Dissociation of H₂ molecule on the β -Ga₂O₃ (100)B surface: The critical role of oxygen vacancy

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Abstract

We systematically study the dissociation of H_2 molecules on the β -Ga₂O₃ (100)B surface, with the influences of surface oxygen vacancy being considered. After introducing the surface oxygen vacancy, the nearest topmost O(I) atom becomes very active, and hydrogen molecules become much easier to dissociate.

Keywords: hydrogen, dissociation, oxygen vacancy, first-principles calculation.

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I. INTRODUCTION

In ambient conditions, the stable form of gallium oxide is the monoclinic structure of β -Ga₂O₃ [1–3], which belongs to the group of transparent oxides with a large band gap of 4.8 eV, and exhibits both conduction and luminescence properties [4–7]. The β -Ga₂O₃ is generally an *n*-type semiconductor due to oxygen vacancies individually compensated by two electrons forming shallow donors [8–10]. However, the number of oxygen vacancies present in the material depends on the growth atmosphere, and so the electrical character of the compound can vary, in a tunable way, from insulating to conductive [11–13]. Because of its tunable optical, magnetic and electrical properties, the β -Ga₂O₃ has attracted much research interest for many technological applications [10]. For example, Ga_2O_3 is useful in the fabrication of masers [1], field-effect devices [14], switching memory devices [15–17], and transmitting ultraviolet light [18, 19]. By monitoring its electronic properties at different chemical atmosphere, the β -Ga₂O₃ can also be used as sensors to detect hydrogen gases [20– 23]. To detect hydrogen molecules, it is revealed that oxygen vacancies are needed on the Ga₂O₃ surface to explain the stretching frequencies of Ga-H bonds observed in the infrared spectroscopy experiment [24]. However, the special mechanism for oxygen vacancies to help dissociate hydrogen molecules has not been discussed yet.

In addition, the H₂-Ga₂O₃ interaction is also important to some catalytic reactions. Catalysts containing supported gallium are known to be active in light alkane dehydrogenation and aromatization [24–27]. Recently, it is highlighted that β -Ga₂O₃ alone is able to dissociate hydrogen molecules at temperatures higher than 500 K and then hydrogenate adsorbed CO₂ stepwise from formate to methoxy groups [28]. Although the oxidation state of gallium ions has been of a matter of debate in catalytic reactions [29, 30], the role of the geometric environment or surface coordinations has not been emphasized.

There are two types of coordination for Ga ions in the β -Ga₂O₃, namely tetrahedral and octahedral, and referred to as Ga(I) and Ga(II). There are also three types of oxygen ions, referred to as O(I), O(II) and O(III). Oxygen O(I) and O(II) lie respectively in and out of the symmetry plane (see Fig. 1(a)). They are both in threefold coordination while O(III) is in fourfold coordination [6, 10]. The most frequent cleavage plane for β -Ga₂O₃ is the (100) plane [23, 24, 31]. A recent theoretical study of the (100) surface presents two possible surface terminations, A and B [23, 31]. Termination A is characterized by rows of oxygen, and termination B by rows of nearest neighbor gallium and oxygen. In our study, we mainly focus on the surface relaxations for the stoichiometric and oxygen vacancy included β -Ga₂O₃ (100)B surfaces, and the dissociation properties of hydrogen molecules on them. The rest of the paper is organized as follows. In Sec. II, we describe our first-principles calculation methods; in Sec. III, we present in detail our calculated results, including the comparisons of the electronic structures of the β -Ga₂O₃ (100)B surface including oxygen vacancy or not, and the dissociation of hydrogen molecules on the surfaces; Finally, the conclusions are given in Sec. IV.

