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First-principles study on the strain effect of the Cu(0 0 1)-$c(2 \times 2)$N self-organized structure

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Abstract

Nitrogen atoms adsorbed on Cu(0 0 1) surface are known to form a self-organized structure, in which islands of nitrogen-adsorbed region are arranged into a square lattice. To clarify the mechanism of the self-organization, the strain effect in this surface is investigated by first-principles theoretical calculations. The difference between the calculated surface stress of Cu(0 0 1)-$c(2 \times 2)$N surface and that of clean Cu(0 0 1) surface is in good agreement with the value estimated from experiments. In the stripe model of the self-organized surface, the top-most Cu atoms are largely displaced in lateral directions, while the nitrogen atoms at the edge of its nitrogen-adsorbed region slightly protrude in the surface normal. These results are consistent with observations. Spontaneous formation of the clean Cu region is also confirmed by calculating the formation energy within the stripe model. The formation energy is fitted well by a function deduced from the theory of elasticity. Nevertheless, the parameter of the fitting cannot be explained only by the difference of the surface stresses.

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Nitrogen atoms deposited on Cu(0 0 1) surface occupy the four-fold-hollow sites and form $c(2 \times 2)$N local structure[1–3]. This $c(2 \times 2)$N local structure forms islands on this surface. In a certain condition, these $c(2 \times 2)$N islands take ~ 5 nm^2 size and are aligned into a regular square lattice separated by a square network of thin and uncovered surface region [4]. This Cu(0 0 1)-$c(2 \times 2)$N surface is recently used as a nano-scale template to construct a lattice of nano-dots of magnetic elements [5,6]. These magnetic elements deposited on Cu(0 0 1)-$c(2 \times 2)$N surface prefer the crossing points in the network of uncovered Cu(0 0 1) region and form nano-dots there.

This self-organization is probably driven by two kinds of forces. One is the attractive interaction among

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nitrogen atoms on Cu(0 0 1) surface, which is mainly electronic one as we clarified previously [7]. The other is the strain generated by the $c(2 \times 2)$N island.

However, it is hardly tractable to perform a first-principles study on the whole $c(2 \times 2)$N island to obtain insight into the strain because of its size. Therefore, in the present study, we tackled the strain effect from two directions. First we examined the difference of the surface stress between the ideal $c(2 \times 2)$N structure and the ideal clean Cu structure. The difference is important since this is one possible explanation of the strain around the $c(2 \times 2)$N island. Secondly, we investigated energetics and structure relaxation of a periodic stripe model made of $c(2 \times 2)$N-adsorbed regions and clean Cu regions to clarify the effect in a tractable geometry. The normal of the boundaries of both regions is in the direction of $\langle 1\,0\,0 \rangle$. Therefore, the stripe is periodic along $\langle 1\,0\,0 \rangle$. In this paper, the period along $\langle 1\,0\,0 \rangle$ is expressed by l in units of a_{L}, the lattice constant of copper.[1]

In this study, the optimized atomic structures of the striped structures were obtained and compared with experiments. In addition, we obtained the energy to form the striped structure by extracting a line of nitrogen atoms from the ideal Cu(0 0 1)-$c(2 \times 2)$N surface. The formation energy (E_{s}) is

$$E_{\mathrm{s}}(l) = (l-1)E(c(2 \times 2)\mathrm{N}) + 2E(\mathrm{clean}) - E(\mathrm{stripe}; l), \quad (1)$$

where $E(c(2 \times 2)\mathrm{N})$, $E(\mathrm{clean})$ and $E(\mathrm{stripe}; l)$ are the total energy per unit cell of $c(2 \times 2)$N, clean, and striped structures, respectively.

The condition of the present first-principles calculation is as follows: the surface was simulated with symmetric slab models whose calculated atomic structures including those of the nitrogen atoms are symmetric about the fixed copper-atom layer at the center. With these slab models we performed a standard density-functional plane-wave-pseudopotential calculation. The Perdew–Burke–Ernzerhof (PBE) type exchange-correlation potential [8,9] was used. Cu and N atoms were simulated by ultrasoft pseudopotentials [10]. The cut off energy, E_{cut} of the plane wave basis set was 49 Ry. All of the available symmetries were utilized. To stabilize the calculation, the filling factors of eigenstates whose energy levels are close to each other within 10^{-4} Hartree (~ 3 meV) were smoothly averaged on each sampled k-point. (This averaging is only effective on the partially filled energy levels.) The decrease of the smoothing range to 10^{-5} Hartree did not affect the total energy of the $c(2 \times 2)$N structure with either non-deformed substrate nor substrate expanded by 2%.

