Improve of p-type conductivity in Al-rich AlGaN substituted by MgGa δ-doping (AlN)$_m$/Ga$_n$ (m≥n) superlattice

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**Abstract**

The challenge of p-type doping in Al-rich AlGaN is investigated based on first-principles calculations. We find that the p-type conductivity can be improved by replacing Al-rich AlGaN with MgGa δ-doping (AlN)$_m$/Ga$_n$ superlattice (SL). The formation energy $E_f$ is the lowest and acceptor activation energy $E_a$ is the smallest for Mg substituting Ga in the SL. The $E_f$ increases if the doping position moves from GaN to AlN layer. Moreover, $E_a$ decreases with increasing the number of GaN monolayers. The $E_a$ can be reduced from 0.48 eV in AlN to 0.26 eV in (AlN)$_5$/Ga$_n$, 0.25 eV in (AlN)$_1$/Ga$_n$, 0.24 eV in (AlN)$_4$/Ga$_2$ and 0.22 eV in (AlN)$_3$/Ga$_3$ SLs. This will lead to a high hole concentration in the order of 10$^{20}$ cm$^{-3}$ at room temperature, which is favorable for AlGaN-based deep ultraviolet optoelectronic devices.

**1. Introduction**

AlGaN alloys are important materials for ultraviolet (UV) and deep ultraviolet (DUV) optoelectronic devices with the spectrum down to 200 nm and can be widely used in the areas of water purification, bio-agents detection, sterilization and medicine [1–3]. Although tremendous progresses have been made in the fabrication of AlGaN materials [4,5], achieving p-type conductivity in Al-rich AlGaN is still of great challenge. The main reasons for the poor p-type conductivity in Al-rich AlGaN are the large acceptor activation energy $E_a$, the strong compensation effects from the intrinsic donor defects, such as nitrogen vacancy [6], and the limited acceptor solubility [4]. In general, the activation energy of the commonly used Mg acceptor increases monotonically from 0.16–0.25 eV in GaN to 0.5–0.6 eV in AlN with increasing Al content in AlGaN alloys [4]. Therefore, realizing p-type doping in Al-rich AlGaN has become a challenging issue for its wide applications in DUV optoelectronic devices.

Many works have been done to study the p-type doping problem in AlGaN alloys during the last few years. Simon et al. proposed the polarization-induced doping by ionizing acceptor dopants using the build-in electronic polarization in wide band-gap semiconductors, which can lead to improvement in p-type electrical conductivity and optical emission efficiency in UV light-emitting diodes (LEDs) [7]. A new alternative co-doping technique was reported to reduce the acceptor activation energy and increase the hole carrier concentration of Al$_{1-x}$Ga$_x$N ($x = 0.4$) and GaN [8]. The pulse supply of the source gases, such as NH$_3$, TMGa and Cp$_2$ Mg, has also been proved to increase the p-type carrier concentration and decrease the acceptor activation energy in AlGaN and GaN epitaxial layers [9]. However, these efforts have not succeeded in solving the p-type doping problem of Al-rich AlGaN, either because the acceptor activation energy is too high or the Al concentration is too low.

It has been known that nanoscale compositional inhomogeneity, such as islands or quantum dots, has an important influence on the luminescence efficiency of group-III nitride semiconductors [10,11]. The atomic-scale compositional superlattice (SL) has also been observed in AlGaN films and has been proved to increase the transverse electric polarized light emission efficiency of Al-rich AlGaN alloys in the DUV spectral region [12–14]. In addition, the p-type conductivity can be enhanced by using Mg δ-doping AlGaN epilayers or Mg and Si δ-doping Al$_{1-x}$Ga$_x$N/Al$_y$Ga$_{1-y}$N SLS [15,16]. According to the tight-binding
approximation [17], we know that the electronic structures of acceptor atom doped in AlGaN can be modified significantly by its nearest atoms. Therefore, we can focus on the nearest neighbors by altering the microscopic atom distributions around the acceptor. In this article, we give the results of Mg doping in short-period (AlN)$_n$/(GaN)$_m$ (m $\geq$ n) SLs with different combinations of m and n, i.e. (AlN)$_3$/(GaN)$_n$, (AlN)$_4$/(GaN)$_2$, (AlN)$_3$/(GaN)$_2$ and (AlN)$_1$/(GaN)$_n$, as a substitution of Al-rich AlGaN alloys. We find that Mg acceptor activation energy $E_A$ can be reduced by about 0.25 eV compared with that in AlN, which leads to a high hole concentration in the order of $10^{18}$ cm$^{-3}$ at room temperature. The $E_A$ is smaller for Mg doping in GaN layer than AlN layer and decreases with increasing n.

