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| Title | Modifying the band gap and optical properties of Germanium nanowires by surface termination |
| Authors | Legesse, Merid;Fagas, Gíorgos;Nolan, Michael |
| Publication date | 2016-11-15 |
| Original Citation | Legesse, M., Fagas, G. and Nolan, M. (2016) 'Modifying the band gap and optical properties of Germanium nanowires by surface termination', Applied Surface Science, 396, pp. 1155-1163. doi: 10.1016/j.apsusc.2016.11.104 |
| Type of publication | Article (peer-reviewed) |
| Link to publisher's version | 10.1016/j.apsusc.2016.11.104 |
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| Download date | 2025-02-07 03:17:23 |
| Item downloaded from | https://hdl.handle.net/10468/3299 |

Accepted Manuscript

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PII: S0169-4332(16)32472-2
DOI: <http://dx.doi.org/doi:10.1016/j.apsusc.2016.11.104>
Reference: APSUSC 34409

To appear in: *APSUSC*

Received date: 13-7-2016
Revised date: 7-11-2016
Accepted date: 14-11-2016



Please cite this article as: Merid Legesse, Giorgos Fagas, Michael Nolan, Modifying the band gap and optical properties of Germanium nanowires by surface termination, *Applied Surface Science* <http://dx.doi.org/10.1016/j.apsusc.2016.11.104>

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Modifying the band gap and optical properties of Germanium nanowires by surface termination

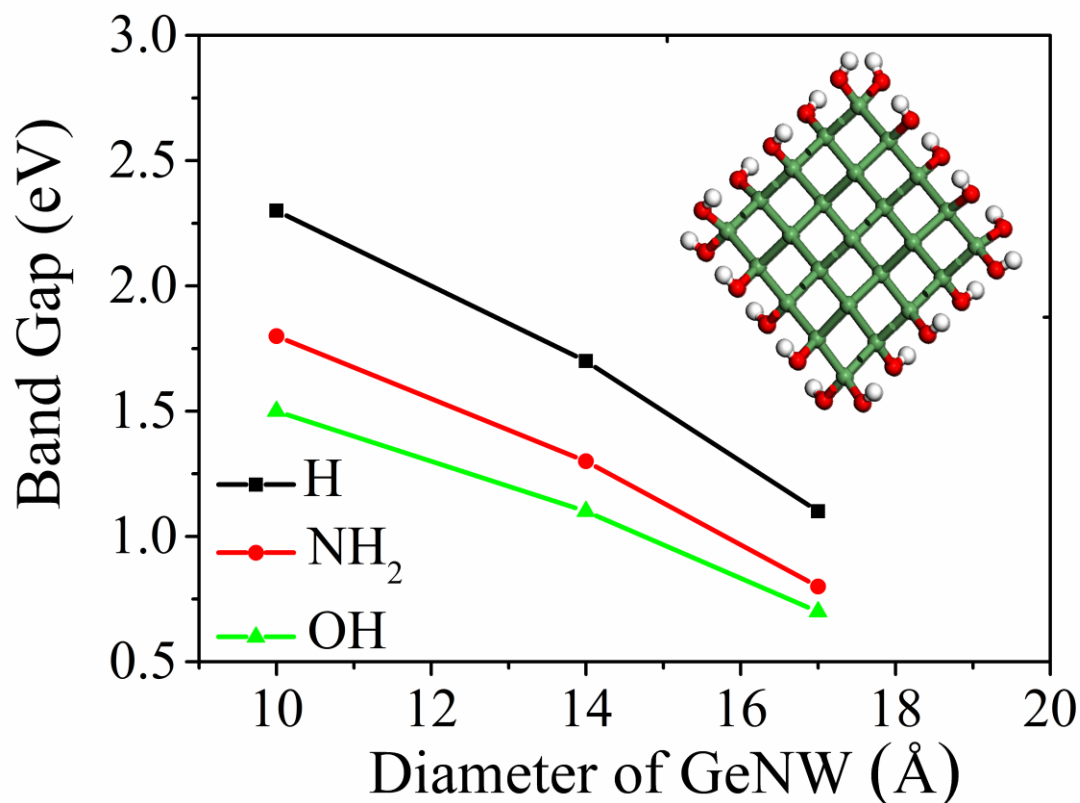
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Graphical abstract



Highlights

- (1) We have shown for a given surface termination (-H, -NH₂ or -OH) the band gap decreases for larger diameter nanowires, while for a given nanowire diameter, terminating with -OH can reduce the band gap by up to 1.1 eV.
- (2) The density of states shows the presence of N 2p and O 2p states above the original VB edge of the Ge nanowire which is the origin of the band gap reduction with these surface terminating groups.
- (3) Our results show for the first time how the nanowire diameter and surface termination shifts the absorption edge in the Ge nanowires to longer wavelengths.
- (4) The combination of nanowire diameter and surface chemistry can be effectively utilised to tune the band gaps and thus light absorption properties of small diameter Ge nanowires

Abstract

Semiconductor nanowires, based on silicon (Si) or germanium (Ge) are leading candidates for many ICT applications, including next generation transistors, optoelectronics, gas and biosensing and photovoltaics. Key to these applications is the possibility to tune the band gap by changing the diameter of the nanowire. Ge nanowires of different diameter have been studied with H termination, but, using ideas from chemistry, changing the surface terminating group can be used to modulate the band gap. In this paper we apply the generalized gradient approximation of density functional theory (GGA-DFT) and hybrid DFT to study the effect of diameter and surface termination using $-H$, $-NH_2$ and $-OH$ groups on the band gap of (001), (110) and (111) oriented germanium nanowires. We show that the surface terminating group allows both the magnitude and the nature of the band gap to be changed. We further show that the absorption edge shifts to longer wavelength with the $-NH_2$ and $-OH$ terminations compared to the $-H$ termination and we trace the origin of this effect to valence band modifications upon modifying the nanowire with $-NH_2$ or $-OH$. These results show that it is possible to tune the band gap of small diameter Ge nanowires over a range of ca. 1.1 eV by simple surface chemistry.

Keywords: Ge-nanowires, Bandgap, surface termination, DFT, adsorption

1 Introduction

Germanium (Ge) nanowires are of great interest because of their unique electronic and optical properties that result from their low dimensionality and the well-known quantum confinement

effect [1]. While silicon (Si) nanowires have tended to dominate in this area, interest in other materials such as germanium nanowires is growing. Germanium nanowires can be used in high quality field effect transistors (FET), sensor applications and in solar cells due to their higher electron and hole mobility and lower band gap compared to Si [2-7]. The intrinsic characteristics of Ge nanowires such as one dimensionality, high surface-to-volume ratio, and biocompatibility as well as the tuneable band gap make it a unique and special class of semiconductors [4].

