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Spatial Variation of Local Work Function of the Au/Cu(111) and Pd/Cu(111) Systems*

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Spatial variation of local work function has been investigated for the Au/Cu(111) and Pd/Cu(111) systems using scanning tunneling microscopy (STM). While the measured work function of the Au adlayer is in the range between the Au(111) and Cu(111)'s values consistent with the results obtained by others, the work function on the Pd adsorbate shows a marked difference. The work function of the first Pd layer exceeds that of the Pd(111) surface and it increases further on its second layer, suggesting an overshooting (possibly oscillatory) behavior, which has never been reported experimentally.

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

1. Introduction

Work function is one of the most commonly used parameters to describe surfaces.[1] Many electronic surface phenomena depend on the work function, such as adsorption, desorption and electron emission. Nevertheless, much remains to be learned since it is not trivial to accurately measure and determine the value. The work function, defined in a macroscopic sense, depends on the chemical (elemental) and structural (morphological) variation of a surface on an atomic scale. It has been known that an adsorbate changes the local work function and a surface step also affects its value.

Local work function has been measured by several techniques. Photoemission from the adsorbed xenon atoms (PAX) has been used to measure the potential exerting on the xenon atoms.[1] It was recently demonstrated that two-photon photoemission (2PPE) is useful to measure local work function precisely.[2, 3] By measuring the image states for each atomic layer separately, the dependence of work function was estimated as a function of Ag thickness on the Pd(111) surface.[3] These methods, however, may not be sufficient to understand local work function since they lack in the needed atomic scale resolution. Scanning tunneling microscopy (STM) may be one of the best techniques to measure *local work function*[4] as pointed out by Binnig and Rohrer.[5, 6] Local work function is important for the STM operation since the height of the tunneling barrier depends critically on it.

In this paper we report spatial variation imaging of work function for the Au/Cu(111) and Pd/Cu(111) surfaces simultaneously taken with their topographic STM images. It is found for the first time that the adsorbed Pd layer exhibits an overshooting behavior in the measured work function, while the Au layer exhibits an ordinary transitional behavior from the Cu to the Au bulk value. We tentatively attribute this observation of the overshooting of the work function for the Pd adlayer on the Cu(111) surface to be a quantum size effect.

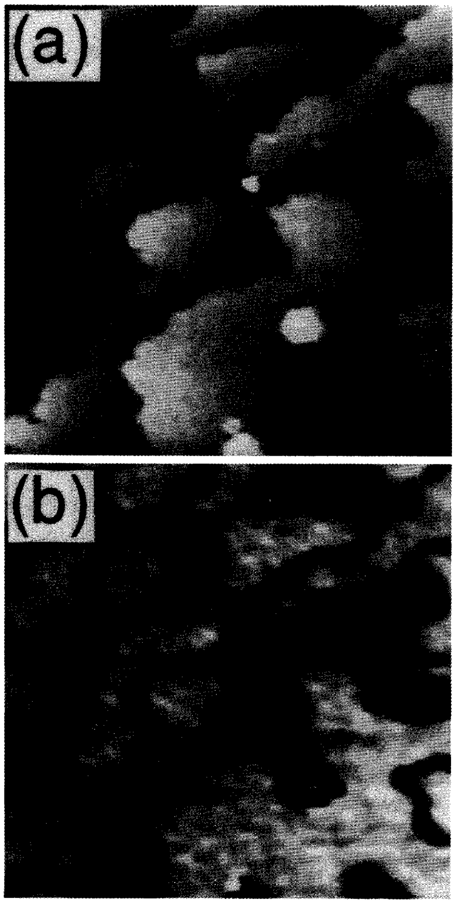

Figure 1. STM (a) and work function (b) images obtained on Au/Cu(111) surface. Applied sample bias voltage is -2.0V and tunneling current is 0.1nA. The size of the observed area is ~ 500Å x 500Å. The coverage of Au is about 0.8ML. Au layer nucleates and grows at the lower side of step edges, making the (111)-oriented plane.

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2. Experimental

All experiments described in this paper were performed with our home-made UHV-STM system,[7] with a base pressure $<1.0\times10^{-10}$ Torr. The Cu(111) sample was cleaned in situ by repeated cycles of Ar^+ bombardment and annealing at 500°C. Gold and palladium were evaporated onto unheated Cu(111) surfaces from an evaporator consisting of a Au/Pd wire wrapped in a Ta foil. The work function of Au(111), Pd(111), and Cu(111) is 5.55eV, 5.44eV, and 4.93eV, respectively,[2] the Cu substrate having the smallest work function. The pressure during deposition was kept lower than 8×10^{-10} Torr. The adsorption rate is estimated to be about 0.2 ML/min based on a evaporation time and STM images. Both adsorbed Au and Pd metals form the (111) oriented terrace over the Cu(111) substrate. All STM images were obtained at room temperature and in a constant-current mode. A (111)-oriented tungsten single crystalline tip was used as a probe of STM.

