ARTICLE

DFT Study of the Effect of Temperature on ZnO Adsorbed on α-Al2O3(0001) Surface

Chun Yang∗, Yi Yu, Lai-cai Li

Key Lab of Computer Software, College of Material and Chemistry, Sichuan Normal University, Chengdu 610068, China

(Dated: Received on March 7, 2005; Accepted on May 12, 2005)

The adsorption and the growth of ZnO on α-Al2O3(0001) surface at various temperatures were theoretically calculated by using a plane wave pseudopotentials (USP) method based on density functional theory. The average adsorption energy of ZnO at 400, 600 and 800 °C is 4.16±0.08, 4.25±0.11 and 4.05±0.23 eV respectively. Temperature has a remarkable effect on the structure of the surface and the interface of ZnO/α-Al2O3(0001). It is found that the Zn-hexagonal symmetry deflexion does not appear during the adsorption growth of ZnO at 400 °C, and that the ZnO[1010] is parallel with the [1010] of the α-Al2O3(0001), which is favorable for forming ZnO film with the Zn-terminated surface. It is observed from simulation that there are two kinds of surface structures in the adsorption of ZnO at 600 °C: one is the ZnO surface that has the Zn-terminated structure, and whose [1010] parallels the [1010] of the substrate surface, and the other is the ZnO[1010] // sapphire [1120] with the O-terminated surface. The energy barrier of the phase transition between these two different surface structures is about 1.6 eV, and the latter is more stable. Therefore, the suitable temperature for the thin film growth of ZnO on sapphire is about 600 °C, and it facilitates the formation of wurtzite structure containing Zn-O-Zn-O-Zn-O double-layers as a growth unit-cell. At 600 °C, the average bond length of Zn–O is 0.190±0.01 nm, and the ELF value indicates that the bond of (substrate)–O–Zn–O has a distinct covalent character, whereas the (Zn)O–Al (substrate) shows a clear character of ionic bond. However, at a temperature of 800 °C, the dissociation of Al and O atoms on the surface of the α-Al2O3(0001) leads to a disordered surface and interface structure. Thus, the Zn-hexagonal symmetry structure of the ZnO film is not observed under this condition.

Key words: ZnO, α-Al2O3(0001) surface, Adsorption, Density functional calculations

I. INTRODUCTION

The thin film of ZnO deposited on the silicon and sapphire substrates by means of pulse laser deposition (PLD) and molecule beam epitaxy (MBE) technology is of high quality. During the process of the film fabrication through MBE, the surface adsorption, diffusion and combination of the deposited particles have an important effect on the nucleation and the properties of the initial growth of thin films, which will further influence directly the quality of the thin films. Temperature is one of the most important factors in controlling the growth of films. There have been many reports on the preparation methods and growth properties of ZnO thin films on the α-Al2O3(0001) surface by means of PLD-MBE [1-5]. Nevertheless, the exploration of the mechanism of the initial growth of ZnO on the α-Al2O3(0001) surface has been extremely inadequate until now.

In our previous study, the calculation of the adsorption of single molecule ZnO on the surface of (1×2) α-Al2O3(0001) [6-8] was made together with the studies of its geometry and electronic structure [9-11]. But in the initial stage of thin film growth, it is necessary to study the surface diffusion and adsorption of a mass of the deposited particles because temperature has a remarkable effect on this process. In this work, the features of the bonding and the adsorption of multi-ZnO molecules on the α-Al2O3(0001) surface are to be investigated in detail, and the influences of temperature upon the surface and interface structure are to be discussed as well.

II. MODELING AND METHODOLOGY

The calculation model of the α-Al2O3(0001) 1×1 surface covered by three ZnO molecules is adopted. The 3×3 side view of this model is shown in Fig.1, in which the first layer ZnO is on the surface [6,7]. The second and third layer ZnO, called newly-added ZnO molecules, drop to the surface from the vacuum, in which the distance between each other is greater than 0.3 nm. Sufficient consideration was given to the impact of short vacuum height, which is set at 2.0 nm. This model can be regarded as the heteroepitaxial growth model of ZnO with the coverage of 1.4 ML on sapphire (0001) surface.

