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A new measurement and ab-initio molecular orbital calculation of wettability

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To clear the mechanism of wetting between materials, the interaction energy of wetting is measured from contact angle between cleaned surfaces, and qualitatively considered by calculating the binding energy using ab-initio molecular orbital method.

A new measurement of wettability is carried out. That is, Ar grow cleaning of specimen in ultra-high vacuum is adopted, and the contact angle at the edge of wetting droplet is measured using scanning electron microscope in high magnification. Consequently, the contact angles of liquid Au, Ag and Cu on each substrate of tungsten and grassy carbon are obtained in good reappearance.

Ab-initio molecular orbital method is used to explain the interaction energy of wettability. Two-atoms model calculation is performed for the system of examination. Calculated binding energy is in good agreement with the interaction energy estimated from the experiment. The hybridization of frontier orbital is also investigated, and a clue for the estimation of wetting interaction is found.

1 Introduction

Wetting phenomenon between two materials is important to many industrial applications such as electronics, printing, dispersion of fine particles, washing and binding. But problems of wetting are not cleared fundamentally as they have been treated empirically and experimentally in many industrial cases. If wetting phenomena are theoretically cleared and can be controlled, we are able to make many useful materials such as functional thin films and ultra-low-friction materials.

Generally, wettability has been evaluated by the contact angle using the sessile drop method.[1)] However, the conventional method may be unsuitable for determining the true interaction energy between pure material surfaces as the contact angle is measured from the macroscopic profile of droplet.

In this study, the contact angle at the edge of wetting droplet is measured using scanning electron microscope in high magnification, furthermore, Ar grow cleaning of specimen is adopted, since the wetting phenomena with chemical binding are very sensitive to surface contamination of specimen.

To find a clue for estimation of wetting interaction, We tried to carry out the ab-initio molecular orbital calculation using the program AMOSS (ab-initio molecular orbital system for supercomputers) which has been developed by the NEC computational chemistry group. Two-atoms model calculation is performed for the system of examination with transient metals.

2 Experiment

To obtain a contamination-free contact of liquid and solid, the experiment must be done in the use of pure specimens under the clean conditions in ultra-high vacuum (UHV) because the wetting phenomenon is based on the chemical bonds of the first-layer atoms of the surfaces.

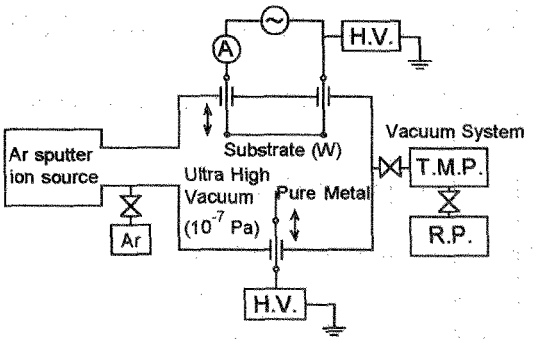

Figure 1 Schematic apparatus of wetting experiment.

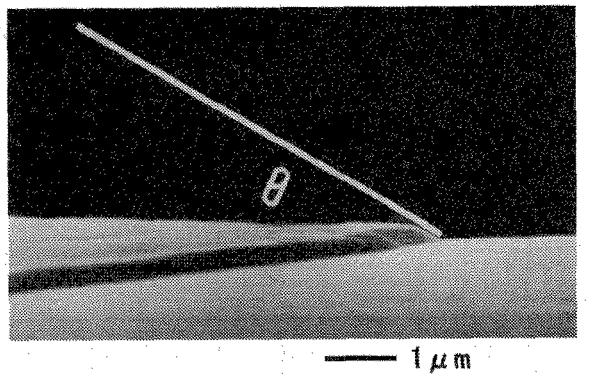

Figure 2 Configulation of measuring of contact angle.

Figure 1 shows the schematic apparatus of wetting experiment. The well annealed tungsten or grassy carbon wire with a purity higher than 99.99% was first cleaned by ultrasonic method and attached in UHV chamber as substrate. And, each wire of Au, Ag, and Cu with a purity of 99.99%, previously flushed in high vacuum, was set as specimen for liquid metal. Then the substrate was outgassed and flushed under UHV condition at 2000 °C for 30 min, and was cleaned together with the liquid metal specimen by the glow discharge of Ar gas (99.9995% in purity). This cleaning process is intended to remove perfectly the slight contamination such as oxide film from the substrate and the liquid metal specimen. The liquid metal specimen was brought into contact with the substrate and was rapidly melted. The liquid metal was cooled after wetting stably. While wetting process, substrate and liquid metal surfaces ware kept bombarding by Ar ion with the energy of 0.5keV. A series of wetting process was recorded by video camera using the microscope of 100 magnifications.

