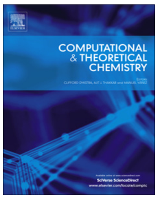
Computational and Theoretical Chemistry 1064 (2015) 51–55

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



Adsorption and dissociation of H_2O on the Ga-rich GaAs(001)-(4 × 2) surface: DFT and DFT-D computations with a $Ga_7As_8H_{11}$ cluster model

Jian-Sheng Zhang [a], Hua-Cheng Liu [a], Feng Shi [b], Feng Yu [a,*], Yang Liu [a], Chen Xiao [a], Qing Lan [a]

[a] *School of Science, Xi'an Technological University, Xi'an, Shaanxi 710021, PR China*
[b] *Science and Technology on Low-Light-Level Night Vision Laboratory, Xi'an, Shaanxi 710065, PR China*

ARTICLE INFO

Article history:
Received 7 March 2015
Received in revised form 23 April 2015
Accepted 23 April 2015
Available online 1 May 2015

Keywords:
H_2O
Ga-rich GaAs(001)-(4×2) surface
$Ga_7As_8H_{11}$ cluster
Adsorption
Density functional theory
Dispersion correction

ABSTRACT

The adsorption and dissociation processes of H_2O on the Ga-rich GaAs(001)-(4 × 2) surface have been investigated at the PBE/def2-TZVPP and PBE-D3(BJ)/def2-TZVPP levels of theory. A $Ga_7As_8H_{11}$ cluster has been employed to model the Ga-rich GaAs(001)-(4 × 2) surface. According to our computations, a chemisorbed state is formed initially. And then, the adsorbed H_2O molecule will dissociate to OH radical and H atom after overcoming the corresponding barriers on the $Ga_7As_8H_{11}$ cluster. Furthermore, the functionals of B3LYP, B3LYP-D3(BJ), and M06-2X have also been compared for evaluating the relative energies.

1. Introduction

Gallium arsenide (GaAs) is an important semiconductor material, and it has been widely utilized in modern advanced technologies. In particular, the GaAs is an excellent material for manufacture of photocathode, and therefore, it has been used in the low-light-level night vision technology and electron accelerator [1,2]. Some atoms and molecules can be easily adsorbed on the GaAs surface, and consequently, the adsorbed atoms and molecules will affect the performance of the GaAs material [3].

The interactions of H_2O with various solid surfaces have been deeply investigated [4,5]. The corresponding adsorption and decomposition mechanisms were elucidated experimentally and theoretically [4,5]. As to the interactions of H_2O with the GaAs surfaces, different mechanisms were obtained with different GaAs surfaces and experimental conditions [6–14]. The dissociation of H_2O on the GaAs surface was found due to the formation of the Ga–O bond [7,11–14]. For example, Chung and coworkers [13] studied the adsorption, desorption, and decomposition mechanisms of H_2O on the GaAs(001)-(4 × 2) surface with the temperature-programmed desorption (TPD), high-resolution electron energy loss spectroscopy (HREELS), and Auger electron spectroscopy (AES). Recently, the dissociation mechanism of H_2O on the GaAs(100) surface was further confirmed by the X-ray photoelectron spectroscopy (XPS) [14].

Cluster model plays a significant role in studying the adsorption problems involving the GaAs surface [15–32]. Cluster model is able to present the essential adsorption character with relatively low computational cost. Different sized clusters have been constructed to model the GaAs surface [15–21]. The adsorption sites and energies of atomic species on the GaAs surface were investigated with the cluster models [15–22]. The adsorption and dissociation mechanisms of molecules on the GaAs surface were also studied with the cluster models [23–32]. The H atom transfer was favorable for the AsH_3 [23], NH_3 [24], CH_3SH [25,28], H_2S [26,27,29], H_2O [29], C_3H_7SH [30], 2-C_3H_7OH [31], and CH_3OH [32] molecules on the GaAs surface.