In this work, the molecular dynamics program [12] of CASTEP software based on the density functional theory (DFT) is used, and the method of ultrasoft pseu-
FIG. 1 The adsorption and growth model of ZnO molecules. (Aimed at the coverage of 1.4 ML). Zn1O1 represents the first deposited layer of ZnO. Zn2O2 and Zn3O3 represent the second and the third newly-added layers of ZnO respectively.

dopentials (USP) proposed by Vanderbilt [13] is employed to describe the interaction between the ion core and valence electrons (O 2s2p3, Al 3s23p1, Zn 3d104s2). The calculation of electronic exchange and correlation energy is based on the general gradient approximation (GGA-PW91) proposed by Perdew et al. [14]. The minimization of the total energy is performed using a preconditioned conjugate gradients technique. The k-point in Brillouin zone is set as 5×5×1, i.e. 25 k-point. The time step for the solution of dynamic KS equation with the accuracy of 5.0 μeV/atom is configured a 1.0 fs. The calculation accuracy is the same as reference [6-9], and the cutoff energy Ecut is 340 eV. In our previous study [6-9], it has been found that the chemisorption of ZnO on α-Al2O3(0001) surface happens mainly in 0-1.2 ps. So, we focus on the initial formation stage of ZnO films in 1.2 ps at 400, 600 and 800 °C respectively in this work.

III. RESULTS AND DISCUSSION

A. Growth stage and adsorption energy

The energy change of ZnO growth on the α-Al2O3(0001) surface at different temperatures is shown in Fig.2. The average swing Eos of system energy change at temperatures of 400, 600 and 800 °C is 0.53, 0.62 and 0.75 eV respectively. This indicates that the average diffusibility of particles rises in accordance with this fact: the higher the temperature, the greater the average energy of particles. The energy change is similar at temperatures of 400 and 800 °C except for the lower system energy at 400 °C. Two energy barriers at 600 °C, E_{con1}=1.7 eV and E_{con2}=1.6 eV lie between 0.3-1.1 ps in the energy change curve. The dynamic trajectories of the adsorption of ZnO at different temperatures (Fig.3) and the system energy change curve (Fig.2) show that the surface adsorption and growth of multi-ZnO molecules can be divided into three stages: (i) Dissociation and collision process (0.0-0.30 ps). In this stage, the adsorbed molecules or the Al and O atoms of α-Al2O3(0001) surface dissociate and collide with the two layers of ZnO being deposited on the surface, and the unstable transitional state is formed. (ii) Diffusion and formation of ZnO film (0.3-0.6 ps). From the analysis of the 3×3 dynamic trajectories (Fig.3), we find that the continuous ZnO thin film is gradually formed with the diffusion and recombination of the surface and interface, and the structures of the surface and interface show distinctive differences at different temperatures. (iii) Diffusion and reconstruction process (0.6 ps). The various diffusion of atoms leads to the reconstruction of the interface structure at different temperatures. The growth trajectories of every stage at different temperatures are shown in Fig.3.

Based on the reaction equation:

\[ \text{Slab} + n\text{ZnO} \rightarrow \text{Slab}/n\text{ZnO} \]

we define the average adsorption energy of ZnO as follows:

\[ E_{ads} = \frac{1}{n}(E_{\text{slab}/n\text{ZnO}} - E_{\text{slab}} - nE_{\text{ZnO}}) \]

where \( E_{\text{slab}/n\text{ZnO}} \) is the system energy after the growth of ZnO thin film; \( E_{\text{slab}} \) is the system energy of the α-Al2O3(0001) substrate before the adsorption of ZnO; \( nE_{\text{ZnO}} \) is ZnO energy before deposition; and \( n \) is the number of ZnO molecules. The average adsorption energy at the lowest system energy at 400, 600 and 800 °C is 4.16±0.08, 4.25±0.11 and 4.05±0.23 eV/ZnO respectively. At 600 °C, the fact that ZnO has the maximal average adsorption energy is in accordance with the calculation of the adsorption of single molecule ZnO on the 1×2 slab of sapphire (0001) (4.4±0.4 eV) [6]. Therefore, 600 °C is the suitable temperature for the growth of ZnO thin films. Temperature influences the kinetic energies of atoms significantly in the procedure of the adsorption and growth. The trajectories of the adsorption and growth of ZnO differ greatly because of the different kinetic energies of atoms at different temperatures, which results in the different diffusibility, surface, interface, and rate of film formation.

![Fig. 2](attachment:image.png)
FIG. 3 The trajectories of ZnO film in three growing stages at different temperatures. The method of listing the stage-temperature-time is applied in every trajectory. For example, II600-630 refers to the trajectory in the second stage of 630 fs at 600 °C. As is shown in Fig.2, Zn$^{+}$O$^{-}$ represents the first deposited layer of ZnO. Zn$^{2+}$O$^{2-}$ and Zn$^{3+}$O$^{3-}$ represent the second and the third newly-added layer of ZnO respectively.

