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Surface structures of atomic hydrogen adsorbed on Cu(1 1 1) surface studied by density-functional-theory calculations

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Abstract

The surface structures of atomic hydrogen adsorbed on Cu(1 1 1) surface have been studied theoretically by using density-functional-theory calculations. The results show that 0.67 ML hydrogen adsorbed on threefold hollow sites forming (3×1) superstructure and 0.5 ML hydrogen adsorbed on threefold hollow sites forming (2×2)-2H superstructure with central H at trigonal sites induce most significant substrate reconstructions and that fits best the observed (3×3) and (2×2) LEED patterns, respectively. The potential energies for the hydrogen in these two models are also lower than those in other competing models. Accordingly, these two models are the most preferable structures for 0.5–0.67 ML and 0.3–0.5 ML hydrogen adsorbed on the Cu(1 1 1) surface. In addition, the calculations also suggest that the lateral H–H interaction is not of simple repulsion and how the adsorbed hydrogen is arrayed is important in modifying the adsorption energy.

Keywords: Adsorption; Atomic hydrogen; Cu(1 1 1); Density-functional-theory calculations; Reconstruction; Adsorption energy

1. Introduction

Adsorption of hydrogen on metal surfaces has been extensively studied in both fundamental and applied researches. In the viewpoint of applications, it is closely associated with a great part of heterogeneous catalysis such as hydrogenation, hydrogen-induced embrittlement and fracture in metallurgy, as well as primary steps in energy storage and/or fuel cell technology [1–8]. By virtue of being the simplest possible adsorbate, hydrogen in the fundamental researches also holds a particular position for attracting theoretical studies such as modelling the gas–surface interaction [1–8]. H–Cu(1 1 1), as a representative model system for the interaction of hydrogen with metal surfaces, has attracted a lot of interests [9–25]. In addition to essential issues on hydrogen adsorption, a number of works go further to investigate absorption of atomic hydrogen into the subsurface and bulk of Cu(1 1 1) [14–21], and some others concentrate on abstraction of hydrogen on the Cu(1 1 1) surface by incident hydrogen atoms [16,22–25]. These works are valuable as the phenomena manifested in these studies encompass most basic concepts of surface science. All of these studies are closely related to the surface structures of H–Cu(1 1 1), which, however, is so far not entirely clear. Although the diffraction patterns for H–Cu(1 1 1) were already reported [10,13,19,20] and the preferential adsorption site was also determined both experimentally and theoretically [10–12,15,17,18], knowledge of how the adsorbed hydrogen arrays are arranged and how the substrate reconstructs is uncertain. The present study thus attempts to illuminate the surface structures of H–Cu(1 1 1) to further our understanding of the adsorption of atomic hydrogen on metal surfaces.

The surface structures of atomic hydrogen adsorbed on the Cu(1 1 1) surface were studied theoretically by using

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density-functional-theory (DFT) calculations. We calculated the energetically most preferable geometries for the structural models of the H–Cu(1 1 1) at different hydrogen coverages. The models were established based on known experimental and theoretical results [10–13,15,17,18,26]. The most likely surface structures were determined finally according to both energetics and substrate reconstructions: the ones with largest adsorption energies and significant reconstructions were favoured. The significant substrate reconstructions are anticipated because hydrogen has a small cross-section for electron scattering. The intense fractional order spots observed in the LEED patterns upon hydrogen adsorption were mainly attributed to pronounced substrate reconstructions [10,13,26]. The current calculations suggest that the (3 × 3) diffraction pattern observed at 0.5–0.67 ML [10,13,19] is primarily produced by hydrogen adsorbed on threefold hollow sites forming (3 × 1) structure. The substrate reconstruction is in a form of buckling with the 3H-coordinated Cu atoms lifted (0.17 Å) relative to the 1H-coordinated Cu atoms. Since the (3 × 1) structure cannot produce (1/3, 1/3) diffraction spots, it should coexist with some $(\sqrt{3} \times \sqrt{3})R30°$-2H structure although such structure has only trivial substrate reconstruction and relatively higher potential energy for the adsorbed hydrogen. The (2 × 2) diffraction pattern observed at 0.3–0.5 ML [10,13,19] arises from hydrogen adsorbed on threefold hollow sites forming (2 × 2)-2H structure with central H at trigonal sites, where the 2H-coordinated Cu atoms are buckled up (0.14 Å) with respect to the non-hydrogen-coordinated Cu atoms. It is noted that these H-induced reconstructions extend slightly into the subsurface layer.

