Orientation dependence of electronic properties of antimony selenide nanowires

Rajasekarakumar Vadapoo1,2,*, Sridevi Krishnan1, Hulusi Yilmaz3 and Carlos Marin4

1 Division of Physics, School of Advanced Sciences, Vellore Institute of Technology, Chennai, 600 127, Tamil Nadu, India
2 Department of Physics, Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, PR 00931, United States of America
3 Dept. of General Education, American University of Phnom Penh, Phnom Penh, Cambodia
4 Department of Engineering Sciences & Materials, University of Puerto Rico - Mayaguez, , Mayaguez, PR 00680, United States of America

* Author to whom any correspondence should be addressed.

E-mail: abraja.v@gmail.com

Keywords: Orientation, electronic, Antimony Selenide, Sb2Se3, nanowires, topological

Abstract

We present a comprehensive DFT study of size-dependent atomic and electronic properties of antimony selenide (Sb2Se3) nanowires in three main crystallographic directions. Our calculations show a significant enhancement in the band gap of wires oriented in [100] and [010] directions due to confinement effects, however the band gap of [001] oriented wires is reduced with respect to bulk. We attribute this anomaly in band gap reduction to the surface reconstructions in these nanostructures. These surface reconstructions are similar to the polyhedral distortions observed in bulk Sb2Se3 under high pressure leading to the insulator-metal transition related to the topological insulating states and then at lower temperature (8K) to superconductivity.

1. Introduction

Antimony Selenide (Sb2Se3) is studied for a myriad of applications owing to its very anisotropic nature. Its unique orthorhombic structure consists of strongly bound one dimensional (1-D) infinite ribbons of [Asb10] units along the [001] direction, which are weakly coordinated between each other [1]. In recent years these structures have been extensively studied for numerous applications including solar cells [2–5], Li-ion batteries [6–8], efficient photodetectors [9–12], flexible electronics [13], thermoelectric applications [14] and efficient two-dimensional antibacterial nanoagents [15]. Besides they are also synthesized as 1D/2D mixed-dimensional heterostructures for functional electronic and optoelectronic devices [16]. Very recently, it was demonstrated that the bulk Sb2Se3 under high pressure becomes a topological insulator [17–21] and further undergoes insulator to metal to superconducting transitions [20].

Nanostructures of Sb2Se3 have been synthesized using various growth methods. Of these nanostructures reported so far, the smallest sizes are 4 nm nanorods [22] & 20 nm nanowires [23] by chemical & physical methods respectively. According to the effective mass approximation (EMA) ([24]), at these sizes, the band gap is expected to be near the bulk value with no significant change. However, a wide range of band gaps from 1.13 eV to 1.49 eV have been reported for these nanostructures [25] with a theoretical study reporting 1.66 eV for a stand alone single ribbon [26].

Most of the nanostructures of Sb2Se3 have been grown by chemical methods and yields [001] oriented structures. Controlling the thermodynamical conditions we were able to grow [010] oriented Sb2Se3 nanostructures employing the VLS growth method [23]. Considering the crystallographic orientations of synthesized nanostructures and anisotropic nature of the crystal structure of bulk Sb2Se3, we have studied the influence of orientation and size on the electronic behaviour of these nanostructures. Here, we explore Sb2Se3 nanowires oriented in the three main crystallographic orientations of the bulk crystal ([100], [010] and [001]) (figure 1).
2. Methods

Calculations were performed using the Vienna ab initio simulation package (VASP) [27, 28] with generalized gradient approximation [29] and projector augmented wave potentials ([30, 31]). We used a kinetic energy cut-off of 300 eV and a gamma centered k-point grid of $1 \times 1 \times 18$. Geometry optimizations were carried out until the force acting on each atom falls below 0.01 eV/Å. Since the surfaces of these nanostructures have dangling bonds, we also studied the structures with hydrogen saturation (Sb- H1.25 & Se- H0.75) to compensate the dangling bonds. A fine grid of up-to 40 K-points were used for band structure calculations. We studied three different sizes in each of the main crystallographic orientations ([100], [010] & [001]) of the nanostructures.

