Creation of a *p*-type $TlBiSe_2$ using photo-induced doping

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Owing to the location of the Dirac point, which is around the center of its wide bulk band gap, $TlBiSe_2$ would be one of the most promising topological insulators for spintronics devices material. However, like many other topological insulators, defects, such as vacancy formed during the crystal growth, dope electrons into $TlBiSe_2$ and make its bulk metallic. Here, we show the achievement of bulk insulating both *n*-type and *p*-type $TlBiSe_2$ by photo-induced doping, a method carried out by a combination of photo-irradiation and H_2O adsorption. We also show that the main trigger of this photo-induced doping is the excitation of the outermost *d* core level of the chalcogen atoms of the topmost layer as in the case of Bi_2X_3, where X = Se or Te.

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I. INTRODUCTION

Three-dimensional topological insulators hold spin-polarized metallic surface states with Dirac cone shape, and have potential applications in high-efficiency spin current devices due to the topological protection and prohibition of 180° backscattering of electron spins by nonmagnetic impurities [1–4]. However, the naturally generated defects dope charge into most topological insulators [5,6], e.g., electrons are doped in Bi_2X_3 (X = Se, Te) [7,8] and holes are doped in Sb_2Te_3 [9], making the bulk of these topological insulators metallic. In such topological insulators, spin-polarized electrons, which flow at the surface only in the ideal case, diffuses into the nonspin-polarized bulk and decreases the efficiency of spin current drastically. This is a serious problem from the point of view of device applications. In order to solve this problem, several methods have been reported to make the bulk insulating, e.g., doping divalent metals in bulk [10,11] or adsorbing gases such as O_2 on the surface [12,13]. However, the bulk becomes metallic again by time due to aging effects when doping the bulk using divalent atoms, and the method of using oxygen adsorption has problems in terms of stability when raising the temperature and also in controlling the amount of doped carriers in atmospheric condition.

The photo-induced doping is a newly developed charge doping method reported for Bi_2X_3 [14]; the doping occurs by irradiating Bi_2X_3 covered with physisorbed H_2O molecules using a photon energy high enough to excite the outermost *d* core level of the chalcogen atoms. The beauty of this method is that the doping is much more stable than those reported previously, and that the doping occurs locally, i.e., only at the area where the light was irradiated. In order to realize high-functionality semiconductor spintronic devices using topological insulators, such as topological *p-n* junction [15–20], it is necessary to make both *n*- and *p*-type topological insulators with insulating bulk. However, the Dirac points (DPs) of Bi_2X_3 are located below the bulk valence band maxima [21,22], and thus it is impossible to make bulk insulating *p*-type topological insulator with these two materials. $TlBiSe_2$ has a wide band gap [23–27] and its DP is located around the center of the bulk band gap [27,28] suggesting that this topological insulator can be both bulk insulating *n*-type and *p*-type by tuning the Fermi level. As in the case of Bi_2X_3, a clean $TlBiSe_2$ is also electron doped [25–27] by defects such as Se vacancies [29] making its bulk metallic.

In this paper, we show that photo-induced doping is adaptable for $TlBiSe_2$ as well, although there is a difference in the surface atomic structure. That is, while the chalcogen layer facing the van der Waals (vdW) gap appears at the

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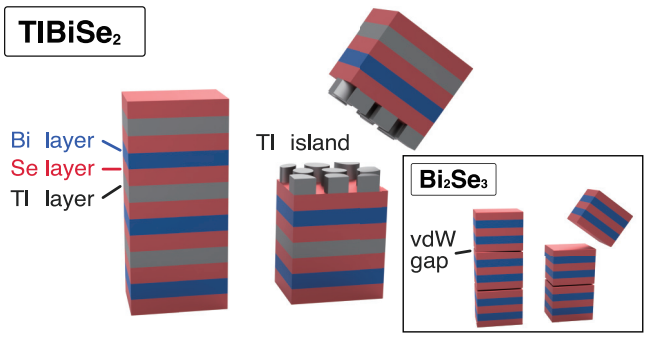

