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Hydrogen, oxygen and hydroxyl on porous silicon surface: A joint density-functional perturbation theory and infrared spectroscopy approach

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ABSTRACT

Based on the density functional perturbation theory (DFPT), infrared absorption spectra of porous silicon are calculated by using an ordered pore model, in which columns of silicon atoms are removed along the [001] direction and dangling bonds are initially saturated with hydrogen atoms. When these atoms on the pore surface are gradually replaced by oxygen ones, the ab-initio infrared absorption spectra reveal oxygen, hydroxyl, and coupled hydrogen–oxygen vibrational modes. In a parallel way, freestanding porous silicon samples were prepared by using electrochemical etching and they were further thermally oxidized in a dry oxygen ambient. Fourier transform infrared spectroscopy was used to investigate the surface modifications caused by oxygen adsorption. In particular, the predicted hydroxyl and oxygen bound to the silicon pore surface are confirmed. Finally, a global analysis of measured transmittance spectra has been performed by means of a combined DFPT and thin-film optics approach.

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1. Introduction

Porous silicon (PSi) is a nanostructured material with interesting properties, such as a huge surface area useful for sensor applications, a tunable refractive index and an efficient photo- and electroluminescence for photonic devices [1], in addition to its compatibility with the current microelectronics based on silicon since it is the second most abundant element in Earth's crust. The extensive surface area of PSi makes it chemically unstable and prone to oxidation in the atmosphere. For crystalline silicon (*c*-Si), the oxidation process has been widely studied, since SiO_2 is one of the best electrical insulators [2]. Such oxidation begins with the adsorption of oxygen atoms on the *c*-Si surface by forming Si – OH and Si – O – Si bonds [3]. In order to identify the nature of oxygen bonds on the nanostructured PSi surface under different oxidation conditions, we develop a microscopic model of PSi oxidation and calculate its effects on the infrared (IR) absorption spectra. The theoretical results are further compared with experimental measurements.

From a theoretical viewpoint, microscopic modeling of porous structures is a difficult endeavor. There are essentially two options: semi-empirical, such as empirical pseudopotentials and tight-binding based on atomic orbitals or Wannier's functions, and ab-initio approaches, through density functional theory with GW correction or quantum Monte Carlo calculations [4]. The former has the advantage of being simple and able to address complex porous structures. However, it is not suitable for studying oxidation since the presence of oxygen atoms distorts the structure and requires a questionable rescaling of the involved microscopic parameters, in contrast to the hydrogen passivation case. On the other hand, the ab-initio calculations are more accurate but allow the treatment of simple porous structures only. In this article we choose the second option, *i.e.*, modeling [5] the PSi structure by using the supercell technique within the density functional theory (DFT), through a double self-consistent procedure: one for the electronic density distribution and another for the geometrical optimization to determine the atomic positions of minimal energy. In addition, the calculation of IR absorption spectra requires the determination of atomic vibrational modes. The density functional perturbation theory (DFPT) [6] provides a natural way of inserting the dynamical-matrix calculation into the mentioned self-consistent procedures. On the other hand, we measure the IR transmittance spectra of oxidized free-standing PSi layers and compare them with the calculated spectra.

2. Ab-initio modeling

PSi possesses a complex morphology and its theoretical modeling has been carried out by using Si clusters [7], Si nanowires [8] and periodic porous structure [9]. In general, oxidation of the c-Si surface produces Si – O – Si and Si – OH bonds [10], which can be detected by means of IR spectroscopy. In order to analyze the IR modes of these bonds in the three mentioned structures, we first performed a comparative study of the IR absorption peaks employing supercells of $16.3 \times 16.3 \times 16.3$ Å^3 for the cluster case and $16.3 \times 16.3 \times 5.43$ Å^3 for nanowire and porous

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structures, where periodic boundary conditions are considered in the x, y and z directions. The supercell of the porous structure was built by joining on the x–y plane nine unit cells of eight Si atoms each.

The calculations were carried out within DFT through the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional and norm-conserving pseudopotentials. A full geometry optimization was performed using the Broyden–Fletcher–Goldfarb–Shanno minimization algorithm for the three structures, where a cutoff energy of 830 eV was used. The Monkhorst–Pack mesh of $1 \times 1 \times 1$ was used for the case of molecule and $1 \times 1 \times 3$ for the nanowire and porous structures. All the ab-initio calculations in this article were performed with the CASTEP codes developed at Cambridge University within Accelrys Materials Studio 7.0 [11] on ultrafine precision, where the convergence criteria are 5×10^{-6} eV/atom for the energy, 0.01 eV/Å for the force and 0.02 GPa for the stress. All the structure sketches in this article are obtained after the geometry optimization. Fig. 1(a) shows the smallest cluster structure to include Si – O – Si and Si – OH bonds. In the nanowire case, we started with a periodic silicon wire lying along the [001] direction with a 3×3 atoms square cross-section. Then, Si – O – Si and Si – OH bonds were added to the wire sidewall at opposite corners, while the surface dangling bonds were saturated with hydrogen, as illustrated in Fig. 1(b). On the other hand, the porous structure was constructed by digging empty columns along the [001] direction in an otherwise c-Si structure, *i.e.*, removing 40 Si atoms from a 72 atom supercell. Fig. 1(c) is a [001] view of the resulting structure. Once the geometrical optimization was performed, we further calculate the structural vibrational modes and the IR absorption spectra by means of the DFPT [6]. The obtained IR spectra are shown in Figs. 1(a′) for cluster, 1(b′) for nanowire and 1(c′) for porous structure.