Work function was measured by applying a sinusoidal voltage on the z-axis piezo in order to modulate the tip-surface distance s and then detecting the response in tunneling current with the same frequency using a lock-in amplifier. The work function Ø is calculated using a formula of $Ø = 0.95(\Delta \ln I / \Delta s)^2$.[5,6] Modulation frequency is set at 2.0 kHz; higher than the cut-off frequency of the feedback loop of the STM system we used (~1kHz) but lower than the response frequency of the current amplifier. We measured frequency dependence of the work function using the Cu(111) substrate, and found the modulation frequency we used is in a range of plateau. The amount of modulation in the gap distance is 0.23Å; much smaller than the gap distance, 5.5Å~6.0Å, which is estimated from the tunneling current (0.1 nA) and bias voltage (-2.0eV on the sample). The gap distance is far from the near-contact regime where the current shows saturation and thus the measured work function is lowered.[8,9] Image potential does not seem to contribute so much to measured work function as was suggested previously.[10-12]

We also checked the bias voltage dependence on the work function. Our measurements with the Cu(111) surface show that it decreases linearly with a rate of 0.2eV per volt in a negative sample bias voltage to about -3V. Since we measure work function with a bias voltage of -2.0V, the measured work function is lowered by 0.4eV, compared with the ideal case of zero-bias voltage. On the clean Cu(111) surface, the measured work function is 4.4±0.3eV. Compensating the bias voltage effect by adding 0.4V, it is 4.8eV in a good agreement with the reported work function.[2]

3. Results and Discussion

Figure 1 is an STM image (a) taken on the Au/Cu(111) system and work function image (b) taken simultaneously with the STM image. Figure 2 shows the magnified images of both topographic and work function of Au/Cu(111) surface with a cross-section profile of the work function. The coverage of Au is approximately 0.8 ML. The STM image shows that the gold layers nucleate and grow from the lower step edges of the Cu substrate, forming the (111)-oriented plane. It is known that alloy formation does not occur at room temperature.[13] Because of the large lattice mismatch between the Au layer and Cu substrate (distance between atoms, Au(111): 2.88Å, Cu(111): 2.55Å), a network of misfit dislocation forms on the Au layers, demonstrated by the triangular dark lines periodically arranged in the STM image (see Fig. 2). The spacing of the dislocation lines corresponds to 15 to 18 times the Cu(111) lattice, implying that the Au layer is compressed by 5 to 6% compared with the Au bulk.

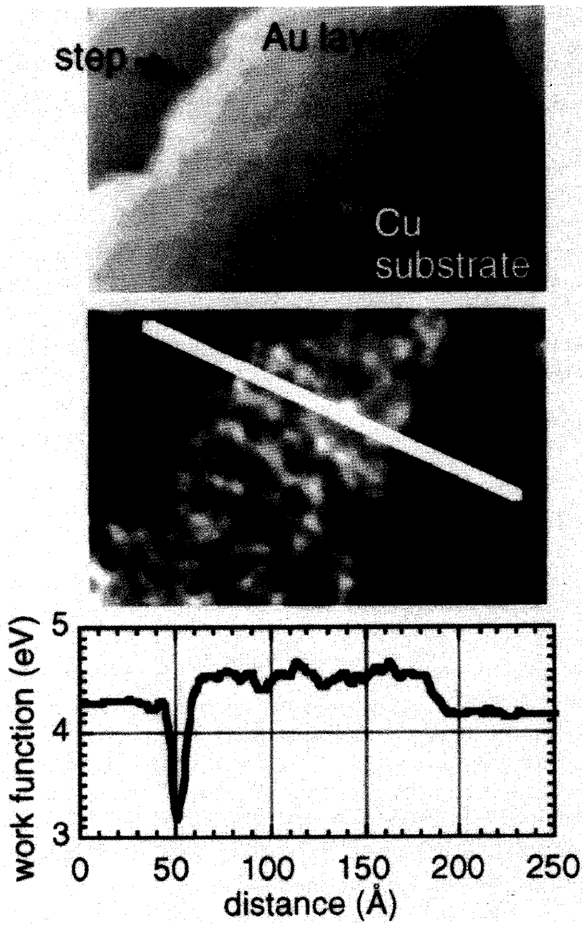

Figure 2. Magnified STM image (upper), work function image taken at the same time (center), and a plot of work function measured along the white line written in the work function image.

Distinct contrast between the Au layer and Cu substrate is observed in the corresponding work function image (Fig. 1(b)) together with the terrace edges. The image indicates that work function is larger on the Au overlayer than Cu substrate. Based on the analysis with more than 100 work function images like Fig. 1(b), we concluded that the measured work function of the 1st Au layer is larger than that of Cu substrate by 7±3%. The step edges show dark contrast in the work function image, which will be discussed later in detail.