II. COMPUTATIONAL METHOD

Our calculations are performed within density functional theory (DFT) using the Vienna *ab-initio* simulation package (VASP) [32]. The PW91 [33] generalized gradient approximation and the projector-augmented wave potential [34] are employed to describe the exchange-correlation energy and the electron-ion interaction, respectively. The cutoff energy for the plane wave expansion is set to 400 eV, which is large enough to make the error from calculations of the adsorption energy below 0.01 eV. The stoichiometric and oxygen vacancy included β -Ga₂O₃ (100)B surfaces are modeled by a slab composed of 30 atomic layers and a vacuum region of 20 Å. The 1×2 supercell with the size of 5.93 Å $~\times$ 6.11 Å ~ is used to study the H_2 adsorption. Our test calculations have shown that this supercell is sufficiently large to avoid the interaction between adjacent hydrogen molecules. Integration over the Brillouin zone is done using the Monkhorst-Pack scheme [35] with $7 \times 7 \times 1$ point grids. A Fermi broadening [36] of 0.05 eV is chosen to smear the occupation of the bands around the Fermi energy (E_f) by a finite-T Fermi function and extrapolating to T = 0 K. During geometry optimizations, the bottom 10 layers of the β -Ga₂O₃ (100)B surface are fixed while other Ga and O atoms are free to relax until the forces on them are less than 0.01 eV/Å. The calculation of the potential energy surface for molecular H_2 is interpolated to 350 points with different bond length $(d_{\rm H-H})$ and molecular height $(h_{\rm H_2})$ of H₂ at each surface site. The calculated lattice constants of the β -Ga₂O₃ crystal are a=12.45 Å, b=3.05Å, and c=5.93 Å, and $\theta=103.9^{\circ}$, in good agreement with the experimental and theoretically calculated values [10, 23]. The calculated bond length of the free H_2 molecule is 0.75 Å, also in good agreement with the experimental value of 0.74 Å [37].

III. RESULTS AND DISCUSSION

First, we do geometry optimizations for the stoichiometric β -Ga₂O₃ (100) surface. There are two different types of (100) surface terminations, respectively called as the β -Ga₂O₃ (100)A and (100)B surfaces [23, 31]. The (100)A surface is formed by cleaving the Ga-O(II) bonds above the O(II) atoms while leaving the below Ga-O(II) bonds intact, and terminated in rows of O(II)'s lying along the [010] direction. The (100)B surface is formed by cleaving the Ga-O(II) bonds below the O(II) atoms, and terminated in nearest-neighbor rows of Ga(II) and O(III) atoms, each singly unsaturated. After geometry optimizations, we find that the topmost O(I) atoms move out on the β -Ga₂O₃ (100)B surface, and form O(I)-Ga(II)-O(II) rows as shown in Fig. 1(a). The calculated surface energies for the relaxed β -Ga₂O₃ (100)A and (100)B surfaces are respectively 1.19 and 0.76 J·m⁻², according well with other *ab initio* results of 1.13 and 0.68 J·m⁻² [23]. The surface energy values indicate that the β -Ga₂O₃ (100)A surface is much more stable than the β -Ga₂O₃ (100)A surface.

There are two kinds of oxygen vacancies on the relaxed β -Ga₂O₃ (100)B surface, respectively the O(I) and O(III) vacancies. After geometry optimizations, we find that the β -Ga₂O₃ (100)B surface with the O(III) vacancy is 0.56 eV lower in total energy than with the O(I) vacancy. The surface geometry of the β -Ga₂O₃ (100)B surface with an O(III) vacancy (Ov-surface) is shown in Fig. 1(c), where the possible adsorption sites near the O(III) vacancy are depicted. On the Ov-surface, the O(I) atom has a relatively large distortion. It moves 0.28 Å along the [001] direction during surface relaxation.

Besides of introducing geometric distortions, the oxygen vacancy also changes the surface electronic structures. Figure 2 shows the surface charge density of the stoichiometric β -Ga₂O₃ (100)B surface and the Ov-surface. The contour map shows the charge density distribution in the plane that is parallel to and 1.50 Å away from the β -Ga₂O₃ (100)B surface. And the values are in the unit of $e/Å^3$. It is clearly shown that the O(I) atom nearest to the O(III) vacancy has more electron distribution than on the stoichiometric β -Ga₂O₃ (100)B surface, and so does the nearest O(III) atoms. Using the Bader topological analysis [38] for the charge density, it is found that the nearest O(I) atom gets 0.28 more electrons on the Ov-surface than on the stoichiometric β -Ga₂O₃ (100)B surface, it is also found that the two nearest Ga(II) atoms and the nearest Ga(I) atom respectively get 0.61, 0.62 and 0.34 more electrons on the Ov-surface. These extra electrons are because that the vacancy of a surface O(III) atom supplies 2 more electrons to its nearby atoms. And the other 0.15 electrons is around the other surface oxygen atoms. The extra electrons around the surface Ga atoms are easy to form Ga-H bonds when hydrogen atoms are introduced.

