Theoretical Study on Adsorption and Diffusion of N Atoms on Cu Low-index Surface

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The adsorption and diffusion of N atoms on the three low-index Cu planes were studied using 5-parameter Morse potential (5-MP) method, and the best theory-experiment agreement was obtained. N atoms of Cu(100) surface sit on the fourfold hollow site with the vertical height of 0.018 nm closely coplanar with the topmost copper layer, and the four Cu—N bond lengths are 0.182 nm and the fifth Cu—N distance is 0.199 nm. For Cu(111) system, the existence of aberrant Cu(100) reconstructed structure is approved at higher coverage, and at low coverage the structure is almost an ideal Cu(111) surface structure. With respect to Cu(110) system, the N atoms are adsorbed at LB and H_3 sites, not at SB site. The diffusion passage and diffusion barrier of adsorbed N atoms were also studied.

Keywords   5-MP, adsorption and diffusion, potential energy surface structure

Introduction

Understanding the local geometry of atomic species on metal surface is of paramount importance, as one of the relevant steps in heterogeneous catalysis. Much effort has been devoted to characteristics of the chemisorption of atomic nitrogen on the Cu(100) surface.[1-7] The chemisorption of atomic nitrogen on the Cu(100) surface for half a monolayer coverage has long been known to be characterized by a c(2×2) overstructure. However, in spite of its apparent simplicity, the quantitative information about the details of structure obtained by different techniques is often contradictory. To our knowledge, DFT,[8-10] HF and corrected Moller Plesset (MP2) methods[11] have been employed for the investigation of N-Cu interactions.

In comparison with Cu(100), the Cu(111) plane has received rather little attention. From the structural point of view, the previous model favored the Cu (100)-c(2×2)-N reconstructed structure.[12-15] Early studies[12] by LEED, RAIRS and EELS confirmed the best overall experiment-theory agreement, which could be obtained by assuming that only the outer layer was reconstructed and all N atoms sat on the Cu(100)-c(2×2) overlayer. However, Toomes *et al.*,[14] using scanned-energy mode photoelectron diffraction method, indicated that it comprised two reconstructed Cu layers. Relatively scarce vibrational frequency data[12] and other geometry structure parameters for N/Cu(111) system have been reported.

The relatively more complicated Cu(110) surface is zigzag, constituted by Cu(111) and Cu(111) surfaces.

From the structural point of view, scanning tunneling microscopy,[16,17] impact-collision ion-scattering spectroscopy,[18] and multiple-scattering LEED[19] investigations suggested a missing-row reconstruction with the N atoms at long-bridge sites. In contrast, the tensor LEED[20] and X-ray reflectivity measurements[21] favored a pseudo-Cu(100)-c(2×2)-N reconstruction, with the N atoms at fourfold hollow site. A slightly different structure for the reconstructed Cu surface, emphasizing fivefold coordination for the N atoms, has recently been proposed by Wilde, Pangher and Haase using SEXAFS measurements[22] on the (2×3)N reconstruction. However, Wende *et al.*[23] presented an angle- and temperature-dependent SEXAFS study of the (2×3)N/Cu(110) phase, and investigations indicated that N atom was primarily bounded only to four Cu atoms, and not to five as previously suggested.

The adsorption geometry of the Cu(110)-(2×3)-N surface as well as Cu(100)-c(2×2)-N surface has received considerable attention. The structural techniques employed to date are able to determine the position of the Cu atoms with some accuracy, while the locations of the N atoms are more difficult to be determined because of the low mass and low *Z* of N relative to that of Cu.[24] So the complicated surface geometry presents a challenge to current methods for structural determination, and that the corresponding theoretical investigations are comparatively scarce. The 5-MP theory of mutual interaction between the adatom and metal surface in this paper is semi-experimental method, which has been successfully used to O-Cu,[25] C-Ni,[26] H-Cu,[27] H-Ni(Pd)[28] and O-Pd[29] systems.

