

Energy band of manipulated atomic structures on an insulator substrate

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Stimulated by recent progress in atom manipulation technology, the electronic properties of periodic structures artificially created with atoms on a substrate surface are studied, where constituent atoms are isolated from substrate atoms and interact with one another through neighboring-atom interactions. By reducing the lattice constant from infinity, the neighboring-atom interaction is gradually turned on, and discrete atomic states broaden to form energy bands. Band structures of a simple one-dimensional atomic chain, a two-dimensional square array, and two parallel atomic chains formed by Si are calculated as a function of lattice constant using the tight-binding theory with universal parameters. For practical lattice constants, these Si structures are all metallic due to the existence of the π band, within which the Fermi energy lies; however, at very low spacings, possible for carbon, the double chain can become insulating. For group-II elements such as Mg, the π band and the conduction band are empty while the valence band is fully occupied. The band-gap variation with lattice constant is reflected in the electronic properties directly: e.g., a Mg atomic chain is insulating for lattice constants greater than or less than 4.2 Å, at which the band gap disappears and the chain becomes metallic. © 1996 American Vacuum Society.

I. INTRODUCTION

Due to the recent progress in atom manipulation technology with scanning tunneling microscopy (STM), it is becoming possible to move atoms one by one and arrange them as desired on a substrate using a STM tip as tweezers.¹ It has been observed experimentally that there are preferred sites for the atoms,² and this suggests that the substrate surface provides an array of potential wells where atoms can be placed. Making use of this potential-well array, it is technologically possible to arrange atoms periodically in one or two dimensions (1D or 2D) on the given substrate. When such arranged atoms are electronically isolated from the substrate surface so that no chemical bonds are formed and the neighboring-atom interaction is practically restricted to that among arranged atoms, they form 1D or 2D electron systems. In these systems, we can change the interaction strength by assigning different values for lattice constant. This can be done, for example, by placing atoms at every one, two, three, etc., potential wells, or changing the periodic directions with respect to the crystal orientation of the substrate surface. When a lattice constant is very large, the neighboring-atom interaction is so weak that electrons are confined to each atom and have discrete atomic energy levels. With reduction in the lattice constant, the neighboring-atom interaction will cause these states to form a band with continuous momentum along the direction in which a periodic structure is made. Since the interaction strength can be changed by changing the lattice constant, the band width and the band gap can be designed, and this will lead to band engineering for atomic structures created on the substrate.

The electronic states of various atomic structures consisting of Si adatoms, one of the most important materials in the

present semiconductor technology, are studied in detail. Since a Si atom has four valence electrons and the highest occupied atomic level is $3p$ and is one-third filled, a simple periodic structure will be metallic if the periodicity just broadens the atomic levels. This simple view is in contrast to the fact that the usual three-dimensional (3D) Si crystal is insulating. This is because the lattice constant is so short that there are crossings of band edges, and a new gap is opened, resulting in the existence of a fully filled highest band; each Si atom is symmetrically surrounded by four neighboring atoms and four covalent σ bonds per atom pair corresponding to four filled valence bands. The number of atoms per unit cell is two, not one, and the problem of accommodating four valence electrons in four states is changed to accommodating eight valence electrons in eight modified states, with all bonding states fully filled. Accordingly, we study a 1D Si atomic chain (the simplest periodic structure), a 2D square Si array (four nearest neighbors), and Si parallel chains where two 1D Si chains are placed in parallel (two atoms per unit cell). We use a tight-binding theory with universal parameters³ to calculate the band structures of these structures. It turns out that all of them are metallic for practically possible lattice constant values, because the Fermi energy lies in the π band originated from $3p$ orbitals perpendicular to the structure, as shown below. Since the Fermi energy is far above the only band gap, the modification of the band gap with lattice constant cannot be reflected in the electronic properties.

If we use group-II elements such as Mg or Be, resultant electronic properties are much more attractive since they can become insulating in principle. This is because s orbitals are fully filled and p orbitals are empty, leading to the formation

of the valence and conduction bands, separated by a band gap. The band gap ranges from a few eV to zero as the lattice constant is reduced, and a Mg chain will show wide variety of electronic properties. The null band gap is realized for one lattice constant $d_0 = 4.2 \text{ \AA}$, at which the chain is metallic. The chain is semiconducting near d_0 , but either greater or less. An insulator, semiconductor, or metal can be realized by manipulating the lattice constant. We have again a strange situation that Mg atomic structures are mostly insulating although the usual 3D Mg crystal with the hexagonal close-packed structure is metallic, and this can be attributed to the difference in the effects of three, rather than one, dimension.

