Investigation of the Origin of Photo-Induced Doping on $TlBiSe_2$

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Topological insulators (TIs) are promising materials for spintronics applications owing to their spin-polarized metallic electronic states that prohibit the 180° backscattering. This peculiar spin-polarized states also shows the possibility to control the direction of spin current by switching the TI from p-type to n-type or vice versa. In order to make this switching, one need to tune the Fermi level. This means that developing an easy way to dope charge into TIs is highly recommended to fabricate highly functional spintronics devices such as topological p-n junctions. In addition, this doping will make the bulk, which is metallic in most TIs due to the presence of defect, insulating, that is another key to make TIs possible for spintronics device materials. Doping of TIs has been studied, for example, by doping Ca in bulk Bi_2Se_3 and making $Bi_{2-\delta}Ca_{\delta}Se_3$ [1] or adsorbing O_2 molecules on Bi_2Se_3 [2], but these doping methods have problems in terms of stability.

Photo-induced doping is a process of holding the bulk of Bi_2Se_3 and Bi_2Te_3 insulating by H_2O exposure followed by VUV and/or SX light irradiation [3]. This method has the possibility of creating devices such as topological p-n junctions by using kind of photomasks like in photolithography. However, Bi_2Se_3 and Bi_2Te_3 have no chance to be bulk insulating p-type TI, because the Dirac point is located below the bulk valence band [4]. In contrast to these TIs, $TlBiSe_2$ has its Dirac point at almost the center of its wide bulk band gap (ca. 300 meV), and thus is one of the most suitable TIs for device applications [4]. Based on these, we tried to do photo-induced doping on $TlBiSe_2$ in our former study. As a result, we succeeded to dope hole into $TlBiSe_2$ by photo irradiation, and making both n-type and p-type $TlBiSe_2$.

In the present study, we performed photon energy-dependent ARPES measurements, at BL-9A of HiSOR, in order to investigate the origin of photo-induced doping on $TlBiSe_2$. In case of Bi_2Se_3 and Bi_2Te_3, the hole-doping were reported to originate by exciting the core-level of the outermost atom, i.e., Se or Te [3]. The surface structure of $TlBiSe_2$ is different from Bi_2Se_3 and Bi_2Te_3, and thus the doping might occur with a different process. As shown in Fig. 1(a), the surface of $TlBiSe_2$ is half covered by Tl islands [5]. $TlBiSe_2$ was cleaved under a UHV condition, exposed to H_2O, and then irradiated with synchrotron radiation light of 10, 20, and 35 eV. As can be seen in Fig. 1(b), 35 eV photon energy allows to excite the Bi core-level, and 20 eV photon energy to excite the Tl core-level. Figures 2(b) and (c) show the results of ARPES measurements after H_2O exposure followed by photo-irradiation at 20 eV and 35 eV, respectively. Compared with the clean $TlBiSe_2$ surface (Fig. 2(a)), the binding energy of the Dirac point (indicated by red line) is shifted to the low binding energy in both cases. However, this shift is smaller than that of the $TlBiSe_2$ surface irradiated at 100 eV(Fig. 2(d)) with the same amount of H_2O exposure. The small shift would originate from the removal of residual gas adsorption, which causes the aging effect, by photo-irradiation [3]. In the present talk, we will explain the mechanism of photo-induced hole doping on $TlBiSe_2$ in more details.