Inspired by the experimental works [13,14], the adsorption and dissociation mechanisms of H_2O on the Ga-rich GaAs(001)-(4 × 2) surface have been reinvestigated with density functional theory. Unlike Ref. [29], a large $Ga_7As_8H_{11}$ cluster is employed to model the Ga-rich GaAs(001)-(4 × 2) surface, and density functionals with dispersion corrections [33] are utilized for computations. As a result, the adsorption and decomposition mechanisms of H_2O on the Ga-rich GaAs(001)-(4 × 2) surface are illustrated in this work.

---

* Corresponding author.
E-mail address: fengyu@xatu.edu.cn (F. Yu).

http://dx.doi.org/10.1016/j.comptc.2015.04.017

2. Computational methods

Based on the previous works [24,30], we selected the $Ga_7As_8H_{11}$ cluster to model the Ga-rich GaAs(001)-(4 × 2) surface. Lu et al. [24] compared the $Ga_4As_5H_9$ and $Ga_7As_8H_{11}$ clusters, and the performances of these two clusters were similar. However, we considered that the $Ga_7As_8H_{11}$ cluster was much better than the $Ga_4As_5H_9$ cluster. The eleven H atoms were used to saturate the dangling bonds of the primary Ga_7As_8 cluster.

All the computations in this work were performed with the ORCA program package [34]. The triple-ζ quality def2-TZVPP basis set [35,36] was utilized throughout this work. At first, the generalized gradient approximation (GGA) PBE functional [37] was employed to map the adsorption and dissociation potential energy profiles. And then, we also used the dispersion corrected PBE-D3(BJ) functional [37–39] to treat the dispersion effect, and the "BJ" stood for the Becke–Johnson damping [40–42]. The dispersion correction was important for describing the adsorption process. The integration grid used in this work was Grid4 [43,44] as defined in the ORCA program [34]. In summary, the geometries of the chemisorption state (CS), transition states (TS), and dissociative states (DS) on the potential energy surface (PES) were optimized at both the PBE/def2-TZVPP and PBE-D3(BJ)/def2-TZVPP levels of theory. And subsequently, the harmonic frequencies and zero-point energies of the obtained geometries were computed at the same level. For each transition state, the only imaginary frequency mode implied its connection properties. As comparisons, the B3LYP [45,46], B3LYP-D3(BJ) [38,39,45,46], and M06-2X [47] functionals were used to compute the single-point energies of the geometries obtained at the PBE-D3(BJ)/def2-TZVPP level. Note that the B3LYP functional mentioned above was different from the B3LYP/G functional in the ORCA program [34]. In order to reduce the computational cost, the resolution of the identity (RI [48] and RI-JK [49,50]) methods were utilized with the auxiliary basis sets of def2-TZVPP/J [51,52] and def2-TZVPP/JK [53] for the computations of the pure and hybrid density functionals, respectively. In addition, the molecular geometries were depicted with the MacMolPlt program [54].

3. Results and discussion

3.1. Adsorption and dissociation pathways of H_2O on the $Ga_7As_8H_{11}$ cluster

The interaction PES of H_2O with the $Ga_7As_8H_{11}$ cluster has been explored at the PBE/def2-TZVPP and PBE-D3(BJ)/def2-TZVPP levels of theory. The relative energies of the key points on the PES are listed in Table 1. The geometries of the key points on the PES are showed in Fig. 1, and the potential energy profile is illustrated in Fig. 2. As the H_2O molecule is adsorbed on the $Ga_7As_8H_{11}$ cluster, a Ga–O dative bond will be formed, and the OH bond will be broken. The dissociated H atom may transfer to the adjacent As and Ga atoms. Based on our computations, three major reaction pathways have been found. The detailed reaction pathways are listed as below.

Table 1
Relative energies of the key points on the interaction PES of the H_2O molecule with the $Ga_7As_8H_{11}$ cluster (in kcal/mol). Note that all the relative energies are computed with the def2-TZVPP basis set.

