First-principles calculations of carrier localization in fluctuated InGaN quantum wells

Toshiyuki Kunikiyo, Shinnosuke Hattori, Raku Shirasawa, and Shigetaka Tomiya

Materials Analysis Center, Fundamental Technology Research and Development Division2, Sony Corporation, Atsugi, Kanagawa 243-0014, Japan

E-mail: Toshiyuki.Kunikiyo@sony.com

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1. Introduction

The spatial distribution of holes and electrons in InGaN-based light emitting devices is an important factor affecting the light emission efficiency. Most InGaN/GaN quantum wells (QWs) in light emitting devices are grown on the c-plane which has polar character in the wurtzite GaN crystal. This is because high-quality GaN can be readily obtained in this growth plane.1,2 In c-plane QWs, a biaxial compressive strain is applied to the InGaN layer because of lattice mismatch at the InGaN/GaN interface. This strain causes vertical piezoelectric polarization in the InGaN layer, which separates the holes and electrons vertically and leads to lower light emission efficiency.2,3 Several structural fluctuations in QWs are being discussed as another factor of carrier localization. For c-plane QWs, three-dimensional atom probe analysis of an InGaN/GaN multiple QW structure revealed monolayer steps in the upper interface of the InGaN layer which would contribute to the localization of carriers at room temperature.4 High-angle annular dark-field scanning transmission electron microscopy (HAADF TEM) and atomic probe tomography studies have indicated that indium (In) composition fluctuation occurs in QW fluctuation.5 In addition to the above-mentioned c-plane case, the QW structure in a semipolar orientation has recently been studied intensively. This has been in attempt to reduce the piezoelectric effect to achieve higher efficiency and/or longer wavelength emission devices.6–14 A comprehensive understanding of the carrier localization in QWs of polar or semipolar orientations with various structure fluctuations is thus required.

There are previous theoretical studies about carrier localization in fluctuated QWs. For c-plane InGaN/GaN QWs, Ref. 15 used the effective mass Schrodinger equation to calculate localization lengths of the electrons and holes. Reference 16 used atomistic tight-binding (TB) model to analyze electronic and optical properties of c-plane InGaN/GaN QWs. For nonpolar InGaN QWs, Ref. 17 used continuum elasticity theory and an eight band k · p model to study the influence of thickness fluctuation in InGaN QWs grown along the [1120] direction in GaN. The calculation methods used in the above studies have the advantage to simulate carrier distribution in QWs with large-scale structural fluctuation. On the other hand, empirical parameters that ensure accuracy for simulation targets are required and continuum model does not include atomistic coordinate explicitly. In recent years, details of the structural fluctuation of QWs such as the range of In composition fluctuation,5 nanofacets structure formed in 201 plane QW interface,18 etc. have been clarified experimentally. However, to the best of our knowledge, simulation taking into account such experimental facts has not been performed.

In this study, we investigate the carrier distributions of band edge states in c-plane QWs and (201) plane QWs with structural fluctuation using first-principles calculations. The ionic relaxation of several supercells comprising thousands of atoms representing a QW with various fluctuations is performed using a Stillinger–Weber (SW) type force field19 whereupon the electronic state analysis of the structure is obtained. From these results, the carrier localization in the polar and semipolar QWs with structure fluctuation is characterized.

2. Methods

The QWs analyzed in this study are constructed from a wurtzite structure and there are no lattice defects such as vacancies and dislocations. To analyze the QW with structure fluctuation, the supercell containing thousands of atoms must be calculated. It is difficult to perform ionic relaxation for this by first-principles calculation, so we use the SW type potential19 for ionic relaxation. The parameter of the SW type potential is taken from Ref.20. It is assumed that the GaN layer is sufficiently thick compared with the InGaN layer, so that supercell lattice vectors which are parallel to the growth plane of QW are fixed to those of the freestanding GaN layers. The lattice vector including growth direction and all atomic coordinates in the supercell are relaxed freely. The width of the InGaN layer is set to about 2.5 nm. In the case of the QW with In composition fluctuation, we assume that the regions of x = 0.25 and x = 0.17 in the InxGa1-xN layer occur periodically along the in-plane direction, as shown in Fig. 1.
The In composition fluctuation range about ±20% was chosen based on the experimental measurement in $\text{In}_{0.25}\text{Ga}_{0.75}\text{N}$ QW.\(^5\) In the case of the QW with well width fluctuation, we assume that the well width varies periodically due to the upper interface of the InGaN layer along the in-plane direction, as shown in Fig. 6. Supercells of the QW structure are relaxed using the SW potential, then a single point calculation without geometry optimization is performed using the projector augmented wave method\(^{21,22}\) with single k-point. This is implemented in the Vienna ab initio simulation package\(^{23–26}\) on the relaxed structure. The Perdew–Burke–Ernzerhof method\(^{27}\) is a kind of generalized gradient approximation and is used for the exchange correlation functional.

