Gas Doping on the Topological Insulator Bi$_2$Se$_3$ Surface

Mohammad Koleini,$^{1,2}$ Thomas Frauenheim,$^1$ and Binghai Yan$^1$

$^1$Bremen Center for Computational Materials Science, University of Bremen, 28359 Bremen, Germany
$^2$Hybrid Materials Interfaces Group, Faculty of Production Engineering, University of Bremen, 28359 Bremen, Germany

(Dated: September 20, 2011)

Gas molecule doping on the topological insulator Bi$_2$Se$_3$ surface with existing Se vacancies is investigated using first-principles calculations. Consistent with experiments, NO$_2$ and O$_2$ are found to occupy the Se vacancy sites, remove vacancy-doped electrons and restore the band structure of a perfect surface. In contrast, NO and H$_2$ do not favor passivation of such vacancies. Interestingly we have revealed a NO$_2$ dissociation process that can well explain the speculative introduced “photon-doping” effect reported by recent experiments. Experimental strategies to validate this mechanism are presented. The choice and the effect of different passivators are discussed. This step paves the way for the usage of such materials in device applications utilizing robust topological surface states.

PACS numbers: 71.20.-b, 73.20.-r, 71.20.Nr

Three-dimensional (3D) topological insulators (TI) have attracted extensive research interest recently\cite{ref1,ref2}. Their novel topological surface states (TSS) in the bulk energy gap open great practical potential in spintronics and quantum computation by realizing the Majorana fermions\cite{ref3}. However, most TI materials available today are poor insulators in the bulk due to heavy defect doping\cite{ref4,ref5} and references therein, hindering the utilization of the TSS in practice. To remove the bulk carriers, surface doping with gas molecules was adopted as a powerful tool in experiments\cite{ref6,ref7}, though the underlying detailed atomistic mechanisms are still unknown. Exploring chemical reactions and understanding the modified surface structures are crucial to comprehend the current experimental results and help finding new methods to achieve the bulk insulating state.

As of today, the most attractive TI material is Bi$_2$Se$_3$\cite{ref8,ref9,ref10}, demonstrating simple Dirac-type TSS along with large bulk energy gap. Presumably due to the Se vacancies, however, it is found to be a n-doped semiconductor. To achieve a real bulk insulator, NO$_2$\cite{ref8,ref11,ref12} and O$_2$\cite{ref13,ref14} gas species were used to dope the surface and successively remove the donated bulk conduction electrons. In particular, the NO$_2$ doped Bi$_2$Se$_3$ surface exhibits a mysterious behavior, in which the surface loses electrons when exposed to photon flux in angle-resolved photoemission spectroscopy (ARPES) experiments\cite{ref6,ref8}. This is very different from the cases of graphene\cite{ref15} and another known TI material Bi$_2$Te$_3$\cite{ref16,ref17}, where the surface gains electrons back through desorbing NO$_2$ by the photon exposure. Though this photon-assisted stimulation or the so-called “photon-doping” method was employed to manipulate the surface bands in experiments\cite{ref18}, the underlying mechanism remains to be defined. In this letter, we have studied from first-principles the reaction of gas molecules on the Bi$_2$Se$_3$ surface containing Se vacancies and conclude how these affect the TSS.

The first-principles molecular dynamic (FPMD) simulation was employed to investigate the dynamic process of chemical adsorption and search for the stable atomic configurations. In bulk Bi$_2$Se$_3$, five atomic layers form a quintuple layer (QL) while the coupling between two such QLs is of the van der Waals type\cite{ref19}. Here we used a two-QL-thick slab model containing $3 \times 3$ primitive unit cells in the $xy$ plane to simulate a surface for

