Ab Initio Evaluation of Capacitance Between Electrodes with a Nanoscale Gap

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We have examined the capacitance of two parallel electrodes with a nanoscale gap, using an *ab initio* method within the density functional theory and taking account of atomic structures of electrode surfaces explicitly by attaching atomic layers to semi-infinite jellium electrodes. The behavior of calculated capacitance exhibits effects of electron spills from the electrodes and tunneling between the two electrodes, which are qualitatively similar to but quantitatively different from the behavior in the case of bare jellium electrodes. The quantitative difference can be understood from the change in the tunneling probability accompanied by the change in surface atomic structure.
Key words: capacitance, density functional theory, aluminum, sodium, tunneling probability

1. INTRODUCTION

The miniaturization of semiconductor devices has been progressed, and reached the nanometer scale recently. On this scale, various quantum effects are expected to be significant. In capacitance, which is one of the important quantities in electronic devices, such quantum effects are expected to appear. Many groups have already studied the quantum effects in capacitance theoretically and experimentally [1-7]. Büttiker *et al.* [1] pointed out that electron tunneling between capacitor plates affects capacitance in their theoretical studies on mesoscopic capacitors. They also pointed out that the experimentally relevant capacitance is not the electrostatic one defined from the potential difference between capacitor plates, but is the electrochemical one defined from the chemical potential difference between electrodes. Hou *et al.* [2] measured the capacitance of a nanoscale junction formed by the tip of a scanning tunneling microscope and a gold cluster on alkanethiol-covered Au (111), and found that as the distance between the tip and cluster decreases, the measured capacitance first increases and then decreases.

Although the general feature of capacitance has been clarified in some extent as mentioned above, the capacitance on the nanoscale has not been understood sufficiently. One reason for this is the difficulty in the measurements of properties of nanostructures and the interpretation of data obtained by such measurements. It may be another reason that theoretical studies on capacitance of nanoscale structures are little and often use method having insufficient reliability. Therefore, further theoretical studies on the capacitance on the nanoscale are highly desirable.

Motivated by the above situation, we have examined previously the quantum capacitance of two parallel jellium electrodes by the *ab initio* method within the density functional theory [7]. The behavior of the

calculated capacitance shows distinct deviation from the classical capacitance, which can be understood from two quantum effects, namely, electron spill from the electrodes and tunneling between two electrodes. Further, we found that the capacitance depends on the electron density in the electrodes. The study, however, is still insufficient in the sense that atomic structures of electrode surfaces are not taken into account.

In this paper, we report the capacitance between two parallel electrodes calculated by the *ab initio* method within the density functional theory [8,9], with taking account of atomic structures of electrode surfaces. We show that the effects of surface atomic structures appear clearly, though the qualitative behavior of the capacitance is the same.

2. METHOD AND MODEL

In the calculation, the two parallel electrodes are described by semi-infinite jellium. We examine two models, namely, aluminum capacitor and sodium one. In the case of the Al capacitor, an Al (100) layer is attached to each surface of the jellium electrodes to examine the effects of atomic structure of electrode surface. The electron density in the jellium electrode is set to be the same as that in the bulk Al, which corresponds to Wigner-Seitz radius (r_s) of 2 a.u. (= atomic unit ; 1 a.u. = 0.0529 nm). The electrode-layer distance is set to be 1.9 a.u., which is optimized by calculating forces acting on the Al layer [10]. In the case of the Na capacitor, Na (100) layer is attached to jellium electrodes. In this case, the electron density of the jellium electrodes corresponds to r_s = 4 a.u., which is the same as that of the bulk Na. The electrode-layer distance is set to be the optimized value, 2.5 a.u. The region between the electrodes is empty, i.e., a vacuum.

It should be noted that not only the surface atomic structure itself but also the arrangement of the two

electrodes in the surface parallel direction may have notable effects. Therefore, we examine two cases of electrode arrangement. In the first one, each atom on an electrode is located just above an atom on the other electrode. On the other hand, in the second one, each atom on an electrode is located just above the center of a square formed by four neighboring atoms on the other electrode. Hereafter we call the first and second arrangements symmetric and asymmetric, respectively.

