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Fundamental concepts to analyze the adsorbed hydrogen over aluminum surfaces

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ABSTRACT
Based on the first principle of density functional theory, the geometric and electronic structures of H atoms adsorbed on Al (110) surfaces with different coverings were studied in combination with the generalized gradient, approximate plane wave pseudopotential, and hyper-unit cell methods. The results show that the adsorption energy of hydrogen atoms on the surface of Al (110) increases with the decrease in coverage, and the length of the Al-H bond and the distance of hydrogen atoms from the surface of Al (110) have no obvious relationship with the change in coverage. The optimal adsorption site of the H atom on the Al (110) surface is affected by the coverage. When the coverage is 1 ML, the H atom is adsorbed at the top position, the adsorption energy is 2.703 eV, the Al-H bond length is 1.600 A, and the H atom is 1.600 A below the Al atom on the surface. When the coverage is 0.5 ML, the H atom is adsorbed in the top position, the adsorption energy is 2.486 eV, the Al-H bond length is 1.600 A, and the H atom is 1.606 A above the Al atom on the surface. The adsorption of the H atom on the surface of Al (110) is called chemisorption. The bonding occurs mainly through the interaction of H1s and Al3p orbitals, and electrons are transferred from the surface Al atom to the H atom.

Keywords: Density Functional, Aluminum Surface, Adsorption, Electronic Structure.

I. INTRODUCTION

Nowadays, with the vigorous development of surface analysis technology and new disciplines such as materials, environment, and energy, the study of gas-solid catalytic reactions has increasingly shown its great basic theoretical value and practical significance and has become a hot topic in scientific research [1]. The adsorption of hydrogen on metal is a key step in the catalytic reaction. An atom is the smallest type of atom. It has only one electron outside its nucleus. It is easily absorbed by metals, forming impurities, and is difficult to observe experimentally. Therefore, the adsorption process of hydrogen on metal is the most representative[2], an in-depth study of this model will help us study more complex systems.

Al is an important transition metal with large reserves on the earth. Due to its excellent performance and low price, it is widely used in building materials, aerospace, and other fields [3]. but it can easily react with gas molecules and atoms in the air [4], therefore, it is in H/Al. It has very important research value and significance in the adsorption system. It can study its adsorption position on the surface, adsorption energy, and surface relaxation caused by it.

Aluminum-based materials as the research object, we adopted the Al (110) crystal plane model, respectively in coverage of 0.5 ML and 1 ML in the case of hydrogen molecules adsorbed on the top, short bridge, and long bridge. Hollow in four positions [5]. Through systematic research on the adsorption characteristics of hydrogen in aluminum-based materials at different levels, the adsorption energy and adsorption sites of hydrogen in aluminum-based materials at different levels are obtained, and the adsorption characteristics at different levels are compared.

CalculationModels and Methods

Computational model

The calculation model uses P(1x1), and P(2x1) of 7layer Al atoms to simulate AL (110) surface, the corresponding coverage rates are respectively1ML,0.5ML. Now with Al1, Al2, Al3, Al4, Al5, Al6, Al7Name the Al atoms in each layer. built an H Cubic model of the structure, three-dimensional edges a=b=c=4.046 Å, ensuring that adjacent H There is no interaction between atoms. Al crystal parameters are taken from X-ray Diffraction data, unit cell constants a=b=c=4.050 Å, the unit cell

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belongs toFM-3M (OH-5) Space group. Figure 1-1 is the Al (110) crystal surface model. Select7indivualAllayer, among which4 individual Al layersare bound, other Al the layer is in a relaxed state, and a vacuum environment is formed on this basis. The thickness of the vacuum layer is15Å.

