

## *Ab initio* study of birefringent porous silicon

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Optical properties of birefringent porous-silicon layers are studied within the density functional theory. Starting from a (110)-oriented supercell of 32 silicon atoms, elliptic columns of atoms in [100] and [010] directions are removed. The dangling bonds are saturated with hydrogen atoms. The results show an in-plane anisotropy in the refractive index and in the absorption coefficient, i.e., a birefringence response. The difference  $\Delta n$  defined as  $n_{[1\bar{1}0]} - n_{[001]}$  is compared with experimental data and a good agreement is observed. Also, the calculated absorption coefficients behave very closely to the measured ones.

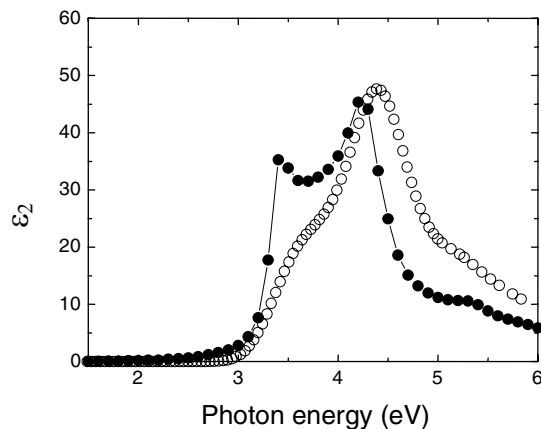
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### 1 Introduction

Since its beginning, the investigation on porous silicon (PSi) has revealed that the pores have a preferential propagation in the equivalent [100] crystallographic direction, for both n- and p<sup>+</sup>-type Si wafers, independent of dopant concentration or anodization conditions [1, 2]. Recently, it has been demonstrated that in (110)-oriented p<sup>+</sup>-doped crystalline silicon (c-Si) samples the pores are preferentially aligned in the [100] and [010] crystallographic directions and therefore, all the pores lie on the planes whose Miller indices are (001). This peculiar geometry causes an in-plane dielectric anisotropy (birefringence) for normal-incident linearly-polarized lights [3]. In addition, the refractive index ( $n$ ) reaches its maximum value when the incident light is polarized along the  $[1\bar{1}0]$  crystallographic direction, i.e., parallel to the planes of the pores. Birefringent PSi provides a sensitive tool for analysing the adsorption of atoms and molecules in negligible quantities [4] and its multilayer arrangements can be used for sensing the linear polarization of light [3].

On the other hand, the density-functional theory (DFT) is nowadays by far the most popular *ab initio* method to calculate ground-state properties of metals, semiconductors, and insulators [5]. The most important approximation in this theory is in the exchange-correlation term of the energy functional, since its exact form is unknown. The optical properties are usually calculated within the local density approximation (LDA) for exchange and correlation, which unfortunately underestimates the band gaps. For semiconductors and insulators they are typically 30–50% less than the experiment data. This discrepancy can be corrected by introducing the many-body *GW* approximation: the first term in an expansion of the self-energy operator in terms of the dynamically screened Coulomb interaction ( $W$ ) and the dressed Green's function ( $G$ ) [6]. However, it is known that shifting the LDA spectrum to higher energies by a scissors operator reproduces the *GW* spectrum [7]. This fact provides an appropriate manner to calculate optical properties of semiconductors. Taken c-Si as an example, we calculate the imaginary part of the dielectric function ( $\epsilon_2$ ) through CASTEP codes [8, 9] within the DFT-LDA framework, using

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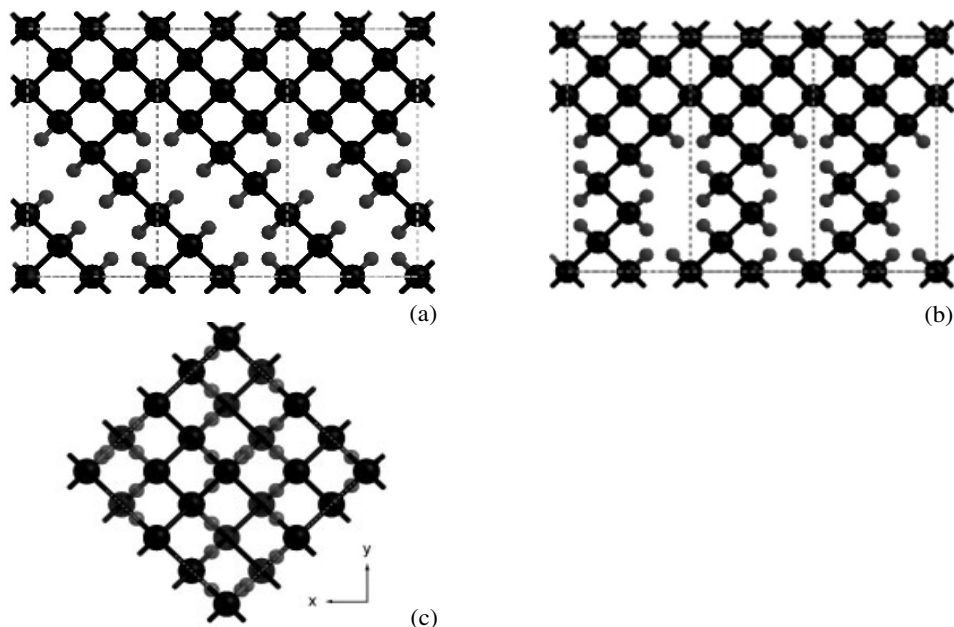


