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Enhancing hole concentration in AlN by Mg:O codoping: *Ab initio* study

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Ab initio study based on density functional theory is performed to study the binding energies of Mg acceptors to single oxygen in AlN and the activation energies of the resultant Mg_n-O complexes (n=2, 3, and 4). It is found that such complexes are energetically favored and have activation energies at least 0.23 eV lower than that of single Mg. The lower activation energies originate from the extra states over the valence band top of AlN induced by the passive Mg-O. By comparing to the well-established case of GaN, it is possible to fabricate Mg:O codoped AlN without MgO precipitates. These results suggest the possibility of achieving higher hole concentration in AlN by Mg:O codoping.

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Ultraviolet light-emitting diodes (LEDs) with wavelengths less than 300 nm are of considerable technological significance. They are potential alternatives to the existing gas lasers and mercury lamps in applications such as disinfection, air and water purification, and biomedicine, where the latter encounter difficulties due to their high operating voltages, low efficiency, large size, and toxicities.[1] They also promise high density optical data storage and high-resolution photolithography.[2] Wide gap semiconductors such as diamond (E_g=5.5 eV) and AlN (E_g=6.2 eV) are the two most studied materials for such LEDs, and AlN is particularly favored due to its direct gap band structure and subsequent high light-emission efficiency. Diamond as well as AlN based LEDs have been fabricated recently.[3,4] However, in view of their low efficiency and high operating voltages, further developments are still required to improve these two LEDs to the point where they can be used as devices.[5]

Fabrication of a homostructured LED requires both p- and n-type doping of a semiconductor. Unfortunately, the asymmetry dopability of wide gap semiconductors makes the fabrication of LEDs very difficult. The asymmetry dopability means that a wide gap semiconductor can be either p- or n-type doped, but not both.[6] AlN can be easily n-type doped with Si. However, p-type AlN is of great challenge. The most promising acceptor for AlN is Mg. Yet, the activation energy (E_A) of the Mg acceptor in AlN is 0.5 eV.[7,8] As the ratio of carrier concentration to impurity concentration follows $\exp(-E_A/k_BT)$, where k_B is the Boltzmann constant and T is the temperature, only a very small fraction $\sim 10^{-8}$ of Mg impurities is activated at room temperature. Since the upper limit of Mg concentration in AlN is $2\times \sim 10^{20}$ cm^{-3},[4] the corresponding hole concentration for Mg-doped AlN would not exceed $\sim 10^{12}$ cm^{-3}. This concentration, however, is still well below that for device applications (which requires a hole concentration of at least 10^{17} cm^{-3}).

Recently, codoping has been proposed and applied to overcome difficulties in p-type doping in some wide gap semiconductors,[9–12] and it has been proved to be an effective method to improve hole concentrations in wide gap semiconductors such as GaN and ZnO. Significant improvements in hole concentrations have been achieved in these two semiconductors. In this approach, p-type dopants (D) are incorporated into the semiconductor along with a small amount of reactive n-type impurities as codopants (CD). Then in the host semiconductors, complexes like D-CD, D_2-CD, D_3-CD, and D_4-CD will form and, more often, they have lower ionization energies than that of monodopant D (except for the passive D-CD complex). Thus, the hole concentration may be greatly enhanced. By this approach, the hole concentration in ZnO was improved from $\sim 10^{13}$ cm^{-3} in N-monodoped ZnO to $\sim 10^{17}$ cm^{-3} or even higher in (Al, Ga, or In)-N codoped ZnO.[13–15] Codoping also enhanced the hole concentration in Mg-doped GaN. The conductivity of Mg-doped GaN could be significantly enhanced by annealing in an environment with oxygen.[16] This enhancement in conductivity was attributed to the decreased activation of Mg acceptors due to the inclusion of oxygen and a corresponding order of magnitude increase of hole concentration (from $\sim 10^{17}$ to $\sim 10^{18}$ cm^{-3}).[17]

