Effect of surface bond-order loss on the dc conductance of a metallic nanosolid

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With the miniaturization of a solid device, quantum and interface effects become dominant not only in the static properties but also in the transport dynamics in the solid. Here we examine the dc conductance of a nanosolid by introducing the depression of the intraatomic trapping potential in the surface skin [Sun, Phys. Rev. B 69, 045105 (2004)] as a perturbation to the conventional “quantum well” for tunneling electrons. It is derived that downshifts of the dc conductance peaks (that is, the incident energies for resonant tunneling) happens in an oscillatory way, depending on the strength of the perturbation. Besides, the downshifts of the peak positions due to the trapping potential well depression decrease as the size of the nanosolid is increased. © 2005 American Institute of Physics.

I. INTRODUCTION

Quantum transport dynamics has attracted tremendous interest owing to its significance in the upcoming technologies such as nanoelectronic devices. Electrons tunneling in a nanosolid exhibit quantized conductance that is often related to the energy level separation in the conduction band, or the Kubo gap, $\delta_k=4E_F/3N$, where $E_F$ is the Fermi level and $N$ is the number of conduction electrons per unit volume. However, the effect of bond-order loss in the surface skin will affect the entire band structure and hence the energy levels, $E_F$, and hence the $\delta_k$ value. Traditionally, a nanosolid is often described by a quantum confinement (QC) potential well:

$$V = \begin{cases} V_0, & |x| \leq L/2 \\ 0, & \text{else.} \end{cases}$$ (1)

The value of $V_0$ is the muffin-tin potential if the conduction electrons are considered, $L$ is the diameter of the nanosolid. If conductivity above the Fermi level is considered, $V_0$ is the potential barrier or the work function of the system.

Recently, we have modified the QC potential well by adding the intraatomic trapping potential $V_{\text{atom}}$ and the effect of surface bond-order loss through a bond-order-length correlation mechanism. The BOLS correlation mechanism indicates that the bond-order loss of atoms in the surface skin causes the remaining bonds of the undercoordinated atoms to contract spontaneously with an association of bond strength gain. As a result of the BOLS correlation, the intraatomic trapping potential $V_{\text{atom}}$ in the surface skin will sink down, as illustrated in Fig. 1(a), where $V_{\text{crystal}}$ and $\Delta_{\text{surf}}$ correspond to the crystal potential and the surface modification, respectively. However, the core interior remains as it is in the bulk materials, as recently noted by Winn. According to the BOLS correlation, densification of mass, charge and energy happens in the surface skin of the nanosolid in a localized way, which dictates the physical properties of nanostructures of which the portion of the undercoordinated atoms increases in a $L^{-1}$ fashion. The BOLS correlation mechanism has been intensively verified and applied to predicting the size dependence of nanostructures. In this article, we report the effect of surface bond-order loss on the dc conductance in a nanosolid by taking into account the sunken part of the intraatomic trapping potential near the surface.

II. THEORY

The BOLS correlation perturbs the potential well of a nanosolid by adding the suppressed intraatomic trapping potential $V_{\text{atom}}$ in the surface skin to the QC potential well given in Eq. (1). This perturbation causes $V_{\text{atom}}$ to sink down near the surface. Therefore, conduction electrons will suppose a trap immediately after tunneling into the QC box through the potential barrier of the surface. In order to simplify the quantum transport calculations, we approximate the depressions of the QC potential well by two square-well depressions in the surface skin [see Fig. 1(b)]. This approximated potential well can be expressed as

$$V = V(x) = \begin{cases} U(x-L/2 + d) - U(x-L/2) + V_{d}U(x-L/2) - U(x-L/2-d) + V_{d}U(x+L/2 + d) - U(x+L/2) + V_{d}U(x+L/2 + d) - U(x+L/2-d), \end{cases}$$ (2)

where $U(z)$ is a step function that jumps from zero to unity at $z=0$. In Eq. (2), $V_0$ is set equal to the crystal potential $V_{\text{crystal}}$ and the $\tilde{V}$ is the depth of the square-well depressions which is used as a parameter for modeling the sunken part of the intraatomic trapping. The conventional QC potential well [given by Eq. (1)] corresponds to $\tilde{V}=0$ (absence of surface bond-order loss). In order to examine the effect of the trap-
pings which are used as an approximation for the sunken part of the intratunneling bulk counterpart.

