Density Functional Theory Calculations on Ag Adatom in the Bi_2Se_3 (111) Surface

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Topological insulator (TI) has non-trivial metallic surface states and has provoked many studies of property of this metarial. One of TI, Bi_2Se_3 is the promising metarial due to application of quantum devices. We investigate the effect of Ag adatom in the Bi_2Se_3 (111) surface. The silver atom prefers to locate within the vdW gap between the QLs rather than on the top surface. The effect of Ag adsorption is the rise of the Fermi level implying that the adsorbed Ag atoms behave like electron donors.

INTRODUCTION

Topological insulators (TIs) such as $Bi_{1-x}Sb_x$ [1], Bi_2Se_3 [2], Bi_2Te_3 [3] constitute a new family of condensed matters which is stabilized by topological order and characterized by its insulating bulk and metallic surface [4]. It is known that the topological metallicity of their surface is robust for impurities and disorders preserving the time-reversal symmetry [4]. Such a robust topological surface metal can be used in novel spintronic devices and quantum computing. Among the TI materials, the most promising one is Bi_2Se_3 with relatively large bulk gap and ideal Dirac cone.

The deformation of electronic and structural properties by adsorbates such as magnetic atoms, water molecules, and transition metals on TI surfaces is interested to explore their effects on the predicted surface metallicity. Ye *et al*. have studied on Ag atoms on Bi_2Se_3 surface [5]. The Ag atoms are found to go into the van der Waals (vdW) gaps between quintuple layers (QLs). It causes an expansion of the vdW gap and the formation of the triangular shaped convexities in STM images.

In this study, we investigated Ag adatoms on Bi_2Se_3 (111) surface to find the stable position of Ag atom by using density functional calculations.

COMPUTATIONAL METHODS

We employed SIESTA code as implemented on the EDISON nanophysics web site [6]. Troullier-Martins norm-conserving pseudopotential was applied with generalized gradient approximation (GGA) [7]. The 2 x 2 surface supercell was used to simulate the adsorption of a single Ag atom on the Bi_2Se_3 (111) surface. The Bi_2Se_3 (111) slab was consisted of 3 QLs. We searched several possible high-symmetry positions of Ag atom both on the surface and in the subsurface regions, and compared the total energies of the local minima structures.

RESULTS and DISCUSSION

There are several positions of silver atom in 3QL-Bi_2Se_3 (111) shown Fig. 1 (c). In between Bi and Se layer, silver atom can be located in hollow, top of Bi and Se atom. The initial positions of Ag atom are top-most surface, each Bi and Se layer and inter QL. The formation energy of these 15 configuration is shown Fig. 2. As shown Fig. 2, the points in blue box including top and subsurface are indicating Ag atom moved from initial position to top-most surface. On the top surface, the Ag atom is higher than the top-most Se atom and the height is similar to the interlayer distance between Bi and Se within the same QL shown Fig. 3 (a). The top surface adsorption site is stable and the corresponding adsorption energy is about -0.15eV. In contrast, the local-minimum interlayer locations (between the second and the third layers and between the third and the fourth layers) within the top QL are calculated to be unstable in the sense that their adsorption energy is negative (~ -1eV) despite the fact that the intercalated Ag atom forms bonds with adjacent Bi and Se atoms. The most stable site for the Ag atom is located within the

vdW gap between the top and the second QLs shown Fig. 3 (c), and the adsorption energy is 0.27eV which is lower than that for the Ag atom on the surface. Although the initial positions of silver atom are between 3rd - 4th layer and 4th - 5th layer, silver atom moves to vdW gap shown green box of Fig. 2. Some of them arrive at stable site and the others lead to extend of vdW gap from 2.9**Å** to 4.6**Å** shown Fig. 3 (b). This implies that Ag atoms may traverse the topmost QL and occupy the most stable location within the vdW gap, provided that a certain energy is supplied to overcome the energy barrier between the two minima. These calculated energetics results are similar to previous experimental and theoretical results [5]. It is noted that the search for the transition state to obtain a plausible estimate for the activation barrier is doable but it is beyond the scope of present work.

