is predicted² to be $E^{(m)}(x) = \Phi(x) - [\Phi(0) - E^{(m)}(0)]$, or, $\alpha = \Phi(1) - \Phi(0)$ if we assume a linear composition variation of $\Phi(x)$. Using the observed³ difference in (110) photothresholds of GaP and GaAs, I find for $\text{GaAs}_{1-x}\text{P}_x$, *independent of the cationic impurity*, $\alpha = \Phi(1) - \Phi(0) = 6.01 - 5.56 = 0.45$ eV (error bars of ± 0.05 eV), in excellent agreement with the results $\alpha = 0.43 \pm 0.03$ eV of Samuelson *et al.* I conclude that their experiment measures essentially the difference in internal photothresholds of the two host materials, providing complementary information to that deduced from core photoemission of clean interfaces (which include, however, interface-specific effects, e.g., recent review by Kroemer⁴). Knowledge of $\Phi(1) - \Phi(0)$ of two semiconductors³ and an impurity level $E^{(m)}(0)$ in one of them^{1,2} hence suffices to predict the level position in the second material as well as its composition dependence in their alloys. For example, I predict for $\text{GaAs}_{1-x}\text{Sb}_x:\text{Cu}$ a slope with a negative sign $\alpha = 4.91 - 5.56 = -0.65$ eV. Caldas, Fazzio, and Zunger predicted $\alpha = 0.68 \pm 0.05$ eV for cation impurities in $\text{ZnS}_x\text{Se}_{1-x}$, in excellent agreement with the new results⁵ for self-activated centers in this alloy, giving an average value $\alpha = 0.61 \pm 0.04$ eV. More predictions are given in Ref. 2. This experiment further pro-

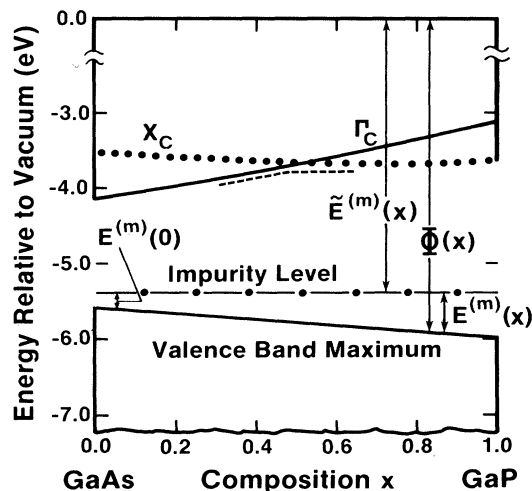


FIG. 1. Energy level diagram for vacuum-related states in $\text{GaAs}_{1-x}\text{P}_x:\text{Cu}$. Data taken from Refs. 1 and 3.

vides a critical test to the idea of Hjalmarson *et al.*^{6a} that the levels of deep cation-site impurities follow the composition variation of the cation vacancy level ("vacancy pinning"). The observation of Samuelson *et al.* is in direct conflict with this suggestion: the calculated Ga vacancy-gap levels in GaP ($E_v + 0.15$ eV)^{6b} and in GaAs ($E_v + 0.06$ eV)^{6c} would suggest a slope of $\alpha = 0.15 - 0.06 = 0.09$ eV, almost five times smaller than the observed slope.

Alex Zunger
Solar Energy Research Institute
Golden, Colorado 80401

Received 14 November 1984

PACS numbers: 71.55.Fr, 71.70.Ch, 78.55.Ds

¹L. Samuelson, S. Nilsson, Z. G. Wang, and H. G. Grimmeiss, *Phys. Rev. Lett.* **53**, 1501 (1984).

²M. J. Caldas, A. Fazzio, and A. Zunger, *Appl. Phys. Lett.* **45**, 671 (1984).

³*Landolt-Börnstein Numerical Data and Functional Relationships*, edited by O. Madelung (Springer-Verlag, Berlin, 1982), Vol. 17, pp. 210, 246, and 273.

⁴H. Kroemer, in *Proceedings of the NATO Advanced Study Institute on Molecular Beam Epitaxy in Heterostructures*, Erice, Sicily, 1983 (Martinus-Nijhoff, to be published).

⁵H. G. Grimmeiss, E. Meijer, R. Mach, and G. O. Müller, *J. Appl. Phys.* **56**, 2768 (1984).

^{6a}H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, *Phys. Rev. Lett.* **44**, 810 (1980).

^{6b}M. Scheffler, J. Bernholc, N. O. Lipari, and S. T. Pantelides, *Phys. Rev. B* **29**, 3269 (1984).

^{6c}G. B. Bachelet, G. A. Baraff, and M. Schlüter, *Phys. Rev. B* **24**, 915 (1981).