FIG. 1. Schematic illustrations of the layer stacking and cleavage plane of $TlBiSe_2$ and Bi_2Se_3. All the layers stacked in the order of -Tl-Se-Bi-Se- are bonded covalently in $TlBiSe_2$, and the quintuple (Se-Bi-Se-Bi-Se) layers are weakly bonded with vdW force in the case of Bi_2Se_3.

surface after cleaving Bi_2X_3, Tl islands with a coverage of 0.5 monolayer (ML) exist on the Se layer in the case of $TlBiSe_2$. This results from the difference in atomic structure; Bi_2X_3 has a vdW gap between each quintuple (Se-Bi-Se-Bi-Se) layer, whereas all layers are bonded covalently in $TlBiSe_2$ [30] as shown in Fig. 1. We also report the success of making a bulk insulating *p*-type $TlBiSe_2$, and the mechanism of photo-induced doping of this topological insulator.

II. METHODS

Single crystalline $TlBiSe_2$ samples grown by the Bridgman method were cleaved in ultrahigh vacuum (UHV) chambers under a base pressure of 1×10^{-6} Pa to obtain a clean surface. The sample quality was confirmed by x-ray diffraction (Fig. S1 within the Supplemental Material [31]). Photoelectron spectroscopy (PES) measurements were performed at different synchrotron radiation facilities, the beamline 4A2 of Pohang light source-II (PLS-II), Korea, the beamlime 13 of SAGA light source (SAGA-LS), Japan, and the beamline 9A of Hiroshima synchrotron radiation center (HiSOR), Japan. The energy resolution was 12 meV in the angle-resolved PES (ARPES) measurements performed at photon energy ($h\nu$) of 20 and 35 eV, below 20 meV in the ARPES measurements at $h\nu = 100$ eV and in measurements of shallow core levels, and 220 meV in the O 1s core-level measurements. The momentum resolution was below 1% of the Brillouin zone in ARPES. All PES measurements were carried out in UHV chambers under a base pressure of $<1 \times 10^{-8}$ Pa and at a temperature lower than 80 K. More detailed informations about sample preparation and measurements are described in the Supplemental Material [31].

III. RESULTS AND DISCUSSION

Figures 2(a)–2(c) show the ARPES images of $TlBiSe_2$ measured with $h\nu = 100$ eV by continuously exposed the sample to H_2O at a partial pressure of 5×10^{-8} Pa. (a), (b), and (c) were measured 22 min, 343 min, and 743 min after starting the photo irradiation, and the light was kept irradiating the same sample position. As clearly seen in the figure, the DP, which is guided by red solid lines, shifts to lower binding energy (E_B) at longer exposure. This result means that the photo-induced hole doping, which was developed for Bi_2X_3 [14], can be applied for $TlBiSe_2$ as well. Taking into account that the bulk band gap is approximately 300 meV and that the DP is located around the center of the bulk band gap [27], the bulk conduction band crosses the Fermi level in Fig. 2(a) indicating this sample to be metallic. On the other hand, the binding energies (E_Bs) of DP in (b) and (c) indicate the bulk states of these two samples to be insulating, and furthermore the $TlBiSe_2$ in (b) and (c) to be a *n*-type topological insulator and a *p*-type topological insulator, respectively. The formation of a *p*-type topological insulator by using

