Gap-like feature observed in the non-magnetic topological insulators

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Abstract

Non-magnetic gap at the Dirac point of topological insulators remains an open question in the
field. Here, we present angle-resolved photoemission spectroscopy experiments performed on
Cr-doped Bi_2Se_3 and showed that the Dirac point is progressively buried by the bulk bands and
a low spectral weight region in the vicinity of the Dirac point appears. These two mechanisms
lead to spectral weight suppression region being mistakenly identified as an energy gap in
earlier studies. We further calculated the band structure and found that the original Dirac point
splits into two nodes due to the impurity resonant states and the energy separation between the
nodes is the low density of state region which appears to be like an energy gap in potoemission
experiments. We supported our arguments by presenting photoemission experiments carried
out with on- and off- resonant photon energies. Our observation resolves the widely debated
questions of apparent energy gap opening at the Dirac point without long range ferromagnetic
order in topological insulators.

Keywords: topological insulators, time reversal symmetry, ARPES

S Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

In topological insulators (TIs), the surface states are protected against non-magnetic perturbations by time reversal symmetry (TRS) [1, 2]. These surface states have helical spin texture and disperse linearly with respect to energy forming the well know Dirac point (DP). Majority of the work in the field concerns the breaking of TRS by a net out-of-plane magnetic moment to open an energy gap at the DP to drive a TI into quantum anomalous Hall state which can be achieved by doping magnetic impurities into the bulk [3–8]. Ambiguously, many angle resolved photoemission spectroscopy (ARPES) experiments reported the existence of a large energy gap ($>$100 meV) in Mn-, V-, and Cr-doped Bi_2Se_3 far above the ferromagnetic transition temperature (T_c) [9–11]. This violates the fundamental theory of TIs which asserts the robustness of the gapless Dirac cone in the non-magnetic state. In theory, impurity resonant states were proposed to be responsible for

such modification of the local electronic structure and the non-magnetic gap at the DP [12–21]. At present, however, the debate about exact nature of the non-magnetic gap continues due to the lack of photoemission experiments addressing the appearance of an energy gap in photoemission experiments without ferromagnetic order, which is inconsistency is still awaiting to be experimentally resolved.

Here, we present a schematic ARPES and tight binding model calculation in Cr-doped Bi_2Se_3 with varied thickness and show that the gap is not due to the magnetization but it is derived from the impurity resonant states which splits the original DP into the two nodes apart from each other by $>$100 meV. Lifetime broadening due to the low crystal quality induced by Cr-incorporation into the bulk leads nodes and the surface states to be buried by the bulk bands. This give rise to misinterpreting the energy separation between the two nodes

as a magnetic gap. We confirmed our results by performing ARPES experiments on high crystal quality films with on- and off-resonant photon energies.

One of the obstacle in earlier works is the dramatic lifetime broadening of the surface states upon impurity deposition into the bulk [13, 22, 23]. This prevents monitoring the evolution of the surface states across the emergence of the gap. As a distinct approach, we grow Cr-doped Bi_2Se_3 on the surface of pristine Bi_2Se_3 samples rather than on a insulating substrate paving a new way to trace the energy bands across the formation of the gap feature. This method subsequently promoted the crystal quality and gave well resolved bulk and surface states in our ARPES experiments. Our method and findings offer a new strategy to study interaction between magnetic impurities and the surface states of TIs and sufficient experimental and theoretical explanation for the non-magnetic gap in TIs.

In our work, we used molecular beam epitaxy (MBE) method to prepare thin films with high crystal quality. Pristine Bi_2Se_3 films were first deposited on Al_2O_3 (0 0 0 1) substrates. Then, Cr-doped Bi_2Se_3 films were grown on 12 quintuple layer (QL) Bi_2Se_3 films at 225 °C. Thickness dependent ARPES experiments were done in a vacuum interlocked MBE-photoemission chamber occupied with a Scienta SES100 electron analyzer and He discharge lamp generating He I-α (21.2 eV) at the surface science labratory of the University of Connecticut. The base pressure in the photoemission chamber was 1×10^{-10} torr and the samples were at the room temperature during ARPES experiment. Binding energies and the size of the gap feature is estimated with a 10 meV error bar. Photon energy dependent high resolution ARPES experiments were done at 21ID-I ESM beamline of National Synchrotron Light Source II (NSLS-II) by using synchrotron radiation and DA30 Scienta electron analyzer at 10 K and with total experimental resolution better than 10 meV. The pressure in the photoemission chamber was kept at 1×10^{-11} torr during the ARPES experiments.

