Layer structures under in-plane compressive strains in $Al_xGa_{1-x}N$/AlN interfaces

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The properties of layer structures in $Al_xGa_{1-x}N$/AlN interfaces were studied by employing first-principles total-energy calculations with density-functional theory. A structural transformation of $Al_xGa_{1-x}N$ overlayers from normal wurtzite structure to zinc blende structure was found when the compressive in-plane strain was between two critical values.

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III nitrides and their related compounds have attracted extensive interests as potential semiconductor materials, especially as building materials for short wavelength optical devices[1,2] and high power electronic devices.[3] In particular, nitride ternaries, such as $Al_xGa_{1-x}N$/AlN alloy systems, which cover a wide ultraviolet spectral range, were used to form strained heterostructures with other appropriate nitrides to construct light emitting diodes,[4,5] laser diodes, and field-effect transistors.[6–8] This has spawned interest in the interactions between adjacent layers where a distribution of strain is involved.

To grow high quality nitrides, one of the main problems is the lack of a thermally and structurally matched substrate. The widely used substrate (0001) sapphire still has a lattice mismatch as large as 16% for GaN and 13.3% for AlN.[9] In order to improve the crystallinity and surface morphology of the nitride main layers, an AlN buffer layer was introduced.[10,11] The process of nitridation and relaxation, which result in cracks, dislocations or defects in buffer layer, will reduce the mismatch strain to some degree. The AlN buffer layer is still, however, under a lot of compressive residual strain.[12] This strain may possibly affect the structure of the overlayers. Recently, a phase transition from wurtzite (WZ) to zinc blende (ZB) GaN was observed in some selective grain boundary areas, where high stress may be regionally concentrated.[13] Another experiment demonstrated nanopipes with dodecagonal pyramidal indentation in the $Al_{0.22}Ga_{0.78}N$/GaN heterostructure, suggesting possible WZ to ZB structural transformation in the interfaces.[14] In this work, $Al_xGa_{1-x}N$/AlN systems was studied using *ab initio* simulation method. We will try to elucidate the influence of strain on the structural formation of $Al_xGa_{1-x}N$ overlayers.

Total energy calculations and geometry optimizations were performed by employing density-functional theory,[15] using the local-density approximation and first-principles norm-conserving nonlocal pseudopotential approach. The Ceperly-Alder formula was adopted to form the exchange and correlation potential.[16] A mixed basis set consisting of plane waves and Bloch sum of local orbitals was used to solve the Kohn-Sham equations. The plane-wave cutoff energy was set to 14 Ry, and the local orbits were constructed from the nitrogen *s* and *p* state pseudo-wave-functions. The program converged after 25 iterations or more. Two systems were calculated in this work. First, the one $Al_xGa_{1-x}N$ layer system was configured with one layer of Al/Ga atoms put on WZ AlN base. After its structural stability was determined, the three $Al_xGa_{1-x}N$ layer system with two additional layers added on was simulated. Both systems were considered under compressive strains.

We first describe our model of the one $Al_xGa_{1-x}N$ layer system and their crystallographic aspects. The equilibrium value a_0 of lattice constant was calculated previously as 0.306 nm ($c/a=1.600$) for bulk AlN unit.[17] The repeated slab was configured as a supercell for $Al_xGa_{1-x}N$/AlN consisting of nine atomic layers and a 14-Bohr-wide vacuum region. This choice of layer number was confirmed to be sufficient to recover the proper bulk conditions, and with the width of vacuum region the influence between surfaces could be neglected. Eight AlN atomic layers in WZ structure are considered as a base, and one layer of Al and Ga atoms mixture resides on the top, whose structure we want to focus on. Generally speaking, there are two possible structures for III nitrides, the WZ structure, which is stable, and the ZB structure, which is metastable. Both structures will be considered in this study. The WZ structured Al/Ga atomic layer [atoms reside on normal hexagonal-close-packed (hcp) structure sites] is shown in Fig. 1(a), and the ZB structured Al/Ga