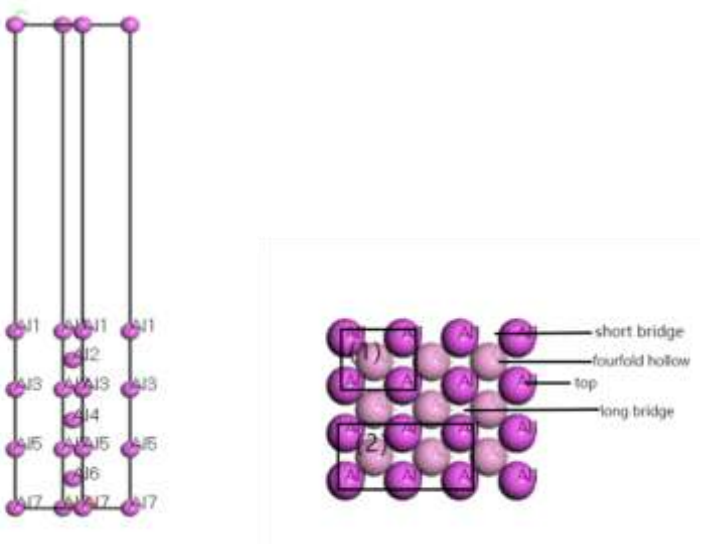
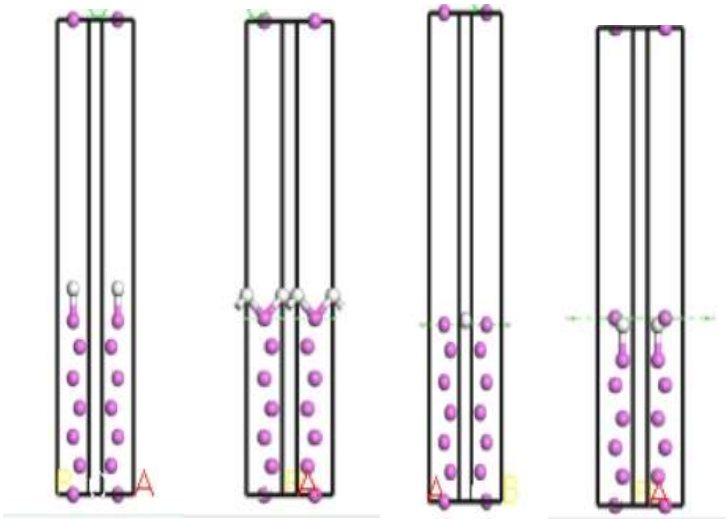


Figure 1-2Al (110) Crystal Plane Model Figure 1-2Al (110) Surface Adsorption Position

Figure 1-2 is Al (110) Main adsorption sites on the surface and super unit structural model. box (1) means P (1x1) Configuration, used to calculate with1MLHydrogen absorption at coverage, (2) is P (2x1) configuration, used to calculate0.5MLcoverage. Figure 1-3 is Al (110) P (1×1)-H The calculation model of the configuration, purple is Al Atoms, white for H atom.



(a) (b) (c) (d)

Figure 1-3 Al (110) P (1×1)-H Computational Model of Configuration, (a), (b), (c), (d) are respectively H atoms adsorbed to Al (110) Surface top, short bridge, long bridge, hollow Case

Calculation method

This study used the density functional theory CASTEP[6]program. in the generalized gradient, approximationPW91The function describes the exchange-correlation energy[7]. The interaction of electrons with atomic nuclei is described by Vanderbilt's "ultra-soft" pseudopotential field, extending it from a fundamental group to a plane wave group, with energy cutoffs adopted for convergence tests420ev. according to Monk Horst-Pack[8]law, the surface Brillouin district K Point is6×6×6. The GGA algorithm is used to optimize the

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geometric structure parameters. The energy convergence condition is 0.001 eV/atom. The convergence standards for interatomic interaction force, stress, and maximum displacement are 0.01 eV/Å, 0.01 GP a, and 0.01 Å respectively. Get its lattice Constanta, band c/arespectively8.094Å,5.7235Åand1.582.