We would like to point out that DFT calculations with GW corrections would lead to more accurate bandgap results. However, in this report, we are interested in the relative variations of the band gap of different size nanowires in different orientations rather than the actual band gap values. Therefore, we will resort to conventional DFT calculations within GGA approximation to circumvent the computational cost involved in study of these large structures.

3. Results and discussion

The cross sectional view of [100] oriented optimized hydrogen saturated Sb$_2$Se$_3$ nanowire (1.8 nm size) is shown in figure 1(a). In this orientation, the 1-D ribbons along [001] are confined by the size of the wire by breaking the strong covalent interactions within the ribbons. The cross sectional sizes (1.2 nm, 1.8 nm & 2.4 nm) of these nanowires were carefully chosen to avoid splitting the ribbons in the [010] direction. These nanostructures could be considered as clusters of molecules (terminated ribbons) infinitely stacked layer by layer (with Van der Waals interaction) along the [100] direction. Due to the inherent nature of the [010] oriented nanostructures, the very small cross sectional wires with cleaved half ribbons were found to be unstable and therefore, we selected a zigzag edged surface along the growth direction for our study (figures 1 (b) & (d)). Also, due to the hefty computational cost, we kept the size along the [100] direction constant (2.2 nm) and varied the size only along [001] direction (i.e., 1.2 nm, 1.8 nm and 2.4 nm) in our study. The cross sectional view of optimized nanowire of [001] orientation (2.4 nm size) is shown in figure 1(c). The 1-D ribbons are made up of $A_4B_6$ units along their cross section, i.e., two molecular units of Sb$_2$Se$_3$ come together to form the cross section of a ribbon. Careful observation of the structure shows that some of the infinite ribbons along the edges of the nanowires are cleaved.
such that they only have a single molecular unit of Sb$_2$Se$_3$ along their cross section. We chose the structures of sizes 1.2 nm, 2.4 nm & 3.6 nm for our studies in this orientation. The optimized structures show surface reconstruction due to the dangling bonds from the termination of ribbons. We also observed the bond formation between the neighboring ribbons in place of Van der Waals interactions. These structures were terminated with hydrogen to compensate the dangling bonds at the surface. Here, we report only the results of hydrogen saturated structures. The overall size changes due to optimization are shown in table 1.

The oriented structures show enlargement in both directions (cross-sectional enlargement) perpendicularly to the growth direction upon relaxation whereas, [010] oriented wires show enlargement in [100] & shrinkage in [001] direction. Examining the energy per atom of these nanowires reveals that their stability increases with increasing size. The [100] nanowires are comparatively most stable and the [001] nanowires are the least stable structures.

The electronic structure of the nanowires were studied with and without hydrogen saturation. Hydrogen saturation removes the bands introduced by the surface dangling bonds between valence and conduction bands and pushes the conduction bands towards a higher energy region in all cases. In the case of [100] oriented wires, the smallest nanowire shows a direct band gap, which changes to a indirect gap with further increase in sizes. These structures exhibit bands of more atomistic nature and it could be explained by the fact that the covalently bonded ribbons along [001] direction have been terminated. Also, in case of [010] oriented structures the band structure looks more atomistic owing to the termination of the strongly bound ribbons in these structures. All the [001] oriented nanowires display indirect band gaps (figure 2). Since the valance band maximum (VBM) near Gamma region has a nearly flat contour, at room temperature these nanowires will exhibit both direct and indirect transitions in a narrow energy range. Interestingly, the band gap of these wires is smaller than that of the bulk, contrary to the simple effective mass approximation (EMA).

The size dependence of the band gaps for all three orientations is presented in figure 3. The variation in band gap is fitted to the following equation for [100] & [010] orientations to explore the confinement effects:

\[ E_g = E_{g,bulk} + A \left( \frac{1}{d^\alpha} \right) \]

where, \( E_g \) & \( E_{g,bulk} \) are the DFT band gap of the nanostructure and the corresponding bulk structure respectively, \( d \) is the size of the structures and \( \alpha \) is the scaling index. The value of constant A and \( \alpha \) were found to be 0.61 and 1.19 respectively for the [100] oriented nanowires, and 0.47 and 1.03 respectively for [010] oriented ones. It should be noted that in simple EMA models the value of \( \alpha \) is predicted to be 2, however this