The energy bands for three Si atomic structures are calculated in Sec. II and the metallic nature is found. In Sec. III, a Mg atomic chain is studied to demonstrate the usefulness of group-II elements in forming an insulator. Discussions of possible experiments are given in Sec. IV.

II. SILICON STRUCTURES

We use a tight-binding theory with universal parameters³ to calculate band structures of various atomic structures. This method may not be as accurate as *ab initio* first-principle methods, but it provides a clear physical picture, which is more to the point. We need to design the band structure, e.g., we often need to know how to change the lattice structure to widen or raise a band of interest. The tight-binding theory with universal parameters provides a clear intuitive answer, and is most suitable for the present purposes. In the application of the theory, how the matrix elements coupling s and p states on neighboring atoms change with an interatomic distance d is crucial. The matrix element connecting an l state and an l' state ($l, l' = s, p$) with m bond ($m = \sigma, \pi$), angular momentum around the internuclear axis, is expressed by

$$V_{ll'm} = \eta_{ll'm} \frac{\hbar^2}{\mu d^2}, \quad (1)$$

where \hbar is the reduced Planck constant, μ is the electron vacuum mass, and d is the interatomic distance. The $\eta_{ll'm}$ are universal dimensionless constants and all the necessary values are tabulated in Ref. 4. It has been found that the electronic structure of sp -bonded materials are described well by Eq. (1).³ This means that the relation is valid for a wide range of d , roughly corresponding to the sizes of smallest to largest atoms, from 1 to more than 5 \AA . Thus, we use this relation throughout the present analysis. Actually, the matrix elements will drop exponentially for larger distances and therefore we may overestimate band widths for lattice constants of order or beyond 5 \AA . This overestimate, however, does not change any qualitative conclusions in this article. For s and p -state atomic energies ϵ_s and ϵ_p , the Hartree-Fock term values are adopted, which are also tabulated in Ref. 5, and only the nearest-neighbor interaction is included as usual.³ The resultant secular equations are solved numerically to obtain band structures.

The band calculations below are performed as if the atomic structures were floating in the vacuum, neglecting the effects from the substrate. Experimentally atomic structures

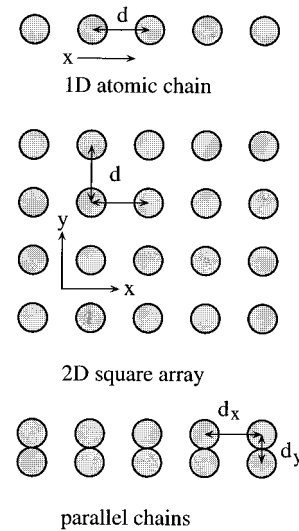


FIG. 1. Schematic of atomic structures studied in this work.

have to be created on the substrate and the presence of the substrate will modify the electronic bands quantitatively, but probably not qualitatively. In 1D structures, a Peierls transition corresponding to a spontaneous distortion of lattice to reduce the total energy by opening a gap at the expense of elastic energy,⁶ or an Anderson localization of electrons due to the random fluctuation of lattice potential,⁷ could be relevant under a certain situation (e.g., depending on substrate surface or temperature) but are assumed not to occur here.

A Si atom has four valence electrons. Since the highest $3p$ state is not fully but one-third occupied, simple periodic structures will be metallic as long as periodicity just broadens discrete atomic energy levels. This may not be the case when the upper p -like bands separate or when there is a significant mixture of $3s$ and $3p$ states. The formation of sp^3 hybrids in 3D Si crystal with diamond structure is an example of the second case, such that each Si atom is surrounded by four nearest-neighbor atoms symmetrically. This is also true for the 2D square Si array, but we shall see that it is metallic. Another way to create a Si insulator would be to change the number of atoms, and therefore electrons per unit cell so that the highest energy band is fully occupied. Actually, 3D Si crystal has two atoms per unit cell and this doubles the number of electrons available to each band. Accordingly, we will study a 1D Si atomic chain (the simplest periodic structure), a 2D square Si array (four nearest neighbors), and Si parallel chains where two 1D atomic chains are placed in parallel (two atoms per unit cell). These structures are schematically shown in Fig. 1.