II. RESULTS AND DISCUSSION

Adsorption position and surface adsorption energy

Adsorption energy is a physical quantity that is often studied in surface adsorption problems. The larger the adsorption energy value, the more stable the surface adsorption. In this paper, the adsorption-Alon energy is calculated by (2-1)sub-

Hequal$E_{ads} = -\frac{1}{N}(E_{H/Al} - E_{Al} - NE_H)$ (2-1)

In the formula, Nfor adsorption H The number of atoms is the total energy of the system after relaxation, the amount after relaxation on the clean surface, and the number of atoms in a single H atom th a sisub-Alngth of$E_{H/Al}$ $_{Al}E_H$ The calculated energy in a cubic vacuum grid of A.By comparing the adsorption energies to determine the H atoms in Al (110) The preferential occupation of surface adsorption, the coverage is0.5MLand1MLA series of simulation calculations were conducted on the adsorption energy of different adsorption positions at different times, and the adsorption energy after adsorption was calculated. Al-H Bond length and distance from H atoms to the Al surface.

Table 2-1Hydrogen atoms are adsorbed to the Al (110) superficial results

	1ML			0.5ML		
	E_{ads}/eV	dAl-H(Å)	dAl/H(Å)	E_{ads}/eV	dAl-H(Å)	dAl/H(Å)
Top	2.703	1.600	1.600	2.486	1.606	1.606
Short bridge	2.659	1.820	1.124	2.366	1.827	1.454
Long bridge	2.494	2.034	0.210	2.390	1.840	1.695
Hollow	2.296	2.080	1.880	2.368	1.826	1.452

It can be seen from Table 2-1 that in1MLor0.5MLIn the experimental model, H atoms have the largest adsorption energy at the top position. When the coverage is1MLWhen, the adsorption energy of H atoms adsorbed at the top position is maximum, which is0.703ev/atom, so H atoms will be preferentially adsorbed at the top position. At this time Al-H The bond length is 1.600 Å, H atoms are located above the Al surface1.600 Å. When the coverage is0.5MLWhen, after comparing the adsorption energies, the adsorption energy of H atoms adsorbed at the top position is the largest, which is2.486ev/atom, so H atoms will be preferentially adsorbed on the top position. At this time Al-H The bond length is1.606 Å, and H atoms are located above the Al surface1.606 Å.

Electronic structure

Differential charge density

Exist1MLUnder the condition of coverage, by calculating the H atoms in Al (110) [9] Differential charge density on the substrate, study the presence of H atoms in Al (110) Transport on the substrate, and then study the transport of hydrogen on the substrate

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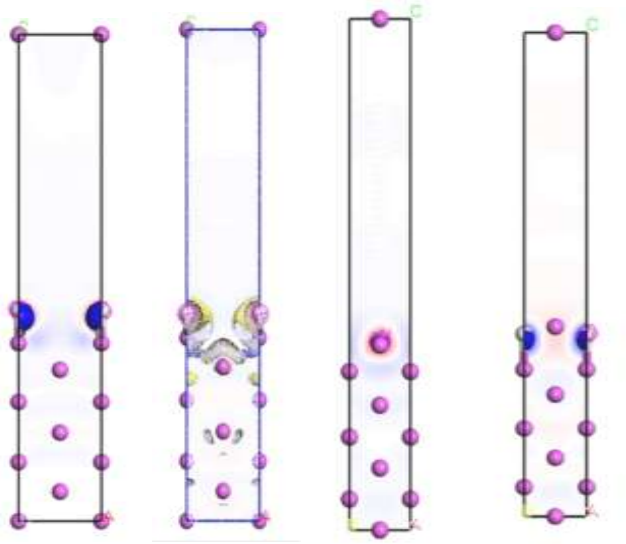

(a) (b) (c) (d)

Figure 2-1The differential charge density of the system, (a), (b), (c), (d)They are hydrogen atoms adsorbed to Al (110) Surface top, short bridge, long bridge, and hollow bit time H Atomic edge Al (110) direction section

Figure 2-1 Differential charge density along Al (110) Directional cutting. It can be seen that all electronic areas surround H atoms, and the electron-losing region mainly surrounds the outermost Al atoms. Therefore, during adsorption, hydrogen gains electrons and exhibits a negative charge, while the Al atoms in the uppermost layer exhibit a positive charge, and there is a significant bonding effect between the two.

Second to seventh floors Al Atoms do not gain or lose electrons, nor do they participate in bonding, so when approaching the bulk phase, Al the relaxation effect of the atoms disappears. From this, it can be seen that when H atoms are adsorbed to Al (110) When the surface of Al arrives H electrons are transferred, and most of the transferred electrons are from the outermost shell H provided by atoms.

