Oxygen diffusion on W(110) : Comparison of experiment and theory

Tschang-Uh Nahm, Jin-Pyo Hong and Chae-Ok Kim

Department of Physics, Hanyang University, Seoul 133-791, Korea
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W(110)면에서의 산소의 확산 : 실험과 이론의 비교

남창우 · 홍진표 · 김채옥

한양대학교 물리학과
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Abstract – The diffusion of oxygen atoms on tungsten (110) surface is studied by comparison of experiment results and recent calculations. It has been suggested that the thermodynamic factor which is inversely proportional to the compressibility has strong temperature dependence which may cause non-Arrhenius behavior of diffusion coefficient. Recent experiments, however, indicate effectively no temperature dependence of this factor and support the view that non-Arrhenius behavior originates from the dynamic factor rather than the thermodynamic factor. Discrepancies in coverage dependence of physical quantities between theory and experiment are discussed.

Keywords : surface diffusion, oxygen, tungsten, field emission microscopy

요   약 – 텅스텐(110)면에서의 산소 원자의 확산을 실험 결과와 최근의 계산과의 비교를 통하여 연구했다. 확산계수의 비 아레니우스적 성질이 압축률에 반비례하는 열역학적 인자에 기인한다는 제안이 있었으나, 최근의 실험 결과는 실질적으로 이 인자가 온도에 대한 의존성을 거의 갖지 않으며, 비 아레니우스적 성질이 열역학적 인자보다는 동적 인자에 의해 주어진다는 관점을 뒷받침해준다. 이 논문에서는 물리적 양들의 증착 정도에 대한 의존도에 대해서도 논의한다.

I. Introduction

Since the surface diffusion had been first observed utilizing field ion microscopy (FIM) or field emission microscopy (FEM) [1], much has been discussed on how individual adatoms or adlayer as a whole diffuse at different adatom coverages and at different phases. The study of adatom diffusion is very crucial in understanding the adlayer morphology such as Si homoepitaxy on hydrogen covered surfaces [2], and in adsorption and desorption during the surface catalytic reactions. Recent studies include tracking the position of individual atoms or dimers using scanning tunneling microscopy (STM) which enables direct determination of the tracer diffusion coefficient [3].

Oxygen adatom diffusion on W(110) plane, one of the most studied systems because of inert behavior of the substrate has recently been investigated more thoroughly owing to the development of digital FEM method [4] and to the availability of fast computers with huge computational capacity. There exist a number of experimental results which mainly determined the activation energy E_a from the Arrhenius plots and the agreement between different groups had been taken as the evidence of a simple Arrhenius behavior of the diffusion constant over a wide range of temperature. The activation energy at low coverage was 0.6 eV/atom and it started to increase when the coverage is close to the p(2×1) phase with the value of 1.1 eV/atom near half coverage [5].

Most interesting feature of all experimental results was the strong temperature dependence of the thermodynamic factor ξ which connects the chemical (collective) diffusion coefficient D_C and its center of mass term, the so-called 'jump diffusion coefficient' $D_{c.m.}$ [6]. This result and the following Monte Carlo (MC) calculations [7, 8] had been regarded as an indication of the importance of the thermodynamic factor in adatom diffusion process rather than of the average microscopic jump rate, a dynamic quantity. This factor is expected to have some singular behavior and may contribute to the non-Arrhenius behavior of diffusion coefficient when phase transition occurs, but the thermodynamic factor of O/Mo(110) system was not found to have any temperature dependence at all except near saturation coverage [9]. Although the measurement was done either below or above the order-disorder transition temperature (T_c), previously observed strong temperature dependence was absent.

Vattulainen et al. have studied the surface diffusion of O/W(110) using MC simulation argued that ξ does not show big anomaly near phase transition and the non-Arrhenius behavior of diffusion coefficient originates mainly from the average microscopic jump rate. These arguments were confirmed by Uebing and Zhdanov [11], but it was stressed that the singularity in the diffusion coefficient really comes from the behavior of ξ.

