

Soft breakdown of an insulating nanowire in an electric field

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Received 21 July 2003, in final form 27 October 2003

Published 8 December 2003

Online at stacks.iop.org/Nano/15/260 (DOI: 10.1088/0957-4484/15/3/004)

Abstract

The study of the properties of nanostructures in an electric field is very important not only from the fundamental point of view but also for practical applications. According to classical physics, an insulating system will be broken down in a large electric field. Can we predict such a behaviour for nanostructures using *ab initio* calculation? Such an attempt is made in this paper. The electronic structure and charge distributions of the thinnest $(\text{SiO}_2)_n$ wire in electric field are studied in detail with a first-principles method. It is found that the HOMO–LUMO gap increases with size and saturates at large values of 6.4 eV when $n \geq 12$, suggesting that the SiO_2 chain can be a very good insulating nanowire. However, when the wire is in an applied electric field, the HOMO and LUMO energies of the wire decrease linearly at different speeds, and the gap approaches zero, at which point the insulating wire is broken down by the electric field.

The discovery of C_{60} [1] and carbon nanotube [2] greatly stimulated the investigations of nanostructures, which have great potential use in nanoscale devices such as quantum dots, quantum wires, nonlinear electronic elements, transistors, molecular memory devices and electron field emitters. There are two important features of nanostructures. Firstly, size can be used as a variable to modulate the structure and properties. Secondly, due to the small size, quantum effects are dominant, and therefore quantum mechanical methods should be used to elucidate their behaviours and properties. Up to now, great effort has been devoted to the evolutions of structure and properties with size. For a metal element system, when the size is small, the energy levels are discrete and result in a large HOMO–LUMO gap. However, when the size becomes large, nonmetal to metal transition will take place resulting from the orbital overlap; this has been well established for many metallic systems [3]. Besides the size induced transition, another kind of transition, that induced by an external field, is an extremely important subject, but one which has not been well explored. In many practical applications, the nanostructure will be in an applied or in a self-produced electric field. According to classical physics, the insulating system will be broken down by a large electric field. Can we predict such a behaviour for nanostructures using a first-principles method? For this purpose, we take the SiO_2 chain as an example against the following background:

(1) bulk SiO_2 is a good insulating material;

- (2) it has been found recently that oxidation can enhance the synthesis of Si nanowires [4], and SiO_2 layer covers on the surface of Si nanowires [5];
- (3) SiO_2 nanowire can be used not only as an intensive blue light emitter [6] but also as a nanosized electronic resonant tunnelling transistor;
- (4) silicon nanostructures attract great attention [7–12].

We use molecular orbital theory in which the wavefunction is represented by a linear combination of atomic orbitals centred at each atomic site. The Gaussian98 package [13] was used and calculations were performed at the B3LYP level of theory [14] with the composite basis set, 3-21G for Si and 6-31G* for O, which have been extensively tested and determined to be the economic basis set for silicon oxide systems [15]. The convergences for energy and force are 0.0001 eV and 0.01 eV \AA^{-1} , respectively.

Based on the previous studies for small $(\text{SiO}_2)_n$ clusters ($n = 1-6$) [16], where the chain configuration was determined to be the most stable geometry, we start with this chain structure and continue to grow by adding SiO_2 units one by one. Figure 1(a) shows the geometry of $(\text{SiO}_2)_{15}$ wire. It should be noted that the ground state geometry may be changed for larger size, and there would be a lot of structural isomers. However, there is no method good enough to guarantee that one can find the real ground state geometry. Therefore, we confine ourselves with this chain configuration, which represents the