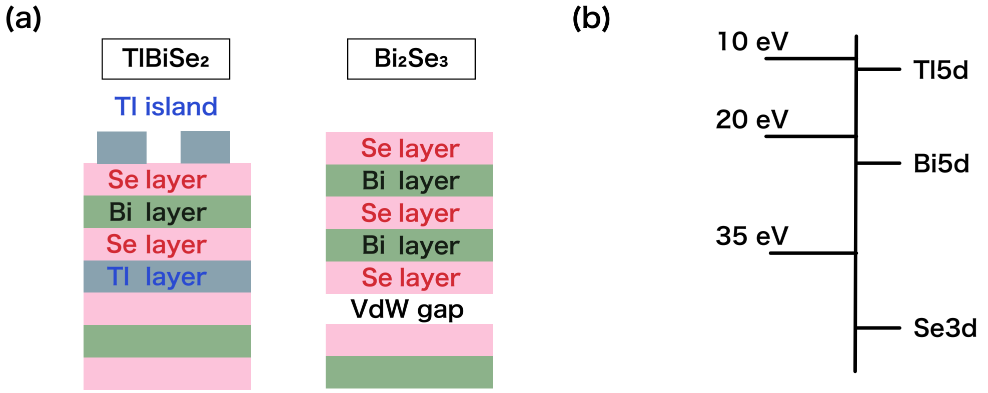

FIGURE 1. (a) Schematic diagram of the surfaces of two different Tis, $TlBiSe_2$ and Bi_2Se_3. (b) Schematic diagram of the relation between the binding energies of Tl5d, Bi5d, and Se3d and the photon energies used in the present study.

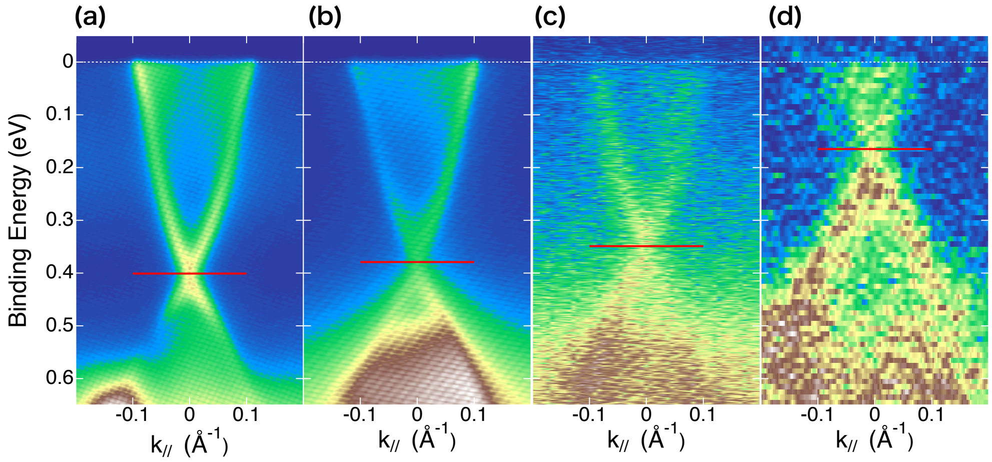

FIGURE 2. Valence bands of (a) a pristine $TlBiSe_2$ ($h\nu$=20 eV), and 5 ML of H_2O exposure followed by (b) $h\nu$= 20 eV, (c) 35 eV, and (d) 100 eV photo-irradiation. (d) has been obtained at the BL13 VLS station of Saga Light Source. Red lines indicate the position of Dirac point.

REFERENCES

1. D. Hsieh,Y. Xia, D. Qian, L. Wray, J. H. Dil, F. Meier, J. Osterwalder, L. Patthey, J. G. Checkelsky, N. P. Ong, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava and M. Z. Hasan , Nature **460**, 1101 (2009).
2. Y. Chen, J.-H. Chu, J. G. Analytis, Z. K. Liu, K. Igarashi, H.-H. Kuo, X. L. Qi, S. K. Mo, R. G. Moore, D. H. Lu, M. Hashimoto, T. Sasagawa, S. C. Zhang, I. R. Fisher, Z. Hussain, Z. X. Shen, Science **329** 659 (2010).
3. K. Sakamoto, H. Ishikawa, T. Wake, C. Ishimoto, J. Fujii, H. Bentmann, M. Ohtaka, K. Kuroda, N. Inoue, T. Hattori, T. Miyamachi, F. Komori, I. Yamamoto, C. Fan, P. Krüger, H. Ota, F. Matsui, F. Reinert, J. Avila, and M. C. Asensio, Nano Lett. **21**, 4415 (2021).
4. O. V. Yazyev, J. E. Moore, and S. G. Louie, Phys. Rev. Lett. **105**, 266806 (2010).
5. K. Kuroda, M. Ye, A. Kimura, S. V. Eremeev, E. E. Krasovskii, E. V. Chulkov, Y. Ueda, K. Miyamoto, T. Okuda, K. Shimada, H. Namatame, and M. Taniguchi, Phys. Rev. Lett. **105**, 146801 (2010).