![Figure 2. Bandstructure of [001] oriented Sb$_2$Se$_3$ nanostructures of sizes (a) 1.2 nm (b) 2.4 nm (c) 3.6 nm.](image)

| Orientation | Size (nm) | Energy/atom (eV) | Change in size (%) |
|-------------|----------|-----------------|-------------------|
|             |          |                 | [100]  | [010]  | [001]  |
| [100]       | 1.2      | −3.84           | *      | 5.6    | 1.8    |
|             | 2.4      | −3.91           | *      | 0.7    | 1.0    |
| [010]       | 1.2      | −3.83           | 7.4    | *      | −3.8   |
|             | 2.4      | −3.90           | 6.3    | *      | −3.2   |
| [001]       | 1.2      | −3.77           | 4.3    | 1.8    | *      |
|             | 3.6      | −3.87           | 2.3    | 1.7    | *      |
The parameter is much lower in our calculations for [100] and [010] directions. For the [001] oriented structures, the change in band gap (ΔE) with size is fitted to the equation $\Delta E = E_{\text{diff}} + A \frac{1}{d^2}$. Here, $E_{\text{diff}}$ represents the reduction in band gap compared to the bulk. The band gap of bulk Sb$_2$Se$_3$ is calculated to be 0.88 eV. An in-depth computational study of the electronic properties of this material is presented earlier ([25]). The values of $E_{\text{diff}}$ and A are found to be $-0.167$ eV and 0.244. All three orientations including [001] oriented structures follow inverse band gap dependence with size, while [001] oriented nanowires show band gaps less than the bulk (figure 3).

In order to understand the reason behind the reduction in the band gap of [001] oriented wires, we investigate the atom resolved partial density of states (p-DOS) of different atoms in these structures. Although all atoms contribute to the bands at the conduction band minimum (CBM), the contribution is much higher for the non-functionalized Sb atoms (Sbnf) of cleaved 5-atom ribbons located at the surfaces (figure 4). Also, it’s interesting to note that the cleaved surface atoms have little contribution to the valence band maximum (VBM). This suggests that the reduction in band gap in these nanostructures is mainly due to restructuring of the lattice with major contributions coming from the surface cleaved atoms.

Further to explore the rationale behind this anomalous band gap reduction in [001] oriented nanostructures, we take a closer look at the bondangle variations. We studied the variation of the polyhedral angles, $\angle \text{Se1} - \text{Sb1} - \text{Se3} \& \angle \text{Se3} - \text{Sb2} - \text{Se3}$ in these nanostructures (figure 5 (b) & (c)). Variations of these angles with respect to the nanowire size are presented in (figure 5 (d) & (e)) for the ribbons located at different spatial positions in the nanowires. We observe large deviation in the polyhedral angles of these nanowires compared to their bulk counterpart. Moreover, the deviations are lower in 10-atom ribbons at the centre (Centre10) but higher in 5-atom cleaved ribbons (Surface5) at the surface, created by the spatial restriction at

Figure 3. Size-dependent band gaps of Sb$_2$Se$_3$ nanowires in three different orientations plotted with respect to the bulk band gap.

Figure 4. Partial density of states (p-DOS) of 5-atom cleaved ribbon which are at the surface of the [001] oriented Sb$_2$Se$_3$ nanostructures. Insert shows the [001] view of the 5-atom ribbon structure with labels. Sef: Selenium H-functionalized atom, Sbf: Antimony H-functionalized atom, Seinf: Selenium intermediate non-functionalized atom, Sbnf: Antimony non-functionalized atom, Senf: Selenium non-functionalized atom.
nanoscale. Compared to the bulk equivalent, up to 9.6° increase in $\angle Se_1 - Sb_2 - Se_3$ and up to 2.3° reduction in $\angle Se_3 - Sb_2 - Se_3$ were observed in the 5-atom ribbons which are the dominant contributors to the band gap reduction. The observed reduction in band gap in the [001] oriented nanowire is a cumulative effect of quantum confinement and the structural distortions of 5-atom ribbon at the surface. The confinement effect would be prominent only up to the length scales of a few nm. Moreover, the contribution of the cleaved 5-atom ribbons would remain with further increasing in size and even up to the bulk level, hence this could be thought of as a complete new structure. Therefore, one would not expect a turn point of the energy gap while increasing the size.

