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Optical vibrational modes of Ge nanowires: A computational approach

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ABSTRACT

Although Ge nanowires (GeNWs) have been extensively studied in the last decade the information about their vibrational modes is still scarce, their correct comprehension could hasten the development of new microelectronic technologies, therefore, in this work we aimed to study the vibrational properties, Raman and IR and spectrum of GeNWs using the first principles density functional perturbation theory. The nanowires are modelled in the [001] direction and all dangling bonds are passivated with H and Cl atoms. Results show that the vibrational modes can be classified in three frequency intervals, a low frequency one (between 0 and 300 cm^{-1}) of mainly Ge—Ge vibrations, and two of Ge—H bending and stretching vibrations (400–500 cm^{-1} and 2000 cm^{-1}, respectively). There is a shift of the highest optical modes of Ge—Ge vibrations compared to their bulk counterparts due to phonon confinement effects, however it is masked by some Ge—H bond bending modes as demonstrated by the IR and Raman responses. The Cl passivated case shows a larger number of modes at lower frequencies due to the higher mass of Cl compared to H, which in turn reduces the red shift of the highest optical modes frequencies. These results could be important for the characterization of GeNWs with different surface passivations.

1. Introduction

Currently technology is incorporated in almost every facet of human life, as the development of new electronic devices for communications, amusement, and work demands more efficient microelectronic components such as transistors, sensors, diodes switches among others. While the capacity of miniaturization of the technology increases, some fundamental physical limits of device fabrications are about to be reached, thus requiring the progress of new materials which would allow a better performance in lower sizes, the nanostructured materials are ideal candidates to this end specially the semiconductor nanowires. In recent years these low dimensional systems have gathered significant attention due to their potential applications, especially Germanium nanowires (GeNWs) could be used in microelectronics devices such as in infrared detectors [1], Schottky solar cells [2], solar cells [3], sensors [4] and lithium-ion batteries [5].

There are numerous experimental investigations of GeNWs, however there have been seldom theoretical investigations, mainly focused on the electronic properties such as the work of Arantes and Fazzio [6] which studies the electronic properties of [110, 111] oriented nanowires, or the work of Jing and coworkers [7] who analyze the effects of surface passivation with ethyl groups and anisotropy on the electronic properties of GeNWs, or the more recent studies that study the effects of halogens on the surface passivation [8], core-shell structures [9–11], and water induced electrical hysteresis [12]. The vibrational properties of GeNWs are much less studied, where are only a handful of works like the one of Peelaers [13] and collaborators which investigate the effects of doping on the vibrational properties, or previous works [14,15] which use semi-empirical potentials to study the Raman response and vibrational properties of GeNWs identifying the effects of the phonon confinement such as a red shift of the highest optical modes and an asymmetrical broadening of the Raman peaks, and there are none, (at the best of our knowledge) that uses first principles methods to model the Raman an IR response of these nanostructures, which would prove to be helpful in the development of new technologies of GeNWs since both spectroscopies provide non-destructive tools for the characterization of these materials and provide insight on the effect of the confinement on their vibrational properties.

Motivated by recent experimental results, in this work a study of the vibrational properties of GeNWs is developed using the first principles density functional perturbation theory, using the generalized gradient approximation and norm conserving pseudopotentials. The results show that the vibrational properties of these structures are heavily influenced by the surface configuration and confinement of the nanowires since a redshift and additional vibrational modes are generated around the highest optical mode frequency of bulk Ge.

2. Model and calculation scheme

The nanowires were modelled using the supercell technique [16,17] by removing atoms outside of a circumference on the [001] direction of an otherwise perfect Ge crystal, at this time this direction was chosen since the [110] direction has already been studied by other group [13], and the other most common growth direction of Ge nanowires the [111] is too computationally expensive whereas the [001] has a

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reasonable computational cost, and although scarcely reported it has been experimentally synthetized [18]. Contrary to previous works using semi empirical potentials [14,15] where the surface was left unpassivated the nanowire surface dangling bonds were passivated with H atoms which have been observed experimentally [19], also to avoid negative frequencies product of the highly reactive surfaces as will be seen in the results section, also a nanowire was passivated with Cl in order to observe the effects of surface terminations on the vibrational properties of the nanowires, however due to computational constraints only one diameter was studied with this surface passivation as depicted in Fig. 1c). To quantify the effects of the quantum confinement on the vibrational properties, three nanowire diameters were modelled: 1.1, 0.9 and 0.6 nm as observed in Fig. 1(a–d). Although the diameters seem too small compared with experimental results [20] recently ultrathin nanowires have been observed [21]. Additionally due to periodic boundary conditions the supercell was chosen so a space of at least 12 Å was left between the nanowires and their replicas.