It is, therefore, reasonable to believe that the hole concentration of Mg-doped AlN can be improved using a similar approach. If the concentration of Mg is equal to that of oxygen, then Mg might be completely compensated by the formation of passive Mg-O complex. However, if the concentration of Mg is two times that of oxygen or even larger, then complexes like Mg_2-O, Mg_3-O, and Mg_4-O would be likely to form, and these complexes might have lower activation energies than a single Mg atom. In this Brief Report, we investigate the possibility of the formation of Mg_n-O (n=2, 3, and 4) complexes, where oxygen is the minor codopant, and the activation energies of such complexes by first principles total energy calculations based on density functional theory (DFT). We first study the possibility of the formation of Mg_n-O (here, n ranges from 1 to 4; atomic O occupies N site and atomic Mg the neighboring Al site, respectively) complexes in AlN. All these complexes under study are assumed to be electrically neutral unless otherwise stated. This is reasonable since even at an activation energy as low as 0.20 eV, only a small portion ($\sim 10^{-4}$) of the acceptors are in the charged state. Then the activation energies of *complex*

TABLE I. Binding energy $\Delta^{(n)}$ for single Mg acceptor attaching to Mg_n-O complex and the activation energy E_A (Mg_{n+1}-O) of the resultant Mg_{n+1}-O complexes. Unit: eV.

n	0	1	2	3
$\Delta^{(n)}$	−5.304	−0.626	−0.412	−0.157
E_A (Mg_{n+1}-O)		0.17	0.14	0.12

acceptor Mg_n-O complexes ($n=2$, 3, and 4 as Mg-O is passive) are calculated. To explain the results obtained, the density of states (DOS) is given. Most of the calculations are done using a $3\times3\times2$ supercell constructed from AlN unit cell using the plane-wave DFT code VASP.[18,19] The lattice constants of the supercell are kept fixed to avoid effects from spurious volume expansion. The Γ-centered $4\times4\times4$ k mesh is used for irreducible Brillouin zone sampling. The ion-electron interaction is described by Vanderbilt ultrasoft pseudopotentials[20] with local density approximation (LDA) for the exchange-correlation potential. The electron wave function is expanded in plane waves with a cutoff energy of 400 eV. These parameters ensure a convergence better than 1 meV for the total energy. In all the doped supercells, atomic coordinates are fully relaxed using the conjugate-gradient algorithm[21] until the maximum force on a single atom is less than 0.03 eV/Å.

For AlN in wurtzite structure, the calculated lattice constants are 3.08 Å for a and 4.94 Å for c, with the internal parameter being 0.382, in good agreement with experimental values. Based on this, the $3\times3\times2$ supercell ($Al_{36}N_{36}$) is constructed. Previous calculations on formation energies have shown that O occupies N site in AlN as a deep donor[22–24] and, consequently, in our supercell, one N atom is replaced by an O atom. This O donor may act as an attraction center to single Mg atom and form complexes such as Mg-O, Mg_2-O, Mg_3-O, and Mg_4-O with Mg atoms occupying the nearest Al sites to O and without destroying the lattice structure. To study whether single Mg atom will bind to Mg_n-O ($n=0$, 1, 2, and 3, respectively) complexes, we define the *binding energy* as the energy required to form the Mg_{n+1}-O complex from well separated Mg dopant and Mg_n-O complex:

$$\Delta^{(n)} = E(Al_{36-n-1}Mg_{n+1}N_{35}O) + E(Al_{36}N_{36}) - E(Al_{35}Mg_1N_{36}) - E(Al_{36-n}Mg_nN_{35}O), \qquad (1)$$

