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Electron Properties of Free-Standing Wires of Porous Silicon: ab Initio Calculation

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We are performed a Monte-Carlo simulation of fabrication processes of porous silicon by electro-chemical etching under 300 K of (100) single silicon and resulted a set of free-standing wires. We are not obtained rebuilding of break bonds as like on the surface. Next we are performed ab initio calculation for elaboration of electron properties of free-standing silicon wires. For this the Car-Parrinello molecular dynamics and ab initio norm-conserving pseudopotential were used. The calculation algorithm means using of atomic basis (it reflects features of the investigating system) which certainly ought to have inverse symmetry. The atomic basis of the primitive tetragonal unit cell of the superlattice represented an infinite silicon free-standing wires with a square cross section at side with 5,43 Å and (100) orientation. An examination of the maps of valence electron density distributions and valence electron spectrum obtained with the help of author program code can explain properties of considered atomic objects. It was indicated that an each atom on surface the wire with a slight thickness had different electron state. This result show anisotropy of electron properties of atoms along free-standing wire surface even if cross section of wire was homogeneous on whole length and explain of wide bar of luminescence not only by means of scatter of parameters of cross section of free-standing wire.

Keywords: free-standing silicon wires, electron properties, ab initio calculation.

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Introduction

Formation of porous space of the composite topology creates interesting object in which different classes of the phenomena both physical and chemical nature are combined. Namely: quantum-dimensional effects, fractal phenomena, which are the reason of photo and electro-luminescence at room temperatures, etc. With the help of the experimental methods, for example by means of a tunnel microscope to trace morphology of pores deep into from the surface is not obviously possible, as the sizes of a tunnel sonde is more, than pores. Therefore adequate simulation is a single expedient to establish actual structure of porous material.

I. Calculation methods and results

In our computer calculation experimental procedure of the fabrication porous layers in silicon was marketed. These layers are traditionally got by way of the anode etching in solution *HF* under room temperature. Realization of model procedure of fabrication *por-Si* consisted in the following. We started at T = 300 K from crystal *Si* (*c–Si*) located in a model cube with linear dimensions of edges 27,1 E, as a film with width in direction Z – 21,68 E and the infinite length in directions X, Y. The (100) surface of a film was considered as the surface of interacting with active substance (solution *HF*). The model volume contained 1000 atoms. Interaction between atoms was modeled by Keating potential [1]. In our models atoms can be under two conditions: in “not etched” state and in “etched” state (vacancy was formed). First all atoms were in not pickled state in crystalline positions. Further the algorithm of etching is realized in which the basis is an analysis of probability of exception of atom from crystal layers. One atom is chosen casually from set of available atom N (N – set available atom comprises of atoms of the surface, which interacts with active material HF, and atoms, which are connected with surface atoms by the etching channel). On the first simulation step the atoms set (N) is equal to quantity of surface atoms. After choice of the atom it is calculated probability of the removing this atom from crystal (the etching). On following step a new set of atoms (N) is defined, which are available to etching, in the manner of percolation cluster. Process of etching was prolonged until percent contents of pores in model volume (~ 50%) have been reached. It is known, that in por-Si from porosity > 50 % during electro-etching are possible to gain quantum points, quantum wires, and devices with various fractal dimensions. Further such model of atomic system was obtained as a

result of a relaxation by Monte Carlo procedure.

On patterns of the radial distribution functions $n(r)$ (fig. 1) of atomic structure crystalline Si and por-Si the differences are fixed. Comparing results of simulation for