2. Calculation details

Our first-principles calculations are performed in the framework of density functional theory (DFT) with the projected-augmented wave (PAW) method [18], as implemented in the Vienna $ab$ initio simulation package (VASP) code [19,20]. The AM05 exchange-correlation (XC) functional [21] is adopted to optimize our lattice parameters and calculate the electronic properties subsequently. This is because the AM05 XC functional can give more reasonable lattice constants than the traditional Perdew–Burke–Ernzerhof (PBE) [22] functional and has shown the same excellent performance for solids as the hybrid functionals [23,24]. A wurtzite supercell with 108 atoms, generated by different combinations of $m$ and $n$ (mn = 33, 42, 11 and 51) are displayed in Fig. 1. It should be noted that the similar short-period (GaAs)$_3$/(AlAs)$_1$ [25], (AlAs)$_3$/(AlSb)$_1$ [26] grown by molecular beam epitaxy (MBE) and GaN/AlN SL [27] with the constituent layers as thin as 1 monolayer grown by switched atomic layer metalorganic chemical vapor deposition (MOCVD) have been obtained previously. We thus believe that our models can also be realized by using MBE or MOCVD technologies. An energy cutoff 550 eV for the plane-wave basis set is used. A non-shifted $\Gamma$-centered $4 \times 4 \times 2$ k-point mesh is employed in the defect-free bulk calculations. The Monkhorst–Pack [28,29] special k-point $2 \times 2 \times 2$ is used for the Brillouin-zone sampling in the defect calculations. Considering that the gap value is seriously underestimated in the usual LDA and GGA calculations, we adopt the LDA-1/2 method [30,31] to revise the band gaps. In the LDA-1/2 scheme, the half ionization is applied to the p-orbital of N atom and d-orbital of Ga atom. We adopt CUT = 2.90 (a.u.) and n = 8 for N atom, and 1.23 (a.u.) and 100 for Ga atom.

The formation energy of a defect in charge state q can be obtained as [32],

$$E^q[D] = E_{\text{tot}}[D^q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + q[E_F + E_V + \Delta V(D)],$$

where $E_{\text{tot}}[D^q]$ is the total energy derived from a supercell calculation with one defect D in the charge state q, $E_{\text{tot}}[\text{bulk}]$ is the total energy of the equivalent bulk supercell, and $n_i$ and $\mu_i$ are the number and chemical potential of atoms of type i, respectively. The Fermi level $E_F$ is referenced to the valence-band maximum (VBM) $E_v$ of the bulk. The correction term $\Delta V$ is introduced to align the average electrostatic potential in the charged defect supercell with that in the bulk. For the neutral defect ($q = 0$), we also need a correction term $E_{\text{corr}}$ accounting for the dispersion of the defect level due to the interaction between defects in different supercells. It is usually obtained from the energy difference between the eigenvalue of the highest occupied state at the $\Gamma$ point and the average of the eigenvalues of the defect-induced band at the special k-points [33]. The Mg acceptor activation energy is defined as the Fermi level position at which the charge states $q = 0$ and $-1$ have equal formation energy and can be calculated as follows,

$$E_A = E_{\text{tot}}\left(D^{-1}\right) - E_{\text{tot}}\left(D^0\right) + E_{\text{corr}} - E_V - \Delta V(D).$$

The chemical potentials depend on the growth condition, which can be either N-rich or N-poor. For the thermal equilibrium, we require the boundary condition, i.e. $\mu_{\text{Ga(Al)}} + \mu_N = \Delta h[\text{Ga(Al)}]$, where $\Delta h[\text{Ga(Al)}]$ is the formation enthalpy of bulk GaN (AIN). For N-poor condition $\mu_{\text{Ga(Al)}}$ is set to the energy of Ga (Al) metal, while for N-rich condition the chemical potential is determined by the energy of N$_2$ molecule. The Mg chemical potential is determined by the formation enthalpy of Mg$_2$N$_2$. It is worthwhile to note that the formation energy under the N-poor condition is merely a shift of the atomic chemical potentials compared with the N-rich condition [see Eq. (1)]. We can also see from Eq. (2) that the activation energy does not depend on the atomic chemical potentials.

3. Results and discussion

To guarantee the reliability of our calculated formation energy and activation energy, we first consider the Mg doping in GaN and AlN. The calculated Mg acceptor activation energy in these two binary alloys are shown in Table 1. For the sake of comparison, we also list some other calculational and experimental results. We can see from Table 1 that our calculated $E_A = 0.20$ eV for Mg acceptor in GaN is in good agreement with well-accepted calculational (0.198–0.26 eV) [34–36] and experimental values 0.16–0.25 eV [4,37,38]. For the Mg doping in AlN, an excellent agreement of $E_A = 0.48$ eV with the previous calculations (0.40–0.58 eV) [39–42].
Table 1  
Comparison of the calculated Mg acceptor activation energy $E_A$ (in unit of eV) in GaN and AlN together with the other calculational and experimental results.

<table>
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<tr>
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<th>This work</th>
<th>Other calc.</th>
<th>Expt.</th>
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<tbody>
<tr>
<td>GaN:MgGa</td>
<td>0.20</td>
<td>0.198 [34]</td>
<td>0.16 [4]</td>
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<td></td>
<td>0.204 [35]</td>
<td>0.208 [37]</td>
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<td></td>
<td>0.26 [36]</td>
<td>0.25 [38]</td>
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<td></td>
<td>0.40 [39]</td>
<td>0.50 [4]</td>
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<td></td>
<td>0.45 [40]</td>
<td>0.51 [43]</td>
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<td></td>
<td>0.58 [41]</td>
<td>0.50 [45]</td>
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and experiments (0.50 eV) [4,43–45] is also observed. This clearly indicates that the present first-principles calculations are accurate and reliable. Therefore, we will also use Eqs. (1) and (2) to calculate the formation energy and activation energy of Mg acceptor in the short-period (AlN)$_m$/(GaN)$_n$ ($m \geq n$) SLs.

To see whether the Mg impurity can stably occupy the Ga site in GaN monolayer and induce a shallow acceptor level, we choose different substitutional positions in our four SLs (see Fig. 1) and calculate their formation energies and activation energies. The calculated formation energies as a function of occupied sites are shown in Fig. 2 for the four SLs. Here the formation energies are obtained under N-rich condition with the Fermi level fixed at the VBM. Both the values for the neutral charge state (solid line) and the $\pm 1$ charge state (dashed line) are given. For the sake of comparison, our calculated formation energies for Mg doping in GaN and AlN are also presented in Fig. 2. It should be pointed out that the Mg acceptor has a lower formation energy in GaN than AlN. This is a common result which can be found in other theoretical calculations [6,36,41,46,47]. We can see from Fig. 1 that the (AlN)$_3$/(GaN)$_3$ and (AlN)$_5$/(GaN)$_1$ SLs have four nonequivalent doping sites. In contrast, the (AlN)$_1$/(GaN)$_1$ SL has three nonequivalent doping sites while the (AlN)$_4$/(GaN)$_2$ SL just has two nonequivalent doping sites. It can be seen from Fig. 2 that the formation energy increases monotonically if the doping site moves from the middle GaN monolayer to the outmost AlN layer. The formation energy is the lowest for Mg acceptor occupying at site 1 in the four SLs. For the same SL structure, the $\pm 1$ charge state has a higher formation energy than the neutral charge state. All the formation energies for the four SLs are in between the values of GaN and AlN. Furthermore, the formation energy has a rapid increase when the Mg impurity moves from GaN layer to AlN layer. The low formation energy at site 1 clearly indicates that it is easier for Mg to substitute the cation in the GaN layer rather than the AlN layer. This guarantees that the Mg impurity can have a GaN-like local environment, which is beneficial for the reduction of its activation energy.

Fig. 3 shows our calculated Mg acceptor activation energy at the different doping sites in the four SLs. As a reference, the calculated values for GaN and AlN are also presented in Fig. 3. It can be seen from Fig. 3 that our calculated Mg acceptor activation energies for the SLs fall in the scope of 0.20 eV for GaN and 0.48 eV for AlN, as it should be [48]. Moreover, we can see from Fig. 3 that the Mg acceptor activation energy increases when the doping position moves away from site 1. The activation energy for Mg $\delta$-doping at site 1 is the smallest. We also note that the activation energy decreases when the number of GaN monolayers increases, i.e. $n$ changing from 1 of (AlN)$_3$/(GaN)$_3$, 2 of (AlN)$_4$/(GaN)$_2$ to 3 of (AlN)$_5$/(GaN)$_1$, for Mg doping at site 1. In other words, Mg has a smaller activation energy in (AlN)$_3$/(GaN)$_3$ SL than that in (AlN)$_5$/(GaN)$_1$ SL. Particularly, the acceptor activation energies for Mg doping in (AlN)$_4$/(GaN)$_2$ and (AlN)$_5$/(GaN)$_1$ SLs fall in between the values of (AlN)$_3$/(GaN)$_3$ and (AlN)$_5$/(GaN)$_1$ SLs. This is because the modulation of the GaN layer becomes stronger if the number of GaN (AlN) monolayers increases (decreases). Both the lowest formation energy and smallest activation energy at site 1 clearly demonstrate that it is more efficient to improve the $p$-type conductivity by using Mg$_{\delta}$-doping in the middle GaN monolayer of the short-period (AlN)$_m$/(GaN)$_n$ SLs instead of traditional AlGaN disorder alloys.