In the electron tunneling theory, electron reservoirs (called contacts) are coupled to the ends of the nanosolid of size $L$. In our approach, the tunneling coupling between the electron reservoirs and the nanosolid is modeled by square potential barriers with width $d$, which is taken to be the thickness of two atomic layers. The overall potential curve used in the electron tunneling theory is shown in Fig. 1(b). In practice, contact resistance between electrode and the nanosolid exists. However, at the junction interface between the electrode and nanosolid, potential well suppression also happens with different width from the case considered her in, which affect the magnitude of the calculated values but not the nature and the general trend of variation.

Notice that the overall potential in Fig. 1(b) consists of two parts: the left part (called the left potential barrier) and the right part (called the right potential barrier). The two parts are equally distant from the origin. The left potential barrier consists of a square barrier followed by a square well (the depression). Also, the right potential barrier is identical to the reflection image of the left potential barrier about its own center. Let $t_l$ and $r_l$ be the transmission and reflection (from the left-hand side) coefficients of the left potential barrier. Similarly, let $t_R$ and $r_R$ be the transmission and reflection (from the left-hand side) coefficients of the right potential barrier. Due to the symmetry of the overall potential mentioned above, we have $t_2 = t_R$ and $r_2 = -r_R(t_l/t_R)$. The transmission and reflection coefficients, as functions of the incident energy $E$, are given by

$$t_l(E) = \frac{1}{N} \left[ \frac{1}{8} \left( k_2/k_1 \right) \left( 1 + k_2/k_3 \right) \left( 1 + k_1/k_2 \right) e^{i (k_2-k_3)d} \right]$$

$$+ \frac{1}{8} \left( k_3/k_2 \right) \left( 1 + k_3/k_1 \right) \left( 1 + k_2/k_3 \right) e^{i (k_3-k_2)d}$$

$$+ \frac{1}{8} \left( k_2/k_1 \right) \left( 1 + k_2/k_3 \right) \left( 1 + k_1/k_2 \right) e^{i (k_2-k_3)d}$$

$$+ \frac{1}{8} \left( k_3/k_2 \right) \left( 1 + k_3/k_1 \right) \left( 1 + k_2/k_3 \right) e^{i (k_3-k_2)d},$$

where $k_1 = \sqrt{2mE}/\hbar$, $k_2 = \sqrt{2m(E-V_0)}/\hbar$, and $k_3 = \sqrt{2m(E-V)}/\hbar$ are the wave numbers in different regions, and $m$ is the mass of the electron.

By considering the transfer matrix of the overall tunneling potential we obtain the total transmission coefficient $t(E)$:

$$t(E) = \frac{t_l t_R}{t_l^2 + r_l^2 e^{2ik_1L}}.$$

The dc conductance $g(E)$ for the electron tunneling through the nanosolid is given by the Landauer formula:

$$g(E) = \frac{2e^2}{h} \left| t(E) \right|^2.$$
TABLE I. BOLS effect on the resonant peaks of dc quantum conductance and the relative change with respect to the case of $\bar{V}$=0 for a metallic nanosolid of $L$=8 nm unless as indicated. The negative sign means the downshift of the resonant peaks, and vice versa.

<table>
<thead>
<tr>
<th>$V/V_0$</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$E_3$</th>
<th>$E_4$</th>
<th>$E_5$</th>
<th>$E_6$</th>
<th>$E_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9861</td>
<td>0.9260</td>
<td>0.8655</td>
<td>0.8062</td>
<td>0.7486</td>
<td>0.6930</td>
<td>0.6392</td>
</tr>
<tr>
<td>-0.05</td>
<td>0.9637</td>
<td>0.9024</td>
<td>0.8421</td>
<td>0.7822</td>
<td>0.7237</td>
<td>0.6685</td>
<td>0.6154</td>
</tr>
<tr>
<td></td>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.136</td>
<td>(-16 nm)</td>
<td>0.141</td>
<td>0.047</td>
<td>-0.076</td>
<td>-0.190</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>-0.15</td>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.2</td>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\[ g(E) = \frac{e^2}{\hbar} |\psi|^2. \]  

The positions of the dc conductance peaks can be determined by plotting $g(E)$ against the incident energy $E$.

III. RESULTS AND DISCUSSION

In the numerical computations of $g(E)$ based on Eqs. (3)–(5), the width of the square potential barrier $d$ is taken to be $d=2$ nm. The nanosolid size $L$ is set to be $L=8$ nm. The barrier height $V_0$ is chosen to be 5 eV. The following values of $\bar{V}$ are considered:

$\bar{V}=0$ (no depression),  
$-0.05V_0$, $-0.136V_0$,  
$-0.15V_0$, $-0.20V_0$.