The contact angle was measured in scanning electron microscope image at the magnitude of more than 10000. The measurement was done at the position first solidified from liquid state as shown in Figure 2. The measured contact angle data were dispersed because of the deference of the crystal faces or the cooling conditions. The average of contact angles were shown in Table 1. It is found that the glow cleaning process strongly

Table 1 Average of contact angle $\overline{\theta}$ with and without glow cleaning process.

	With cleaning	Without cleaning
Au on W	21.8 °	25.3 °
Ag on W	24.7 °	58.6 °
Cu on W	38.6 °	53.5 °
Au on C	No wetting	No wetting
Ag on C	No wetting	No wetting
Cu on C	No wetting	No wetting

affects on the average contact angles of metals wetting on W, especially for Ag on W, which seems to be due to the difference of surface oxidization. And no liquid metal wet on grassy carbon substrate regardless of with or without glow cleaning. The interaction energy or the adhesion energy γ_0 of each wetting system is given by the equation;

$$\gamma_0 = \gamma_\ell(1 + \cos\theta) \tag{1}$$

where γ_ℓ is the surface energy of liquid metal, and the θ is the contact angle. To obtain γ_0, the experimental value of γ_ℓ is required, so we used the Semenchenko's experimental values.[2)]

3 Qualitative consideration of wettability

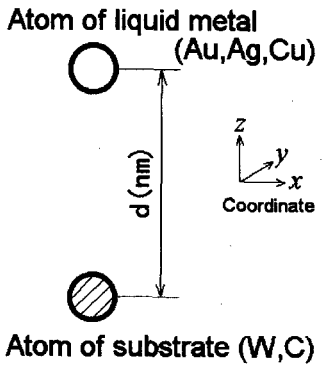

Figure 3 The two-atoms model for calculating.

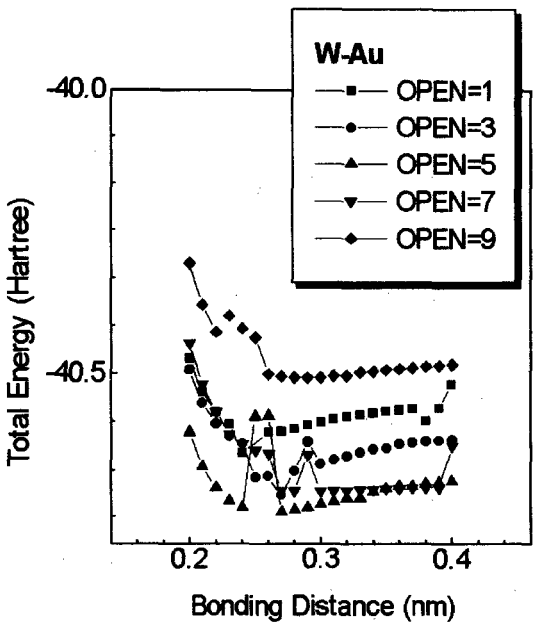

Figure 4 The example of calculated adiabatic potential carves.

The first step for understanding wetting phenomenon is to estimate the interaction energy that closely relates to the formation of the contact angle at the triple junction consisting of substrate, liquid metal and their interface. In this section, the interaction energy is estimated qualitatively by calculating the one-electron levels and the binding energy of two-atoms molecular model using AMOSS. Transient metal is stable with several open shell, thus the restricted open-shell Hartree-Fock (ROHF) method was used to calculate the energy levels. In AMOSS, the Christiansen's effective core potential[3] is used and the correlation correction to the energy is calculated using the Møller-Plesset second-order perturbation theory. The basis sets for each atom consist of the atomic orbitals that are the linear combinations of Gaussian functions. Only the Gaussian function of each orbital which has the lowest exponent is separated and used as the deferent basis for expressing accurately the spreading wave functions far from the atomic core.