![Figure 1](attachment:fig1.png)  
FIG. 1. (a) Schematic of NO$_2$ molecule adsorption and dissociation processes and (b) corresponding reaction energetics on the Bi$_2$Se$_3$ surface with a Se vacancy. The Se vacancy is indicated by the white dot (step I) and donates two electrons that can dope the surface. During NO$_2$ exposure, the molecule occupies the vacancy site quickly with one O binding to three Bi atoms from the second atomic layer (step II). The corresponding N-O bond becomes weaker compared to before adsorption (step I). The stable adsorption structure is shown in (b) together with charge density difference before and after adsorption. The donor electrons transfer partially from the vacancy to NO$_2$. Under external photon exposure (step III), the weakened N-O bond breaks, resulting in the NO$_2$ dissociation into NO + O (step IV). The NO molecule leaves the surface, while O passivates the vacancy. In this case, two donor electrons transfer to the O atom and the vacancy is compensated. White balls stand for Bi atoms, red for O, and blue for N. In the isovalue surface plots of the charge difference, solid blue (wired gray) color denotes charge depletion (gain).

\[\text{(step I)} \quad \text{Se vacancy} \rightarrow \text{doped BiSe}_{3}\text{ surface} \quad \text{(step II)} \quad \text{NO}_2 \text{ molecule} \rightarrow \text{BiSe}_{3}\text{ surface} \quad \text{(step III)} \quad \text{NO}_2 \text{ molecule} \rightarrow \text{BiSe}_{3}\text{ surface} \quad \text{(step IV)} \quad \text{NO}_2 \text{ molecule} \rightarrow \text{BiSe}_{3}\text{ surface} \]
FIG. 2. Atomic structures and band structures for (a) a perfect Bi$_2$Se$_3$ surface, (b) a surface with a Se vacancy, (c) NO$_2$ adsorption, (d) O adsorption from the dissociated NO$_2$, (e) O$_2$ and (f) H$_2$ adsorption. Bands are aligned to their valence band maximum at $\Gamma$. The Fermi energy is shifted to zero. (a)-(d) show structures from side view, whereas (e)-(f) from the top view. Red lines indicate the surface states. White balls stand for Bi, yellow for Se, red for O, blue for N and small gray for H atoms. The transparent ball indicate the missing Se at the vacancy in (b). Band structures are calculated from a 3$\times$3 supercell of seven QLs thick. Colored circles denote Dirac points.

The results are shown in Fig. 2. The pristine surface has a single pair of Dirac-like TSS with the Fermi level $E_F$ crossing the Dirac point at $\Gamma$, consistent with previous calculations. When a Se vacancy forms on the surface, $E_F$ shifts to the bulk conduction band bottom, resulting in n-type doping as observed in experiments. Interestingly, the surface states are energetically changed considerably by the existing vacancies. The original Dirac point at $\Gamma$ shifts upward and almost merges into the conduction band, while a new Dirac point forms at the $\bar{M}$ point (Fig. 2(b)). In the bulk gap, $E_F$ still intersects the TSS odd times, indicating the topological nontrivial character. It should be noted that in our model Se vacancies distribute periodically on the surface, reflecting the employed supercell periodic boundary condition. However due to the vacancy random distribution on the real sample surfaces, the ARPES measured only a single Dirac point at $\Gamma$ in the primitive Brillouin zone. This illustrates a possible way to engineer the Dirac point by designing well-ordered surface potential.

NO$_2$ and NO. In the FPMD simulations, NO$_2$ molecules are placed above both the pristine surface and the surface with vacancy. NO$_2$ moves freely above the pristine surface whereby no strong binding effect is observed. The total energy calculation reveals that NO$_2$ physisorbs on this surface with a weak adsorption potential energy (APE) of $-0.4$ eV, resulting in tiny charge transfer from the surface to the molecule. However, on the defected surface NO$_2$ chemisorbed at the vacancy site quickly. One of the NO$_2$ oxygens, labeled as O1, adsorbs and binds to three Bi atoms from the second atomic layer, see Fig. 1(a) step II. The equilibrium bond length of N-O1 is elongated to 1.6 Å compared to the other N-O bond of 1.3 Å, indicating weakened N-O1 bond upon adsorption. Proceeding further, different FPMD replicas resulted into two situations. Firstly, in the majority of the simulations, stable adsorption of NO$_2$ at the vacancy with the APE of $-2.0$ eV took place. The corresponding band structure is depicted in Fig. 2(c), whereby the Dirac cone is recovered at $\bar{\Gamma}$. However, the surface is yet slightly electron-doped with $E_F$ 0.15 eV above the Dirac point. This indicates that NO$_2$ can not take away all donor electrons from the vacancy. In the other situation, localized vibrations cause the weakened N-O1 bond to break. Subsequently,
NO₂ dissociates into NO which leaves the surface, while the O1 atom passivates the vacancy. The respective APE decreases to -1.6 eV. To estimate the dissociation energy barrier, we performed density-functional calculations using the nudged elastic band method [21] and monitor dissociation to happen smoothly at a barrier of about 0.4 eV. From the related band structure in Fig. 2(d), we see the O1 atom passivation shifts $E_F$ further down to the Dirac point and totally restores the band structure of the pristine surface. This can be understood by the fact that the single O1 atom can accommodate all two extra electrons from the Se vacancy, more than NO₂ in the former case, as illustrated by the charge density change in Fig. 1(b). Contrary to NO₂, NO binds weakly (APE of -0.6 eV) and does not yield a similar good passivation of the vacancy, due to its much lower electron affinity.