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Theoretically calculated method and surface cluster models

Theoretical calculated method (5-MP)

5-MP has been introduced in detail in Refs. 25—29, and it is simply illuminated as follows. On the assumption that the metal cluster is frozen, the interaction energy $U(\vec{R})$ between an adsorbed atom and the whole metal surface cluster can be written in the following form:

$$U(\vec{R}) = D \sum_{i=1}^{\text{Cluster}} (\frac{h_i + Q_1}{R_i + Q_2})\{\exp[-2\beta(R_i - R_0)]$$
$$-2\exp[-\beta(R_i - R_0)]\}$$

where, $\vec{R}$ and $\vec{r}_i$ specify the coordinate of adsorbed atom and the ith metal surface atom respectively, R_i is the distance between the adatom and the ith metal surface atom and denoted as $R_i = |\vec{R} - \vec{r}_i|$, h_i is the vertical distance between the adatom and the surface where the ith metal atom is.

The summation runs over all the atoms from the metal surface cluster, and the potential function $U(\vec{R})$ only consists of 5 parameters: D, β, R_0, Q_1 and Q_2. The defined details are found elsewhere.[25,26] According to available experimental data the parameters in this paper were adjusted and shown in Table 1. Once the parameters are confirmed, the interaction potential function $U(\vec{R})$ is also constructed successfully and applicable to all kinds of complex surfaces including stepped and reconstructed faces. In summary, the main characteristic of 5-MP is that the parameters are independent of surface cluster structure.

**Table 1** 5 parameters of N-Cu surface system

System	D/eV	β/0.1 nm^{-1}	R_0/0.1 nm	Q_1/0.1 nm	Q_2/0.1 nm
N-Cu	0.73	2.45	1.892	1.655	0.138

The movement of N atom on Cu cluster surface has three free degrees, namely, 5-MP function $U(\vec{R})$ is four-dimensional energy hypersurface. Generally, critical points were determined according to λ, which denotes the number of the negative eigenvalues from Hessian matrix and is used to represent the critical characteristics of potential energy hypersurface. For the atom-surface adsorption system, there are three kinds of critical points corresponding to different λ values. Among them, the one $\lambda=0$ corresponds to the surface adsorption state for adsorbed atoms. The one $\lambda=1$ corresponds to the surface diffusion transitional state. The one $\lambda=2$ corresponds to the surface diffusion maximum point. That is to say, our calculation can directly give out the adsorption state, transitional state, *etc.* of the adatom on the cluster surface by the λ value of critical points. Moreover, eigenvalues from Hessian matrix are relevant to the vibration frequency of the adatom on the cluster surface, and the adsorption geometry was also determined by the information of adsorption state.