3. Results and discussion

3.1. Indium composition fluctuation

Figure 1(a) shows the iso-surface of the valence band maximum (VBM) and conduction band minimum (CBM) densities in the case where the In composition of the InGaN layer varies periodically in the c-plane QW, as shown in Fig. 6. Supercells of the QW structure are relaxed using the SW potential, then a single point calculation without geometry optimization is performed using the projector augmented wave method\(^{21,22}\) with single k-point. This is implemented in the Vienna ab initio simulation package\(^{23–26}\) on the relaxed structure. The Perdew–Burke–Ernzerhof method\(^{27}\) is a kind of generalized gradient approximation and is used for the exchange correlation functional.

Figure 1(b) shows the case of the (20\(\overline{21}\)) plane QW with In composition fluctuation. For the (20\(\overline{21}\)) plane QW, we construct a zigzag shaped interface composed of two nanofacets, which is based on reported HAADF TEM observations of the (20\(\overline{21}\)) plane QW.\(^{18}\) The well width of the InGaN layer is uniform at \(\sim 2.5\) nm. We assume that the In composition varies in the [1\(\overline{1}14\)] direction. The CBM and VBM tend to concentrate in the region of high In composition as in the case for the c-plane QW. However, the CBM and VBM separate from each other in the in-plane direction in addition to in the perpendicular direction, in the region of high In composition in the (20\(\overline{21}\)) plane QW. Separation of the CBM and VBM in the perpendicular direction is the opposite to the behavior observed in the case of the QW in the c-plane. Reported theoretical calculations\(^{30,31}\) have shown that the piezoelectric polarization of the (20\(\overline{21}\)) plane QW inverts (i.e., becomes upside down) with respect to the
c-plane QW. Our results obtained using first-principles calculations are consistent with these theoretical calculations.

To clarify the reason why in-plane separation appears in the (201) plane QW, we investigate the possibility of it being caused by the in-plane component of the piezoelectric polarization. Figure 2(b) shows the orientation dependence of piezoelectric polarization of In$_{0.25}$Ga$_{0.75}$N rotated by the angle $\theta$ around the (11\overline{2}0) axis with biaxial compression at the $xy$ surface described in Fig. 2(a). This is calculated in the same way as in Ref. 31. The $x$ component is constant at 0, and the $y$ component is generated except for a specific angle. The $x$ component is constant at 0 even when the In composition changes. It can be seen that the in-plane component of polarization occurs along [1014] ($/\gamma$) in the (20\overline{2}1) plane QW. However, when the structure fluctuation of QW is small and the polarization is nearly constant in the InGaN QW, the influence of the electric field on the in-plane component is considered to be small.

The potential distribution with the polarization $P$ is governed by the Poisson equation, $-\nabla \cdot \varepsilon \nabla \phi = -\nabla \cdot P$, where $\varepsilon$ is the dielectric constant and $\phi$ is the electrostatic potential. In the case where polarization is constant in the InGaN QW, the right side of the equation is 0 except for at the InGaN/GaN interface or the edge surface of InGaN QW. Furthermore, if the InGaN/GaN interface is perfectly flat, the in-plane component of the polarization generates polarization charge only at the edge surface of InGaN QW. In the perfect flat case, the in-plane component of the polarization usually does not become a major issue when considering carrier localization by the piezoelectric effect. In the case of the (22\overline{1}0) plane QW, it is possible that the periodic fluctuation of polarization charges occurring at the zigzag shaped InGaN/GaN interface could affect the distribution of carriers. However, the current results show that there is no correlation between the CBM and VBM density distribution and the period of the zigzag interface structure. The polarization charge at the interface does not appear to be the dominant factor in their separation.

We now investigate the possibility that the polarization in the InGaN layer becomes non-uniform due to the fluctuation of the In composition. To obtain the polarization distribution, we calculate the strain tensor of the InGaN. The freestanding In$_{0.17}$Ga$_{0.83}$N and In$_{0.25}$Ga$_{0.75}$N crystal structures are taken as reference for the region of $x = 0.17$ and $x = 0.25$ respectively. The analyzed in-plane and perpendicular direction strains are shown in Fig. 3. The in-plane component of Fig. 3 shows no noticeable change even if the In composition changes. This means that the actual lattice spacing in the in-plane direction in the region of $x = 0.17$ is narrower than in the region of $x = 0.25$. Because the lattice parameter $a,c$ of freestanding In$_{0.17}$Ga$_{0.83}$N are smaller than that of freestanding In$_{0.25}$Ga$_{0.75}$N. The strain of the perpendicular component tends to increase in the region of low In composition.

