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Electron dynamics of unoccupied states in topological insulators

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ABSTRACT

The topological insulators Bi_2Se_3 and Bi_2Te_2Se have been shown to possess unoccupied topological surface states at the center of the surface Brillouin zone at energies around 1.3 eV above the Fermi level. Using time-resolved two-photon photoemission we study the electron dynamics of the unoccupied topological surface states, image-potential states and conduction bands on these surfaces.

1. Introduction

Topological insulators are semiconducting as bulk materials and metallic at the surface. This is due to topological surface states with a linear dispersion of energy versus momentum parallel to the surface. The states on this Dirac cone are spin-polarized and spin and momentum are intrinsically locked [1,2]. Such properties have the prospect for application in spintronics. Bismuth chalcogenides are known to have topological surface states and their dispersion and spin polarization has been studied by angle-resolved two-photon photoemission [3,4]. The carrier dynamics of topological surface states is of particular interest because the spin structure prevents backscattering [5] and long lifetimes are expected [6]. Time- and angle-resolved photoelectron spectroscopy has been performed for several bismuth chalcogenides [7–11]. The *n*-doping of bismuth chalcogenides prevents the study of the electron dynamics of the topological surface states on the Dirac cone by pump-probe techniques such as time-resolved two-photon photoemission (2PPE). This can be overcome by *p*-doping with foreign dopant atoms such as Mg [7] or by choosing different materials in the antimony telluride class like $SnSb_2Te_4$ [12].

It has recently been found that surfaces of bismuth chalcogenides Bi_2Se_3, Bi_2Te_2Se, and Bi_2Te_3 possess additional unoccupied topological surface states at energies around 1.3 eV above the Fermi level [13]. The observed states were shown by 2PPE using circularly polarized light to be spin-polarized and were confirmed by band-structure calculations. The existence of such states was also predicted for topological insulators with more complex structure and composition $SnSb_2Te_4$ [12], $PbSb_2Te_4$, and $Pb_2Bi_2Te_2S_3$ [14]. Fig. 1(a) shows the calculated band structure of Bi_2Se_3 with the shaded regions of the projected bulk band structure. The topological surface states are plotted in red and green to indicate the different spin orientation. The red arrows represent a 2PPE transition which proceeds from the bulk valence band to the unoccupied topological surface state, because optical transitions from the occupied topological surface state are allowed only between states of same spin orientation [13,15]. The 2PPE transition with the reversed sequence of the laser pulses is also allowed and proceeds via an image-potential state as indicated by the blue arrows in Fig. 1(a). These two pathways may be overlapping and can be distinguished by the photon energy dependence or time-resolved 2PPE [16].

In this work we present time-resolved 2PPE results for the unoccupied topological surface states on Bi_2Se_3 and Bi_2Te_2Se. The lifetimes are found to be relatively short due to the narrow band gap and the possibility of the electrons in the topological surface state to decay into the lower-lying conduction bands. For the same

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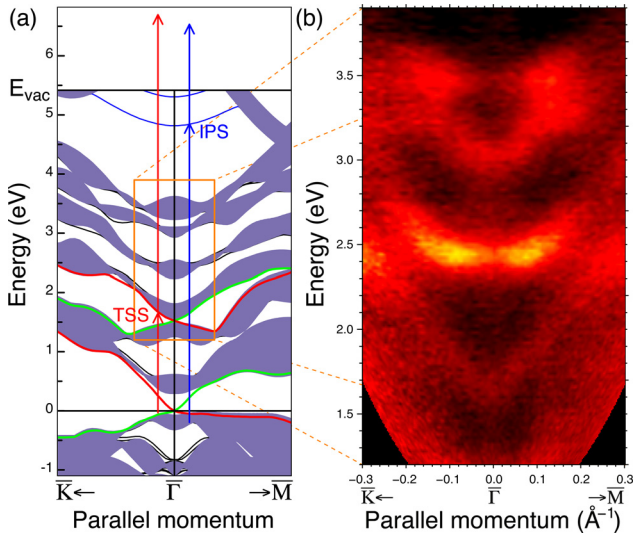

Fig. 1. (a) Band structure of Bi_2Se_3 with the occupied and unoccupied topological surface states marked in red and green. The blue parabolas show the image-potential states near the vacuum level E_{vac}. The arrows indicate the corresponding two-photon photoemission processes. (b) Monochromatic 2PPE results using UV photons (4.65 eV) for intermediate states in the area marked in (a) by an orange rectangle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

reason the lifetimes of the image-potential states are also rather short. After a short description of the experimental setup and procedures we report results on the unoccupied electronic states. The electron dynamics of the states are discussed in the main part of the paper.