**Fig. 1** Imaginary part of the dielectric function of c-Si. The open circles represent the spectra calculated within the DFT-LDA and the solid circles correspond to experimental data of Ref. [10].

a scissors operator of 0.7 eV and a smearing width of 0.2 eV. These results are shown in Fig. 1 (open circles) next to experimental data (solid circles) obtained from Ref. [10].

## 2 Calculation details

Our starting point is a c-Si (110)-oriented supercell of 32 atoms (black dots in Fig. 2). Eight-atoms elliptic columns are removed in the [100] and [010] directions simulating the structure of birefringent PSi with 25% porosity, which is defined as the ratio of the number of removed Si atoms over the total number of Si atoms in the supercell. All the dangling bonds are saturated with 20 hydrogen atoms (dark gray dots), as done in Ref. [11]. The resulting supercell is shown in Figs. 2(a) and (b) for its [100] and [010] direction views, respectively. Figure 2(c) has a [001] sight of the supercell and indicates the crystallographic  $x$ - and  $y$ -axis.



**Fig. 2** (online colour at: [www.pss-a.com](http://www.pss-a.com)) (a) [100], (b) [010] and (c) [001] views of the supercell, indicated by the dashed lines, containing 24 silicon (black dots) and 20 hydrogen (dark gray dots) atoms.

The numerical calculation of PSi is carried out by using the norm-conserving non-local Troullier–Martins pseudopotential [12] within the DFT-LDA. In particular, CASTEP codes developed at Cambridge University are used [8, 9], in which the electronic wave functions are expanded in a plane-wave basis set with periodic boundary conditions. A full geometry optimisation is done within the quantum molecular dynamics method developed by Car and Parrinello [5], leading the atoms to their equilibrium positions and releasing the internal stress of the supercell. A  $60 \times 60 \times 90$  Fourier transform grid was used and due to the presence of hydrogen atoms the cutoff energy was set at 900 eV. Convergence parameters are the same as in Ref. [11].

Optical properties of the system are calculated by evaluating  $\epsilon_2$ , which is given by [13]

$$\epsilon_2 = \frac{2e^2\pi}{\Omega\epsilon_0} \sum_{k,v,c} \left| \langle \psi_k^c | \hat{u} \cdot \mathbf{r} | \psi_k^v \rangle \right|^2 \delta(E_k^c - E_k^v - E),$$

where  $\mathbf{u}$  is the vector defining the polarization of the incident electrical field. For the optical-property calculation we have used 82 electronic bands, a  $\mathbf{k}$ -point spacing of  $0.04 \text{ \AA}^{-1}$  in the first Brillouin zone, a self-consistence tolerance of  $10^{-4}$  eV and a smearing width of 0.6 eV. The number of electronic bands was chosen to insure certainty in the optical spectra until 10 eV.

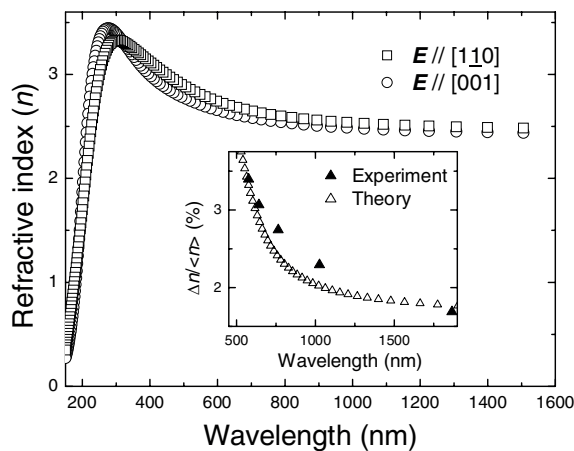
The real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of the dielectric function are linked together by a Kramers–Kronig transform, therefore, if the complex refractive index ( $N$ ) is written as  $N = n + ik$ , we have

