Journal of the Korean Vacuum Society
Vol. 1, No. 1, February 1992 pp.78-82

〈연구논문〉

Work Function Change of W(123) Plane Due to Hydrogen and Deuterium Adsorption at 78 K

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(Received November 29, 1991)

78 K에서 수소 혹은 중수소 흡착으로 인한 W(123)면의 일함수 변화

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(1991년 11월 29일 받음)

Abstract—The changes in work function due to hydrogen and deuterium adsorption on W(123) plane are measured by means of Field Emission Method. In the case of hydrogen or deuterium adsorption, work function of W(123) plane at 78 K increase and after a maxium value, it decrease and saturated as increasing coverage. After annealing the tungsten emission tip at 200 K, the coverage corresponding to maximum change in work function was shifted toward low coverage and the effect of work function by terraces or steps of which orientation is [011] was observed.

요 약—W(123) 표면위에 수소와 중소수가 흡착될 때 일함수의 변화를 장방출(Field Emission) 방법으로 측정하였다. 78 K에서 이 분자들이 흡착될 때 일함수의 변화는 처음에는 증가하다가 최대치에 이른 후 감소하였고, 덮임율(coverage)이 증가함에 따라 포화되었다. 텅스텐 tip의 온도를 200 K까지 올렸을 경우에, 일함수의 변화가 최대가 되었을 때의 덮임율은 78 K일 때의 비해 낮은 덮임율 쪽으로 이동하였고, [011] 방향을 갖는 step 혹은 terrace에 의한 일함수의 효과도 동시에 관측되었다.

1. Introduction

The W(123) plane is consist of terraces and steps of [011] orientation, i.e., (123) plane in not close packed surface. The physical and chemical properties and behavior of adsorbate on such a stepped surface have long been interested[1]. But very little work seems to have been done on the change in work function due to adsorbates on such surfaces, specifically on the coverage dependence of change in work function at low temperature.

Hydrogen or its isotopes adsorbed on the W(123) plane diffuse at the temperature higher than 100 K. But at the temperature lower than 100 K, tunneling diffusion was observed[2]. Therefore at lower temperature than 100 K, the change in work function due to adsorbate is different from that of room temperature. Namely at low temperature, hydrogen could be adsorbed on the step edge and at high temperature, the adsorbate diffuse to the steps of close packed or terraces of which orientation is [011]. Thus we investigated the work function changes of W(123) plane due to hydrogen and deuterium adsorption at 78 K.

2. Experiment

Field Emission Tube is designed and construct-

ed orginally for the study of surface diffusion. But this equipment is usefull for measuring work function of local area of tip. And W tip, a part of Field Emission Tube was made by chemical etching method. The tip radius was measured from the slopes of $\ln(i/V^2)$ plots versus 1/V using the following Fowler-Nordheim equation[3].

$$\ln(i/V^2)=\ln B-6.8\times10^7\phi^{3/2}/k_rV,\ k_r=Cr_t \quad (1)$$

here i is the total current from tip, ϕ is the work function of tip, V is the applied potential to tip, r_t is the tip radius, B is a field dependent term and C is a correction factor for the shape of the tip. By inserting the average work function of W into above equation, and comparing the dimension of image of tip obtained from electron microscope, C was determined as 3.5.

The average work function of W is 4.5 eV[4] and the values of W(011) and (112) are 5.3 eV[5] and 4.947 eV[6] respectively, therefore, the (011) and (112) images are darker than others and the shape of (011) image is a rectangle because W has a bcc structure. Therefore one can distinguish a particular image from each others. To measure a work function of a particular plane, 4-deflecting electrodes were used. There are (257), (123) and (235) planes between (011) an (112) planes. The theoretical directions of (257), (123) and (235) are 16°, 19° and 24.4° with respect to the (011) direction respectively. But because of compression factor $\beta=1.5$[7] which is obtained by observing the field emission images, real directions become 10.7°, 12.7°, and 16.3° respectively. With applying proper potential to the deflecting electrods, the image of (123) plane could be moved to the slit of a detector. As mentioned above, because this equipment was designed for the study of anisotropic surface diffusion, a new slit of dimension 2 mm×0.3 mm is designed to select one image from tip and also we use this slit to investigate anisotropic diffusion. But in this study, the results of anisotropic diffusion which shall be appeared in our separate paper[2] are not considered. As a detector for field emission current, a fluorescent screen and PM tube system was used. Slit direction can be changed by using a magnet. The average tip radius is found to be increased from 2133 Å to 2150 Å during the work function measurement. The probed dimension is also obtained from following equation,

