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Atomistic description of wave function localization effects in $In_xGa_{1-x}N$ alloys and quantum wells

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ABSTRACT

We present a detailed analysis of wave function localization effects in $In_xGa_{1-x}N$ alloys and quantum wells. Our work is based on density functional theory to analyze the impact of isolated and clustered In atoms on the wave function localization characteristics in $In_xGa_{1-x}N$ alloys. We address the electronic structure of $In_{0.25}Ga_{0.25}N$/GaN quantum wells by means of an atomistic tight-binding model. Random alloy fluctuations in the quantum well region and well-width fluctuations are explicitly taken into account. The tight-binding model includes strain and built-in field fluctuations arising from the random In distribution. Our density functional theory study reveals increasing hole wave function localization effects when an increasing number of In atoms share the same N atom. We find that these effects are less pronounced for the electrons. Our tight-binding analysis of $In_{0.25}Ga_{0.75}N$/GaN quantum wells also reflects this behavior, revealing strong hole localization effects arising from the random In atom distribution. We also show that the excited hole states are strongly localized over an energy range of approximately 50 meV from the top of the valence band. For the quantum wells considered here we observe that well-width fluctuations lead to electron wave function localization effects.

Keywords: Nitrides, $In_xGa_{1-x}N$, alloy fluctuations, density functional theory, electronic structure, quantum wells

1. INTRODUCTION

Semiconductor quantum wells (QWs) based on $In_xGa_{1-x}N$ alloys have attracted considerable interest due to their band gap spanning the whole visible range and their correspondingly large potential for optoelectronic devices.[1] Compared to other III-V materials, such as $In_xGa_{1-x}As$, $In_xGa_{1-x}N$ QWs have the very unique characteristic that despite high defect densities, efficient radiative recombination can still be achieved in the blue spectral regime. The origin of this surprising feature is attributed to strong wave function localization effects, that keep the carriers away from the defects.[2] Experimental studies reveal clear fingerprints of these carrier localization effects.[2–6] However, even though highlighted by experimental studies, these effects are still widely ignored in the theoretical modeling of $In_xGa_{1-x}N$-based structures. In the present atomistic study we investigate directly the effects of deviations from an ideal structure, taking both random alloy and well-width fluctuations explicitly into account. Our analysis reveals that random alloy fluctuations, already in bulk systems, can lead to localized states in the valence band. We also show that in $In_xGa_{1-x}N$/GaN QWs well-width fluctuations can lead to localization effects in the conduction band.

2. THEORY

In this section we briefly outline the ingredients of our theoretical framework to study the impact of In atoms on the electronic structure of $In_xGa_{1-x}N$ bulk alloys and quantum wells.

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2.1. Density functional theory calculations

To analyze the impact of isolated In atoms and of In atoms sharing the same N atom, we first use the density functional theory (DFT) in the framework of the local density approximation (LDA). It is well known that LDA-DFT underestimates the band gap. An improved description of the band gap can be achieved by using hybrid functional DFT schemes or GW calculations.[7,8] However, here we are interested in localization effects introduced by different In atom configurations rather than an accurate description of the band gap. Recently, we have shown for $In_xAl_{1-x}N$ alloys that LDA-DFT gives a good description of such effects in comparison with the computationally far more expensive hybrid functional approaches.[9] Therefore, LDA-DFT is a reasonable choice within the scope of the present study. The LDA-DFT is furthermore computationally much cheaper than a HSE framework and thus allows us to study larger systems, which then provide a better approximation of isolated In atoms in a larger GaN matrix.

Our LDA-DFT calculations were performed using the plane-wave-based ab initio package *VASP*.[10] The supercells (SCs) under consideration contained 1024 atoms. The energy cutoff for the plane waves was 400 eV and the semi-core *d* electrons of In and Ga have been treated as valence electrons. The structure was relaxed using a valence force field (VFF) model.[11,12]

2.2. Tight-binding model

To provide a microscopic insight into the impact of alloy and well-width fluctuations on the electronic structure of $In_{0.25}Ga_{0.75}N$/GaN QWs, we use an sp^3 tight-binding (TB) model, taking input (local strain and built-in fields) from our recently established local polarization theory.[13] This framework has already been validated by comparison with both DFT and experimental data,[13,14] with the results of our semi-empirical TB model showing excellent agreement both with DFT and with experiment. More details of the model are given in Caro *et al.*[13] and Schulz *et al.*[12]

3. RESULTS

In this section we present the results of our DFT and TB calculations for $In_xGa_{1-x}N$ alloys and $In_{0.25}Ga_{0.75}N$/GaN QWs, respectively.