We then calculate the piezoelectric polarization from the strain tensor using the piezoelectric coefficient $^{31}$ The average in-plane component in the region of high In composition is 0.010 C m$^{-2}$, and that in the region of low In composition is 0.015 C m$^{-2}$. Figure 4 shows a schematic of the polarization distribution in the InGaN QW. When the polarization vector $P$ changes by $\Delta P$ at the interface whose perpendicular vector is $n$ in the InGaN QW, the surface polarization charge $\sigma_{b}$ occurs for which the density is expressed by $\sigma_{b} = -n \cdot \Delta P$. Comparing the results in Fig. 1(b) and Fig. 4 shows that the CBM and VBM are biased toward the boundary side of $\sigma_{b} > 0$ and $\sigma_{b} < 0$, respectively. The surface polarization charge generated in the InGaN layer may generate an internal electric field in the in-plane direction which hardly occurs in the c-plane QW or (201) plane QW without structural fluctuation. As a result, carriers may separate in the in-plane direction. As shown in Fig. 2, there is in-plane anisotropy of the piezoelectric polarization in the (201) plane QW. If the cause of the in-plane separation of the CBM and VBM is fluctuation of polarization, their distributions must reflect the polarization charge distribution. In the (201) plane QW, polarization charges mainly occur at the boundary where the In composition changes perpendicular to the y direction.

To verify this, we construct the (201) plane supercell shown in Fig. 5(a), in which the In composition of the InGaN layer is arranged in the checkered pattern shown in Fig. 5(b). The calculated distributions of the VBM and CBM projected along the growth direction are shown in Fig. 5(c). The CBM and VBM tend to concentrate in the region of high In composition. Their separation appears along the [1014] direction, and separation along the $a$-axis direction is not apparent. This result corresponds to the in-plane anisotropy of the polarization shown in Fig. 2, and confirms that the in-plane separation of the CBM and VBM is due to the in-plane component of polarization.

3.2. Well width fluctuation

Figure 6(a) shows the calculated VBM and CBM distributions in the c-plane QW whose local well width in the InGaN layer changes periodically along the $m$-axis due to the upper interface of the InGaN layer. The CBM tends to localize in the thick well width region.

In the theoretical calculations in Refs. 15 and 16, the electronic carrier is susceptible to the roughness of the upper interface. Though our approach is different from these previous studies, our results exhibit a similar tendency to them. Figure 6(b) shows the case of the (20\overline{2}1) plane QW
where the well width of the InGaN QW varies periodically along the [1\overline{0}14] direction. The CBM and VBM tend to separate in the in-plane direction in addition to in the perpendicular direction.

Figure 7 shows the strain distribution of the (20\overline{2}1) plane QW with the well width fluctuation calculated in the same manner as in Sect. 3.1. The region of narrow well width is strongly compressed in the in-plane direction compared with the region of the wide well. This can be interpreted that it is strongly elongated in the perpendicular direction due to the reaction of in-plane compression. The average in-plane component of the polarization in the wide well width region is 0.015 C m\(^{-2}\), and that in the narrow well width region is 0.017 C m\(^{-2}\). The polarization change between these regions causes polarization charge and it may generate an internal electric field in the in-plane direction as in the case of In composition fluctuation. However, the localization of VBM and CBM due to In composition fluctuation does not occur in this case. This can be understood by the CBM and VBM distributing around the interface of \(\sigma_b > 0\) and \(\sigma_b < 0\), respectively.

4. Conclusions
We have characterized the carrier localization in fluctuated polar and semi-polar QWs using first-principles calculations. In both the c-plane QW and (20\overline{2}1) plane QW, the CBM and VBM tend to localize in the region of high In composition. In the case of the c-plane QW, the CBM localizes in the region

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**Fig. 4.** Schematic of piezoelectric polarization and polarization charge (\(\sigma_b\)) distribution in the (20\overline{2}1) plane QW including In composition fluctuation. Plus and minus sign indicate the sign of \(\sigma_b\) occurring between regions of different In composition.

**Fig. 5.** (Color online) Analysis of the (20\overline{2}1) plane QW with In composition fluctuation in a checkerboard pattern: (a) supercell of QW consisting of 9600 atoms, (b) In composition pattern of the InGaN layer, (c) iso-surface of the CBM (red) and VBM (blue) density. The region of \(x = 0.25\) is indicated by the green frame.

**Fig. 6.** (Color online) Iso-surface of the CBM (red) and VBM (blue) density in the QW with well width fluctuation: (a) c-plane QW, (b) (20\overline{2}1) plane QW.
of wide well width due to the upper interface of the InGaN layer. In the (20\ 21) plane QW, the CBM and VBM can separate in the in-plane direction as well as in the perpendicular direction, when In composition fluctuation or well width fluctuation exist. The cause of these is considered to be the polarization charge generated by the non-uniform piezoelectric polarization inside the InGaN layer due to the structural fluctuation of the QW. It is well-known that the semipolar plane QW can suppress the separation of holes and electrons in the perpendicular direction, compared with the c-plane QW. However, our results imply that carrier separation in the in-plane direction could contribute to lowering the light emission efficiency in semi-polar plane QWs.

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