In theoretical calculations, we consider a 5 QL thin film of Bi_2Se_3 with non-magnetic impurities substituting Bi on the surface. Due to computational limitations, we do not aim to model quantitatively the experimental system consisting of a doped TI thin film grown on top of a pristine 12 QL film. Instead, we use a model of a thin film with surface doping to qualitatively describe the impurity resonant states observed in the experiment. Note that our mode applies in the regime when the resonance overlaps with the Dirac point and leads to the appearance of the gap-like feature in the spectral function, which happens in 5–7 QL thin films. We do not consider ultrathin films of 1–3 QLs which are characterized by gapped Dirac states. For modeling of the electronic structure of Bi_2Se_3 we employ the sp^3 TB model with Slater–Koster parameters obtained by Kobayashi [26–28] by fitting to bulk band structures calculated with density functional theory (DFT). Interactions between atoms in the same atomic layer and between atoms in first and second nearest-neighbor layers are included. Spin–orbit interaction with strength λ is incorporated in the intra-atomic matrix elements. For surface calculations, we consider a slab consisting of 5 QL and we use the

same Slater–Koster parameters obtained by Kobayashi [26]. To model the effect of doing, we use a supercell approach in which we consider a 3×3 surface supercell with one impurity atom per supercell. Furthermore, we use a simplified model in which the non-magnetic impurity is described by an on-site potential U. More specifically, the impurity is treated as a host atom (Bi in this case since Cr substitutes Bi), whose s- and p-orbitals are modified by an additional on-site potential U uniform for all orbitals. Since we are interested in the effect of Cr doping above the ordering temperature, we neglect the magnetic part of the impurity potential in the calculations. The energy at which the impurity resonance occurs is controlled by the parameter U. Although the position of the resonance is fixed in a real material, in the present experiment the binding energy at which DP appears changes with increasing the film thickness. Therefore, it is possible that the impurity resonance states overlaps with DP, leading to the appearance of the gap-like feature. In order to address precisely this situation, we change the value of U to move the impurity resonance across the DP. The resulting TB band structures are qualitatively similar to DFT band structures where impurity states appear as localized bands at certain energy with respect to DP (see [28]). For the results presented in the current work, we choose the value $U = 6$ eV since it produces the impurity resonance at the DP to provide a plausible explanation for the appearance of the gap-like feature observed in our experiments.

