The recently discovered topological insulators exhibit topologically protected metallic surface states which are interesting from the fundamental point of view and could be useful for various applications if an appropriate electronic gating can be realized. Our photoemission study of Cu-intercalated Bi$_2$Se$_3$ shows that the surface-state occupancy in this material can be tuned by changing the photon energy and understood as a photoemission-induced gating effect. Our finding provides an effective tool to investigate the new physics coming from the topological surface states and suggests intercalation as a recipe for synthesis of a material suitable for electronic applications.

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The conelike dispersion of surface states with a spin-degenerate Dirac cone, recently observed in photoemission experiments, is now considered as a hallmark of topological insulators. In this sense, the compound Bi$_2$Se$_3$ with single Dirac cone in the Brillouin zone can be considered as the most elementary in the rapidly growing family of topological insulators. This, together with their easily tunable charge carrier concentration by surface doping and realization of superconductivity with Cu intercalation, makes the Bi$_2$Se$_3$ class of materials the most promising for applications in spintronic and computing technologies. The main obstacle here is that, unlike graphene, the three-dimensional (3D) topological insulators cannot be easily tuned to the zero-carrier-density regime through standard electrical gating, although some successful attempts have already been reported. In this Rapid Communication, using ultralow-temperature synchrotron-based angle-resolved photoemission spectroscopy (ARPES) in a wide photon energy range from $h\nu=20$ to 110 eV, we report the observation of the photoemission-induced gating of Cu-intercalated Bi$_2$Se$_3$. This finding opens the possibility of exploring directly and on the same sample the effect of the surface-state occupancy on the low-energy electronic structure, as well as suggesting intercalation as a recipe for synthesis of topological insulators suitable for electronic applications.

Single crystals of Bi$_2$Se$_3$ and Cu$_{0.07}$Bi$_2$Se$_3$ were grown using the Bridgman method starting with high-purity Bi, Cu, and Se elements. Samples in the form of rectangles with typical dimensions of $5 \times 5 \times 1$ mm$^3$ were cut for measurements. According to energy-dispersive X-ray (EDX) analysis, the Bi$_2$Se$_3$ samples from different batches show different amounts of Se in the range 1%. The sample we measured by ARPES is characterized by typical metallic in-plane resistivity with $\rho_{10K}=0.3$ m$\Omega$ cm and $\rho_{300K}=0.5$ m$\Omega$ cm. The Cu-doped crystals, which exhibit a large photoinduced gating effect, have been characterized by EDX analysis as Cu$_{0.07}$Bi$_2$Se$_3$. They reveal much higher resistivity, as shown in Fig. 1, with a semiconductor-like upturn at low temperature (see the inset). The out-of-plane resistivity for the Cu-doped samples reveals purely semiconducting behavior, increasing monotonically with decreasing temperature from 10–18 m$\Omega$ cm at 300 K up to 7–38 $\Omega$ cm at 10 K. It is known that Cu doping of Bi$_2$Se$_3$ can be realized in two ways: (1) singly ionized interstitial Cu atoms, which go between Se or Bi layers, act as donors; (2) its substitutional defects on bismuth sites, which carry double negative charge, act as acceptors. Both the composition and resistivity data indicate that Cu, in the studied samples, appears mainly as interstitial atoms. Also, we observe an increase of the electronic occupation of the surface states in Cu$_{0.07}$Bi$_2$Se$_3$ compared to Bi$_2$Se$_3$, which is consistent with Cu intercalation.