When the Ag atom is in the vdW gap between the QLs, the electronic structure of 3QL-Bi_2Se_3 (111) is modified. The slightly unoccupied band of the clean surface near □-point becomes occupied as seen in Fig. 2. Whilst the completely-unoccupied band along K-□ direction for the clean surface is partially occupied (see the W-shape band in Fig. 2). Overall, the effect of Ag adsorption is to supply electrons to Bi_2Se_3 (111) that leads to the apparent rise of the Fermi level. At the investigation of projected density of states (PDOS) about Ag, Bi and Se atom, Se atoms involve the surface states near Fermi level shown Fig. 5. The charge density of Ag atom is located in the bulk-like range. However, we should stress that the present calculations do not include the spin-orbit coupling (SOC) and the inverted band structure (which is the characteristics of TI) is missing. In addition, the detailed change in the electronic band structure due to Ag adsorption might be further modified if the SOC is explicitly included.

CONCLUSION

In summary, from DFT calculations, we found that the Ag adatom prefers to locate within the vdW gap between the QLs rather than on the top surface. Electronically, the most prominent effect of Ag adsorption is the rise of the Fermi level implying that the adsorbed Ag atoms behave like electron donors.

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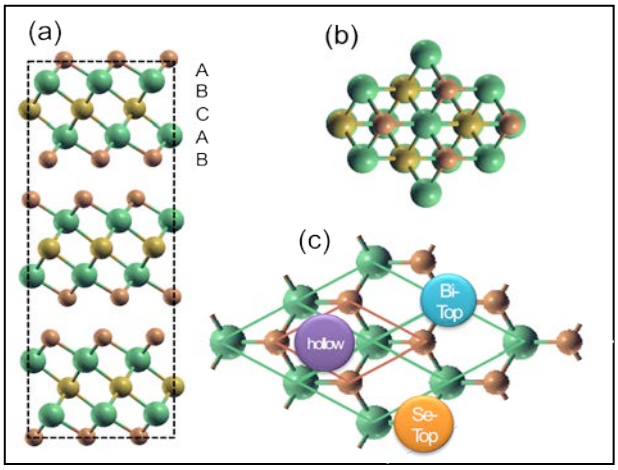

Fig. 1. Structure of Bi_2Se_3 (111) surface. Yellow and red balls are Se atoms, green balls are Bi atoms. (a) Side view and (b) top view of the slab. Bi_2Se_3 slab has hexagonal stacking structure like A-B-C-A-B. (c) It is high-symmetry positions of Ag atom, which locates hollow, Bi-top and Se-top site on each layer of 1 QL.

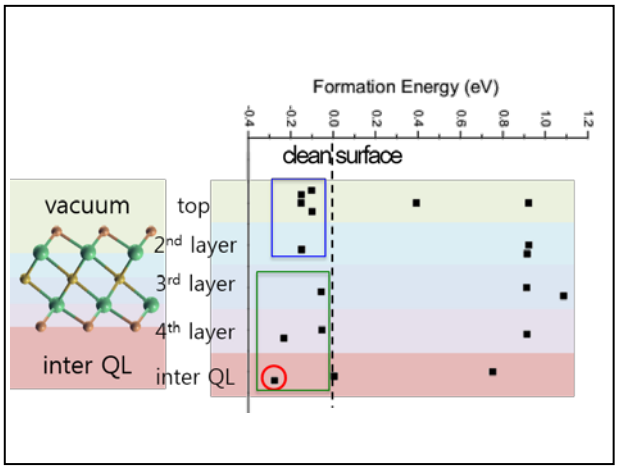

Fig. 2. Formation energy of Ag atom on Bi_2Se_3 (111) surface. Y-axis of graph is consist of five intervals from the topmost surface to interlayer (inter QL) of 1 QL. The interval of top

and subsurface is light green color, 2nd and 3rd layer, 4th layer and inter QL is light blue, pink and light red color, respectively. Reference of formation energy is total energy of clean surface and is marked dash line. The points in blue (green) box indicate Ag atom which moves from initial position to top surface (inter QL) after relaxtion.