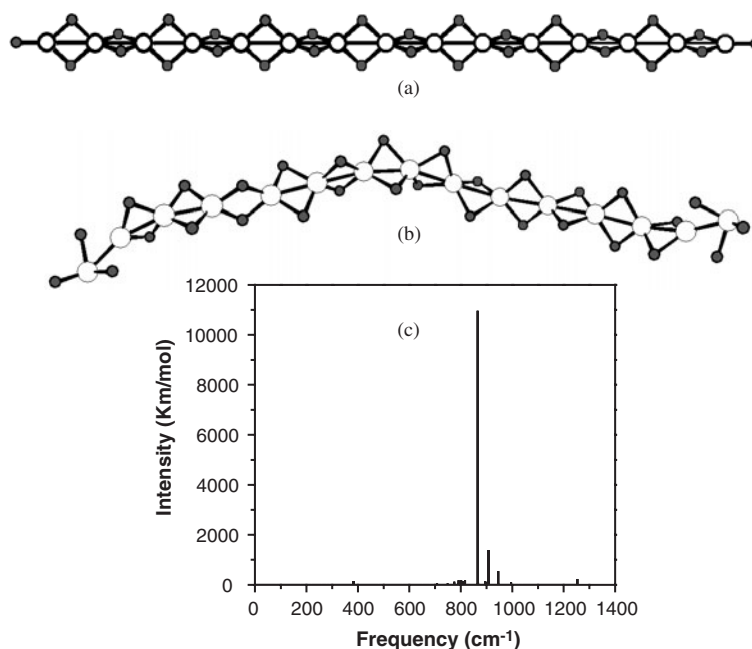


Figure 1. Equilibrium geometry (a), the distorted initial structure (b), and the vibration spectrum (c) for $(\text{SiO}_2)_{15}$ wire. The empty big balls represent Si atoms, and the small solid balls denote O atoms.

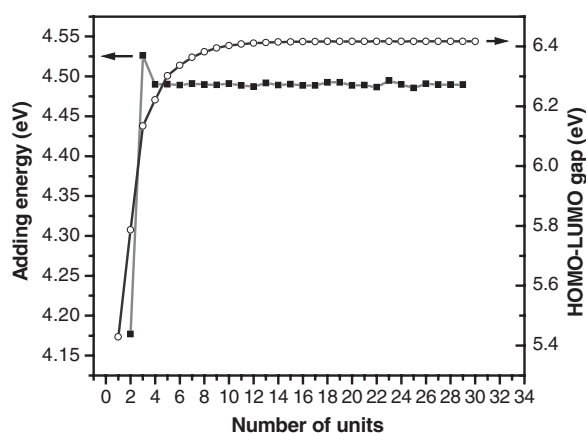


Figure 2. The size evolution of adding energy (squares) and the HOMO-LUMO gap (circles).

thinnest SiO_2 wire and can be used as a simple model for the theoretical studies.

We define the adding energy as

$$\Delta E(n) = E(n) + E(1) - E(n+1) \quad (1)$$

where the $E(i)$ is the total energy of i units. The changes for ΔE are shown in figure 2 (curve with squares). We can see that there is a big jump from $(\text{SiO}_2)_2$ to $(\text{SiO}_2)_3$. In $(\text{SiO}_2)_2$, the two SiO_2 units are respectively at the two ends; the binding is enhanced by adding a SiO_2 unit. When the size becomes larger, the saturation in ΔE begins at $n = 4$ with the value of 4.49 eV, and there are no meaningful oscillations there, indicating no magic behaviours existed, quite different from the pure Si clusters [17]. Therefore, oxidation provides an effective way to modulate behaviour in nanostructures.

The results for the HOMO-LUMO gap are shown in figure 2 (curve with circles). From $n = 1$ to 11, the gap

increases with size. This can be understood on the basis of charge transfer and bonding characteristics. Mulliken population analysis indicates that the atoms in the end part of the chain have lower charge. For different size, the charge transfers are different. For example, for $n = 3, 10$ and 15 , the average charge of Si atom is 1.77, 1.90 and 1.92, respectively. The corresponding charge at O atom is $-0.88, -0.95$ and -0.96 , respectively. We can see that as the size increases more electrons are transferred from Si atoms to O atoms, making the chain more ionic and resulting in a larger gap. On the other hand, going from $n = 12$ the gap begins to saturate in 6.4 eV; this is larger than the gaps of α -quartz and β -quartz, and is comparable with the gap of the β -tridymite phase in bulk SiO_2 [18]. Therefore, this SiO_2 nanochain would be a very good insulator. Compared with the previous results for small clusters [10], the HOMO-LUMO gap that we obtained is larger. This can be attributed to the different basis set and different exchange correlation functionals, especially as we used a hybrid method, which has been shown in other systems to dramatically improve the HOMO-LUMO gap with respect to experiment [19, 20].

