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Substrate polarization effect on the band gaps of one-dimensional semiconducting atomic wires

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ABSTRACT

The dielectric screening induced modulation of the electronic structure of model SiH_2 and GeH_2 one-dimensional atomic wires is investigated using graphene as a prototypical substrate. A combination of first-principles density functional theory and many-body perturbation theory within the GW approximation is employed to investigate how the substrate alters the electronic structure of the weakly bounds wires. The quasiparticle GW band gaps of the atomic wires are reduced by ~1 eV when supported by a graphene substrate. The band gap reduction is attributed to a change in the correlation energy of the frontier orbitals of the atomic wires due to the increased effective screening of the Coulomb interaction as a result of the polarization of the dielectric substrate. This work indicates that the band gaps of semiconducting nanowires composed of Si and Ge can be engineered via the interaction with the substrate in addition to conventional approaches such as adjusting size and crystal orientation.

1. Introduction

While a number of potential candidates for the miniaturization of active integrated circuit components have been explored over the last two decades, none have shown more promise than Si and Ge semiconducting nanowires [1]. Not only do such wires present a number of options for tuning their electronic properties, such as size, orientation, and composition [2–6], but the ability to experimentally fabricate small diameter (down to ~1 nm) wires and implement them in prototypical devices has already been achieved [7–12]. It has even been experimentally demonstrated that such nanowires can be used as the basic building blocks in more complicated circuit components [7,11]. Similar potential surrounds carbon-based nanoelectronics [13], but carbon-based devices lack the ease of integration and natural compatibility of Si and Ge with current semiconductor technology.

Whereas the effect of geometry, size, orientation, composition, and surface passivation on the electronic structure of Si and Ge nanowires has been exhaustively studied [2–4,14–21], the role played by the dielectric environment surrounding the wire, in particular the substrate upon which the wire is supported, has seen considerably less attention [21–24]. This is thought to be rather important though since both experiments and devices involving such wires will require supporting them on a substrate. Using a combination of tight-binding (TB) and a semi-analytical self-energy correction model, Niquet et al. found that a dielectric mismatch between the nanowires and their environment can substantially open up the band gap when the dielectric constant of the wire exceeds that of its environment [21]. On the other hand, when the dielectric constant of the environment was allowed to exceed that of the wire the self-energy corrections were reduced compared to the previous case. Although this trend is consistent with the understanding of other reports for the effect of the dielectric environment on the band gap [25–30], the results of Ref. [21] were found to be of limited quantitative accuracy in the regime where the dielectric constant of the wire is less than that of the environment. Rather, a more complete quantitative description of such trends requires the use of many-body perturbation theory (MBPT).

In this work, ultrathin, H-passivated, and [1 1 0]-oriented one-dimensional (1D) atomic wires (AWs) composed of Si and Ge are studied with and without a graphene substrate (dielectric) from first-principles. The small model atomic wires are chosen to reduce computational cost in the MBPT calculations. Graphene is chosen as a substrate for the following reasons: lack of surface dangling bonds, weak interaction with the fully passivated wire, and minimal number of unit cell atoms which again makes the MBPT

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calculations more tractable. The weak interaction between the wire and graphene is required such that the electronic structure modulation can be ascribed to the dielectric screening, and not any strong, chemical interaction. In any case, since our goal is to focus on this effect when the wire-substrate interaction is weak, graphene provides a good model. The band gaps in the free-standing configuration are found to be in good agreement with the previously reported trends for Si and Ge nanowires [2–4,15–20]. For the graphene-supported AWs, it is found that the substrate-induced polarization renormalizes the AW energy levels such that the band gap is suppressed by ~1.1 eV, in agreement with the previously reported trend [21]. The gap renormalization is ascribed to a reduction in the screened Coulomb interaction and is compared to other systems where substrate-induced band gap suppression has been reported [25–30].

2. Methods

The density functional theory (DFT) [31,32] and MBPT calculations were performed using the abinit code [33,34]. The electron–ion interaction is described using norm-conserving pseudopotentials generated using the Trouiller–Martins scheme [35]. The local density approximation (LDA) of Teter-Pade et al. [36] is employed to describe the exchange–correlation energy. Convergence testing for the DFT results for the free-standing wires revealed that an energy cutoff of 38.0 Ha, a $1 \times 1 \times 30$ k-point sampling, and at least 10 Å of vacuum separating periodic images is necessary to pin down the total energy to within 0.5 mHa. Identical parameters were employed for the DFT calculations where the wires are supported by a graphene substrate.

Here it is pointed out that rather than strain the AW to match the lattice of the substrate, the substrate has been strained such that the AW can simply be placed atop it. At its maximum, this compressive strain is approximately 11% and does not drastically alter the electronic structure of the substrate. For example, the Dirac cone present at the k-point in the band structure of graphene, and hence the semi-metallic nature of the substrate, is preserved (see Fig. 2(b) and (d)), consistent with the results of Ref. [37]. A similar methodology has been adopted in Ref. [38].

