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Modelling of electronic and phononic states of Ge nanostructures

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ABSTRACT

The electronic band structure of ordered porous germanium (PGe) and germanium nanowires (GeNW) are studied by means of an sp^3s^* tight-binding approach. Within the linear response theory, a local bond-polarization model based on the displacement–displacement Green's function and the Born potential including central and non-central interatomic forces are used to investigate the Raman response and the phonon band structure of PGe and GeNW. This study is carried out by means of a supercell model, in which along the [0 0 1] direction empty-column pores and nanowires are constructed preserving the crystalline Ge atomic structure. An advantage of this model is the interconnection between Ge nanocrystals in PGe and then, all the electronic and phononic states are delocalized. However, the results of both elementary excitations show a clear quantum confinement signature. Moreover, the highest-energy Raman peak in both PGe and GeNW shows a shift towards lower frequencies with respect to that of bulk crystalline Ge, in good agreement with the experimental data.

1. Introduction

Nanostructured materials and devices are important for both fundamental research and applications, because they provide the possibility to observe quantum phenomena at macroscopic scale and have the potential to reach far higher devices densities compared with traditional semiconductor technology. In particular, the nanostructured semiconductors could be used as building blocks for many nanodevices in microelectronics [1,2]. Although silicon (Si) has replaced germanium (Ge) in microelectronic largely because of the superior structural and electrical characteristics of the Si/SiO_2 interface, recent works on the ordered porous germanium (PGe) and germanium nanowires (GeNW) suggest that Ge may again become an important material for high-performance transistors [3–5]. The potential of GeNW as building blocks for nanoscale three-dimensional (3D) integrated circuits has been demonstrated by successful fabrications of field-effect transistors based on p-type GeNW with deposited high dielectric constant films as gate insulator [6]. For optical applications, Ge has the largest dielectric constant among Si and most semiconductor materials [7] and then, is particularly suitable for photonic devices.

In this work, we model the Raman scattering by phonons in both PGe and GeNW using a local polarization model of bonds, in which the displacement–displacement Green's function, the Born potential including central and not central forces are utilized. This approach has the advantage of being simple and providing a direct relationship between the microscopic structure and the Raman response. For the electronic band structures of PGe and GeNW, we use an sp^3s^* tight-binding model. In both electron and phonon studies, the supercell technique is employed in order to include the 3D and one-dimensional translational symmetries in PGe and GeNW, respectively.

2. Model and calculation scheme

The ordered PGe are modelled by means of the supercell technique, in which columns of Ge atoms are removed in [0 0 1] direction. For modeling GeNW, we start from a cubic supercell with eight Ge atoms of side $a = 5.65$ Å, taking the periodic boundary condition only along z-direction and free boundary conditions in x and y directions. Ge atomic layers are further added in these directions to obtain GeNW with larger cross-sections.

Nowadays, Raman scattering is becoming a widely used non-destructive technique for the analysis of chemical composition, bonding, and microstructure of materials. From the local polarization model of bonds, the Raman response $[R(\omega)]$ by phonons can be expressed as [8–10]

$$R(\omega) \propto \omega \,\mathrm{Im} \sum_{\mu,\mu'} \sum_{i,j} (-1)^{i-j} G_{\mu\mu'} \quad (i,j,\omega), \tag{1}$$

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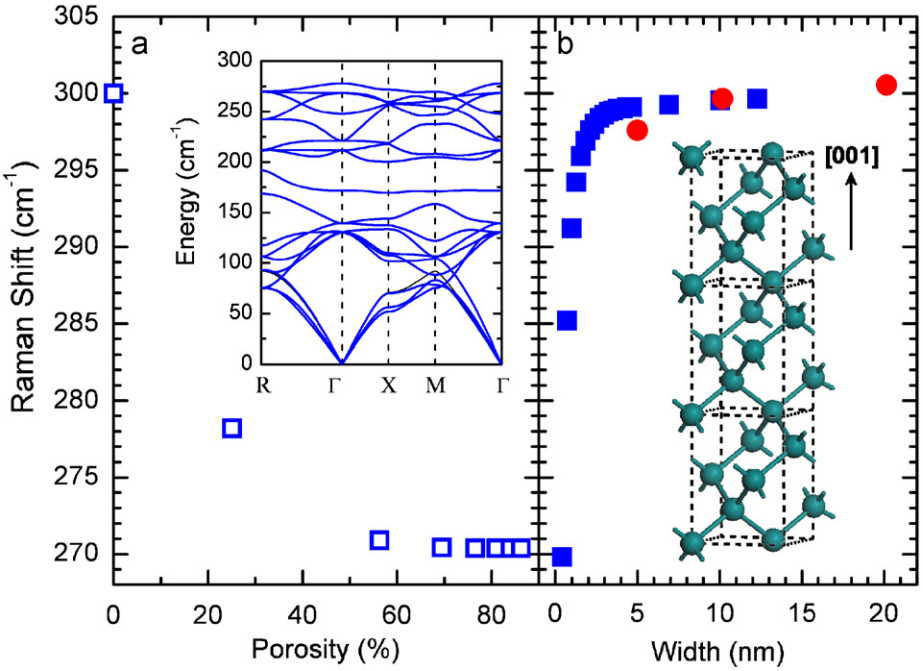