$$\alpha=\alpha_s/M=\alpha_s\beta r_t/x \quad (2)$$

here, α is the probed length, α_s is the slit dimension, $\beta=1.5$ is the compression factor, and x(4 cm) is the distance between tip and screen. The obtained probed dimensions were 24 Å×160 Å. The distance from (123) plane to (257) and (235) plane are 110 Å and 170 Å respectively and distances from (123) plane to another planes are longer than these planes, therefore another planes could not affect, if any, very little, on the work function of probed region.

The base pressure in the system was 3×10^{-11} torr. For desorption the carbon from the tip surface, tip was exposured to oxygen of 1 Langmuir and flashed. And for desorption other impurities from the tip surface, flashing method was imployed. The field emission image is changed very sensitively by the impurities adsorption. Even a few number of adsorbate, it can change the field emission image. So one can easily distinguish a clean surface from an contanminated surface by observing the field emission image. Adsorption of hydrogen or deutrium was carried out by dosing at a nomial ion gauge pressure of 1×10^{-9} torr and the tip temperature at 78 K. Work functions and mean tip radius were determined from the plots of $\ln(i/V^2)$ versus 1/V in the usual manner using the Fowler-Nordheim equation. The correlation factors of all obtained values using least square fitting method are bigger than 0.99999. To investigate the coverge change during experiment, current passing through the slit hole was measured for one hour after cleaning the tip. During the experiment the probe hole current. While, in case of field on the emission tip, probe hole current was found to be increased a little bit and became constant after 1000 second as shown Fig. 1. This phenomenon is considered as the redistribution of adsorbate by the field. So, work function measurement were carred out 1000 second after field on and tip temperature at 78 K. And also work function measurements were carried out with and without annealing the tip. Tip tem-

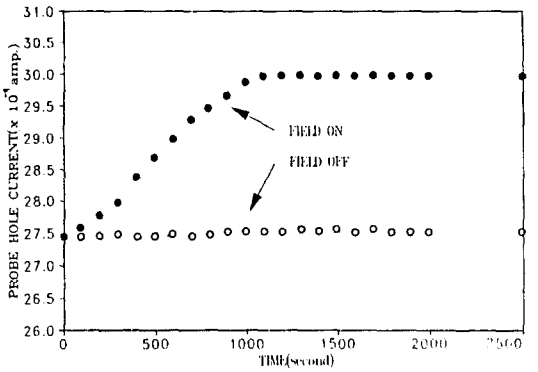

Fig. 1. Probe hole current vs. time.

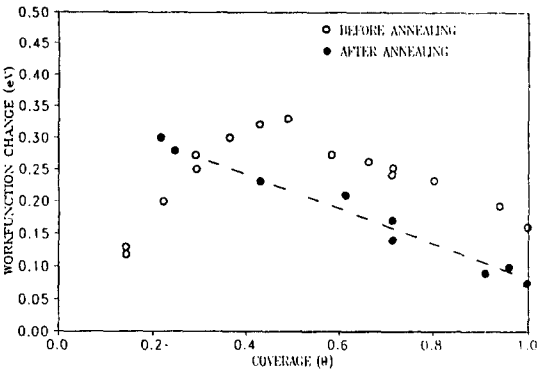

Fig. 2. Work function change due to hydrogen adsorptuion on W(123) plane.

perature was determined by measuring the resistivity of the W-filament which the tip is attached on. And tip was annealed at 200 K.