For the calculation of surface stress, $c(2 \times 2)$ super cell was used. The number of the sampled k-points in the first Brillouin zone, N_k was 8×8. The thicknesses of the slab and the vacuum region were 7 and 11 atomic layers, respectively.

For the striped structures, the number of the sampled k-points along the stripes in the first Brillouin zone, N_{ky}, was eight. The numbers of the sampled k-points across the stripes, N_{kx}, were 6, 4, 4, 4 and 2 when l were 3, 4, 5, 6 and 8, respectively. The thickness of the slab and the vacuum region were seven and eleven atomic layers except for $l = 8$ stripe. For $l = 8$ stripe, they were nine and five atomic layers, respectively.

Atomic structures were optimized so that the maximal force acting on each atom (F_{max}) became smaller than 10^{-3} Hartree a.u.$^{-1}$. Judging from our previous calculation [7], the present condition for F_{max} is enough to obtain fully relaxed structures. Our calculation was performed with an extended version of Tokyo Ab-initio Program Package (TAPP) [11] which has been developed in our group. A preconditioning method for the updates of the local potential was utilized to accelerate the convergence [12].

Actual calculations of E_{s} were performed using supercells with the same size to minimize the error. In the calculations, the total energies of the slabs were divided by two since each slab has two identical surfaces.

The convergence of E_{s} was as follows: for the $l = 3$ stripe, the increase of E_{cut} to 64 Ry and the increase of N_{ky} to ten varied E_{s} less than 1 meV/a_{L}, respectively. The change of the N_{kx} to 4, 6, 2, and 2 for l are 3, 4, 5, and 6 varied E_{s} less than 7 meV/a_{L}. The variation of the thickness of the slab and the vacuum region for $l = 6$ to nine and nine atomic layers, respectively, varied E_{s} less than 2 meV/a_{L}.

In case of the stripe model of $l = 8$ with the clean Cu region of width a_{L}, the change in the displacement of the top-most copper atoms is less than 0.005 Å in

[1] Needless to say, the period along $\langle 0\,1\,0 \rangle$ of the unit cells of stripes is a_{L}.

$\langle 1\,0\,0\rangle$ direction even when the thickness of the slab is increased from nine to eleven atomic layers. The increase of the thickness of the vacuum region from five to seven atomic layers increased $F_{\max}$ by less than 10^{-4} Hartree a.u.$^{-1}$. The decrease of $F_{\max}$ to 0.5×10^{-3} Hartree a.u.$^{-1}$ displaced the top-most copper atoms less than 0.016 Å in $\langle 1\,0\,0\rangle$ direction.

The surface stresses of the clean and $c(2 \times 2)$N structure are obtained by expanding or contracting the unit cells of their slabs in $\langle 1\,0\,0\rangle$ direction. The total energy of a slab, E, as a function of the strain, u_{xx}, can be fitted with two parameters p and q as,

$$E(u_{xx}) = E(0) + 2A(\tfrac{1}{2}pu_{xx}^2 + qu_{xx}), \tag{2}$$

where A is the area of the surface of the slab. The prefactor two means that each slab has two identical surfaces. Here, q is the surface stress.

For the calculation of the surface stresses, the convergence was as follows: the decrease of E_{cut} to 42.25 Ry varied them less than 0.06×10^{-3} Hartree a.u.$^{-2}$. The increase of N_k to 12×12 varied them less than 0.04×10^{-3} Hartree a.u.$^{-2}$. The variation of the thickness of the slab and the vacuum region to nine and nine atomic layers varied them less than 0.02×10^{-3} Hartree a.u.$^{-2}$. $\Delta E = E(u_{xx}) - E(0)$ is shown in Fig. 1. The fairly good fitting results show that the convergence of the calculation is good enough.

The obtained surface stresses of $c(2 \times 2)$N structure and clean surface are -3.4×10^{-3} and 0.9×10^{-3} Hartree a.u.$^{-2}$, respectively. For clean surface, 0.886×10^{-3} and 1.350×10^{-3} Hartree a.u.$^{-2}$ have been previously reported by embedded-atom method [13] and modified embedded-atom method [14], respectively. The present first-principles result supports the former one. The negative surface stress of $c(2 \times 2)$N structure means that $c(2 \times 2)$N structure tends to expand on copper surface as it is believed. From the obtained surface stresses their difference $\delta\sigma$ is calculated to be 2.4×10^{-9}N/a_{L}, which is rather close to the experimentally suggested values, 2.2×10^{-9}[15] and 2.4×10^{-9} N/a_{L}[16].