From the perspective of modifying the band gap of nanowires, the focus for both Si [4, 8-11] and Ge nanowires [4, 8, 10, and 12] has been on exploiting the quantum confinement effect for H-terminated nanowires. Ref [11], investigated the electronic structure of SiNWs with different diameters and with H, Br, Cl, and I surface termination. Leu et al., concluded that the origin of band gap reduction comes from the surface species weakly interacting with the SiNW and they also claim that due to the formation of surface states associated with halogen binding, the band gap was found to increase in the order of $\text{Cl} < \text{Br} < \text{I}$. We have previously shown¹⁰, using density functional theory (DFT) calculations, that the band gap of small diameter Si nanowires can be tuned by up to 1 eV by changing the nature of the nanowire surface terminating group, from -H to -NH₂ or -OH. Since then, there have been a number of papers focussing on the effect of the surface terminating group in Si nanowires [4, 13, and 14]. In ref [13] studies found that the magnitude of the band gap reduction in -OH-terminated Si nanowires was surface-facet dependent and Ng et al. also investigated 50% substitution of H-termination on a (100) Si nanowire by -OH or -F atoms and predicted that the band gap to changes from direct to indirect. In Ref [15] it was shown that the band gap narrowing of SiNWs can be achieved by changing surface passivation from H to OH and correlated the reduction to the electronegativity of the passivating species.

By contrast, for Ge nanowires, the focus has been on the effect of quantum confinement in H-terminated nanowires. In refs [4, 16-19] the band gap of H terminated Ge nanowires was shown to increase with decreasing diameter, due to quantum confinement. The influence of functional groups such as halogens [8, 20, 21], SH [22] alkenes and alkyne [8, 22, 23] was studied. Ref [21] showed that for (100) GeNWs, the band gaps are reduced with F and Cl surface passivations as compared to that of H passivation. Refs [8, 22, and 23] studied experimentally the prevention of oxidation and hysteresis in electric current of GeNWs. In Ref [24] the effect of surface defects (which act as charge traps) on the electronic properties of (100) oriented OH-terminated GeNWs was investigated. The band gap and effective electron mass of the (100) OH-GeNW with surface trap state defects was calculated and the presence of charge traps decreased the band gap and modified the effective electron mass. Perhaps surprisingly, there have been no studies analogous to ref. [10] for Ge nanowires.

The purpose of this paper is therefore to present DFT studies of Ge nanowires for different diameter Ge nanowires (10, 14 and 17 Å) with three different surface terminating chemical groups, -H, -OH and -NH₂. We apply the generalised gradient approximation to DFT (GGA-DFT) and hybrid DFT (screened exchange HSE06 functional) to compute the band gaps. We examine how the diameter and surface termination determine the magnitude and nature of the nanowire band gap and study for first time the influence of these parameters on the absorption edge of the nanowires. We show that the band gap of Ge nanowires can be modified by up to 1.1 eV by changing the surface termination from -H to -OH, that this effect is most prominent for small diameter nanowires. The absorption edge is shifted to longer wavelength with the -OH and -NH₂ surface terminations. Finally, these results also show the ability of GGA-DFT to qualitatively

describe the change in the band gap of semiconductor nanowires with both diameter and surface termination.

2 Methods

All calculations were performed in a three dimensional periodic supercell model of the nanowires, using a plane wave basis set to describe the valence electron wavefunctions within the VASP.5.2 code [25, 26]. The Perdew Burke Ernzerhof (PBE) GGA approximation to the exchange correlation functional [27] was applied. To test the performance of this GGA-DFT functional, we also carried out hybrid DFT calculations for the smallest diameter modified nanowires using the screened exchange HSE06 [28] functional, with 25% exact exchange and a screening length of 0.2 Å⁻¹, at the PBE geometry. A plane wave cutoff energy of 400 eV is used and the core-valence interaction is described by the projector augmented wave (PAW) method [29], with a [Kr] core for Ge and a [He] core for O and N, while a 1 electron H potential is applied. The calculations are performed with cell dimensions normal to the wire axis chosen large enough to reduce interactions between neighbouring wires and induce quasi-1-dimensional periodicity along the wire axis. A full relaxation of the ionic positions with no symmetry constraints has been performed on all nanowire structures with the forces on each atom converged to less than 0.01 eV/Å. k-point sampling is performed with a (1 x 1 x 4) Monkhorst-Pack sampling grid. We examined the effect of the k-point sampling grid on the properties of the Ge nanowires and the results in the supporting Information show that the (1 x 1 x 4) grid is sufficiently converged. A Gaussian smearing of width 0.1 eV is applied to determine the band occupations and electronic density of states within the Methfessel-Paxton scheme.

We also investigate the optical properties of the Ge nanowires through the absorption coefficient, α (E), which is the fundamental quantity that characterises light absorption in the material. We compute the real and imaginary parts of the dielectric function, ϵ_1 and ϵ_2 , using the VASP post-processing routines of Furthmueller [30]. We then compute κ , the extinction coefficient, using

$$\kappa = \frac{1}{\sqrt{2}} \left(\sqrt{\epsilon_1} + \sqrt{\epsilon_1^2 + \epsilon_2^2} \right) \quad (1)$$

and the absorption coefficient, α (E,) is determined from

$$\alpha = \frac{2\kappa\pi}{\lambda} \quad (2)$$

Where λ is the free space wavelength of light.

3 Results

3.1 Structural Analysis of Ge Nanowires with Different Terminal Groups

For all GeNWs, the initial atomic structure is constructed from diamond structured bulk Ge, by selecting all the Ge atoms that fall within a virtual cage placed around bulk Ge, while Ge atoms falling outside this virtual cage are removed. The surface dangling bonds were terminated with different terminal groups at full coverage, that is -H, -NH₂ and -OH, to form Ge-H, Ge-N and Ge-O bonds, with starting bond lengths of 1.56 Å, 1.92 Å and 1.84 Å respectively. The passivation groups are stable and simple to deposit on the germanium nanowire surface and also allow us a further reduction of the band gaps of H-terminated GeNWs. From our calculation -OH termination is stable on GeNWs and these are hydroxyl groups rather than GeO_x species; we have not observed any GeO₂ on the surface. According to our knowledge there is some literature in -OH terminated Ge nanowires are studied [24] and GeO₂ formation on GeNWs surface is not reported.