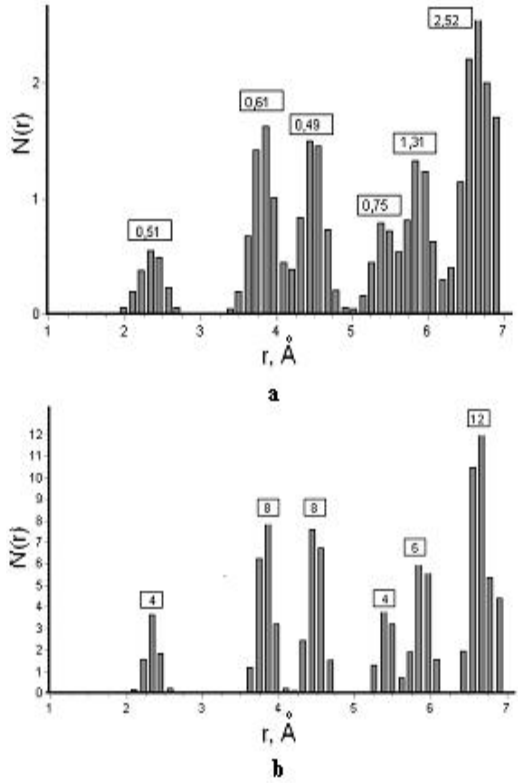

Fig.1. Radial distribution functions, $n(r)$, for porous silicon (a) and Si crystal (b) (T=300 K).

c-Si and por-Si, it is visible, that first coordination sphere of crystal Si contains 4 atoms, por-Si – 0,51, the second accordingly – 8 and 0,61, the sixth – 12 and 2,52 (fig. 1). Herewith, profiles of radial pair distribution functions $g(r)$ for c-Si and por-Si (fig. 2) show a similar location of peaks on distance, for example, the first peak is apart 2,34 E, second – 3,75 E, the third – 4,5E, etc. (see Fig. 2). The results obtained by us, prove to be true experiments [2] which mount, that in *por-Si* in basic the order of the location of the atoms, inherited from a silicon substrate is saved.

The spatial pattern of arranging of atoms (Fig. 3) shows, that the nano-dimensional formations in por-Si are shaped as the ramified isolated clusters. Growth of silicon wires occurs perpendicularly to surface of etching. Pores in porous silicon destroy atomic chain that gives in formation of broken bonds. But reconstruction of atoms, similarly to the surface, for closure of broken bonds does not occur as evidenced by improved chemical activity por-Si and change of its electronic and optical properties by contrast to zero-defect silicon. Absence of essential atomic reorganizations in the field of the free-standing silicon wires in an array of porous material prove to be true by our additional calculations with use of methods from the first principles – theory of functional of electron density and a ab initio norm-conserving pseudopotential within the framework of algorithm of quantum-mechanical molecular dynamics –

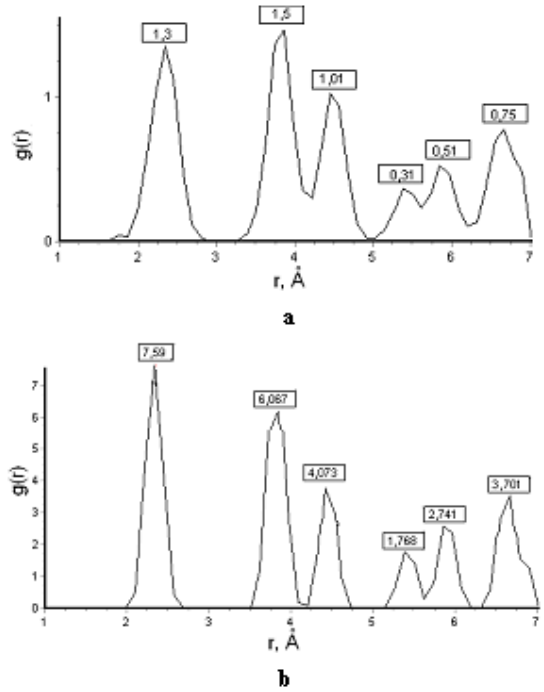

Fig.2. Radial pair distribution functions, $g(r)$, for porous silicon (a) and Si crystal (b) (T=300 K)

