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Ordered arrays of quantum wires through hole patterning: *ab initio* and empirical electronic structure calculations

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We propose an approach to the fabrication of one-dimensional nanostructures, based on the design of a pattern of channels onto a semiconductor surface. The feasibility of this approach is demonstrated by means of *ab initio* and empirical electronic structure calculations. When the channel diameter is sufficiently larger than the interstitial space, the resulting pillars constitute an ordered array of electronically independent, though mechanically connected nanowires. In the opposite regime a tunable metamaterial results. The proposed method provides a path to the realization of uniform quantum wires—both in size and doping characteristics—while easing electrical contacting. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2696774]

Semiconducting nanowires (NWs) are among the most exciting and promising building blocks for future applications in nanoelectronics. Many significant advances have been achieved in recent years concerning their fabrication and NWs of diameters below 100 nm can be routinely grown.[1–7] However, the fabrication of ordered arrays of nanowires—with the same crystallographic orientation and homogeneous sizes—remains at a large extent elusive. This is a crucial problem for a myriad of practical applications, ranging from sensor arrays and light emitters to the realization of templates for NW-based electronics. Semiconducting nanowires are normally grown by vapor-liquid-solid reaction, using metallic nanoparticles as catalysts.[8,9] Thus, the growth of ordered arrays of NWs is subordinated to the ability of patterning a substrate with a homogeneous set of nanoparticles,[10] which can be tackled by means of e-beam lithography. Attempts at NW fabrication by direct chemical etching have resulted in disordered highly porous Si.[11]

We propose a catalyst-free method to fabricate ordered arrays of NWs from bulk material in a top-down approach. The method is based on the design of a pattern of channels perpendicular to a semiconductor surface, as illustrated in Fig. 1, by any advanced lithography technique, such as e-beam or scanning probe, in a manner similar to photonic crystals.[12] We present *ab initio* and empirical calculations showing that when the channel diameter is sufficiently larger than the interstitial (interchannel) space, the resulting pillars between the channels [dashed circles in Fig. 1(a)] may constitute an ordered array of electronically independent, though mechanically connected NWs. The quantum wires obtained in this manner have all the typical characteristic of conventionally grown NWs, but in addition they should benefit from a superior control of the crystallographic orientation and from the homogeneity of the properties of the whole ensemble. Far less than an inconvenience, the fact that the wires are connected provides them with an enhanced mechanical stability and, in a regime with finite interwire coupling, can lead to an original class of two-dimensional superlattices with tunable properties.

We have performed *ab initio* electronic structure calculations with the SIESTA package,[13] which implements the density-functional theory (DFT), within the generalized gradient approximation,[14] using an optimized single-ζ polarized basis set.[15] We have considered Si and GaAs substrates, designing square or hexagonal channel networks perpendicular to the [100] and [111] surfaces, using a grid of $1\times1\times6$ **k** points. The simulation cells employed range from 359 to 952 atoms. The dangling bonds of the channels' internal surface have been passivated with (pseudo) hydrogens.

At first we have considered channels arranged in a square network in a silicon substrate, such that the spacing between neighboring channels is of approximately 5.5 Å. The channels have been designed following Si natural cleavage planes. The resulting array of NWs has also a square lattice symmetry, as illustrated in Fig. 1(b). We have calculated this structure with interconnects of increasing thicknesses to test their confinement properties. The size of the interchannel pillars, on the other hand, is kept at 15 Å, the order of the thinnest nanowires reported.[1] The wave functions of the states at the top of the valence band (TVB) and at the bottom of the conduction band (BCB) are illustrated in Figs. 2(a) and 2(b), demonstrating the confining properties of this architecture. A more quantitative estimate is obtained by the analysis of the band structure diagram [Fig. 3(a)] where we recover the typical band dispersion of a ⟨100⟩ wire, featuring a direct band gap, when the wave vector moves along the wire axis (k_z), while the bands are fairly dispersionless when moving along k_x and k_y, i.e., perpendicular to the pillar axis. Doubling the thickness of the interconnects [Figs. 2(c) and 2(d)], a coupling between neighboring wires starts to appear. The situation is rather different, depending on the type of carrier considered: holes in the valence band still

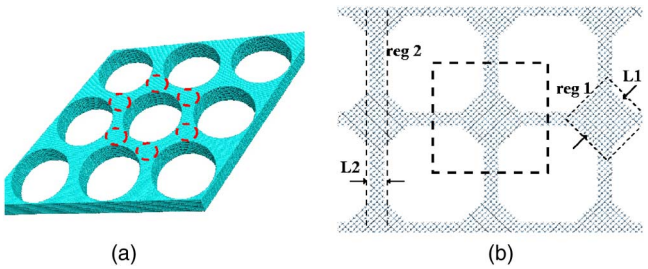

FIG. 1. (Color online) (a) Sketch of the method proposed and (b) top view of a Si supercell used in the calculations.