The adsorption energies of the atomic hydrogen at different coverages are also discussed in this report. The calculations show that in the lower coverage regime the hydrogen adsorption energy does not decrease monotonically with the coverage and thus imply that the lateral H–H interaction is not of simple repulsion.

2. Computational method

Our total-energy calculations for the atomic hydrogen adsorbed on the Cu(1 1 1) surface were based on the density functional theory. The total energies for the various models under studies were computed in a super-cell geometry using a plane-wave and pseudopotential code, CASTEP [27], in which the generalised gradient approximation (GGA) proposed by Perdew et al. [28] was used for the exchange correlation energy. In our calculations, the Cu(1 1 1) surface was represented in the super-cell by a slab of four or five atomic layers in a ABCA stacking and the vacuum region was six-layers thick [15,17]. The Cu slab was from the top four or five layers of a slab of ten atomic layers with a lattice constant of 3.61 Å that had relaxed and reached the energetically most favourable geometry with bottom three layers fixed to include surface-induced interlayer relaxation. The interlayer distance between the first and second layers contracted by 1.7% with respect to the bulk value (2.087 Å), while the relaxation in other interlayers was negligible and the in-plane inter-atom distance remained the same as bulk value (2.556 Å). These lattice parameters are quite comparable with the experimental characterisation [29]. The unit cells employed in the calculations depend on the hydrogen coverages under investigation, which will be illustrated in next section. Uniform sampling in the reciprocal space was used (with a density of $0.04\ \text{Å}^{-1}$). Symmetry was taken into account to reduce sampling *k*-points. For different unit cells, the surface Brillouin zone was sampled by different numbers of *k*-points, ranging from 8 to 33. The adsorbed hydrogen and the Cu atoms in the top two layers are allowed to relax to achieve the energetically most preferable geometries, i.e., with the lowest total energies, through BFGS geometry optimisation steps [30]. Typically, the total energies were converged after about 15 iterations of the BFGS geometry optimisation steps.

The reference energy, that is the energy for the separated Cu surface and the hydrogen atoms, was derived from two separated calculations in the super-cell: one for the isolated slab and one for the hydrogen atoms. To get an accurate description for the hydrogen atoms, we need to perform a spin-polarised calculation, giving a value of −13.536 eV for the hydrogen atom energy.

3. Results and discussions

Diffraction measurements, including low energy electron diffraction (LEED) and helium atom scattering (HAS), have shown that atomic hydrogen adsorbed on Cu(1 1 1) surface formed coverage-dependent superstructures: the (2 × 2) pattern in a lower coverage regime (0.3–0.5 ML), a mixture of the (2 × 2) and (3 × 3) patterns at higher coverages (0.5–0.67 ML) and a pure (3 × 3) pattern near saturation (0.67 ML) [10,13,18,19]. Moreover, vibrational spectroscopy measurements and theoretical calculations suggest consistently that the atomic hydrogen adsorbed on threefold hollow sites of the Cu(1 1 1) surface (no evident difference can be distinguished between hcp and fcc hollow sites) [11,12,15,17,18]. On the basis of these reported results, we propose structural models accounting for the observed diffraction patterns at various coverages.