The aim of the surface terminating groups is to maintain the original tetrahedral bond angles and to prevent surface reconstructions that would otherwise be present upon relaxation of a structure with dangling Ge present at the surface. We construct all of the GeNWs with a square cross-section. The square and rectangular cross-section Ge and Si nanowires are stable and well proved by experiment. And also the experimental results suggested that corner in the rectangular or square cross-section nanowires played important roles on the enhancement of the electrical performances of the electronic device [31]. Figure 1 (a – c) shows the atomic structure of the (001) oriented Ge nanowire with 17 Å diameter and terminated by the three different terminating groups, namely –H (H is indicated by gray spheres), –NH₂ (N is indicated by blue spheres) and –OH (O is indicated by red spheres). The supporting information (Figure S1, S2) shows the atomic structures of Ge nanowires with 10 Å and 14 Å diameter with these terminal groups.

We consider firstly the effect of surface termination on the Ge-Ge bond distances, which are shown in table 1, with a particular emphasis on the difference between Ge-Ge distances in the core region, which have no bonding to the surface terminating group, and the Ge-Ge distances on the surface, which directly bind to the surface terminating group. Taking firstly the –H terminated 17 Å diameter nanowires, the Ge-Ge distances in the core region are 2.48 Å and in the surface the Ge-Ge distances are 2.47 Å; there is thus little difference between the bonding geometry in the core and surface regions for H-terminated nanowires, irrespective of the nanowire diameter [31].

In the case of the –OH terminating group, the Ge-Ge distances in the core region and at the surface are quite different. The Ge-Ge distance of 2.52 Å at the surface of the largest diameter nanowire

is notably longer than the Ge-Ge distance of 2.47 Å in the core region, with a similar difference persisting for the other nanowire diameters. This is due to the strong Ge-O interaction which distorts the surface Ge-Ge bonds more than the Ge-H interaction. Finally, the effect of the NH₂ terminating group lies between the -H and -OH terminations, reducing the surface Ge-Ge distances to 2.46 Å with the core Ge-Ge distances being 2.48 Å. It is clear that the interaction of surface Ge with oxygen has a much stronger effect on the local atomic structure than the interaction of Ge with the other surface terminating groups. The trends in the Ge-Ge core and surface distances for the 10 and 14 Å nanowires are the same as the 17 Å diameter nanowires for each surface termination.

3.2 Electronic Properties of Surface Modified GeNWs

In this section, we describe the band gap of Ge nanowires with different diameters and terminal groups, calculated using GGA-PBE and HSE06 to examine the dual effects of nanowire diameter and surface termination on the nature and the magnitude of the band gap. Bulk Ge has an experimental, indirect band gap of 0.74 eV [32]. Theoretical calculations using several techniques have led to band gaps of Ge in the ranges of -0.02 to 0.35 eV for LDA and GGA [33, 34] and hybrid DFT calculations reported an indirect gap in the range 0.63–0.77 eV [35–37]. Thus, local DFT functionals underestimate the band gap, whereas band gaps from hybrid DFT are closer to the experimental results.

Figures 2 – 4 show the computed GGA-PBE band structures for the -H, -OH and -NH₂ terminated Ge nanowires of 10 Å (Fig. 2), 14 Å (Fig. 3) and 17 Å (Fig. 4) diameters. The valence-conduction band gaps (and their nature, either direct or indirect) are shown in table 2. For a given terminating group the quantum confinement effect is clearly observed, with the smallest diameter nanowire

having the largest band gap for all surface terminations. For $-H$ terminated nanowires the band gap reduces by 1.3 eV as the diameter changes from 10 Å to 17 Å. Our computed values for the H - terminated nanowires are consistent with those reported in reference [38].

The nature of the band gap for $-H$ terminated nanowires appears to show some dependence on the diameter. From GGA-PBE, we see that the smallest diameter H -terminated nanowire has a direct band gap, consistent with other theoretical studies [39, 12], however, the smallest indirect gap is only 0.15 eV larger, and as the nanowire diameter increases, the band gap changes to an indirect gap, similar to bulk Ge.

Examining the band structures of $-NH_2$ and $-OH$ terminated GeNWs, we see that these surface terminations also show the quantum confinement effect, with a band gap reduction of 0.8 eV for the $-OH$ terminated nanowires and 1 eV for the $-NH_2$ terminated nanowires on going from the smallest to the largest diameter nanowire. We note that the magnitude of the band gap change as the nanowire diameter increases is smallest for the $-OH$ terminated nanowires and largest for the $-H$ terminated nanowires.

In terms of the nature of the band gap, we find an indirect band gap for 10 Å nanowires terminated with NH_2 (the smallest indirect gap is 0.2 eV larger) and a direct band gap for the 14 Å and 17 Å nanowires. A direct band gap is found for all $-OH$ terminated nanowires. Thus, it is possible to modify the magnitude and the nature of the band gap by chemistry that changes the surface termination of the nanowire.

We now compare the effect of the surface termination on the band gap of nanowires of a fixed diameter. Figure 5 (a) plots the band gap against nanowire diameter for the $-H$, $-OH$ and $-NH_2$

terminating groups from GGA-PBE and figure 5 (b) shows the band gap against nanowire diameter for 10 Å nanowires with the three surface terminations from HSE06, comparing with the GGA-PBE values.

Figure 6 shows the band structure for the 10 Å diameter nanowire with the –H, –OH and –NH₂ surface terminations from HSE06 to compare with the GGA-PBE results GGA-PBE. The first observation is that for a given nanowire diameter, the –OH surface termination strongly reduces the magnitude of the band gap, with a reduction of 1.1 eV over the –H terminated 10 Å diameter nanowire. While the magnitude of this difference reduces as the nanowire diameter increases, it still persists for the 17 Å diameter nanowire and this surface termination always reduces the band gap compared to –H termination.

We attribute the fall off in the magnitude of the band gap reduction with increased nanowire diameter to the surface to volume ratio in the nanowires – the smallest diameter nanowire has the largest surface to volume ratio and the interaction of the surface Ge atoms with oxygen will show the largest perturbation of the band edges and thus the largest change to the band gap. As the wire diameter increases the surface to volume ratio decreases and the effect of the Ge-O bonding reduces so that the change to the band gap is smaller. The –NH₂ terminating group reduces the band gap by 0.8 eV for the 10 Å diameter nanowire indicating that the effect of this surface termination is weaker than the –OH termination.

Similarly to –OH termination, the difference between the band gaps for –NH₂ and –H terminated nanowires reduces as the nanowire diameter increases, with a similar origin in terms of surface to volume ratio as a function of nanowire diameter. These results do show clearly that the band gap

of Ge nanowires can be modified over a wide range (up to 1.1 eV) by suitable surface termination chemistry.

