Doping Induced Carrier and Band-gap Modulation in Bulk versus Nano for Topological Insulators: a Test Case of Stibnite

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Abstract: We aim at comparing the electronic properties of topological insulator Sb₂S₃ in bulk and Nanorod using density-functional scheme and investigating the effects of Se-doping at chalcogen-site. While going from bulk to nano, there is a drastic change in the band gap due to surface-induced strain. However, the trend of band gap modulation with increased Se doping is more prominent in bulk. Interestingly, Se-doping introduces different type of carriers in bulk and nano.

INTRODUCTION

Nanostructures of narrow band gap V₂VI₃ semiconductors have been widely studied nowadays because of their special thermoelectric and optoelectronic properties. Due to their promising photoconducting and thermoelectric behavior, they are widely used in television cameras, microwave and switching devices, solar cells etc.¹ Antimony trisulfide (Sb₂S₃), commonly known as Stibnite, is a prospective candidate for solar energy conversion and thermoelectric technologies.¹

Nanoparticles, because of their high surface to volume ratio, are well-known to possess interesting properties significantly different from their bulk counterpart. The size reduction is often associated with drastic change of fundamental properties.² For Stibnite, a significant part of recent experimental research focuses on nanoscale systems, where the effect of surface states are more prominent than bulk.²

In the present work, we intend to study a comparison of electronic behavior of Stibnite for bulk and nanorod after a substitutional doping with Se at S-site. We have used first-principles density functional theory (DFT) calculations to extract the electronic structure of bulk Sb₂S₃ and Sb₂S₃ Nanorod and its various doping profiles.

COMPUTATIONAL DETAILS

First-principles spin-polarized plane-wave pseudopotential calculations are performed using Projector augmented wave (PAW) potentials for bulk-supercell and nanorod cluster of Sb₂S₃. Initial aspect ratio of the nanorod was taken as 10:1 to resemble a realistic experimental system. Se ions replace the S ions, to obtain the required doping percentages. Keeping the experimental site-preference for doping in nano-systems in mind, the Nanorod is doped only at its surface.

The exchange-correlation interactions are treated by the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange functionals using Vienna Ab-initio Simulation package (VASP).³ The cutoff energy for the planewave expansion is set at 500 eV and the k-mesh for bulk calculations are taken as 7×5×3. Keeping in mind the large box-size and the corresponding tiny Brillouin zone for Nanorod cluster, we have
employed only single k-point (Γ-point) for its complete geometry optimization and electronic structure calculations. Van der Waal’s interactions are incorporated in this calculation by using DFT-D2 method of Grimme, as implemented in VASP. The bulk Sb$_2$S$_3$ and the Nanorod are fully relaxed until the absolute value of force acting on each atom is less than 0.01eV/Å.

RESULTS AND DISCUSSIONS

Bulk crystalline structure used for the host semiconductor is a 120 atom Sb$_{48}$S$_{72}$ supercell of size ~12×12×22 Å$^3$, whereas Nanorod system consists of 100-atom assembly of Sb$_{40}$S$_{60}$, placed in a rectangular box of size ~15×50×22 Å$^3$. For bulk system, Se-doping sites are randomly chosen, whereas Nanorod doping sites are intentionally kept on the surface. Se-doping, in principle, should be associated with a size-induced chemical pressure because of the difference in the ionic radii of Se$^{2-}$(1.84Å) and S$^{2-}$(1.7Å). After structural relaxation, the Nanorod is observed to undergo huge surface reconstruction. As a result, the Sb-S-Sb bond angle near Nanorod surface is ~15 degrees higher than the bulk. A direct consequence of this surface induced strain is manifested in the direct band gap of the system. The band-gap of all Nanorod systems is one order of magnitude smaller than the bulk. Band gap of doped and the pristine systems are listed in table 1. In addition, Se incorporation within the system leads to an increase of bond-length for both Nanorod and bulk.

The impact of Se-doping on the electronic structure of bulk Sb$_2$S$_3$ and Nanorod has been shown in the atom projected density of states (APDOS) Figure 1 and 2 respectively. For both systems, Se doping percentage is varied from ~3 – 10%.

Bulk Sb$_2$S$_3$ is semiconducting with a bandgap of ~1.18 eV, with highly hybridized Sb-5p and S-3p states, mostly contributing the bottom of the conduction band and top of the valence band. The highest occupied valence bands below E$_F$ is mainly dominated by S-3p states with a lesser contribution of Sb-5p, whereas the bottom of the conduction band has almost equal weightage of Sb-5p and S-3p states. The spin up and spin down components of the DOS are symmetrical, indicating that the pure system is nonmagnetic in nature. From the DOS of Se-doped Sb$_2$S$_3$, strong $p$-$p$ hybridization is observed between Se-4p and Sb-5p orbitals. The amount of charge transfer is more from Sb-5p to Se-4p than to S-3p because of higher electron affinity of Se than S. Presence of filled 3d orbitals in Se leads to more effective shielding than S. The charge density plot for corresponding Se doped bulk Sb$_2$S$_3$ presented in Figure 3a also supports this fact. Therefore, with increasing concentration of Se, the system manifests more $p$-type doping.

![Figure 1](image1.png)

**Fig 1:** Figure 1a, b, c and d shows the APDOS of pure Sb$_2$S$_3$ bulk structure and 2.77%, 5% and 10% Se doped systems respectively.
Fig 2: Figure 1a, b, c and d shows the APDOS of pure Sb$_2$S$_3$ bulk structure and 2.5\%, 5\% and 10\% Se doped systems respectively.

Fig 3: Charge Density plot of a) Bulk doped Sb$_2$S$_3$ and b) doped Sb$_2$S$_3$ Nanorod.
TABLE 1. Variation of Band gap of Sb$_2$S$_3$ upon doping with different concentration of Se atom

<table>
<thead>
<tr>
<th>Doping concentration</th>
<th>Bandgap (in eV)</th>
<th>Doping concentration</th>
<th>Bandgap (in eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>1.18</td>
<td>0%</td>
<td>0.17</td>
</tr>
<tr>
<td>2.77%</td>
<td>1.13</td>
<td>3%</td>
<td>0.17</td>
</tr>
<tr>
<td>5.5%</td>
<td>1.13</td>
<td>6%</td>
<td>0.17</td>
</tr>
<tr>
<td>10%</td>
<td>1.09</td>
<td>10%</td>
<td>0.16</td>
</tr>
</tbody>
</table>

For Nanorod, due to surface reconstruction, additional surface states are generated at top of the valence band, which will be evident from a comparison of Fig. 1 and 2. Thus, effects of surface reconstruction shield the effect of surface-doping induced chemical pressure, keeping the hybridization picture intact. Doping induced band-gap modulation is much less prominent for Nanorod, as the surface doping effects of Se is masked by huge charge reordering at the surface of the Nanorod. The picture of carrier doping too is exactly opposite to bulk. Increasing Se-doping percentage leads to an increase of $n$-type doping within the system. This happens because of increased surface charge introduced as a result of Se-doping.

CONCLUSION

In summary, we have compared the effects of Se doping in Sb$_2$S$_3$ bulk and Nanorod using first principles DFT calculations. There is an order of magnitude change in the band gap while going from bulk to Nanorod system due to surface induced strain. Increasing doping percentage of Se leads to $p$-type doping in bulk. On the contrary, Nanorod manifests an increase of $n$-type doping. The present investigation may offer a new perspective to effectively control the band gap and doping nature of topological insulators.

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