Nahm and Gomer [5] repeated the autocorrelation function measurement on O/W(110) using digital method and found no temperature dependence of thermodynamic factor. The measurement was not accomplished near the phase transition temperature, but the strong temperature dependence in Ref.[6] could not be reproduced. Furthermore, their thermodynamic factor showed similar behavior with previously studied O/Mo(110) system [9] and the inverse of this quantity did not have its minimum at relative coverage [12] of 0.5 as predicted by MC calculations [8, 13], but at 0.2, which is very close to the order - disorder phase boundary. The coverage dependence of activation energy derived from D_C was not in agreement with the calculated values from D_C, but roughly with those from $D_{c.m.}$

[13]. These results suggest that current status of MC calculation to understand the surface diffusion phenomena of oxygen on W(110) or Mo(110) surface is not perfect.

In this paper, we compare the existing experimental results on O/W(110) with on O/Mo(110), and those with the MC calculations to show discrepancies and agreements between them. In Sec. II, we briefly describe the fluctuation method to measure the autocorrelation function with which E_A^C and ξ have been determined and then the experimental results on O/W(110) and O/Mo(110) are compared in Sec. III. In Sec. IV, we compare these experimental results with the calculations and concluding remarks are added as Sec. V.

II. The fluctuation method

This method is basically measuring the time autocorrelation function of field emission current fluctuation fi(t) from a small region of the field emitter. Since the emission current fluctuation is the result of adatom density fluctuation within the measured region, we can relate these two quantities. Also, it is well known that the time autocorrelation function of density fluctuation can correctly yields the chemical diffusion coefficient [1]. This enables one to obtain the chemical diffusion coefficient from the time autocorrelation function of current fluctuation.

When the probing region has a radius of r_0 which is usually 7~10 nm, the behavior of fi(t) which is related to the autocorrelation function of number fluctuation $f_n(t) = <\delta N(0) \; \delta N(t)>$ can be described by a single time parameter tau-0 where N is the number of adatoms within the probed area. Then chemical diffusion coefficient D_C can be determined using the relation $\tau_0 = r_0^2 / 4D$, and the activation energy by assuming Arrhenius behavior of D_C as

$$D_C = D_o \exp(-E_A^C / k_B T),$$

where D_0 is a prefactor and k_B the Boltzmann constant.

The chemical diffusion coefficient is given by the Kubo-Green equation

$$D_C = \frac{1}{2<(\delta N)^2>} \int_0^\infty dt<\sum_{i=1}^N \mathbf{v}_i(0). \sum_{j=1}^N \mathbf{v}_j(t)>,$$

and is related to the jump diffusion coefficient $D_{c.m.}$ by

$$D_C = \xi \cdot \lim_{t \to \infty} \frac{1}{4Nt} <|\sum_{i=1}^N \triangle \mathbf{r}_i|^2> = \xi \cdot D_{c.m.},$$

The thermodynamic factor ξ is the inverse of the mean square fluctuation $<(\delta N)^2>/<N>$ by the relation

$$\xi = \frac{\partial(\mu/k_B T)}{\partial \ln \theta} = \frac{<N>}{<(\delta N)^2>} = \left[k_B T K \frac{<N>}{A}\right]^{-1},$$

where μ is chemical potential, θ the adatom coverage, A the probing area, and K the adlayer compressibility.

One of the serious shortcomings of this method is that since filed emitter is a tip with many planes of different directions at its end, the coverage of the plane one is interested in can be changed during equilibrium measurement when some of adatoms migrate to or emigrate from adjacent planes. This has been the main reason the fluctuation method could not be used across T_c in some cases.

Another problem is that in general it is not easy to determine the coverage of adatom layer. Sometimes relative coverage to the saturated layer is determined assuming constant sticking coefficient at low substrate temperature except near saturation as in Ref.[9] for O/Mo(110), but one cannot know the amount of adatoms of the saturated layer exactly. The best way to overcome this is relying on work function vs. coverage relation of the macroscopic layer as employed in Ref.[5] for O/W (110).

An inherent shortcoming of analog method originating from the frequency cutoff had been removed by digital method in which one can measure the emission current $\delta i(t)$ rather than $i(t)$ and calculate the autocorrelation function afterwards.