Population number

The population analysis can give the total number of electrons gained and lost by atoms, and then the transfer of electrons in the system can be analyzed. The charge and its population on each atomic orbital can determine the local structure and interactions formed between atoms in the adsorption system [10].

Table 2-2Al (110) P (1×1)-H population of the system

	H	Al1	Al2	Al3
Free	$1S^{1}$	$3S^{1.40}3P^{1.51}$	$3S^{1.16}3P^{1.85}$	$3S^{1.14}3P^{1.86}$
Top	$1S^{1.16}$	$3S^{1.30}3P^{1.60}$	$3S^{1.13}3P^{1.81}$	$3S^{1.11}3P^{1.87}$
Shortbridge	$1S^{1.30}$	$3S^{1.32}3P^{1.61}$	$3S^{1.17}3P^{1.80}$	$3S^{1.12}3P^{1.88}$
Long bridge	$1S^{1.29}$	$3S^{1.38}3P^{1.53}$	$3S^{1.10}3P^{1.89}$	$3S^{1.13}3P^{1.85}$
Hollow	$1S^{1.28}$	$3S^{1.33}3P^{1.56}$	$3S^{1.15}3P^{1.87}$	$3S^{1.16}3P^{1.89}$

Table 2-2 is in1MLUnder the coverage of Al (110) The population of the system after absorbing H atoms on the surface. Taking the H atom adsorbed to the top position as an example and analyzing it, the results show that the valence electron configuration of the H atom before adsorption is:1S1, the valence electron configuration after adsorption becomes1S1.16, the number of electrons localized in the H atom is1.16e, Got0.16e, therefore, the H atom is the electron acceptor. ExistAl1Localized2.90electrons, lost0.01electrons as donors. ExistAl2Atomically localized2.94electrons,

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lost0.07An electron is also an electron donor. Al1 and Al2 contributed a similar number of electrons respectively. When the H atom enters the hole, its electron donor is Al1, and Al2 only occupy0.01e, which has little impact on it. When H atoms are adsorbed to short bridge sites, Al1got 0.02e, soAl1Be is the electron acceptor. When H atoms are adsorbed to long bridge sites,Al1No electron gain or loss occurs,Al2 loses 0.02e,thereforeAl2 is an electronic donor. ExistAl (110) On the crystal surface, after H atoms are adsorbed on the crystal surface, electrons are transferred from H atoms on the crystal surface to H atoms, while there is no electron transfer to the aluminum atoms deep in the crystal surface. This is consistent with the conclusion obtained using differential charge density observations above.

Density of states

Electronic density of states (intensity of states,DOS) describes the energy distribution of electrons. Al is an easily conductive metal material, so the energy gap is 0 (There is a certain overlap in the energy range between the part in the conduction band and the part in the valence band). Observing Figure 2-2, we can see that the upper limit of the Al conduction band is 10, and the lower limit of the price band is 15.

