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A density functional study of Br on Cu(100) at low coverages

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1 Introduction

Since the realization that the tips of scanning probe microscopes can interact with atoms and molecules at surfaces, so as to manipulate them there has been much interest in the possibility of constructing or modifying nanostructures using this technique [1]. There has been a great deal of work on the manipulation of both atoms [2,3] and molecules [4–6] on surfaces. Most of the work on the construction of complex structures [7,8] has been performed at cryogenic temperatures using systems where the interaction between the adsorbate and the surface is weak, allowing the atoms to be manipulated with a weak tip-atom interaction. Bromine on copper (100) is of great interest as a system where controlled room temperature nanomanipulation has been achieved[9]. An understanding of systems such as this one is essential if we are to succeed in “manufacturing” nanoscale devices.

The experiments on this system, however, raise many questions about our understanding of the processes that are important during nanomanipulation.

In the present communication we have employed *ab-initio* density-functional-theory (DFT) to address two key issues relating to the adsorption and tip-induced motion of Br on Cu(100). The first is identification of the adsorption site. It is generally believed that Br on Cu(100) must occupy fourfold hollow sites as shown in figure 1, but a surprising result of the STM experiments is that the topographic features assigned to adsorbed bromine atoms appear in registry with the greyscale maxima of the STM images [9,10] (figure 2). This registry is preserved under a wide range of differing tip conditions which lead to imaging the bromine induced features as greyscale maxima, minima or Mexican hat sombreros [10]. If the substrate maxima correspond to Cu positions, the implication is that Br atoms occupy sites on top of individual Cu atoms. The present calculations demonstrate unambiguously that the fourfold hollow site has the lowest energy amongst possible sites for binding of a Br atom to a defect-free Cu(100) surface. The second issue concerns the barriers to atomic motion. In the STM experiments, tip induced motion is always along $\langle 011 \rangle$ directions. Thus if the tip is rastered along the $[011]$ direction, the Br atoms move away from the tip along the orthogonal $[0\bar{1}1]$ direction (figure 3a). By contrast if the tip is rastered along the $[010]$ direction the Br atoms move in zig-zag tracks, alternating between $[011]$ and $[01\bar{1}]$ directions (figure 3b). Thus although the net motion is along the $[001]$ direction and is therefore again orthogonal to the scan direction, the Br atoms avoid direct hops in this direction. We have calculated the barriers to motion between fourfold hollow sites along $\langle 001 \rangle$ and $\langle 011 \rangle$ directions. The activation barrier is found to be much higher along $\langle 001 \rangle$. However the barrier to hopping along $\langle 011 \rangle$ is only 0.23 eV. This value is so low as to suggest that it should not be possible to image Br in fourfold hollow sites by STM at room temperature in the first place. The discrepancies between the calculations and

the experiments can be reconciled to some extent if it is assumed that Br atoms bound in Cu vacancy sites are imaged in the STM experiments.

2 Calculation Details

All the calculations were performed within DFT formalism [11,12] with a plane wave basis set and using pseudopotentials to describe the ionic potentials. The generalised gradient approximation (GGA) [13] was used for the exchange correlation potential. The plane wave code CASTEP [14–16] was used, this code is based on the iterative diagonalization of the Kohn-Sham Hamiltonian [17] in a plane wave basis using the ultrasoft pseudopotentials of Vanderbilt[18]. We have shown that this gives good values for the bulk lattice parameter and the bulk modulus (see table 1), the calculated lattice parameter is only 0.3% too small, whilst allowing a modest energy cutoff, 320eV, to be used.

The k-points used in the calculations were generated according to the scheme of Monkhorst and Pack [19]. For the bulk calculations a $16 \times 16 \times 16$ k-point mesh was used for the 1 atom primitive cell. For the surface studies a $12 \times 12 \times 1$ k-point mesh was used for the $p(1 \times 1)$ surface unit cell with equivalent meshes used in the larger cells. This k-point mesh was found to give well converged results when compared with calculations using a $16 \times 16 \times 1$ k-point mesh; the surface energy changes by less than 0.02 J m^{-2} . The surface calculations were all performed at the experimental lattice parameter of $3.615 \text{ \AA}$.

3 Results

There are three possible high-symmetry binding sites for bromine atoms on a copper (100) surface at low coverage: these are the fourfold hollow site, the twofold bridge site and the on-top site

(figure 1). We investigated the relative stability of the bromine atom in these three sites to determine the most stable surface site. In order to calculate the energies of the three sites a 7 layer thick $p(3\times3)$ cell of copper was used, containing 63 Cu atoms and a single Br atom. A vacuum layer equivalent to a further 7 layers was used to separate the surfaces. The top three layers of the copper and the bromine atom were allowed to fully relax whilst the lower layers were held fixed at the bulk separation. These results are compared against calculations using a $p(2\times2)$ cell to investigate the effects of any interaction between periodic images particularly due to strain in the copper lattice induced by large bromine atoms. The $p(3\times3)$ cell is equivalent to a $\frac{1}{9}$ of a monolayer coverage, the $p(2\times2)$ cell $\frac{1}{4}$ of a monolayer coverage, in both these cells no bromine atom is bonded to any copper atom that is also bonded to by a periodic image of the bromine atom. The results for the three sites using the two different cells are given in table 2.