Energetically, the [001] oriented nanowires with 5-atom ribbons at the surface could be considered as a metastable structure and potentially realized by adopting appropriate physical methods. Nonetheless, this work intends to show that the drastic variations in the polyhedral angles of the 5-atom cleaved ribbons at the surface of [001] wires and the resultant peculiar electronic properties closely resemble the recent experimental study of structural and electronic properties of bulk $Sb_2Se_3$ under high pressure [20]. This similarity is interesting because the above experimental study has shown that $Sb_2Se_3$ goes through semiconductor-metal transition around 3 GPa and then becomes superconductive for pressures above 10 GPa. Our results here provide important clue in understanding of the above observation and thus, the anomaly of reduction in band gap of our [001] oriented nanostructure could be attributed to this insulator-metal transition related to the topological insulating transition.

4. Conclusion

We have studied nanowires of $Sb_2Se_3$ with three different orientations and sizes for their stability and dependency on electronic structure. We found that the [010] oriented nanowires were stable only for the zigzag edged surface along the growth direction. All of the studied nanowires show confinement effect with inverse dependence on size. The [001] oriented structures show reduction in band gap compared to the bulk. This anomalous band gap reduction could be attributed to the insulator-metal transition related to the topological insulating transition observed in bulk $Sb_2Se_3$ at high pressure $\sim$ 3 GPa.

Acknowledgments

This research was supported in part by the National Science Foundation through TeraGrid resources (TG-DMR100006) provided by the National Center for Supercomputing Applications (NCSA). Computations were also performed using the High Performance Computing facility (HPCF) at the University of Puerto Rico (UPR) and the Holland Computing Center of the University of Nebraska-Lincoln.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
ORCID iDs

