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Study on Initial Growth Mechanism of $(ZnO)_{1-x}(InN)_x$ Using First Principles Calculations

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Abstract

We investigated theoretically the initial growth mechanism of $(ZnO)_{1-x}(InN)_x$ (=ZION) using first principles calculations. It was found that the most probable first-step in the growth is that an In atom adsorbs on an O-polar ZnO(0001) substrate. We also revealed the origin of a pseudo binary growth mechanism of ZION by comparing the self-surfactant energies of several adsorption patterns.

1. Introduction

Recently a novel category of $(II–VI)_{1-x}(III–V)_x$ semiconductor alloys has been fabricated and attracted much attention. Itagaki *et al.* synthesized $(ZnO)_{1-x}(InN)_x$ (=ZION) as a pseudo binary random alloy consist of ZnO (E_g = 3.3 eV) and InN (E_g = 0.7 eV) in the wurzite structure [1]. The band gap energy, E_g, of ZION is expected to be widely modified by changing the x value, then it has many potential applications, such as excitonic light-emitting devices, solar cells, and so on. In the previous study, we calculated the electronic structure of ZION using the Interacting Quasi-Band theory based on the tight-binding calculations [2] and elucidated the overall concentration dependence of E_g.

It has been reported that ZION, which is originally a quaternary system $(Zn_{1-x}In_x)(O_{1-y}N_y)$, grows as a pseudobinary system (x=y). ZION is synthesized by coherent growth using RF-magnetron sputtering on ZnO substrate [3]. In order to grow a high-quality thin film of ZION and establish the associated film formation technology, it is important to understand the growth process, in particular the initial growth mechanism. For this purpose, this study focused the absorption energies of In or N atoms on ZnO substrate and the self-surfactant energies using first principles calculations.

2. Theory and calculation model

Figure 1 shows the calculation model for evaluating the adsorption energies. We adopt a 8-layered 2×2 and 3×3 ZnO(0001) slab as a substrate. Generally, the surface of the ZnO(0001) exhibits either an O-polar (000-1) or Zn-polar (0001) character. Depending on its polarities, the back-surface is terminated with pseudo hydrogens with +0.5e or +1.5e. According to Ref. [4], the ZnO (0001) surface retains the 1×1 structure without reconstruction. There are three high symmetry sites (T4, H3, Top) for both O and Zn polarity surfaces. To investigate the initial growth mechanism of ZION we consider a simple situation: one of two elements (In or N) adsorbs

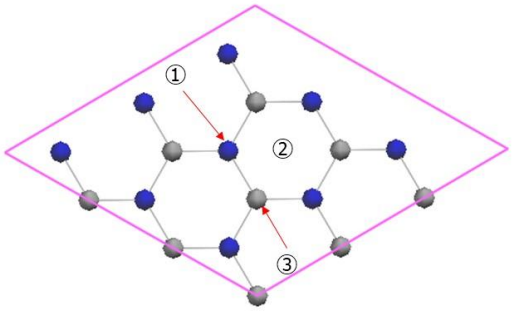

Fig. 1 Top view of the surface structure of ZnO(0001) (blue: O atom, gray: Zn atom). Highly symmetrical sites, T4, H3, and Top sites are indicated as 1 to 3, respectively.

on one of three sites. Then, there are 12 combinations of adatoms and surface sites in all (Figure 2). The total energy was calculated for all the combinations, and the adsorption energy E_{ad} was calculated by the following equation.

$$E_{ad} = E_{tot} - E_{substrate} - E_{N(In)}. \quad (1)$$

E_{tot} is the total energy of the surface with adatoms, $E_{substrate}$ is the total energy of the surface without adatoms, E_N is the total energy of a N_2 molecule per N atom, and E_{In} is that of bulk-In per In atom. By this definition, the negative value of E_{ad} indicates that such adsorption will be realized. The larger $|E_{ad}|$ means more preferable for adsorption. On the other hand, positive E_{ad} indicates that such adsorption is difficult to be realized thermodynamically.

