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Metallization induced by nitrogen atom adsorption on silicon nanofilms and nanowires

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First-principles calculations on the electronic properties of silicon nanofilms and nanowires that were adsorbed with nitrogen atoms on (110) facets revealed the formation of N–Si–N–Si chains, which causes the conduction and valence bands to intersect and metallizes the system. The interaction between the nitrogen and silicon atoms on the surface was found to induce energy bands near the Fermi level. The metallic electronic states induced by surface adsorption could be expected to significantly improve the conducting properties of the Si nanostructures due to their large surface-to-volume ratio and thus has great implications for SiNWs in nanoelectronic applications. © 2009 American Institute of Physics. [DOI: 10.1063/1.3098455]

Silicon is a dominant material in the electronics industry, and low-dimensional silicon nanomaterials are being developed to extend their electronic application to optical applications. Silicon nanomaterials, such as nanowires (SiNWs)[1,2] and quantum dots (SiQDs),[3] have been intensively investigated because of their promising properties for electronic applications, which were also used as model systems for demonstrating quantum confinement effects.[4] These low-dimensional nanomaterials extend the physics of reduced dimensions and offer the opportunity for fundamental study of the regime between nanostructure and bulk states.

The electronic band structure of SiNWs depends strongly on the wire diameter, and the light emission or absorption of SiNWs covers the visible range, indicating the possibility of fabricating Si-based visible optical devices. Recently, large quantities of SiNWs have been synthesized using different methods, with controllable sizes and morphologies.[5–7] The direct band gap characteristic confirms effective light emission, which is important for optoelectronic applications. An indirect-to-direct energy gap transition for $\langle 111 \rangle$ SiNWs at a diameter of less than 2.2 nm has been reported;[4] however, the energy band gap of $\langle 112 \rangle$ SiNWs remains indirect for the wire even with a small diameter.[8] In our previous work,[9] we found that an indirect-to-direct band gap transition in $\langle 112 \rangle$ SiNWs can be induced by changing the wire cross-section shape, that is, changing the cross-sectional aspect ratio of the (111) and (110) facets that enclose the wire. In addition, the uniaxial strain driven on SiNWs can modulate the band structure and induce the indirect-to-direct band gap transition, which is dependent on the crystal orientation and the diameter of the SiNWs.[10,11]

Nanomaterials exhibit a large surface-to-volume ratio, and surface becomes more important as size decreases. It has been demonstrated that surface oxidization could make SiQDs, which initially emit above 3.0 eV in the blue and emit near 2.0 eV in the yellow-red region,[3] and that SiQDs become more stable in the presence of double-bonded oxygen on the surface.[12] Systematic investigation shows that the optical properties of SiQDs can be tuned by different termination groups, where capping SiQDs with an alkyl group (–Si–C–) induces minimal changes in the optical spectra, while covering the surface with NH_2, SH, and OH results in evident changes compared with hydrogenated SiQDs.[13,14] For small-diameter SiNWs with a fixed cross section, the functional group used to saturate the silicon surface significantly modifies the band gap, which is traced to details of the hybridization between the silicon valence band and the frontier orbitals of the terminating group, in competition with quantum confinement.[15] Besides the band gap energy modification, atom (such as phosphorus) adsorption on the surface of SiNWs could change the local density of states (LDOS) distribution near the Fermi level and induce the indirect-direct band gap transition.[16]

Band gap tuning is important in Si-based visible optical devices, while good conducting is required for efficient electronic nanodevices. Rurali and Lorente[17] reported that reconstructions on a particular surface could make SiNWs metallic and that the electronic-structure behavior is dictated by the surface states of reconstruction. For bulk Si, both *p*-type and *n*-type doping increases the density of carriers and enhances conductivity. But for hydrogen-saturated SiNWs, conductivity does not rise rapidly with doping, and the different behaviors of P versus B doping indicates that *n*-type or *p*-type doping may lead to significantly different conductance properties in wires as compared with bulk.[18]