The apparatus for $i(t)$ measurement was fully described by Whitten and Gomer [4]. It uses a spiraltron as electron multiplier, and the base pressure of the vacuum system was $4\text{-}5 \times 10^{-11}$ Torr. O_2
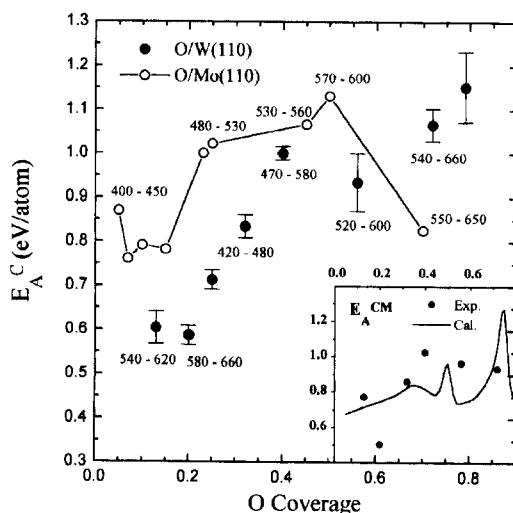

Fig. 1. Activation energy E_A^c vs. coverage for O/W (110) from Ref.[5] and for O/Mo(110) from Ref.[9]. The temperature range over which E_A^c was determined are indicated. The inset shows experimental [5] and theoretical [13] values of E_A^{CM}. The theoretical values at 590 K are shifted by 0.6 eV for comparison.

was introduced by backfilling via a leak valve to pressure less than 6×10^{-9} Torr.

III. The experimental results

Fig. 1 shows the activation energy E_A^c of O/W (110) and O/Mo(110) from Ref.[5] and [9]. The temperature ranges from which the Arrhenius plots had been made is indicated. It is clear that E_A^c has low values in disordered phase and starts to increase as the coverage is close to the phase boundary. The oxygen atom coverage of O/Mo (110) might be inaccurate because the linear relation between coverage and work function was assumed and because only relative coverage to the saturated surface was indicated, but the main trend is that there is big increase in E_A^c near the phase boundary and slight dip near half coverage for O/W(110) and decrease at high coverages for O/Mo (110).

Since the measured activation energy at high coverage within disordered phase using profile characterization [14] and that at ordered phase using fluctuation method were nearly the same, it
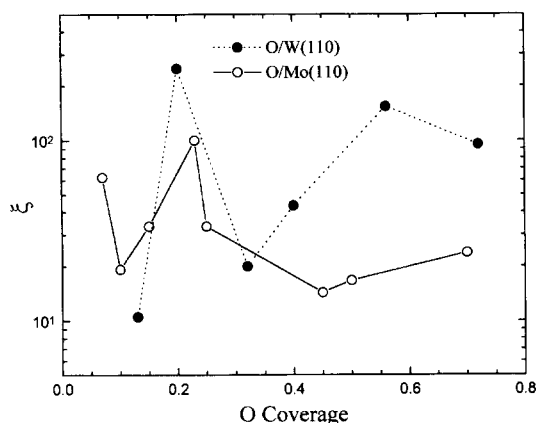
Fig. 2. Thermodynamic factor ξ vs. coverage for O/W (110) from Ref.[5] and for O/Mo(110) from Ref.[9]. Because there was effectively no dependence on temperature, only the average values are shown. Note the cusps at coverage of 0.2.

had been suggested that the activation energy is almost the same below and above T_c. However, the dynamic measurement of ordering process using low energy electron diffraction (LEED) [15] showed only small increase in E_A^C even at half coverage and the measured values were interpreted as non-equilibrium quantities. It was argued that diffusion during nucleation is not the same as diffusion of adatoms in ordered phase and we believe the measured E_A^C might be rather close to that of disordered phase.

The thermodynamic factor ξ was found to be almost independent of temperature for both systems [5, 9], but its coverage dependence has some structure as in Fig. 2. The thermodynamic factor ξ of O/Mo(110) and of O/W(110) surfaces were plotted together to show the similarity of these systems, but because ξ was almost constant, only the average values are shown. Unlike the calculation which predicts only a sharp cusp at half coverage, both systems have smaller cusp at coverage of 0.2 which is close to the phase boundary at the measured temperature range. Since the coverage determination of O/Mo(110) may be incorrect, one cannot be sure about whether this coverage corresponds to that of disordered phase or p(2×2) phase, but it seems that this nominal coverage is well below that of p(2×1). Because it is not easy

to prepare exactly half covered surface at least for O/W(110), the experiment could not see the predicted cusp at half coverage, but the slight increase of ξ at high coverage of O/Mo(110) might be the half coverage cusp since the assumed coverage vs. work function relation can cause some error. If the coverage vs. work function relation of O/Mo(110) is similar to that of O/W (110), we believe the nominal coverage of 0.7 in Ref.[9] would correspond to relative coverage of about 0.5, while 0.2 would still be close to relative coverage of 0.2.