It is interesting to compare these results with recent ARPES measurements [6, 15]. In experiments, the Fermi level is 0.3 eV above the Dirac point. Supposing all doped electrons are due to the Se vacancies, a dosage of 0.1 Langmuir (L) of NO₂ can shift $E_F$ down by 0.15 eV. After dosing with NO₂, in experiment two additional non-dispersive peaks appear at the binding energies of -4.0 eV and -7.5 eV [6]. This agrees with our calculated density of states (DOS) projected onto NO₂ (Fig. 3(b)), where partial DOS analysis (not shown here) indicates that the peak at $\sim -4.0$ eV is mainly due to both O atoms and the other at $\sim -7.5$ eV due to all N and O atoms. The ARPES results are found to remain stable with temperature varying from 10 K to 300 K. This can be explained by the large APE and the dissociation barrier (0.4 eV), much too high to be overcome by RT thermal fluctuations. Thereby NO₂ will neither desorb nor dissociate at 300 K. Moreover, the surface with a dose of 0.1 L can also be further hole-doped by extensive photon (energy 28-55 eV) exposure until $E_F$ reaches the Dirac point [15], called as “photon-doping”. Considering that NO₂ molecules dissociate into NO + O under laser pulse irradiation [22], the above experimental observation may be explained by the NO₂ dissociation process (Fig. 1 step III). High-energy photons stimulate the N-O₁ bond to break and subsequently transfer remaining electrons from the vacancy to the O₁ atom, finally downshifting $E_F$ to the Dirac point. We conclude that a dosage of 0.1 L of NO₂ passivates most of the Se vacancies on the surface, as the experimental $E_F$ position (0.15 eV above the Dirac point) is the same as our calculated one, see Fig. 2(c). Therefore photon exposure induces an O-passivated surface without extra donor electrons. In addition, without photon exposure a dosage of 2.0 L more can also shifts $E_F$ down to the Dirac point. This can be attributed to the weak adsorption of NO₂ on the pristine surface, see above, where much less electron transfer happens compared to that of the strong adsorption on the vacancy.

The proposed dissociation mechanism can be easily checked in experiments. One way is to monitor whether

![FIG. 3. Density of states (DOS) for (a) the perfect pristine surface and the one with a Se vacancy, (b) NO₂, (c) a single O atom, (d) O₂, and (e) H₂ passivated. To be more clear the adsorbates PDOS have been scales by $N_X/N_{Tot}$, where $N_X$ is the number of atoms in the adsorbate and $N_{Tot}$ is the total number of atoms in the supercell.](image)
one can find that the monoatomic oxygen, which is generally used in semiconductor industry for plasma ashing, can be an excellent passivator to Se vacancies, if under controllable exposure.