2. Experiment

Angle-resolved monochromatic 2PPE experiments used the third harmonic (UV, 4.65 eV photon energy) of titanium:sapphire oscillators with pulse lengths downto 75 fs [17,18]. For bichromatic and time-resolved measurements the fundamental (IR, 1.55 eV photon energy) was added. The laser beams were *p*-polarized with an incidence angle of 45° unless stated otherwise. Circular polarization of the third harmonic necessary for circular dichroism experiments was obtained using a λ/4-waveplate. Two-dimensional momentum distribution patterns (MDCs) at constant kinetic energy were recorded using an ellipsoidal "display-type" analyzer at an energy and angular resolution of 50–100 meV and 3°, respectively [19]. Angle-resolved spectra for the intensity maps were acquired by a hemispherical analyzer with resolution of 34 meV and 1.6°, respectively [18]. Energies are given for intermediate states or as final-state energies when different excitation paths contribute to the spectra. In both cases energies are referred to the Fermi energy E_F.

Bi_2Te_2Se was prepared from mixtures of Bi_2Te_3 and Bi_2Se_3 synthesized from elementary Bi, Te, and Se of 99.999% purity. Crystals were grown in sealed quartz ampoules coated with a carbon layer. For recrystallization a vertical variant of the modified Bridgman method was used [20]. The resulting ingots consisted of one or several single-crystalline blocks and were stable to oxidation in air [21]. The samples were naturally *n*-doped with carrier concentrations in the range of $(1-9)\times10^{18}$ cm^{-3}. Samples were cleaved in vacuum at a pressure $<5\times10^{-6}$ Pa and then transferred to ultrahigh vacuum (pressure $<1\times10^{-8}$ Pa) where they were cooled to 90 K for measurements. Sample quality and orientation was checked by low-energy electron diffraction (LEED) showing a sharp threefold pattern. According to LEED patterns the samples were oriented with the laser beams incident parallel to the $\bar{\Gamma}\bar{M}$ mirror plane.

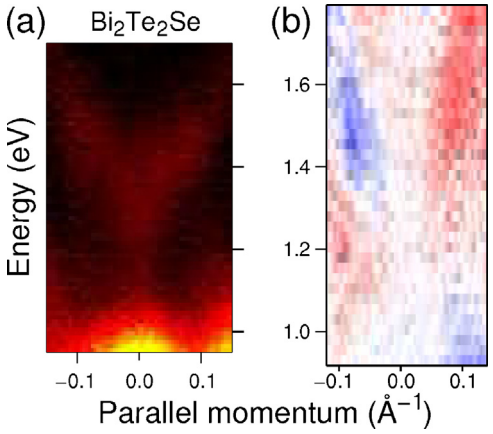

Fig. 2. (a) Two-photon photoemission and (b) circular dichroism from the unoccupied Dirac cone of Bi_2Te_2Se using UV photons (4.65 eV). The parallel momentum is perpendicular to the plane of light incidence.

The electronic structure calculations were performed within the density functional formalism and the details have been outlined in Ref. [13].

3. Results

3.1. Electronic band structure

Fig. 1(b) shows a 2PPE intensity map for Bi_2Se_3 excited with UV photons covering a large energy and momentum range. Five bands can be clearly identified and their dispersion agrees well with the calculated unoccupied conduction bands presented in Fig. 1(a). This proves that the 2PPE is dominated by the intermediate states of the unoccupied band structure. The occupied initial states have a minor influence and might be responsible for the intensity enhancements observed along the individual bands. Similar observations have been reported for Bi_2Te_2Se [13].

The unoccupied topological surface states are found around 1.3 eV near the $\bar{\Gamma}$ point ($k_{||}=0$) where a linear dispersion is observed [13]. This region has been investigated with higher energy resolution and bulk and surface bands were resolved [15]. In Fig. 2(a) we show the unoccupied topological surface state for Bi_2Te_2Se with its linear dispersion. The higher intensity at the bottom stems from the second conduction band. Note that the band structure of Bi_2Te_2Se [13] is very similar to the one of Bi_2Se_3 shown in Fig. 1(a). While Fig. 2(a) (and Fig. 1(b)) presents actually the sum of measurements with left and right circularly polarized light, the difference is shown in Fig. 2(b). This dichroism signal clearly shows the opposite sign between positive and negative parallel momenta. In addition the dichroism does not change along the two linear branches. At the crossing (Dirac) point the dichroism vanishes. The dichroism is a clear proof of spin polarization of the observed bands. This signal must come from topological surface states, because the bulk bands are not spin-polarized. Note that this holds also, when the 2PPE signal is dominated by emission from bulk bands overlapping the topological surface state.

In bichromatic 2PPE both photons can serve as pump and as probe pulse. Therefore, the energy of the intermediate state cannot be determined without additional information. Fig. 3 shows spectra from Bi_2Te_2Se in normal emission for different polarization of the UV and IR laser beams. In addition the monochromatic UV spectra are shown by dotted lines. These contributions are always present as a background in the bichromatic data, but are relevant only for *p*-polarized UV light. The peaks at 5.55 and 6.16 eV final-state energy are observed in the monochromatic and bichromatic spectra and must therefore be due to emission by the UV photon. The

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