B. The structure of the surface and interface

Analyzing the dynamic trajectories in Fig.3, we find that at different temperatures, the adsorption of ZnO, the desorption of the α-Al$_2$O$_3$(0001) surface atoms, and the surface and interface structures have distinctly different characters, which are fully illustrated in the following.

(i) At a temperature of 800 °C, the bonded ZnO molecules desorb rapidly, and the bonds of Al and O on the α-Al$_2$O$_3$(0001) surface break down and secede from the surface, then the Al and the O atoms combine with the newly-added ZnO molecules swiftly. This process is presented in I 800-260 in Fig.3. The arrows in I 800-260 show the diffusion direction of the Al and the O atoms. But the surface atoms of the α-Al$_2$O$_3$(0001) substrate are very stable at 400 and 600 °C.

(ii) At 400 °C, with the decrease of the atomic diffusibility, a longer time is consumed in the formation of ZnO film which has Zn-hexagonal symmetry structure. There is no deflexion between the hexagonal symmetry of Zn and that of O on the α-Al$_2$O$_3$ (0001) surface, and it is obvious that ZnO [1010] is parallel with the [1010] of α-Al$_2$O$_3$ (0001) slab (Fig.4 III 400-980T). The lowest system energy facilitates the film formation whose outmost layer atoms are Zn (see Fig.3 III 400-980). At 800 °C, the dissociation happens vigorously because of the high temperature, which accelerates the diffusion of the Al and O atoms. As a result, a lot of vacancies are formed in the amorphous interface due to the strong diffusibility of the Al and the O atoms. The formation of the Zn-hexagonal symmetry structure at 800 °C is not observed (Fig.4 III 800-1120T).

(iii) At 600 °C, the lowest energy $E_{\text{low1}}$ occurs first at the time of 0.63 ps, and at the same time, the ZnO film of the O-terminated surface is formed, where the interface configures Zn-O double layers (Fig.3 II 600-630) and has an obvious Zn-hexagonal symmetry structure (Fig.4 II 600-630T). While the system energy reaches the lowest point after the time of 0.83 ps at 400 °C, the ZnO film with Zn-terminated surface tends to form Zn-hexagonal symmetry structures, as is shown in Fig.3 II
FIG. 4 The top view of Zinc-hexagonal symmetry structure at different temperatures. The method of listing the stage-temperature-time is adopted in the figure. For example, III 600-1060T refers to the planform of the trajectory in the third stage of 1060 fs at temperature 600°C. The dark thick hexagon shows the Zn-hexagonal symmetry, and the thin line of the hexagon shows the O-hexagonal symmetry on α-Al2O3 (0001) surface. The stick-ball represents ZnO, and the stick at the bottom represents Al2O3. It is shown from III 800-1120T that the interface of ZnO thin film at 800°C is in disorder, and the Zn-hexagonal symmetry (III 800-1120T) is not formed.

400-980 and Fig. 4 II 400-980T respectively. However, at 800°C, the interface is in a chaotic state (see Fig. 3 II 800-630, II 800-1120 and Fig. 4 II 800-1120T).

(iv) The diffusion of O atoms at the interface plays a very important role in the plane growth of ZnO film at 600°C. A nascent ZnO film, characterized by non-symmetry and a lot of vacancies, is formed before the first $E_{con1}$, and the terminated atoms on the surface is Zn. The system energy becomes lower after surpassing $E_{con1}$ (1.7 eV). At the time of 0.63 ps ($E_{low1}$) is formed ZnO film whose formation of Zn-hexagonal symmetry superimposes that of O on the substrate surface, which means that the ZnO [1010] parallels the substrate [1010], as seen in Fig. 4 II 600-630T.
A phase transition happens during the process of the film formation at the time of 0.63-1.07 ps at 600 °C, which corresponds to the structure of $E_{\text{con}2}$ (0.83 ps) and $E_{\text{low}2}$ (1.06 ps). The surface structure terminated by Zn atom is formed at the maximum peak (0.83 ps) with the energy barrier $E_{\text{con}2}$ (1.6 eV), and the ZnO film [1010] parallels the substrate [1120] (Fig.3 III 600-1060T). When the system energy gets across the energy barrier $E_{\text{con}2}$ (1.6 eV) and lies at $E_{\text{low}2}$, the O-terminated surface is formed (Fig.3 III 600-1060), and it has a more regular surface and interface structure. Comparing the two surface structures (Fig.4 III 600-830T and III 600-1060T), we find that there is a clear deflexion of about 30° between the hexagonal symmetry structure of Zn and that of O after the system energy across the energy barrier $E_{\text{con}2}$. The ZnO film [1010] tends to parallel the substrate [1120] (Fig.4 III 600-1060T). The result discussed above indicates a possible existence of both ZnO(0001)-Zn and ZnO(0001)-O structures. That is to say, a surface phase transition occurs in the growth of ZnO film, which confirms the experimental suggestions [2-4]. Comparing the shape and stack of ZnO in Fig.3, it is obvious that a temperature of 600 °C is helpful with the formation of (0001)-O surface structure, and that the ZnO film with the (0001)-O structure is more stable.