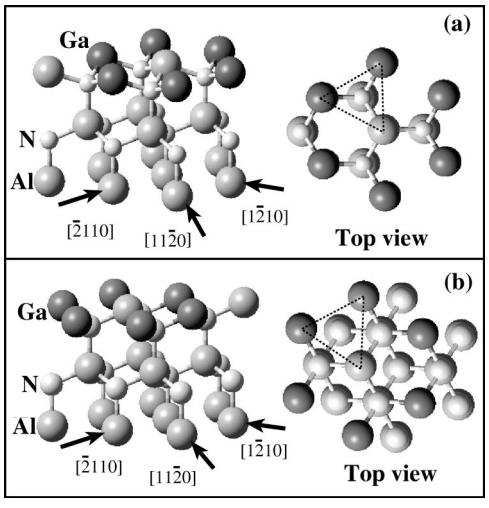

FIG. 1. One $Al_xGa_{1-x}N$ layer systems with one layer of Al/Ga atoms on WZ AlN base. Two different structures are considered under compressive strains in $\langle 11\bar{2}0\rangle$ directions. (a) Normal WZ structure with top layer atoms at hcp structure sites. (b) Translated structure with top layer atoms at the fcc structure sites.

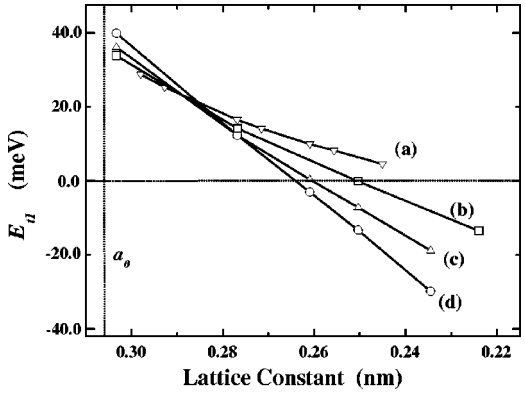

FIG. 2. The average translation energy E_{t1} as a function of lattice constant a for the one $Al_xGa_{1-x}N$ layer systems. (a) $x=0.00$, (b) $x=0.25$, (c) $x=0.50$, and (d) $x=0.75$. a_0 is the equilibrium lattice constant of bulk AlN.

atomic layer [atoms reside on face-centered-cubic (fcc) structure sites] is shown in Fig. 1(b). In order to observe the influence of in-plane compressive strain on the structural formation of the Al/Ga atomic layer, the lattice constant a is varied from the equilibrium value a_0 down to about 20% smaller while the lattice constant c remains unchanged. For the convenience of analyzing the structural stability of these two structures, we will define an average translation energy E_t per top layer atom as

$$E_t=(E_a-E_b)/n, \tag{1}$$

where E_a is the total energy of the system when the top layer atoms are at the normal hcp structure sites (WZ structure) as shown in Fig. 1(a), E_b is the total energy when the top layer atoms are at the fcc structure sites (ZB structure) as shown in Fig. 1(b), and n here is the number of atoms in the top layer. Positive E_t means WZ structure is preferable, while negative E_t means ZB structure is preferable.

The one $Al_xGa_{1-x}N$ layer system has been examined with different Al mole fraction x of 0.00, 0.25, 0.50, and 0.75. Figure 2 shows the translation energy E_{t1} as a function of lattice constant a. In curve (a) where $x=0.00$ (i.e., a pure Ga layer), although E_{t1} decreases with the decreasing of a, it still remains positive with strain less than 20%. This indicates that the WZ structure is still energetically more stable. In curve (b), Al percentage is 25%, the turning point of E_{t1} can be found at a_1 about 0.250 nm, i.e., under a compressive strain of 18.3%. Thus, E_{t1} would dive into the negative region if the strains keep increasing continuously, but this is still not an easily realizable situation. More acceptable results are observed in curves (c) and (d) with x of 0.50 and 0.75, respectively. The translation will occur above the critical value a_1 of 0.261 and 0.264 nm, corresponding, respectively, to the 15 and 13% in-plane compressive strain. It could be seen from all these four curves that the higher the Al mole fraction is, with the induced strain ascending, the steeper the decreasing slope of E_{t1} goes. As is already known, compared to Ga-N bond, the Al-N bond has a stronger interaction, i.e., has a larger formation energy.[18] This helped us to understand above results with a reasonable explanation: The translation will lower the formation energy of the Al-N bonds more than that of the Ga-N bonds under compressive strains.