Fig. 1. Raman response calculated by Eq. (1) for (a) PGe and (b) GeNW, in comparison with experimental data from Ref. [14] (solid circles). Inset of (a) phonon band structure for the porosity of 25%. Inset of (b) the narrowest nanowire analyzed in this paper.

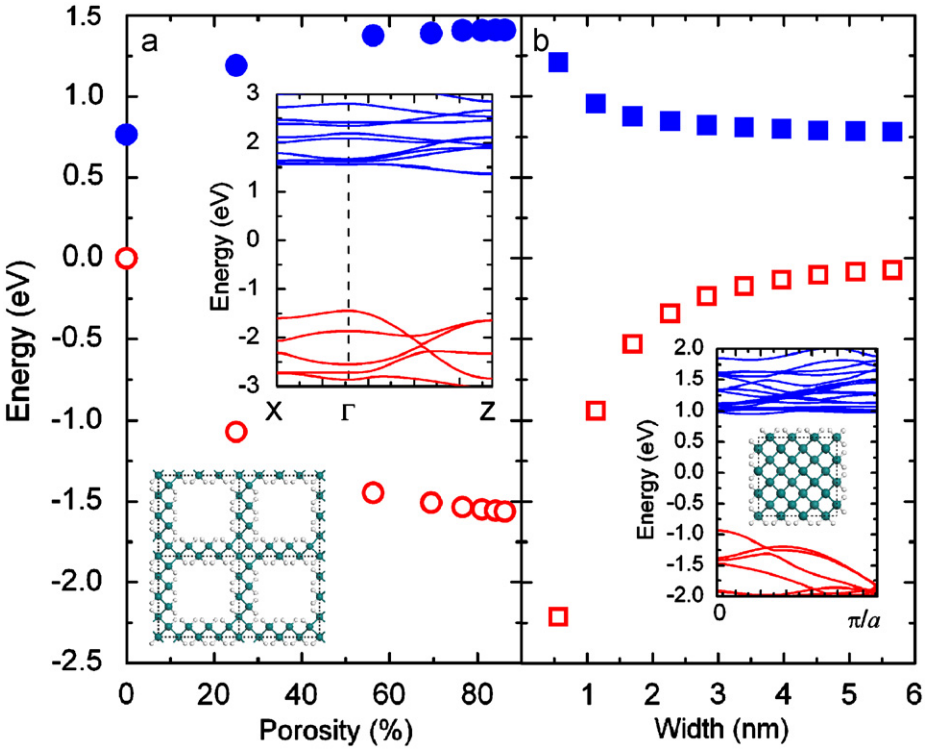

Fig. 2. Shifts of the conduction and valence band edges of (a) PGe and (b) GeNW as functions of porosity and width, respectively. Insets: electronic band and atomic structures for (a) a PGe with porosity of 56.25% and (b) a GeNW with a unit cell of 32 atoms.

where μ, $\mu' = x, y,$ or z, i, and j are index of atoms, and $G_{\mu\mu'}(i,j,\omega)$ is the displacement–displacement Green's function calculated within the Born model, as done for Si nanowires in Ref. [10] except $\alpha = 0.957\,\mathrm{N\,cm^{-1}}$ and $\beta = 0.244\,\mathrm{N\,cm^{-1}}$ obtained by fitting the phonon band structure of crystalline Ge (c-Ge) [11].