Lastly, we compare the HSE06 calculation of the band gaps for the different terminal groups in 10 Å diameter Ge nanowires to the GGA-PBE band gaps. While the GGA-PBE band gaps are clearly underestimated compared to hybrid DFT, figure 5 (b), the change in the band gap when -H is substituted for -OH or -NH₂ is the same, with a significant change of 1 eV in the magnitude of the band gap with -OH termination from both DFT approaches. The nature of the band gap for the -OH and -NH₂ terminated nanowire is also unchanged when comparing GGA-PBE and HSE06. Although the 10 Å diameter H-terminated NW shows an indirect band gap with HSE06 and direct with GGA, there is a rather small energy difference between the direct and indirect band gaps, which may be sensitive to the DFT method employed. However, given that hybrid DFT generally provides accurate band gaps for semiconductors, we can be confident that for determining trends in the value of band gap modification of Ge nanowires with different surface terminating groups and wire diameter, GGA-PBE would be entirely suitable.

To compare any effects arising from the orientation of the Ge nanowires, the computed band gap for the different terminating group of 10 Å diameter Ge nanowires along the [100], [110], and [111] orientations is shown in figure 7. We see that the magnitude of the band gap of GeNWs depend on the nanowire orientation. The magnitude of band gap of hydrogen terminated germanium nanowires with orientation follows: (100) > (111) > (110) and this is consistent with reference [12]. In terms of the surface terminating groups, the effect of the nanowire orientation is similar for -OH and -NH₂ surface terminations. However, the key finding is that there is not effect of the nanowire orientation on the band gap change with different surface terminating groups,

which has not been discussed in the literature. As it has been pointed out in reference [39], orientation effects are related to the different geometrical structure of the wires in the (100), (111), and (110) orientations. Indeed the [100], [111] wires appear as a collection of small clusters connected along the axis, while the (110) wires resemble a linear chain. So we expect that quantum confinement effects are much bigger in the (100) and (111) wires than (110). But band gap modulation via surface terminating groups is independent of the nanowire orientation.

To understand in more detail the effect of the surface terminating group on the band gap of Ge nanowires we examine the electronic density of states projected (PDOS) onto the Ge 4p, H 1s, O 2p and N 2p electronic states. The PDOS plot for the Ge nanowires with -H, -NH₂ and -OH termination are shown in figure 7 (a), (c) and (d) for 10, 14 and 17 Å diameter nanowires. The PDOS shows that the valence and conduction band edges of H-terminated Ge nanowires are derived from Ge states, with no significant contribution of the H 1s states to either the valence or conduction bands.

For the -OH and -NH₂ surface terminations the valence band edge is shifted upwards with the largest shift being found for the -OH termination. This results in the reduction of the valence-conduction band energy gap with the largest reduction for -OH termination and the band gap for -NH₂ termination lying between the band gaps of the -OH and -H terminated nanowires. We also observe that in the VB region, the offset of the highest energy O 2p and N 2p states from the Ge 4p states decreases as the nanowire diameter increases, which is consistent with the smaller change in the band gap with these surface terminations compared to -H termination as the diameter of the nanowire increases.

Comparing the PDOS from GGA-PBE with HSE06 for the 10 Å diameter nanowires, figure 8 (a) and figure 8 (b), we see that the same upwards shift of the valence band edge is found from both DFT approaches, giving further confidence in using GGA-PBE to examine the changes in the band gap of semiconductor nanowires with surface modification.

3.3 Optical properties of GeNWs with different terminal groups

Figure 9 (a) – (c) shows the computed absorption coefficient plotted against energy for the –H, –NH₂ and –OH surface terminating groups for the 10, 14 and 17 Å Ge nanowires. The supporting information also shows the absorption coefficient versus energy for different diameter nanowires with a given surface termination.

These plots show that the position of the absorption edge is red shifted to lower energy (longer wavelength) as the surface terminating group changes from –H to –NH₂ to –OH, in a fixed diameter nanowire, consistent with the change in the band gap for these surface terminations. This behavior was also observed for modified SiNWs [41, 42], but has not been described for Ge nanowires. We find this result at all nanowire diameters and we also see that the shift in the absorption edge with –OH and –NH₂ termination is smaller for the largest diameter nanowire compared to the smallest diameter nanowire, which is also consistent with the results for the computed band gaps. Thus, the surface environment has a significant role in determining the optical properties of the nanowires.

4 Conclusions

In summary, we have shown from for a given surface termination (–H, –NH₂ or –OH) the band gap decreases for larger diameter nanowires with (001) orientation, while for a given nanowire

diameter, terminating with –OH can reduce the band gap by up to 1.1 eV. This surface terminating effect weakens for larger diameter nanowires as a result of the smaller surface to volume ratio, but it is independent of the nanowire orientation. The density of states shows the presence of N 2p and O 2p states above the original VB edge of the Ge nanowire which is the origin of the band gap reduction with these surface terminating groups. We have also shown how the surface termination shifts the absorption edge in the Ge nanowires to longer wavelengths. Thus, the combination of nanowire diameter and surface chemistry can be effectively utilised to tune the band gaps and thus light absorption properties of small diameter Ge nanowires

Acknowledgements

We acknowledge support from The European Commission, through the 7th Framework ICT-FET-Proactive program, Project: SiNAPS (contract no 257856). MN acknowledges the Science Foundation Ireland (SFI) Starting Investigator Research Grant Program, project EMOIN” grant number SFI 09/SIRG/I1620. We also acknowledge computing resources provided by SFI to the Tyndall National Institute and by the SFI and Higher Education Authority Funded Irish Centre for High End Computing.

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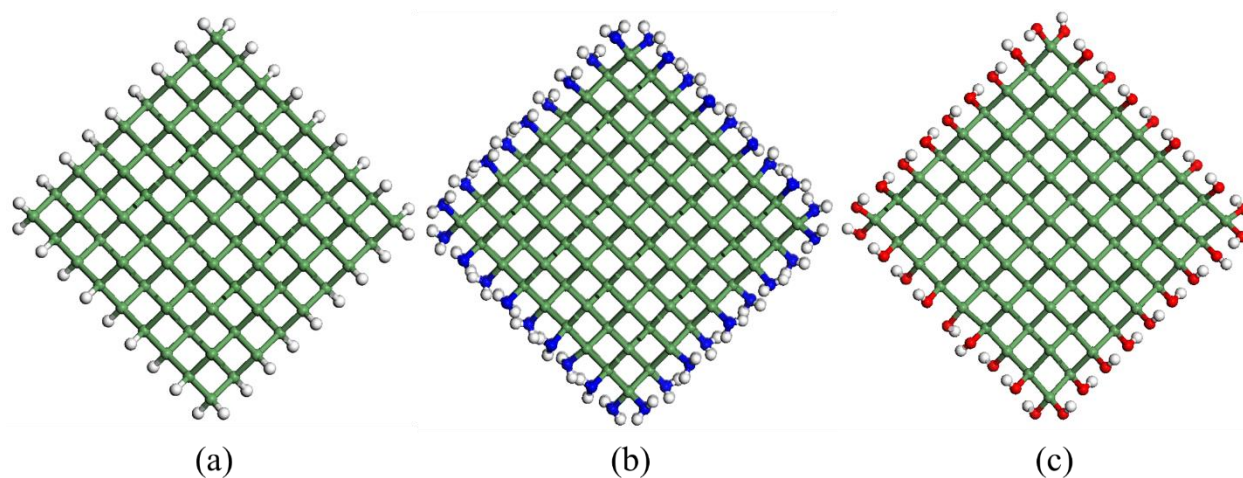