The value of $-0.136V_0$ is derived by considering the bond strength gain due to a 12% contraction at a flat surface: $|\bar{V}|/V_0=(0.88)^{-1}-1=0.136$. Numerical results for the positions of the dc conductance peaks in various cases of the depression depth $\bar{V}$ are shown in Table I. There are more than 20 peaks found in each case. For discussion convenience, Table I lists only the seven peaks that are nearest to $V_0$. In unit of $e^2/\hbar$, the amplitudes of all the conductance peaks are equal to 1. Also, in Table I, we use $E_i$, $i=1,2,\ldots,7$, for the positions of the seven peaks, in the order that $E_2<E_6<\cdots<E_2<E_1<V_0$. All the $E_i$'s are expressed in units of $V_0$. Table I also shows the relative shift of the peaks with respect to the case of $\bar{V}=0$ for the $L=8$ nm nanosolid. A case of $L=16$ nm is also compared.

Results in Table I shows that the addition of the BOLS depressions to the QC potential well has caused a significant change in the incident energies for resonant tunneling (peak positions) in the nanosolid. There are three interesting points for the results. First, the presence of the depressions in the well causes the conductance peaks to shift down. The relative downshift in the peak positions are remarkably large (around two to three percent) for a small depression depths such as $\bar{V}=0.05V_0$. This finding demonstrates the significance of the surface bond-order loss. Second, the percentage changes in the peak positions do not increase monotonically with $\bar{V}$. For instance, the percentage changes in the peak positions start to drop when $\bar{V}$ is sufficiently large, but then the changes increase again when $\bar{V}$ is increased, demonstrating that the resonant tunneling incident energies vary in an oscillatory way with $\bar{V}$. Third, the resonant features are weakened by increasing the feature size of the nanostructure such as $L=16$ nm. The numerical result shows that the percentage changes in the peak positions become smaller compared to the case with $L=8$ nm. The result is consistent with our expectation that the resonant features will be less pronounced as the nanosolid feature size is increased. The energy gaps in the nanosolid decrease when the $L$ is increased; hence we expect smaller percentage changes for the energy levels when $L$ is larger.

The resonant tunneling in the nanosolid corresponds to the dc conductance peaks. By Eq. (4), the condition of resonant tunneling is given by

\[ 2\phi + 2k_L L = 2n\pi, \]  

where $\phi$ is the phase of $r_R$ and the $n$ is an integer. Equation (6) means that the total phase change when the electron wave function travels to and fro between the left and right tunneling barriers must be equal to an integral multiple ($n$) of $2\pi$ or that there are an integral number ($n$) of half-wavelengths in the confinement potential well. The presence of the depressions $\bar{V}$ near the surface of the nanosolid would cause the wavelength $2\pi/\sqrt{2m(E-\bar{V})/\hbar^2}$ to decrease (leading to a number of half-wavelengths greater than $n$) should the incident energy $E$ be fixed. In order that the number of half-wavelength $n$ in the well is maintained, the incident energy $E$ for resonant tunneling (the dc conductance peak positions) needs to decrease (compared to the case of $\bar{V}=0$). Hence we expect a downshift in the peak position in the presence of the BOLS potential well depressions.

As is mentioned previously, the condition of resonant tunneling is that the total phase change must satisfy the relation: $2\phi + 2k_L L = 2n\pi$, where $\phi$ is the phase of the reflection coefficient $r_R$. The oscillatory way of variation of the peak positions with $\bar{V}$ indicates that the phase $\phi$ also varies with $\bar{V}$ in an oscillatory way. It is not easy to see this from the explicit formula of $r_R$ [Eq. (3b)] which is complicated. Let us consider for simplicity the case that $V_0\rightarrow \infty$ (very hard tunneling barriers). In this case Eq. (3b) reduces to
From Eq. (7), we have \( \tan(\phi + 2k_1d/2) = k_1/k_3 \tan k_3d \), where \( k_1 = \sqrt{2mE/\hbar^2} \) and \( k_3 = \sqrt{2m(E-V)/\hbar^2} \). From this expression, we clearly see that the phase \( \phi \) of \( r_R \) varies in an oscillatory way when \( |V| \) increases.

**IV. CONCLUSION**

The effect of surface bond-order loss on the surface trapping plays a significant role in determining the dc conductance in nanosolids by changing the incident energies for resonant tunneling inside the QC box. It has been found that the shift of the incident energies for resonant tunneling varies in an oscillatory way with the depth of the depressions. The extent of peak shift increases with the reduction of the QC box size. Understanding may provide guidelines for nanosolid device design.

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