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## A STUDY OF POROUS Si & Ge USING Ab-Initio METHODS

R. Khatri\*

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**Abstract:** *First-principles and semi-empirical methods are employed to calculate electronic and optical properties of porous silicon and porous germanium. In order to test the parameters used in this work, the crystalline case has been taken as a starting point, where the  $sp^3 s^*$  tight-binding and the density functional theory with the local density approximation approaches show a good agreement in the electronic band structures. For the dielectric function, the tight-binding approach demonstrates a better behavior in comparison with the experimental data. For porous systems, this tendency is preserved, showing strong quantum confinement effects.*

**Keywords:** *Porous semiconductor materials; density functional theory; semi-empirical methods.*

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\*Department of Physics, DAV College, Abohar, India



## 1. INTRODUCTION

The quantum mechanics established in the early twentieth century has allowed a microscopic understanding of the materials, despite the fact that the many-body problem is still unsolved. Nowadays, there are essentially three kinds of theories; they are empirical, semi-empirical and abinitio ones, in which the ab initio theory is the most desirable since it could lead to the design of new materials. However, neither the electronic correlation nor the extremely high degrees of freedom ( $10^{23}$ ) can be properly addressed with the current computing capacity. In consequence, the abinitio theory usually involves a large number of approximations and their effects on the results are not clear. The density functional theory (DFT) is currently the most popular abinitio method, since it can be applied to relatively large systems and includes some effects of the electronic correlation and exchange. On the other hand, in the semi-empirical theories, one needs experimental data to fix the parameters of the theory in order to predict macroscopic properties of a specific material. These experimentally determined parameters usually contain complex many-body correlation effects of the system. In addition, the semi-empirical tight-binding (TB) approach, based on the Wannier functions, has the advantage of being simple and able to address large systems with extended defects, contrary to the reciprocal space methods that require crystalline symmetries.

In the last two decades, the quantum confinement observed in nanostructured semiconductors has motivated a great quantity of theoretical and experimental investigations because it has many potential applications in optoelectronics devices. In particular, a uniform layer of porous silicon (PSi) can be obtained from a substrate of crystalline silicon (c-Si) when it is anodized in a solution of hydrofluoric acid with an appropriate current density. This PSi layer consists of a skeleton of c-Si whose typical thickness is of nanometer order. Usually, PSi is modeled as a collection of quantum wires in which the quantum confinement effects are emphasized. However, the interconnection between nanowires present in real PSi samples is ignored in this kind of models. Hence, a model that includes these two effects could be based on supercells where columns of silicon atoms are removed and the dangling bonds saturated by hydrogen atoms [1]. Furthermore, this model predicts a growth of the lattice parameters in PSi, in contrast to the quantum wire model in which a decrease of the lattice parameters is observed after a geometry



optimization process [2]. Moreover, X-ray experimental results have shown an increase in the lattice parameter along the pore-growing direction [3,4]. On the other hand, little research has been done about porous germanium (PGe) [5] since pores of good quality have not been produced until recently [5,6]. The bulk Ge has a larger dielectric constant and smaller carrier masses compared to the bulk Si. Moreover, in Ge, the direct gap ( $E_0 = 0.9$  eV) is close to the indirect gap ( $0.76$  eV). Then, it is considered that quantum confinement effects would appear more pronounced in Ge than in Si, and Ge nanocrystals would exhibit a direct-gap semiconductor nature [7]. Takeoka and coworkers [8] have observed a size dependent photoluminescence (PL) from nanostructures of indirect-gap in the near-infrared region which is closer to the band gap of bulk Ge and which seems more compatible with the quantum confinement model. In this work, we present a comparative study of the DFT and TB approaches to electronic and optical properties of PSi and PGe, by means of the supercell model.

## 2. CALCULATION SCHEME

The porous semiconductors are modeled by starting from a crystalline supercell of eight atoms, removing columns of atoms along the [001]-direction, and saturating the dangling bonds with hydrogen atoms. The CASTEP codes [9] developed in Cambridge University, within the DFT and the local density approximation (LDA), are used to perform the geometry optimization of the supercell and the calculations of the electronic band structure and the dielectric function. We are using norm-conserved, nonlocal, Troullier-Martins pseudopotentials generated by the Kerker method. The electronic wave functions are expanded in a plane wave basis set with periodic boundary conditions and a plane wave energy cut-off of 900 eV, due to the presence of hydrogen atoms. The Monkhorst-Pack method has been used to select the k points set, with a 4 x 4 x 4 grid. Also, a scissors operator of 0.7 eV for Si and 0.2 eV for Ge has been considered since the DFT-LDA systematically underestimates the semiconductor band gap. On the other hand, the  $sp^3s^*$  tight-binding Hamiltonian [10] is used and the interaction parameters between hydrogen atoms and the semiconductor surface are taken from AH4 molecular calculations being A=Si [11] or Ge [12]. The imaginary part of the dielectric function ( $\epsilon_2$ ) is calculated from