To evaluate capacitance of the above systems, first we calculate electronic states under finite bias voltages self-consistently. For this purpose, we adopted a method developed by our group [11,12], which takes account of semi-infinite electrodes explicitly. In this method, an entire system is divided into three regions, namely, deep insides of the two electrodes and the middle region between them, and wave functions in the middle region are determined so that they are connected properly to wave functions in the electrode regions. Effective potential and electron density are determined self-consistently while keeping the difference in Fermi level between the two electrodes according to the applied bias voltage. We use the local density approximation [13,14] for the exchange-correlation potential and local pseudopotential for the ionic potential [15,16]. The cutoff energy for Fourier expansion in the directions parallel to the surface is set to be 10.73 Ry (1 Ry = 13.6 eV) and 4.93 Ry for the Al and Na systems, respectively.

Capacitance is estimated using

$$C = \frac{\Delta Q}{\Delta V}.$$ (1)

Here, ΔQ is the change in the induced charge due to the change in the applied bias voltage ΔV, defined using the electron density at the applied bias voltage $V, \rho(V,\mathbf{r})$, as

$$\Delta Q = \int_{\Omega_+} [\rho(V + \Delta V, \mathbf{r}) - \rho(V, \mathbf{r})] d^3 \mathbf{r}.$$ (2)

As for Ω_+, it is defined as the region on the side that includes the positively biased electrode from the middle of the vacuum region. In the present calculation, V and ΔV are set to be 0 and 0.3 V, respectively.

3. RESULTS AND DISCUSSIONS

Before presenting the calculated results, we would like to comment on the definition of the distance between the two electrodes. Though the distance defined by the positions of nuclei of the attached layers, d_{nuc}, is unambiguous, they are not necessarily suitable to compare the calculated capacitances with those estimated classically. This is because the distribution of the electron clouds extends to the region outside the nuclei. Therefore, we define the effective distance between the electrodes d so that the calculated capacitance coincides with the classically estimated one in the cases where the distance between the electrodes are sufficiently long. The values of d defined in this way are shorter than d_{nuc} by 5.4 and 7.7 a.u. for the cases of Al and Na, respectively. Since halves of these values are comparable to the ionic radii of Al (2.7 a.u.) and Na (3.6 a.u.), we can say our definition of the effective distance is reasonable. It is noted that d is defined similarly in the case of the bare jellium electrodes [7]: because of electron spill from an electrode, the position of the effective surface does not coincides with the jellium
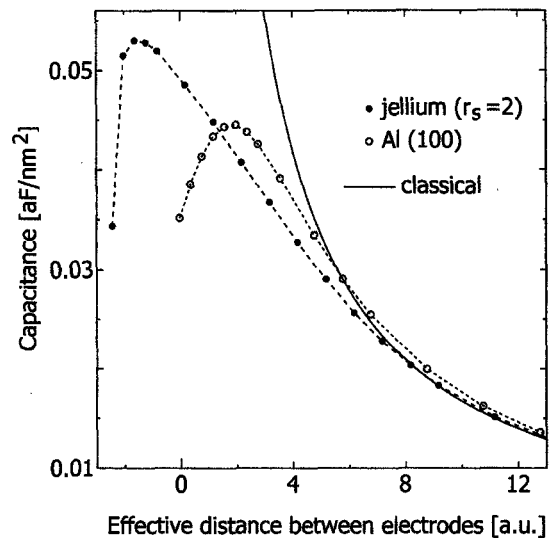

Fig.1. Calculated capacitance of the bare and atomic-layer attached jellium electrodes for the Al case as a function of the effective distance between electrodes. The results for bare and atomic-layer attached electrodes are shown by white circles and black ones, respectively.

edge.