$O_2$ and $H_2$. The $O_2$ molecule also gets adsorbed in the vacancy site quickly with an estimated APE of ~ 3.4 eV. The two O atoms still remain connected to each other with one O (labeled as O1) binding to one Bi atom and the other O (O2) binding to the other two Bi atoms, as Fig. 2(c) shows. In the equilibrium structure, the O1-Bi bond length is ~ 2.2 Å, while two O2-Bi bonds form at ~ 2.4 Å. Concluding from the band structure analysis, $O_2$ captures two extra electrons from the vacancy and recover the neutral-charged TSS very well. After adsorption no $O_2$ dissociation was observed in any of our MD simulations, clearly due to stiffness of O=O bond. This suggests why photon exposure had not any improving effect in experiments with $O_2$ [9]. In contrast, $H_2$ does not occupy the vacancy site in the MD adsorption simulations. However after artificially saturating dangling bonds with hydrogens, the relaxed structure shows similar bondings with three below Bi atoms as in the $O_2$ case, see Fig. 2(f). This passivation can also restore a perfect Dirac-type band structure (Fig. 2(f)). Though $H_2$ adsorption is not favored in dynamics, single $H$ atoms can be an ideal passivation to Bi dangling bonds in theoretical studies, removing nontrivial surface dangling bond states and simplify the physics underlying.

In summary, we have studied the chemical adsorption of gas molecules ($NO_2$, $NO$, $O_2$ and $H_2$) on the Bi$_2$Se$_3$ surface. The passivation of common Se surface vacancies is found to gain the donor electrons much more effectively than weak adsorption on the pristine surface. The local atomic structures after adsorption are revealed and the band structures are compared. $NO_2$ is observed to passivate the vacancy and accommodate partially the vacancy-doped electrons. By overcoming a moderate energy barrier (e.g., with laser stimulation), $NO_2$ dissociates into NO and a single O atom, whereby the latter occupies the vacancy and accommodates all donor electrons. This dissociation and charge transfer can explain the mysterious “photon-doping” effect seen in ARPES experiments. As well, both $O_2$ molecule and the single O atom are found to passivate the vacancy very well and restore the surface band structure to the charge neutral state. In contrast, NO and $H_2$ are not favorable adsortates on the Bi$_2$Se$_3$ surface. The combination of MD with electronic structure analysis is shown to be versatile in explaining experimental observations along with suggesting new routes for device engineering, by tailoring different dopants and TI materials.

B.Y. acknowledges the financial support from Alexander von Humboldt Foundation in Germany. Computational time has been allocated at the University of Bremen.

X. Qi and S. Zhang, Physics Today 63, 33 (2010).

J. Moore, Nature 464, 194 (2010).

M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. 82, 3045 (2010).

Y. Xia, D. Qian, D. Hsieh, R. Shankar, H. Lin, A. Bansil, A. Fedorov, D. Grauer, Y. Hor, R. Cava, et al., Arxiv preprint arXiv:0907.3089 (2009).

Y. Xia, D. Qian, D. Hsieh, R. Shankar, H. Lin, A. Bansil, A. Fedorov, D. Grauer, Y. Hor, R. Cava, et al., Arxiv preprint arXiv:1008.2020 (2010).

H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nature Physics 5, 438 (2009).

Y. Xia, D. Qian, D. Hsieh, R. Shankar, H. Lin, A. Bansil, D. Grauer, Y. Hor, R. Cava, and M. Z. Hasan, Nature Physics 5, 398 (2009).

Y. Xia, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Phys. Rev. B 81, 041307 (Jan 2010).

H.-Z. Lu, W.-Y. Shan, W. Yao, Q. Niu, and S.-Q. Shen, Phys. Rev. B 81, 115407 (Mar 2010).

FPMD calculations have been performed by employing fully relativistic density-functional calculations including spin-orbit coupling (SOC) as implemented in the openMX code [24]. GGA-PBE for exch.-corr. [25] with grid cutoff of 250 Ry have been used.

G. Henkelman, B. Uberuaga, and H. JóNSSon, The Journal of Chemical Physics 113, 9901 (2000).

G. E. Busch and K. R. Wilson, J. Chem. Phys. 56, 3626 (1972); ibid. 56, 3638 (1972).

J. Vandevondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, and J. Hutter, Computer physics commu-
[24] T. Ozaki and H. Kino, Phys. Rev. B \textbf{72}, 045121 (Jul 2005).

[25] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. \textbf{77}, 3865 (1996).