**Ab Initio** Study of Al Atomic Chains with Na Impurity Atom

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We have carried out *ab initio* calculations on the electrical properties of Al chains with a substitutional Na impurity, focusing on the potential drop due to the applied bias voltage. Besides the expected electric current reduction by the introduction of Na impurity, we have found that the effective potential almost drops at the Na atom position wherever Na atom is located. This behavior is maintained when the applied bias voltage is increased. These results can be understood from the strength of interactions between atoms and between atom and electrode.

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The remarkable progress in fabrication technology enables us to shrink the size of electronic devices to nanometer scale. In this scale, the electron conduction mechanism is different from that in large-scale conductors. For example, it is reported that the conductance of atomic point contacts has been quantized in the unit of \( G_0 \) (=2\( e^2/h \), where \( e \) is the electron charge and \( h \) is Planck’s constant) [1–3]. Further, it is reported that the conductance of single row of Au atomic chain between electrodes has also been quantized [4, 5]. There are also several reports of conductance quantization for other atom species such as Al [6, 7].

Many theoretical studies have been performed concerning electrical properties of the atomic chains, too. Their current(\( I \))-voltage(\( V \)) characteristics is one of the focused topics of the theoretical studies on the atomic chains. One of the important behaviors which may provide a clue to understand their electric properties is the potential drop due to the bias voltages between electrodes. However, there are only few reports focused on the potential drop. Moreover, different behaviors of the potential drop are seen among the reported studies. In a carbon atomic chain, Brandbyge *et al.* reported that the potential drop concentrates at one of the ends of the chain [8]. On the other hand, Lang *et al.* reported that the potential drop is spread over the chain and also into the electrodes by examining another carbon atomic chain [9]. In the case of Al atomic chains between jellium electrodes, the potential drop is reported to concentrate at a certain position in the chain [10, 11]. Further, in the case of a Na atomic chain between jellium electrodes, the potential drop concentrates at one of the ends of the chain [12]. In the above investigations, all the atomic chains were constructed by the same atomic species. On the contrary, Hirose *et al.* examined Al atomic chains where the Al atom next to a jellium electrode was replaced by a Na atom, and found that the potential drop concentrates at the Na atom [13]. Although their results clearly show that the replacement of the Al atom with Na enhances the degree of localization of the potential drop region, the effects of the Na impurity are not well separated from those of the contact between chain and electrode. To investigate the potential drop behavior in more detail including this point would be of great interest not only from the viewpoint of fundamental science, but also from technological application: the understanding, control and design of the potential drop lead to the control and design of the electrical properties of nanostructure, and thus we may be able to obtain guiding principles to design nanoscale devices.

In this letter, we report the impurity effects on the electrical properties of the Al atomic chains, focusing on the behavior of the effective potential drop. In the present analysis, we carried out *ab initio* calculations using the boundary-matching scattering-state density functional (BSDF) method developed by our group [10, 14, 15]. This method is based on the density functional theory [16, 17] incorporating scattering states, and can calculate electronic states including semi-infinite electrodes under applied bias voltage self-consistently. We used the local density approximations for the exchange-correlation potential [18, 19], and local pseudopotentials suggested by Chelikowsky *et al.* for Al [20] and Ashcroft for Na [21] for the ionic potentials.

In the calculation, we examined an Al atomic chain consisting of six atoms between jellium electrodes, and substitute one of the atoms with a Na atom. The Al\(_6\) chain without Na impurity was also examined as a reference. The Al chains with a substitutional Na impurity may be difficult to be fabricated, but we expect that the essence of the behavior of the potential drop can be seen in these...
TABLE I: The notation of the atomic chains examined in this letter.

| symbol       | order of the atoms                                      |
|--------------|---------------------------------------------------------|
| NaAl$_5$     | jellium-Na-Al-Al-Al-Al-jellium                          |
| AlNaAl$_4$   | jellium-Al-Na-Al-Al-Al-Al-jellium                       |
| Al$_2$NaAl$_3$| jellium-Al-Al-Na-Al-Al-Al-jellium                      |
| Al$_6$       | jellium-Al-Al-Al-Al-Al-Al-jellium                       |

![Graph](image1.png)

FIG. 1: Calculated electric current through the atomic chains as a function of the applied bias voltage.

The notation given in Table I for example, the AlNaAl$_4$ chain denotes a chain where Al, Na, Al, Al, Al and Al atoms are placed between electrodes with this order. The Wigner-Seitz radius of the jellium is set to be 2.0 atomic units (a.u.), which is the same as that of bulk aluminum. In principle, we choose the geometrical parameters referring to the bulk crystal: the distances of jellium-Al, jellium-Na, Al-Al and Al-Na are set to be 2.5 a.u., 2.9 a.u., 5.4 a.u. and 6.2 a.u., respectively. The positions of atoms are fixed throughout the calculations. We impose the periodic boundary condition in the directions parallel to the surface, and the size of supercell is set to be 15.0 a.u. x 15.0 a.u.

Figure 1 shows the calculated I-V characteristics of the NaAl$_5$, AlNaAl$_4$, Al$_2$NaAl$_3$ and Al$_6$ chains. From this figure, we can see that the existence of Na atom much reduces the electric current. We can also see that the electric current through the NaAl$_5$ chain is slightly higher than the other chains which include Na atom. This can be understood by the difference in electronic states of Na atom: Na atom of NaAl$_5$ is located between Al atom and jellium, while that of AlNaAl$_4$ and Al$_2$NaAl$_3$ is located between Al atoms. It should be noted that these I-V characteristics hardly depend on the applied bias voltage within the examined range.

