An ab initio investigation of Bi$_2$Se$_3$ topological insulator deposited on amorphous SiO$_2$

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Abstract
We use first-principles simulations to investigate the topological properties of Bi$_2$Se$_3$ thin films deposited on amorphous SiO$_2$, Bi$_2$Se$_3$/a-SiO$_2$, which is a promising substrate for topological insulator (TI) based device applications. The Bi$_2$Se$_3$ films are bonded to a-SiO$_2$ mediated by van der Waals interactions. Upon interaction with the substrate, the Bi$_2$Se$_3$ topological surface and interface states remain present, however the degeneracy between the Dirac-like cones is broken. The energy separation between the two Dirac-like cones increases with the number of Bi$_2$Se$_3$ quintuple layers (QLs) deposited on the substrate. Such a degeneracy breaking is caused by (i) charge transfer from the TI to the substrate and charge redistribution along the Bi$_2$Se$_3$ QLs, and (ii) by deformation of the QL in contact with the a-SiO$_2$ substrate. We also investigate the role played by oxygen vacancies ($V_O$) on the a-SiO$_2$, which increases the energy splitting between the two Dirac-like cones. Finally, by mapping the electronic structure of Bi$_2$Se$_3$/a-SiO$_2$, we found that the a-SiO$_2$ surface states, even upon the presence of $V_O$, play a minor role on gating the electronic transport properties of Bi$_2$Se$_3$.

Keywords: topological insulator, deposition, first-principles, amorphous

(Some figures may appear in colour only in the online journal)
on a-SiO2 by different experimental techniques [12, 13], and it has recently been shown to present topologically protected surface states [14–16].

To better understand the interaction between Bi2Se3 thin films and the a-SiO2 substrate, we perform a first-principles investigation for increasing number of Bi2Se3 quintuple layers deposited on a-SiO2, (Bi2Se3)n/a-SiO2. We find that the Bi2Se3 layers are bonded to the a-SiO2 surface mediated by vdW interactions; where the lattice structure of the Bi2Se3 QLs is preserved. At the interface region we have found a net electronic charge transfer from the bottom-most Bi2Se3 QL to the a-SiO2 surface. There is a down-shift (up-shift) of the metallic TSSs (TISs), promoting electronic transport mediated by electrons (holes) on the surface (interface) Bi2Se3 QLs.

We have also considered the presence of oxygen vacancies (VO) on the surface, a-SiO2[VO], which is a quite common intrinsic defect. The strength of Bi2Se3/a-SiO2[VO] interaction is the same as that of Bi2Se3/a-SiO2, as well as the maintenance of the Bi2Se3 lattice structure. Further electronic structure calculations show that the a-SiO2 surface states, even upon the presence of VO, play a minor role on gating the electronic transport properties of Bi2Se3; where the VO defect level is resonant within the valence band of Bi2Se3, lying below the topologically protected metallic states.

2. Computational details

The calculations are performed based on the density-functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP) [17]. We use the generalized gradient approximation (GGA), in the form proposed by Perdew, Burke and Ernzerhof [18], to describe the exchange-correlation functional. The Kohn–Sham orbitals are expanded in a plane wave basis set with an energy cutoff of 400 eV. The electron–ion interactions are taken into account using the projector augmented wave (PAW) method [19]. The Brillouin Zone is sampled according to the Monkhorst–Pack method [20], using at least a $2 \times 2 \times 1$ mesh. We have also used a functional that accounts for dispersion effects, representing van der Waals (vdW) forces, according to the method developed by Tkatchenko–Scheffler (TS) [21], which is implemented on VASP [22]. The inclusion of van der Waals forces in the simulations is necessary to obtain the correct vdW gap between consecutive QLS [23], the interaction between the a-SiO2 substrate and Bi2Se3 is also better described with the inclusion of vdW interactions.

The amorphous structure was generated through ab initio molecular dynamics (MD) simulations based on the DFT approach as implemented in the VASP code. In [24], we present details on the generation procedure of amorphous SiO2 bulk structure. In order to generate the a-SiO2 surface, we have considered a a-SiO2 slab, where the boundary condition perpendicular to the surface plane (z direction) has been removed by introducing a vacuum region of 10 Å. The atomic positions have been relaxed until atomic forces were lower than 25 meV Å$^{-1}$.