IV. Comparison with calculations

There have been many MC calculations on the surface diffusion of O/W(110) as described briefly in Sec. I. One of the early calculations in Ref.[7] which tried to interpret the erroneously huge temperature dependence of thermodynamic factor of Ref.[6] is now unreliable, but there has been sometimes good agreement of diffusion coefficient values between calculations [8].

Recent studies by Uebing and coworkers [11] have included thermodynamic scale laws to show the singular behavior at T_c which is not easy to see experimentally. In Ref.[8], the values of E_A^C at many different coverages were calculated, but since their ln D versus 1/T curves showed nearly no slope within the ordered phase, they had to compare their activation energy of disordered phase with the experimental results assuming that E_A^C has the same values for all temperature at a fixed coverage. As discussed above, there is good explanation of different values of E_A^C at different phases, and the coverage at which E_A^C starts to increase was near the phase boundary. Also, the values of ξ from the experiment did not have temperature dependence predicted by the calculation and had a maximum at coverage of 0.2, very close to the phase boundary.

Another recent calculation of the surface diffusion coefficient at coverage of 0.45 [10] showed that the non-Arrhenius behavior is pronounced near T_c and as a result E_A has singular behavior at T_c. It was also predicted that E_A has smaller values

in disordered phase, which can be understood as a result of reduction of the adatom - adatom interaction. The experimentally observed high E_A^C values from ln D vs. 1/T curve of p(2×1) ordered phase and low values of low coverage disordered phase might be explained by this temperature dependence of E_A.

The calculated ξ has a dip at Tc, but there are flat region above and below the dip which is in good agreement with the experiments. The fluctuation method results did not include data points near T_c due to the change of coverage, and a dip of ξ or inversely a cusp of $<(\delta N)^2>/<N>$ could not be detected. Although the coverage dependence has not been fully studied, the temperature dependence of thermodynamic factor along with that of E_A in Ref.[10] seems more correct than other calculations.

The coverage dependence of E_A^C and that of ξ were recently calculated by Vattulainen et al. [13]. The trend of E_A^C was that it increases at low coverage until the order-disorder phase transition occurs, and then it is decreased rapidly and has very small value at half coverage. Although the fluctuation measurement at exactly half coverage was impossible in Ref.[5], it is apparent that the sharp decrease in calculation after entering p(2×1) phase was experimentally absent. Vattulainen et al. compared their E_A^{CM} at 590 K, that is the activation energy derived from $D_{c.m.}$ with the experimental values in Ref.[5] and argued that there is good agreement between them. The increase of E_A^{CM} at low coverage roughly agrees when we shift the calculated values by 0.6 eV as in the inset of Fig. 1, but the experimentally observed values at higher coverages than 0.5 were nearly constant, while the calculation predicted sharp rise of E_A^{CM} as approaching p(2×1) to p(1×1) phase transition.

Also, there is some discrepancy between theory and experiment about the thermodynamic factor. Due to lack of data points near half coverage, it is not sure whether there really was a cusp in ξ, but one thing clear is that calculation predicts a monotonic decrease in ξ near order - disorder phase boundary rather than a small cusp.

All these indicate that the current calculations

do not represent the real O/W(110) system properly. Polaron formation, that is the participation of the substrate during the adatom diffusion process was suggested to interpret the disagreement between theory and calculation [8], but this may not be a plausible explanation because the substrate is very inert unlike W(100) plane.

V. Conclusion

The understanding of surface diffusion has been greatly improved by recent calculations, but as shown in this work, there are still many discrepancies between theory and experiment even for relatively simple system O/W(110). The issue of how important the thermodynamic factor is in diffusion coefficient was not fully considered until quite recently. It seems now apparent both from calculation and from experiment that the temperature dependence of the thermodynamic factor is far less important than that of microscopic jump rate in the behavior of chemical diffusion coefficient.

For the coverage dependence of the activation energy, the theory has been less successful. It may simply result from the different adatom - adatom interaction in ordered and disordered phases, but this has not been well predicted by calculations. The non-Arrhenius behavior in Ref.[10], however, shed some light on this issue and some agreement has been achieved. If the calculation can fully explain the experimentally observed coverage dependence of the thermodynamic factor as well as that of the activation energy, we will be able to understand more of surface diffusion phenomena in connection with ordering mechanism.

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