For the case of electrons, the dangling bonds on the surface are saturated with hydrogen atoms having a H–Ge bond length of 1.52 Å. It is well known that within the tight-binding approximation, sp^3s^* is the minimal basis capable to reproduce the indirect band-gap. In this work, the parameters of Vogl et al. [12] are used, which reproduce an indirect-gap of 0.76 eV for bulk c-Ge. In addition, the study of GeH_4 leads to a H on-site energy of 0.205 eV, hopping integrals between H and Ge of $ss\sigma_{\mathrm{H-Ge}} = -3.618$ eV and $sp\sigma_{\mathrm{H-Ge}} = 4.081$ eV [13]. The electronic states of

Table 1
Raman shifts and electronic band edges of ordered porous Ge

Supercell size/removed atoms	8/2	32/18	72/50	128/98	200/162	288/242	392/338
Porosity (%)	25	56.25	69.45	76.57	81	84.03	86.23
Raman shift (cm^{-1})	278.19	270.9	270.43	270.375	270.375	270.375	270.375
Valence band edge (eV)	−1.07	−1.447	−1.507	−1.534	−1.549	−1.557	−1.563
Conduction band edge (eV)	1.191	1.377	1.391	1.408	1.408	1.409	1.409

Table 2
Ge nanowires built from unit cells with periodic boundary only along [0 0 1] direction

Number of atoms in unit cell	8	32	72	128	200	288	392	512	648	800
Width (nm)	0.5666	1.132	1.698	2.264	2.830	3.396	3.962	4.528	5.094	5.660
Raman shift (cm^{-1})	269.8	291.2	295.9	297.6	298.4	298.8	299	299.1	299.15	299.25
Valence band edge (eV)	−2.152	−0.938	−0.530	−0.340	−0.236	−0.173	−0.133	−0.103	−0.083	−0.073
Conduction band edge (eV)	1.210	0.955	0.877	0.846	0.823	0.808	0.798	0.790	0.785	0.782

both PGe and GeNW are determined by diagonalizing the tight-binding Hamiltonian matrix, whose dimension is $5N_{Ge}+N_H$, being N_{Ge} and N_H numbers of Ge and H atoms in the supercell, respectively.

3. Results

An example of the phonon band structure of PGe is shown in the inset of Fig. 1(a), obtained by using a supercell of six Ge-atoms, i.e., two neighbor Ge atoms are removed from an eight-atom c-Ge cubic supercell. Note that the highest-frequency optical phonon is located at 278 cm^{-1}, which is an active Raman mode. In Fig. 1(a), the highest-frequency Raman shift (ω_R) is plotted as a function of the porosity for square pores, obtained by increasing the size of supercells and maintaining the thickness of two atomic layers in the skeleton, as shown in the lower inset of Fig. 2(a). The porosity is defined as the ratio of the removed Ge-atom number over the original number of Ge atoms in the supercell. In Fig. 1(a), we have removed 2, 18, 50, 98, 162, 242, and 338 atoms from supercells of 8, 32, 70, 128, 200, 288, and 392 atoms, respectively. The values of ω_R obtained from Eq. (1) are presented in Table 1. Observe that there is an exponential decay of ω_R with porosity and its limiting value is around 270 cm^{-1}.

For GeNW, we have calculated the Raman response of unit cells of 8–800 Ge atoms and the results of ω_R are summarized in Table 2. In Fig. 1(b), ω_R (solid squares) is plotted as a function of GeNW width and compared with experimental data obtained from Ref. [14] (solid circles). Note the excellent agreement between the theory and experiment without any adjustable parameters.

Figs. 2(a) and 2(b) show the edges of valence (E_v) (open symbols) and conduction (E_c) (solid symbols) bands for PGe and GeNW, as functions of the porosity and of the width, respectively. In their insets, a *z*-view of the atomic positions for a PGe with porosity of 56.25% and a GeNW built from a unit cell of 32 Ge atoms, as well as their electronic band structures are presented. Observe that the band edges move away and bring close asymmetrically as the porosity and the width increase, respectively. This asymmetry is originated from the difference of electron and hole effective masses in c-Ge. The values of this band-edge variation are summarized in Tables 1 and 2 for PGe and GeNW, respectively.

4. Conclusions

We have presented a comparative study of electron and phonon in PGe and in GeNW. Both elementary excitations have shown a clear quantum confinement signature, in spite of the presence of a supercell model, where the wavefunctions are definitively delocalized. In the case of PGe, the confinement is originated by the nodes of wavefunctions at the pore surface and the states with wavelengths longer than the distance between nodes will not be accessible for the system. In fact, the variations of E_c, E_v, and ω_R are in good agreement with the effective mass theory.

For the Raman scattering, the results obtained from GeNW show that this microscopic theory based on the local bond-polarization model reproduces main features of the measured Raman response and offers a direct relationship between the microscopic structure and the macroscopic physical quantity. In consequence, the Raman scattering could provide useful information about the structure and vibrational modes of PGe and GeNW, which are basic in the design of future microelectronics.

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