A. 1D Si atomic chain

Figure 2 shows the calculated band width as a function of lattice constant. The 1D Si atomic chain is metallic for all lattice constants d , since the Fermi energy always lies inside the doubly degenerate π band which is originated from $3p_y$ and $3p_z$ orbitals perpendicular to the chain direction x . The

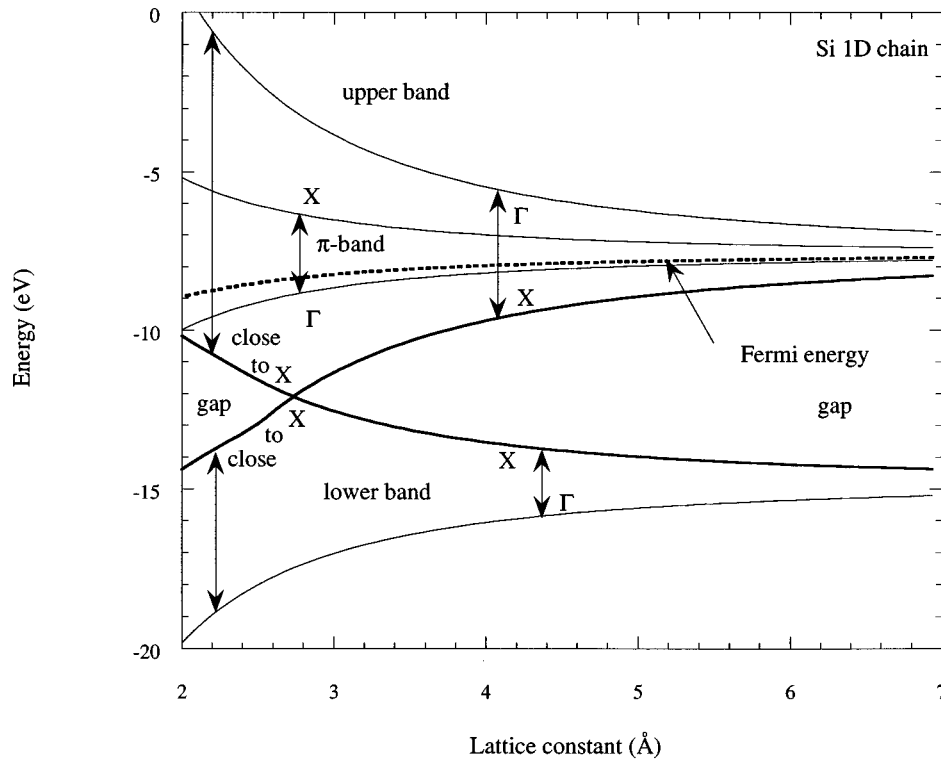


FIG. 2. Band width of a 1D Si atomic chain as a function of lattice constant. The broken line indicates the Fermi energy.

lower and upper bands are originated from $3s$ and $3p_x$ and can accommodate two electrons per unit cell, respectively, while the π band can accommodate four electrons. There is one atom per unit cell, so four valence electrons have to be accommodated in four states and this explains the position of Fermi energy indicated by the broken line. Although there is a band gap between the lower and upper σ bands, it will not be directly reflected in the electronic properties due to the high position of Fermi energy. The bottom of the lower band, the bottom of the π band, and the top of the upper band are at Γ , while the other edges of these bands are at X (or its neighbor for small d), as seen by the dispersion plots for different d in Fig. 3.

