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Study on the local barrier field variations for electron tunneling in field ionization at a step edge of W(112) with a micro-probe hole field ion microscope

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The local field ion densities of W(112) surface have been observed using a micro-probe hole field ion microscope (μ PH-FIM) combined with a pulse counting analysis. The mapped field ion densities clarified the anisotropic emission property within a single bright spot of a surface W atom site at a step edge. Based on the most relevant formula for tunneling barrier strength provided by B. Halpern and R. Gomer, we derived the local “across-atom” barrier field variations in the same step edge area. We found that the location of maximum barrier field strength is noticeably shifted towards the step side, rather than being on the top of the substrate surface atom site. The result indicates that the locus in which most highly promoted field ionization events take place is much smaller than previously estimated because of the extremely localized barrier field produced by the field adsorption of helium imaging gas atom.

1. Introduction

Field ion microscopy (FIM), the development of which was earlier than Scanning Tunneling Microscopy (STM) by about three decades,¹⁾ provides a direct method of examining the atomic structure of metal surfaces. Just like STM, FIM images are quite straightforward to understand the existence of atoms and to see how atoms are arranged in real space on metal surfaces. Contrary to the simplicity of getting the images of atom, there has been a long-drawn-out debate on the questions concerned with field ion image formation, such as why two adjacent surface atoms are imaged with different contrast or why the addition of a trace of second gas atom in the presence of the principal imaging gas atom improves the quality of FIM image.²⁾ In this context, with the recent advent of remarkable progresses in both theory and experiment, it is now well established that the local field ionization density (FID) variations, within any very small area of the image, is chiefly determined by the electron transition rate constant variation for field ionization (FI) across the surface at least at normal operating temperatures (near 20 K or above).^{3,4)} Since the electron transition rate constant for FI is defined as an amount of field ionized gas atoms generated per unit volume per unit time near some point in space and thus depends on the electric field at that point, the local image contrast in field ion micrographs could be regarded as the reflection of relative amplitudes of the lateral field variations across the surface. It should be noted here that the key parameter for electron tunneling is the net volume of potential barrier that determines the transmission of electrons. Particularly, at a protruding atom site, classical electrostatic theory and simple consideration of topological effects tell us that considerable narrowing of spacing between the adjacent equipotential lines occurs and the local field enhancement is promoted. Consequently, the width of potential barrier above the protruding atom will be reduced locally and the tunneling rate constant for FI will increase. Field enhancement calculations based on the classical electrostatic model of a hemisphere on a flat plane or on a curved surface have been

performed and estimated the values of field enhancement factor to be in a range of 1.0 to 3.0.⁵⁻⁷⁾ However, such calculations are inadequate to deal with the effect of redistribution of electron charges in a protruding atom under the external field and thus overestimate the field enhancement factor. Self-consistent calculations based on a model of a single adatom on a flat jellium surface have revealed that the partial field penetration into the adatom could reduce the field enhancement factor from the classical value.⁸⁾ A further atomic scale field enhancement effect has been predicted to arise at a step on a planar surface by density functional calculations.^{9,10)} The results indicated that substantial charge redistribution in the vicinity of the step edges could be induced by the application of external field. These theoretical works were building better “atomic-view” models of local image contrast involving new analyses of charged surface as well as renewed Jeffreys-Wentzel-Kramers-Brillouin (JWKB) type rate constant formula. Unfortunately, experimental data that enable us to make a detailed examination of field variations across a single surface atom have not yet been reported on the extent of the local FID variation in last two decades.

Now, with the questions of how the presence of field adsorbed imaging gas atoms at protruded surface atoms produces a further atomic scale field enhancement effect and how the mapped barrier field variations relate to the surface electronic structure, it is of great interest to conduct a reliable high precision experiment on local FID in the vicinity of a single surface atom site. Particularly, we are interested *not* in a change in FID between two separate bright spots in FIM image *but* in a variation in FID between two different characteristic points over a single surface atom site.

In this paper, we report experimental results of our μ PH-FIM mapping of local FID variations at a step edge site of W(112). The mapped FIDs clearly show a site-specific strong spatial anisotropy above a step edge atom, unlike the usual concentric bright spot obtained with the conventional fluorescent screen. We found that this anisotropic emission

is caused by the extremely site-specific localization and amplification of barrier field for electron tunneling produced by the field adsorption of helium imaging gas atom on the substrate tungsten atom. By analyzing the mapped FIDs data based on a most relevant and the “best simple” barrier field model proposed by Halpern and Gomer,¹¹⁾ we derived the detailed geometric configuration of field adsorbed helium atom on the metal surface atom at a step edge site.

The results will stimulate further renewed interest in developing and/or re-examining surface FI theory that could explore accurate knowledge of the detailed electronic structure of highly charged metal surfaces. Moreover, the precise information on the local barrier field variations would be greatly helpful to improve reconstruction process in atom-probe tomography in which our knowledge of the degree of uncertainty in electrostatic field at each *individual* surface atom site severely affects the preciseness of placing the field evaporated ions on the correct lattice sites in the specimen.

2. Experimental

Figure 1 is a schematic diagram of our home-made μ PH-FIM combined with a pulse counting analysis.¹²⁾ The spectrometer could pulse count the field ions emitted from a sample surface inside the circular area with a diameter of 30 μ m by utilizing the idea of spatial selectivity adopted in the atom-probe technique. The magnification ratio of the spectrometer ($\sim 1.7 \times 10^6$) was evaluated from the comparison of the observed FIM image with the known lattice structure of a tungsten sample. The detection area of this size is only about 12 % of the area occupied by a single tungsten atom on a sample surface, which ensures that we could collect the field ions at most from sixteen different sampling positions as coming from separate points within a specific single bright spot area under study. The probe hole which was fabricated as a circular through-hole in the center of a stainless steel electrode using a focused ion beam equipment serves as the entrance

aperture to the flight tube region with a single ion detector at the end. The two-stage microchannel plate in a chevron configuration was used as the detector to convert an ion impact into an electric pulse signal, and randomly arriving pulse signals were recorded as a function of time. Therefore, we could analyze the recorded data not only as an array of pulse signals which directly tells us about the time intervals between the actual instant of field ion production but also as the net amount of ions produced during a certain period of time that accounts for the yield of field ions. The probe hole electrode was manually manipulated within a plane (x - and y -directions) perpendicular to the beam line (z -direction) of the field ions, and its displacement is operated both in x - and in y -direction independently with the micrometers. The minimum displacement accuracy in x -direction is 10 μm which corresponds to the maximum movement error of the center position of detection area by 6 pm. Similarly, the minimum displacement accuracy in y -direction is 25 μm which corresponds to the maximum movement error of the center position of detection area by 15 pm. In the present experiment, considering the fact that the detection area of our spectrometer is a circle of 30 pm in diameter, the distance between the two adjacent sampling positions of FID in x -direction over a single surface atom is set to be 60 pm and y -direction over a single surface atom is set to be 75 pm, thereby avoiding the overlap of detection area.

Other experimental procedures generally follow in accordance with the normal FIM operation. The spectrometer has a base pressure of about 3×10^{-7} Pa and helium was admitted as an imaging gas into the vacuum chamber to a pressure of approximately 5×10^{-3} Pa for obtaining the field ion images. FIM tips of polycrystalline tungsten with a diameter of 0.2 mm were electrochemically polished in a solution of 1N of KOH. The tips so prepared were ultrasonically rinsed in ethyl alcohol before loading into the UHV chamber. The tips were then mounted on a pre-cooled stage (~ 80 K) with the gimbal mechanics in the UHV chamber and in turn field evaporated until an atomically clean

surface with a well-developed endform is obtained prior to an FIM measurement. Thus, all the FIM images presented in this paper were observed at a temperature of approximately 80 K with helium imaging gas ambient. An applied voltage to the FIM tip for imaging was chosen to give the best resolution (the best image voltage: BIV, which thereby gives the best image field: BIF).

3. Results and discussion

Figure 2 shows a portion of a W(112) field ion micrograph where the images of individual atoms are seen. This micrograph was taken at BIV=4.91 kV. In the present study, we have measured the variations of FID inside the area enclosed by a red colored rectangle. This region of interest (ROI) contains a step edge atom that is located in the upper-terrace side of the (112) plane and is on the line of the $\langle 111 \rangle$ crystallographic direction. The field ion image is a map of the protruding atoms on the sample surface and the arrangement of the bright spots on the microscope screen is the copy of crystallographic lattice site of the sample surface.

Figure 3(a) is the two-dimensional map of FIDs around the step edge atom designated by the ROI in Fig. 2. The label (+) defines the center position of tungsten nucleus at the step edge site. The left-hand side from this atom is the direction towards the center of the upper terrace, while the right-hand side is the step-down direction towards the lower terrace. The sampling positions of each FID are indicated by small black dots with approximately 50 pm spacing. Fig. 3(b) is the cross section of FIDs taken along the line (white solid line) in Fig. 3(a). The line is drawn as passing through the maximum position of FIDs. The origin of the horizontal axis corresponds to the center position of tungsten nucleus at the step edge site. As is clear from Figs. 3(a) and 3(b), FIDs show the characteristic features in spatial variation around the step edge atom. Looking at the behavior of FIDs from the peak position, the decay of FIDs towards the center of the upper

terrace (the first layer facet) is relatively slow and their profiles extend over the middle point of the adjacent inner facet atom. On the contrary, the decay of FIDs towards the step down direction from the peak position of FIDs is surprisingly fast. In addition, the most prominent feature in the step-down direction is that the intensive quantities of FIDs are maintained about 120 pm away from the position just above the tungsten step edge atom and then rapidly diminish in confined space down to the lower terrace. In this way, mapped FIDs with the μ PH-FIM clearly show a strong spatial anisotropy around the step edge atom, unlike the usual concentric bright spot obtained with the conventional fluorescent screen.

Following the well-established formalism of field ionization based on the most relevant expression for the tunneling barrier strength provided by Halpern and Gomer,¹¹⁾ the local FID measured with our μ PH-FIM spectrometer is given as the one-dimensional approximation by

$$I_{\text{FID}} = C \cdot P_e , \quad (1)$$

where C is the concentration of imaging gas atom at some point in space where the field ionization takes place and P_e the electron transition rate constant, respectively. Here, P_e is given by

$$P_e = \nu_e \cdot D(F_b) , \quad (2)$$

where ν_e is the expected number of tunneling attempts per unit time being estimated using a Bohr orbit,¹³⁾ and $D(F_b)$ is the JWKB barrier penetration probability. Note that P_e depends on the gas atom position in space at the instant of ionization via the position dependence of F_b . As for the position dependence of C , it is confirmed that, at least in the quasi-thermodynamic-equilibrium approximation, gas distribution effects at two adjacent characteristic points in the closely defined area of an image spot is quite small at operating temperatures near liquid-nitrogen temperature¹⁴⁻¹⁶⁾ as in the case of the present study, so that the local FID variations would be determined primarily by the variations of P_e .

The barrier penetration probability $D(F_b)$ can be expressed in the form,¹¹⁾

$$D(F_b) = \exp[-(b/F_b)(\nu_{\text{FI}}I_1^{3/2} - \phi_S^{3/2})] , \quad (3)$$

where b is the second Fowler-Nordheim constant. The constant $b \equiv (4/3)(2m_e)^{1/2}/e\hbar$, where e is the elementary charge and m_e is the electron mass. Its value is $b \cong 6.830890 \text{ (eV)}^{-3/2} \text{ V/nm}$. The parameter F_b is the surface “barrier field” that defines the tunneling barrier and is physically some sort of *average field* between the critical surface (i.e., the location of the imaging gas atom nucleus when field ionization occurs at the closest permissible distance) and the end of the tunneling barrier that is closer to the metal surface. The parameter ν_{FI} is a correction factor associated primarily with the particular shape assumed for the tunneling barrier which has been called the “Burgess correction” in Ref. 17 and now is known to be a special solution of the Gauss Hypergeometrical Differential Equation.^{18,19)} In the case where helium is used as an imaging gas and in the BIF condition, ν_{FI} takes the value of about 0.51. The parameter I_1 is the effective first ionization energy of the imaging gas atom, and ϕ_S is the work function of the metal. Note that, for helium at the BIF condition and with a value of local work function of tungsten, the following values are obtained: $\phi_S = 4.6 \text{ eV}$,²⁰⁾ $\nu_{\text{FI}}I_1^{3/2} \approx 62.4 \text{ (eV)}^{3/2}$ and $\phi_S^{3/2} \approx 9.7 \text{ (eV)}^{3/2}$. Therefore, the first term in Eq. (3) dominates the variations of $D(F_b)$. In addition, if we take account of the argument that the parameters ν_{FI} and ϕ_S are slowly varying quantities across the region of space above an imaged emitting atom,^{18,19)} the variations in $D(F_b)$ are primarily driven by the variations in the $1/F_b$ term. Therefore, the interpretation that the FID data in FIM primarily map barrier field variations is plausibly acceptable.

Figure 4 is a map of surface barrier field (F_b) variations calculated from Eqs. (1), (2), and (3) of the same area shown in Fig. 3(a) and the typical values of F_b are denoted at several positions within the area. In this calculation, a small dipole is superimposed above the protruding substrate atom to reproduce the local field enhancement effect observed in the map of FIDs. For comparison, we also calculated the electric field variations above the

“bare” protruding substrate atom without any extra dipole field caused by the field adsorbed atom and the result is shown in Fig. 5. It is apparent that the simple concentric distribution with small amplitude of decay in field strength centered just above the position of substrate atom nucleus is formed. Therefore, this symmetric field distribution seems unlikely to become any cause of the anisotropic distribution of FIDs. These results confirm that field adsorption of imaging gas atom plays an essential role of amplifying image contrast by increasing F_b at the critical surface, then by affecting the barrier penetration probability $D(F_b)$, and eventually by increasing the electron transition rate constant P_e .

Moreover, it is of great interest to note that the location of maximum F_b exhibits a noticeable shift towards the step side with a lateral distance of about 60 pm away from the top position of the substrate tungsten atom underneath, as is also shown in Fig. 4. Since the background field variations produced in space across the “bare” substrate atoms without field adsorption are basically identical both in Fig. 4 and Fig. 5, there is no doubt that the image gas atoms do not simply reside on the top of the substrate atoms, but change their sitting configuration most appropriately adjusting for field adsorption under the given field conditions. Taking account of the argument that helium imaging gas atoms are field adsorbed at high field site above metal substrate atoms,^{21,22)} the most probable interpretation for the configuration of field adsorbed helium atom that could cause the shift of maximum barrier field location would be the case where the polarized helium gas atom under high field is field adsorbed pointing its one end towards the position just at the high field site above the substrate tungsten atom and is aligned along the field line pointing its other end outwards in vacuum. Note that the highest electric field direction above a metal substrate atom produced by the applied tip voltage does not necessarily coincide with the direction perpendicular to the facet that includes the metal substrate atom, but rather orients towards the most protruding direction outside the sample surface. With various possible attempts concerned with the alignment of polarized helium atom during the

calculations to reproduce the map of FIDs (Fig. 3(a)), we obtained the following important result on the detailed configuration of field adsorbed helium atoms on the substrate surface atoms, i.e., the dipole model of the polarized helium gas atom adsorbed at the high field site above the step edge atom with a tilted angle of $9.45 \pm 1.38^\circ$ and the electric dipole moment of $\rho_{\text{He}} = 0.36 \pm 0.02 \text{ D}$ ($1\text{D} = 3.33564 \times 10^{-30} \text{ C} \cdot \text{m}$) gives the best match between the simulation and the observed map of FIDs with the accuracy of more than 95 % over all 88 sampling points inside the ROI ($600 \text{ pm} \times 525 \text{ pm}$). Cross section of the geometric configuration of helium atom adsorption on the tungsten substrate atom in the layer that contains the center of the substrate tungsten atom nucleus and that of the dipole moment of helium atom is depicted in Fig. 6 with the best match parameters determined in the calculation.