Construction and adsorption site of the Cu surface cluster

Metal copper belongs to FCC lattice with the lattice constant $a_0 = 0.3615$ nm. Considering the local geometrical symmetry in a point group for surface crystal cell and the whole surface lattice displacement symmetry, the Cu plane was simulated by a copper cluster with at least 5 layers of cell atoms, and every layer contains at least 6 (length)×6 (wide) atoms, which contains about 300 copper atoms. The size of the cluster was defined by the principle that there was no boundary effect in our calculations. Coordinate orientation is shown in Figure 1, and the surface normal direct is also z-axis direct. As to reconstructed Cu(111) surface, according to the experimental model proposed by Higgs *et al.*[12], it could be assumed that only the topmost Cu-atoms gave rise to obvious shift and relaxation, namely, the distance between the top-layer and the second-layer normal to the surface lay between Cu(100) and ideal Cu(111) surface, which in this paper was 0.190 nm, was confirmed by optimization. On the level orientation, taking the top site of second-layer at H_r site as coordinate origin, Cu(100) surface, which was the top-layer structure of reconstruction model, 0.3 lattice unit (taking the distance between two neighboring rows or lines as unit length of x-axis or y-axis) was moved to y-axis and 0.3 lattice unit to x-axis, respectively. To be pointed out, the reconstructed model in this paper was similar to the experimental model,[12] but had obvious differences from that one. The radical difference is that the experimental model gave no concrete data of relaxation and shift.
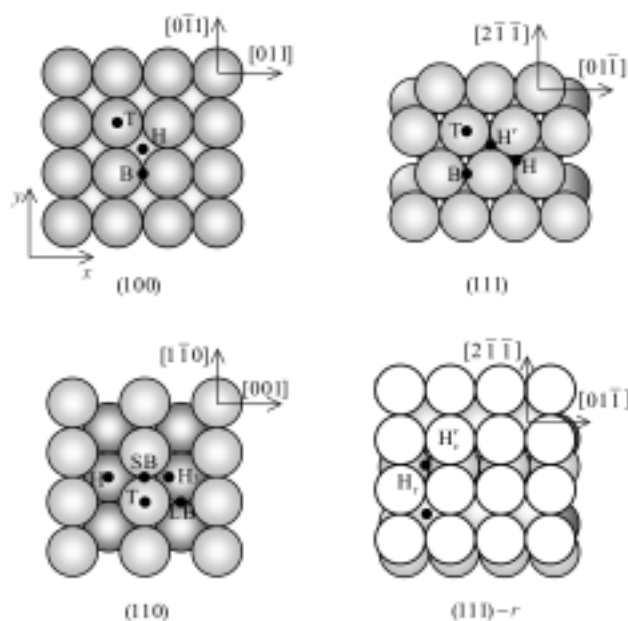
Figure 1 Cluster model of Cu(100), (111), (110) and reconstructed Cu(111)-*r* low-index planes.

The adsorption sites of N atoms on Cu planes were defined as in Figure 1. They are hollow site (H), bridge

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site (B), and top site (T) for Cu(100) plane; Fcc hollow site (H) and Hcp hollow site (H') for Cu ideal (111) plane; fourfold hollow site (H_r and H_r') for reconstructed Cu(111) plane; pseudo-3-fold hollow site (H_3), long-bridge (LB) site, short-bridge (SB) site and the transitional state (S) between LB and H_3 for Cu(110) plane, respectively.

There was still one question to be clarified: R_{N-Cu} (distance between the adatom and its nearest neighbor coordination) was defined in the range of less than 0.25 nm.

Results and discussion

The adsorption of N atoms

The N atomic adsorption on copper three low-index surfaces was studied using 5-MP method respectively, and the results are shown in Table 2. For the N-Cu surface system, binding energies (E_b), bond length between N adatom and its nearest neighbor Cu atom (R_{N-Cu}), the vibrational frequency (f) and the distance of N atom to the surface (Z_{N-Cu}) for N adsorption on all sites of Cu plane mentioned above were gained. From Table 3, the calculated results can well reproduce the measured data. The quantities of these sites can be seen apparently from Figures 2—5.

For N on Cu(100), the surface relaxation was rather small, and although cluster size may influence the exact extent of the surface relaxation, the calculated values nicely followed the experimental trends. The fourfold hollow adsorption state with $\lambda=0$ had a C_{4v} local geometrical symmetry, which was the same to that of the crystal cell, and the surface diffusion transitional point

lay on the B site with $\lambda=1$. The T site with $\lambda=2$ was the surface diffusion maximum point. The eigenvalue was determined for N-Cu vibration mode parallel to the surface as 91.9 meV corresponding to the degenerate irreducible representation E in C_{4v} point group, and the mode perpendicular to the surface was 39.8 meV which belongs to the full-symmetrical A_1 representation in C_{4v}, which are in good agreement with the EELS experiment[6] by Ibach and his co-workers.