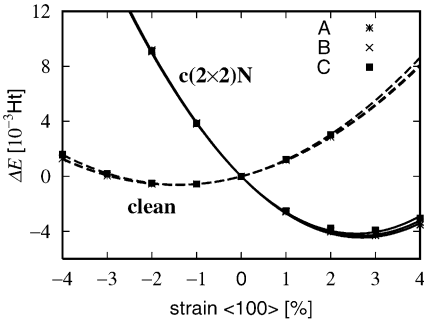

Fig. 1. Total energy variation as a function of the strain $\langle 1\,0\,0\rangle$ for $c(2 \times 2)$N structure and clean surface. The capitals in the figure specify the condition of the calculation. (A) $E_{\text{cut}} = 42.25$ Ry, $N_k = 8 \times 8$. (B) $E_{\text{cut}} = 49$ Ry, $N_k = 8 \times 8$. (C) $E_{\text{cut}} = 49$ Ry, $N_k = 12 \times 12$.

The obtained lateral displacements of the top-most Cu atoms of striped structures from the positions of clean surface are shown in Fig. 2 (a) and (b), where the widths of the clean Cu regions are a_{L} for (a) and 3 a_{L} for (b), respectively. This result is consistent with the experimental result in Ref. [15] which claimed the large root-mean-squared displacements at the very surface, 0.15 and 0.11 Å, depending on condition. Such large displacements are also found by an STM experiment [17]. The displacements are in the outward direction of the $c(2 \times 2)$N stripes and they are the largest at the edges of the stripes.

It is also found for the slabs in Fig. 2 (a) and (b) that the nitrogen atoms at the edges of the $c(2 \times 2)$N stripe protrude by 0.03–0.07 Å compared with the inner nitrogen atoms, while the height differences among the inner nitrogen atoms were less than 0.01 Å. Thus the nitrogen atoms at the edges are seen brightly in a simulated STM image of a stripe as shown in Fig. 2 (c). These results are consistent with an STM observation [17], while they mainly attributed the observation to an artifact of STM.

The obtained E_{s} is shown in Fig. 3. Positive E_{s} means the spontaneous formation of clean Cu regions in large enough $c(2 \times 2)$N islands.

From the theory of elasticity E_{s} should be fitted by,

$$E_{\text{s}}(l) = C_1 + C_2 \log\left(\frac{l}{\pi}\sin\left(\frac{\pi}{l}\right)\right), \tag{3}$$

which is derived for the $1 : l - 1$ striped structure [18–20]. Fitted lines are shown in Fig. 3. Since the fitting is fairly good, E_{s} is possibly understood by elasticity.

To consider the effect of the non-zero width of the clean Cu regions we also used another fitting function,