Fig. 1a–d show the structural models proposed to account for the (3 × 3) and (2 × 2) diffraction superstructures, respectively. These models are proposed by assuming that the adsorbed hydrogen atoms are ordered at low temperature and may induced substrate reconstructions of long-range order. Fig. 1a illustrates 0.67 ML (3 × 1) structure with hydrogen at fcc threefold hollow sites, which may exist in domains of three orientations related by a 60° rotation. Fig. 1b shows 0.67 ML $(\sqrt{3} \times \sqrt{3})R30°$-2H structure which also has hydrogen at the fcc threefold hollow sites [10–12,15,18]. Fig. 1c shows 0.5 ML (2 × 1) structure with hydrogen at the fcc threefold hollow sites, existing in

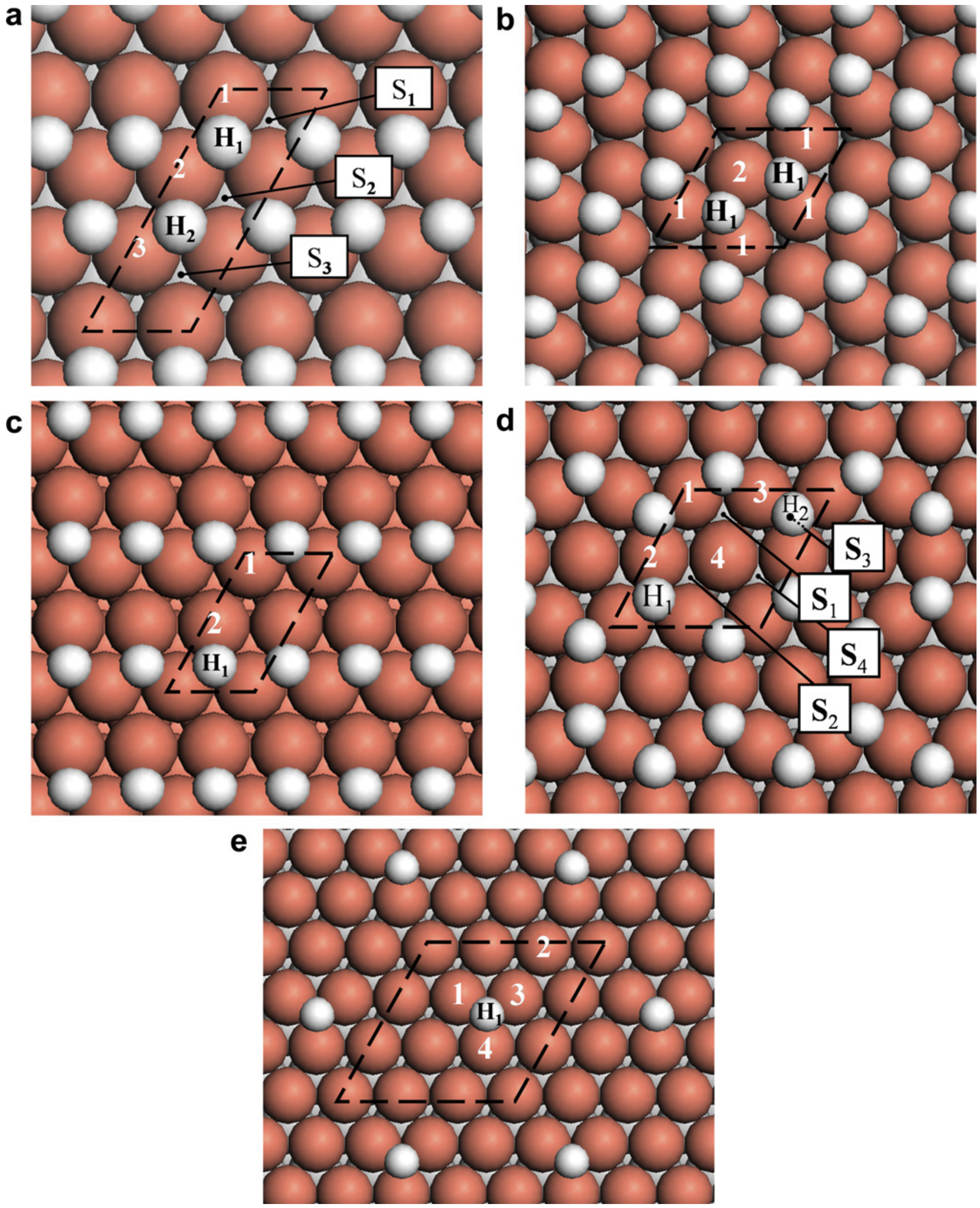

Fig. 1. Schematic diagrams illustrating (a) 0.67 ML (3 × 1) model, (b) 0.67 ML $(\sqrt{3}\times\sqrt{3})R30°$-2H model, (c) 0.5 ML (2 × 1) model, (d) 0.5 ML (2 × 2)-2H model and (e) 0.11 ML. The smaller balls in the figure denote the hydrogen atoms and the larger ones denote the copper atoms. The dash lines indicate the unit cells used for the computation. The atoms are marked for convenience of describing their movement. Their corresponding ones in the side views are shown in Fig. 2. The configuration of 0.11 ML is used to represent the low coverage case in which the hydrogen is well isolated from each other. In (e), the H–H distance is about 7.65 Å.

domains of three orientations rotated by 60° from each other, and Fig. 1d demonstrates 0.5 ML (2 × 2)-2H structure, in which hydrogen atoms occupy both fcc and hcp threefold hollow sites [10–12,15,18,26]. The dash line in each figure indicates the unit cell used to compute the total energy for this model. What models are the most likely surface structures are determined by whether or not the energetically most preferable geometries in these models, derived from the DFT calculations, can give H-induced substrate reconstructions that agree best with the observed LEED patterns. This criterion is used as the hydrogen atom has a small cross-section for electron scattering, due to its small atomic number. The contribution in the LEED intensities from the hydrogen overlayers is thus much smaller (typically a few percent) than that from a transition or noble metal substrate [26]. The fractional order spots in (2 × 2) or (3 × 3) patterns should be all very faint, in comparison with integral order spots, if they were solely due to the hydrogen arrays [26]. However, the relative intensities of the fractional order spots to the integral order spots in the LEED patterns of H–Cu(1 1 1) [10,26] are much larger than those from (2 × 2) H–Ni(1 1 1), where the substrate was found to reconstruct slightly [31,32]. Accordingly, ones believe there must be evident H-induced substrate reconstructions at H–Cu(1 1 1) surface, which contribute to the intense fractional order diffractions.