B. 2D square Si array

Figure 4 shows the band width of a 2D square Si array as a function of lattice constant. The lower σ band and the upper two σ bands are originated from $3s$, $3p_x$, and $3p_y$ orbitals, where x and y are parallel to the array plane, and the π band is originated from $3p_z$ orbital. Each of these σ bands as well as the π band can accommodate two electrons. We have one atom per unit cell and thus four valence electrons. The Fermi energy indicated by a broken line is inside the π band, and this makes the 2D Si square array always metallic. If an insulator is sought in the context of four symmetrically arranged nearest neighbors, four σ bonds have to be created using all the $3s$ and $3p$ orbitals, as in the case of 3D Si crystal with the diamond structure. In the present square array, there is no way for $3p_z$ state to couple with $3s$, $3p_x$, or

$3p_y$ state on the neighboring atoms since the matrix elements are mathematically zero due to symmetry. This creates an isolated π band, and the Fermi energy lies inside this band. Energy extremals in the present case are observed to occur at $\Gamma:k=(0,0)$ or at zone boundaries. The top and the bottom of the lower band are at $M:k=(1,1)\pi/d$ and Γ , respectively. The top and the bottom of the upper two bands are at $X:k=(1,0)\pi/d$. The bottom of the π band is at Γ and the top is at M . For clarity, energies at Γ , M , and X are shown as a function of the lattice constant. The top of the lower band and the bottom of the upper bands change abruptly at small lattice constants where there is a crossing of two energy lines. Due to the existence of the π band, it is expected that 2D Si rectangle ($d_x \neq d_y$) arrays are also metallic. This is observed for several combinations of d_x and d_y (figures not shown).

C. Si parallel chains

Changing the number of atoms per unit cell could allow us to realize an insulator. The structure considered here is two parallel atomic chains with the same lattice constant d_x , and the separation of two chains is d_y , as shown in Fig. 1. Or in other words, we first form a molecule Si_2 in the y direction with the separation of d_y and arrange it periodically in the x direction with a period of d_x . If we can fully fill the highest energy level of Si_2 , then the parallel atomic chains will be a good candidate for an insulator. In Si_2 , there are four σ -orbital states $\sigma_g, \sigma_g^*, \sigma_u$, and σ_u^* originated from $3s$ and $3p_y$, and two doubly degenerate π -orbital states π and π^*