The model for calculating the binding energy is illustrated in Figure 3. We first calculate the adiabatic potential in all the cases of calculatable open shell with ROHF method by slightly varying the distance between the atoms of substrate and liquid metal. The example of the calculated adiabatic potential is shown in Figure 4. The discontinuity seen in Figure 4 is explained that the starting wave function is not suitable for converging the most stable electron state. Therefore the lowest plot may be adopted as the basic stable state of the bound atoms. The binding energy of the system is thought to be the difference energy between the basic stable states of bound atoms and of completely separated atoms. The estimated binding energy values and the equilibrium distance of the most stable states in each cases are shown in Table 2.

The binding energies of tungsten-metal systems are much higher than those of carbon-metal systems. This result corresponds to the experimental results that the tungsten substrate is well wetted by the liquid metals and the grassy carbon substrate cannot be wetted. It is also cleared that the equilibrium distances of tungsten-metal systems are longer than those of carbon-metal systems. This is thought that the valence electron orbital *6s* of tungsten dispersed further than that of carbon *2s*, thus the stable binding easily occurs in the cases of tungsten-metal systems.

To clear the binding structure, the coefficient of wave function of the binding orbital selected by Mulliken's population analysis is investigated. Figure 5 shows the examples of the calculated energy level of tungsten-metal and carbon-metal

Table 2 Binding energy (E_0) and equilibrium distance (d_0) of each system. The parenthesized value is the number of open shell. Interaction energy (γ_0) obtained from the measured contact angle using equation (1) is also shown. In the case of metal-carbon, no value is presented because of no wetting. A hyphen may be thought to represents zero.

	E_0 (a.u.)	d_0 (nm)	γ_0 (J/m^2)
W-Au(5)	0.193	0.27	2.16
W-Ag(5)	0.158	0.28	1.89
W-Cu(5)	0.157	0.26	2.00
C-Au(1)	0.056	0.20	-
C-Au(3)	0.045	0.21	-
C-Ag(1)	0.015	0.19	-
C-Ag(3)	0.046	0.22	-
C-Cu(1)	0.031	0.21	-
C-Cu(3)	0.017	0.19	-

systems before and after binding. This diagram shows the degree of hybridization. The diagrams of W-Ag and W-Cu were similar to that of W-Au, and those of C-Ag and C-Cu were similar to that of C-Au. Many binding orbitals of W-Au which have lower energy than the HOMO are hybridized from the atomic orbitals which have higher energy than each LUMO of tungsten and gold atoms. But this result is not obtained in the case of C-Au. So it is thought that the hybridization of valence orbital is the prime cause of the higher binding energies of the tungsten-metal systems than the carbon-metal systems.

4 Conclusions

With Ar glow cleaning and by measuring the contact angle in high magnification, the contact angles of liquid Au, Ag and Cu on each substrate of tungsten and graphite can be obtained in good reappearance.

By calculating the one-electron levels and the binding energy of two-atoms molecular model using ab-initio molecular orbital calculation program AMOSS, it is found that the binding energies of tungsten-metal systems are much higher than those of carbon-metal systems. This corresponds to our experimental results of wetting. Furthermore it is thought that the hybridization of frontier orbital is the prime cause of the higher binding energies of the tungsten-metal systems than the carbon-metal systems.

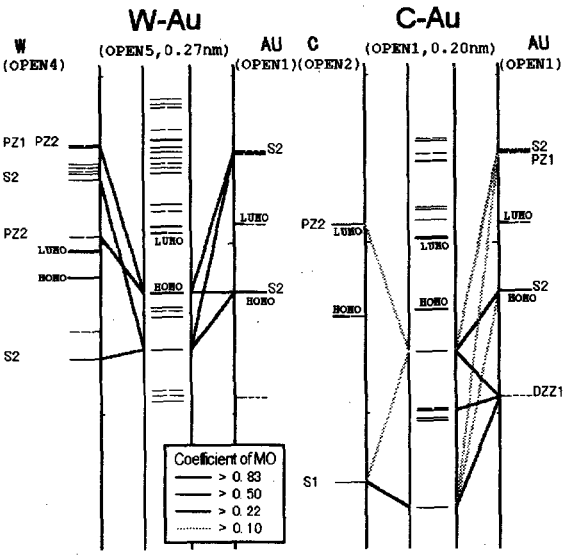

Figure 5 The relation of calculated energy levels between before and after binding.

5 Acknowledgments

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