For the (3 × 3) diffraction pattern, the calculations show that the 0.67 ML (3 × 1) structure involves pronounced substrate reconstruction. The Cu atoms coordinated with three hydrogen atoms (denoted by 2 in Fig. 1a) are uplifted by 0.17 Å, with respect to the lowest Cu atoms at the surface (coordinated with one hydrogen and denoted by 1 in Fig. 1a). The Cu atoms coordinated with two hydrogen atoms (denoted by 3 in Fig. 1a) are also raised by 0.06 Å relative to Cu atoms 1 (see Table 1). The lateral movement is negligible. The reconstructed substrate also forms long-range order of (3 × 1) as the hydrogen overlayer. In contrast, in the 0.67 ML $(\sqrt{3}\times\sqrt{3})R30°$-2H model, all the Cu atoms at the surface are equally high (see Table 1), although the hydrogen adsorption causes slight expansion of the interlayer distance. The subsurface Cu layer is as flat as that without hydrogen adsorption. That is perhaps due to the highly symmetric configuration of this superstructure. We should note that these reconstructions are by no means due to the Cu slab in an unoptimised state, since allowing the same relaxation without hydrogen, we see only negligible interlayer contraction (<0.01 Å). According to the reconstruction criterion discussed above, the (3 × 1) structure in Fig. 1a should predominate the surface at higher hydrogen coverages (0.67 ML). The result is further supported by the energetics, in which the adsorption energy per hydrogen atom in the (3 × 1) model is larger than that in the $(\sqrt{3}\times\sqrt{3})R30°$-2H model (see Table 2). To corroborate the conclusion, we also expanded doubly the unit cell for the calculations to see if there are other reconstructions and we obtained the same result as above. The (3 × 1) model may have hydrogen adsorbed at hcp hollow sites. Similar substrate reconstruction and adsorption energy are derived (see Tables 1 and 2). For instance, the 3H-coordinated Cu atoms (denoted by 2) are lifted by 0.16 Å relative to the 1H-coordinated Cu atoms (denoted by 1). As the differences between the fcc and hcp hollow sites are minor, both structures could be present at the surface. However, three domains of the (3 × 1) structure cannot produce (1/3, 1/3) diffraction spots. One of plausible reconcilements is that the (3 × 1) structure coexist with some $(\sqrt{3}\times\sqrt{3})R30°$-2H structure on the surface to yield an entire (3 × 3) diffraction pattern. While, this speculation may from certain viewpoints contradict with the observation that the (1/3, 1/3) spots in the (3 × 3) LEED pattern are not so weak in comparison with other spots, e.g., (1/3, 0) and (2/3, 0) [10,13]. We accordingly cannot rule out the existence of a pure (3 × 3) phase with other unknown structure.

For the (2 × 2) diffraction pattern, both (2 × 1) and (2 × 2)-2H models exhibit substrate reconstructions. In the (2 × 1) model, the Cu atoms (denoted by 1) coordinated with two adsorbed hydrogen are uplifted by 0.085 Å, relative to the rest, coordinated with one hydrogen (denoted by 2). Whilst, in the (2 × 2)-2H model, we see that the Cu atoms (denoted by 1) coordinated with two adsorbed hydrogen are buckled up by 0.14 Å, with respect to the uncoordinated Cu atoms (denoted by 2), or alternatively we view the Cu atoms 2 are buckled down. Both reconstructions can result in long-range order of (2 × 2), however, the (2 × 2)-2H model is favoured because its more remarkable reconstruction can give rise to intense fractional order spots in the diffraction patterns. Moreover, in view of the calculated potential energies for the adsorbed hydrogen, the (2 × 2)-2H is also more preferable (see Table 2). The result is similar to those obtained from H–Ag(1 1 1) and H–Ni(1 1 1), although the Cu(1 1 1) surface reconstructs more than Ni(1 1 1) (uplifted by 0.04 Å) [26,31,32]. From the above calculations, we notice a trend that more hydrogen the Cu atom is coordinated with, more the Cu atom is induced to move. For instance, in the (3 × 1) model 3H-coordinated Cu atoms are lifted by 0.17 Å, apparently larger than that for the 2H-coordinated Cu atoms in the same model (0.06 Å) and also that in the (2 × 2)-2H model. For isolated hydrogen atoms, exemplified in Fig. 1e where the hydrogen is well separated from each other with a H–H distance of about 7.65 Å, the 1H-coordinated Cu atoms are raised up by only 0.044 Å (see Table 1).

Table 1
H-induced Cu(1 1 1) substrate reconstructions for a variety of models

	0.67 ML fcc (3 × 1)	0.67 ML hcp (3 × 1)	0.67 ML $(\sqrt{3}\times\sqrt{3})$ $R30°$-2H	0.5 ML (2 × 1)	0.5 ML (2 × 2)-2H	0.11 ML
1	0.000	0.000	0.000	0.085 Å	0.141 Å	0.044 Å
2	0.173 Å	0.160 Å	0.000	0.000	0.141 Å	0.000
3	0.060 Å	0.047 Å			0.141 Å	0.044 Å
4					0.000	0.044 Å
S1	0.000	0.000			0.000	
S2	0.022 Å	0.007 Å			0.000	
S3	0.036 Å	0.009 Å			0.019 Å	
S4					0.000	

Since the lateral movement is negligible, only changes of the vertical positions are reported. The numbers shown in the columns indicate the vertical positions relative to the lowest atoms in that layer ("0" indicates the atom at the lowest position in that layer). The atoms marked by 1, 2, 3 and 4 or S_1, S_2, S_3 and S_4 are shown in Figs. 1 and 2.