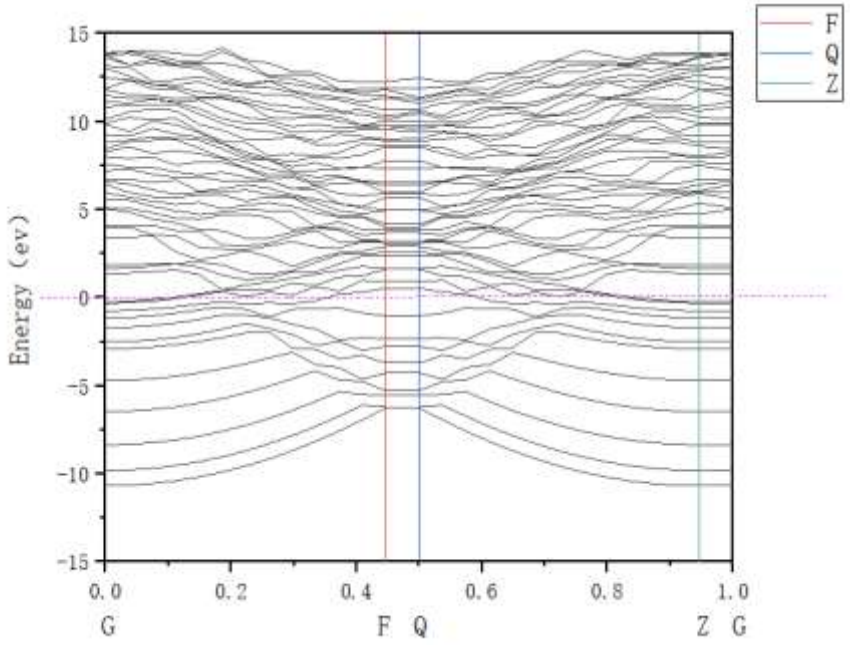

Figure 2-2 Al (110) P (1×1)-H Band structure diagram of the system by Al (110)-H The system is the research object and adopts1MLofH2existAl (110)-H Adsorption in the system, research H2 exist Al (110)-H Bonding in the system. Figure 2-3(a)shows the total state density of the system and Ha and Al the projected state density of atoms have a coverage of1MLstate density at a time.in, -10evThe nearby spectral lines are almost all composed of each layer Al atomics, P orbital contribution, whileA3sThe orbit is very close to the nucleus, so it is highly localized and isolated. Moreover, the peak here is very small, indicating that there are only a few electrons in the system at this energy level, so the impact on bonding is very small. The peak position near 2 electron volts is the product of H atoms, H atoms, H atoms, and H atom hybridization.H1sandAl3pexist5evFive resonance peaks are generated between the Fermi level and the Fermi level.H1sandAl3pthe sum of the resonance peaks is approximately equal, indicating that there are significant ionization features at these two energy levels. In this area, A3sorbitals are more fragmented, which facilitates bonding. In this system, H and Al an ionic bond is formed, the main reason for its formation being the mixing of hydrogen gas with aluminum. When hydrogen is Al (110) on the surface with 0.5ML When the coverage is adsorbed on its top position, it also exhibits the same bonding characteristics.

When H atoms are adsorbed on Als surface T opposition, on the Fermi surface, the state density of the adsorbed hydrogen atoms is not 0, which indicates that the adsorbed H is also metallic. Adsorbed H atoms 1sThe orbit is approximately below the Fermi surface-5evwhere two peaks aresurface localized, and the surface atomsAl1There is also the same peak at this position, indicating that