$$\epsilon_1 = n^2 - k^2 \quad \text{and} \quad \epsilon_2 = 2nk.$$

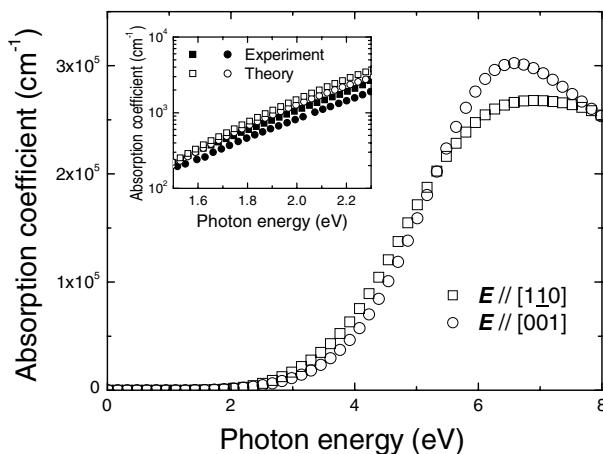
Furthermore, the absorption coefficient ( $\alpha$ ) is related to the imaginary part of the refractive index by  $\alpha = 2\omega k/c$ . Numerical results of the refractive index and the absorption coefficient are presented in the next section using the PSi model discussed above.

### 3 Results and discussion

For a [110] incident light, Fig. 3 shows the calculated refractive index ( $n$ ) of a birefringent PSi, drawn in Fig. 2, for polarizations along  $[1\bar{1}0]$  (open squares) and  $[001]$  (open circles) directions. Observe that for wavelengths around 200 nm both  $n_{[1\bar{1}0]}$  and  $n_{[001]}$  are practically the same and in the static limit  $n_{[1\bar{1}0]} = 2.45$  and  $n_{[001]} = 2.41$ , in comparison with respective measured values of 2.55 and 2.39 for a PSi sample with 40% porosity [3]. Notice that the difference  $\Delta n = n_{[1\bar{1}0]} - n_{[001]}$  is in general proportional to the porosity as discussed in Ref. [14]. In the inset of Fig. 3 the variation of  $\Delta n$  in units of  $\langle n \rangle = (n_{[1\bar{1}0]} + n_{[001]})/2$  (open triangles) is plotted as a function of the light wavelength, beside experimental data (solid triangles) from Ref. [15].



**Fig. 3** Refractive index for polarized light along  $[1\bar{1}0]$  (open squares) and  $[001]$  (open circles) directions. Inset: spectral dependence of  $\Delta n/\langle n \rangle$  for the theoretical (open triangles) and experimental (solid triangles) taken from Ref. [15].



**Fig. 4** Absorption coefficient ( $\alpha$ ) spectra for  $[1\bar{1}0]$  (open squares) and  $[001]$  (open circles) polarized lights. Inset: these spectra are compared with experimental data [14] for  $\alpha_{[1\bar{1}0]}$  (solid squares) and  $\alpha_{[001]}$  (solid circles).

Figure 4 illustrates the absorption spectra of the same system as in Fig. 3 for light polarized along  $[1\bar{1}0]$  (open squares) and along  $[001]$  (open circles) directions. These results are compared in the inset with experimental data [14], where solid squares and solid circles respectively represent the absorption spectra for  $[1\bar{1}0]$  and  $[001]$  polarized lights. Observe that the theoretical and experimental  $\alpha$  follow almost the same photon-energy dependence and  $\alpha_{[1\bar{1}0]} > \alpha_{[001]}$  for both, experimental and *ab initio* calculation results. We have also found a cross in the two polarization responses for many optical properties, for example such cross is located at 320.3 nm for the refractive index and at 5.3 eV for the absorption coefficient.

## 4 Conclusions

In this work, a DFT-LDA calculation of birefringent PSi has been performed including a full geometry optimisation to find the structural ground state. This *ab initio* approach, containing a scissors operator, seems to be a simple and appropriate way to quantify optical properties of PSi. In particular, for birefringent PSi the calculated refractive index and absorption coefficient reveal an in-plane optical anisotropy as observed experimentally. Moreover, these first-principle results have a good quantitative agreement with experimental data, even though the difference in the porosity and the periodical arrangement of pores supposed in the supercell model. This porosity difference is diminished by the fact that the simulated pores are much smaller than the experimental ones. Furthermore, the supercell limitation is negligible probably because the light wavelength is much larger than the size of pores. The numerical calculation has been done at zero temperature and some thermal effects are considered through the smearing width. Finally, this study can be extended to investigate surface adsorptions of atoms and molecules in birefringent PSi by saturating the dangling bonds with different particles. This investigation is currently being carried out.

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