Table 2
Adsorption energies per hydrogen atom for a variety of coverages

	1 ML	0.67 ML fcc(3 × 1)	0.67 ML hcp(3 × 1)	0.67 ML $(\sqrt{3}\times\sqrt{3})$ $R30°$-2H	0.5 ML (2 × 1)	0.5 ML (2 × 2)-2H	0.33 ML $(\sqrt{3}\times\sqrt{3})$ $R30°$-1H	0.11 ML
Potential energy (eV)	−2.477	−2.534	−2.525	−2.501	−2.528	−2.561	−2.542	−2.534

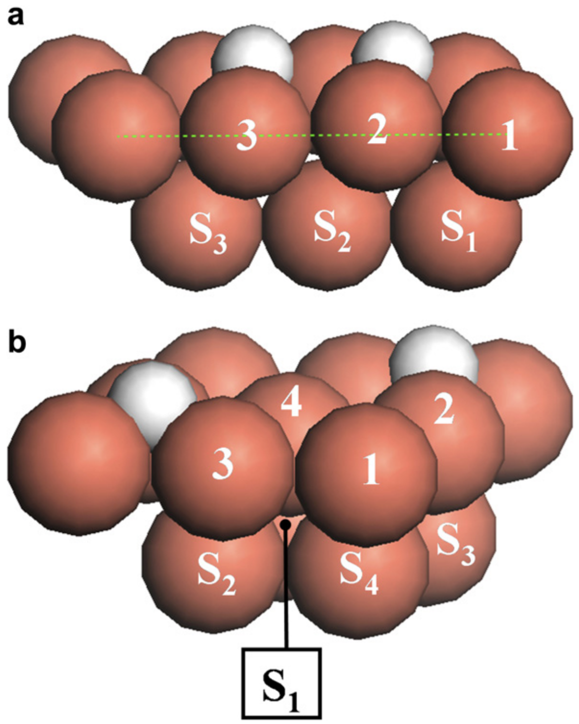

Fig. 2. Schematic diagrams showing the side views for (a) 0.67 ML (3 × 1) model and (b) 0.5 ML (2 × 2)-2H model. The smaller balls in the figure denote the hydrogen atoms and the larger ones denote the copper atoms. The labelling for the atoms is described in the text and the corresponding atoms for top views are shown in Fig. 1.

It is evident that the reconstructions extend slightly into the subsurface layer. In the fcc(3 × 1) model, the subsurface atoms coordinated with Cu atoms 2 and 3 (demoted by S_2) and coordinated with atom 3 and 1 (denoted by S_3) are lifted by 0.022 Å and 0.036 Å, respectively, with respect to the lowest Cu atoms at this subsurface layer (demoted by S_1), as shown in Fig. 2a. The average distance between the first and second Cu layers is enlarged. For instance, the interlayer distance between the lowest atoms of these top two layers, Cu atom 1 and S_1, is about 0.02 Å larger than that before the hydrogen adsorption. Such slight interlayer expansion is also seen in the hcp(3 × 1) model, but H-induced corrugation at the subsurface layer is negligible. The structural changes of the subsurface in the (2 × 2)-2H model are more complex. The subsurface atoms beneath the adsorbed hydrogen (denoted by S_3) are 0.019 Å higher than other subsurface Cu atoms (denoted by S_1, S_2 and S_4). The interlayer distance between subsurface atoms (S_1, S_2, S_4) and Cu atoms 4 contracts by 0.048 Å, in comparison with that before the hydrogen adsorption. Whilst, the interlayer distance between subsurface atoms S_3 and the Cu atoms (1,2,3) expands by 0.074 Å, as shown in Fig. 2b. These results are confirmed in the calculations where the top three atom layers are allowed to relax.