Based on experimental IR absorption bands of Si – O – Si in siloxanes [12], Si – H in silanes [13], and Si – OH in silanols [12], Table 1 summarizes the corresponding calculated absorption peaks and bands obtained from Fig. 1(a′–c′), where the peak with the highest wavenumber within the band near 1000 cm^{-1} is associated to the Si – O – Si vibrational modes. Observe a systematic shift towards lower wavenumbers of the peaks corresponding to the nanowire and porous structures in comparison with the molecule absorption peaks. This fact could be related to the higher mass involved in these vibrational modes for these two structures.

Now we focus on the porous structure model to analyze the oxidation process in PSi by starting from a fully hydrogenated surface and gradually substituting hydrogen atoms by oxygen. Fig. 2(a)–(i) respectively illustrate the progressive addition of oxygen atoms from zero to eight, modeling different oxidation stages by forming Si – O – Si bonds in an originally 32 Si-atom supercell. The corresponding calculated IR transmittance spectra are shown in Fig. 2(a′–i′), obtained from the same calculation procedure used in Fig. 1.

Observe the absorption band at 2070–2200 cm^{-1}, which is related to the Si – H vibrational modes, and that its amplitude diminishes as the hydrogen content decreases. The 917–938 cm^{-1} band is associated to coupled hydrogen–oxygen vibrational modes on the PSi surface. In fact, this band disappears when the surface is fully passivated by oxygen atoms.

Another radical found in the oxidation process of c-Si is hydroxyl (OH) [12]. For its analysis, larger supercells are needed since the pores contained in a 32-Si-atom supercell, as in Fig. 2, are not big enough to fit several of these radicals without a significant interaction between them. Thus, we resort to a 72-Si-atom supercell, as shown in Fig. 1(c), to study the effects of OH on the IR response. Fig. 4 illustrates the studied structures passivated by (a′) hydrogen and OH, as well as (b′) hydrogen, OH and oxygen. The corresponding calculated IR transmittance spectra are shown in Fig. 4(a) and (b), respectively.

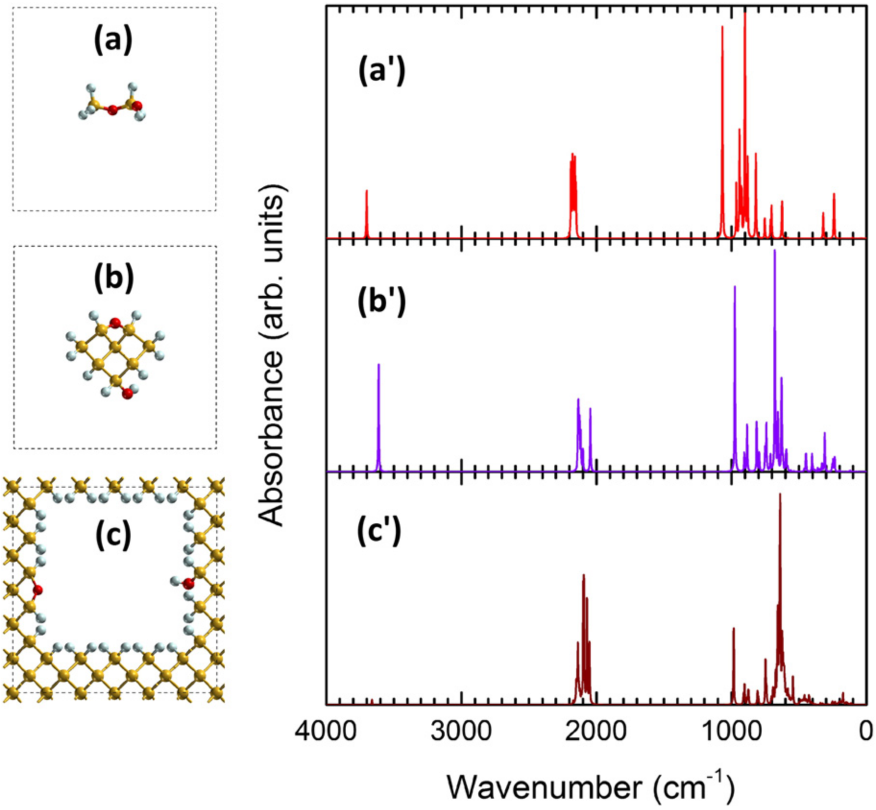

Fig. 1. Sketches of Si (yellow spheres), H (gray spheres) and O (red spheres) in (a) $H_6Si_2O_2$ molecule, (b) nanowire and (c) porous structure, where the dashed lines indicate the supercell boundaries of $16.3 \times 16.3 \times 16.3$ Å^3 for (a) and $16.3 \times 16.3 \times 5.43$ Å^3 for (b) and (c). The calculated IR absorbance spectra (a′–c′) are shown for (a–c), respectively.

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