The results demonstrate that for both the $p(3\times3)$ and $p(2\times2)$ cells, the binding energy for the fourfold hollow site is greater than for the twofold bridge site which is in turn greater than for the on-top site. The binding energies for the $p(3\times3)$ cell are greater than for the $p(2\times2)$ cell for the twofold bridge and on top sites, but the energy is somewhat smaller for the hollow site. However the dependence on surface coverage is not very strong with binding energy differences of less than 0.1eV between the two cells. This suggests that the binding energies would not change significantly using even larger supercells. Thus we can be reasonably confident that the $p(3\times3)$ supercell provides a reasonable basis for understanding the energetics of isolated Br atoms.

Referring to the results from the $p(3\times3)$ cell, the bromine in the hollow site forms directional bonds with the four surrounding copper atoms at a Cu-Br distance of 2.59 Å. This value may be compared with an estimate of 2.54 Å extrapolated from copper halogen bond lengths measured in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ reconstruction of Br and Cl [20] on Cu(111) and in the $c(2\times2)$ reconstruc-

tion of Cl [21] on Cu(100). For the case of the bridge sites the bond lengths were 2.38 Å and for the on-top site 2.30 Å. Thus the bond length increases as the coordination number increases as would be expected by bond order arguments. The binding energies for hollow, bridge and on-top sites are 1.94 eV, 1.71 eV and 1.57 eV, giving energy differences above the ground state of 0.23 eV and 0.37 eV for the bridge and on-top sites respectively.

To investigate whether these energies can be interpreted as activation barriers for motion of bromine atoms between fourfold hollow sites along $\langle 001 \rangle$ and $\langle 011 \rangle$ directions, we have calculated energies at intermediate points along the line joining fourfold hollow and bridge sites and the line joining bridge and on-top sites using a quasi-static approach. For convenience the calculations for the energy of the bromine as it moves along these lines were performed with the smaller $p(2 \times 2)$ cell. In addition the bottom copper layers were frozen. However as the bromine moves in the x-y plane its height and the positions of the copper atoms in the topmost atomic layer were allowed to relax. The results of these calculations are shown in figure 4. It can be seen that the bridge and on-top sites are stable local energy minima. The on-top site is in fact an energy maximum and the bridge site a saddle point. Thus the energy differences of 0.23 eV and 0.37 eV should represent the activation barriers for hopping of Br atoms between adjacent sites.

It is superficially gratifying to find that there is an anisotropy of $(0.37-0.24)$ eV = 0.13 eV in the barriers to hopping along $\langle 001 \rangle$ and $\langle 011 \rangle$ directions because this is at first sight consistent with anisotropy in tip induced hopping in STM. However, the very low magnitudes of the barriers suggests that the lifetime of a Br atom in a hollow site at room temperature should be much too short to allow observation of Br atoms of this sort in STM. The thermal hopping rate may be estimated crudely as the product of a frequency factor ν and a Boltzman factor $\exp(-\Delta E/kT)$. Since kT at room temperature is about 25 meV, the latter is about 10^{-4} . Values for the frequency factor can be derived in two

ways. Firstly the energy versus displacement curve in figure 4 can be interpreted in terms of a force constant of 4.54 Nm^{-1} for the parallel vibration of Br in the fourfold hollow site. Assuming that the mass of a Br atom can be used as the effective mass, this gives a vibrational frequency of $5.8 \times 10^{12} \text{ s}^{-1}$. Alternatively we can use the vibrational energy of 20 meV measured [22] by HREELS for Br on Cu(111). Although this energy is for a normal vibration on a different Cu surface, the associated frequency factor of $4.8 \times 10^{12} \text{ s}^{-1}$ is very close to that derived from our calculations. Based on these considerations it seems the frequency factor must be around $5 \times 10^{12} \text{ s}^{-1}$: it is inconceivable that the frequency factor can be below 10^{12} s^{-1} , giving a lifetime for Br in a hollow site at room temperature of at most 10^{-8} s . A lifetime of the order of 500 s is required to account for the observation that the Br features are stable in sequentially scanned STM images over periods of several minutes. This in turn implies a barrier to hopping of at least 0.85 eV or a very much lower frequency factor.

The calculations thus appear at odds with experimental observations on two counts. First the barrier to hopping is quantitatively wrong. Second the calculations appear to identify the wrong binding site: recall the experimental observation that Br induced features appear to occupy on-top for a wide range of different tip conditions [10]. Of course we could explain the STM observations in terms of contrast inversion of STM images of the Cu(100) substrate. Whilst atypical tip structures may occasionally produce contrast inversion in STM images, consistent and invariable inversion seems implausible.

