Resonant hole localization and anomalous optical bowing in InGaN alloys

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Using large supercell empirical pseudopotential calculations, we show that alloying of GaN with In induces localization in the hole wave function, resonating within the valence band. This occurs even with perfectly homogeneous In distribution ~i.e., no clustering!. This unusual effect can explain simultaneously exciton localization and a large, composition-dependent band gap bowing coefficient in InGaN alloys. This is in contrast to conventional alloys such as InGaAs that show a small and nearly composition-independent bowing coefficient. We further predict that ~i! the hole wave function localization dramatically affects the photoluminescence intensity in InGaN alloys and ~ii! the optical properties of InGaN alloys depend strongly on the microscopic arrangement of In atoms. © *1999 American Institute of Physics.* @S0003-6951~99!00613-0#

Low-In content $(x, 0.1)$ $In_xGa_{12x}N$ alloys exhibit ~i! localized excitons

atomic shells around GaN:In, and at larger distance the wave function is extended. To see this, we calculate the charge enclosed within a sphere of radius R from the impurity $Q_i(R) = 4p^* \int_0^R r^2 c_i^2 dr$ for electronic level i (Fig. 2). We see that (i) GaN:As has a deep *gap* level with exponentially localized c_i, so $Q_i(R)$ increases rapidly, reaching 90% already at a radius of 5 Å from the impurity. (ii) GaAs:In has a wave function that is an extended Bloch-like state, so $Q_i(R)$ increases slowly. (iii) GaN:In has a state with resonant character, so the behavior of $Q_i(R)$ is intermediate between the two extremes (i) and (ii), indicating the dual character of the wave function: short-range localization and long-range delocalization. This behavior leads to exciton localization (since the hole is localized) even if there is no *chemical* clustering of In atoms. In conventional alloys such as In_xGa_{12x}

valence band maximum in In-dilute $In_xGa_{12x}N$ (part a) and $In_xGa_{12x}As$ (part b). We see hole wave function localization around In in $In_xGa_{12x}N$ but not in $In_xGa_{12x}As$. In fact, this localization exists not only for the alloy VBM state, but also extends for states below the alloy VBM (~ 100 meV range). Thus, the state shown in Fig. 1(a) has a *resonant* character. It can be thought of as a combination of the In ''impurity'' wave functions hybridized with a continuum of GaN valence bands. In this regard GaN:In is different from the cases of isovalent *traps* of GaN:As[13] that show localized states *inside the band gap*, with exponentially decaying wave function. As a result, there is strong localization on a small number of

clustering; we find that the bowing coefficient of $In_{0.125}In_{0.875}N$ changes more than 30% even if we change only 10% of the first-shell short-range order parameter.[15]

Our results agree with the recent experimental investigations finding large ~3.8–4.4 eV! bowing coefficients in low-In content InGaN alloys.[4,5] Our results also agree qualitatively with the recent local density approximation ~LDA! calculations.[5] However, our values for $b(x)$ are even larger than the LDA derived values at small x, 0.1 In compositions. We believe that this difference can be attributed partly to the fact that the LDA calculations have been performed with small supercells. The choice of supercell size and symmetry should not greatly affect the predicted alloy properties if all states are delocalized. Indeed, in a conventional alloy such as InGaAs, we find b; 0.4 eV, nearly independent of the supercell size and shape used. If, however, the alloy has some localized states, the choice of the supercell size and shape is crucial, ~unless one uses a very large cell!. This reflects the fact that, depending on the supercell geometry, different Brillouin zone ~BZ! points fold into the $\bar{G}$ point. For example, the $\bar{G}$ point of a 16 atom fcc cell contains the G 1 4L 1 3X