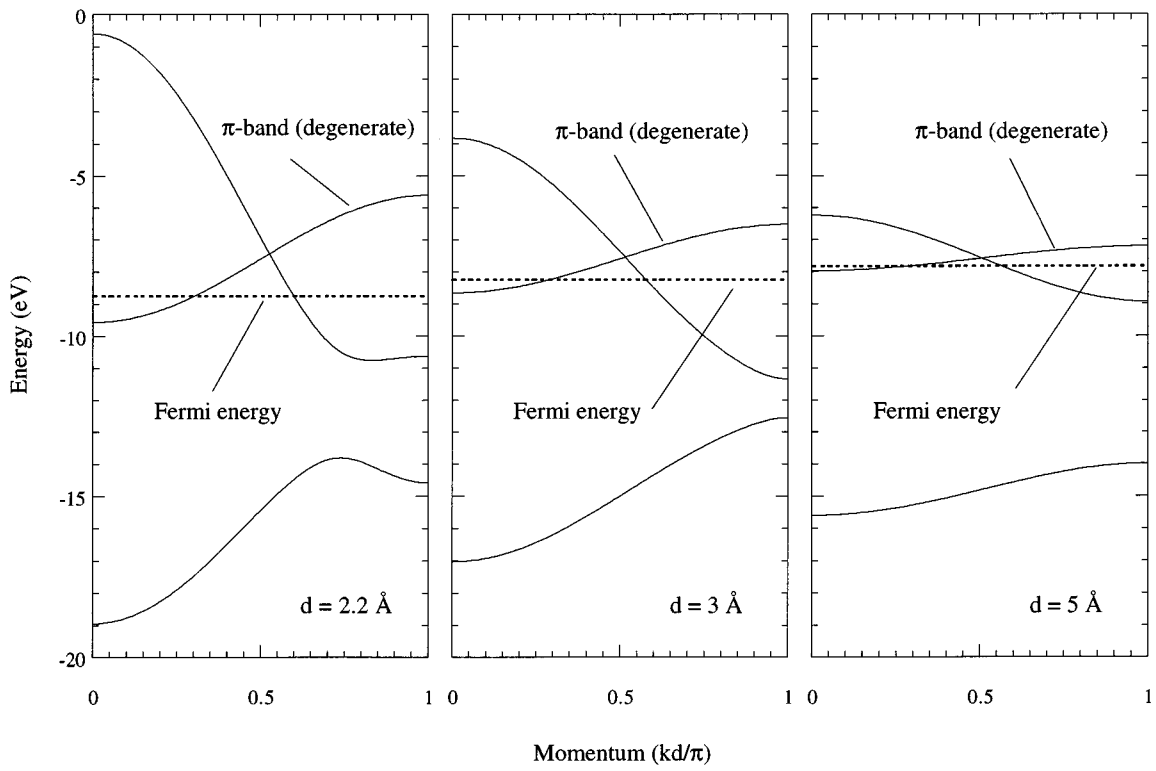


FIG. 3. Dispersion of a 1D Si atomic chain for lattice constant values of 2.2, 3, and 5 Å.

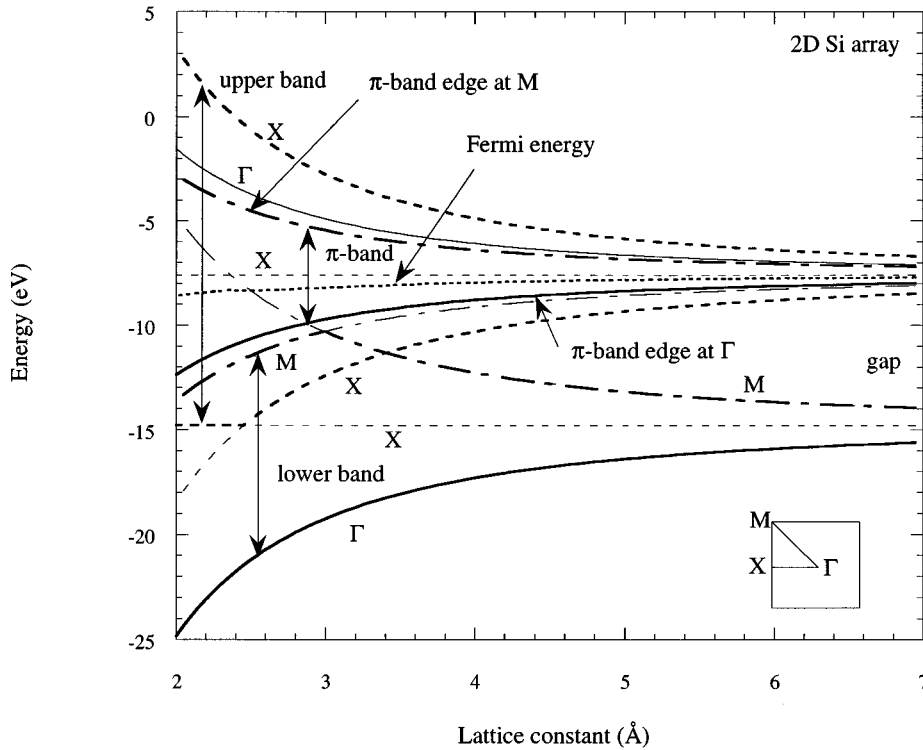


FIG. 4. Band width of a 2D Si square array as a function of lattice constant. The broken line indicates the Fermi energy.