A scenario where state-of-the-art density functional theory fails to reproduce the true activation barrier to Br hopping by at least 0.5 eV and there is consistent contrast reversal in STM seems untenable. The alternative is to question the interpretation of the original STM experiments. Surface EXAFS is clearcut in establishing that Cl on Cu(100) in the $c(2 \times 2)$ reconstruction occupies fourfold hollow sites [21] and we believe this must also be the case for Br on defect-free Cu(100). A simple way of accounting for the

registry in STM is to postulate that the Br atoms imaged by STM are not in hollow sites but are instead trapped by Cu vacancy sites. The Br then effectively replaces a Cu atom *within* the surface plane, rather than occupying a site *above* the plane of surface Cu atoms. The substitutional Br atoms are 8 coordinate. This structure has clear affinities with a substitutional $c(2 \times 2)$ reconstruction we have proposed [23] for Br on Cu(100) below half monolayer coverage. The Br in 8-coordinate substitutional sites is expected to be slightly larger than Cu [23] so that strain is introduced by this reconstruction, leading to a break up into islands which are arranged in a mesoscopic chequerboard superstructure. There are also affinities with structures proposed for Br on Ni(110) [24] and Pt(110) [25] where adsorbed bromine atoms occupy hollow sites but etch metal atoms out of the close packed rows to end up in sites flanked by an additional pair of in-plane metal atoms. In addition we note that Altman and coworkers have made extensive studies of Br and Cl on Cu(100) in the medium coverage regime using LEED, thermal desorption and STM [26–32]. It was found that STM imaging of adsorbate-induced superstructures was not possible for Br coverages below 85% of that required to saturate the $c(2 \times 2)$ reconstruction. This was ascribed to dynamic thermal fluctuations in the adsorbate layer below saturation coverage. The dynamic effects are strongly attenuated when the $c(2 \times 2)$ reconstruction completely covers the surface. At this stage step edges align along 100 directions rather than the 110 directions found on the clean substrate. These observations concur with the view that Br atoms which are not trapped in vacancy sites are highly mobile. The energy for creation of a Cu vacancy on the (100) surface is estimated to be 0.51 eV, so that at equilibrium at room temperature only 1 Cu site in 6×10^9 is empty [33]. Thus it is unlikely that an impinging Br_2 molecule will land near to a vacancy or that there will be many subsequent binary encounters between Br adatoms and vacancies. However we have seen that Br diffusion between four-fold hollow sites across Cu(100) surfaces should be rapid at room temperature and an adsorbed Br atom will be able to make its

way rapidly to up step edges, where substitutional incorporation into the next Cu layer is possible. This mechanism allows incorporation of In into the Cu(100) surface [34,33]. Moreover the activation energy for vacancy migration is only 0.29 eV. The resulting high mobility of the vacancies provides a mechanism for thermal diffusion of in plane Br atoms away from step edges via a “slide-puzzle” mechanism [34,33]. It is unclear to us at present whether surface Cu vacancies may be involved in the tip driven motion observed in STM experiments, but further calculations are in hand to explore the energetics of adsorption and diffusion of substitutional Br atoms on Cu(100).

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Fig. 1. Schematic diagram showing fourfold hollow, bridge and on-top binding sites for Br on Cu (100) and the $p(2 \times 2)$ and $p(3 \times 3)$ supercells used in the DFT calculations. The crystallographic axes used for the (100) surface are based on the bulk fcc cell.

Fig. 2. $3\text{nm} \times 3\text{nm}$ STM image of Br on Cu (100) taken at -20mV sample bias and a 1 nA tunnel current. The two Br-induced features appear as greyscale minima in the image. Note the apparent top registry between the greyscale maxima of the substrate and the Br induced features. Reproduced from reference [10]

Fig. 3. 5nm $\times$ 6nm images of Br on Cu (100) taken at a -10mV sample bias and a 3nA tunnelling current showing distinctive atom tracks due to tip induced motion. (a) image taken with the tip rastered along $[011]$ direction (b) image taken with tip rastered along $[010]$ direction. Images taken from reference [10].

Fig. 4. Graph showing the calculated variation in energy as a Br atom moves from a fourfold hollow site along a line to the bridge position and then from the bridge to an on-top site.

	a_0 (Å)	B_0 (GPa)
CASTEP	3.604	157
Experiment	3.615	171.5 ± 3.4

Table 1

Bulk properties of Cu as calculated in the present work compared with experiment. a_0 is the lattice parameter in Å, B_0 is the bulk modulus at the equilibrium lattice constant.

Site	Cell Size	Number of Layers	Binding Energy (eV)	Br-Cu distance (Å)	Height above Surface (Å)
Top	2x2	7	1.49	2.27	2.27
Bridge	2x2	7	1.83	2.40	2.03
Hollow	2x2	7	1.98	2.58	1.84
Top	3x3	7	1.57	2.30	2.30
Bridge	3x3	7	1.71	2.38	2.01
Hollow	3x3	7	1.94	2.59	1.81

Table 2

The binding energy, the bromine-copper separation and the height of the bromine above the surface for the bromine in the three sites. Results are given both for a $p(2 \times 2)$ and a $p(3 \times 3)$ cell