The projected density of states (PDOS) for the nearest surface O(I) atom on the Ovsurface is shown in Fig. 3, together with the PDOS for a surface O(I) atom on the stoichiometric β -Ga₂O₃ (100)B surface. From detailed wavefunction analysis, we find that there are strong s-p hybridizations in the electronic states for Ga(I) and Ga(II) atoms on the β -Ga₂O₃ (100)B surface, but the electronic states of surface O(I) and O(III) atoms do not hybridize at all. In the PDOS of an O(I) atom on the stoichiometric β -Ga₂O₃ (100)B surface, the s states lie around 15 eV below the p states, and the p electronic states contribute the majority part of the electronic states around the Fermi energy. As shown in Fig. 3, in the PDOS of the nearest O(I) atom on the Ov-surface, there is a new peak (peak 1) below the Fermi energy, which represents for the electronic states of the 0.28 extra electrons due to the O(III) vacancy. Since electrons near the Fermi energy are easier to join in electronic hybridizations, the extra electrons around the surface O(I) atom make it more active than on the stoichiometric Ga_2O_3 surface. Moreover, it is found from wavefunction analysis that the electronic states of peak 1 tend to occupy the oxygen p_z orbital. These facts indicate that the electronic states around the O(I) atoms are very easy to interact with a parallel hydrogen molecule. As we will see later, hydrogen molecules adsorbing around the surface O(I) atom on the Ov-surface do dissociate more easily.

After analyzing the surface electronic structures, we then study the adsorption and dissociation of hydrogen molecules, both on the stoichiometric β -Ga₂O₃ (100)B surface and the Ov-surface. As shown in Fig. 1(b), there are five high symmetry sites on the relaxed β -Ga₂O₃ (100)B surface, respectively on top of the Ga(I), Ga(II) and oxygen atoms, and in the middle of two Ga(I) atoms and two oxygen atoms. In following discussions, we call them as the TG1, TG2, TO, BG and BO sites. At each surface site, there are three possible orientations for an adsorbing hydrogen molecule, respectively along the x ([001]), y ([010]) and z ([100]) directions. After employing these notations, we will use TG1-x, y, z, TG2-x, y, z, TO-x, y, z, BG-x, y, z, and BO-x, y, z to represent the considered adsorption channels for hydrogen molecules. While studying the adsorption and dissociation of hydrogen molecules on the Ov-surface, we choose TO to be the site directly on top of the O(III) vacancy, and TG1 and TG2 sites to be the sites on top of the nearest Ga(I) and Ga(II) atoms. To study the adsorption properties of H₂ molecules, we do geometry optimizations after initially putting an H₂ molecule 4.00 Å away from the stoichiometric β -Ga₂O₃ (100)B surface and the Ov-surface along all the above mentioned high symmetry channels. During the geometry optimizations, the bottom 10 layers of the β -Ga₂O₃ (100)B surface are fixed while other H, Ga and O atoms are free to relax until the forces on them are less than 0.01 eV/Å. From these relaxation calculations, we find that there are no chemisorption states for H₂ molecules on both the stoichiometric β -Ga₂O₃ (100)B surface and the Ov-surface. All the H₂ molecules will finally evolve into the physisorption states, with the adsorption energies of several tens of meV.

We calculate the two-dimensional (2D) potential energy surface (PES) cuts to evaluate the dissociation properties of hydrogen molecules. Along each adsorption channel, $h_{\rm H_2}$ ranges between 0.40 Å and 4.00 Å, and $d_{\rm H-H}$ ranges between 0.45 Å and 2.40 Å. From the calculated 2D PES cuts for H₂ on the stoichiometric β -Ga₂O₃ (100)B surface, we see no direct dissociation. As examples, the 2D PES cuts along the TG1-*x*, *y*, TG2-*x* and TO-*y* channels are listed in Figs. 4(a)-(d). As shown in Figs. 4(a)-(c), on the stoichiometric β -Ga₂O₃ (100)B surface, hydrogen molecules are very hard to get close to surface Ga atoms. The energy barrier for a hydrogen molecule in its molecular length of 0.75 Å to be 1.00 Å from the surface Ga(I) and Ga(II) atoms is over than 12 eV. However, hydrogen molecules might be easier to get close to the O atoms on the β -Ga₂O₃ (100)B surface. The energy barrier for a hydrogen molecular length to be 1.00 Å from the surface O(I) atom is 5.2 eV, as shown in Fig. 4(d). In total, hydrogen molecules can not dissociate on the stoichiometric β -Ga₂O₃ (100)B surface. Even the energy barriers for hydrogen to get closer to the surface is huge. These results indicate the inactivity of the stoichiometric β -Ga₂O₃ (100)B surface to hydrogen molecules.