Figure 1: Atomic structure of 17 Å Germanium nanowire oriented along the [100] direction with different surface terminating groups: (a) -H (white gray = H), (b) -NH₂ (deep blue = N) and (c) -OH (red = Oxygen).

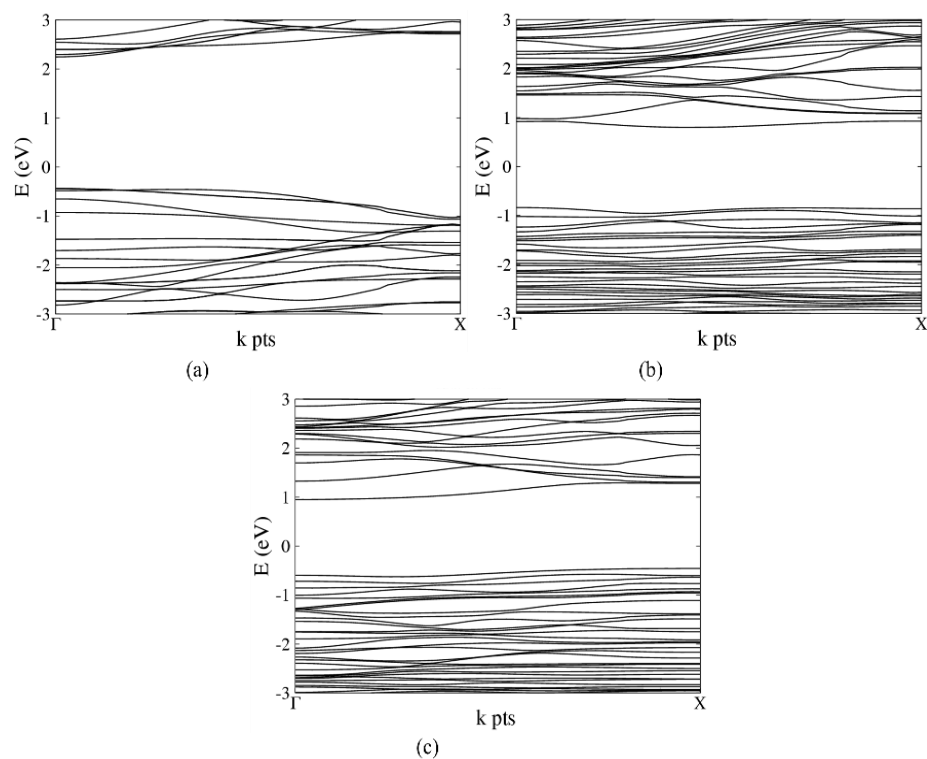


Figure 2: One-dimensional GGA-PBE band structure for [100]-oriented Germanium nanowires with -H termination. The Germanium nanowire diameters are 10 Å in part (a), 14 Å in part (b) and 17 Å in part (c).

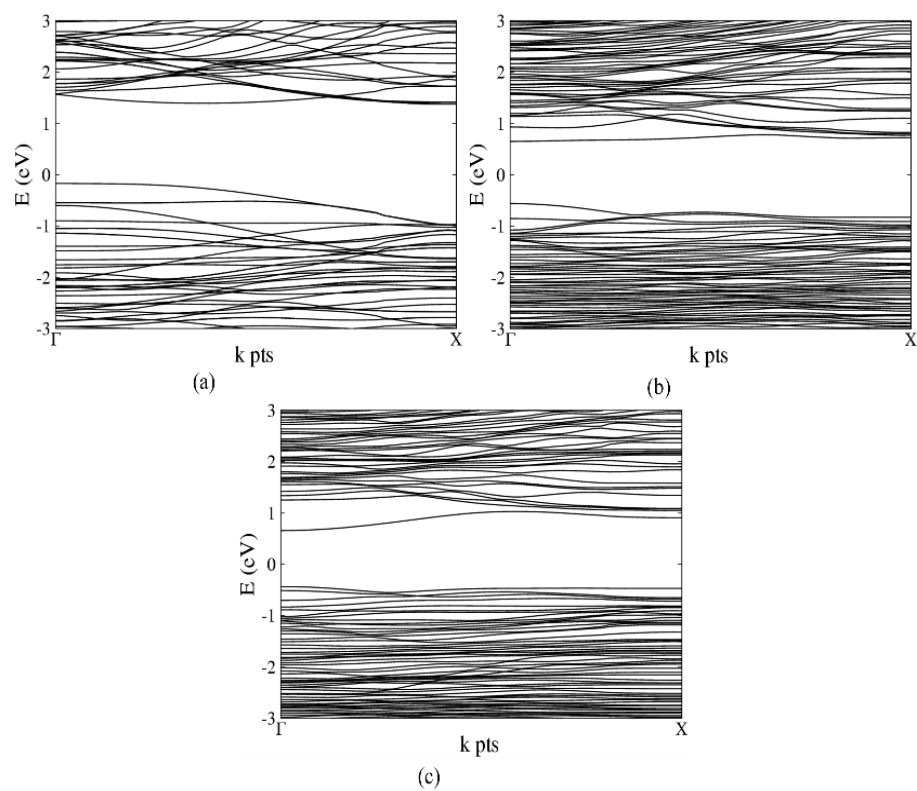


Figure 3: One-dimensional GGA-PBE band structure for [100]-oriented Germanium nanowires with $-\text{NH}_2$ termination. The Germanium nanowire diameters are 10 Å in part (a), 14 Å in part (b) and 17 Å in part (c).