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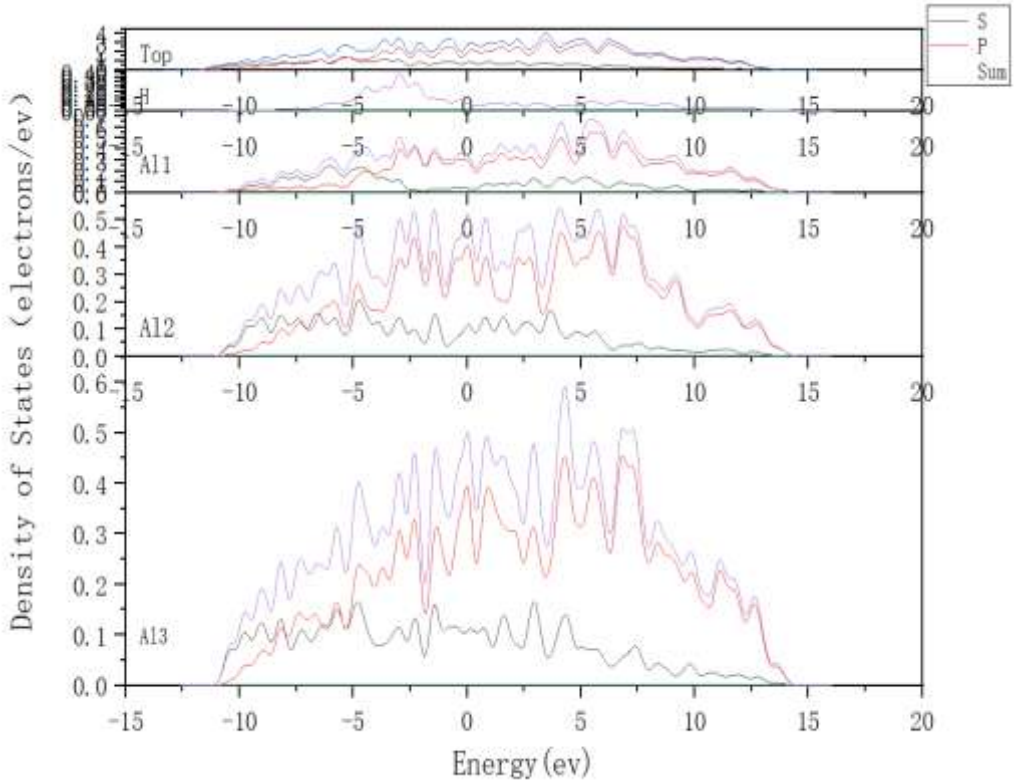
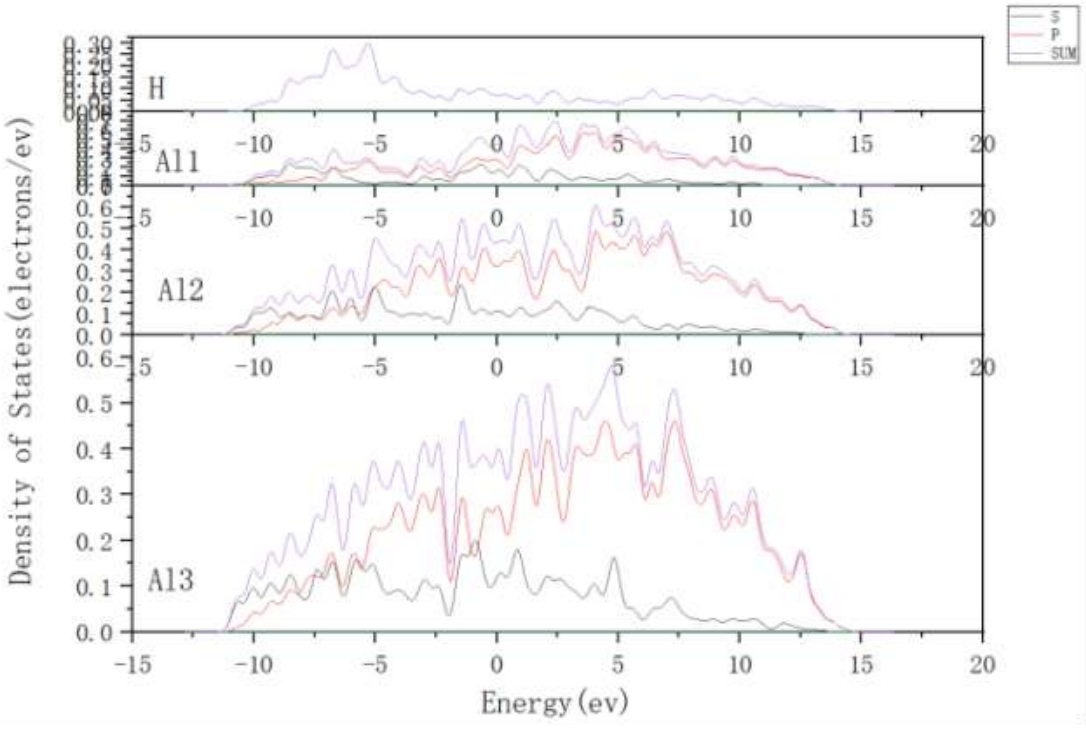
this surface localized state isAl1-HThe result of hybridization. BecauseAl2, Al3 two Al2, Al3It is further away from the H atoms on the surface and have a lower degree of hybridization with the atomic orbitals on the surface, its 3PThe density of orbital states is closer to that of the bulk phase.