3.1. Impact of In atoms on the electronic structure of $In_xGa_{1-x}N$ alloys

As a qualitative measure, we use the participation ratio PR to quantify the impact of isolated In atoms and of In atoms sharing the same nitrogen atom on the wave function localization characteristics,[15] where the participation ratio is given by

$$\mathrm{PR} = V \int |\psi(\mathbf{r})|^4 \, \mathrm{d}^3 r \ , \tag{1}$$

with V being the volume over which the wave function ψ is normalized. The stronger the localization of the wave function, the larger the value of PR for a given volume V. Here we have calculated the values of PR within LDA-DFT for the conduction band edge (CBE) and the valence band edge (VBE) for an isolated In atom and two, three and four In atoms sharing a N neighbor. The results for the *normalized* $\overline{\mathrm{PR}} = \mathrm{PR}/\mathrm{PR}^{\mathrm{GaN}}$ values, where $\mathrm{PR}^{\mathrm{GaN}}$ is the PR of the equivalent pure GaN state, are summarized in Table 1. We see from Table 1 that in the isolated In case (1 In) the CB state is practically delocalized and only very weak localization effects are observed in the VBE since $\overline{\mathrm{PR}} \approx 1$. It is important to note that these weak localization effects are in strong contrast to $In_xAl_{1-x}N$ alloys where already an isolated In atom introduces a strongly localized state in the CB.[9] This localized state in the CB hybridizes with the CBE, leading therefore to strong localization effects at the CBE. The differences in the basic physical properties, such as the band gap for example, are even more extreme between AlN and InN than they are between GaN and InN. Therefore, one could expect weaker effects in $In_xGa_{1-x}N$ compared with $In_xAl_{1-x}N$. While the localization effects at the $In_xGa_{1-x}N$ CBE are very weak (even in the case of four In atoms, $\overline{\mathrm{PR}}$ is only slightly larger than the $\overline{\mathrm{PR}}$ value for VBE in the isolated In case), Table 1 indicates stronger localization effects in the $In_xGa_{1-x}N$ VBE. When more than two In atoms share the same N atom in GaN, $\overline{\mathrm{PR}}$ increases significantly at the VBE. However, these numbers are still significantly smaller than in $In_xAl_{1-x}N$.[9] The CB remains delocalized even for four In atoms sharing the same N atom.

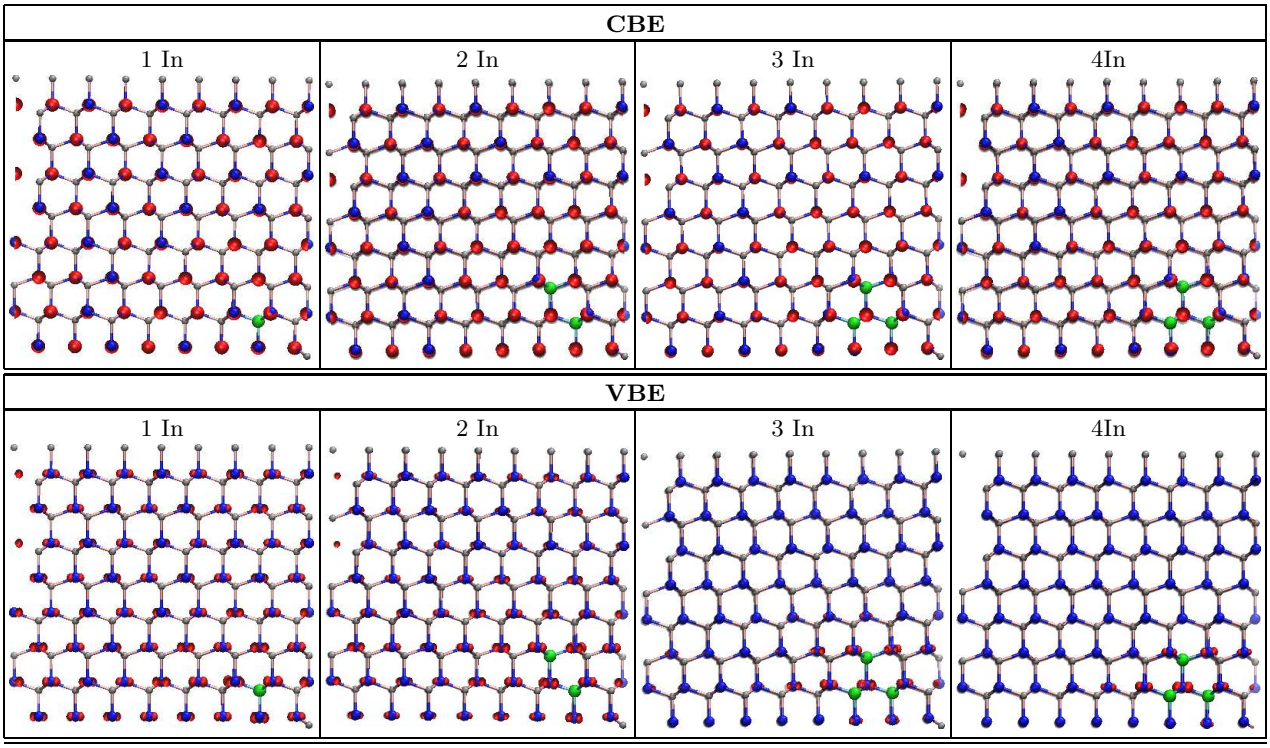

Figure 1. Isosurfaces (red) of the charge densities for CBE and VBE states at 25 % of the maximum value. The In atoms are shown in green, the Ga atoms in silver while N atoms are indicated in blue.

To visualize the increase in $\overline{\text{PR}}$, Fig. 1 shows isosurfaces (red) of the charge densities of the CBE and VBE states at $\mathbf{k} = \mathbf{0}$. The charge density is shown in red at 25% of the maximum charge density. In atoms are indicated in green, Ga atoms in silver and N atoms are given in blue. Figure 1 reflects the trends observed in Table 1. The CBE exhibits only very weak indications of wave function localization effects, since the charge density is spread over the entire SC, even in the case of four In atoms. The situation is different for the VBE, for which the wave functions become localized in the vicinity of the In atoms, as an increasing number of In atoms share the same N neighbor. Also when looking at the symmetry of the charge densities we observe an expected behavior: While the CBE is composed mainly by s-like orbitals, the VBE – when neglecting the weak spin-orbit coupling – is calculated to remain mainly a linear combination of p_x- and p_y-like orbitals.

We note here that calculations by other authors on $In_xGa_{1-x}N$ alloys reveal also indications that the highest valence states tend to become localized in these systems.[2, 15–18] Our calculations here are therefore consistent with previous results. It should also be noted that the here observed localization effects should also impact the band gap bowing in $In_xGa_{1-x}N$ alloys. Due to these localization effects one could expect that the band gap

Table 1. Normalized CBE and VBE wave function participation ratio $\overline{\text{PR}}$ for one, two, three and four In atoms sharing the same N atom in GaN.

	# In atoms			
	1 In	2In	3 In	4 In
VBE	1.006	1.029	1.118	1.305
CBE	1.002	1.005	1.010	1.016

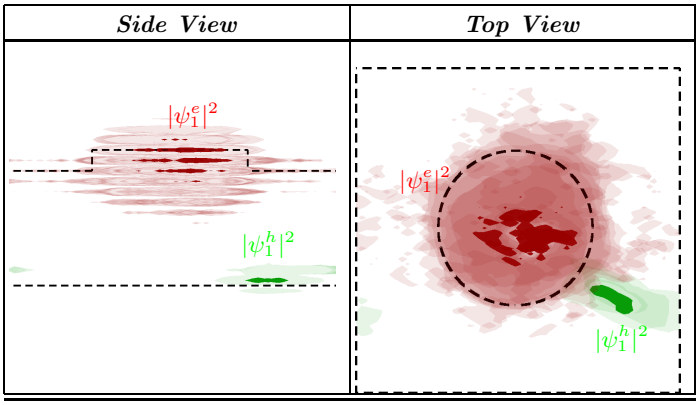

Figure 2. 5 % (bright) and 50% (dark) of the maximum charge density of electron (red) and hole (green). The QW interfaces are indicated by the dashed lines.