The hydrogen adsorption energies computed for various coverages and structures are valuable to understand why these particular surface structures are formed. Table 2 lists the potential energies per H atom for each case we discussed above and also some other cases that do not truly occur at the surface, such as 0.33 ML $(\sqrt{3} \times \sqrt{3})R30^\circ$-1H and 1 ML. The values derived are close to previous results [15,17]. We note that the potential energy for the hydrogen in the 0.5 ML (2 × 2)-2H model (Fig. 1d) is lowest (−2.561 eV), evidently lower than that in 0.11 ML (−2.533 eV), representing the low coverage cases where the hydrogen is well separated from each other. The comparison implies that even at the coverages far lower than 0.5 ML, the hydrogen atoms would rather form the (2 × 2)-2H structure than being widely dispersed or form other ordered structures and explains that the (2 × 2) diffraction pattern was observed not only at 0.5 ML but also at the coverages between 0.3 ML and 0.5 ML [10,13,19]. These calculated potential energies shown in Table 2 also indicate that the adsorption energy is not subject to simple coverage dependence due to lateral H–H interactions, conventionally regarded as a major role in modifying the adsorption potential [1,2]. The adsorption energy decreases from 0.5 ML to 0.67 ML, or to 1 ML (although it does not occur), which suggests repulsive H–H interactions and that is in line with the experiments [13]. However, the potential energy for 0.11 ML is clearly higher than that for 0.5 ML (2 × 2)-2H and nearly equivalent to that for 0.67 ML fcc (3 × 1). Ruling out the reconstruction effect (by assuming no reconstruction), we obtain the potential energies with a similar trend shown in Table 3. The potential energies are enhanced by 0.2–0.4 eV, while the adsorbed hydrogen in 0.5 ML (2 × 2)-2H structure still has the lowest potential energy. Even the potential energy for the hydrogen in 0.33 ML $(\sqrt{3} \times \sqrt{3})R30^\circ$-1H (does not really occur) is lower than that in 0.11 ML. The results in consequence suggest that in the lower coverage regime the H–H interaction may not be simply repulsive [1] and how the adsorbed hydrogen is arrayed is essential in modifying the energetic structure at the Cu(1 1 1) surface.

4. Conclusion

We have studied the surface structures of atomic hydrogen adsorbed on Cu(1 1 1) surface by using density-functional-theory calculations. The results indicate that the

Table 3
Adsorption energies per hydrogen atom for a variety of coverages without involving substrate reconstruction

	1 ML	0.67 ML fcc(3 × 1)	0.67 ML $(\sqrt{3} \times \sqrt{3})R30^\circ$-2H	0.5 ML (2 × 1)	0.5 ML (2 × 2)-2H	0.33 ML $(\sqrt{3} \times \sqrt{3})R30^\circ$-1H	0.11 ML
Potential energy (eV)	−2.451	−2.491	−2.485	−2.499	−2.539	−2.528	−2.503

hydrogen 0.67 ML (3 × 1) model and 0.5 ML (2 × 2)-2H model induce significant substrate reconstructions, and that agrees best with the observed LEED patterns. The hydrogen atoms in these two models also have the potential energies lower than those in other competing models. We therefore conclude that these two structures are most preferable, respectively, for 0.5–0.67 ML and 0.3–0.5 ML hydrogen on the Cu(1 1 1) surface. The calculations also show that the repulsive H–H interaction on the Cu(1 1 1) surface plays a role in modifying the adsorption potential at high hydrogen coverages; while, at lower coverages the H–H interaction is not simply repulsive and how the adsorbed hydrogen is arrayed is crucial.

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