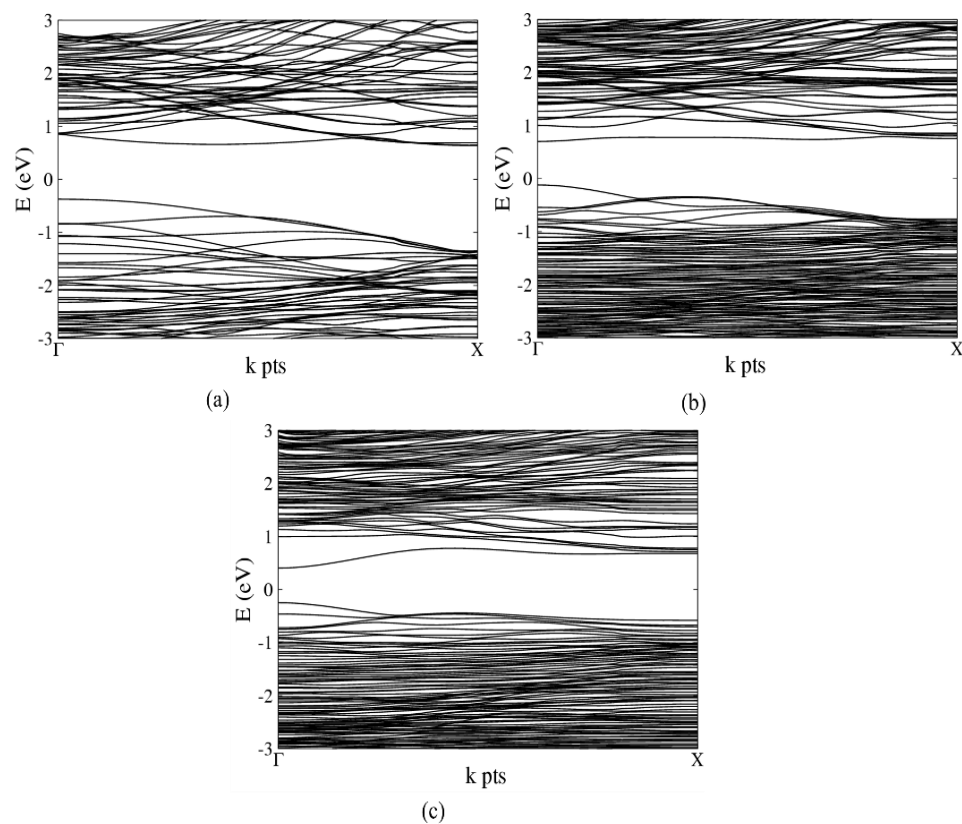


Figure 3: One-dimensional GGA-PBE band structure for [100]-oriented Germanium nanowires with $-\text{NH}_2$ termination. The Germanium nanowire diameters are 10 Å in part (a), 14 Å in part (b) and 17 Å in part (c).

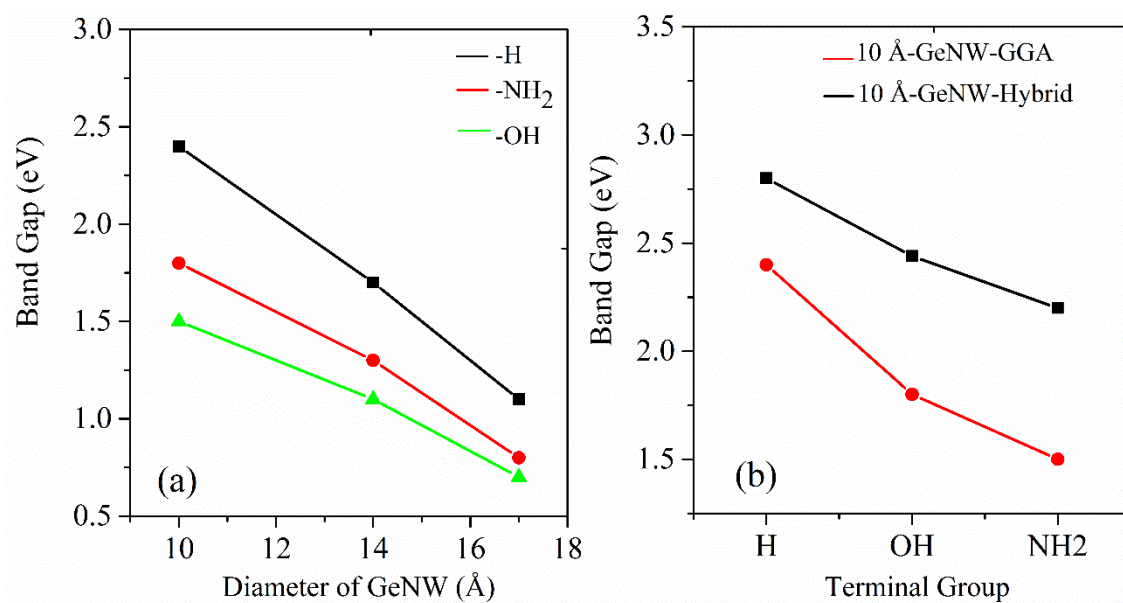


Figure 5: Computed band gap as a function of the diameter for (100) oriented Germanium nanowires for the surface terminations studied in this paper. (a) GGA-PBE results. (b) GGA-PBE and HSE06 results for 10 Å diameter nanowires.