It has been known that the formation of native donor defects can reduce the $p$-type doping efficiency due to the compensation effect. The formation energies of various native defects in GaN and AlN have been systematically investigated previously [33,41,49,50]. In $p$-type materials, the nitrogen vacancy ($V_N$) is predicated to have low formation energy and can induce donor levels to compensate the acceptor defects [6]. Moreover, we also need to know whether the Mg impurity can stably remain at the substitutional site instead of becoming the interstitial or antisite defect. Therefore, it is necessary to have a comprehensive understanding of the behavior of both acceptor and native defects in AlGaN alloys. Considering that the vacancies always have low formation energy in GaN and AlN and may become important compensating centers [41,50], we will thus focus our attention on the $N$ vacancy ($V_N$), Ga vacancy ($V_{Ga}$), Al vacancy ($V_{Al}$) and Mg-related defects in the SLs. As a representative of Al-rich AlGaN, the calculated formation energies for the selected native and Mg-related defects in (AlN)$_3$/(GaN)$_1$ SL

![Fig. 2. Defect formation energy for Mg $\delta$-doping in (AlN)$_3$/(GaN)$_3$ (Olive), (AlN)$_4$/(GaN)$_2$ (Red), (AlN)$_1$/(GaN)$_1$ (Blue) and (AlN)$_5$/(GaN)$_1$ (Magenta) SLs as a function of doping sites (see Fig. 1) under N-rich condition. Here $E_F$ is fixed at the VBM. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 3. Acceptor activation energy for Mg $\delta$-doping in (AlN)$_3$/(GaN)$_3$, (AlN)$_4$/(GaN)$_2$, (AlN)$_1$/(GaN)$_1$ and (AlN)$_5$/(GaN)$_1$ SLs as a function of doping sites (see Fig. 1). For the sake of comparison, the acceptor activation energies in bulk GaN and AlN (see the dashed line) are also given.](image)
AlGaN alloys. The MgGa substitutional defect in the middle GaN is stabilized by substituting Al-rich AlGaN with MgGa. It is much easier for MgGa to form spontaneously under N-rich condition and is close to the VBM. This indicates that under N-poor condition, the MgGa defect will be compensated by MgGa and VAl. The MgGa and VAl calculations. We can see from Fig. 4 that the MgGa defect has the lowest formation energy compared with other defects if the Fermi level moves from the intersection of MgGa and Mg0 and VAl (E_F(1)) under N-rich condition. For the intersection of MgGa and VN is denoted as E_F(1). The Fermi level range between E_F(1) and E_F(2) under N-rich condition is larger than that under N-poor condition and is close to the VBM. This indicates that it is much easier for MgGa to form spontaneously under N-rich condition. Therefore, the MgGa defect can effectively lead to the p-type conductivity if E_F is close to the VBM under N-rich condition. Under N-poor condition, the MgGa defect will be compensated by Mg, Mg0 and VN defects for E_F getting close to the VBM. The above results clearly indicate that the N-rich condition is favorable for the formation of MgGa defect and the p-type conductivity can be realized by substituting Al-rich AlGaN with MgGa δ-doping (AlN)m/(GaN)n SLs.

4. Conclusion

In conclusion, the p-type doping problem in Al-rich AlGaN has been investigated using first-principles approach. We find that the p-type doping bottleneck can be broken through by using Mg δ-doping short-period (AlN)m/(GaN)n (m ≥ n) SLs to substitute Al-rich AlGaN alloys. The MgGa substitutional defect in the middle GaN monolayer (site 1) has the lowest formation energy compared with other substitutional, interstitial and antisite defects. For E_F varying within special range in the band gap, the MgGa at site 1 also has the lowest formation energy compared with the native vacancy defects. Moreover, the Mg acceptor activation energy has an increasing tendency with the doping position moving from the middle GaN monolayer to the outmost AlN layer. The smallest activation energy at site 1 is attributed to the GaN-like local environment around the Mg acceptor. For different combinations of m and n (m = 33, 42, 11 and 51), the acceptor activation energy E_a decreases with the increase of n. The E_a can be reduced from 0.48 eV in AlN to 0.26 eV in (AlN)3/(GaN)4, 0.25 eV in (AlN)7/(GaN)8, 0.24 eV in (AlN)14/(GaN)15 and 0.22 eV in (AlN)22/(GaN)23 SLs. This will lead to a high hole concentration up to 10^{18} cm^{-3} at room temperature. The present results indicate that MgGa δ-doping in (AlN)m/(GaN)n (m ≥ n) SLs, as a substitution of Al-rich AlGaN alloys, is a very promising method for achieving p-type conductivity. We hope that this study would motivate further experiments on the p-type Al-rich AlGaN and related optoelectronic devices.

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References