The theory in this paper considered the direction of the d electrons and obtained the bonding energy of 4.13 eV, which was in accord with other theoretical results.[8,11,30,31] The participation of the metal d orbital to the covalent part of the bond is not negligible, and the second layer metal atom is important to a more realistic simulation of the surface, but does not participate in the chemical bond with the adsorbate.[8]

Whether fourfold or fivefold coordination ascertained to some extent depends on the range of the R_{N-Cu} value. Therefore, from our results (see Table 2), this paper obtained that N atoms are deep into the expected hollow sites and become closely coplanar with the topmost copper layer with the vertical height of 0.018 nm, then the four Cu—N bond lengths are 0.182 nm and the fifth Cu—N distance is 0.199 nm, which are in good agreement with LEED studies by Zeng and his co-workers.[1,7] And in a sense it can be considered that N atoms sit in the fourfold hollow site and have the fivefold coordination.

The Cu(111) surface is the most compact surface among three single crystal surfaces. This paper firstly studies the ideal Cu(111) surface system, and then also

Table 2 Critical characteristics of N-Cu surface system

System	Site	N	λ	E_b/eV	f/meV		R_{N-Cu}/0.1 nm	Z/0.1 nm
					//	$\perp$		
	H	5	0	4.13	91.9×2	39.8	1.82×4, 1.99	0.18
N-Cu(100)	B	2	1	2.54	65.9	69.8	1.87×2	1.36
	T	1	2	1.61		77	1.85	1.85
	H	3	0	3.35	58.8×2	67.3	1.88×3	1.17
N-Cu(111)	H′	3	0	3.36	59.1×2	67.2	1.88×3	1.17
	B	2	1	2.86	70.4	72.7	1.85×2	1.34
	T	1	2	1.71		79.5	1.84	1.84
	H_r	3	0	5.62	84.5, 52.2	92.0	1.86, 1.80, 1.83	1.14
N-Cu(111)-*r*	$H_r′$	4	0	5.65	81.0, 48.1	93.4	1.84, 1.81 1.88, 1.93	1.12
	H	1	2	3.15		82.6	1.85	0.57
	H_3	3	0	3.36	46.5, 43.9	72.0	1.91×2, 1.88	0.53
N-Cu(110)	LB	4	0	3.82	93.1, 49.8	58.8	1.81×2, 1.92×2	0.15
	S	2	1	3.25	42.6	78.0	1.91, 1.85	0.54
	SB	2	1	2.41	65.5	69.0	1.87×2	1.36
	T	1	2	1.49		75.9	1.86	1.86

Table 3   Comparison between our results and literatures

	System	Theoretical prediction	Experimental data	This work
E_b/eV	(100)-H	4.12,[11] 4.05,[11] 4,[31] 4.055,[8] 4.142[30]		4.13
	(100)-H	1.84,[10] 1.84,[31] 1.82,[11a] 1.86,[11b] 2.18,[10]	1.85,[5] 1.81,[7] 1.91,[6] 2.29,[5] 1.98,[7] 2.41,[6]	1.82 1.99
R_{N-Cu}/ 0.1 nm	(111)	1.85×4, 2.0[14]		1.84, 1.81 1.88, 1.93
	(110)		1.89±0.03,[22] 1.88±0.04, 1.92±0.05, 1.80±0.10[23]	1.91, 1.88, 1.92, 1.81
Z/0.1 nm	(100)-H	0.36,[31] 0.6±0.1,[11] 0.21[10]	0.4,[5] 0.0,[7] 0.6,[6]	0.18
	(110)		0.18,[1] 0.36[1]	0.15, 0.53
f/meV	(100)-H	230.2,[11d] 30.1,[11c] 33.7[11b]	40.2,[33] 39.5,[6] 34.3,[5] 39.7$_\perp$, 91.7$_{//}$[6]	39.8$_\perp$, 91.9$_{//}$
	(110)		(H)$\perp$45.5, 54.5[24] $//$75[24] (subsurface) 105[24], 50[5]	H_3 72.0$_\perp$, 46.5$_{//}$, 43.9$_{//}$, LB 93.1$_{//}$, 49.8$_{//}$, 58.8$_\perp$
	(111)-r		50, 80.5, 92.9[12]	H_r 48.1$_{//}$, 81.0$_{//}$, 93.4$_\perp$, H_r' 52.2$_{//}$, 84.5$_{//}$, 92.0$_\perp$