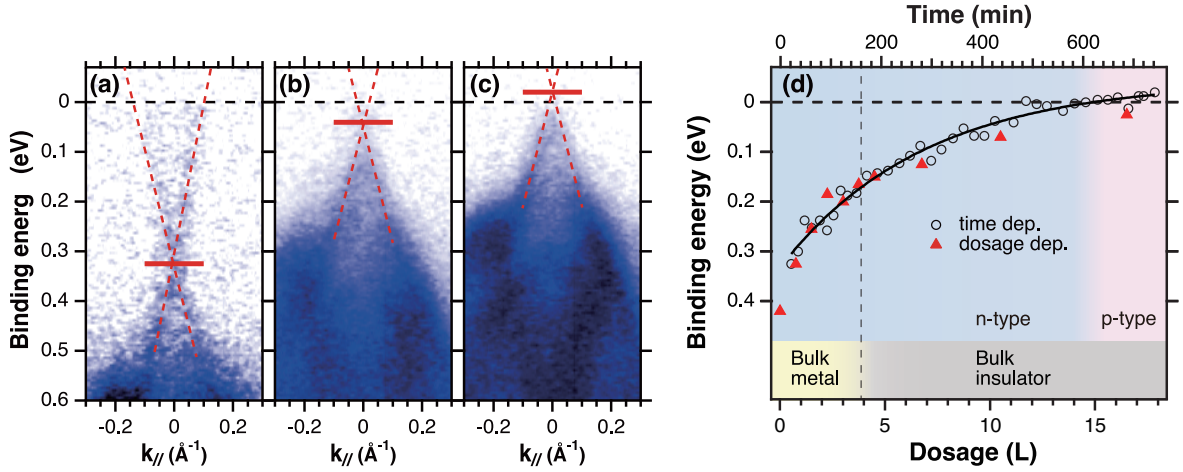

FIG. 2. [(a)–(c)] ARPES images obtained by continuously exposing $TlBiSe_2$ to H_2O. The photon energy was $h\nu = 100$ eV and the partial H_2O pressure was 5×10^{-8} Pa. (a), (b), and (c) were obtained 22 min, 343 min, and 743 min after starting the photo irradiation, respectively. The red dashed lines indicate the Dirac cones and the red solid ones indicate the DP in (a)–(c). The black open circles in (d) show the time-dependent E_{DP} obtained with $h\nu = 100$ eV by continuously exposing the sample under a partial H_2O pressure of 5×10^{-8} Pa, and the red triangles in (d) are the results of the dosage-dependent E_{DP}. The black solid line overlapping the experimental data is the fitting result. The dosage-dependent E_{DP}s were obtained by photo-irradiating 30 min the $TlBiSe_2$, which was exposed to a certain amount of H_2O.

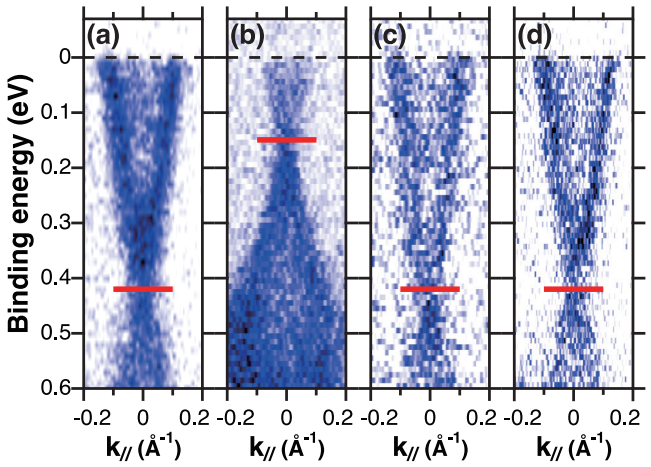

FIG. 3. ARPES images of (a) a pristine $TlBiSe_2$, (b) a 30-min photo-irradiated 4.5 L H_2O exposed $TlBiSe_2$, and (c) a 4.5-L H_2O exposed $TlBiSe_2$ measured soon after moving the light spot 300 μm from the position of (b). (d) $TlBiSe_2$ irradiated 40 min without H_2O exposure. $h\nu = 100$ eV was used in (a)–(d).

photo-induced doping was proposed in Ref. [14] but not realized so far.