$$\text{Im}[\epsilon(\omega)] = \frac{2\pi^2}{\Omega\epsilon_0} \times \sum_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} |\langle \Psi_{\mathbf{q}} | \hat{\epsilon} \cdot \mathbf{q} | \Psi_{\mathbf{q}'} \rangle|^2 \delta(\epsilon_{\mathbf{q}'} - \epsilon_{\mathbf{q}} - \hbar\omega) \quad (1)$$



in which the intra- and inter-atomic dipole matrices are considered [13].

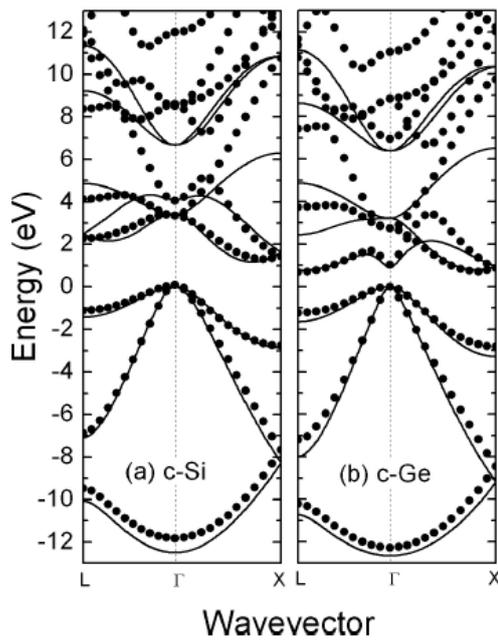


FIGURE 1. Electronic band structure of (a) c-Si and (b) c-Ge obtained from DFT-LDA (dots) and TB (lines).

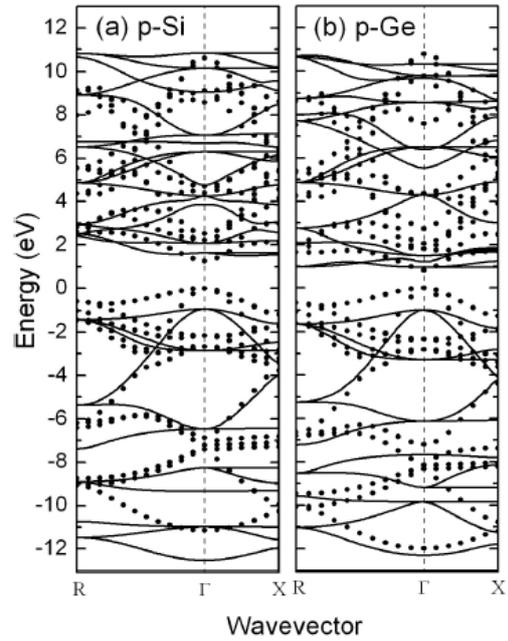


FIGURE 2. Electronic band structure of (a) p-Si and (b) p-Ge obtained from DFT-LDA (dots) and TB (lines).

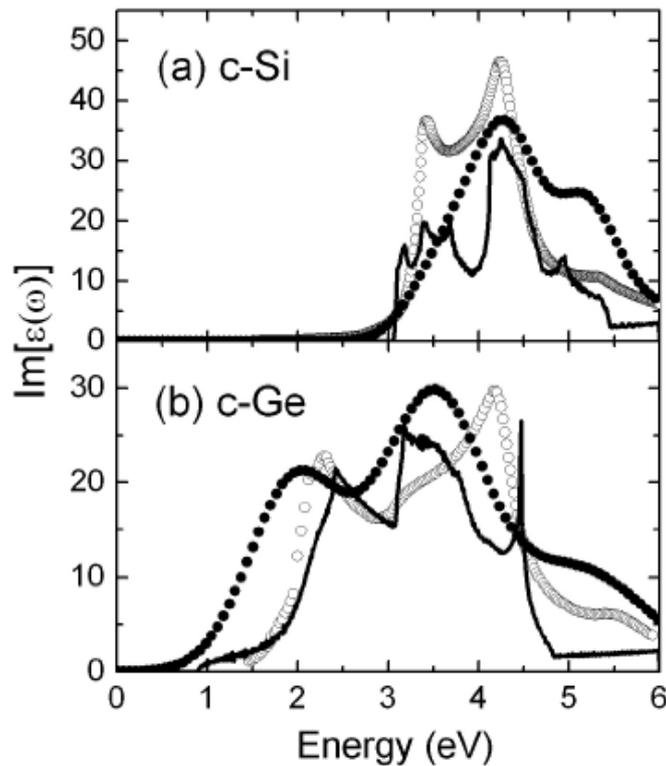


FIGURE 3. Imaginary part of the dielectric function ( $\epsilon$ ) vs. photon energy in (a) c-Si and (b) c-Ge obtained from experiments (open circles), DFT (solid circles) and TB (lines).