[11a] Not considering d trajectory of atom. [11b] Considering d trajectory of atom. [11c] Represents the results by MR-MP2 method. [11d] Represents by MP2.
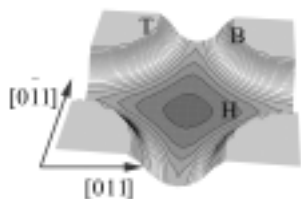
Figure 2   Three-dimensional PES sketch map of N adsorption and diffusion on Cu(100).
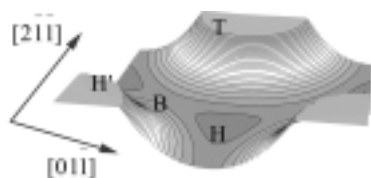
Figure 3   Three-dimensional PES sketch map of N adsorption and diffusion on ideal Cu(111).
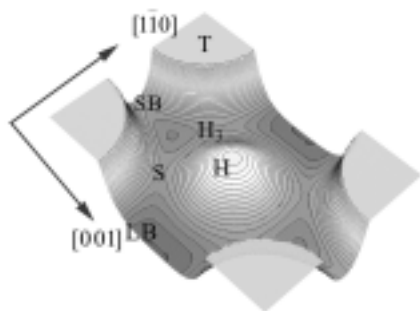
Figure 4   Contour map of N/Cu(110) surface system at the height of 0.0 nm.

studies the reconstructed Cu(111)-*r* model system as shown in Figure 1. The calculated results of frequency were in good agreement with the investigations of Higgs
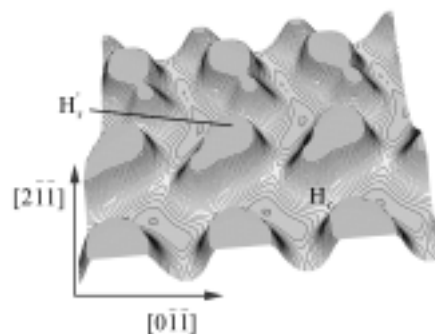
Figure 5   Three-dimensional PES sketch map of N adsorption and diffusion on reconstructed Cu(111).

et al.[12] by EELS experiment, and proved the existence of aberrant Cu (100) structure. Moreover, only the topmost Cu-layer appeared to be reconstructed, not two layers. As it is the results of the Ref. 16 that Cu(100)-c(2×2)-N islands were formed even at low coverage, so the desorption of N atoms might occur either from the unreconstructed Cu(111) terraces or from Cu(100)-c(2×2)-N islands. That is to say, at very low coverage the Cu (111) surface either was partly reconstructed, or the degree of reconstruction was very small so that it was almost the ideal Cu(111) surface. While at high coverage the surface was almost completely reconstructed and formed an ordered stable overlayer. Since structure was similar to that of Cu(100), and the spectral data should be reproduced as those of N/Cu(100) system. In fact, the results recurred as expected (see Table 2).

Calculations showed that there were four different non-equivalent critical points on ideal Cu(111) surface. H' and H threefold hollow sites were the surface adsorption states with $\lambda=0$ in a C_{3v} local geometrical symmetry. B site was the surface diffusion transitional state. T site was the diffusion state. Considering the structure of the Cu(111) surface, although H' and H were different types of adsorption sites, the difference between their