In this study, we explore the possibility of metallizing the Si nanostructure with nonmetal atom adsorption. In general, delocalized electronic states are required to achieve metallization. It is known that the delocalized $d\pi – p\pi$ bonds are formed by the p_z orbit of a nitrogen atom and the empty *d* orbit of silicon, for instance in the case of the $N(SiH_3)_3$ molecule,[19] which makes the molecular planar. Earlier theoretical studies showed that[20] saturation atoms such as nitrogen on the surface of Si nanostructures could stabilize the structures and clean the gap states, important for the visible luminescence in the silicon-based nanostructured material. Experimentally, after dissociation of NO or NH_3, nitrogen atoms can adsorb stably onto the Si surface,[21,22] suggesting the possibility of a new process design for controlling N-rich layers. In the following, we focus on the nitrogen adsorption on Si nanostructures and study how the metallization occurs.

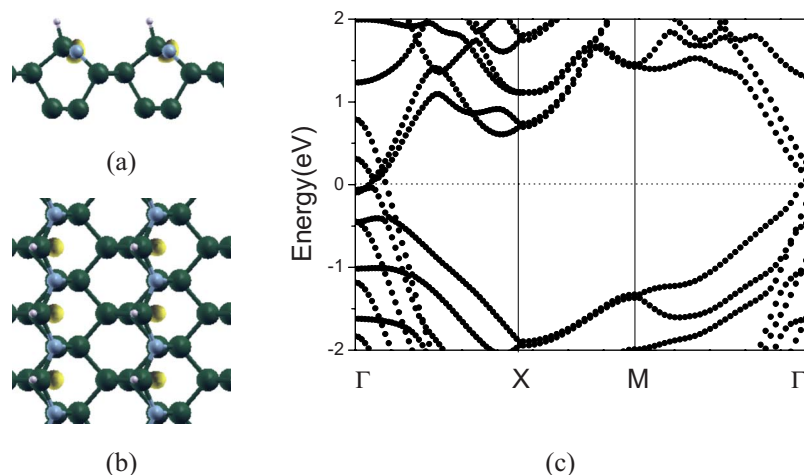a)Electronic mail: aprqz@cityu.edu.hk.

FIG. 1. (Color online) The geometry and band structures of Si thin films with nitrogen adsorption: (a) side view, (b) top view, and (c) band structures. The Si, H, and N atoms are denoted by green, white, and blue, respectively. The isosurfaces are 35% of the maximum of the density. The Fermi level is set at zero.

Our calculations were conducted using density functional theory with the generalized gradient approximate (GGA) that is available in the VASP method.[23,24] The energy cutoff was set at 420 eV, and the GGA was used with the PW91 exchange-correlation functional. The distance between neighboring wires was greater than 9 Å to reduce the cell-to-cell interaction. For Si thin films, we adopted Monkhorst–Pack sampling with a $6 \times 6 \times 1$ k-point grid, and used a $1 \times 1 \times 6$ k-point grid for the SiNWs. Using the conjugate gradient method, we fully optimized both the atomic configurations and the lattice constant of SiNWs along the wire axis, where the force criteria were 0.01 eV/Å. The wave function analysis on the characteristics of electronic band structures was obtained with the SIESTA code.[25]

We first considered the (110) Si thin film with a thickness of 11.5 Å, whose surface is saturated by hydrogen atoms. The film showed a band gap of 0.91 eV. When one silicon monohydride (–SiH) was replaced by one nitrogen atom, the average N–Si bond length was 1.87 Å, which is slightly larger than the one for the N(SiH$_3$)$_3$ molecule (1.73 Å). For the case where two –SiH were replaced by N atoms, we found that the N–Si–N–Si chain is energetically preferred and that the N–N dimer forming increases the total energy by 0.42 eV. As the number of nitrogen atoms increased, we obtained the structure with half the –SiH on the surface replaced by nitrogen atoms, as shown in Figs. 1(a) and 1(b). The band structure in Fig. 1(c) shows that this nitrogen-adsorbed Si thin film is metallic since the valence and conduction bands evidently cross near the Fermi level. We obtained similar results when we considered a thicker Si film (19.2 Å), which shows an intrinsic band gap of 0.81 eV.

