Fabrication of ordered arrays of quantum wires through hole patterning

X Cartoixà¹, R Rurali¹, I Fernández-Cuesta², F Pérez-Murano², J Suñé¹
¹ Departament d’Enginyeria Electrònica, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain
² Centro Nacional de Microelectrnica - Institut de Barcelona, (CNM-IMB, CSIC) - Campus UAB, 08193 Bellaterra, Spain
E-mail: Xavier.Cartoixa@uab.es

Abstract. We present empirical tight-binding calculations of the electronic structure of an array of mechanically connected silicon nanopillars. Structural parameters are chosen so that electrons are confined within each pillar, obtaining an array of effectively decoupled one-dimensional states. We address fabrication issues and present results demonstrating the suitability of the process.

1. Introduction

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 [1–4]. 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 (VLS), using metallic nanoparticles as catalysts[5, 6]. Thus, the growth of ordered arrays of NWs is subordinated to the ability of patterning a substrate with a homogeneous set of nanoparticles [7], 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 [8].

Some of us have recently proposed a catalyst-free method to fabricate ordered arrays of NWs based on the etching of a hole pattern onto a bulk substrate [9]. By appropriate design of the structure, the material that is left behind may constitute an array of thicker material (interstitials) capable of supporting one-dimensional states without coupling to states located at other interstitials, even though the interstitials may be mechanically connected by thinner regions of material (interconnects) [see below for further explanation]. In this paper we report on the progress towards the experimental realization of these ideas on a silicon substrate. Silicon is interesting because its processing is very mature, it possesses a natural high quality oxide that can lessen the demands on the nanolithography and, when the interstitials are small enough it becomes a direct bandgap material [10], opening possibilities for its use in optoelectronic
devices. In the second section we present calculations for silicon substrates determining the target dimensions that, in future work, we will try to obtain using the processes described in the third section.

2. Calculations
Calculations have been carried out using the empirical tight-binding method [11], using a basis comprised of \{ |s\rangle, |p_x\rangle, |p_y\rangle, |p_z\rangle \} antibonding (conduction band) states located on an fcc lattice, following the antibonding orbital model (ABOM) by Chang et al. [12]. This is a full zone model that, therefore, takes into account the intervalley couplings that can give rise to energy splittings in reduced dimensionality structures [13]. The lower number of states in the ABOM basis allows for faster calculations with respect to atomic orbital-type tight binding calculations.

We design a structure with a centered rectangular arrangement of the holes in order to avoid the appearance of states extending over aligned interconnects [cf. Ref. [9], Fig. 2(d)]. On the other hand, Si [110] substrates provide atomically flat \{111\} walls after anisotropic TMAH wet etching [14], minimizing the presence of potentially disturbing surface defects. Thus, the walls of the holes are chosen to coincide with \{111\} planes, making the top view of the structure look like Fig. 1.

Figure 2(a) shows the charge density of the first eigenstate of the structure in Fig. 1 with \( t = 7.8 \) nm and \( d = 10.9 \) nm. We observe that the charge density is confined to the interstitial
regions; consequently this structure is expected to behave as an array of quantum wires from the point of view of the electronic structure. Figure 2(b) refers to the fifth eigenstate, showing the appearance of a nodal plane, as would be expected for an excited state in a mechanically isolated nanowire. Due to the multiplicity arising from the six equivalent conduction band (CB) minima in bulk Si, this is the first excited state differing significantly from the ground CB state. The energy splitting between the fifth and first eigenstates $\Delta_{5-1}$ is only 5.3 meV, this low value coming from the relatively large confinement sizes and the heavy CB effective masses in Si.

Figure 3 is similar to Fig. 2, except that the interconnects have widened to $t=12.2$ nm. We see that, while the ground state is still confined in the interstitials, the fifth eigenstate, only 3.7 meV above the ground state, presents an extended behavior. From this study we conclude that, in order to observe experimentally unidimensional states, either we need to go to cryogenic temperatures or the interconnect needs to be effectively shut off. This last requirement may be easier to obtain by wet oxidation of the structure after the hole patterning. By regulation of the oxidation parameters (time, temperature), the thickness of the oxide growing into the silicon structure can be controlled, thus oxidizing completely the interconnects and leaving only part of the interstitial unoxidized. We have also carried out calculations with structures with a larger hole pitch ($p=68.2$ nm), still showing confinement for the first few states above the CB minimum.