Figure 1 gives ARPES maps of the $Bi_{1.95}Cr_{0.05}Se_3$ films for different thicknesses deposited on the surface of 12 QL pristine Bi_2Se_3 films. A 1 QL $Bi_{1.95}Cr_{0.05}Se_3$ film does not exhibit an electronic structure different from a pristine Bi_2Se_3 film in terms of the gapless surface states. The prominent difference between the two cases is that the DP is observed at the higher binding energy of -254 meV in 1 QL $Bi_{1.95}Cr_{0.05}Se_3$/12 QL Bi_2Se_3. Increasing $Bi_{1.95}Cr_{0.05}Se_3$ thickness to 3 QL results in the DP appearing even at a higher binding energy of -285 meV and two sharp quantum-well states which appear at -105 meV (E2) and -190 meV (E1). These quantum-well states have been observed in adsorbate-covered Bi_2Se_3 and its origin is attributed to the downward bending of the bands near the surface [29]. The films with thickness up to 3 QL do not exhibit a clear gap feature at or around the DP, yet. Here, the observation of the gapless surface states and the well-separated E1 and E2 are notably different than the corresponding $Bi_{1.95}Cr_{0.05}Se_3$ films grown directly on an Al_2O_3 (0 0 0 1) substrate (see supplementary figure 1 (stacks.iop.org/ JPhysCM/32/145503/mmedia)). Increasing the $Bi_{1.95}Cr_{0.05}Se_3$ film thickness to 5 QL leads to appearance of 40 meV wide spectral weight suppression (SWS) region resembling an energy gap marked with two solid red lines in figure 1. In our earlier work, we showed that the T_c of the Cr-doped Bi_2Se_3 is about 10 K with a 1.3 μ_B for out of plane orientation [32]. Therefore, a magnetic gap opening at the DP is not expected at room temperature. It should be also noted that the bulk band-gap has not vanished indicating the absence of a topological phase transition (see supplementary figure 2). Furthermore, another sharp state also appears just 55 meV above E2 for 5 QL film. For the thicker films, the energy bands experience significant lifetime broadening and they cannot be well-resolved
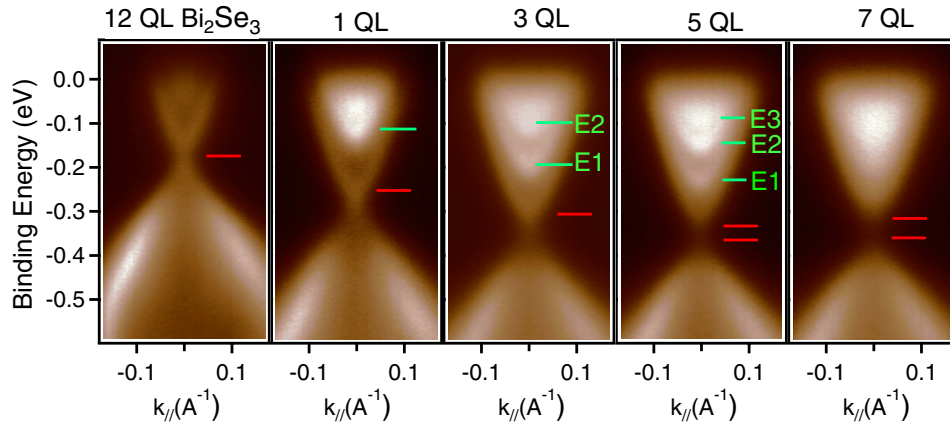
Figure 1. ARPES maps of $Bi_{1.95}Cr_{0.05}Se_3$ films with different thicknesses grown on the 12 QL Bi_2Se_3 films. Thicknesses of the $Bi_{1.95}Cr_{0.05}Se_3$ films are given above the images. Green and the red lines represent bulk states of E1–E3 and the gap feature, respectively. ARPES maps were collected at room temperature with a He I-α (21.2 eV).

in the 7 QL film. Therefore, increasing the $Bi_{1.95}Cr_{0.05}Se_3$ film thickness has a strong impact on the electronic structure which leads to a strong overlap of bulk and surface states along with the appearance of a gap feature. The correlation between the apparent gap and the thickness is indeed the consequence of the progressive overlapping of the impurity resonant states and the DP. We will further discuss in the proceeding section that the gap-like feature appears in the spectra once the DP shifts to the vicinity of the impurity states.