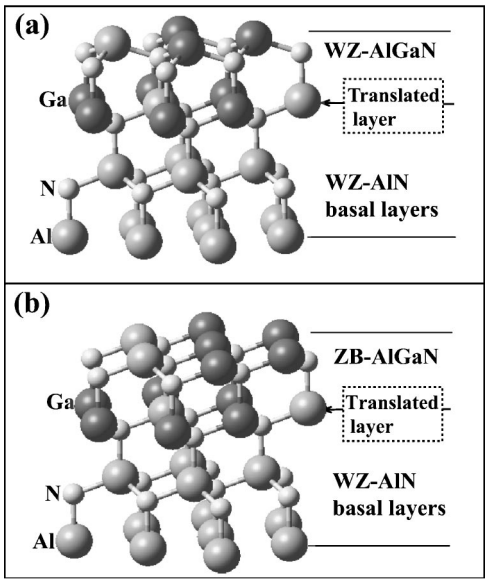

FIG. 3. Three $Al_xGa_{1-x}N$ layer systems with two additional layers on the translated first $Al_xGa_{1-x}N$ atomic layer. (a) $Al_xGa_{1-x}N$ in WZ structure, (b) $Al_xGa_{1-x}N$ in ZB structure.

In order to determine whether the translated ZB structure of the Al/Ga atomic layer will continue when additional atomic layers are added, simulations of the three $Al_xGa_{1-x}N$ layer systems were carried out with the same calculation method. We have compared the formation energies of the three layer system with or without translation of the first Al/Ga atomic layer. The simulation results always showed a lower formation energy for systems with a translated atomic layer, whether the structures of the additional layers were transformed or not. This indicates that the three $Al_xGa_{1-x}N$ layer systems with a translated first overlayer are more stable. We will now concentrate on the structure of the third $Al_xGa_{1-x}N$ atomic layer in such systems. The slab models encompass 11 layers and a 14 Bohr vacuum region. The schematic models are illustrated in Fig. 3. Both WZ and ZB structures of the $Al_xGa_{1-x}N$ overlayers are configured for comparison.

Results of the average translation energy E_{t2} of the third atomic overlayer as a function of lattice constant a are illustrated in Fig. 4. In contrast to E_{t1}, E_{t2} increases with a decreasing. E_{t2} becomes positive when a becomes larger than a critical value a_2, which is different from a_1. In order to make it easier for analysis, lattice constant is divided into two regions marked as I and II in Fig. 4. In region I, which is between the critical lattice values a_1 and a_2, E_{t1} and E_{t2} are both negative. This indicates that the atoms in the third $Al_xGa_{1-x}N$ layer are inclined to translate and form a stable ZB phase. Thus, the heterostructure will become a combination of ZB $Al_xGa_{1-x}N$ and WZ AlN. In region II, however, E_{t2} for both (a) and (b) goes positive while E_{t1} remaining negative, which means that the WZ to ZB transformation is not following up to the third layer. In this situation, the

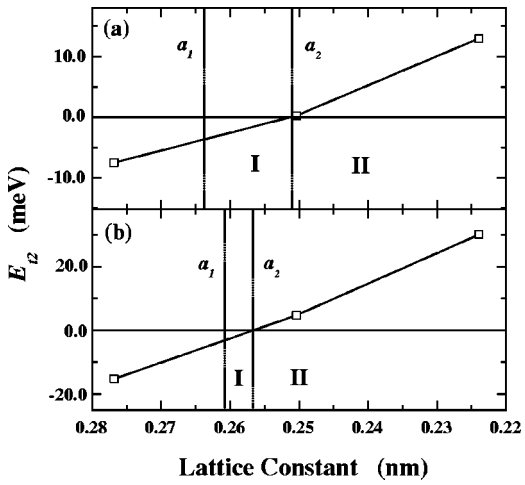

FIG. 4. The average translation energy E_{t2} as a function of lattice constant a for the three $Al_xGa_{1-x}N$ layer systems, where a_1 and a_2 are the critical lattice constants for the one and three $Al_xGa_{1-x}N$ layer systems, respectively. (a) $x=0.50$ and (b) $x=0.75$.

$Al_xGa_{1-x}N$/AlN heterostructure would appear as two WZ structures sticking together with a structural translation in the interface layer.