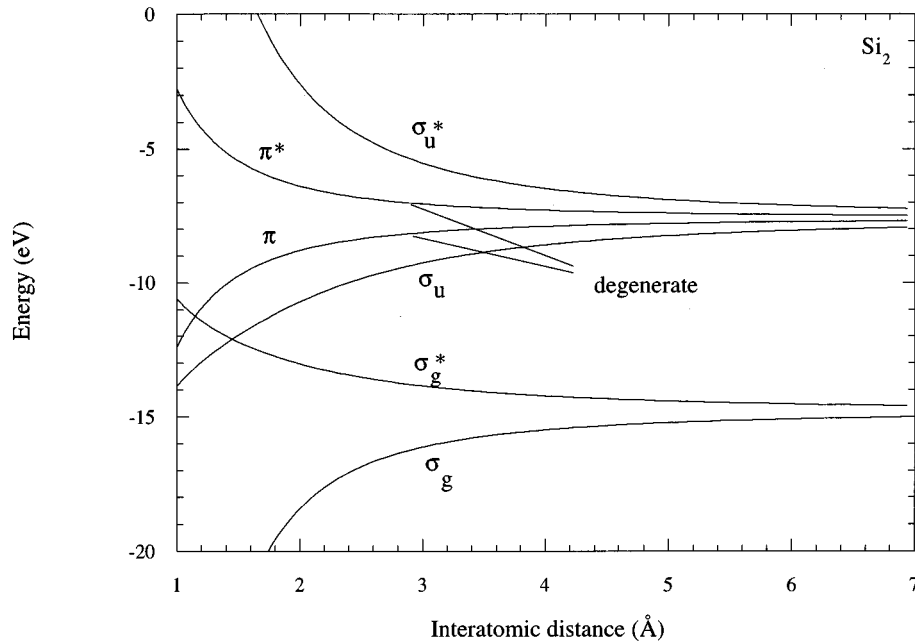


FIG. 5. Energy levels of a Si_2 molecule as a function of interatomic distance.

originated from $3p_x$ and $3p_z$,⁸ where states with and without an asterisk are antibonding and bonding, and g and u stand for even and odd, respectively. π and π^* states are degenerate since $3p_x$ and $3p_z$ are symmetric with respect to the diatomic axis y . Each σ state can accommodate two electrons and each π state can accommodate four electrons including degeneracy. There are eight valence electrons and eight states in Si_2 . For large interatomic distance d_y , the order is $\sigma_g, \sigma_g^*, \sigma_u, \pi, \pi^*$, and σ_u^* from the bottom. Thus, the highest occupied level is π and is half-filled. Simple tight-binding consideration indicates that by reducing d_y there is a possibility that we can realize the ordering of $\sigma_g, \sigma_u, \pi, \sigma_g^*, \pi^*$, and σ_u^* , so that the highest band is π and is fully filled.

Figure 5 shows energy levels of Si_2 as a function of interatomic distance d_y . The tight-binding method is sometimes inaccurate in predicting the ordering of energy levels in diatomic molecules, but gives the correct ordering⁹ for the present Si_2 case. The figure shows that the ordering of $\sigma_g, \sigma_u, \pi, \sigma_g^*, \pi^*$, and σ_u^* needed for an insulator occurs at an extremely short d_y around 1.2 Å, much shorter than the natural interatomic distance of 2.2 Å for Si_2 ,⁹ or crystalline spacing of 2.35 Å, and is not practically realizable. This ordering is known to occur in the molecule C_2 ,⁸ and the same idea can be pursued for C atomic structures to form an insulator. In case of Si parallel chains, it is expected that the structure is always metallic because the highest occupied band in Si_2 is partially filled. This is confirmed in Fig. 6, where the dispersion curves are shown for some d_x values with d_y fixed at 2.2 Å. The band structure is understood in connection with that in Fig. 3. The discrete molecular levels of $\sigma_g, \sigma_g^*, \sigma_u, \pi, \pi^*$, and σ_u^* broaden to form bands, totaling eight states per unit cell. The degeneracy of π and π^*

levels are lifted since $3p_x$ and $3p_z$ are not symmetric after the parallel chains are formed in the x direction. The Fermi energy indicated by a broken line lies inside the bands. Although the molecular π level is half filled in Si_2 , the highest occupied bands in the parallel chains are not half-filled, so that the Mott transition,⁶ which causes a metal with a half-filled band in a 1D system to become an insulator due to the Coulomb interaction, is irrelevant here.

III. STRUCTURES BY DIVALENT ATOMS

As shown above, all three Si atomic structures are consistently metallic, although the usual 3D Si crystal is an insulator. The main reason for this is the π band originating from $3p$ orbitals perpendicular to the structures (the chain direction or the array plane), inside which the Fermi energy lies. In the 3D Si crystal, this π band is eliminated due to the formation of 3D bands, often associated with sp^3 hybrid.