Figure 2(d) shows the time-dependent E_B of the DP (E_{DP}) obtained by continuously exposing the sample to H_2O, together with the DP obtained after photo-irradiating 30 min a sample exposed to a certain amount of dosage. [The unit of dosage is described in Langmuir (L: 1 L = 1.33×10^{-4} Pa $\times 1$ s).] The time-dependent (black open circles) E_{DP} shows that the DP gets closer to the Fermi level and moves above it at longer time. The shading indicate the region where the $TlBiSe_2$ is n-type or p-type, and the scale bar at the bottom of the figure indicate the region where the bulk is metallic or insulating. The E_{DP} also becomes smaller at higher dosage as indicated by red filled triangles. (The E_Bs of red triangles are obtained by irradiating the H_2O exposed $TlBiSe_2$ 30 min, a time long enough to saturate the E_{DP} shift.) In order to obtain more details information about the change in E_B of the DP, we have fitted the experimental data. The black solid line overlapping the experimental data in Fig. 2(d) is the least-squares fit obtained using $E_{DP}(t) = A\exp(-Bt) + C$, where A corresponds to the difference between the initial and the saturated E_{DP}, B is a constant corresponding to the doping mechanism, and C corresponds to the E_{DP} at the saturation condition. The obtained values were $A = 375$ meV, $B = 0.0043$ min^{-1}, and $C = -43$ meV, which prove the possibility of forming a p-type $TlBiSe_2$.

To confirm the effect of photo-irradiation, we have measured the Dirac cone of a $TlBiSe_2$ before starting the H_2O exposure [Fig. 3(a)], that of a sample exposed to 4.5 L of H_2O [Fig. 3(b)], and soon after moving the light spot by 300 μm from the original position [Fig. 3(c)]; the size of the light spot was 140 μm in the direction that the light was moved. As shown in Figs. 3(a)–3(c), the DP is located at $E_B \sim 150$ meV at a position irradiated with $h\nu = 100$ eV for 30 min, whereas it has the same E_B as that of a pristine $TlBiSe_2$ at a nonirradiated position. In the case of irradiating a clean $TlBiSe_2$ with $h\nu = 100$ eV for 40 min, the E_B of the DP hardly changed [Fig. 3(d)]. Since the whole sample was exposed to H_2O in Figs. 3(b) and 3(c) and because no shift is observed in Fig. 3(d), these results indicate that both the photo-irradiation and the adsorption of H_2O are indispensable to this doping method. Furthermore, these experimental results also show that local doping is possible, and spintronics devices such as topological p-n junctions can be realized by controlling the amount and position of photo-irradiation.

In order to obtain more detailed information about the doping process, we have measured the shallow d core levels of the three elements composing the topological insulator, and the core level of oxygen that was reported to play a key role to photo-induced doping in the case of Bi_2X_3 [14]. Figure 4(a) shows the core levels of a pristine $TlBiSe_2$ obtained using $h\nu = 680$ eV. No peak except those from the core levels of Tl, Bi, and Se are observed in the spectrum. This means that the pristine $TlBiSe_2$ is clean and not contaminated by neither C nor O. Taking into account that photo-induced doping of Bi_2X_3 occurs by the chemisorption of O species [14], we have measured the O 1s core level of a $TlBiSe_2$ kept under a partial H_2O pressure of 5×10^{-8} Pa using $h\nu = 750$ eV. The O 1s core level obtained approximately 5 and 40 min after starting the irradiation is shown in Fig. 4(b). Three peaks are observed in each spectrum. By fitting the two spectra using Voigt functions, we obtained the E_B of the peaks to be 532.3. 529.5, and 528.2 eV in the lower spectrum, and 532.2, 529.4, and 528.1 eV in the upper one. The number of O 1s component and their relative E_Bs agree well with those of photo-induced hole doped Bi_2Se_3 [14]. Taking these agreements and the origin of the peaks reported in Ref. [14] into account, we assign the O 1s component with the highest E_B to originate from the physisorbed H_2O, and the two components with lower E_B to result from the chemisorbed species that are in the form of -O or -OH. Furthermore, by considering the change in the relative intensity of O 1s components upon photo irradiation, which indicates the photo-induced dissociation of the physisorbed H_2O and the dissociated O species to chemically bond to $TlBiSe_2$, we conclude that the origin of the photo-induced hole doping is this chemisorbed O species like the case of Bi_2Se_3 [14].