Similar to what we do for the 2D PES cuts of hydrogen molecules on the stoichiometric β -Ga₂O₃ (100)B surface, we also calculate the 2D PES cuts of hydrogen molecules on the Ov-surface. To make a comparison, we list the 2D PES cuts along the TG1-*x*, *y*, TG2-*x* and TO-*y* channels in Figs. 5(a)-(d). One can see from Figs. 5(a)-(c) that the adsorption of hydrogen molecules does not change too much on top of Ga(I) and Ga(II) atoms on the Ov-surface, comparing with that on the stoichiometric β -Ga₂O₃ (100)B surface. However, the adsorption of hydrogen molecules change a lot on top of the O(I) atom. As shown in Fig. 5(d), there is a clear dissociative adsorption state for hydrogen on the Ov-surface, in which

the bond length and molecular height of H_2 are respectively 1.80 and 0.50 Å. The dissociation energy barrier for a hydrogen molecule to reach this adsorption state is 2.97 eV, which is much smaller than the approaching energy barrier on the stoichiometric β -Ga₂O₃ (100)B surface, indicating a big enhancement of the surface reactivity to hydrogen molecules. The PES results also approves our previous hypothesis that due to the extra electrons from the surface O(III) vacancy, the nearby O(I) atom are easier to interact with hydrogen molecules. We also notice that the dissociation energy barrier of hydrogen molecules is still very large. But more importantly, we point out that surface oxygen vacancies can greatly enhance the activity of the β -Ga₂O₃ (100)B surface to interact with hydrogen. Given more surface oxygen vacancies, and an environment with larger hydrogen enthalpy, hydrogen molecules can be further easier to dissociate on the β -Ga₂O₃ surface.

IV. CONCLUSION

In summary, we have systematically studied the electronic structures of the stoichiometric and oxygen vacancy included β -Ga₂O₃ (100)B surfaces, and the dissociation properties of hydrogen molecules on them. It is found that due to the oxygen vacancy, the neighboring surface Ga and O atoms get some extra electrons than on the stoichiometric Ga₂O₃ surface. The extra electrons around the surface O(I) atom are very near to the Fermi energy, and distribute on the p_z orbital, which are thus very active to hydrogen molecules. By calculating the 2D PES cuts for hydrogen molecules on the stoichiometric and oxygen vacancy included β -Ga₂O₃ (100)B surfaces, we find that hydrogen molecules are very hard to get close to the stoichiometric Ga₂O₃ surface, but much easier to dissociate on the oxygen vacancy included Ga₂O₃ surface. Our results indicate the enhancement of surface activity to hydrogen molecules by introducing surface oxygen vacancies.

Acknowledgments

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List of captions

Fig.1 (color online) The β -Ga₂O₃ (100)B surface viewed along the (a) [010] and (b) [100] directions, and (c) the β -Ga₂O₃ (100)B surface with an O(III) vacancy viewed along the [100] direction. Grey and red balls respectively represent Ga and O atoms. The black squares in (b) and (c) represent the surface unit cells in our calculations.

Fig.2 (Color online) Contour map of the charge density distribution on the (a) stoichiometric and (b) oxygen vacancy included β -Ga₂O₃ (100)B surfaces. The mapping plane is 1.5 Å from the Ga₂O₃ (100)B surface. The back squares in dashed lines represent the surface unit cells.

Fig.3 (Color online) The projected density of states for the O(I) atom on the stoichiometric and oxygen vacancy included β -Ga₂O₃ (100)B surfaces. Fermi energy is set to be the energy zero.

Fig.4 The 2D PES cuts for the adsorption of hydrogen molecules along the (a) TG1-x, (b) TG1-y, (c) TG2-x and (d) TO-y channels on the stoichiometric β -Ga₂O₃ (100)B surface. The total energy of a free H₂ molecule plus that of the β -Ga₂O₃ surface is set to be the energy zero.

Fig.5 The 2D PES cuts for the adsorption of hydrogen molecules along the (a) TG1-x, (b) TG1-y, (c) TG2-x and (d) TO-y channels on the oxygen vacancy included β -Ga₂O₃ (100)B surface. The total energy of a free H₂ molecule plus that of the oxygen vacancy included β -Ga₂O₃ surface is set to be the energy zero.



FIG. 1:



FIG. 2:



FIG. 3:

FIG. 4:

FIG. 5: