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Scanning Tunneling Microscopy Measurements of the Local Work Function around Steps on the Au/Cu(111) Surface*

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With a scanning tunneling microscope we have taken local work function images of the Au/Cu(111) surface. The local work function measured from large Au-covered terraces is in good agreement with the result obtained by non-local techniques, and the local work function around step edges is significantly lower than that on terraces. The experimental details of the local work function lowering around a step can be reproduced nicely with a simple simulation if a dipole moment row with a proper linear density is put at the center of the step and if the influence of the topographic change of the step due to formation of the dipole moment is taken into account. It is demonstrated that STM has the ability to reveal the details of how local work function varies around steps and other defects on metal surfaces.

KEYWORDS: local work function, scanning tunneling microscopy, surface steps, gold, copper

1. Introduction

Basically, work function is a macroscopic value; which is defined as the minimum energy needed to remove an electron from the material and to bring it far away from the surface. As one of the most fundamental properties of surfaces, work function is involved in many surface phenomena, such as adsorption, desorption, electron emission etc., in which electrons come in or out of surfaces.1) Although it has thus been extensively studied, there still remains difficulty in determining its value accurately by experiments and understanding its physics. One of the experimental problems arises from the fact that work function depends on both chemical (elemental) and structural (morphological) properties of surfaces. One way to solve this problem is measuring work function locally and studying local work function of each structure (terrace, adsorbates or steps).

Local work function has been measured with several techniques. Photoemission from adsorbed xenon atoms (PAX) has been used to measure the potential that xenon atoms feel on surfaces, and to investigate the potential difference between terraces and steps.2) Recently, it was demonstrated that 2 photon photoemission (2PPE) is quite powerful for measuring local work function very precisely.3) It measures image states localized on each atomic layers, and from the data the dependence of work function on Ag thickness on a Pd(111) surface was deduced. Although these techniques are quite useful for measurement of work function of surfaces they are not powerful enough to reveal local work function because of the lack of a high spatial resolution. Recently, we demonstrated that scanning tunneling microscopy (STM) can be used for measuring local work function in nano-scale spatial resolutions.4) Using the method we can directly find correlation between the work function and local chemical and/or structural properties of surfaces.

As an intrinsic morphological property of surfaces, steps are attracting more and more interests of physicists due to their interesting and important properties.5-8) Previous studies showed that steps could affect the growth of crystal materials, adsorption, diffusion and catalytic reaction kinetics, etc..5-7) Recently, steps are found to act as barriers for surface electrons, and this property is utilized to confine them and form structures of low dimensionality.8)

Steps also have some influence on the local work function of metal surfaces. Previous works on stepped surface showed that the work function decreases linearly with increasing step density.9) The effect were interpreted by the so-called "smoothing effect".10) Since on metal surfaces the lateral density variation of electrons is smoother than that of the atoms electric dipoles, which has a sign opposite to that of the surface dipole, may form at places where some surface atoms protrude and, as a result, the work function becomes smaller for rough or stepped surfaces.9,10) However, these works were not able to disclose how the work function varies around individual monatomic steps and how far the influence of a monatomic step on the local work function can extend. However, such information is important if one wants to know the local modifications of surface properties due to steps as well as the physics of local work function.

In this paper, we will report local work function measurements around the step edges using STM with a sample of Au/Cu(111). Our measurements show that work function around step edges is lower than that on terraces. The mean full width at half minimum (FWHM) and depth of the low work function troughs at Au-Au monatomic steps are 6.5 ± 1Å and 0.9 ± 0.3 eV, respectively. This agrees well with the simulation in term of the formation of dipole moment at step edge and influence of topography. This work suggests that the influence of step dipole moment on local work function can extend to about 10 Å on both sides of the step edge and that STM is able to reveal the details of how local work function is related to morphology of metal surfaces.

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2. Experiments

All experiments described in this paper were done with our home-made UHV-STM system,11) which has a base pressure lower than 1×10^{-10} Torr. The Cu(111) sample was cleaned in situ by several cycles of Ar^+ bombardment and annealing at 500°C. Gold was deposited onto the clean Cu(111) surface at room temperature from an evaporator consisting of a Au wire wrapped with a piece of Ta foil. The deposition rate was about 0.2 ML/min (for the calibration, see below). The pressure during deposition was kept lower than 8×10^{-10} Torr. A [111]-oriented single crystalline tungsten STM tip was used. Since work function is closely related to the tip condition in-situ tip cleaning function is quite important for obtaining stable and reliable work function images. The field-ion microscopy (FIM) function equipped in the vacuum chamber was thus used to clean the tip in-situ. The constant-current mode was used throughout the work, and the sample was kept at room temperature during measurements.

The work function is measured by applying a small sinusoidal voltage to the z-piezo to give the gap distance s a small modulation ds and then measuring the small response variation in the tunnel current d(lnI) by means of a lock-in amplifier.12) The work function then can be calculated simply using the formula of $\text{Ø} = 0.95[d(\ln I)/ds]^2$. 12) To obtain a local work function image simultaneously with a STM image, what we have to do is measuring the d(lnI) at each image point, in addition to measuring the tip height.

In our experiment, the modulation frequency was set at 2.0 kHz which is higher than the cut-off frequency of the feedback loop of the STM (~1kHz) but lower than the response frequency of the current amplifier of the STM. The dependence of the work function on the modulation frequency had been measured using Cu(111) substrate, and it was found that when the modulation frequency is around 2.0 kHz the measured work function has a plateau. The amplitude of the modulation was such that the correspondent ds was 0.23 Å, much smaller than the gap distance of about 5.0 Å (estimated from the tunnel current (0.1 nA) and the sample bias voltage (-2.0 eV)). Note that this gap distance (5.0 Å) is much larger than the minimum gap distance below which the tunnel current would be saturated and hence the measured work function would be reduced.13,14)

3. Results and Discussion

A. Surface morphology

A typical STM image collected from the as-deposited Au/Cu(111) surface is shown in Fig. 1(a). The imaged area consists of many terraces separated by winding steps. Inspecting the image carefully one can see, though vaguely, many triangular features surrounded by a darker line. These triangular features form a quasi-periodic arrangement on most areas of the terraces. Similar features have been observed from some other metal/metal systems such as Ag/Pt(111),15) and the mechanism of such features has been suggested to be networks of misfit dislocations induced by mismatch of the distance between neighboring atoms of the involved metals.15) In the present case, the distance is 2.88 Å and 2.55 Å for Au(111) and Cu(111), respectively. According to these features areas covered by a Au(111) layer are discernible from uncovered terraces of the Cu(111) substrate. A statistic shows that about 80% of the total area of the surface was covered by a (111) layer Au. Taking also into account the fact that no alloying occurs for this system at room temperature,16) we know that the surface had a Au coverage of 0.8 ML and that the deposition rate was 0.2 ML/min.

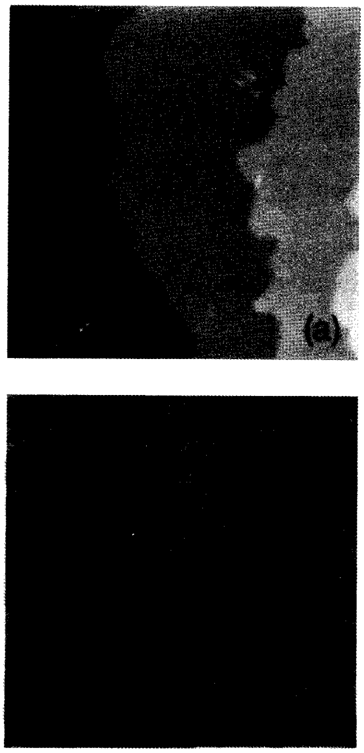

Figure 1. STM (580 Å x 580 Å, sample bias -2.0 V, and tunnel current 0.1 nA) (a) and work function (b) images obtained simultaneously from the Au/Cu(111) surface. In the work function image a higher brightness represents a higher work function.

B. Local work function

Shown in Fig. 1(b) is the local work function image taken simultaneously with the STM image shown in Fig. 1(a). According to the above discussion, obviously, the Au-covered areas, i.e., the brighter areas in the image have a higher local work function than that of those uncovered areas. It is consistent qualitatively with the fact that Au(111) surface has higher work function than Cu(111).

Because our previous work has shown that with an increasing sample bias voltage (in the range of -0.2 V to about -3 V) the measured work function decreases linearly with a rate of about 0.2 eV per volts,4) we know that our measured values must be 0.4 eV lower than the real values, which could be obtained with only a null bias voltage, as a -2.0 V bias voltage was used in our work function measurements. From our clean Cu(111) surface, the work function measured with the STM was 4.4 ± 0.3 eV. By adding 0.4 eV to this value to compensate the lowering due to the non-zero bias voltage, we obtained 4.8 ± 0.3 eV, which is in good agreement with the value of 4.93 eV obtained with a more accurate technique.17)

Apart from the difference between the Au and Cu areas, in Fig.1 (b) one can also see dark valleys along step edges, indicating that the local work function at step edges is much lower than that on terraces. This is in consistent with the results that stepped surfaces have lower work function than flat ones.9) A line scan crossing a step that separates two Au terraces is shown with a solid line in Fig.

2 (a). According to the statistic based on more than 100 work function images like Fig. 1 (b), the mean FWHM and depth of the work function valley is 6.5±1 Å and 0.9±0.3 eV, respectively for Au-Au monatomic steps. We suggest two possible facts to be responsible for the formation of the valleys: dipole moments at step edges and the related topographic change of steps.

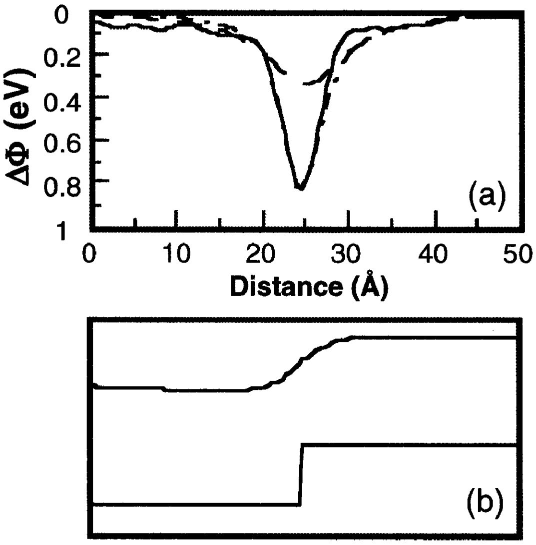

Figure 2. (a) Comparison of the experimental local work function valley crossing a Au-Au monatomic step (solid line) with its simulated counterpart (dashed-dotted line). The dashed line shows the local work function lowering induced by the step dipole moment alone. (b) STM line scan (top), corresponding to the solid line in (a), and the idealized step (bottom), showing the location of the step.

Firstly, it has long been known that around step edges the electron distribution is smeared compared with the atomic structure and thus that electrons are accumulated at the lower side of the steps and depleted at the upper side of steps, resulting in formation of dipoles pointing from the bulk to the surface. As a result, the potential is lowered and the local work function is reduced around steps.[10)]

According to the above picture, a simple simulation was made in the present work. An infinite row of dipole moments is used to simulate a step. If this row is put along the y-axis of a right-hand coordinate system with the center of the dipole moments at z = 0 and their direction pointing to +z then the potential that an electron at a point (x,z) feels is given by:

$$\phi(z,x)=(Q/4\pi\varepsilon_0)\ln[(z+\alpha/2)^2+x^2]/[(z-\alpha/2)^2+x^2], \quad (1)$$

where Q is the linear density of charge, α is the distance between the positive and negative charges, d is the atomic spacing, and thus $Q\alpha d$ is the dipole moment per atom. This potential ought to be responsible for the work function variation caused by dipole moments at step edges.

Secondly, to be able to reproduce the experimental curve of the local work function valley along steps, we must further consider the topographic change of steps caused by formation of dipole moments, as in the measurement the tip followed the surface rather than staying at a constant height. An experimental STM line scan crossing a step is shown in Fig. 2(b). As one can see from the line scan, the tip starts to change its height even several Angströms before it reaches the step edge since the tip follows the contour of the density of states, which is smoothed near the step edge.[18)] So, we have to calculate the potential along the STM line scan, rather than along a line parallel to the surface or along a line, which reflects the atomic structure of the step, like the lower line in Fig. 2(b). However, the step topography has one more effect on the measured values of work function, as pointed out by Binnig and Rohrer,[19)] since in STM measurements of work function we measure, as mentioned above, the response d(lnI) to the modulation of gap distance ds, which ought to be in the normal direction of the surface. If at a point the normal of the surface is not in the z direction but tilted away by an angle θ then the real ds is reduced by a factor of $\cos\theta$ even if the modulation of the tip height dz is constant.[19,20)] As a result, the measured local work function of that point is reduced by a factor of $\cos^2\theta$. Since the surface normal changes its direction around step edges (see the upper line in Fig. 2(b)), to reproduce the local work function curve measured along a line scan crossing a step we must take this topographic effect into account. The work function variation around a step is then given by:

$$\Delta\varnothing(x) = \varphi_0-(\varphi_0-\phi(z,x))\cos^2\theta, \quad (2)$$

where φ_0 is the measured work function of the terraces that are separated by the step, and $\phi(z,x)$ is given by formula (1).

Using formulas (1) and (2), according to the STM line scan given in Fig. 2 (b), we have calculated $\Delta\varnothing(x)$. In the calculation the value of θ at each point was determined from the line scan. By optimizing the gap distance and the linear density of dipole moment, a good agreement between the calculated and experimental curves was achieved. The calculated $\Delta\varnothing(x)$ and $\phi(z,x)$ are shown in Fig. 2(a) with the dotted-dashed and dashed line, respectively, along with the experimental curve (solid line) for comparison. The tip height is 4.9 Å, which is also in good agreement with the gap distance of about 5 Å estimated from the tunnel current and bias voltage, and the dipole moment was derived to be about 0.12 D per edge atom. The final result obtained from many similar fittings is 0.16 ± 0.05 D per edge atom. We note that from the experiment on stepped Au(111) surface, Besocke et. al.[9)] derived the dipole moment to be 0.2-0.27 D per edge atom.

It is interesting that although the net contribution of the dipole moment itself to the work function is only 0.3 eV (see Fig. 2(a)) we still can detect it with the STM. Another interesting thing of our result is that the influence of a monatomic step on local work function can extend to about 10 Å on both sides of the step edge, in agreement with the result of Avouris et. al. obtained recently from their STM spectroscopic data of step edges.[21)] This suggests that some step-step coupling may come into play if terraces are narrower than 20 Å.

4. Conclusions

With a scanning tunneling microscope we have obtained images of local work function of the Au/Cu(111) surface. The local work function measured from large Au-covered terraces of the sample is 4.8 ± 0.3 eV, which is in good agreement with the result of 4.93 eV that was obtained by a more accurate non-local technique. The local work function around step edges is much smaller than that on large terraces and that the mean full width at half minimum and depth of the local work function valley at Au-Au monatomic steps are 6.5 ± 1.0 Å and 0.9 ± 0.3 eV, respectively. The experimental details of the local work function valley can be reproduced nicely with a simple simulation if a dipole moment row with a linear density of 0.16 ± 0.5 Debye per edge atom is put at the center of the step, if the local work function along the STM line scan of the step is considered, and if the apparent work function reduction caused by the local surface declination is calculated from the line scan and taken into account in the simulation. It is thus demonstrated that STM is able to reveal the details of how local work function is related to steps and, very likely, other morphological features on metal surfaces.

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