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characteristic critical points was very little from our calculations, nearly the same R_{N-Cu}, Z_{N-Cu} as well as a considerably low discrepancy with 0.01 eV in binding energy, 0.30 meV in parallel and 0.10 meV in perpendicular vibrational frequencies, so they can be considered approximately equivalent. The ideal Cu(111) system obtained the vibrational frequencies of //58.8 meV and ⊥67.3 meV at threefold H site, both were basically in accord with 50.0 meV in the investigations of low coverage in EELS experiment[12] which was attributed to the N-Cu stretch. It would give better results to consider the N-N interaction, which is the work in our group hereafter. And the results of the aberrant Cu(100) structure indicated that there were two different non-equivalent adsorption sites H_r and $H_r^'$. And the parallel vibrational frequencies of 81.0 and 48.1 meV as well as the vertical vibrational frequencies of 93.4 meV at $H_r^'$ site were obtained, which corresponded to 80.5, 50, 92.9 meV in the results of EELS experiment,[12] respectively. At the same time, the parallel vibrational frequencies of 84.5 and 52.2 meV as well as the vertical frequency of 92.0 meV at H_r site were also obtained, and these values seemed to be similar to those of bulk Cu_3N.[31] The above analysis to some extent indicated the rationality of Cu(111) reconstructed model. The adsorption of nitrogen atoms on Cu(111) led to the formation of an ordered nitride overlayer in which the surface was reconstructed to a slightly distorted Cu(100) structure, and it was assumed that the nitrogen atoms occupy the four-coordinate site and the corresponding bond lengths are shown in Table 2 in detail with the adsorption height of 0.112 nm. To be pointed out, the agreement of the three parallel vibrational frequencies calculated at an H_r site with the spectra of bulk Cu_3N is not purely fortuitous. Because the approach was validated by many systems,[25-29] which not only reproduced simultaneously the experimental data on three low-index surfaces, but also was applicable to stepped faces even to reconstructed surfaces.

For N/Cu(110) system, firstly, the missing-row N/Cu(110) model systems[16-18,20] at nearly zero coverage were calculated, but the corresponding vibrational modes and adsorption geometry were not reproduce. Secondly, the ideal Cu(110) surface system was studied, and almost all spectra in the high-resolution electron-energy loss spectroscopy (HREELS) experiment were found,[24] which indicated that the adsorption of N atoms had little effects on Cu(110) surface, and at least it is not the missing-row structure as Mitchell *et al.*[18] proposed. However, the lateral shift of surface Cu atoms in the small range was not excluded and the surface aberrance was brought, which led to the calculated results in this work to be in disagreement with the experiments. Then whether on earth the model was the Cu(100)-c(2×2) structure as proposed [19,21] previously, it cannot be confirmed only from our results to date.

Though the calculated results in this paper reproduced almost all spectral data above, the spectra above 100 meV were not obtained. Our calculation results

showed that the adsorption at LB site was the most stable adsorption state. There was a discrepancy of 0.46 eV on binding energy between the LB and H_3 adsorption states with $\lambda=0$. The parallel vibrations of N adsorbed on LB site were 93.1 and 49.8 meV with the perpendicular one of 58.5 meV, and the H_3 site had the parallel vibrations of 46.5 and 43.9 meV as well as the perpendicular one of 72.0 meV. These modes corresponded to 45.5, 54.5 and 75 meV in HREELS experiment.[24] With respect to 93.1 meV, on the one hand, from the off-specular EELS spectra[24] of the Cu(110)-(2×3)-N surface, the peak of 80—90 meV can be seen to appear clearly. On the other hand, the geometry characteristics of LB site were similar to those of the H site of Cu(100) to some extent, so the appearance of 93.1 meV (analogy with 91.9 meV on Cu(100)) was not surprising.

It was assumed that these spectra of 100 meV above originated from molecular vibrations, not from the subsurface N as Hannon *et al.*[24] proposed. And that the assumption was in accord with the investigations by Zeppenfeld *et al.*[32] In addition, the local density of N or N_2 was very large, which led the peak intensity of (70±6) meV to be distinctly strengthened. After ascertaining the static adsorption geometry, the dynamics of N atoms on metal surface was further studied.