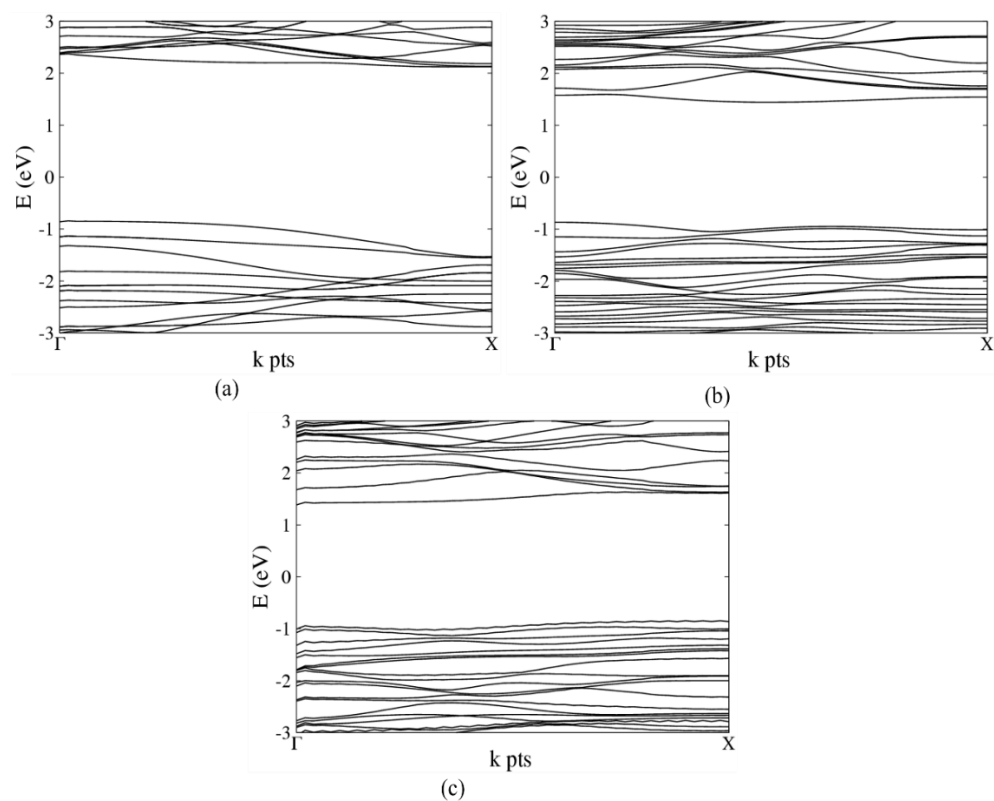


Figure 6: One-dimensional band structure for 10 Å diameter Germanium wires along [100] with different surface terminations (a) -H (b) -NH_2 and (c) -OH . Result from hybrid DFT (HSE06) calculation.

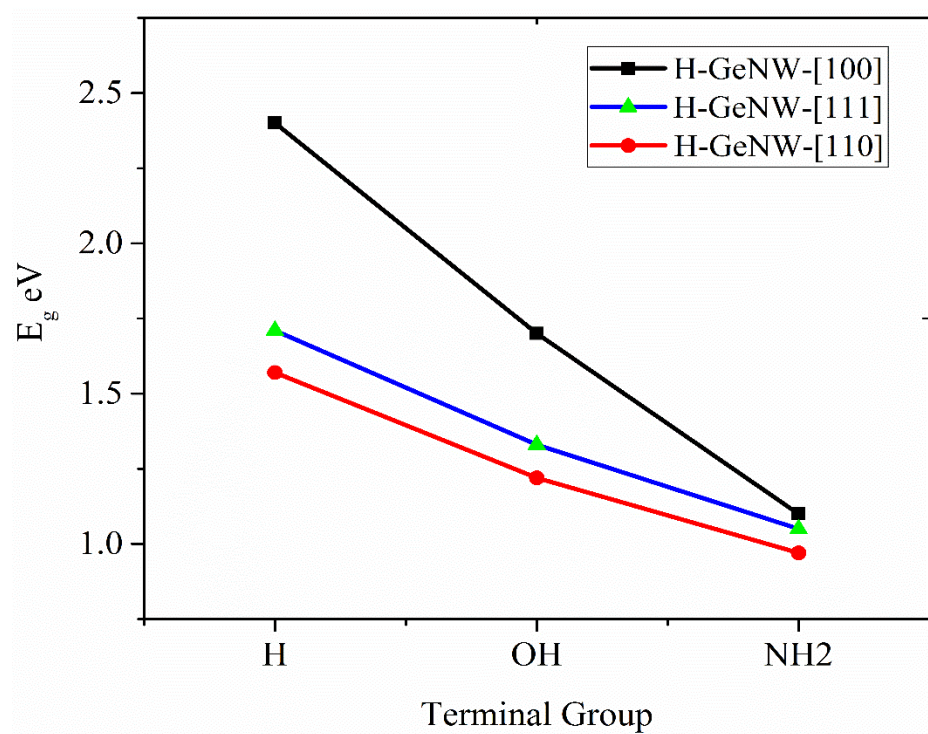


Figure 7: Computed band gap as a function of the Terminal group for (100) (110) and (111) oriented Germanium nanowires of 10 Å nm diameter

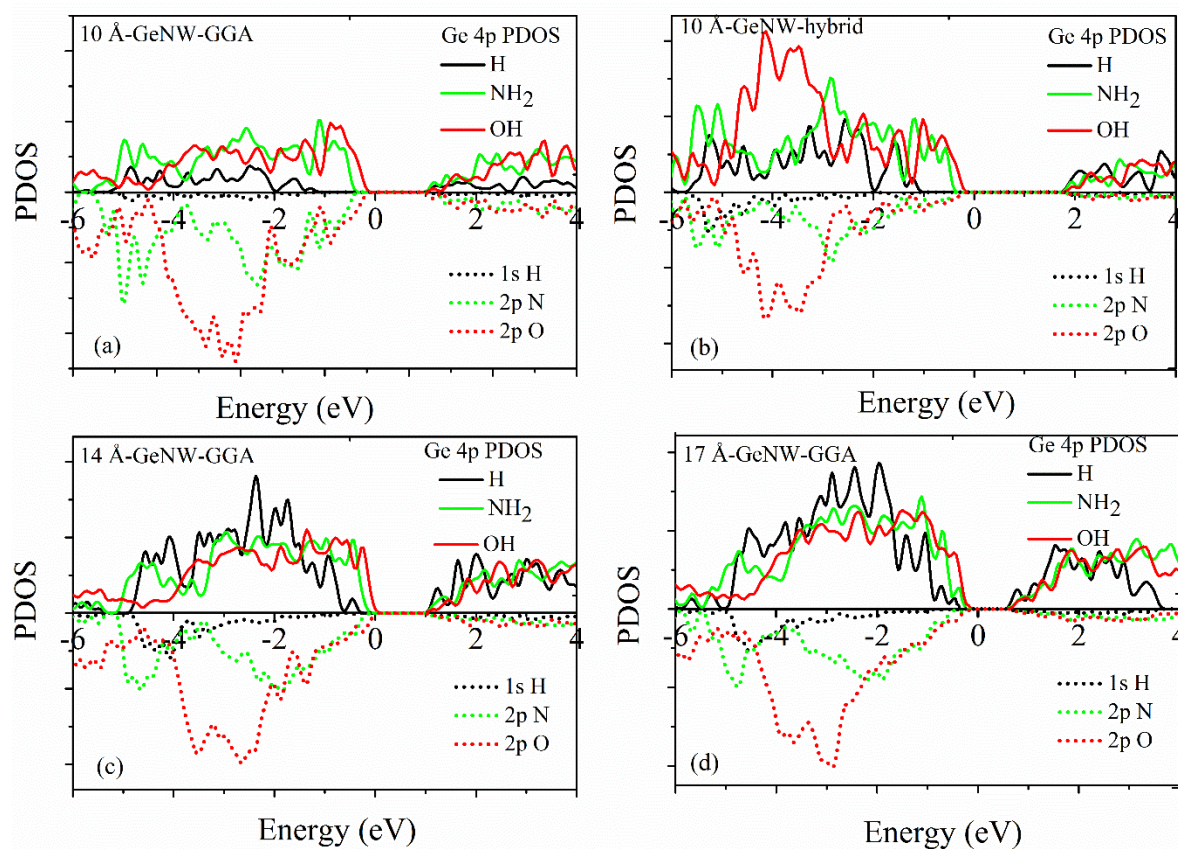


Figure 8: Projected electrons density of states (PDOS) for (a) 10 Å (from GGA-PBE), (b) 10 Å (from HSE06), (c) 14 Å (from GGA-PBE) and (d) 17 Å (from GGA-PBE) diameter Ge (100) nanowires, with different surface terminations (-H, -OH, -NH₂) decomposed into orbital contributions of Ge 4p, H 1s, O 2p, and N 2p as indicated. Energies are referenced with respect to the conduction band edge.