bowing parameter exhibits a composition dependence. Such an effect was, for example, observed by Moses *et al.*[19] in the framework of hybrid-functional DFT. However, these calculations were performed on small SCs (32 atoms), for which localization effects might therefore be difficult to identify. We have recently applied the TB model introduced in Sec. 2.2 to analyze the band gap bowing of $In_xGa_{1-x}N$ alloys over the full composition range. Our TB results show also a weak composition dependence of the band gap bowing parameter and are therefore in good agreement with the hybrid functional DFT results from Moses *et al.*[19] and consistent with the here presented LDA-DFT data in terms of localization effects. Given this good agreement, and since the TB model allows us to study much larger systems, we use it to analyze the electronic properties of $In_xGa_{1-x}N$/GaN QWs in the next section.

3.2. Electronic structure of $In_xGa_{1-x}N$/GaN QWs

In this section we analyze the electronic structure of $In_{0.25}Ga_{0.75}N$/GaN QWs by means of our TB model. As a model system we assume a 3.5 nm thick $In_{0.25}Ga_{0.75}N$/GaN QW. All QW calculations have been performed on SCs containing $\approx$ 82,000 atoms ($\approx$ 10 nm $\times$ 9 nm $\times$ 10 nm) with periodic boundary conditions. Following experimental data,[20–23] we treat $In_xGa_{1-x}N$ as a random alloy and include well-width fluctuations at the upper QW interface.[22] The experimentally reported lateral size of these well-width fluctuations is $\approx$ 5–10 nm.[22, 24, 25] The height of the well-width fluctuation is between one and two monolayers. Here, we approximate well-width fluctuations as disk-like structures with a diameter of 5 nm and a height of two MLs, residing on the 3.5 nm wide $In_{0.25}Ga_{0.75}N$/GaN QW. In the following we focus our attention on one microscopic random configuration since it describes already the main features introduced by well-width and random alloy fluctuations. A more detailed analysis of the impact of different microscopic configurations on the electronic and optical properties, including Coulomb effects, will be presented elsewhere.[12]

Figure 2 shows the ground state electron $|\psi_1^e|^2$ and hole $|\psi_1^h|^2$ charge densities in the structure considered. The light and dark isosurfaces correspond to 5% and 50% of the maximum charge density. Several features are clearly visible from Fig. 2. Firstly, since we are dealing with *c*-plane QWs, electron and hole states are spatially separated by the built-in field along the *c*-axis. Secondly, we observe that the electron ground state wave function is localized by the well-width fluctuation. However, the random alloy fluctuations also perturb the wave function, since the circular symmetry introduced by the well-width fluctuation is not fully preserved. Turning to the hole ground state $|\psi_1^h|^2$, we find that the random alloy fluctuations in the QW lead to strong localization effects in the valence band. This behavior is not a particularity of the here chosen microscopic configuration, as we show elsewhere.[12] From Fig. 2 we conclude also that in comparison with the electrons, the holes are more strongly localized.