To closely examine the appearance of the gap feature at or around the DP seen in ARPES maps, we present energy dispersive curves (EDC) obtained along the $k_{\parallel} = 0$ A^{-1} for different thicknesses of the Cr-doped Bi_2Se_3 films in figure 2(a). To avoid confusion, we marked the lowest intensity points just below the DP with cyan colored lines for the 1 QL, 2 QL, and 3 QL films in order to trace where the gap feature starts to appear. Here, the DP is identified from ARPES maps as convergence point of linearly dispersing surface states at $k_{\parallel} = 0$ A^{-1} in figure 1. For pristine Bi_2Se_3, the DP exhibits a sharp peak located at a binding energy of -165 meV marked with a red line. With increasing $Bi_{1.95}Cr_{0.05}Se_3$ film thickness, the DP appears at a higher binding energy. It can be also seen that the E1 moves to higher binding energies even more rapidly with increasing film thickness and gets closer to the DP. However, the spectral intensity of the DP does not exhibit any dramatic change indicating that the gap feature appears below the DP. With increasing film thickness, the DP, E1, and E2 strongly overlap especially for 7 QL and thicker films. This leads to the DP becoming buried by the bulk bands which obstructs its observation of it in the EDCs taken from the thicker films. In the films directly grown on the substrates, however, this trend cannot be resolved due to the rapid lifetime broadening of the energy states. In previous studies, this led to the conclusion that the DP is destroyed even in the non-magnetic state. Both the overlapping of the DP with E1 and the SWS just below the DP lead to treating the gap feature as a magnetic energy gap in ARPES measurements. Hence, our observations provide an experimental evidence that the large gap feature observed in the ARPES maps is a consequence of the SWS taking place just below the DP and broadening of energy bands. We also

obtained similar results for higher Cr-content and presented in supplementary figures 5–7. To visualize the emergence of relative SWS below the DP, we plotted the changes of DP, E1, and E2 as a function of the $Bi_{1.95}Cr_{0.05}Se_3$ film thickness by selecting narrow slices around the Γ (0 0 0) point in figure 2(b). In the regime from 1 QL to 6 QL, the E1 (dotted black line) and the DP (dotted pink line) are well separated from each other. Above 6 QL, these two states start to overlap leading to spectral region (between green dotted lines) appear as an energy gap in ARPES maps. Furthermore, the DOS within this spectral region is far from zero even though ARPES maps suggest the appearance of the gap feature which is in the line with recent experimental findings [13, 24, 25].

Furthermore, in figures 3(a)–(c), EDCs are given for the 3 QL, 6 QL, and 8 QL films with Gaussian fitted peaks are given to demonstrate the overlapping progression. In the 3 QL film, the DP (red fitting line) and E1 (green fitting line) are well separated in energy. With increasing thickness E1 peak exhibits lifetime broadening and at 8 QL it almost fully masks the DP. This leads the low density of the states in the spectrum that appears as if a large energy gap opened at the DP in ARPES maps.