3. Fabrication

For a preliminary attempt, an ordered array of holes was fabricated in silicon, by a combination of electron-beam lithography (EBL) and anisotropic wet etching. First, the holes were defined by e-beam exposure at 20keV in a 100 nm thick PMMA 950k film, spun onto a (110) silicon wafer. After EBL, the exposed PMMA was developed in a MIBK:IPA, 3:1 solution. The features are transferred into the silicon substrate by selective wet etching, using the non-exposed PMMA as a mask. First, a short dip (1s) in HF is performed, in order to remove the native oxide on the silicon surface, and then, the sample was rinsed in a TMAH solution (25\%) at 80° during 10 s, in order to achieve a depth of 70 nm. The main reason for using anisotropic wet etching in TMAH is that the etching ration strongly depends on the crystallographic planes of the substrate (the etching ratio of \{111\} planes is tens of times slower than \{100\} planes and \{110\} planes [14]), so after the etching, the round-shaped holes that were defined in the mask became wider and hexagonal, and the whole matrix resembles the desired structure, shown in Fig. 1.

Figure 4 shows a SEM image of an example of a structure fabricated following the process described above. In this case, the holes were defined with a diameter of 300 nm and the pitch of the array is 450 nm, and resulting depth is 72 nm. Here, it can be observed that sidewalls
corresponding to the \{111\} planes at \(\pm 54^\circ\) with respect to the horizontal line of the image have vertical sidewalls, but the others, in the horizontal direction, are sloped, leading to a limitation in the depth of the holes attainable by wet etching. Possible solutions include working with a silicon-on-insulator substrate, yielding an array of quantum dots instead of quantum wires, or performing a reactive ion etching (RIE) to obtain high aspect ratio holes followed by isotropic wet etching, to smoothen the surface of the sidewalls.

4. Conclusions
In summary, we have studied theoretically the confining properties of an array of holes patterned onto Si [110] substrates. We have identified a set of design parameters that make the first few eigenstates in the conduction band behave as an array of electronically independent states, with transport taking place only along the hole axes. A first structure fabricated along these guidelines is presented.

Acknowledgments
This work was supported in part by the European Commission’s Marie Curie International Reintegration Grant No. MIRG-CT-2005-017198. The authors also acknowledge the Spanish Ministry of Science and Technology for funding under contract number TEC2006-13731-C02-01 and the GICSERV Program for access to the nanofabrication facilities. JS acknowledges the support of the DURSI of the Generalitat de Catalunya. XC (RR) acknowledges financial support from Spain’s Ministry of Education and Science Ramón y Cajal (Juan de la Cierva) program.

References
[1] Ma D D, Lee C S, Au F C K, Tong S Y and Lee S T 2003 Science 299 1874–1877
[2] Holmes J D, Johnston K P, Doty R C and Korgel B A 2000 Science 287 1471–1473
[3] Coleman N, Morris M, Spalding T and Holmes J 2001 J. Am. Chem. Soc. 123 187–188
[4] Wu Y, Cui Y, Huyhn L, Barrelet C, Bell D and Lieber C 2004 Nano Lett. 4 433–436
[5] Westwater J, Gosain D P, Tomiya S, Usui S and Ruda H 1997 J. Vac. Sci. Technol. B 15 554–557
[6] Morales A M and Lieber C M 1998 Science 279 208–211
[7] Hsu J H, Huang M H, Lin H H and Lin H N 2006 Nanotechnology 17 170–173
[8] Cullis A G and Canham L T 1991 Nature 353 335–338
[9] Rurail R, Suiñé J and Cartoixà X 2007 Appl. Phys. Lett. 90 083118 (pages 3)
[10] Huo J, Solanki R, Freecouf J L and Carruthers J R 2004 Nanotechnology 15 1848–1850
[11] Slater J C and Koster G F 1954 Phys. Rev. 94 1498–1524
[12] Chang Y C, Chiou A E and Khoshnevisan M 1992 J. Appl. Phys. 71 1349–1360
[13] Cartoixà X and Chang Y C 2005 Phys. Rev. B 72 125330
[14] Tabata O, Asahi R, Funabashi H, Shimaoka K and Sugiyama S 1992 Sens. Actuators A 34 51–57