3. Result and discussion

Work function of the clean W(123) surface was determined from the slope of $\ln(i/V^2)$ versus 1/V, which is normalized to the slope of plots corresponding to the average work function (4.5 eV) of clean W. The resultant values were 4.95 eV for the slit with its long axis parallel to steps, and 4.72 eV for the slit with its long axis perpendicular to steps. This should be compared to the value of 4.85 eV found with a round probe hole by Gong and Gomer [8]. The difference arises because the slit samples slightly different regions of the surface in its two orentations, as discussed previously[7]. Relative coverages were estimated from the curves of change in work function after annealing. Assuming that the change in work functions are proportional to coverage, the relative coverage could be obtained from following equations[9],

$$\Delta\phi = -4\pi\Delta P,\ \Delta P = P_o N \tag{3}$$

here, P_o is a dipole moment of a adsorbate on the surface and N is the number of adsorbate per unit area. Assuming N is proportional to coverage, relative coverages were then estimated by comparing the obtained values with maximum value, assuming a linear decrease or increase in ϕ with coverage. Thus relative coverage θ would be assumed to be

$$\theta = (\phi_{max} - \phi)/(\phi_{max} - \phi_s) \tag{4}$$

where ϕ_s corresponds to the observed value of ϕ at saturation condition ($\theta \geq 1$) and ϕ_{max} is the extraplotted value at $\theta = 0$.

This estimates obtained in this way are obviously rather crude but give at least a qualitative idea of adsorbate population. Fig. 2 shows the change in work function due to hydrogen adsorption with and without annealing. Although the data are scattered and it seems that the tip was contaminated by the impurities, we confirmed that only hydrogen was adsorbed on the tip surface by observing the field emission images. When oxigen is adsorbed on the W(123) plane, the field emission image becomes progressively cross-bone shape i.e. along the zone (011)-(112), the work function increase and when carbon is adsorbed on the tungsten surface, a bright lump appears near the boundary of W(011) image and hydrogen adsorption makes the W(011) image small. And adsorption of the other impurities also strongly effect the field emmission images[10]. This figure shows that before annealing, work function increase and after passing a maximum value, decrease and saturate with increasing coverge. But after annealing at 200 K, except at very low coverge, work function decrease linearly with the coverge. The most notable feature of that figure is that work function initially rises and drops. This can be understood as follows : As mentioned above, when hydrogen is adsorbed on the W(011) surface, the W(011) image becomes bright and the work func-

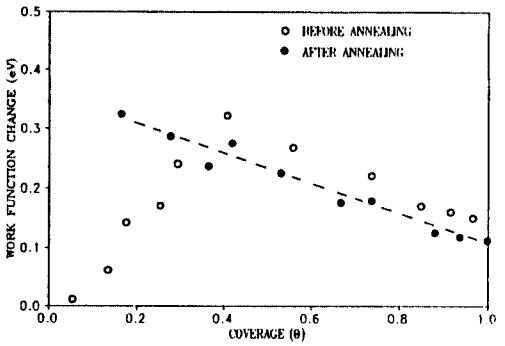

Fig. 3. Work function change due to deuterium adsorption on W(123) plane.

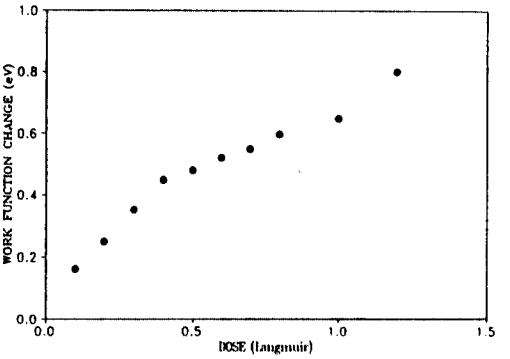

Fig. 4. Work function change due to oxygen adsorption on W(1123) plane.