In order to shed light on the possible origin of the gap feature observed in these measurements, we use a tight-binding model for doped Bi_2Se_3 films [26–28]. To be in the line with the experiment, M is set to be 0 since ARPES maps were recorded at temperatures well above the T_c of Cr-doped Bi_2Se_3 [30]. In figure 4(a), the band structure of a pristine sample for only top surface states is presented and it exhibits gapless feature as expected. The presence of Cr impurities, however, leads to impurity resonant states that appear as nearly flat bands in the calculated electronic band structures (see figure 4(b) and supplementary figure 8). Our calculations show that the electronic states near the DP are dramatically modified when the impurity resonant falls in the vicinity of the original DP of the pristine slab. This is demonstrated in figure 4(b) which shows the band structure for the slab doped with non-magnetic impurities with $U = 6$ eV. In this case, a flat impurity bands extend just below the DP. The segment of the electronic states between the energy just below the top
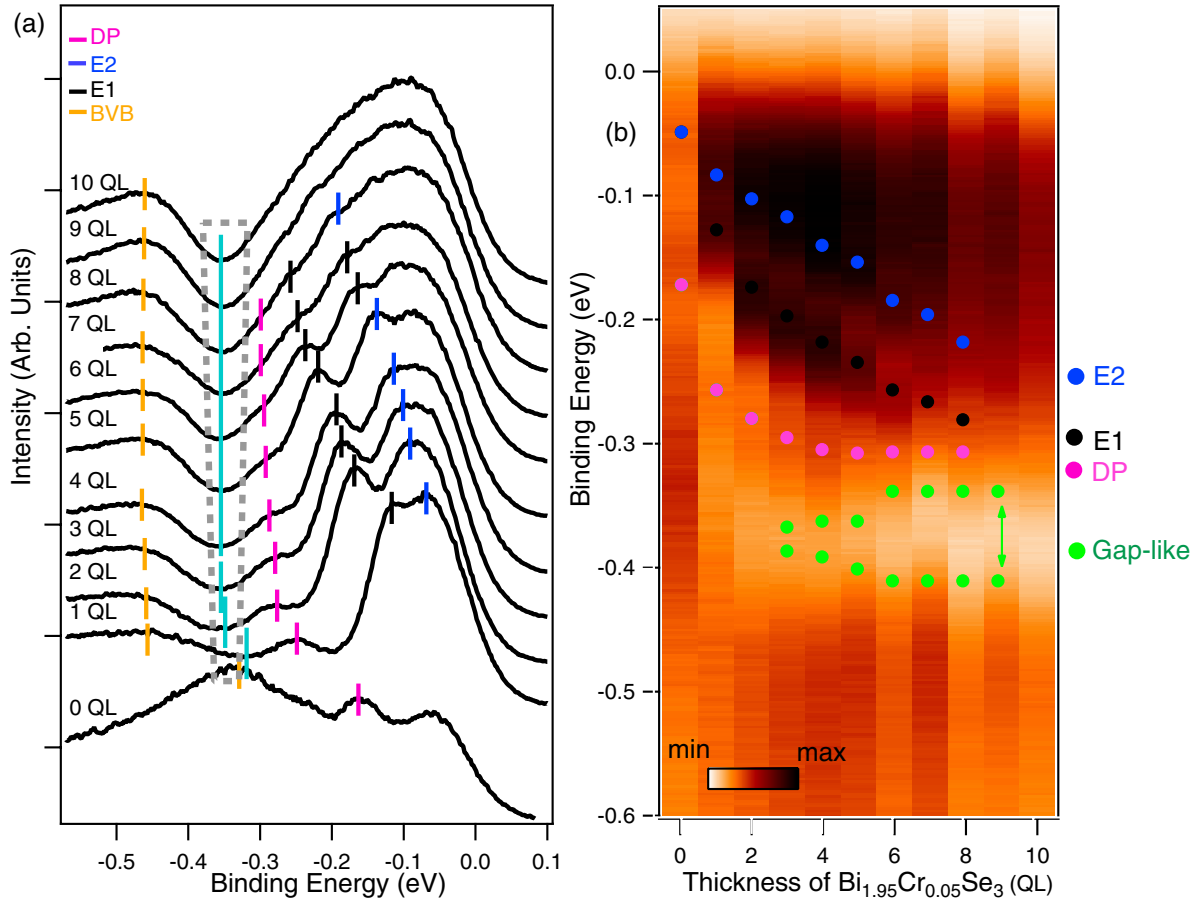
Figure 2. (a) EDC for different thicknesses of $Bi_{1.95}Cr_{0.05}Se_3$ on pristine Bi_2Se_3 along the $k_\parallel = 0\ \text{Å}^{-1}$ in figure 1. Dashed gray rectangular area represents the gap region. pink, black, and blue lines represent the DP, E1, and E2, respectively. Orange lines are the bulk valance band (BVB) high intensity points. Low intensity point of the gap feature is indicated with cyan line. Full set of ARPES maps can be found in supplementary figure 3. (b) Dispersion of the bulk and the surface states as a function of the thickness.
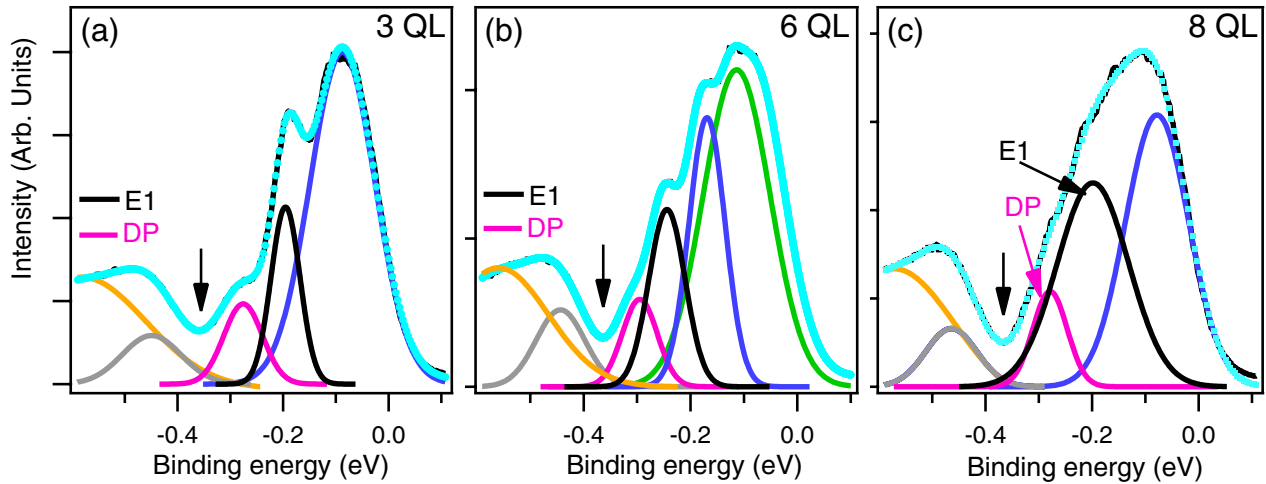