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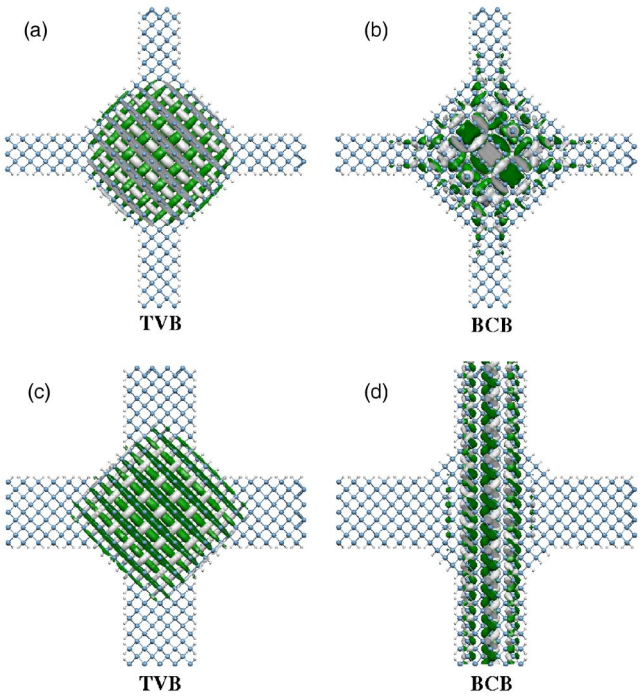

FIG. 2. (Color online) Si substrate, interconnect thicknesses of ~5.5 Å (upper row) and ~11.0 Å (lower row): TVB and BCB wave functions.

travel in reasonably confined states, while electrons in the conduction band would move in extended states. Once again, this is easily understood from the band structure [Fig. 3(b)], where it can be seen that the highest state in the valence band is still fairly flat, while the very first empty states of the conduction band already start dispersing when moving in the k_x-k_y plane. Calculations for thicker interconnects maintaining the wire size constant indicate that the hole confinement

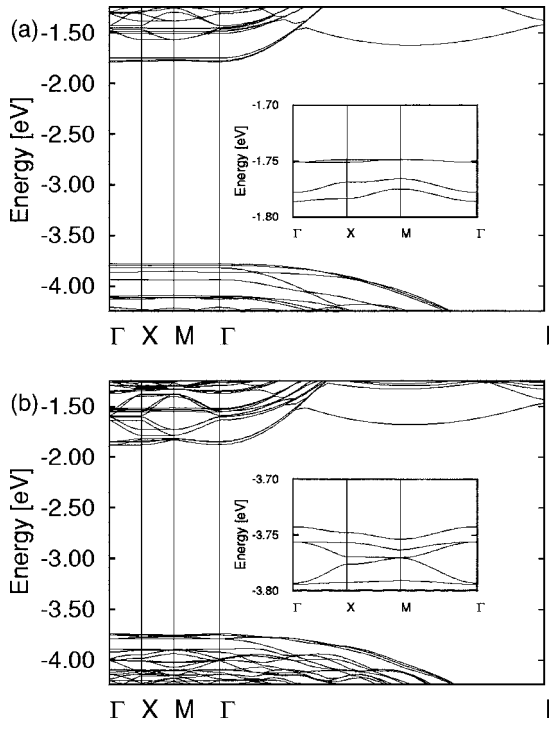

FIG. 3. Si substrate, band structure diagrams for interconnect thicknesses of (a) ~5.5 Å and (b) ~11.0 Å, showing direct band gap. The insets show a magnification of the BCB (a) and TVB (b). Flat bands indicate decoupling.

is more persistent than the electron confinement effect. All these structures have been also calculated with a GaAs substrate to test the robustness and generality of the approach. No significant differences were detected from the viewpoint of the confining properties, and thus both materials are suited for the fabrication of these structures.

The predominance of localized or extended states at the band extrema is easily understood in the square topology as a competition in the confinement energy between the two-dimensional electron/hole gas formed in the interconnects [cf. region 2 in Fig. 1(b)] and the one-dimensional structures of interest [region 1 in Fig. 1(b)]. An effective mass approximation analysis yields a condition for the existence of NW-like states in the square topology,

$$\sqrt{1+\frac{m_h^*}{m_l^*}}L_2 < L_1, \tag{1}$$

where m_h^* (m_l^*) is the heaviest (lightest) of the in-plane effective masses under consideration (i.e., longitudinal and transverse CB effective masses for Si), L_2 is the thickness of the interconnect, and L_1 is the wire typical size. We see from Eq. (1) that, for materials with spherical effective masses, having NW states at the band extrema is based on geometrical considerations only, and thus it should be a robust effect with respect to material variations. In the case of Si, the elliptical character of the CB minima contributes to the preferential delocalization of electrons with respect to holes. Although Eq. (1) is strictly valid for systems without strong confinement, it does predict the electron (hole) ground state delocalization (localization) in the Si structures discussed so far, in agreement with the *ab initio* calculations.