Similar measurements have been performed for the Pd/Cu(111) system. Figure 3 is STM and work function images obtained for the Pd/Cu(111) system. The area observed in these figures is ~ 500Åx500Å. The growth of Pd on Cu(111) is similar to the Au case, although the Pd overlayers are more dendritic. The dark contrast along step edges is also observed in work function images. A similar network of the misfit dislocation is observed on the Pd layer but it is not so ordered as the case of the Au layer. From the periodic spacing of the misfit dislocation, the Pd overlayer is estimated to be compressed by 2 to 3%.

The islands of the 1st Pd layer form on the wide Cu substrate terraces and several small islands of the 2nd Pd layer form on the 1st Pd layer. In the corresponding work function image (Fig. 3(b)), the islands of the 2nd Pd layer are imaged brighter than the 1st Pd layer. A surprising observation is that the work function measured on the Pd overlayer is much larger than that of the Cu substrate and is indeed *even larger than the pristine Pd(111) value.* Our analysis yields that the 1st Pd layer has a larger work function than Cu(111) by 19±5%, while the work function of the ordinary Pd(111) surface is larger only by 10% . Furthermore, that the 2nd Pd layer shows an even higher work function than that of the 1st Pd layer by 6±5%. (We did not observe such a behavior on layer thickness for the Au/Cu(111) system.)

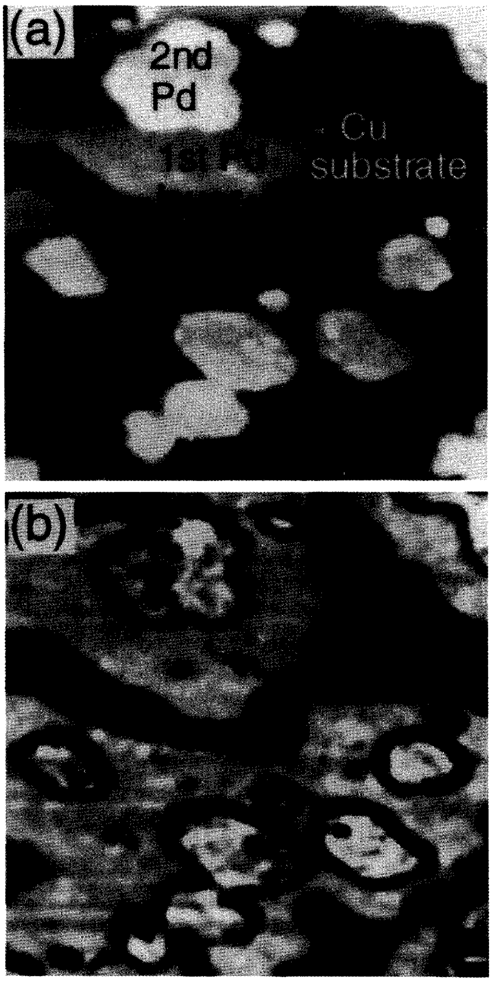

Figure 3. STM (a) and work function (b) images obtained on the Pd/Cu(111) surface. Applied sample bias voltage is -2.0V and tunneling current is 0.1nA. The size of the observed area is ~ 500Å x 500Å. The coverage of Au is about 1.0ML.

Measured work function values are summarized in Fig. 4 together with the reported values of the Cu(111), Au(111) and Pd(111) surfaces.[2] For the Au/Cu(111) system, Wallauer et al. has already studied on thickness dependence of work function with 2PPE.[13] Their results are also included in the figure. All the measured data points plotted in Fig. 4 are shifted upward by 0.4eV in order to compensate the bias voltage effect. The obtained number on the 1st Au layer shows a good agreement with the data obtained by Wallauer et al. with 2PPE,[13] which shows gradual and monotonic increase toward its bulk value with increasing Au thickness. The reason we could not observe the thickness dependence in the Au/Cu(111) system is probably due to its small thickness dependence.[13]

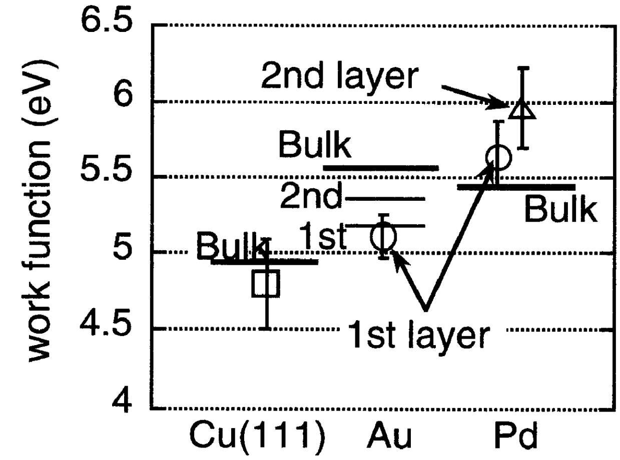

Figure 4. Summary of the measured work function. The data obtained by 2PPE [2] including those of each Au layer on Cu(111) [13] are also plotted for comparison.