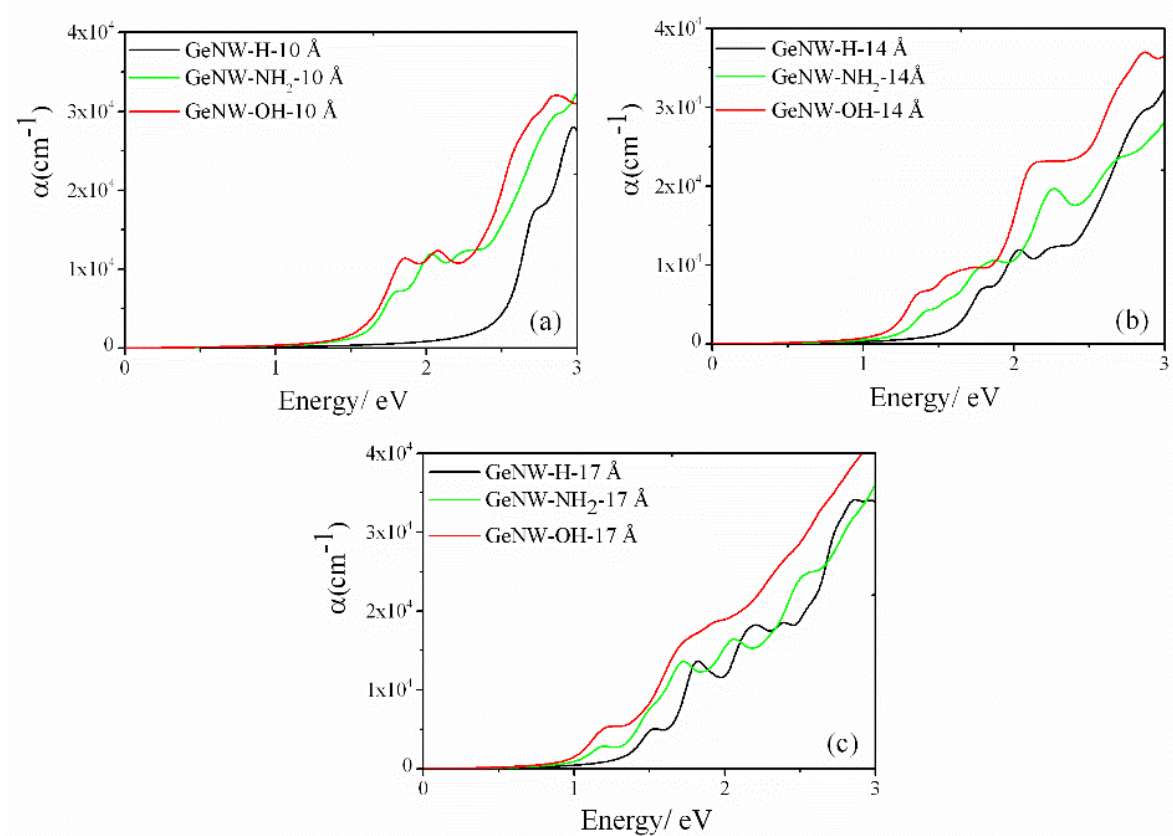


Figure 9: Calculated absorption coefficient plotted against energy for (100)-oriented Ge nanowires from GGA-PBE. (a) 10 Å diameter with the three surface terminating groups, (b) 14 Å diameter with the three surface terminating groups and (c) 17 Å diameter with the three surface terminating groups.

Table 1: Relaxed Ge-Ge bond lengths, in Å, in the core and surface regions of the Ge nanowires.

| | Diameter (Å) | Bond length (Å) | Diameter (Å) | Bond length (Å) | Diameter (Å) | Bond length (Å) |
|---------------------------|---------------------|-------------------------------|---------------------|-------------------------------|---------------------|------------------------|
| Hydrogen (-H) | | | | | | |
| Ge-Ge (surface) | 10 | 2.46 | 14 | 2.46 | 17 | 2.47 |
| Ge-Ge (core) | | 2.47 | | 2.48 | | 2.48 |
| Ge-H | | 1.52 | | 1.53 | | 1.53 |
| Amino (-NH ₂) | | | | | | |
| Ge-Ge (surface) | 10 | 2.47 | 14 | 2.46 | 17 | 2.46 |
| Ge-Ge (core) | | 2.49 | | 2.49 | | 2.48 |
| Ge-N | | 1.91 | | 1.92 | | 1.92 |
| Hydroxyl (-OH) | | | | | | |
| Ge-Ge (surface) | 10 | 2.51 | 14 | 2.52 | 17 | 2.52 |
| Ge-Ge (Core) | | 2.48 | | 2.48 | | 2.48 |
| Ge-N | | 1.84 | | 1.85 | | 1.86 |

Table: 2 The magnitude and nature (direct or indirect) of the band gap of (100) oriented Ge nanowires for different wire diameter and different terminal groups.

| Diameter of GeNW (Å) | Eg (eV) GGA-DFT | Eg (eV) Hybrid-DFT | Nature of band gap |
|--------------------------------|-----------------|--------------------|--------------------|
| Hydrogen (-H) | | | |
| 10 | 2.45 | 2.80 (Indirect) | Direct |
| 14 | 1.70 | | Indirect |
| 17 | 1.11 | | Indirect |
| Amino (-NH₂) | | | |
| 10 | 1.80 | 2.45 (Indirect) | Indirect |
| 14 | 1.30 | | Direct |
| 17 | 0.80 | | Direct |
| Hydroxyl (-OH) | | | |
| 10 | 1.50 | 2.20 (Direct) | Direct |
| 14 | 1.10 | | Direct |
| 17 | 0.70 | | Direct |