where E is the total energy of the system indicated in parentheses. A negative $\Delta^{(n+1)}$ suggests that the Mg_{n+1}-O complex is energetically favorable and stable, while a positive $\Delta^{(n)}$ suggests that Mg_{n+1}-O cannot form. The calculated $\Delta^{(n)}$ are summarized in Table I. As can be seen, single Mg atom will bind to single O atom for a large energy decrease of 5.304 eV. This large energy decrease can be attributed to the passivation of the extra electron of O by Mg. This suggests that Mg will be completely compensated by O if their concentrations are very close. However, the concentration of Mg is larger and, therefore, extra Mg acceptors are present, then these extra Mg atoms will bind to the Mg-O complex, forming Mg_2-O, Mg_3-O, and Mg_4-O complexes depending on the ratio between Mg and O. The energy decrease from single Mg atom binding to Mg-O complex is 0.626 eV, suggesting that Mg_2-O complex will form provided the amount of Mg exceeds that of O. If there are still extra Mg acceptors available, then Mg_3-O will form with an energy decrease of 0.412 eV, and Mg_4-O complex with an energy decrease of 0.157 eV. The binding of single Mg atom to the O atom in Mg_n-O complexes can be attributed to the larger electronegativity of O than that of N. The local environments around Mg_n-O are given in Fig. 1. There are only minor changes in Mg-O and Al-O bond lengths. This is reasonable as atomic Mg and Al are very close in atomic size, and so with O and N. Thus, formation of these Mg_n-O complexes does not destroy the lattice in AlN.

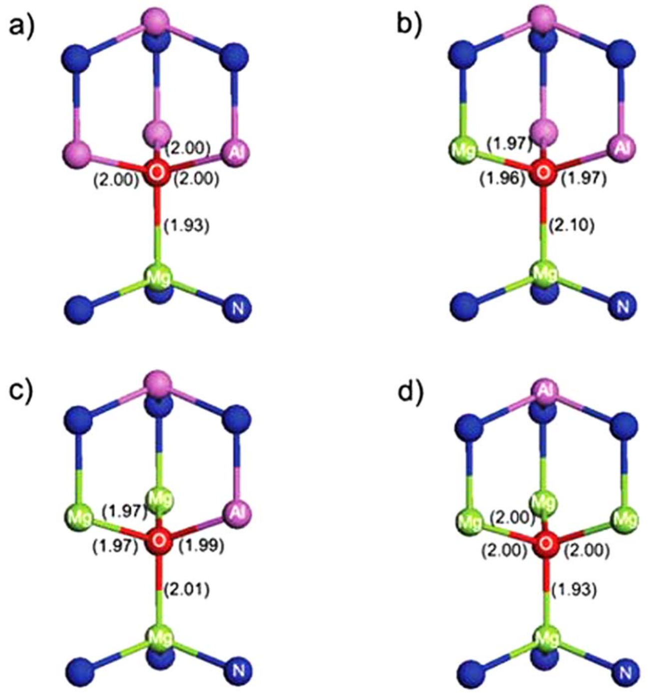

FIG. 1. (Color online) Bond-and-stick models of the local environment around Mg_n-O complexes: (a) Mg-O, (b) Mg_2-O, (c) Mg_3-O, and (d) Mg_4-O. Bond lengths of Mg-O and Al-O are given in parentheses. Unit: Å.

Now we calculate the activation energy of the Mg_n-O ($n=2$, 3, and 4, respectively) complexes, which can be made abundant by appropriate ratio between Mg and O. The method proposed by Van de Walle and Neugebauer is applied for the activation calculation:[25]

$$E_A = E_{tot}[D^-] - E_{tot}[D^0] - E_v - \Delta V[D] + E_{corr}, \qquad (2)$$

where E_A is the activation energy of the defect (donor) D. $E_{tot}[D^-]$ and $E_{tot}[D^0]$ are the total energies of the supercell with defect in charged (−) and neutral (0) states, respectively. E_v is the valence band maximum of the bulk semiconductor; $\Delta V[D]$ is a correction term to align the reference potential in the charged defected supercell with that of the bulk and it is derived from the electrostatic potential difference between the bulk and that of the defected supercell far away from defect site. Using a $5\times5\times3$ supercell, a value of