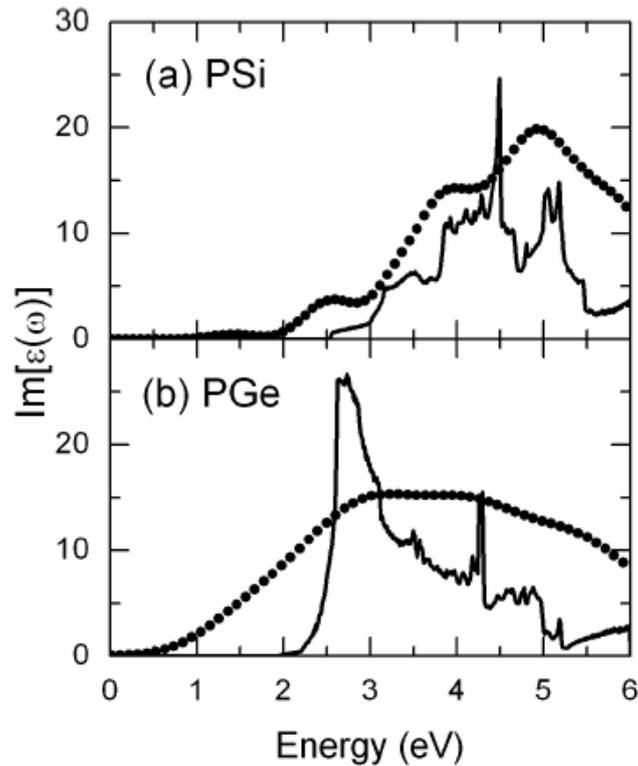


FIGURE 4. Imaginary part of the dielectric function ( $\epsilon$ ) vs. photon energy in (a) PSi and (b) PGe obtained from DFT (solid circles) and TB (lines).

### 3. RESULTS

In order to validate the calculation parameters used in this work, we have performed electronic band-structure calculations for crystalline silicon (c-Si) and germanium (c-Ge), as correspondingly shown in Figs. 1a and 1b, where the lines and dots correspond to the TB and DFT results, respectively. Notice the good agreement between abinitio and semi-empirical results around the band gap.

As first approximation to the porous systems, an eight-atom supercell of silicon (germanium) is considered, where the central atom is removed to simulate a pore as discussed in the previous section.

Figures 2a and 2b show the electronic band structure for the case of one atom pore in eight-atom supercells of silicon and germanium, respectively. Notice that in this case the DFT-LDA calculations give smaller band gaps for the porous structures in comparison with those obtained within the tight-binding approach. This difference could be due to the inherent smoothing of the hydrogen and silicon (germanium) wave functions within DFT, allowing



for a greater overlap between them than in the case of the TB approach and then, reducing the quantum confinement effects in the DFT picture.

In Figs. 3a and 31D, the imaginary part of  $\epsilon$  is plotted as a function of x-polarized photon energy for c-Si and c-Ge, respectively, where the open circles, solid circles and lines correspondingly represent the experimental, DFT and TB results. It can be observed that in general the TB approach gives a closer agreement with experimental data of Si [14] and Ge [15], since the parameters used in the semi-empirical theory contain many electronic correlation effects that ab-initio calculations cannot easily include.

Figures 4a and 4b respectively show the imaginary part  $E$  of porous silicon (PSi) and porous germanium (PGe), calculated by DFT-LDA (circles) and TB (lines). Observe that the DFT calculation leads to a weaker effective quantum confinement in comparison with the TB one. It is worth mentioning that we have found no experimental data in the literature for the porosity of 12.5% considered in this work.

#### 4. CONCLUSIONS

Both DFT and TB approaches can reproduce the main features of the experimental results, revealing the quantum confinement effects on the electronic and optical properties. However, the abinitio scheme still requires external information of the system, such as the scissor operator that simulates many-body interactions. Also, the semi-empirical approach uses parameters obtained from the crystalline case and their transferability to porous materials is not clear. Hence, a systematical study in larger supercells with different pore morphologies, porosities and pore distributions must be performed in order to compare the available experimental data of porous semiconductors. This work is currently in progress.

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