Figure 3. (a)–(c) EDC for the 3-6-8 QL $Bi_{1.95}Cr_{0.05}Se_3$ films with fitting lines. Black arrows show the low-intensity points within the gap feature. Pink and black fitting lines are the DP and E1, respectively. Blue and green fitting lines are the bulk bands and gray fitting line represents the lower surface state of the gapped Dirac cone (see figure 4).

Dirac point (upper dashed line in figure 4(b)) and the second band crossing (lower dashed line in figure 4(b)) would appear as a gap in the ARPES spectra. Remarkably, the energy separation is about 100 meV between the two dashed lines which is in excellent agreement with the experimentally claimed

gap size. Hence, we believe that this is the feature consistent with the gap feature observed in Cr-doped Bi_2Se_3 films as discussed above. Therefore, the modification of the electronic states due to impurity resonant at the Dirac point can provide the explanation for the observed gap feature in the similar
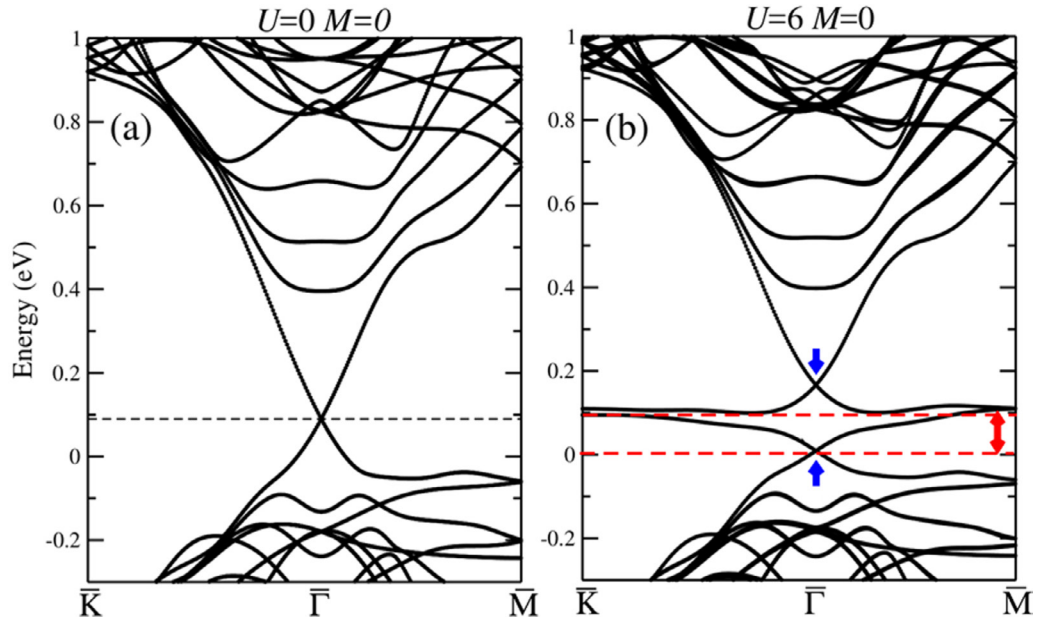