![Graph](image2.png)

FIG. 2: Shift in effective potential along the chain axis by an applied bias voltage of 0.1 V for the (a) NaAl$_5$, (b) AlNaAl$_4$ and (c) Al$_2$NaAl$_3$ atomic chains.

![Graph](image3.png)

FIG. 3: Shift in effective potential at each atom of the atomic chain as a function of the applied bias voltage for the (a) NaAl$_5$, (b) AlNaAl$_4$ and (c) Al$_2$NaAl$_3$ atomic chains.

There are two energy peaks in local density of states within the range of 0.4 eV from the Fermi level in the Al$_6$ and NaAl$_5$ but not in others.

Figure 2 shows the shift in effective potential by an applied bias voltage of 0.1 V along the chain axis. From this figure, we can see that the effective potential drop due to the applied bias voltage always concentrates at the Na atom wherever it is placed. From the dependence of the effective potential on the applied bias voltage shown in Fig. 3, we can see that the features of the above concentration of potential drop do not depend on the bias voltage within the examined range. Further, all the chains show the common feature of the potential shift: the potential shifts of the atoms at the left of the Na hardly change, while those of the atoms at the right of the Na shift nearly...
the same amount of the applied bias voltage.

We also examined the shift in the local density of states (LDOS) around each atom of the Al$_2$NaAl$_3$ chain as shown in Fig. 4. From this figure, we notice that the peak of LDOS hardly changes by the applied bias voltage for the atom located just at the left of the Na, while the peak of LDOS shifts about 0.5 eV for the atoms located at the right of the Na. This means that the atoms at the left of the Na behaves as if they do not feel the applied bias voltage, while the atoms at the right of the Na behave as if they feel the applied bias voltage fully.

On the basis of the above results, we can speculate the trend of the effective potential drop as follows. In the Al$_2$NaAl$_3$ chain, there are strongly hybridized states between the Al atoms, and also Al atom and electrode. However, in the case of the Al atomic chain as a function of the incident electron energy for the atom located just at the left of the Na, while the peak of LDOS shows about 0.5 eV for the atoms located at the right of the Na. This means that the atoms at the left of the Na behaves as if they do not feel the applied bias voltage, while the atoms at the right of the Na behave as if they feel the applied bias voltage fully.

In summary, we report the impurity effects on the electrical properties of the Al atomic chains, focusing on the concentration of the effective potential drop. We found that the shift in effective potential due to the applied bias voltage concentrates at the substitutional Na impurity atom wherever the Na atom is located. The analysis of the local density of states around each atom shows that the electronic states behave as if the bias voltage is absent at one side of the Na atom, while they behave as if they feel the bias voltage fully on the other side. We expect that the potential drop concentration also appears in more complicated nanostructures, and thus the present findings would be useful in controlling and designing electric properties of nanoscale devices.

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[1] N. Agraït, J.G. Rodrigo and S. Vieira, Phys. Rev. B 47, 12345 (1993).
[2] J.I. Pascual, J. Méndez, J. Gómez-Herrero, A.M. Baró, N. García and V.T. Binh, Phys. Rev. Lett. 71, 1852 (1993).
[3] J.M. Krans, C.J. Muller, I.K. Yanson, Th.C.M. Govaert, R. Hesper and J.M. van Ruitenbeek, Phys. Rev. B 48, 14721 (1993).
[4] H. Ohnishi, Y. Kondo and K. Takayanagi, Nature 395, 780 (1998).
[5] A.I. Yanson, G.R. Bollinger, H.E. van den Brom, N. Agraït and J.M. van Ruitenbeek, Nature 395, 783 (1998).
[6] J.C. Cuevas, A.L. Yeyati, A. Martín-Rodero, G.R. Bollinger, C. Untiedt and N. Agraït, Phys. Rev. Lett. 81, 2990 (1998).
[7] J. Mizobata, A. Fujii, S. Kurokawa and A. Sakai, Phys. Rev. B 68, 155428 (2003).
[8] M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor and K. Stokbro, Phys. Rev. B 65, 165401 (2002).
[9] N.D. Lang and Ph. Avouris, Phys. Rev. Lett. 84, 358 (2000).
[10] S. Furuya, Y. Gohda, N. Sasaki and S. Watanabe, Jpn. J. Appl. Phys. 41, L089 (2002).
[11] Y. Asari, J. Nara, N. Kobayashi and T. Ohno, Jpn. J. Appl. Phys. 44, 6317 (2005).
[12] S. Tsukamoto and K. Hirose, Phys. Rev. B 66, 161402 (2002).
[13] K. Hirose, N. Kobayashi and M. Tsukada, Phys. Rev. B 69, 245412 (2004).
[14] Y. Gohda, Y. Nakamura, K. Watanabe and S. Watanabe, Phys. Rev. Lett. 85, 1750 (2000).
[15] Y. Gohda and S. Watanabe, J. Phys.: Condens. Matter 16, 4685 (2004).
[16] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
[17] W. Kohn and L.J. Sham, Phys. Rev. 140, A1133 (1965).
[18] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. 45, 566 (1980).
[19] J.P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
[20] J.R. Chelikowsky, D.J. Chadi and M.L. Cohen, Phys. Rev. B 23, 4013 (1981).
[21] N.W. Ashcroft, Phys. Lett. 23, 48 (1966).
[22] C.P. Hu, Y. Gohda, S. Furuya and S. Watanabe, Jpn. J. Appl. Phys. 42, 4639 (2003).