At a second stage we have tested the confinement properties of a hexagonal lattice of channels. This arrangement is a promising solution from the viewpoint of the envisaged applications because it seems that a more efficient confinement can be achieved, given the difficulties in forming fully delocalized two-dimensional states such as that of Fig. 2(d). We have considered a structure equivalent to Figs. 2(a) and 2(b) in terms of interconnect and wire size. We find that the formation of two-dimensional-like states is indeed frustrated for the few first states above the ground CB level, whereas for the square lattice of channels these states do appear at the same energy range.

In order to address whether the hexagonal lattice is capable of supporting even a more favorable wire size to interconnect size ratio, thus possibly relaxing the needed specifications for experimental realization, the use of *ab initio* methods becomes prohibitive. Therefore, we have used the effective bond orbital model[16] (EBOM)—a computationally lightweight (eight orbitals per Ga–As pair) method based on the empirical tight-binding method valid for medium-to large-sized structures[17]—to study systems with a hexagonal array of channels on a GaAs substrate with larger characteristic sizes. In Fig. 4(a) we have plotted the charge density associated with the BCB state for a structure with a channel diameter and an interconnect thickness of 37.2 and 3.2 nm, respectively. The interstitial pillars still act like independent quantum wires, as expected from the superior confining properties of the hexagonal lattice. Dielectric confinement effects,[18] not included in this calculation, can add to quantum confinement, thus possibly easing the structural requirements to achieve the wirelike behavior. An appreciable coupling

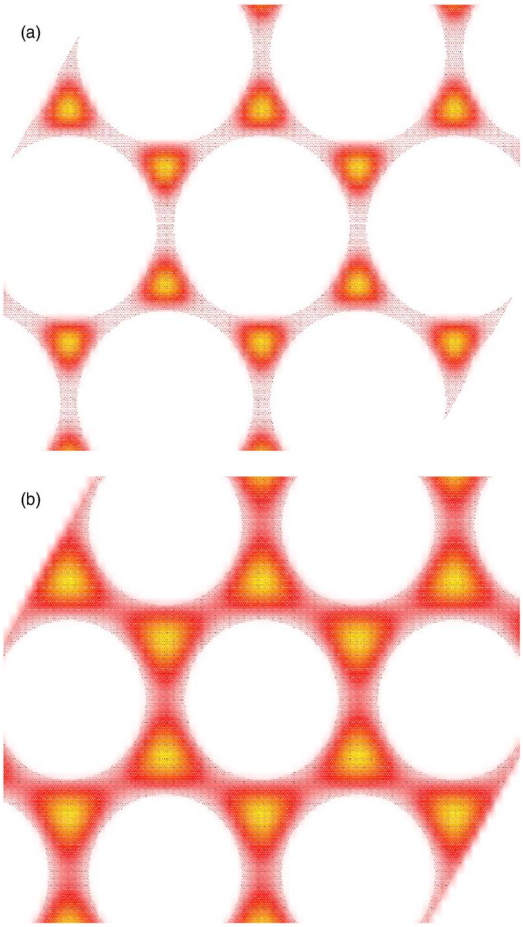

FIG. 4. (Color online) GaAs substrate, (a) interconnect thickness of ~3.2 nm and hole diameter of ~37.2 nm and (b) interconnect thickness of ~8.4 nm and hole diameter of ~32.0 nm: charge density corresponding to the BCB state, featuring (a) independent and (b) coupled NW behavior.

between the NWs appears when moving to a structure with interconnects of 8.4 nm and channel diameter of 32.0 nm [see Fig. 4(b)]. A more quantitative estimation of the coupling for electrons between instances can be given by the CB effective mass at the zone center. Perpendicular to the wire axis we obtain values of $9.1m_0$ and $0.38m_0$ for the uncoupled and partially coupled structures, respectively. This is to be compared to the almost bulklike value of $0.072m_0$ along the wire axis. We have checked that the isolation can be restored by increasing the channel diameter to about 64 nm. Note that these feature sizes are within current lithographic capabilities. Experimental verification of the predictions here made might involve scanning tunneling spectroscopy on an interstice, where observation of $2e^2/h$ quanta of conductance would be a signature of confined vertical transport. Angle-resolved photoemission spectroscopy could equally be employed to measure the dispersion relation perpendicular to the channels.

In conclusion, we have shown by means of electronic structure calculations that an appropriately designed lattice of channels in a semiconductor substrate can give rise to an ordered array of nanowires if the channel diameter is sufficiently larger than the remaining interstitial pillars. The confining properties of the structures depend on the distribution of channels and on a subtle interplay between the thickness of the interconnects and the diameter of the pillar, with a hexagonal array of channels making the confinement much more efficient. The nanowires obtained should have uniform properties, concerning the diameter, length, crystallographic orientation, and dopant concentration, and would be suitable for integration in nanodevices, while their electrical contacting would be enormously facilitated by depositing the top metal layer before the hole patterning. The proposed procedure could be easily extended to quantum well or superlattice substrates, e.g., GaP/InGaAs or GaAs/AlGaAs, resulting in regular arrays of (stacked) quantum dots with several potential applications as optoelectronic devices.

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