The Se 3d, Bi 5d, and Tl 5d core levels of a pristine and a photo-induced hole-doped $TlBiSe_2$ are shown in Figs. 4(c)–4(e). The hole-doped sample was obtained by irradiating a 10.5-L H_2O exposed $TlBiSe_2$ with $h\nu = 100$ eV until the shift in E_B of the core levels saturated. While the core-level spectra of Se 3d and Bi 5d show two peaks originating from the $d_{5/2}$ and $d_{3/2}$ components, the core-level spectrum of Tl 5d shows four peaks. These four Tl 5d peaks result from the $d_{5/2}$ and $d_{3/2}$ components of bulk Tl and those from the Tl atoms forming islands on the surface [30]; the lower E_B $d_{5/2}$ and $d_{3/2}$ components originate from bulk Tl, and the higher E_B ones from Tl forming islands. As shown in the figure, all these shallow d core levels shift to lower E_B after photo-irradiation. The shift in E_B of the Bi 5d and bulk-Tl 5d is 340 meV, a value that agrees well with the DP shift of a 10.5-L exposed $TlBiSe_2$ [Fig. 2(d)], and the O 1s shift in Fig. 4(b) also agrees with the DP shift of a 40 min irradiated $TlBiSe_2$ [Fig. 2(d)], given that these shifts result from band bending such as the case of Bi_2Se_3 [14]. On the other hand, the Se 3d and island-Tl 5d core levels show shifts of 390 meV and 400 meV, i.e., values