Therefore the growth of $Al_xGa_{1-x}N$ in either ZB or WZ structure initiating from a translated interface layer will minimize the energy within an appropriate strain range. We know that different structures may lead to different photoelectric properties. It has been reported that the bandgap of $Al_xGa_{1-x}N$ alloy is related to its composition and strain.[19] Furthermore, WZ $Al_xGa_{1-x}N$ has a direct band, while ZB $Al_xGa_{1-x}N$ may have a indirect band, which depends on the AlN fraction. Understanding these effects is meaningful for configuration of material properties. For instance, narrowing bandgap will diminish the band offset between AlGaN and other III nitrides. So by engineering alloy composition and induced strain, the electronic structure and photoelectric characteristics of $Al_xGa_{1-x}N$ heterostructure can be effectively managed.

In summary, we have examined the structures of the interface layers of $Al_xGa_{1-x}N$/AlN systems by employing *ab initio* method with density-functional theory. The translation of the first $Al_xGa_{1-x}N$ layer atoms from normal hcp structure sites to the fcc structure sites is preferred under the appropriate compressive in-plane strain. This structural translation is also likely to spread into the upper overlayers and form ZB $Al_xGa_{1-x}N$ if the induced strain is between two critical values. When the strain is larger than the critical value for the third $Al_xGa_{1-x}N$ layer, formation of WZ $Al_xGa_{1-x}N$ on WZ AlN base with a structural translation in the interface layer is found. This transformation in AlGaN alloy may provide a realizable engineering of material structure and photoelectric properties for either epilayers or heterostructures.

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[1] S. Nakamura, T. Mukai, and M. Senoh, Appl. Phys. Lett. **64**, 1687 (1994).
[2] S. Nakamura, M. Senoh, S. Nagahama, N.I. Wasa, T. Yamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, T. Kozaki, H. Umemoto, M. Sano, and K. Chocho, Jpn. J. Appl. Phys., Part 2 **36**, 1568 (1997).
[3] O. Aktas, W. Kim, Z. Fan, A. Bothkatev, A. Salvador, S.N. Mohammad, B. Sverdlov, and H. Morkoc, Electron. Lett. **31**, 1389 (1995).
[4] T. Nishida, H. Saito, and N. Kobayashi, Appl. Phys. Lett. **78**, 3927 (2001).
[5] A. Kinoshita, H. Hirayama, M. Ainoya, Y. Aoyagi, and A. Hirata, Appl. Phys. Lett. **77**, 175 (2000).
[6] O. Aktas, Z.F. Fan, S.N. Mohammad, A.E. Botchkarev, and H. Morkoc, Appl. Phys. Lett. **69**, 3872 (1996).
[7] N. Maeda, T. Saitoh, K. Tsubaki, T. Nishida, and N. Kobayashi, Jpn. J. Appl. Phys. **38**, L987 (1999).
[8] I. Daumiller, C. Kirchner, M. Kamp, K.J. Ebeling, and E. Kohn, IEEE Electron Device Lett. **20**, 448 (1999).
[9] Daudin and F. Widmann, J. Cryst. Growth **182**, 1 (1997).
[10] S. Yoshida, S. Misawa, and S. Gonda, Appl. Phys. Lett. **42**, 427 (1983).
[11] H. Amano, N. Sawaki, I. Akasaki, and Y. Toyoda, Appl. Phys. Lett. **48**, 353 (1986).
[12] T. Kehagias, P. Komninou, G. Nouet, P. Ruterana, and T. Karakostas, Phys. Rev. B **64**, 195329 (2001).
[13] L. Cheng, G. Zhang D. Yu, and Z. Zhang, Appl. Phys. Lett. **70**, 1408 (1997).
[14] J. Kang, S. Tsunekawa, B. Shen, Z. Mai, C. Wang, T. Tsuru, and A. Kasuya, J. Cryst. Growth **299**, 958 (2001).
[15] P. Hohenberg and W. Khon, Phys. Rev. **136**, B864 (1964); W. Khon and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
[16] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[17] D. Cai, J. Kang, and Z. Zhu, in *Proceedings of the 2001 IEEE 6th International Conference on Solid-state and Integrated-circuit Technology*, edited by B. Li and G. Ru (IEEE, Shanghai, 2001), p. 2445.
[18] C.I. Wu and A. Kahn, J. Vac. Sci. Technol. B **16**, 2218 (1998).
[19] G. Steude, D.M. Hofmann, B.K. Meyer, H. Amano, and I. Akasaki, Phys. Status Solidi B **205**, R7 (1998).