In Fig.1, we show the calculated capacitances of the bare [7] and atomic-layer attached jellium electrodes per unit area for the Al case as a function of d, together with the ones estimated using the classical electrostatics. Here, the arrangement of the Al electrodes is the symmetric one. When $d > \sim 5$ a.u., the calculated capacitances of the bare and atomic-layer attached jellium electrodes agree well with the classically estimated ones, which are proportional to d^{-1}. In the region $d < \sim 5$ a.u., where the deviation of the calculated capacitances from the classical ones is clearly seen, the behavior of the capacitances of the jellium with an atomic layer is qualitatively the same as those of the bare jellium: when d is very small, the capacitances increase as d increases. This behavior can be understood from the electron tunneling between the electrodes [7]. Quantitatively, however, distinct difference is seen between the bare and atomic-layer attached jellium cases. In the case of the jellium with an attached layer, the capacitances are smaller than those of the bare jellium electrodes.

This quantitative difference can be understood from the electron density and induced charge distribution of the jellium electrode with the attached Al (100) layer for $d \sim 10$ a.u., which are shown in Fig. 2. As can be seen easily, both the distributions of the electron density (Fig. 2(a)) and induced charge (Fig. 2(b)) are not uniform. They are quite different from those in the bare jellium case, where the distributions are completely uniform in the direction parallel to the surface. Since the localization of induced charges accompanies the local reduction of the potential barrier for tunneling electrons [17], the tunneling probability in the cases of the atomic-layer attached jellium is larger than that in the bare jellium. Therefore, the capacitance of the former case becomes smaller than the latter one.
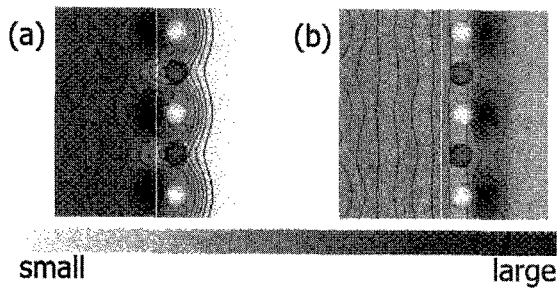
Fig.2. Distributions of (a) electron density and (b) induced charge for the jellium with the attached Al (100) layer. The vertical white line shows the jellium edge. White circles are Al ionic cores, centers of which are in the plane shown in the figure, while the Al cores denoted by black circles are out of plane. The interval of contour lines is (a) 25 nm^{-3} and (b) 0.1 nm^{-3}.

In Fig. 3, we show the calculated capacitances per unit area as a function of the effective distance between the two parallel electrodes d, together with the classical one. Here, the capacitances for both symmetric and asymmetric arrangements of electrodes are shown in the Al case, while only that for the symmetric one is shown in the Na case. We can see that the qualitative behavior of the capacitance is the same for all the three cases shown in Fig. 3. We can also see that the capacitance of the Na case is always smaller than those of the Al cases. The origin of this discrepancy is considered to be the same as the origin of the electron-density dependence of the capacitance of the bare jellium electrodes [7]. Namely, a smaller work function of Na than that of Al involves higher tunneling probability for electrons at the
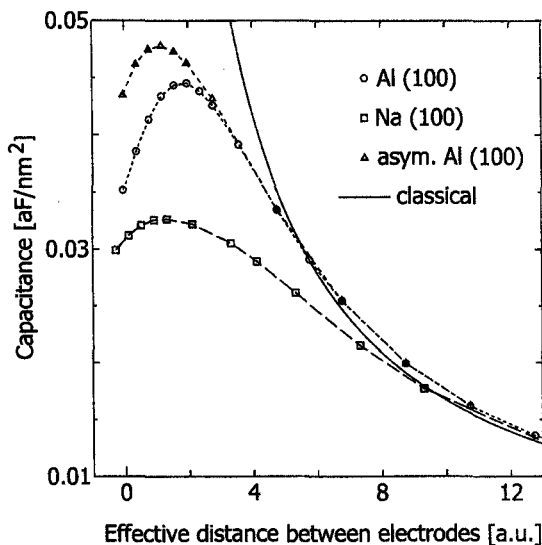