Replacing –SiH with an N atom did not induce dangling bonds on the surface, and no isolated gap states were created. Thus, the metallization was not caused by the gap states. Considering the states near the Fermi level (with a range of 0.80 eV), we found that the LDOS distribution is concentrated on the surface, as shown in Figs. 1(a) and 1(b), which indicates that the metallization is attributed to the interaction between the nitrogen and silicon atoms on the surface. By examining the projected density of states (PDOS) per atom, we investigated the mechanism of metallization in detail. Figure 2 shows the average PDOSs of the core Si atoms, the surface Si atoms, and the N atoms. The DOS near the Fermi level is mainly from the surface Si atoms, especially the p orbit. The PDOSs between the core and surface Si atoms evidently differ. For the core Si atom, the density of electrons

in the s and d orbits is much less compared to the one in the p orbit. However, the density of electrons in the d orbit is large for the surface Si atom, which is comparable to the one in the p orbit at the energy range from -1.2 to -0.3 eV. For the N atom, the density of electrons in the p orbit is dominant compared with the one in the s and d orbits. It can be concluded that N atom adsorption modifies the p orbits of surface Si atom significantly, which induces the states near the Fermi level and sequentially metallizes the system.

Further, we extended our investigation to the $\langle 110 \rangle$ SiNWs with a rectangular cross section, which is enclosed by the (110) and (100) facets.[26] The SiNW we adopted possesses a diameter of 12 Å and shows a band gap of 1.12 eV. When an N–Si chain was introduced on the (110) facet, the SiNWs became metallic. Based on the PDOS of three kinds of nonequivalent atoms, we found that the density of electrons near the Fermi level comes mainly from the surface Si atoms and N atoms. Similar to the case of Si films, the system is metallized because of the states induced on the surface.

We also considered the case of nitrogen atoms adsorbed on both the (110) and (100) facets. We replaced the silicon dihydrides (–SiH$_2$) on the (100) facet with the nitrogen monohydride (–NH) and found that there were no dangling bonds. From the band structures (not shown), we found that the conduction bands were drawn down significantly and are intersected with the valence bands near the Γ point. Thus,
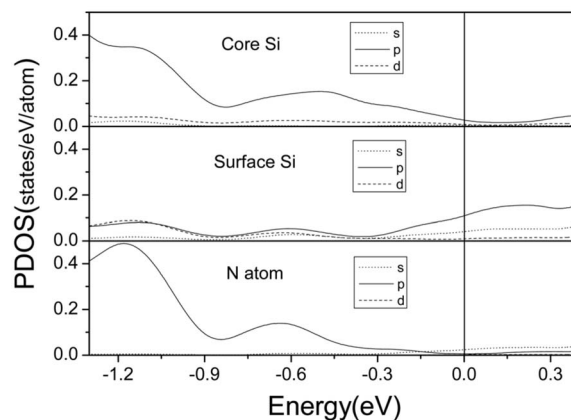