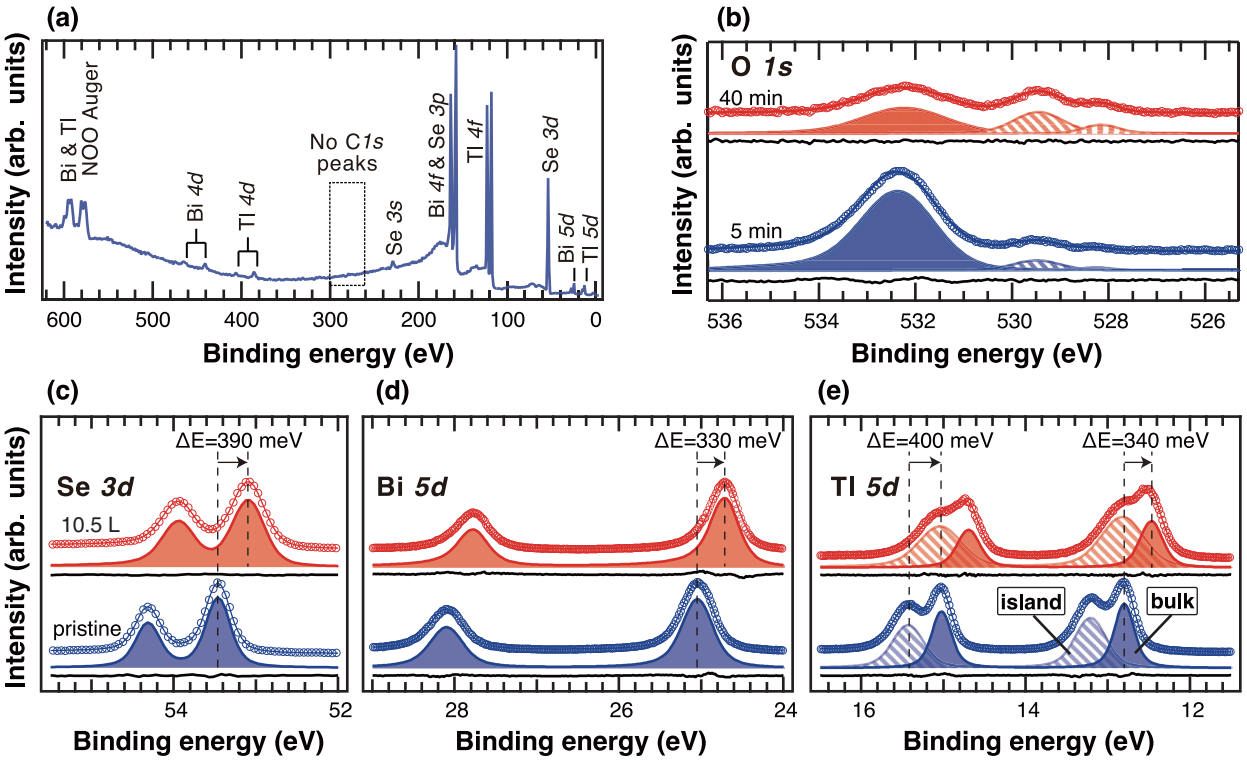

FIG. 4. (a) Core-level spectrum of a pristine $TlBiSe_2$ obtained with $h\nu = 680$ eV. (b) O 1*s* core level measured 5 and 40 min after starting the photo irradiation with $h\nu = 750$ eV under a partial H_2O pressure of 5×10^{-8} Pa. (c), (d), and (e) show the Se 3*d*, Bi 5*d*, and Tl 5*d* core levels of a pristine $TlBiSe_2$ and a hole-doped $TlBiSe_2$ by 10.5 L H_2O exposure and $h\nu = 100$ eV light irradiation. The open circles on (b)–(e) are the experimental data, and the lines overlapping the circles are the fitting result. The areas indicated by different hatching are the components used in the fitting procedure. The shaded components in (b) represent the chemisorbed oxygen, and those in (e) are the components from Tl forming islands. The black line under each spectrum is the residue

larger than that of the DP shift, and the widths of these two core levels become broader after photo-induced hole doping. The larger shift and broadening of the Se 3*d* and island-Tl 5*d* core levels indicate the coexistence of band bending and presence of positively charged Se and Tl atoms, and therefore the adsorption of O species to the outermost atoms.

In the case of Bi_2Se_3, the saturated E_{DP} is reported to change significantly when changing the photon energy from $h\nu = 40$ to 60 eV, indicating the necessity of exciting the core level of the element of the outermost layer, i.e., the Se 3*d* core level. Unlike Bi_2Se_3, however, there are two elements as the outermost atoms in the case of $TlBiSe_2$, i.e., Tl and Se as shown in Fig. 1, and as mentioned above both outermost elements are oxidized. In order to determine the mechanism, especially the trigger of photo-induced doping on $TlBiSe_2$, we have measured the E_{DP} shift using different $h\nu$. $h\nu = 20$, 35, and 100 eV are used by considering the E_Bs of the shallow core levels of Tl, Bi, and Se. Figure 5 shows the Dirac cone obtained after irradiating an approximately 5-L H_2O exposed $TlBiSe_2$ using $h\nu = 20$, 35, and 100 eV for 30 min, i.e., until the saturation of E_{DP}. As shown in Figs. 5(a) and 5(b), the DP shows only a small E_B shift of 40 meV and 70 meV from the pristine sample when using $h\nu = 20$ and 35 eV, while the shift is much larger, 270 meV, in the case of using $h\nu = 100$ eV. Since the E_{DP} shift was approximately 75 meV when irradiating a 10-L H_2O exposed sample using $h\nu = 20$ and 35 eV, no further shift can be expected at higher H_2O exposure using these photon energies. We therefore conclude that exciting the Se 3*d* core level is essential for photo-induced doping the $TlBiSe_2$ as the case of Bi_2Se_3 [14]. In other words, the excitation of the Se 3*d* core level is the main trigger for photo-induced doping on $TlBiSe_2$ as well.