In the case of the Pd/Cu(111) system, however, the work function of a thin Pd adsorbate layer overshoots before reaching the bulk Pd value, since the work function of the 1st Pd layer is already larger than that of bulk Pd(111). All the previous works so far concluded that the work function changes monotonically to reach the bulk value for the cases of Ag on Pd(111), Au(111), and Cu(111), and Au on Pd(111) and Cu(111) systems.[4, 5, 13] Therefore, the present observations must imply that the behavior of work function of the Pd overlayer is new and distinctively different from those of Au and others.

We have considered two possible situations to account for the unique behavior of the Pd/Cu(111) system. First, the different atomic density in the overlayer from those of nominal surfaces may be responsible. In general, a densely packed surface has a high work function compared with the loosely packed surface, which is explained by the electronic smoothing effect proposed by Smoluchowski.[14] A good example is the work function variation among three basic Cu planes of (111), (100), and (110). Since copper has the fcc structure, the (111) plane is the most close-packed surface, and has the highest work function among them. If the atomic density in the overlayer is larger than the bulk due to the compression, the work function may become higher and the overshooting behavior may occur. From the STM images, we can determine how much the Pd overlayer is compressed from the nominal surfaces, and find that it is 2-3%, not enough to cause a significant change in work function.

Another possibility is a quantum size effect since film thickness of the overlayer is smaller than Fermi wavelength of the metal. Schulte [15] calculated the work function of a thin film suspended in vacuum and its thickness dependence using LDA and Jelium model.[16] He concluded that the work function oscillates as the film increases in thickness with a periodicity of the Fermi wavelength, and that the oscillation decays while the work function approaching its bulk value. Under this scheme, the work function of thin film can be larger or smaller than that of the bulk, depending on the relationship between the thickness, the Fermi wavelength and charge density. Realizing the fact that the neither Pd or Cu is not the so-called simple metal, the Jelium model may not be completely applicable to the present case. Nevertheless, we believe that a quantum size effect best accounts for the observed (oscillatory) work function variation of the Pd/Cu(111) system. Obviously, we need further quantitative investigation both theoretically and experimentally to elucidate this intriguing phenomenon.

Another interesting observation is that dark lines are observed at the positions corresponding to step edges in the work function image. The width and depth of the trough is 13±2Å and 0.9±0.3eV, respectively for the Au steps and 12±3Å and 1.1±0.4 eV, respectively for the Pd steps. This is likely due to two effects; dipole moment formation at step edges and the topographic effect. If the dipole moment pointing into the bulk forms on a surface, the potential is lowered and thus the local work function is reduced. It is known that such dipole moment forms at steps by the electron smoothing effect, the same as the one used for explaining atomic density dependence of the work function. Around a step edge the electron distribution is smeared, and thus electron are accumulated at the lower side of the step, while depleted at the upper side of the step, forming a dipole moment which reduces the work function. It has been reported that a step reduces work function,[17, 18] and recently the dipole moment formation was detected directly by STM from the spectroscopic data obtained around step edges.[19] The effect of dipole moment formation with vicinal surfaces is measured to be 2.7 to 3.6 eV·Å for the Au step.[17, 18].

In addition, we also have to consider a topographic effect in the work function measurements with STM, pointed out by Binnig and Rohrer.[20, 21] We measure the work function by modulating a tip position in the z direction and detecting its response in the tunneling current. If the surface is tilted by θ , the actual modulation in the gap distance is reduced by a factor of $1/\cos\theta$. As a result, the measured work function is reduced by a factor of $1/\cos^2\theta$. Since a slope changes around the step edge, the step edge appears dark in work function images. We estimated numerically how much work function drops apparently by the topographic effect from the STM images, and found to be 1.5 to 2.0 eV·Å if integrated in a perpendicular direction to the step edge. The sum of these two is in agreement with our experimental result of 6.0eV·Å.

4. Conclusions

In conclusion we have demonstrated that STM allows us to take work function images in nanometer-scale spatial resolution, and using this technique we have observed the overshooting of the work function for the Pd/Cu(111) system. With both topographic and work function images on the same area obtained simultaneously, it will provide direct and unambiguous information on how nanometer-size structures are related with local work function. This technique can also be used for elemental and material identification and may be more useful than the technique utilizing the image states with STM,[22] because the present measurement does not require a high bias voltage which adversely affects the potential and shifts the energy levels of the image states.

Acknowledgments

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