DFT Investigation on the Adsorption of KCl on the Surface of ZnO

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Abstract. The growth of ZnO crystal has been an interesting problem for functional material researches. Based on experimental investigation, it is found that addition of KCl can be used to control the growth of ZnO crystal by passivating the [002] facets. However, it is difficult to observe the mechanism affecting the passivation at atomic scale experimentally, hence a computational DFT investigation is chosen as the methodology in this study. Using electronic structure calculation, we have mapped the potential energy surface of [002] ZnO using KCl adsorbant to investigate the possible dissociation path of KCl on ZnO surface. We found out that Cl atom adsorbed on the surface of ZnO and caused some surface reconstruction which could prohibit crystal growth and causing the passivation of the surface.

Key words: ZnO, KCl, adsorption, potential energy surface

1. Introduction

ZnO is a functional material that can be used for variety of purposes, such as gas sensor [1] [2], hybrid and organic solar cells [3]. ZnO thin film can be used as sensor for poisonous gases [4] [5], or as the hole blocking layer for solar cell [6]. The sensitivity of ZnO as gas sensor depends a lot on its surface area which directly interacts with gases. We can also increase its efficiency in solar cell by increasing the surface area. Hence controlling the growth of ZnO crystal is an interesting issue to be solved in order to increase its efficiency in solar cell or gas sensor [7] [8] [9].

The growth of ZnO thin films can take a lot of forms. One of them is nanorod, which usually have large surface area. These variety in forms can be controlled by using different synthesis method and the type of solvent used during synthesis process. In this study we will investigate the effect of KCl as the ionic additive to the growing phase of ZnO [10], which we hypothesized will work as passivation agent on several surfaces. The passivation agents will be adsorbed on the surfaces and reduce the adsorption of Zn2+ and O2- on the surface and hence stopping the growth.

2. Computational Details

The calculation in this paper is carried out using Quantum Espresso PWscf package [11]. We investigated the potential energy surface of ZnO [002] surface with K+ and Cl- adsorbant. Generalized Gradient Approximation with Perdew, Burke, and Ernzerhof [12] exchange correlation is used. We do not include spin factor or any starting magnetization in this study. For the wavefunction, we use plane wave basis set with kinetic energy cut off of 340.14 eV (25 Ry) and 4081.71 eV (300 Ry) for charge density and potential. Energy calculations are sampled using 2 x 2 x 1 Monkhorst-Pack grid [13]. We calculate the potential energy surface by subtracting the total energy from the energy of its constituents, as written in equation 1.
The calculated energy is then plotted over the atom coordinates to produce a contour map of potential. This contour map will be able to provide some information on K⁺ or Cl⁻ absorption on the surface of ZnO.

3. Result and discussion
ZnO has a hexagonal wurtzite structure [14]. In this case we use a surface of ZnO with 32 atoms which is comprised of 8 ZnO unit cells in 2x2x2 repetition in each direction. A visualization of the ZnO system is provided below in Fig.1.

The system was prepared with optimized cell parameter of c/a = 1.6125 (which differ by 0.64% from the experimental cell parameter c/a = 1.6024 [14]). We then scan the surface by putting a K atom or Cl atom at 2.4 Angstrom above the surface as visualized in Figure 2. By mapping the adsorption energy at that distance, we can map a potential energy surface on top of ZnO surface. We can minimize the amount of sampling point needed by utilizing the symmetry of ZnO [002] surface. The potential energy (PES) is calculated using equation 1.

\[ E_{pot} = E_{total} - E_{\text{surface}} - E_{K^+ \text{or } Cl^-} \]  

Figure 1. Top view of the ZnO[002] system used in this calculation. Gray is Zn atom while red is Oxygen atom

Figure 2. The location of adsorbate (in this case K atom) on one of the possible adsorption site
Figure 3. The potential energy surface of Cl on top of ZnO. We can see that there are two local minima (the purple area on the left picture) which could be the possible adsorption site of Cl on ZnO surface. Any Cl atoms moving close to the surface will tend to go to the minima (path drawn using red arrow).

As we can see in Figure 3, the minima of PES is in the hollow area. We expect that a Cl atom approaching the surface will move closer toward the minima. We then calculate the adsorption energy of Cl on top of ZnO. Calculation was done using the relaxation method applied in Quantum Espresso to minimize the forces between atoms. For the adsorption of Cl on ZnO surface, the adsorption energy is -8.99 eV. This amount of energy shows that Cl is adsorbed quite strongly on the surface. However, the adsorption of Cl also brings quite a significant surface reconstruction, which is visualized on Fig. 4.

Figure 4. The adsorption of Cl (green atom) on the hollow site (as predicted by PES). The adsorption is followed by some surface reconstruction.

As for the PES of K atom on top of ZnO also has similar minima with the Cl at the hollow site. However, there is a periodic potential wall on x direction as we can see on Fig. 5.
Figure 5. The PES of K on the surface of ZnO. The site for minima is similar with Cl, but with high potential wall. The potential wall is located around O atom in the area enclosed within the blue rectangle on the right. The high potential wall is due to strong repulsive interaction between K atom and oxygen on top of ZnO due to the radius of K atom. A K atom hovering near the potential will be very close to the two oxygen atoms there and be repulsed to find a path to minima. One of such paths is drawn using the red arrow on the PES in Fig.5. The adsorption of K atom on surface does not occur. We minimized forces of the interaction between K atom and ZnO surface using relaxation method similar to Cl. The adsorption energy is +1.45 eV, which does not show adsorption onto ZnO surface. The existence of K atoms actually attracts some of the oxygen atom on the surface, but does not concluded in significant surface reconstruction. The adsorption is visualized on Fig. 6.

Figure 6. The adsorption of K atom (purple) on the surface of ZnO. The adsorption changes some part of the structure by attracting the oxygen atoms on the surface toward K atom.

4. Summary
We have mapped and calculated the potential energy surface and interaction of K and Cl atom on top of ZnO [002] surface. Both atoms interact with surface with the same site for potential minima. However, Cl atom interacts quite strongly with the surface with energy of -8.99 eV (adsorption) while K is slightly repulsed with energy of +1.45 eV. The adsorption of Cl on the surface also reconstructs the surface significantly. Using this result we can develop our initial hypothesis. Initially we suspected that either K or Cl will be the surface passivation agent by adsorbing into surface and blocks further growth of ZnO. Since K tends to be repulsed, it is possible that with introduction of Zn$^{2+}$ and O$^{2-}$ precursors it will just be removed from the surface and doesn’t affect the crystal growing phase. However, with the strong adsorption of Cl on the surface of ZnO and the surface reconstruction it caused, it is possible that the surface will stop growing even with introduction of Zn$^{2+}$ and O$^{2-}$ precursors and then the surface is passivated for further growth. To understand the passivation mechanism, we will need to simulate the crystal growth phase on the surface in future works.

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