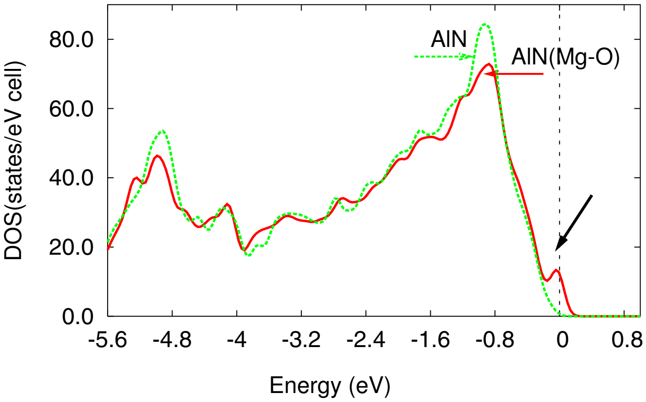

FIG. 2. (Color online) Total DOS of supercells with pure AlN (curve marked by AlN) and AlN containing one passive Mg-O complex [curve marked by AlN(Mg-O)]. The bold arrow indicates the extra states on top of the VBM of pure AlN. The Fermi level of pure AlN is indicated by the vertical dashed line.

-0.15 eV is calculated for both $\Delta V[\text{Mg}]$ and $\Delta V[\text{Mg}_2\text{-O}]$. Calculation obtained using a larger $6\times6\times4$ supercell does not result in any significant change in these values. E_{corr} is a correction term for the use of Γ-included k-mesh sampling for the hexagonal lattice. In practice, this is derived from the energy difference between the highest occupied level at Γ point and other special k points (averaged) in the supercell containing the neutral defect D. The calculated E_{corr} is 0.26 eV for a supercell containing only Mg defect, and 0.03 eV for the supercell containing Mg_2-O complex. The calculated ionization of a single Mg acceptor in AlN is 0.40 eV, which is in agreement with previous DFT-LDA calculation [$\sim$0.45 eV (Ref. 26)] and experiments [$\sim$0.5 eV (Refs. 7 and 8)]. For the Mg_2-O complex, the calculated E_A is only 0.17 eV. Similar calculations are performed for Mg_2-O and Mg_3-O complexes, and the obtained results are summarized in Table I. The activation energies of Mg_3-O and Mg_4-O are lower than that of Mg and also of Mg_2-O, suggesting better doping efficiency than pure Mg. We can see that at least a decrease of 0.23 eV in activation energy can be obtained in this codoping approach compared to single Mg in AlN. If we apply this decrease to the experimental value, then following $\exp(-E_A/k_BT)$, the hole concentration can be increased by at least a factor of 10^3. This is a significant improvement, although the total carrier concentration is still below the value desired. Other complexes Mg_3-O and Mg_4-O have slightly lower activation energies to that of Mg_2-O. Thus, incorporation of some amount of oxygen into Mg-doped AlN can improve the hole concentration.

The decreased activation energy in the Mg acceptors after attaching to O-Mg complex can be understood from the density of states of the defected supercell as shown in Fig. 2. Although O-Mg complex is passive and cannot accept the host valence electrons, it induces extra fully occupied states right on the valence-band maximum (VBM) as indicated by the DOS curve of AlN supercell containing Mg-O complex. In the Mg-O complex, some electrons have higher energy than that of the host valence electrons. Thus, Mg atoms binding to this complex may be activated by electrons from these *complex states* rather than from the host states. So the activation energy is decreased.