Fig.3. Calculated capacitances of the Al and Na capacitors as a function of the effective distance between electrodes. Capacitances of both the symmetric (circles) and asymmetric (triangles) arrangements are shown in the case of the Al, while only the symmetric one (squares) in the Na case. Solid line shows the capacitance estimated classically.
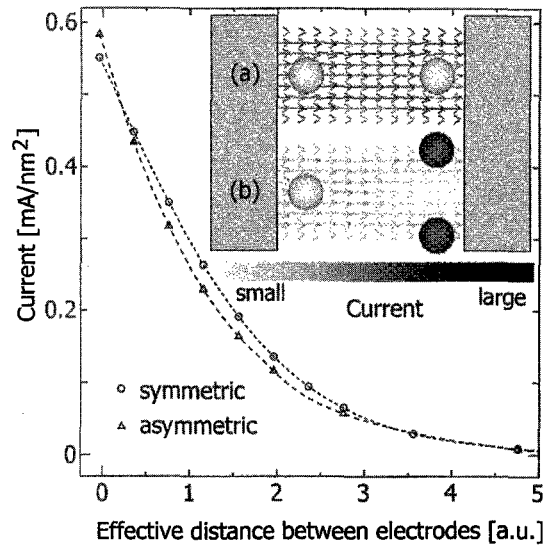

Fig.4. Tunneling current in the Al capacitor with the symmetric (circles) and asymmetric (triangles) arrangements as a function of the effective distance between the electrodes. The inset shows the current distributions for (a) symmetric and (b) asymmetric capacitors, respectively. Definitions of the white and black circles in the inset is the same as those in Fig.2.

Fermi level if other conditions are the same, and thus leads to a smaller capacitance in the Na case.

Another interesting feature seen in Fig.3 is the difference of capacitance between the symmetric and asymmetric arrangements of the Al electrodes. The capacitance of the asymmetric case is larger than the symmetric one when $d < 3.0$ a.u. This can be understood from the fact that the effective tunneling path is longer in the asymmetric arrangement than in the symmetric one for the same value of d. In general, the longer tunneling path causes smaller tunneling probability, and thus leads to a larger capacitance. This idea is confirmed by the current distribution between the two electrodes shown in the inset in Fig.4, for the case where $d \sim 3$ a.u. Distinct difference in the current distribution seen in the inset between the symmetric and asymmetric arrangements suggests that the currents flow through the topmost atoms of the two electrodes, and that the current direction is not necessarily vertical to the surface. The calculated currents between the electrodes shown in Fig. 4 also support the idea. In the range 0.4 a.u. $< d < 3.5$ a.u., the current is larger in the symmetric arrangement than in the asymmetric one.

It is worth mentioning that the current in the asymmetric arrangement becomes larger than in the symmetric one when $d \sim 0$ a.u. This may be understood from the facts that the two electrodes almost contact at such an effective distance, and that the asymmetric arrangement is nearly the same as the bulk crystal without defects while the symmetric one has a stacking fault. It should also be noted that the reversal of the order of currents at $d \sim 0$ a.u. does not seem to affect the capacitance shown in Fig. 3. The reason for this is under investigation.

4. CONCLUDING REMARKS

We have examined the capacitance of two parallel electrodes with a nanoscale gap, using an *ab initio* method within the density functional theory and taking account of atomic structures of electrode surfaces explicitly. The calculated capacitance exhibits two quantum effects, namely, the electron spills from the electrodes and tunneling between the two electrodes, which are qualitatively similar to but quantitatively different from the behavior in the case of bare jellium electrodes. The quantitative difference can be understood from the change in the tunneling probability accompanied by the change in surface atomic structure.

The present results show that capacitance of nanoscale structure is very sensitive to its atomic structure. Even if the atomic structures of the electrodes are the same, capacitance changes by arrangements of the electrodes in the direction parallel to the surface. On the other hand, our results also show that the effects of the atomic structures on capacitance appear only when the gap distance is as short as a few a.u. This may be partly due to the very flat structures examined in the present study: when the electrode surfaces are rougher, another quantum effect in capacitance, the effect of density of states [1], is expected to appear.

ACKNOWLEDGEMENTS

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