![Figure 1](image.png)

**Figure 1.** Binding energy of 1QL-Bi2Se3/a-SiO2 as a function of separation distance along the perpendicular direction ($d_z$), as represented in the structure shown in the inset. Green (light red) balls represent Bi (Se) atoms, and yellow (dark red) balls represent Si (O) atoms.

3. Results and discussion

Our study starts by calculating the energetic stability and the equilibrium geometry of Bi2Se3 on the a-SiO2 substrate, Bi2Se3/a-SiO2. The binding energy ($E^b$) of Bi2Se3/a-SiO2 is defined as,

$$E^b = E[\text{Bi}_2\text{Se}_3/a-\text{SiO}_2] - E[\text{Bi}_2\text{Se}_3] - E[a-\text{SiO}_2],$$

where $E[\text{Bi}_2\text{Se}_3]$ and $E[a-\text{SiO}_2]$ are the total energies of the separated components: a QL of Bi2Se3 and the a-SiO2 surface; and $E[\text{Bi}_2\text{Se}_3/a-\text{SiO}_2]$ represents the total energy of the final system, a single QL of Bi2Se3 adsorbed on the a-SiO2 surface, as indicated in the inset of figure 1. Our results of $E^b$, as a function of the vertical distance $d_z$, are presented in figure 1. We find $E^b = -8.68$ meV Å$^{-2}$, for an (averaged) equilibrium distance of $d_z = 2.90$ Å. As observed for the QLS in the Bi2Se3 bulk, there is no chemical bonding between the Bi2Se3 and the a-SiO2 substrate, where the Bi2Se3/a-SiO2 interaction is ruled by vdW forces. Similar picture has been verified for graphene on the a-SiO2 surface, where we found $E^b = -6.3$ eV Å$^{-2}$ [25], which is in good agreement with the experimental estimation of Ishigami et al., $-6$ meV Å$^{-2}$ [26].

The absence of chemical bonding between the Bi2Se3 QL and the a-SiO2 surface has been maintained even upon the presence of oxygen vacancies (VO) on the a-SiO2 surface (a-SiO2[VO]); VO is a quite common intrinsic defect in SiO2. We obtained practically the same values of binding energy, $E^b = -9.00$ meV Å$^{-2}$, and an equilibrium distance $d_z$ of 2.96 Å. For both systems, Bi2Se3/a-SiO2 and /a-SiO2[VO], the atomic displacements at the interface region are very small, preserving the lattice structure of Bi2Se3, supporting recent experimental results of scanning transmission electron microscopy [15]. Further comparisons indicate that, (i) the distance between the substrate and the Bi2Se3 QL is approximately 9% larger than the separation distance between consecutive QLS in the Bi2Se3 bulk phase [23, 27], and (ii) the Bi2Se3/a-SiO2 binding energy is about 40% lower (in absolute
value) compared with the one between QLs in Bi2Se3 bulk phase. That is, the Bi2Se3–Bi2Se3 interaction is stronger than that between Bi2Se3 and the a-SiO2 surface.