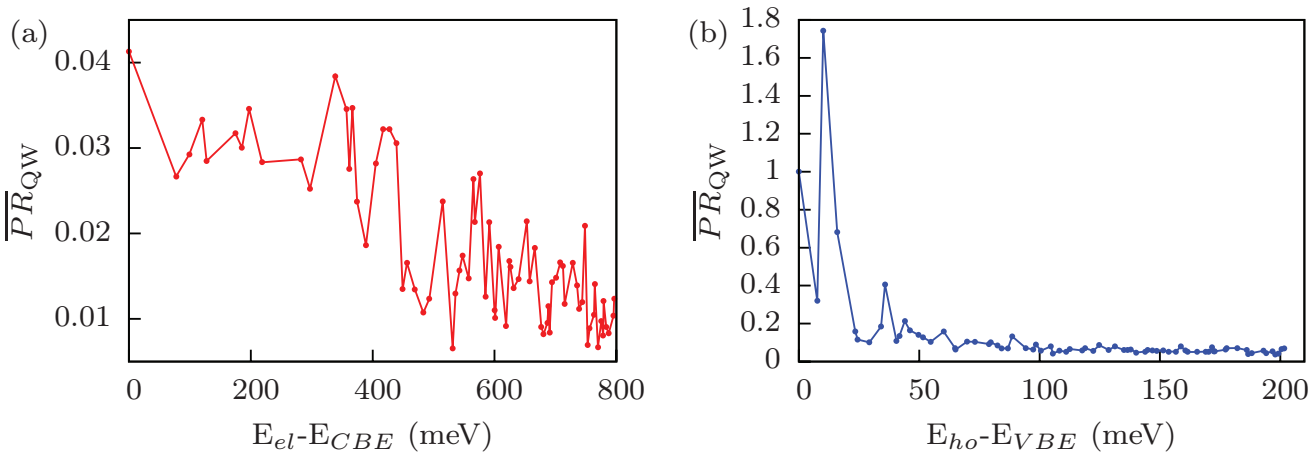

Figure 3. The PR values for (a) electron and (b) hole states in a $In_{0.25}Ga_{0.75}N$/GaN QW. Here, PR values are normalized to the PR value of the hole ground state. The energies are given with respect to CBE and VBE, respectively. Note the different scales for electrons and holes.

Furthermore, the excited hole states also reveal strong localization effects. To support this conclusion, we have calculated PR values for not only the electron and hole ground states but also for a larger number of excited states. The results are shown in Fig. 3 (a) for electrons and (b) for holes. To compare the PR values for electrons and holes more easily, the data is normalized to the PR value of the hole ground state. The reference energy is the CBE and VBE, respectively. Note the different scales for the PR values in Figs. 3 (a) and (b). Figure 3 confirms that the hole state localization is generally stronger than that of the electrons. This finding is in agreement with our LDA-DFT results presented in Sec. 3.1.

Figure 3 (b) reveals that not only the hole ground state wave function is localized but also the excited states. For example, the second excited state is even more strongly localized than the hole ground state. It should be noted that the large localization effect in the hole states is in part introduced by the strong built-in field along the *c*-axis. However, Fig. 2 indicates already that the hole wave functions are also strongly localized in the *c*-plane. We find, that the first 10–20 hole states (45–65 meV) are also localized in-plane (not shown). The energy difference between these states and the VBE indicates that these localization effects play a role up to room temperature. From hole state 20 on, the hole wave functions become also more delocalized within the *c*-plane.

Our current study presents only one microscopic configuration; similar results have however been obtained across a series of $In_{0.25}Ga_{0.75}N$/GaN QWs that we have investigated. In future work we will extend our analysis to these other configurations and discuss the impact of the InN content in the well on the results.

4. CONCLUSION

In summary, we have presented an atomistic analysis of the wave function localization effects in $In_xGa_{1-x}N$ alloys and $In_{0.25}Ga_{0.75}N$/GaN QWs with random In distributions and well-width fluctuations. We applied the DFT method to study the impact of one, two, three and four In atoms sharing the same N neighbor. Our results show that the In configurations considered here affect the CBE wave function only slightly, while the VBE state becomes increasingly localised as an increasing number of In atoms share a N atom.

To study the wave function localization effects in $In_{0.25}Ga_{0.75}N$/GaN QWs with realistic dimensions, we applied an atomistic TB model. The TB model includes local strain and built-in potential fluctuations arising from the random alloy fluctuations considered here. Our analysis reveals that the electron ground state wave function in the $In_{0.25}Ga_{0.75}N$/GaN QW is mainly localized by well-width fluctuations, with random alloy fluctuations being of secondary importance. This is in contrast to the hole states. Here we find that the hole states are already strongly localized by the presence of the random In fluctuations. This finding is in very good agreement with the above discussed DFT results, indicating that the TB model applied here gives a good description of the localization effects in $In_xGa_{1-x}N$/GaN QWs.

Furthermore, we have also used our TB analysis to gain insight into the localization behavior of excited states. This study reveals that not only the hole ground state is strongly localized but also higher hole states. This observation is consistent with the experimentally observed "S-shape" dependence of photoluminescence (PL) spectra with temperature,[5,6] which is a clear indication of localization effects in $In_xGa_{1-x}N$ QWs.

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