tion of W(011) plane decreases. And the region near W(123) plane consists of terraces of (110) orientation whose work function would be ~5.3 eV if they were of infinite extent, and step edgs, which lower the work function to the observed clean surface value of 4.8~4.9 eV. It is also well known that H_2 does not easily dissociate on W(011)[11]. If initial dissociative chemisorption occurs at the step edges, thereby raising the work function of (123) plane or at least suppressing emission from them, i. e. the effect on the work function from the steps or terraces becomes more dominant than that from step edges (field emission current from step edges decreases), the resultant value will be approximately 5.3 eV, i. e. work function of (011) plane. And it is known that H on W(011) plane lower the work function of (011) plane[12], therefore as adsorption proceeds the terraces acquire more H and the overall work function consquently drops. Presumably H can diffuse even at 78 K from the step edges where H_2 is dissociatively adsorbed to the terraces, which are only 1~2 lattice spacing wide. With considering above explanation, it is highly probable that before annealing, most of adsorbate would be adsorbed on the step edge and after annealing, the adsorbate on the step edges would diffuse to the middle area of steps or terraces resulting to the lowering the work function of (123) plane. This phenomenon suggests the anisotropic diffusion which shall be appeared in our separate paper[2]. But at very low coverage, the concentration of adsorbate is not enough to change the emission current (work function) strongly from the step edges. Therefore at the low coverge, the change in the work function with annealing is bigger than that of without annealing, while at the high coverge, the change in the work function without annealing is bigger than that of with annealing. This phenomenon also suggests that the tip annealing makes the adsorbates on the step edges diffuse to steps. Fig. 3 shows the changes in the work function due to deuterium adsorption on the W(123) surface. This result is slightly different from the result of hydrogen. Because of finite slit dimension, slit sample different region and it could make an expermental error. But the slit dimensions are very small compared to the tip radius, so it still makes sense. The estimated equation of change in work function versus coverage from Fig. 2 and Fig. 3 are

$$\Delta\phi_H = -0.245\theta + 0.35, \quad 0.1 < \theta < 1 \tag{5}$$

$$\Delta\phi_D = -0.240\theta - 0.35, \quad 0.4 < \theta < 1 \tag{6}$$

Here, H denotes hydrogen and D denotes deuterium.

For investigating experimental error, oxygen were adsorbed on the W(123) plane and work function change is measured. The result shown in Fig. 4 is different from those of hydrogen or deuterium, but similar to the Gomer's result[13]. Therefore this result confirms the fact that the phenomenon of increasing and decreasing work function change is not experimental error.

4. Conclusion

This study confirms that before annealing, at low

coverage of hydrogen or deuterium on W(123) plane at 78 K, the change in work function increases up to 0.3 eV and then decreases and saturates at high coverage. But after annealing at 200 K, the relative coverage corresponding to maximum change in work function is shifted toward low coverage. Both of hydrogen and deuterium adsorption the saturated changes in work function ($\theta \approx 1$) is -0.1 eV and the maximum change in work function ($\theta = 0$) is -0.35 eV. At low coverage and without annealing, the change in work function is strongly affected by step edges, while at high coverage and with or without annealing, the change in work function is strongly affected by the middle area of steps or terraces of which orientation is [011]. The result of change in work function and the annealing effect confirm that hydrogen or its isotopes are adsorbed not uniformly on the W(123) plane at 78 K and it is highly probable that hydrogen or its isotrope diffuse anisotropically on W(123) plane. It is preassumed that the change in work function due to hydrogen and its isotrope are similar because of their similar atomic structure and this study confirms it.

Acknowledgements

This study was supported in part by the Korea Science and Engeering Foundation. One of the authors (D. S. Choi) wishes to express deep thanks to Prof. R. Gomer, University of Chicago, for his valuable discussions and encouragements for this study.

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