The chain configuration is very graceful, but is it stable dynamically? In other words, can this chain configuration be maintained under some disturbance? This is a very critical point, but one that has not been checked for small clusters [15, 16]. Conventional geometry optimizations generally converge to a structure in a local minimum of the potential energy surface or a saddle point, and dynamic stability analysis becomes an important tool. In the case of a saddle point, the system displays one or more imaginary vibration frequencies, suggesting that the energy of the system can be lowered by structural displacements. Such an instability in structure cannot be easily detected with conventional total energy calculations. Therefore, calculations of the vibration spectra are necessary, which are given in figure 1(c) for

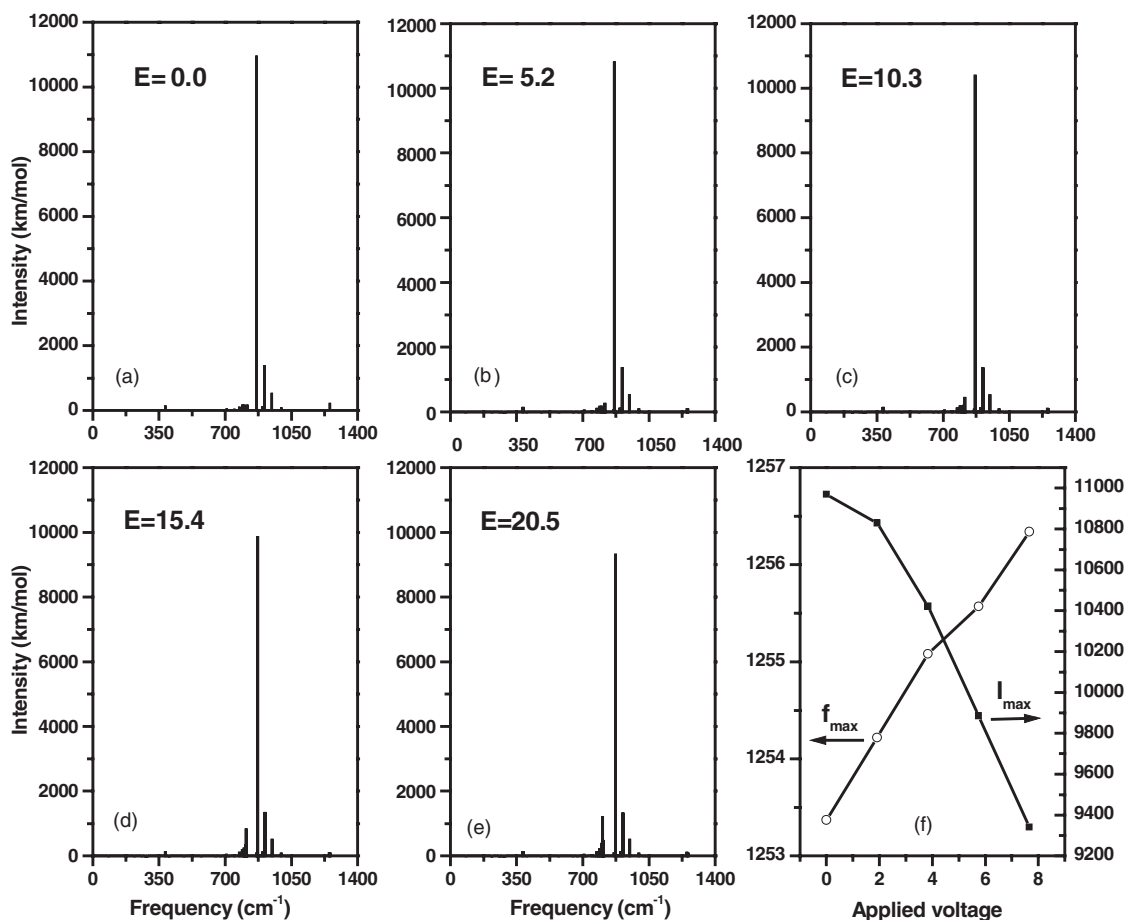


Figure 3. Vibration spectrum for $(\text{SiO}_2)_{15}$ wire in several applied fields: 0.0 (a), 5.20 (b), 10.3 (c), 15.4 (d) and 20.5 MV cm^{-1} (e). The corresponding maximum frequency f_{\max} and the maximum infrared intensity I_{\max} are shown in (f), where the field is expressed as voltage.

$(\text{SiO}_2)_{15}$. All the frequencies are real, suggesting that this chain structure is stable dynamically. To confirm this point further, we distort the structure as shown in figure 1(b). When reoptimized, it is very encouraging to find that the final geometry converges to the structure in figure 1(a). In the frequency spectrum, the maximum frequency corresponds to the relative vibrations along the chain for the Si and O atoms in the two ends, while the maximum intensity corresponds to the relative vibrations along the chain for the Si and O atoms in the mid-part of the chain.

