Atom manipulation of bright and dark spots on Cu(111) surface by scanning tunneling microscope*

Masanori Ono,[†] Takahiro Nishio, and Toyoaki Eguchi

Institute for Solid State Physics, the University of Tokyo, 5-1-5 Kashiwa-no-ha, Kashiwa 277-8581, Japan

Yukio Hasegawa

*Institute for Solid State Physics, the University of Tokyo,
5-1-5 Kashiwa-no-ha, Kashiwa 277-8581, Japan and*

PRESTO, Japan Science and Technology Corporation, Kawaguchi 332-0012, Japan

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Using a low-temperature scanning tunneling microscope, atom manipulations were performed on Cu(111) surface. We succeeded in manipulating single Cu atoms which were deposited on the Cu substrate at low temperature, and arranging them in an intended pattern. Besides the brightly contrasted Cu adatom, we also successfully moved single dark spots, presumably an adsorbed molecule of carbon monoxide, by using the same manipulation technique. [DOI: 10.1380/ejssnt.2004.165]

Keywords: Scanning tunneling microscope; Atomic manipulation; Copper adatom; Cu(111)

I. INTRODUCTION

In 1990, Eigler *et al.* [1] surprised the world by demonstrating a single atom manipulation. Using low-temperature scanning tunneling microscope (LT-STM), they moved several Xe atoms one by one on Ni(110) surface to create nano-size characters. A decade later the atom manipulation technique using scanning probe microscope (SPM) is one of the key technologies for constructing nanostructures in a bottom-up manner. It has been used to confine surface electrons [2], to form low-dimensional structures [3], and recently to investigate a frictional force in an ultimate atom-atom interaction [4].

In this paper, we present atom manipulation on Cu(111) surface. A designed pattern was formed by arranging Cu atoms which are intentionally deposited on the surface. We also demonstrate manipulation of darkly contrasted species. A motion of the dark spots in the manipulation process suggested us that those are adsorbates, not defects, and presumably CO molecules. This demonstrates capability of atom manipulation to identify unknown entities observed in STM images [5].

II. EXPERIMENTAL

Our experiments have been carried out using a commercial LT-STM produced by Unisoku Co.(USM-1300). The system can be operated in ultrahigh vacuum (UHV, $< 5 \times 10^{-9}$ Pa at room temperature), low temperature (cooled by liquid helium) and high magnetic field (up to 11 T). In fact, the vacuum around the sample must be further better because most of the residual gases have negligibly low vapor pressure at the liquid helium temperature. The sample temperature, which is measured with a resistive temperature sensor (Cernox, cx-1030), can be controlled from 3K to 30K by activating a heater or

FIG. 1: STM images taken during manipulation of single Cu atoms. A brightly contrasted Cu atom is moved from site A in (a) to B in (b). The atoms indicated with dashed circle C in (b) are accidentally transformed into the Cu cluster as shown as B' in (c) during moving tip from site C to B'. The parameters for the STM imaging are following; scanned area: $18 \text{ nm} \times 10 \text{ nm}$, I_t : 300 pA, V_b : 350 mV.

pumping liquid helium in a dewar like a lambda-point refrigerator. The magnetic field up to 11 T can be applied perpendicular to the sample surface by a superconducting coil.

In this study, we used an electrochemically etched polycrystalline tungsten tip as a probe. After degassing in the UHV chamber, the oxide layer on the tip was removed by field evaporation with *in-situ* field ion microscope (FIM).

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[†]Corresponding author: m-ono@issp.u-tokyo.ac.jp

FIG. 2: Using the atom manipulation technique an alphabet letter of 'M' was constructed. These images are parts of a series of the STM images taken at intervals in each step of the construction process. A large bright protrusion pointed by a green arrow in (a) indicates identical sites in these images as a marker. A yellow arrow is one example of dark spots. The imaging parameters are $10\text{ nm} \times 12\text{ nm}$, $I_t = 250\text{ pA}$, $V_b = 200\text{ mV}$. A complete set of the drift-corrected images is shown in a form of animation, which you can find in the electronic appendix.

Before introduced into the UHV chamber, the Cu(111) sample was etched electrochemically using nitric acid solution. Clean Cu(111) surface was prepared by repetitive Ar-ion sputtering and annealing around 750 K. We confirmed the cleanness of the Cu(111) surface by STM observation.

In order to locate individual metal atoms on the metal substrate the substrate has to be cooled down during the deposition, because at room temperature (RT) deposited metal atoms diffuse over the surface and stick each other to make clusters or islands. During the copper deposition the substrate was refrigerated on a stage cooled by flowing liquid helium. The substrate temperature was kept below 30 K during the deposition, which was measured with AuFe(0.07%)-chromel thermocouple.