The composite system is generated by first straining the substrate cell to match the periodicity of the AW. It is reiterated here that even at a compressive strain of 11%, the fundamental electronic properties of the graphene substrate are preserved, i.e., no gap is opened up at the Dirac cone and graphene remains semi-metallic. A rectangular supercell is then built from the strained, hexagonal unit cell and the AW is combined with the substrate at a separation of $z = 3.25$ Å. In total, each composite system contains 42 atoms: 36 substrate (C) atoms and 6 AW (2 Si/Ge, 4 H) atoms. For the remainder of this work the composite systems which feature a graphene (G) substrate shall be referred to as SiH_2/G and GeH_2/G.

The geometry of the [1 1 0] free-standing AWs (Fig. 1(a)) [39] and bare graphene substrate was allowed to fully relax (with the lattice constant fixed) until the maximum force was less than 1×10^{-5} Ha/Bohr. The wire was then combined with a rectangular graphene supercell by placing it at a separation of $z = 3.25$ Å from the substrate (Fig. 1(b)). The wire-substrate separation z was chosen to reflect the weak, van der Waals interaction that is expected to exist between the dangling-bond-free graphene surface and the hydrogenated AWs. Fig. 1(c) shows the total relative energy as a function of z and as expected, shallow minima are observed in the range of 3.1 Å for SiH_2 and 3.4 Å for GeH_2, which is characteristic of a weak van der Waals interaction. Any further lattice mismatch or rotations with respect to the substrate have not been considered and are outside the scope of this work, although based on the results of Ref. [27], small changes in the wire/substrate orientation are not expected to dramatically influence the electronic structure. The length of the supercell b was chosen so that the separation between wires along the substrate surface was almost 18 Å. The supercell length also ensures that the Dirac cone associated with the k-point of the hexagonal unit cell of graphene is mapped to the Γ-point of the rectangular supercell (Fig. 2(b) and (d)).

The tolerance for the energy calculations was set at 1×10^{-6} Ha and the band structure calculations utilized a wavefunction squared residual tolerance of 1×10^{-12} Ha^2. This combination of convergence and cutoff parameters allowed the DFT predicted gaps for the free-standing and graphene supported AWs to be converged to within 10 meV or better. Note that the motivation behind examining a composite of an ultrathin [1 1 0] wire and a one atom thick substrate is to capture the role of the substrate in altering the electronic structure of the weakly bound wire while maintaining a model which is both computationally tractable and efficient. Similar simple models have been shown to provide converged results while also lending insight into the underlying physics [30].

Since it is well known that DFT drastically underestimates the band gap [40,41], quasiparticle corrections to the DFT electronic structure employing MBPT within the GW (G = Green's function, W = screened Coulomb potential) approximation [42] have been carried out. For all GW calculations the Coulomb cutoff scheme proposed by Ismail-Beigi [43] is employed and screening is calculated using the Hybertsen–Louie plasmon pole model [44]. To converge the quasiparticle gaps to within ~0.2 eV, it is necessary to employ a much more aggressive k-point sampling. A $1 \times 1 \times 78$ k-point grid was used for the free-standing wires and a $30 \times 4 \times 1$ grid for the wires on graphene. A similar, dense k-point sampling was adopted in Ref. [20,45]. A double-check of the convergence of the GW gaps with respect to the vacuum was also performed and it was found that increasing the vacuum by 5 Å only changes the GW gaps by ~30 meV or less for both the free-standing and substrate supported AWs. All the GW simulations employed an energy cutoff of 3 Ha and 300 bands in the dielectric and self-energy calculations.

3. Results

The geometry of the free-standing and substrate supported systems are featured in Fig. 1 and Table 1. The free-standing [1 1 0] AWs are composed of either Si or Ge and each atom of the wire has been passivated with two H atoms. The [1 1 0] direction has been selected since it has been found to be a favorable growth orientation in experiment [46,47]. Both the SiH_2 and the GeH_2 wires adopt a wide zigzag geometry (Fig. 1(a)) with almost identical bonding (Table 1). The geometry for the SiH_2 wire is in good agreement with the theoretical results of Ref. [14,48], as well as the experimental bonding parameters reported in Ref. [2] for Si nanowires of larger cross-sectional area.

The results for the electronic structure of both the free-standing and graphene supported AWs are featured in Fig. 2 and Table 2. Before analyzing the electronic structure, it is pointed out that a number of characteristics can be ascertained from the extensive literature on Si and Ge nanowires. For example, both [1 1 0] AWs are expected to be direct band gap semiconductors because of their small size and the fact that the bulk conduction band minimum will be mapped to the Γ-point for the [1 1 0] wire orientation [4,15,16,18]. The DFT/GW gaps and GW corrections of the AWs are also expected to be much larger than that of their bulk, or larger cross-sectional area nanowire, counterparts due to quantum confinement [2–4,15–20]. Furthermore, the uppermost valence band and lowest conduction band should show a relatively large dispersion due to the delocalized nature of these states along the axis of the wire [16,18].