Figure 4. Calculated band structures of a Bi_2Se_3 thin film: (a) pristine structure, (b) potential impurity with $U = 6\,eV$ and $M = 0$. Horizontal dashed line in (a) marks the position of the Dirac point. In panel (b), only the top Dirac states are shown since the bottom surface states are unaffected by the dopants. Horizontal dashed lines in (b) mark the energy region where the gap feature appears. The vertical red arrow in (b) demonstrates the gap feature.
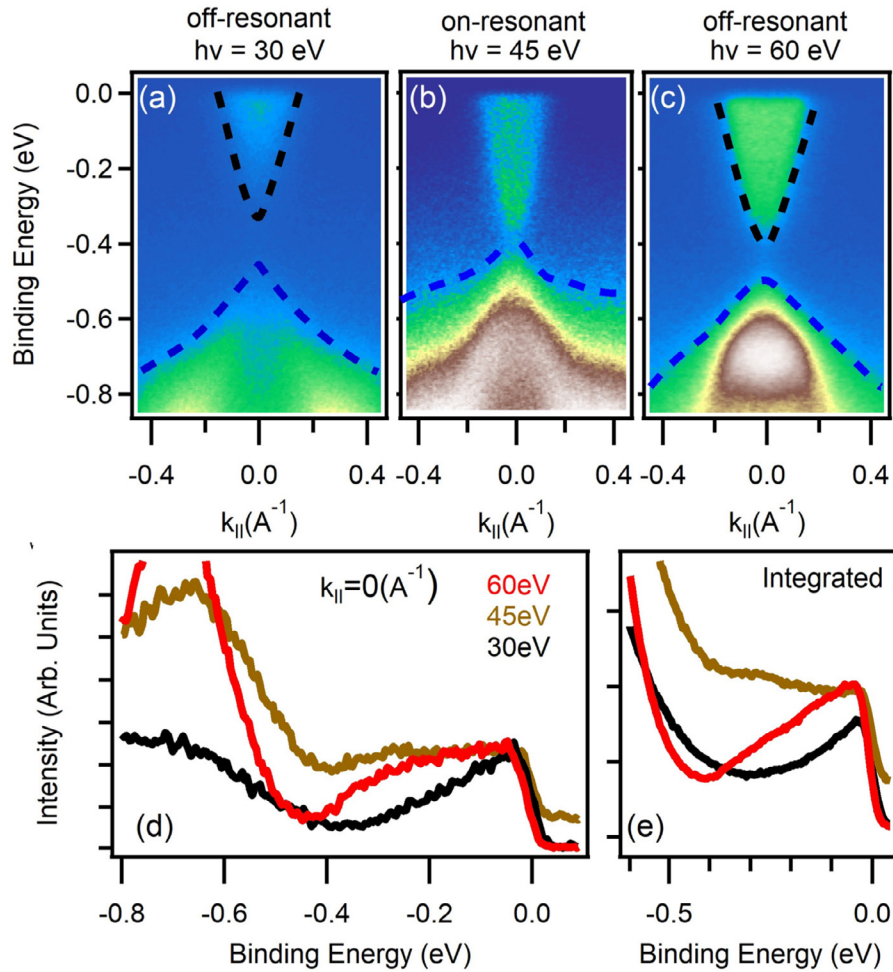

Figure 5. (a)–(c) ARPES spectra of 3 QL $Bi_{1.78}Cr_{0.22}Se_3$ on a 12 QL Bi_2Se_3 taken with 30 eV, 45 eV, and 60 eV photons. (d) Corresponding EDCs taken along the $k_\| = 0\,A^{-1}$. (e) Integrated EDCs within $k_\| = \mp0.45\,A^{-1}$. Dashed black and blue lines are to guide eyes.

systems as well. Our calculation also explains the appearance of the obvious gap feature in the thicker films. The DP shifts to the higher binding energy with increasing thickness of $Bi_{1.95}Cr_{0.05}Se_3$ sample. Therefore, it is most likely that the DP overlaps stronger with the impurity resonant states leading to observation of a clear gap feature at thicker $Bi_{1.95}Cr_{0.05}Se_3$ films. However, in few QL of $Bi_{1.95}Cr_{0.05}Se_3$ sample, ARPES map exhibits gapless Dirac like dispersion due to the well separated DPs and the impurity resonant states.