All vibrational properties IR and Raman spectrum calculations were performed using the first principles density functional perturbation theory as implemented in the CASTEP code [22,23], with a Perdew Burke Ernzerhof functional [24] within the generalized gradient approximation and norm conserving pseudopotentials [25]. The converged cutoff was of 720 eV for an error of 0.01 eV in the energy calculation of crystalline Ge, and the Monkhorst-Pack [26] grid was of $1 \times 1 \times 7$ for the Brillouin zone sampling. The structures were optimized using the BFGS algorithm [27] where the convergence was achieved when the interatomic forces were less than 0.001 eV/Å, whereas the vibrational properties were converged to an error of 0.1 cm^{-1} with a difference of $+0.6$ cm^{-1} of the highest optical mode of germanium compared to the experimental value of 300.7 cm^{-1}.

The calculation parameters were tested on bulk crystalline Ge, the results can be observed in Fig. 2, where the theoretical calculations are compared with experimental results taken from [28,29]. It can be seen that there is an excellent agreement between the theoretical description

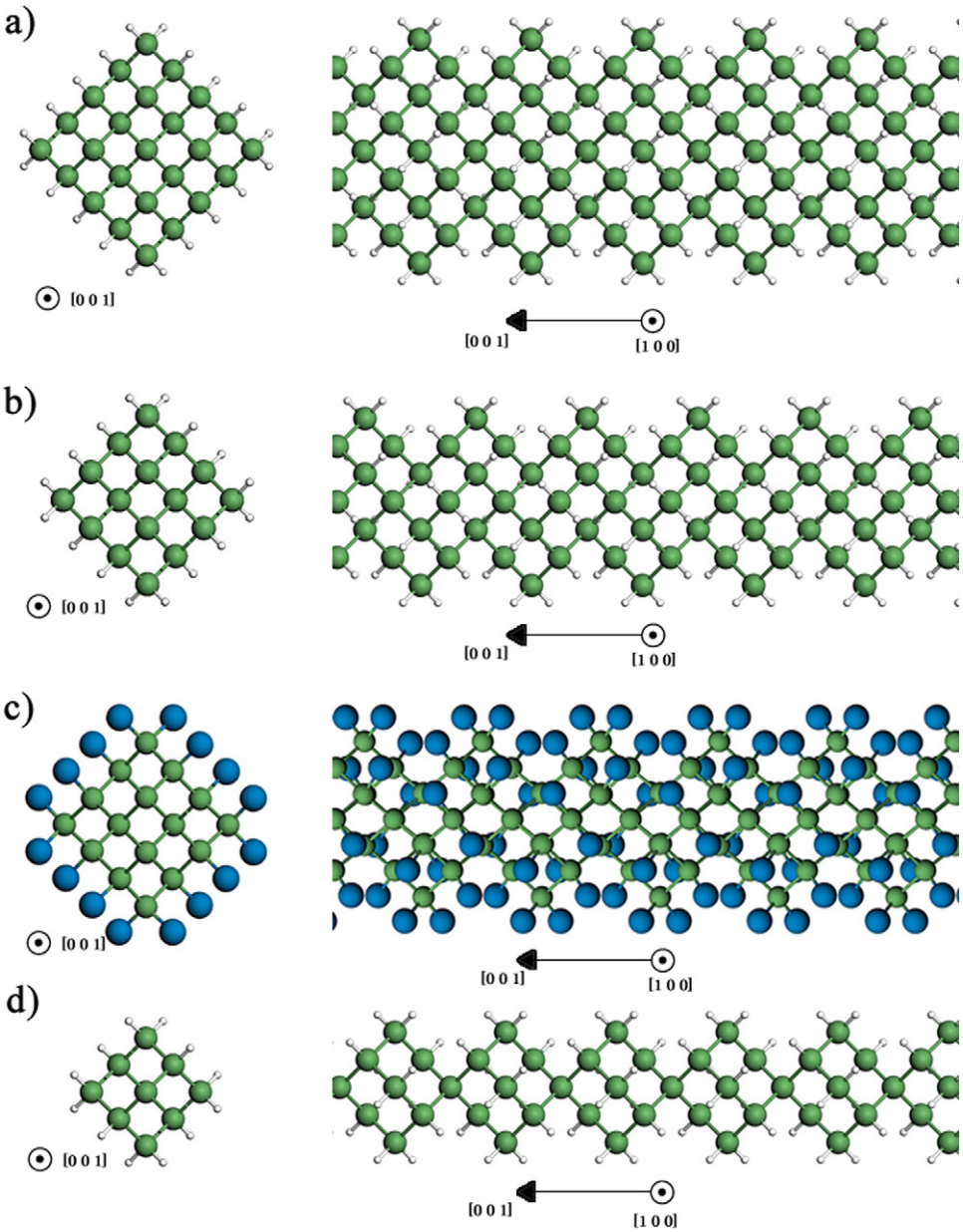

Fig. 1. Top and side view of GeNWs orientated on the [001] direction with diameters of: a) 1.1, b) 0.9 c) 0.9 Cl-passivated and d) 0.6 nm.