In the above discussion of Eq. (3), the interpretation that a FIM primarily maps barrier field variations is plausibly acceptable. However, that argument could be done by assuming the parameters ν_{FI} and ϕ_{S} are slowly varying quantities across the region of space above an imaged emitting atom. As mentioned above, ν_{FI} is purely mathematical quantity and the exact mathematics of the function ν_{FI} is well established.^{18,19)} On the contrary, ϕ_{S} is a “real” physical quantity that relates to a work function of substrate surface. In our calculations, ϕ_{S} is treated as a free parameter to obtain the best match between the simulation and the observed map of FIDs, and the map of ϕ_{S} is shown in Fig. 7. In the upper terrace area (the left-hand side from the label (+) atom), ϕ_{S} exhibits slow variations, which is in good agreement with the above mentioned argument about the behavior of ϕ_{S} across the surface atom. On the contrary, at the step edge side, ϕ_{S} shows an abrupt decrease towards the step down directions. Generally, the kinetic energy of the electrons largely determines the nature of surface electronic properties by influencing the charge distribution at metal surfaces. In other words, the electron charge density is likely to be less corrugated to achieve lower kinetic energy of the electrons, and then to minimize

the total energy of the surface. Following this explanation, surface protrusions such as steps should induce charge transfer towards the step down direction forming a relatively “smooth” electron distribution at step edge site. Consequently, the resultant step dipole formation reduces the local work function $\phi_s^{23)}$ at the upper step edge as observed in Fig. 7.

4. Conclusions

We presented a novel method to measure the spatial variations of FIDs on the atomic scale over a single atom at the step edge site on W(112) with a μ PH-FIM combined with a pulse counting analysis. Our spectrometer could realize pinpoint measurement of FIDs at a specific atom site on sample surface. In fact, we clearly observed the anisotropic emission property of field ions within a single bright spot of a surface tungsten atom site at the step edge. The mapped barrier field variations indicates that field adsorption of imaging gas atom plays an essential role of forming extremely localized barrier fields and the barrier field variations are much more greater than previously realized. By analyzing the data, we have obtained the detailed geometric configurations of field adsorbed helium atom on a substrate tungsten surface atom.

At present, we do not fully understand how the barrier field strength is locally affected by the surface electronic structure. In particular, we need greater understanding of the effect of field adsorption on the barrier penetration probability to build an accurate model of the field adsorption state itself. Although the conditions of field adsorption at each surface atom site differ from one place to another, the progress of this type of discussion could eventually lead us to the development of better charged surface models. For this purpose, further experimental and theoretical studies are strongly desired.

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Figure Captions

Fig. 1. Schematic diagram of μ PH-FIM system combined with a pulse counting analysis.

Fig. 2. Portion of a W(112) field ion micrograph taken at BIV=4.91 kV with helium imaging gas. The region of a red colored rectangle corresponds to a ROI where the variations of FID were measured.

Fig. 3. (a) Two-dimensional map of FIDs around the step edge atom designated by the ROI in Fig. 2. The label (+) defines the center position of tungsten nucleus, and the white dotted lines displays the radius of each tungsten atom (137 pm) and the step edge of the W(112) surface. The sampling positions of each FID are indicated by small black dots with approximately 60 pm spacing in x -direction and 75 pm spacing in y -direction. (b) Cross section of FIDs taken along the line (white solid line) in Fig. 3(a).

Fig. 4. Map of F_b variations derived from Eqs. (1), (2), and (3) of the same area shown in Fig. 3(a). The white dotted lines are the same as those in Fig. 3(a). The numbers in the map are the values of F_b (V/nm).

Fig. 5. Colored and contour map of electric field variations above the “bare” protruding substrate atom without any extra dipole field caused by the field adsorbed atom. The white dotted lines are the same as those in Fig. 3(a). The numbers in the map are the values of calculated electric field (V/nm).

Fig. 6. Cross section of the geometric configuration of helium atom adsorption on the tungsten substrate atom in the layer that contains the center of the substrate tungsten atom nucleus and that of dipole moment of helium atom. Best match values of dipole moment

configuration for helium atom adsorption are indicated within the figure.

Fig. 7. Colored and contour map of the ϕ_S variations obtained in the best match conditions between the simulation and the observed map of FIDs (Fig. 3(a)). The white dotted lines are the same as those in Fig. 3(a). The numbers in the map are the values of ϕ_S (eV).

Fig. 1.

Fig. 2.

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7