(a)



(b)

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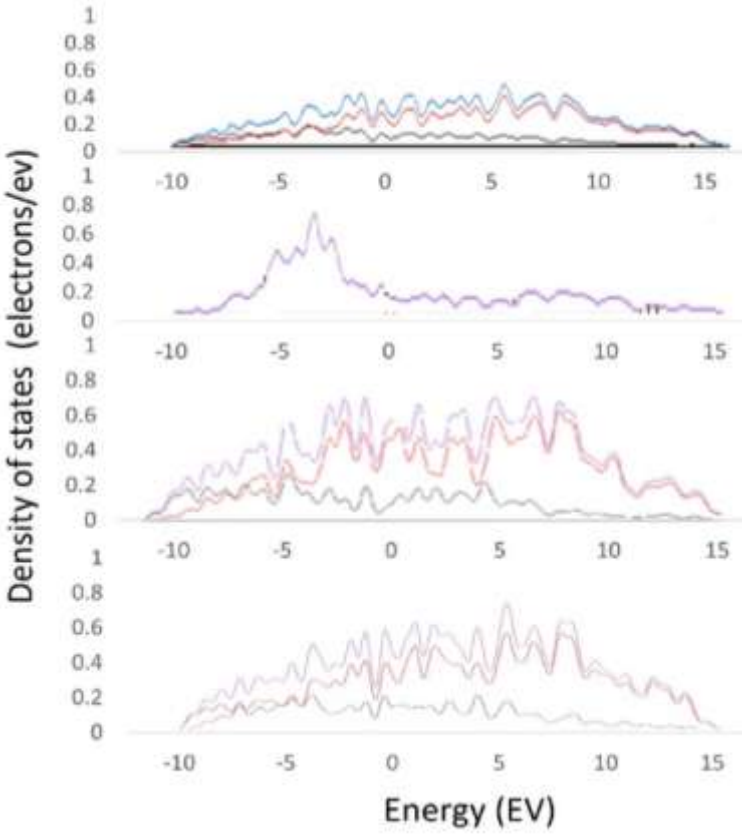
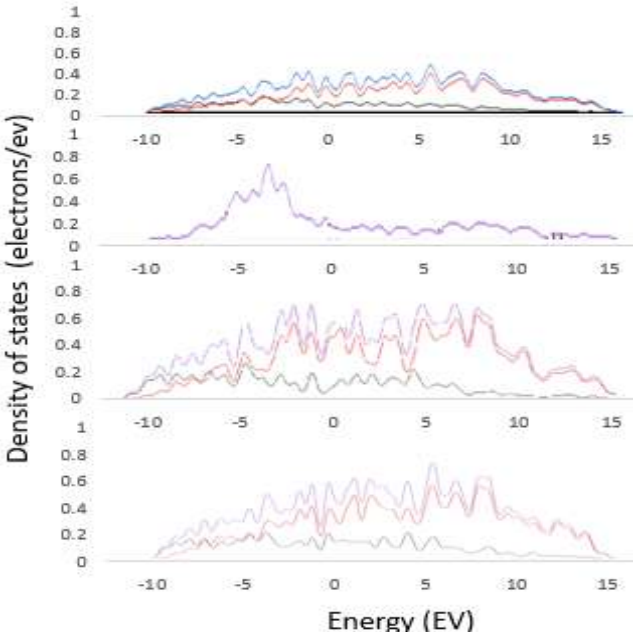


(c)



(d)

Figure 2-3 (a), (b), (c),(d) respectively (110)P(1×1)-HsystematicTop,Short bridge,Long bridge,Hollowdensity of states

As shown in Figure 2-4, based on the state density of H atoms when H atoms are adsorbed to different positions with different coverage and the projected state density of H atoms before adsorption, the problem of hydrogen's preferential adsorption site is analyzed from the perspective of electronic