The diffusion of N adatoms

For the N/Cu(100) system, the energy barriers were obtained through the B site and the T site, 1.59 and 2.52 eV respectively, which were in accord with the first-principle calculations by Yoshihide Yoshimoto and Shinji Tsuneyuki[10] with 1.5—1.7 and 3.0 eV, respectively. From the three-dimensional diffusion potential energy surface (PES) (Figure 2) it can be made out that the energy of the H site was the lowest, and the B site was the surface diffusion transitional point and the T site was surface diffusion maximum point (the darker the color is, the lower the energy is). Clearly, the lowest energy passage was H-B-H with diffusion barrier of 1.59 eV.

With regard to the diffusion of N atom on the Cu(111) surface, a potential energy barrier of 0.49 eV (0.50 eV) existed on the diffusion channel H-B-H' (see Figure 3). It was much lower than that of Cu(100) plane for the N atom to get through. To give more obvious evidence, this paper also scanned the contour map of Cu(111)-*r* reconstructed system (see Figure 5) at the height of 0.12 nm. It was not difficult to make out that the N atom sat at fourfold coordinated H_r and $H_r^'$ sites. Furthermore, the diffusion along [2$\bar{1}$$\bar{1}$] orientation and [01$\bar{1}$] orientation had much higher barrier. Therefore it was more difficult for adatom N to diffuse, and the adsorption was more stable. It was the reason that the adsorption energy is much higher than that of other systems.

As to the diffusion of N atom on Cu(110) surface, the situation was much more complex. So the three-dimensional contour map was also scanned (see Figure 4), and the lowest energy diffusion channels of

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H$_3$-SB-H$_3$ and LB-S-H$_3$-S-LB were analyzed. A potential energy barrier of 0.95 eV was found on the H$_3$-SB-H$_3$ diffusion channel, which gave an obvious clue that the diffusion on H$_3$-SB-H$_3$ channel was quite difficult to take place, and the curvature of the counter map was larger than LB-S-H$_3$-S-LB. Otherwise, analytical results showed that along LB-S-H$_3$-S-LB channel N atom needed to get across two potential barriers of 0.57 and 0.11 eV respectively, which indicated that the potential barrier between H$_3$ and LB was considerably low and the diffusion between the two stable adsorption states was much easier, and the curvature was smaller. In other words, our calculation results predicted a low-energy surface diffusion channel for N atom along the zigzag on the Cu(110) surface. From the analysis above, a conclusion that the diffusion of N atom on Cu(110) surface displayed a distinct anisotropy. In addition, clearly, the H site was a local peak point, not an adsorption site. It was expected to obtain the corresponding experimental and theoretical supports in this field.

Conclusions

This paper studied the adsorption and diffusion of N atoms on the three low-index Cu planes by 5-MP method, and obtained the best theory-experiment agreement (see Table 3). The results are shown as follows:

(1) For N—Cu(100) system, N atoms sat at the fourfold hollow site with the vertical height of 0.018 nm, closely coplanar with the topmost copper layer, then the four Cu—N bond lengths were 0.182 nm and the fifth Cu—N distance was 0.199 nm. The N atoms had five-fold coordination. At the same time the energy barriers obtained through the T site and the B site were 1.59 and 2.52 eV, respectively.

(2) For Cu(111) system, the existence of aberrant Cu(100) structure was proved, and the adsorption of N atoms led to the reconstruction only at high coverage. However, at very low coverage the structure almost did not change. In addition, only the topmost Cu atoms produced obvious shift and relaxation.

(3) With respect to Cu(110) system, the calculated results in this paper were in good agreement with experiments,[24] and it was confirmed that the N atoms were in LB and H$_3$ sites not at hollow site. Accordingly, the missing-row model was excluded.

(4) The diffusion passage and barrier of adsorbed N atoms by three-dimensional PES were studied and the available experimental and theoretical data supported them. It was hoped that our prediction on interactions could stimulate further experimental and theoretical studies.

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