III. RESULTS AND DISCUSSIONS

An atom manipulation process performed in this study is basically the same method as that developed by Eigler *et al.* [1]. The tip is set above an atom we wanted to move. Then the tip is moved vertically toward the target atom by increasing the tunneling current with the STM feedback circuit kept active, until significant interaction is formed between the tip and the atom. We can detect the interaction formation by monitoring the tunneling current: A wave form of the tunneling current changes at

the moment of the atom trapping. One can thus judge whether the atom is trapped or not by listening sound produced with the current. With lateral motion of the tip below which the target atom is trapped, the atom moves following the tip. After being moved to a designated site, the tip is retreated back to normal tunneling condition, releasing the atom from the trapping. Before and after the controlled tip motion, STM images are taken to check whether the atom was indeed moved in an intended manner.

A series of STM images demonstrating our atom manipulation of copper atoms on the Cu(111) substrate is shown in Fig. 1. The sample bias voltage (V_s) and tunneling current (I_t) was set at 370 mV and 300 pA, respectively for the imaging. In these images the smallest bright protrusions are single Cu atoms and large bright spots are Cu clusters. In addition to those bright features, there are some dark spots. Using the atom manipulation method mentioned above, we moved a single Cu atom on the surface as is shown in the STM images.

From Fig. 1(a) to (b), one atom is moved from site A to B. And then the atom at site B formed a cluster by collecting atoms around site C (Fig. 1(b) and (c)). In the upper left of the images there is a monatomic step acting as a marker to prove the identical location.

According to Hla *et al.*[2], tunneling resistance (R_t), which is a measure of the distance between the tip and sample, is a key parameter deciding whether the atom will

FIG. 3: The manipulation of a dark spot indicated by green arrows. The dark spot is moved downwards from (a) to (b).

follow the tip motion when the tip is laterally moved. In our manipulation process, we fixed the target atom with a parameter of $V_s = 1$ mV and $I_t = 6 \sim 8$ nA. These values corresponds to a tunneling resistance of $R_t \sim 142$ k Ω , comparable to that reported for the case of Ag atom on Ag(111) surface ($R_t = 210 \pm 19$ k Ω) [2]. In our case, however, a hysteresis is found in the tunneling current at the trapping and releasing of an atom: For instance, with a sample bias voltage of 1 mV, we usually need to raise the current more than 6 nA for trapping an atom, but the atom cannot be released until the current is lowered less than 5 nA, suggesting additional factors are involved in our manipulation process different from the reported one.

To demonstrate capability of our setup to move single atoms as we desire, we constructed a shape of an alphabet letter 'M' (the initial letter of one of the authors) by arranging atoms one by one by the manipulation technique (Fig. 2). As is the case of Fig. 1, STM images were taken sequentially at an interval of each step of the construction process (I_t : 250 pA, V_s : 200 mV, scanning rate: 4 min/frame), and some of them (not all) are shown in Fig. 2. An animation of sequential images taken during the manipulation process is found in the electronic appendix. A large bright Cu cluster pointed out with a green arrow in Fig. 2(a) works as a marker.

In the cases of both Fig. 1 and Fig. 2, the observed area shifts slightly during each manipulation processes. This is not due to thermal drift, since the identical area can be imaged even after several hour interval. The image shift is probably induced by creep or hysteresis of a piezo actuator used for the STM scanning. This occasionally causes accidental unexpected cluster formation, as shown in Fig. 1, and creation of distorted pattern like the case of Fig. 2. During the formation of the 'M' character, 2-atom clusters are occasionally formed by the reason mentioned above. Since we wanted to make the character with single atoms and the dimers cannot be dissociated by the manipulation technique, we moved them away from the construction site when they are formed.

After deposition of Cu atoms we found not only Cu atoms and clusters but also darkly contrasted spots in the

STM images, as is pointed out with a yellow arrow in Fig. 2(a). As shown Fig. 3, the dark spot can also be moved by sliding the probe tip over the spot. In the present case we slid the tip from the upper to lower positions in the image over the spots, and the spot moved in the same direction. If the dark spot is a defect, the motion of the spot means that the original defect site is filled with an atom which was originally situated at the newly formed defect site, that is, the involved atom moved in the direction opposite to the tip motion. Since such motion is not likely to occur the assumption that the dark spots are due to defects can be ruled out. The manipulation process provides us a hint on an identity of the unknown species. They are presumably adsorbates on the surface.

We speculate that the dark spots are carbon monoxide molecules since the image contrast is quite similar with those reported previously [6]. Because of the reduced local density of states, the adsorbates look darker than the substrate on Cu(111) surface. The number of the spots decreases when the substrate was heated up slightly (~ 150 K), which is consistent with the previously reported desorption temperature [7]. The CO molecules probably came from the inside wall of the UHV chamber by a heating during the Cu deposition.

IV. CONCLUSIONS

By using a low-temperature STM we succeeded in manipulation of single Cu atom and presumably CO molecule, demonstrating a construction of atom-made nano letter 'M' using 11 Cu atoms. This technique will make us possible to control and manipulate electron motion, which is crucial for investigation of nanometer scale science.

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