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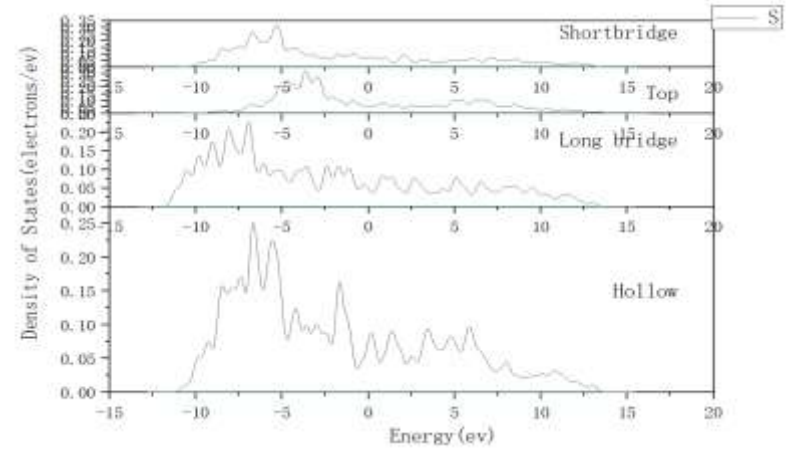
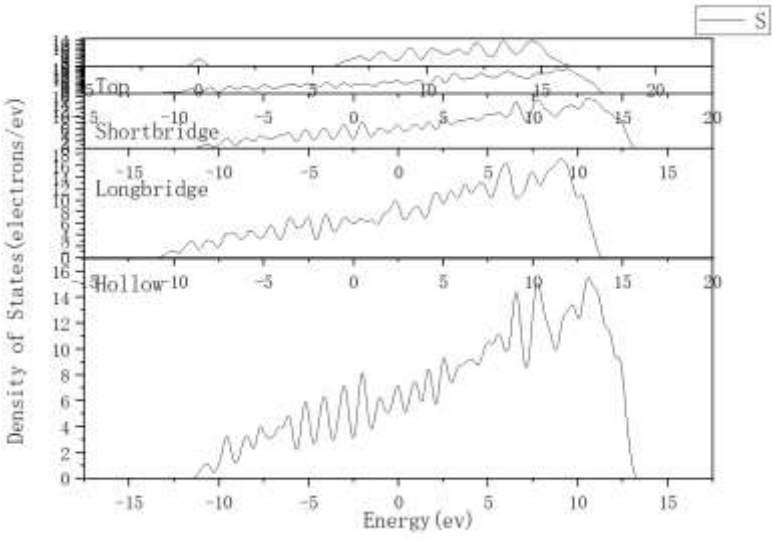
structure. After adsorption, H1sthe orbits all shift to lower energy levels, causing the energy of H to decrease, making H more stable. Figure 2-4(a), the density of the state curve after H atoms are adsorbed at different positions [11]. The upper limit is set to the Fermi level. It can be seen that the density of the state curve when H atoms are adsorbed at the long bridge position has the maximum value is2.24. This shows that when H atoms are absorbed by the long bridge position, the number of electrons below the Fermi surface is the largest, giving the structure the greatest stability [12], [13], [14]. The same integration is performed for the H atom state density in Figure 2-4b, and it is found that when H is absorbed in the short bridge position, the maximum value of the integration is 2.46. As explained in0.5MLUnder the coverage of, the hydrogen absorption at the short bridge position is the most stable [15]. This is consistent with our conclusions from the absorbed energy analysis.



(a)



(b)

Figure 2-4 (a), (b) H The projected state density and coverage of atoms are,0.5MLadsorbed to Al (110) The density of states of hydrogen atoms at different positions on the surface

III. CONCLUSION

(1) H atoms are in Al (110) The adsorption energy of surface adsorption increases as the coverage decreases. Al-H The bond length and the distance from H atoms to the Al surface have no obvious relationship with the change in coverage.

(2) Hydrogen atoms are in Al (110) The preferred adsorption sites for surface adsorption are affected by coverage. When the coverage is1MLWhen, the hydrogen atom is adsorbed on the top position, and the adsorption energy at this time is2.703eV, Al-H The bond length is1.600 Å, H electrons are located below the Al atoms on the surface1.600 Å; When the coverage is0.5MLWhen H atoms are adsorbed at the top position, and the adsorption energy at this time

is2.486eV, Al-H the bond length is1.600 Å, H atoms are located above the surface Al atoms1.606 Å.
(3)H atoms are in Al (110) The adsorption on the surface is chemical, mainly throughH1sandAl3pThe orbitals interact to form bonds, and electrons are transferred from surface Al atoms to H atoms.

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