(vi) The atomic structure at 600 °C shows a better hexagonal stacking of AaBbAaBb, a smooth surface with the Zn-O–Zn-O–Zn-O double layers and a good formation of wurtzite ZnO film. Consequently, a temperature of 600 °C will be favorable for the layer-by-layer growth of ZnO thin film. From Fig.3 III 400-980 and III 600-1160, although there is a good Zn-hexagonal symmetry structure at 400 °C, the arrangement of the interface atoms is not as regular as that at 600 °C because there are more dislocations and more defects at 400 °C.

(vii) It can be found from Fig.3 III 400-980 and III 600-1060 that a temperature of 400 °C tends to be favorable for the atom O in ZnO to become the first layer interface atoms, and to form the (0001)-Zn surface of ZnO film. But at 600 °C where the (0001)-O surface structure is easily formed, it is favorable for the Zn atoms to become the first layer of the interface. The growth direction of ZnO film is c-axis at both temperatures. The results are in agreement with the experimental results [2-5]. We find that the former (400 °C) has more vacancies of Zn, which makes the surface structure sparse and the quality of the film worse.

C. The ELF and bonding in the interface

The interface structure of the heteroepitaxial growth of ZnO thin film is further observed. The bond formation and bond length of Zn on the surface of $\alpha$-Al$_2$O$_3$(0001) at 600 °C are listed in Fig.5. Electron localization function (ELF) is used to analyse the chemical bonding characteristics such as metallic bonding, ionic bonding, covalent bonding, and dangling bonding [15-18]. Figure 6 shows the ELF distribution value of the bonding in the surface and interface.

![Figure 5](image-url)  
**FIG. 5** The chemical bonds of the surface and interface of ZnO/$\alpha$-Al$_2$O$_3$(0001).

![Figure 6](image-url)  
**FIG. 6** The ELF for the adsorption growth of ZnO on the $\alpha$-Al$_2$O$_3$(0001) surface. (a) and (b): The ELF of the single-ZnO adsorbed on a sapphire(0001) surface (1×2) (Ref.[6]). (c): The bonding electron density of the O-Zn-O-Al bond on the surface and interface, and the chemical bond is vertical to the surface in direction of [1120], under the condition of multi-ZnO molecules chemisorbed on the sapphire(0001) surface (1×1).

The top view of the Zn-hexagonal symmetry structure in Fig.4 shows that the growth position of Zn has a 30° deflexion angle from the O-hexagonal symmetry on the substrate surface, and a strong chemical bond is formed between the Zn atom and the substrate O atoms, which is in excellent agreement with our previous results [6]. The average bond length of Zn–O in ZnO film is 0.190±0.01 nm, and it is close to the Zn-O
IV. SUMMARY

The result also accords with our former studies [6-8]. Figure 6 (a) and (b) show the ELF of the single-ZnO molecule adsorbed on the surface of (1×2) α-Al2O3(0001) [6-8], and Fig.6(c) displays the ELF of multi-ZnO molecules in this work. The chemical bond parameters (bond length, bond angle) of the multi-ZnO molecules' adsorption are similar to those of the single-ZnO one. The bond angle of Al—O—Zn is about 90°, whereas the bond length of the adsorbed multi-ZnO is slightly longer than that of the single ZnO adsorbed on the surface of (1×2), and the ELF of the substrate shows that the O—Zn—O has the clear characteristic of covalent bond, and (Zn)O—Al(substrate) has the character of ionic bond. The adsorption position of ZnO (Fig.4 II 600-830T and III 600-1060T) facilitates the formation of the tetrahedral coordination by the sp³ hybridization that comes from the Zn 4s orbital and the 2p orbitals of the surface oxygen atoms, which is favorable for forming the wurtzite structure of ZnO film. The result also accords with our former studies [6-8].

V. ACKNOWLEDGMENT

This work was supported by the Application and Basic Research of Sichuan Province (No. 02GY-006), the Key Foundation of Sichuan Province Education Bureau (2002A086) and the Project of SZD0406.