To evaluate theoretically the total energies and adsorption energies, we used the PHASE code [5], which is a program

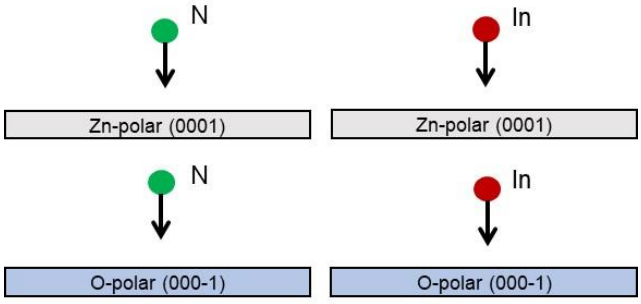

Fig. 2 Schematic side view image of the combinations of adatoms and the surface (green: N atom, red: In atom). There are three sites with high symmetry per combination on each surface (see Fig. 1).

package for performing first-principles calculations based on the density functional theory (DFT) and the ultra-soft pseudo-potential scheme. The generalized gradient approximation was used as the exchange-correlation term [6]. The cutoff energies for the wave function and charge density were 30 and 120 Ry, respectively.

3. Results and discussions

Table 1 shows calculated values of E_{ad} for 12 possible combinations. When an In atom is adsorbed to three possible sites of O-polar surface (000-1), all of E_{ad} are found to be negative, while an N atom is adsorbed, all are positive. These results indicate that the mixing of InN into ZnO starts from the adsorption of In atoms on the O-polar surface (000-1). The most stable adsorption site is found to be H3 with E_{ad} =−2.67 eV, although it leads a stacking fault lattice mismatch. To realize the wurtzite structure the suitable site for an In adatom is the Top site, where E_{ad} is slightly 0.58 eV higher than H3.

Table1. Calculated adsorption energies E_{ad} (in eV). Negative value favors the adsorption.

Surface + adatom	T4	H3	Top
Zn-polar (0001) + In atom	−0.12	−0.13	0.33
Zn-polar (0001)+ N atom	1.09	0.73	3.50
O-polar (000-1) + In atom	−2.29	−2.67	−2.09
O-polar (000-1) + N atom	0.60	0.39	1.30

On the crystal growth of pure ZnO, it is theoretically reported that O atoms adsorbed on the H3 site at first and then, move to the top site by the self-surfactant effect of Zn atoms adsorbed near the O atom [7]. A similar mechanism could be expected in the growth of ZION. We next calculated the self-surfactant energy for several adsorption patterns. Figure 3 shows a typical situation: an In atom and next layer atoms are adsorbed on the ZnO(0001) surfaces. Table 2 shows the energy difference between the H3 site and the Top site due to the self-surfactant effect. The self-surfactant energy ΔE was calculated by the following equation.

$$\Delta E = E_{\mathrm{Top}} - E_{\mathrm{H3}}. \quad (2)$$

Here, E_{Top} is the total energy with an In atom at the Top site and self-surfactant atoms at the adjacent T4 sites. E_{H3} is the total energy with an In atom at the H3 site and self-surfactant atoms at T4 sites.

Table2. Calculated self-surfactant effect energy ΔE.

	Surface patterns	ΔE [eV]
(a)	In atom + O atom + O atom	−0.85
(b)	In atom + N atom + N atom	0.72
(c)	In atom + O atom + N atom	−3.35

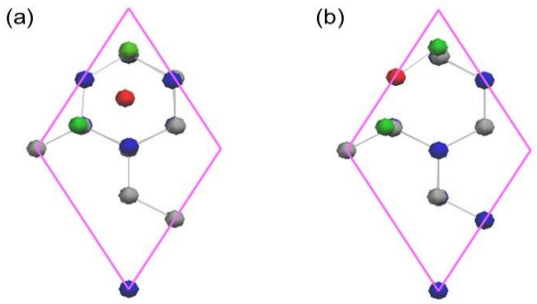

Fig. 3 Schematic top view image of the self-surfactant effect (green: N atom or O atom, red: In atom). (a) is the In atom at H3 site. (b) is the In atom at Top site.

We calculate three patterns in which (a) two O atoms, (b) two N atoms, (c) one O and one N atom, are adjacent to the adsorbed In atom. We found that patterns of (a) In-O-O and (b) In-O-N exhibit the self-surfactant effect. (The Top site of the In atom is more stable than the H3 site.) On the other hand, (c) In-N-N pattern does not exhibit the self-surfactant effect. It is found that two N atoms are likely to form a N_2 molecule. Comparing self-surfactant energies, we find that the pseudo-binary In-O-N has strong self-surfactant effect. These results indicate that the growth of ZION as a pseudo-binary system is related to the self-surfactant effect.

4. Conclusions

On the basis of first-principles calculations based on the density functional theory (DFT), we have investigated the initial growth mechanism of ZION. We have found that the first-step of the growth is that In atoms are adsorbed on the O-polar surface of ZnO substrate. It is also shown that the pseudo binary system of ZION is promoted by the self-surfactant effect of the next layer atoms.

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