Rajasekarakumar Vadapoo 🌐 https://orcid.org/0000-0003-2251-3854

References

[1] Tideswell N W, Kruse F H and McCullough J D 1957 The crystal structure of antimony selenide, Sb$_2$Se$_3$, Acta Crystallogr. 10 99
[2] Gujjarro N, Lutz T, Lana-Villarreal T, O’Mahony F, Gomez R and Haque S A 2012 Toward Antimony Selenide Sensitized Solar Cells: Efficient Charge Photogeneration at spiro-OMeTAD/Sb$_2$Se$_3$/Metal Oxide Heterojunctions J. Phys. Chem. Lett. 3 1351
[3] Wang K, Chen C, Liao H, Wang S, Tang J, Beard M C and Yang Y 2019 Both free and trapped carriers contribute to photocurrent of Sb$_2$Se$_3$ Solar Cells J. Phys. Chem. Lett. 10 4881
[4] Tiwari K J, Ren M Q, Kamalakar Vajandar S, Osipowicz T, Subrahmanyan A and Malar P 2018 Mechanochemical bulk synthesis and e-beam growth of thin films of Sb$_2$Se$_3$ photovoltaic absorber Sol. Energy 160 56
[5] Li Z et al 2019 9.2%-efficient core-shell structured antimony selenide nanorod array solar cells Nat. Commun. 10 1235
[6] Choi J-H, Lee M-H, Choi H-Y, Park C-M, Lee S-M and Choi J-H 2019 Investigation of electrochemical reaction mechanism for antimony selenide nanocomposite for sodium-ion battery electrodes J. Appl. Electrochem. 49 207
[7] Wang X, Wang H, Li Q, Li H, Xu J, Zhao G, Li H, Guo P, Li S and Sun Y-K 2017 Antimony selenide nanorods decorated on reduced graphene oxide with excellent electrochemical properties for li-ion batteries J. Electrochem. Soc. 164 A2922
[8] Tian Y et al 2020 Low-bandgap se-deficient antimony selenide as a multifunctional polysulfide barrier toward high-performance lithium-sulfur batteries Adv. Mater. 32 1904876
[9] Zhang L, Li Y, Li C, Chen Q, Zhen Z, Jiang X, Zhong M, Zhang F and Zhu H 2017 Scalable low-band-gap Sb$_2$Se$_3$ thin-film photocathodes for efficient visible-near-infrared solar hydrogen evolution ACS Nano 11 12753
[10] Choi D, Jang Y, Lee J H, Jeong G H, Whang D S, Cho K S and Kim S W 2014 Diameter-controlled and surface-modified Sb$_2$Se$_3$ nanowires and their photodetector performance Sci. Rep. 4 6714
[11] Wu W, Li Y, Liang L, Hao Q, Zhang J, Liu H and Liu C 2019 Enhanced broadband responsivity of ni-doped Sb$_2$Se$_3$ nanorod photodetector J. Phys. Chem. C 123 14781
[12] Xue H, Chen K, Zhou Q, Pan D, Zhang Y and Shen Y 2019 Antimony selenide/graphene oxide composite for sensitive photoelectrochemical detection of DNA methyltransferase activity J. Mater. Chem. B 7 6789
[13] Hasam M R et al 2016 An antimony selenide molecular ink for flexible broadband photodetectors Adv. Electron. Mater. 2 1600182
[14] Ko T-Y, Shellaiah M and Sun T W 2016 Thermal and thermoelastic transport in highly resistive single Sb$_2$Se$_3$ nanowires and nanowire bundles Sci. Rep. 6 35086
[15] Miao Z, Fan L, Xie X, Ma Y, Xue J, He T and Zha Z 2019 Liquid exfoliation of atomically thin antimony selenide as an efficient two-dimensional antibacterial nanosheet ACS Appl. Mater. Interfaces 11 26664
[16] Sun G et al 2019 Direct van der Waals/DS$_3$/WF$_3$/mixed-dimensional p-n heterojunctions Nano Res. 12 1139
[17] Liu W, Peng X, Tang C, Sun I, Zhang K and Zhong J 2011 Anisotropic interactions and strain-induced topological phase transition in Sb$_3$Se$_5$ and Bi$_3$Se$_5$, Phys. Rev. B 84 245105
[18] Bera A, Pal K, Muthu D V, Sen S, Guptasarma P, Waghmare U V and Sood A K 2013 Sharp Raman anomalies and broken adiabaticity at a pressure induced transition from band to topological insulator in Sb$_3$Se$_5$, Phys. Rev. Lett. 110 107401
[19] Efthimiopoulos I, Zhang J, Kucway M, Park C, Ewing R C and Wang Y 2013 Sb$_2$Se$_3$ under pressure Sci. Rep. 3 2665
[20] Kong P P et al 2014 Superconductivity in strong spin orbital coupling compound Sb$_2$Se$_3$, Sci. Rep. 4 6679
[21] Li W, Wei X-Y, Zhai J-X, Ting C S and Chen Y 2014 Pressure-induced topological quantum phase transition in Sb$_2$Se$_3$, Phys. Rev. B 89 035101
[22] Tian Y, Sun Z, Zhao Y, Tan T, Liu H and Chen Z 2018 One-dimensional Sb$_2$Se$_3$ nanorods synthesized through a simple polyol process for high-performance lithium-ion batteries J. Nanomater. 2018 9273945
[23] Farfán W, Mosquera E, Vadapoo R, Krishnan S and Marin C 2010 Vapor-liquid-Solid synthesis of [010]-oriented Sb$_2$Se$_3$ nanowires J. Nanosci. Nanotechnol. 10 5847
[24] Brus L 1986 Electronic wave functions in semiconductor clusters: experiment and theory J. Phys. Chem. 90 2555
[25] Vadapoo R, Krishnan S, Yilmaz H and Marin C 2011 Electronic structure of antimony selenide (Sb$_2$Se$_3$) from GW calculations Phys. Status Solidi B 248 700
[26] Vadapoo R, Krishnan S, Yilmaz H and Marin C 2011 Self-standing nanoribbons of antimony selenide and antimony sulfide with well-defined size and band gap Nanotechnology 22 175705
[27] Kresse G and Hafner J 1993 Ab initio molecular dynamics for liquid metals Phys. Rev. B 47 558
[28] Kresse G 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set Phys. Rev. B 54 11169
[29] Wang Y and Perdew JP 1991 Correlation hole of the spin-polarized electron gas, with exact small-wave-vector and high-density scaling Phys. Rev. B 44 13258
[30] Kresse G 1999 From ultrasoft pseudopotentials to the projector augmented-wave method Phys. Rev. B 59 1758
[31] Blochli P E 1994 Projector augmented-wave method Phys. Rev. B 50 17953