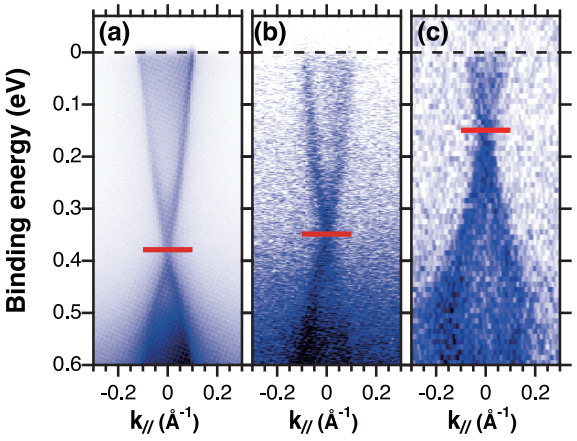

FIG. 5. Photon energy dependent E_{DP} shift. (a) and (b) were obtained after irradiating a 5-L H_2O exposed $TlBiSe_2$ with light of $h\nu = 20$ eV, 35 eV for 30 min. (c) was obtained after irradiating a 4.5 L H_2O exposed $TlBiSe_2$ with light of $h\nu = 100$ eV for 30 min.

Together with the necessity of exciting the Se 3d core level of Bi_2Se_3 covered with H_2O, the presence of C atoms, which positively charge the surface, was reported to be the key for photo-induce hole doping the Bi_2Se_3 [14]. However, as shown in Fig. 4(a), no signal from C was detected in the present case. Due to the difference in electron negativities of Tl and Se, the presence of Tl islands, which means the loss of half of the Tl bonded to Se, leads to slightly positive charged surface Se atoms, and thus renders the effect of carbon adsorption on Bi_2Se_3 unnecessary. This means that there is one process less in the case of photo-induced doping $TlBiSe_2$ compared to the case of Bi_2Se_3.

Finally, we discuss the charge carrier induced by the present doping process. Although it is difficult to discuss the change in carrier density inside the bulk, the carrier induced at the surface can be discussed based on the change in Fermi wave vector of the Dirac cone [32]. That is, by assuming the shape of Fermi surface to be circular, the surface carrier density can be expressed as $Ns = {k_F}^2/2\pi$, where N_s is the surface carrier density and k_F is the Fermi wave vector. This equation leads to a surface carrier density of $2.1 \times 10^{13}\,\mathrm{cm}^{-2}$ for the pristine $TlBiSe_2$ and of $3.7 \times 10^{12}\,\mathrm{cm}^{-2}$ for the $TlBiSe_2$ exposed to H_2O and irradiated with photon with $h\nu = 100$ eV for 172 min. These values indicate that a hole density of $1.7 \times 10^{13}\,\mathrm{cm}^{-2}$ was injected to the surface for making the bulk of $TlBiSe_2$ insulating, and $2.1 \times 10^{13}\,\mathrm{cm}^{-2}$ for making p-type $TlBiSe_2$. Furthermore, by assuming the injection of one hole per one adsorbate, the hole density suggests the $TlBiSe_2$ surface to be covered by approximately 0.033 ML of chemisorbed O species when the Dirac point reaches the Fermi level. (This coverage is much smaller than that expected from the dosage of H_2O, and thus suggests that most physisorbed H2O desorbs from the surface by photostimulation.)

IV. CONCLUSIONS

In conclusion, we have performed time- and dosage-dependent PES study using different photon energy to understand the mechanism of photo-induced doping $TlBiSe_2$, a doping method originally found on Bi_2Se_3. By combining H_2O adsorption and photo-irradiation with a photon energy high enough to excite the Se 3d core level, we succeeded to achieve both n-type and p-type bulk insulating $TlBiSe_2$. Since the doping occurs only at spots where photons were irradiated, this doping method can be used as photolithography, and therefore suggests the possibility of realizing a topological p-n junction by tuning the irradiation time. Furthermore, the present result suggests the universality of the photo-induced doping method in topological insulators containing chalcogen atoms, and the potential of tuning other thallium-based topological insulators such as $TlBi_xSb_{1-x}Te_2$ [26,33] and magnetic topological insulators [34] as well.

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