$$E_{\text{s}}(l) = C_1 - \frac{C_2}{6}\left(\frac{\pi}{l}\right)^2, \tag{4}$$

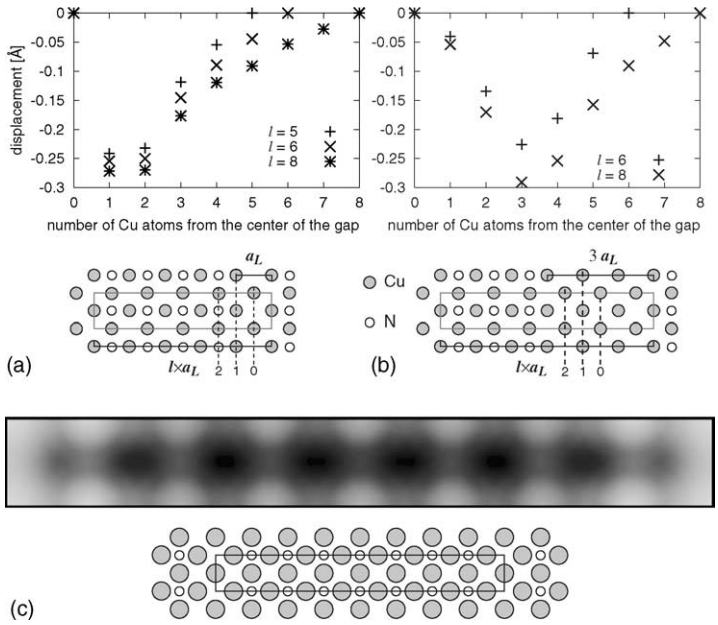

Fig. 2. (a, b) Lateral displacements of the top-most Cu atoms of stripes from the positions of clean surface toward the N adsorbed region. The widths of the clean Cu regions are a_L (a) and 3 a_L (b). (c) A simulated STM image of a $l = 8$ striped structure on the plane at a distance of 3 Å from unrelaxed clean surface with a sample bias of −0.5 V. The atomic structure of the striped structure is shown below with the frame of the image indicated by a rectangle. The nitrogen atoms which are adjacent to the clean Cu region protrude slightly.

which is derived for regularly arranged line defects on surface whose period is l. This corresponds to the situation when the width approaches zero ($\pi/l \to 0$).

The obtained fitting parameters for the fitting functions are shown in Table 1. Both fitting produced approximately equivalent results. Moreover, both fitting curves were hardly distinguishable in the figure. This means that the clean Cu region treated here can be understood as a zero-width line defect on the surface about elasticity. The fitting of data from $l =$ 4 to 8 is better than that from $l = 3$ to 8. This may be because both two nitrogen atoms in $l = 3$ stripe are on the boundaries. Judging from the height of the nitrogen atoms, the nitrogen atoms on the boundary have different character from that of the inner ones.

The stable period of the stripe is determined from E_s per a nitrogen atom shown in the inset of Fig. 3. The maximum is around $l = 4-5$. The experimental width of the island is $l \sim 14$. In the striped structure, the strain can be relaxed only one-dimensionally. We

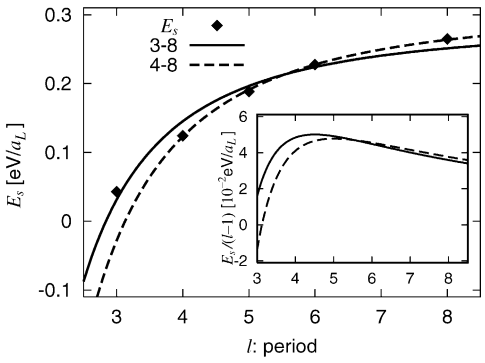

Fig. 3. E_s as a function of l. The solid line and the dashed line are fitted using the data from $l = 3$ to 8 and $l = 4$ to 8, respectively. Inset: E_s per a nitrogen atoms as a function of l derived from the fittings.

Table 1
The parameters, C_1 and C_2 for the fitting of E_s in units of eV/a_L

Fit by	Range of l	C_1	C_2
Eq. (3)	3–8	0.29	1.3
Eq. (3)	4–8	0.31	1.8
Eq. (4)	3–8	0.29	1.4
Eq. (4)	4–8	0.31	1.8

Eqs. (3) and (4) specify the fitting functions in the text.

suppose that experimental structures can grow wider since two-dimensional strain relaxation is more effective and the clean Cu region can be wider also.

Meanwhile, C_2 is obtained in a naive manner using the elastic Green's function of point force acting on a surface of an isotropic medium[18] as

$$C_2 = \frac{2(1-\nu^2)}{E\pi}(\delta\sigma)^2, \tag{5}$$

where E and ν are Young's modulus and Poisson's ratio of copper, respectively[21,22]. From the obtained $\delta\sigma$, $C_2 = 0.44$ eV/a_L. We also performed a finite-element calculation for elastic medium to take in the effect of cubic symmetry of copper crystal. From the calculation, $C_2 = 0.53$ eV/a_L. (The calculation with the elastic constants that corresponds to isotropic copper gives $C_2 = 0.46$ eV/a_L with the same condition of the calculation.) The reason of the difference of the values of C_2 may be an additional force that originates from electronic structure at the edges of $c(2 \times 2)$N stripe or surface specific elasticity of $c(2 \times 2)$N structure that are not considered.

In summary, the surface stresses of $c(2 \times 2)$N structure and clean Cu surface were obtained. Their difference was consistent with the experiments. In the striped structures with narrow and clean Cu regions, their top-most Cu atoms were largely displaced. From the formation energy of clean Cu region in the striped structures, its spontaneous formation was confirmed. The formation energy can be fitted by a function deduced from the theory of elasticity.

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