For such a codoping, the enthalpy effect should be taken into consideration for experimental study as MgO may appear as a competitive precipitate. In this study, we evaluate the feasibility of overcoming MgO precipitate by comparing the enthalpy effect to an established case. The formation energy of a defect is given by

$$E^f[D(q)] = E^{tot}[D(q)] - E^{tot}[bulk] - \Sigma_i n_i \mu_i + q(E_f + E_v), \tag{3}$$

where the $E^{tot}_{defect}(q)$ is the total energy of the supercell containing the defect, $E^{tot}(bulk)$ is the total energy of a similar supercell containing the pure crystal, and n_i is the number of atoms that is involved in the formation of the defect, with μ_i being the corresponding chemical potentials. E_f is the Fermi energy which is set to zero at the valence-band maximum E_v. A low formation energy suggests a high concentration of the defect without competing precipitates under thermal equilibrium. In our system, the chemical potentials depend on the experimental growth conditions, which can be either Al-rich or N-rich. Formation of AlN crystal under thermal equilibrium requires $\mu_{\text{Al}}+\mu_{\text{N}}=\mu_{\text{Al}}[bulk]+\frac{1}{2}\mu_{\text{N}}[\text{N}_2]+\Delta H[\text{AlN}]$, where $\Delta H(\text{AlN})$ is the formation enthalpy of AlN. In the N-rich condition, which is preferred for incorporating Mg at Al sites, the upper limit of μ_{N} is given by $\mu_{\text{N}}[\text{N}_2]$, i.e., the energy of N in a N_2 molecular. $\Delta H[\text{AlN}]$ is calculated to be -3.58 eV. The formation energy of Mg on Al site at neutral state is $E^f[\text{Mg}_{\text{Al}}(0)]=1.76$ eV, with the solubility limit imposed by $3\mu_{\text{Mg}}+2\mu_{\text{N}}=3\mu_{\text{Mg}}[bulk]+2\mu_{\text{N}}[\text{N}_2]+\Delta H(\text{Mg}_3\text{N}_2)$. However, if O_2 is present in N_2 flux, to avoid the formation of MgO precipitate, the upper limit of μ_{Mg} is as follows:

$$\mu_{\text{Mg}} + \mu_{\text{O}} = \mu_{\text{Mg}}[bulk] + \mu_{\text{O}}[\text{O}_2] + \Delta H(\text{MgO}),$$

where $\Delta H(\text{MgO})=-6.69$ eV from our calculation for rocksalt MgO. Under this constraint, the formation energies of Mg_n-O complexes become rather high. The formation energy of Mg_2-O complex is calculated to be 4.81 eV, suggesting an ignorable concentration of Mg_2-O complex in AlN in a growth process under thermodynamic equilibrium. However, this solubility limit can be overcome by proper growth conditions, i.e., low growth temperature and high growth rate.[27] For example, in the case of Mg:O codoping of GaN by gas-source epitaxy method, the inclusion of oxygen did not result in the MgO precipitate in GaN, but it improved the hole concentration significantly.[17,28] By calculation, the formation energy of Mg_2-O complex in GaN is 6.31 eV, significantly higher than that of AlN (4.81 eV). Thus, in AlN, the solubility limit problem is less severe and can be overcome in comparison to that of Mg:O codoping of GaN. This suggests the possibility of Mg:O codoping in AlN without MgO precipitate.

While in our study on the formation of Mg_n-O complexes the activation energies of these complexes and the possibility of overcoming the MgO precipitate suggest the improvement of hole concentration in AlN, there are still other important issues remaining unaddressed. The optimum ratio between Mg and O is very important, but is very difficult to predict theoretically and can only be determined experimentally. In view of the extremely low $\sim10^{10}$ cm^{-3} hole concentration in

AlN reported up to date, our proposal of Mg:O codoping of AlN might be a way to improve the hole concentration and require further experimental study.

To summarize, we have studied the electronic properties of Mg acceptors in AlN at the presence of oxygen by *ab initio* study. Our calculations suggest the formation of Mg_n-O complexes and their lower activation energies compared to Mg. Compared to the well-established case of GaN, the MgO precipitate problem can be overcome. Our results suggest that the hole concentration in AlN:Mg can be greatly enhanced by oxygen codoping.

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