Resolving the impurity states and the nodes in the ARPES experiments will be challenging due to the broader and weak spectral nature of the states, especially for the low concentration as adopted in this study. Nevertheless, these states will contribute spectral weight in the vicinity of the original DP which can be realized by performing ARPES experiments with on-and off-resonant photon energies. The resonant photoemission process is based on photoexcition of a core level electron to the empty state between the Fermi level and Vacuum level. The relaxation of the photoexcited electron leads to enhance the photoemission intensity of the Cr d states. Therefore, the photon energy is in close proximity to the binding energy of the core level [31]. Therefore, in figures 5(a)–(c) we presented ARPES maps of a 3 QL $Bi_{1.78}Cr_{0.22}Se_3$ film grown on a 12 QL Bi_2Se_3 obtained with 30 eV and 60 eV (off-resonant), and 45 eV (on-resonant) photons collected at 10 K with synchrotron radiation. At 30 eV photon energy, a large apparent energy gap within the dashed black and blue lines can be seen in the spectrum. At resonant photon energy of 45 eV, however, gap shrinks in the spectrum due to the spectral contribution of the impurity resonant states. Once the photon energy is increased away from the resonant photon energy, gap-like feature reappears in the spectrum taken with 60 eV photons (figure 5(c)). This directly indicates that the gap-like feature between the dashed blue and black lines is the consequence of the spectral modification of the DP by the impurity resonant states. We can further confirm the presence of the resonant states by the observation the flatter band edge marked with dashed blue line in figure 5(b) at resonant photon energy which is expected feature of the impurity resonant states. Furthermore, in figure 5(d), we presented EDCs along the $k_{\parallel} = 0$ A^{-1} for each photon energies to better visualize the spectral changes in the vicinity of the apparent gap with changing photon energy from off- to on-resonant. It is clear that relative spectral weight within the claimed gap increases with tuning photon energy to on-resonant. Particularly, at 45 eV photon energy, the apparent gap almost disappears. Increasing spectral weight in the vicinity of the gap-like feature for resonant photon energy is more obvious in the EDC integrated within $k_{\parallel} = \pm 0.45$ A^{-1} in which no measurable gap is present in the EDC taken with 45 eV resonant photon energy (figure 5(e)). This observation provides strong evidence that the DP is strongly modified by the impurity resonant states. By even tuning the photon energies, the claimed gap can be as large as 100 meV for 30 eV photons while no observable gap is present in the ARPES map for 45 eV photon energy.

In summary, we have carried out a series of photoemission measurements on Cr-doped Bi_2Se_3 films deposited on pristine Bi_2Se_3 samples in order to explain a long-puzzling observation

of the gap opening at the DP without the presence of long range ferromagnetic order. Our spectroscopic study revealed that claimed magnetic gap is the energy region between the two nodes formed as a result of the modified DP by impurity resonant states. We supported our finding by theoretical calculations and angle resolved photoemission spectroscopy by using ultra high quality thin film materials and variety of photon energies. In particular, our photoemission spectroscopy with on- and off-resonant photon energies showed the modified spectral region by the impurity resonant states. We also clarified why the earlier studies claimed that the feature was a magnetic gap by stating that the overlapping of the bulk bands and surface states as a consequence of doping induced strong lifetime broadening leads to the mistaken identification of energy difference between the two nodes as a magnetic energy gap. We believe that this observation can clear up many misinterpretations involving ARPES experiments performed in TIs and pave the way for further studies regarding the breaking of TRS.

Acknowledgments

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