Next we investigate the electronic and topological properties of Bi2Se3/a-SiO2, as a function of the number of Bi2Se3 QLS (n) on the a-SiO2 surface, (Bi2Se3)n/a-SiO2. In (Bi2Se3)n/a-SiO2, the opposite sides of Bi2Se3 are in contact with different environments (with different dielectric constants), viz.: one (top-most) is in contact with a vacuum region, and the other (bottom-most) in contact with the a-SiO2 surface. There is no inversion symmetry in (Bi2Se3)n/a-SiO2, and thus the energy degeneracy between the edge (QL) states can be removed. Indeed this is what we verify in figure 2, where we present the electronic band structure of (Bi2Se3)n/a-SiO2 for n = 3, 4, 5, 6, and 8. The size of blue (red) circles (in figure 2) is proportional to the contribution of the Bi–p, orbitals of the bottom-(top-)most QL of the (Bi2Se3)n. We find that the surface states present an energy gap for n = 3 and 4, characterized by a Rashba-like band splitting near the Γ point. Those Rashba-like energy bands present similar spatial distribution, and spin-texture (not shown) when compared with the ones observed for thin films of Bi2Se3 on SiC(0001) and InP[111] [28, 29]. In addition, it is worth noting that electronic contributions from the edge QLS to the band apex, indicated by arrows near the Γ point in figure 2(a), are reduced for n = 3 and 4. Those states are delocalized, spreading out along the Bi2Se3 layers, as verified for Bi2Se3 on InP[111] [29]. Such a delocalization is suppressed upon the formation of gapless Dirac bands for n = 5, 6 and 8 (figures 2(c)–(e)), i.e. the topologically protected metallic bands become fully localized on the top-most surface, and bottom-most interface QLS of (Bi2Se3)n/a-SiO2.

As shown in figures 2(c)–(e), the topological surface/interface states (TSSs/TISs) move downward/upward with respect to the Fermi level. Those results suggest that there is a local p-type (n-type) doping of the edge QLS of Bi2Se3. Indeed, based on the Bader charge analysis method [30], with the code developed by the Henkelman’s group [31], we find a net charge transfer from the bottom-most Bi2Se3 QL to the a-SiO2 surface atoms, giving rise to an electrostatic dipole at the interface region, as well as an electronic charge density rearrangement along the Bi2Se3 slab. In order to provide a measurement of the charge density imbalance along the Bi2Se3 layer, we compare the total charge densities at the edge QLS of (Bi2Se3)n/a-SiO2 with the ones of a free standing (Bi2Se3)n film. We find that the charge density reduces by 5.5–6.0 × 10¹² e cm⁻² in the bottom-most QL, while it increases by 0.2–1.0 × 10¹² e cm⁻² in the top-most QL. Thus, supporting the down-shift (up-shift) of the TSSs (TISs) lying on the surface (interface) QL of (Bi2Se3)n/a-SiO2.

The separation between the Dirac points (V' in figure 2(g)) increases almost linearly with the number of QLS, even one QL before the closing of the energy gap, n = 4. Such a dependence of V' with the width (d) of (Bi2Se3)n, can be attributed to the presence of a net electric field (E net) along the (Bi2Se3)n film, V' ∝ E netd [32]. Where E net comes from the charge density imbalance discussed above, and the band bending due to the charge transfer at the (Bi2Se3)n/a-SiO2 interface. By changing

Figure 2. (a)–(e) Band structures for nQLs-Bi2Se3 deposited on a-SiO2, where n ranges from 3–8. Blue circles are contributions of Bi p-orbitals from the bottom-most QL (interface with the substrate), and red circles for the top-most QL (vacuum interface). The circle size is proportional to the orbital contribution for each computed k-point. (f) Band structure for (Bi2Se3)n/a-SiO2. (g) Energy gap at the Γ-point between Dirac-like cones from Bi2Se3 topological surface and interface states, as a function of the number of QLS deposited on the a-SiO2 substrate. The electronic structure at the Bi2Se3/a-SiO2 interface region, we may have different values of V' for a given (Bi2Se3)n width; for instance, the presence of oxygen vacancies on the a-SiO2 surface. As shown in figure 2(f), V' increases by 37 meV, V' = 47 – 84 meV in (Bi2Se3)n/a-SiO2 [VO].

Tuning the electron chemical potential within the energy window given by V', the energy separation between the opposite edge states of Bi2Se3/a-SiO2 will promote topologically protected electron (hole) currents on the top-most surface (bottom-most interface) states of Bi2Se3. In addition, the up-shift of the interface states in Bi2Se3/a-SiO2 indicates that
the scattering rate between the TSSs and the bulk continuum states will be reduced, while the TSSs will face an increase of such a scattering rate [33]. Further control of the energy positions of those TSSs and TSIs can be done by an external electric field. Indeed, top-gate structures have been used to control the topological transport properties in thin films of Bi$_2$Se$_3$ on dielectric substrates [14, 16, 34, 35].