FIG. 2. The PDOS of atoms for Si thin film and SiNWs with nitrogen adsorption: the dotted line shows the PDOS for the s orbit, the solid line for the p orbit, and the dashed line for the d orbit. The Fermi level is set at zero.
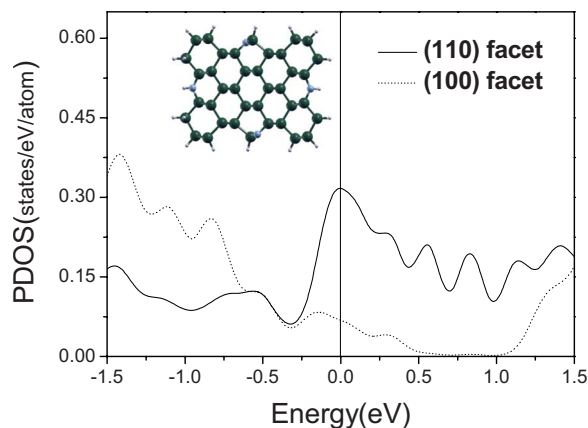
FIG. 3. (Color online) The PDOS of atoms for SiNWs with nitrogen adsorption. The solid line shows the PDOS for the silicon atom in the (110) side facet and the dotted line for the silicon atom in the (100) side facet. The Fermi level is set at zero.

this SiNW would exhibit metallic properties. Figure 3 shows the average PDOS of the surface Si atoms on the (110) and (100) facets, respectively. We found that the metallization is attributed mainly to the Si(110) facet with N atoms adsorption, which induces the delocalized states of Si atoms on the surface. With the band structure and PDOS, we can see that the conduction bands are from the N–Si chain on the (110) facet. For the (100) facet, the PDOSs of the core and surface Si atoms are similar near the Fermi level, which is much smaller compared with that of the Si atoms on the (110) facet. We found that the nitrogen adsorption on the (100) facet did not induce metallization.

Based on our calculations, we have shown the metallization mechanism of the Si nanostructure by nitrogen atoms adsorption. In addition, we extend our discussion to the possibility of achieving the metallization in experiments. When the silicon monohydride (–SiH) is replaced by the nitrogen atom, the average N–Si bond length is slightly changed compared with the one for the $N(SiH_3)_3$ molecule. The replacement does not induce dangling bonds on the surface, and the system remains stable. In the N-rich condition, the number of nitrogen atoms increases, but the N–N dimer forming is not energetically favorable. Thus, the N–Si–N–Si chain is probably achievable, sequentially inducing the metallization.

For SiNWs along different growth directions, many low-index facet configurations and cross sections are possible.[26] Besides the rectangular cross section, the ⟨110⟩ SiNWs could possess the hexagonal or octagonal cross section, enclosed by the (100), (110), and (111) facets. When the N–Si chain forms on the surface of the Si(110) facet, the system becomes metallic. Nitrogen atoms on other facets have a slight effect on the electronic properties of SiNWs; thus, metallization could be achieved under suitable N-rich conditions. To confirm metallicity, the N–Si–N–Si chain should be extensive and along the wire axis. However, for the ⟨112⟩ SiNWs enclosed by the (110) and (111) facets, the N–Si chain on the (110) facet is not along the wire axis, and the nitrogen adsorption only modifies the band gap energy instead of inducing the metallization.

In summary, we have shown that metallization can be induced by adsorbing nitrogen atoms on the surface of Si

nanostructures. Replacing –SiH with an N atom induces neither extra electrons nor dangling bonds, which differs from that of n-type doping. We found that the N–Si–N–Si chain is energetically favorable on the (110) facet and that the metallic states near the Fermi level are attributed mainly to the nitrogen and silicon atoms on the surface, according to the wave function analysis. The PDOS examination showed that the p orbits of surface Si atom are modified by the N atom and the states are induced near the Fermi level, which sequentially metallizes the system. For SiNWs, whether metallization occurs or not depends on the growth direction and the index of the SiNW facet. By controlled deposition or epitaxial growth methods, the N–Si chain could form on the ⟨110⟩ SiNWs with the (110) facet enclosed, which would induce metallization in experiments under the N-rich condition. The revealed mechanism of introducing metallic electronic states on an Si nanostructure with nonmetal atom adsorption could guide us to fabricate SiNWs with good conducting properties using surface modifications. This finding should have great implications for SiNWs in nanoelectronic applications.

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