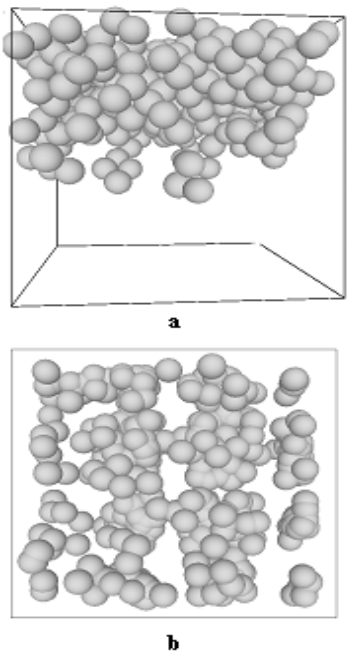

Fig.3. Spatial pattern of arrangement of atoms in *por-Si*: in the plane of perpendicular surface (100) (a), on the part of the surface (100) (b) (T = 300 K).

which allow to estimate the basic state of atomic system [3].

The calculation algorithm means using of atomic basis (it reflects features of the investigating system) which certainly ought to have inverse symmetry. The atomic basis of the primitive tetragonal unit cell of the superlattice represented an infinite silicon free-standing wires with a square cross section at side with 5,43 Å and (100) orientation. It comprised 8 atoms of silicon.

Using the author program code [3], the performances of the basic state of atomic systems for center of Brillouin zone have been received with such variants of experiment requirements: (1) number of plane waves in decomposition of the complete wave function of system was defined by the cutoff energy 12 Ry and has made 705; value of fictitious mass for orbitals – 300 atomic unities, a time step in algorithm of the molecular dynamics – 2 atomic unities, number of iterations of the self-coordination – 20; starting conditions for electronic orbitals were defined by random values of coefficients in decomposition of the lowest states and zero velocities of their change; interaction of valence electrons with an ion of a atom core was calculated with the help of Hartwigsen, Goedecker, Hutter ionic pseudopotential from first principles which took into account contributions *s*-, *p*-, *d*- orbitals [4]; (2) under other identical requirements, starting conditions for electronic orbitals were defined Hamiltonian matrix diagonalization, which has consisted from functional of a kinetic energy and the Bachelet–Hamann–Schluter ionic pseudopotential which took into account contributions *s*-, *p*-, *d*-orbitals [5] and have been screened by the dielectric function ***ε(G)*** in Thomas-Fermi approximation. Calculations on different starting conditions yielded the similar results.

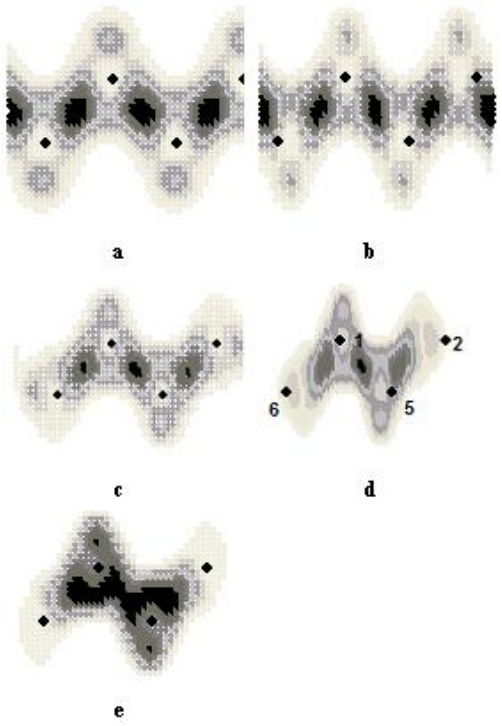

Fig.4. The (110) section of the space valence electron density distribution: (a) for bulk silicon; (b) for thin silicon film with thickness 5,43 Å (not relaxed); (c) for free-standing silicon wire (section along a wire); (d) for free-standing silicon wire (section across a wire with the indication the numbers of atoms of basis); (e) for a cluster from 8 *Si* atoms

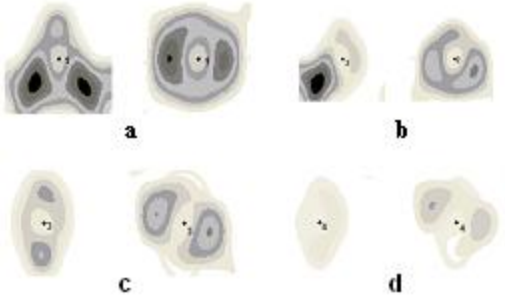

Fig.5. Sections in crossly perpendicular planes of the space valence electron density distribution for free-standing silicon wire in a neighbourhood of atoms of basis with numbers 1(a), 2(b), 3(c), 4(d)

The analysis of density distribution of valence electrons for the free-standing silicon wires of the infinite length has allowed revealing main features in its spatial structure. Interaction between hairlines which were apart 3,06 Å, is not observed, atoms practically maintain the arrangement as it was in a crystal with inappreciable displacements (about 2%), that reduces thickness of the free-standing wires.

For observation of transformation of electron density at change of dimensionality of substance of silicon from volumetric to a thin film thickness 5,43 Å, is farther to the free wire, and in the end, to a cluster from 8 atoms, on Fig. 4-5 sections of a spatial distribution of electron density of termed objects are given.

Atoms with numbers 1 and 5 of atomic basis are interior atoms of a wire and for them, as it is clear from fig. 5, sp^3-hybridization is maintained, and the surface of a wire is created by atoms 2, 3, 4, 6, 7, 8. From Fig. 4 it is visible, that at that small thickness of a wire, which was explored, each pair of atoms of the surface (presence of pairs is defined by inverse symmetry in atomic basis) has different electronic state which shows distinction in the valence-electron distribution in a neighbourhood of termed atoms. This result shows anisotropy of electron properties of atoms along free-standing wire surface even if cross section of wire was homogeneous on whole length and explains bar wide of luminescence not only by means of scatter of parameters of cross section of free-standing wire.

Conclusions

We obtained by computer Monte-Carlo simulation with atomic potential and methods from the first principles that in por-Si in basic the order of the location of the atoms, inherited from a silicon substrate is saved. Growth of silicon wires occurs perpendicularly to surface of etching. Reconstruction of atoms, similarly to the surface, for closure of broken bonds does not occur. We are appeared anisotropy of electron properties of atoms along free-standing wire surface even if cross section of wire was homogeneous on whole length. This anisotropy explains the bar wide of luminescence not only by means of scatter of parameters of cross section of free-standing wire.

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Електронні властивості вільних ниток пористого кремнію: розрахунок із перших принципів

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За допомогою методу Монте-Карло ми відтворили процес виготовлення пористого кремнію шляхом електрохімічного травлення зразка кремнію і отримали масив вільних ниток. Ми не спостерігали перебудови обірваних зв'язків, що характерне для поверхні. Для з'ясування електронних властивостей вільних ниток кремнію ми виконали розрахунки з використанням методів із перших принципів: молекулярної динаміки Кар-Парінелло і теорії псевдопотенціалу. Алгоритм обчислень передбачає використання атомного базису (це відображають топологічні особливості досліджуваної системи), який повинен мати зворотну симетрію. Атомний базис примітивної татрагональної комірки суперрешітки представляє собою нескінченну вільну нитку з квадратним поперечним перерізом із стороною 5,43 Å орієнтовану в напрямку [100]. Аналіз карт розподілу густини валентних електронів і спектру валентних електронів, отриманих за допомогою авторського програмного коду, дозволяє пояснити властивості об'єктів, що розглядаються. Так, було визначено, що кожний атом на поверхні нитки малої товщини має різний електронний стан. Це дає можливість визначити наявність анізотропії електронних властивостей атомів уздовж поверхні вільної проволоки пористого кремнію навіть при однорідності перерізу проволоки по всій довжині і пояснити широку смугу фотолюмінесценції не тільки через розкид параметрів перерізу вільних проволок.

Ключові слова: вільні нитки кремнію, електронні властивості, розрахунок із перших принципів.