Now we study the behaviour of $(\text{SiO}_2)_{15}$ chain in the electric field. We apply a uniform electric field along the chain axis, and fully optimize the geometry. Figures 3(a)–(e) show the vibration spectra in different fields. The results suggest that the chain-like SiO_2 nanowire is still stable dynamically in the field. The changes of maximum vibration frequency (f_{\max}) and maximum infrared intensity (I_{\max}) with the field are displayed in figure 3(f). We can see that with the increase of field, the maximum intensity is reduced, while the maximum frequency is almost linearly increased, indicating that the Si and O atoms at the two ends vibrate more quickly along the wire axis in the field.

It is well known that the HOMO–LUMO gap is a very important quantity for understanding and predicting the properties and behaviours of nanostructure. But how does the gap change with the applied field? As shown in figure 4, it

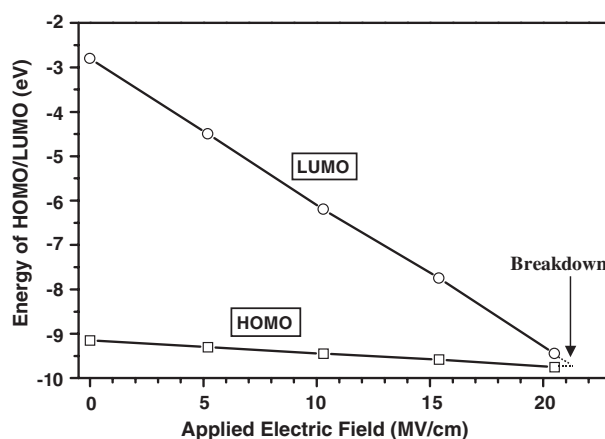


Figure 4. Energies of HOMO and LUMO change with applied field for $(\text{SiO}_2)_{15}$ wire.

is quite interesting to note that the energies for both HOMO and LUMO levels decrease linearly but at different speeds, and that therefore a crossover occurs, which corresponds to the breakdown of this insulating wire. The breakdown field of this insulating wire is 22 MV cm^{-1} (or 8.1 V), which is comparable with the values for SiO_2 film, which were found to be in the region of $18\text{--}27 \text{ MV cm}^{-1}$ [21]. The geometric structure of the wire is still maintained in the breakdown state, and the process is