If we wish to form an insulator, it will be better to use divalent atoms belonging to group II, since their highest occupied level is valence s and is fully filled while all the valence p levels are empty. Thus, we can empty the unwanted π band, and the band gap between the lower and upper bands which we discuss above is reflected directly in the electronic properties. In order to demonstrate the attractive features of group-II elements, a Mg atomic chain is studied. Figure 7 shows the band width as a function of lattice constant d . The lower band is completely filled and the upper band is empty at zero temperature, so we call them the valence and conduction bands, respectively. HOMO and LUMO stand for highest occupied molecular orbit and lowest unoccupied molecular orbit, respectively. The Mg atomic

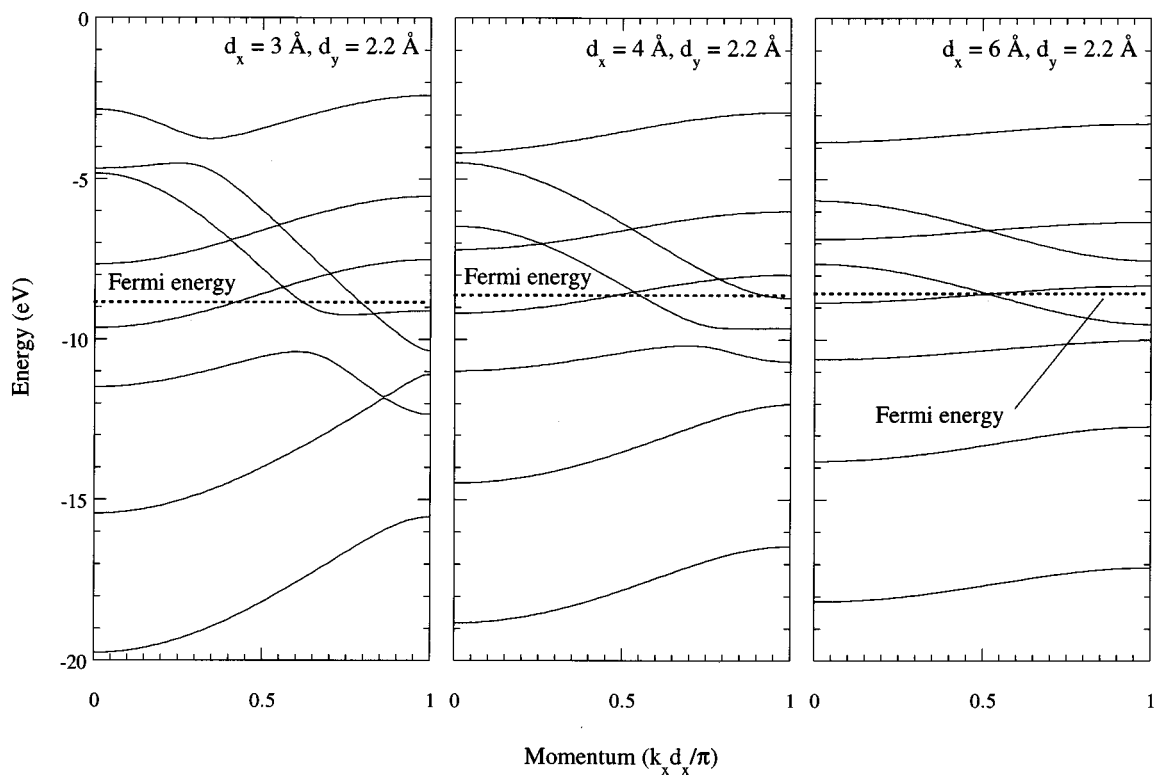


FIG. 6. Dispersion of Si parallel chains for some combinations of d_x and d_y , where x is the chain direction and y is the molecular direction, as depicted in Fig. 1.