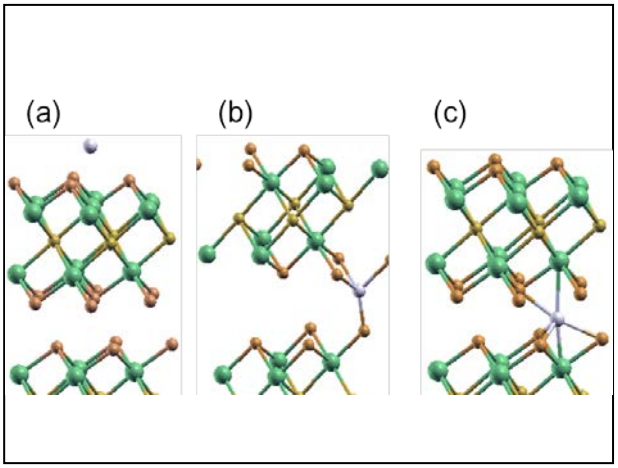

Fig. 3. Structure of Ag adatom on Bi_2Se_3 (111) surface after relaxation. Ag atom on the (a) top surface, (b) and (c) inter QL. (b) VdW gap is extended from 2.9Å to 4.6Å due to Ag atom.

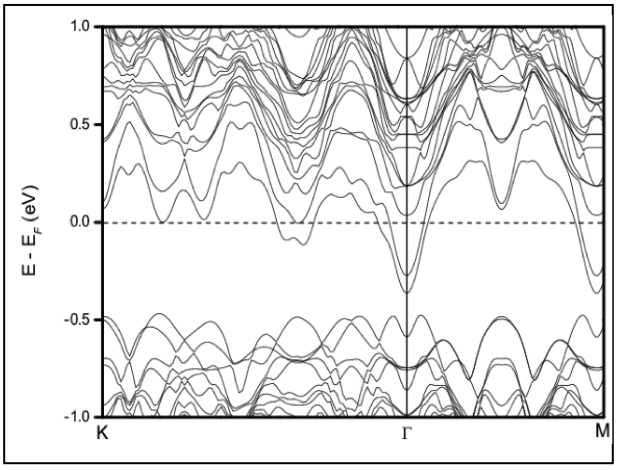

Fig. 4. Band structure of Bi_2Se_3 3QL with one Ag atom located within the vdW gap between the top and the second QLs. In comparison with the clean Bi_2Se_3 3QL, the Fermi level moves upward and the highest occupied band near □-point is deformed to form a M-shaped energy dispersion.

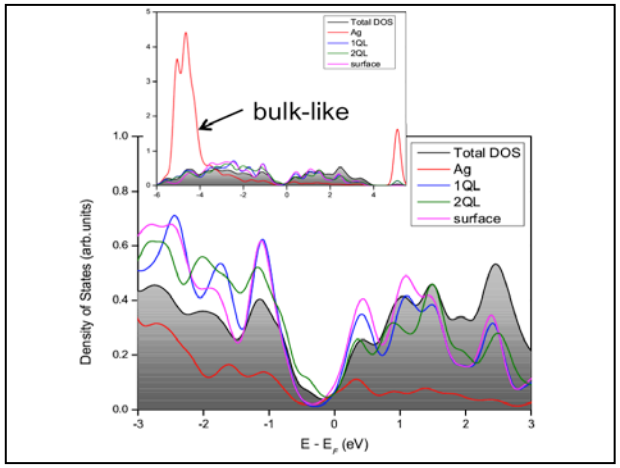

Fig. 5. Density of States (DOS) of Ag on Bi_2Se_3 (111) surface. In the range near Fermi level, total DOS is resulted by nearest neighbor Se in vdW gap and surface Se atom not by Ag atom. Charge density of Ag atom is localized in bulk-like region.