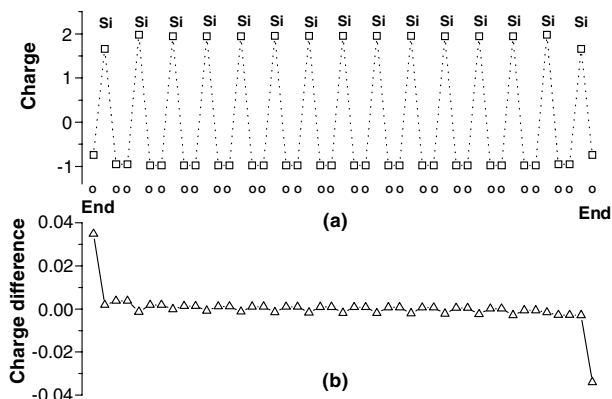


Figure 5. (a) Charge distributions and (b) charge difference between $E = 20.5 \text{ MV cm}^{-1}$ and $E = 0.0$ for $(\text{SiO}_2)_{15}$ wire.

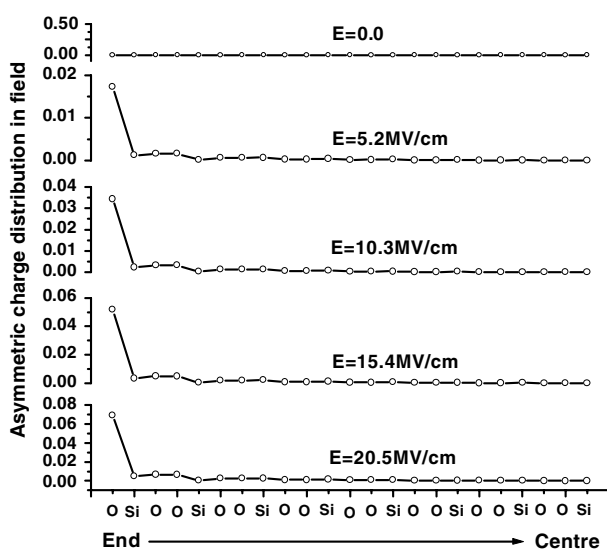


Figure 6. Asymmetric charge distribution for $(\text{SiO}_2)_{15}$ wire in the electric field.

reversible. In this sense, the breakdown for this SiO_2 nanowire can be classified as soft breakdown [22].

From Mulliken population analysis, it is found that the charges are redistributed in the field. Figure 5(a) shows the charge distribution for the wire of $(\text{SiO}_2)_{15}$ with no field: except for the Si and O atoms at the two ends there are nearly two electrons transferred from each Si atom, and each O atom gets one electron. When the electric field is applied, the situation changes. Figure 5(b) displays the charge difference of corresponding atoms of the wire in the field of 20.5 and 0.0 MV cm^{-1} . The big difference occurs for the O atoms at the two ends: the charges decrease at one end while they increase at the another end, resulting in an asymmetric distribution of charges along the wire. In the $(\text{SiO}_2)_{15}$ wire, starting from one end, we label the atoms 1, 2, 3, ..., 45, where the first and the 45th sites are the O atoms at the two ends, and the 23th site is the Si atom in the centre of the wire. If the charge on the i th atomic site is $q(i)$, we define a parameter Q as $Q(i+1) = q(1+i) - q(45-i)$ ($i = 0, 1, \dots, 22$), which

measures the asymmetric charge distribution along the wire, as shown in figure 6. When there is no applied field, the charges are symmetric with respect to the centre of the wire, so Q is zero. When a larger field is applied, Q becomes larger especially for the O atoms in the ends, and the dipole moment of the wire is increased.

In summary, detailed studies on the behaviour of an insulating nanowire in an electric field are performed on a SiO_2 chain, which is the thinnest wire and provides the simplest model for theoretical study with a first-principles method. In practical applications, the nanowires may be assembled by interconnecting with each other or being attached to some electrodes, and then the situation will be much more complicated. However, the present study on isolated nanowire sheds light on the mechanism and behaviour of nanowire in an electric field, and provides a little fundamental understanding of the complicated nanostructures.

Acknowledgment

The authors would like to express their sincere thanks to the crew of the Centre for Computational Materials Science, the Institute for Materials Research, Tohoku University, for their continuous support of the HITAC SR8000 supercomputing facility.

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