Species	PBE (0 K)	PBE-D3(BJ) (0 K)	PBE-D3(BJ) (298.15 K)
$H_2O + Ga_7As_8H_{11}$	0.0	0.0	0.0
CS	−9.9	−11.8	−11.7
TSa1	4.9	2.6	2.0
TSb1	8.1	5.4	4.8
TSb2	−10.1	−12.7	−13.4
TSc1	9.5	6.5	6.1
TSa2	38.0	35.7	35.3
TSa3	15.2	13.0	12.7
DSa1	−13.8	−16.2	−16.1
DSb1	−16.6	−18.7	−19.1
DSb2	−18.6	−21.0	−21.6
DSc1/DSa3	−11.1	−13.2	−13.3
DSa2	2.9	0.6	0.3

Pathway (a): A chemisorption state denoted as CS is firstly formed when the H_2O molecule is adsorbed on the $Ga_7As_8H_{11}$ cluster. Subsequently, the reactive system will overcome the transition state TSa1 to form the dissociative adsorption state DSa1. For the dissociative adsorption product DSa1, OH(2) radical is adsorbed on the Ga(1) atom, and the dissociated H(1) atom is adsorbed on the As(1) atom at the second layer. This pathway is simply referred as CS → TSa1 → DSa1.

Pathway (b): Following the chemisorption state CS, the H(2) atom decomposed from the adsorbed H_2O molecule inserts into the Ga(1)–Ga(2) bond through the transition state TSb1. As a result, the dissociative state DSb1 is formed. After passing the transition state TSb2, the reactive system isomerizes to the dissociative state DSb2. This pathway is summarized as CS → TSb1 → DSb1 → TSb2 → DSb2.

Pathway (c): This reaction pathway also starts at the chemisorption state CS. The dissociated H(2) atom transfers to the As(2) atom at the second layer via the transition state TSc1. The corresponding dissociative adsorption state is DSc1. As to the dissociative adsorption product DSc1, OH(1) radical is adsorbed on the Ga(1) atom, and the H(2) atom is adsorbed on the As(2) atom at the second layer. This pathway can be summarized as CS → TSc1 → DSc1.

As shown in Fig. 2, starting from the dissociative adsorption state DSa1, the reactive system could further overcome the transition state TSa2 to form the dissociative adsorption product DSa2. The H(2) atom transfers to the Ga(2) atom after the H(1) atom has transferred to the As(1) atom. Furthermore, the dissociative adsorption product DSa3 could be formed via the transition state TSa3. In this reaction process, the H(1) atom hops from the As(1) atom to the As(2) atom. In fact, the dissociative adsorption product DSa3 is identical to the DSc1 state. However, the relative energies of the transition states TSa2 and TSa3 are relatively high, and thus, these further reaction processes are very hard to occur. The reactive system will stay at the dissociative adsorption product DSa1.

The reaction pathways mentioned above are similar to those of the small molecules on the GaAs surface [23,24,26,27,29,32] and even GaP surface [55]. In terms of the potential barriers of the reaction pathways (as shown in Table 1 and Fig. 2), the pathway (a) has a relatively low potential barrier. Therefore, the DSa1 is the most favorable dissociative adsorption product for the interaction of the H_2O molecule with the $Ga_7As_8H_{11}$ cluster.

3.2. Relative energy and geometry changes during the adsorption and decomposition of the H_2O molecule on the $Ga_7As_8H_{11}$ cluster

In this work, both the PBE and PBE-D3(BJ) functionals were employed for studying the interaction PES of the H_2O molecule with the $Ga_7As_8H_{11}$ cluster. Generally speaking, the functional with dispersion correction is much more suitable for describing the adsorption process. In the following discussion, comparisons will be presented between the results obtained with the PBE and PBE-D3(BJ) functionals.

The chemisorption state dubbed as CS is first formed when the H_2O molecule approaches the $Ga_7As_8H_{11}$ cluster. As to the CS, the O atom of the H_2O molecule will interact with the Ga(1) atom at the first layer of the $Ga_7As_8H_{11}$ cluster to form the Ga(1)–O dative bond. This character is similar to that of the interaction between