In figure 3(a), we present the energy positions of the isolated systems, valence band maximum (VBM) and the conduction band minimum (CBM) of pristine a-SiO$_2$ (left), and defective a-SiO$_2$[V$_0$] (right) surfaces. Here, we have considered the vacuum level as the energy reference. The doubly occupied V$_0$ defect level ($\varepsilon_0 = -5.84$ eV) lies at 1.46 eV above the valence band maximum $\varepsilon$. In the (Bi$_2$Se$_3$)$_8$ film (figure 3(a) (center)), the Fermi level is given by the crossing on the TSSs; it lies in the energy gap of a-SiO$_2$, and above the VBM $\varepsilon$. The position of the Fermi energy ($E_F$) with respect to the vacuum level, corresponds to the work function ($\Phi_0$) of free standing (Bi$_2$Se$_3$)$_8$, $\Phi_0 = 4.90$ eV. Meanwhile, the work function of the final systems (\Phi), (Bi$_2$Se$_3$)$_8$/a-SiO$_2$ and /a-SiO$_2$[V$_0$], increases with respect to $\Phi_0$. Comparing those work functions, $\Delta E_F = \Phi - \Phi_0$, we can infer the band bending of (Bi$_2$Se$_3$)$_8$ upon the formation of the Bi$_2$Se$_3$/a-SiO$_2$ interface [36]. We find positive values of $\Delta E_F$, 0.30 and 0.21 eV for (Bi$_2$Se$_3$)$_8$/a-SiO$_2$ and /a-SiO$_2$[V$_0$], respectively, and thus supporting the electron transfer from Bi$_2$Se$_3$ to the a-SiO$_2$ surface.

Aiming the development of electronic devices composed by thin films of Bi$_2$Se$_3$ with a-SiO$_2$ as the dielectric gate, it is important to get a picture of the energy positions of the TSSs and TSIs in Bi$_2$Se$_3$/a-SiO$_2$. In figures 3(b) and (c) we present the electronic band structures of the final systems, (Bi$_2$Se$_3$)$_8$/a-SiO$_2$ and /a-SiO$_2$[V$_0$], respectively, including the orbital projection to the a-SiO$_2$ surface. Those energy band diagrams show that (near the $\Gamma$ point) the TSSs and TSIs states lie at about (i) 2.6 eV above the VBM of the a-SiO$_2$ surface ($\Delta E_{\text{vBM}}$ in figure 3(b)), and (ii) 0.9 eV above the V$_0$ defect level ($\Delta E_{\text{VO}}$ in figure 3(c)), which is resonant within the valence band of Bi$_2$Se$_3$. Thus, indicating that the electronic states of the a-SiO$_2$ surface, even upon the presence of intrinsic defects like V$_0$, will play a minor role on gating the electronic transport properties, mediated by the topological states, for Bi$_2$Se$_3$ films.

4. Conclusions

We have performed an ab initio investigation of Bi$_2$Se$_3$ topological insulator deposited on amorphous a-SiO$_2$ substrate. The Bi$_2$Se$_3$ layers are bonded to the a-SiO$_2$ surface through vdW interactions; preserving the lattice structure of the Bi$_2$Se$_3$ QLs. Topologically protected edge states are observed on the surface as well as at the interface layers of Bi$_2$Se$_3$, however they are no longer degenerated. The TSSs exhibit an energy-down-shift, followed by the up-shift of the TSIs. The degeneracy break is caused by the combination of two effects: (i) charge transfer from the TI to the substrate and charge redistribution along the Bi$_2$Se$_3$ QLs, resulting in electron depletion (accumulation) at the closest (furthest) QL from the substrate; and (ii) the Bi$_2$Se$_3$ deformation due to the a-SiO$_2$ interaction. Such an energy separation is increased by the presence of V$_0$. Finally, by mapping the energy positions of the Bi$_2$Se$_3$ edge states, the VBM, CBM, and the V$_0$ defect level of a-SiO$_2$, we verify that the a-SiO$_2$ surface states will play a minor role on gating the electronic transport properties in Bi$_2$Se$_3$/a-SiO$_2$ systems.

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