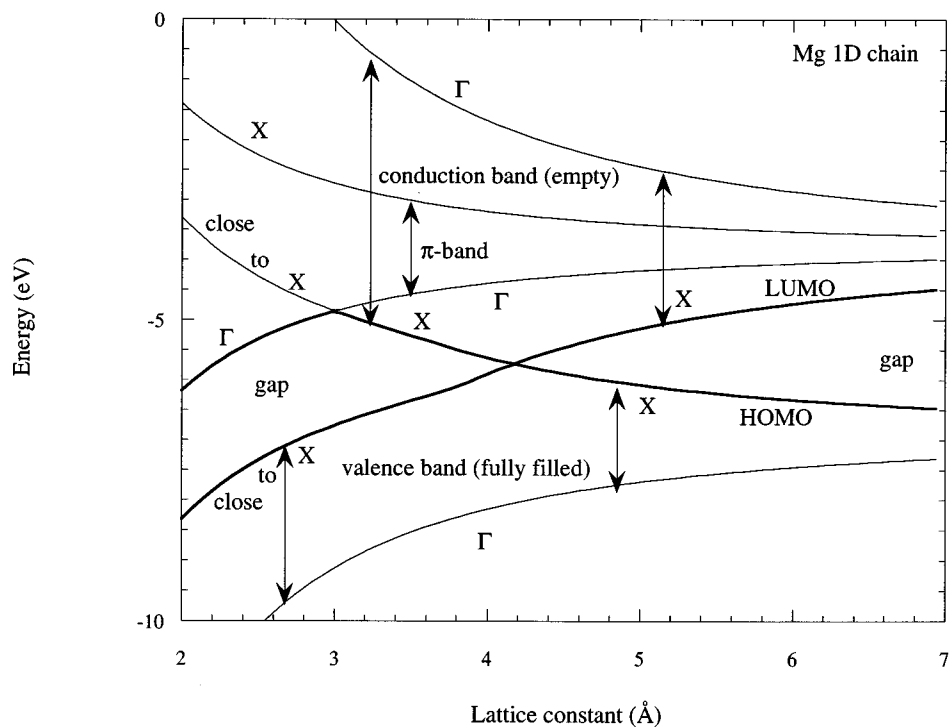


FIG. 7. Band width of a 1D Mg atomic chain as a function of lattice constant.

chain is almost always insulating, except around $d=4.2$ Å, where the band gap becomes zero and the chain behaves as a metal with a finite density of states at the Fermi energy. For Be, the corresponding d is 4.5 Å (not shown). Again, we encounter a strange situation since the 1D Mg atomic chain is an insulator while the usual 3D Mg crystal with hexagonal close-packed structure is a metal. The difference can be attributed to crossing of the s and p bands at small spacing.

IV. EXPERIMENTAL FEASIBILITY

Atomic structures have to be created on the substrate experimentally, although the above band calculations are performed for an ideal situation so that all the substrate effects are negligible, as if the structures were floating in the vacuum. A Si substrate could be available for this purpose, but we need to passivate the dangling bonds of the surface atoms since they would otherwise create chemical bonds with the atomic structure. We may use hydrogen atoms to terminate.¹⁰ After successful termination, all the dangling bonds are saturated and the atoms are arranged at potential minima determined by the Van der Waals interaction, without creating any chemical bonds with the substrate atoms. The arranged atoms are subject to the thermal diffusion on the surface, and therefore, low temperature environment is preferred.

There are conventionally two characterization techniques to distinguish metal from insulator—optical and electrical ones. The former is promising since a near-field optical microscope approaching the atomic system size is now being developed.¹¹ The spot size is currently on the order of 500 Å in diameter, which is two orders of magnitude larger than a typical lattice constant. The input light causes a vertical (momentum conserving) transition of electrons from the lower filled band to the upper empty band in an insulator, and from the lower filled band to the states above the Fermi energy in the upper band in a metal, both via dipole interaction. Detecting signals from an atomic system without having unwanted response from the bulk substrate is not trivial because of the spot size. We may study the second-harmonic generation (SHG), or the generation of light with double the input-light frequency.¹² The significant advantage of this measurement is that SHG does not occur in the bulk substrate, due to the presence of space inversion symmetry, and can occur only at the surface, where the symmetry can be made absent. Thus, we can only detect the surface atomic

structure and avoid the unwanted response from the substrate automatically by making use of the nature of the SHG process.

Electrical characterization is not easy since there is no obvious way to obtain ohmic contacts. If an atomic structure makes chemical bonds with surface atoms of the conductor substrate, there will generally be a potential barrier at the junction, which usually shows nonlinear I - V characteristics. Since there is no simple way to place electrical leads to the atomic structure, plural STM tips could be used in place of lead lines to feed current and detect voltage to estimate conductance. The temperature dependence of the conductance will determine the phase of the atomic structure—an exponential dependence for an insulator with the activation energy corresponding to the band gap, and practically no temperature dependence for a metal. It is also of interest to check experimentally whether the conductance for a 1D atomic chain in the metallic phase is quantized as in mesoscopic 1D conductors.

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