ARPES experiments have been performed at the “13” beamline at BESSY, equipped with a SES 4000 analyzer and He cryomanipulator with the base temperature on the sample less than 1 K. The data are summarized in Fig. 2. The presented spectra were recorded along cuts through the center of the Brillouin zone close to the $\Gamma M$ direction. The band position was reproducible with 20 meV accuracy when measured at 1 K and under $8 \times 10^{-11}$ mbar pressure on the time scale of the experiment (about 6 h) as well as after keeping the cleaved sample at room temperature and at $2 \times 10^{-10}$ mbar for 34 h. This reproducibility can be seen even from the data presented. For example, the protocol for recording the spectra for Cu$_{0.07}$Bi$_2$Se$_3$ presented in Fig. 2(b) is the following: sample cleavage; $+2$ h 40 min; $50$ eV spectrum; $+40$ min; $33$ eV spectrum; $+2$ h 40 min; $20$ eV spectrum; $+1$ h; $100$ eV spectrum; $+1$ h; $30$ eV spectrum. One should note that for several Bi$_2$Se$_3$ samples measured at higher temperatures (10–30 K) we indeed observe a change in the binding energy of the Dirac point as a function of exposure time, about $30$ meV during 20 min, which is in agreement with other reports. However, the spectra are recovered when the position of the light spot on the sample surface is changed.

Figure 2 presents the two key observations: (1) The number of topological charge carriers depends on the excitation energy. (2) This dependence correlates with the total current of photoelectrons. The $h\nu$ dependence of the binding energy of the Dirac point, or, in other words, of the surface-state occupancy, can be seen on the raw ARPES spectra presented.
FIG. 1. (Color online) In-plane resistivity of the pure (black dashed line) and Cu intercalated (red solid line) Bi$_2$Se$_3$ crystals; the low-temperature region of the later is zoomed in the inset.

in Figs. 2(a) and 2(b) for pure Bi$_2$Se$_3$ and a Cu-intercalated sample, respectively. It is summarized in Fig. 2(c) for both samples in terms of the surface-state Fermi surface area. While the effect is weak for the pure crystal, it appears as a clearly detectable step at about 30 eV for Cu$_{0.07}$Bi$_2$Se$_3$. The error bars include both the accuracy of the estimation of the Fermi surface area and its detected variations during the experiment.

Taking into account the 2D nature of the surface states, the observation (1) is very surprising. Despite the earlier reported time shift of the surface states that was associated with band bending, the absence of essential $h\nu$ dependence of those states has been considered as a proof of their surface origin. Unlike the exposure-time-dependent band bending, the described effect is much larger (150 vs 50 meV) and perfectly reproducible. The observed $h\nu$ dependence also cannot be explained by possible three-dimensionality of the bands because it is monotonic rather than oscillating. Actually, the earlier conclusion about the surface-state origin of the Dirac cone dispersion was based on measurements in the low-excitation-energy range, 19–31 eV. So our result confirms the conclusion about two-dimensionality of the Dirac-cone-forming states on the basis of data from a much wider energy range.

Ruling out the three-dimensionality issue, it is natural to assume that the observed change of the electronic occupation of the surface states is caused by the photoemission process. Due to the discrete energy spectrum of electrons in atoms, the absorption of light and, consequently, the photoemission current from solids, exhibit a stairlike dependence on photon energy, with the steps, known as absorption edges, occurring at the binding energies of the core electrons plus the work

![Graph showing in-plane resistivity and Fermi surface area](image)

FIG. 2. (Color online) Excitation energy dependence of the surface-state occupancy. A weak decrease of the binding energy of the Dirac point in Bi$_2$Se$_3$ (a) is contrasted to a 150 meV steplike change in Cu$_{0.07}$Bi$_2$Se$_3$ (b). (c) The step at 30 eV in the surface-state occupancy, shown in units of the Fermi surface area, corresponds to the lowest photon energy enabling photoemission from Bi 5$d$ core levels and consequent manifold increase of the photocurrent [see underlying plot of integral density of states (DOS)].
The photovoltage effect on semiconducting surfaces and interfaces has been studied since the late 1940s, 18 and the surface photovoltage method has been used as an extensive source of surface and bulk information on various semiconductors and semiconductor interfaces19,20 but, despite the great body of work, a microscopic description of the effect and related band bending is missing. In this regard, ARPES studies of the topologically protected surface states can provide indispensable information for understanding the macroscopic parameters of the photovoltage effect, starting from the electronic band structure of the surface states. On the other hand, the observed effect is peculiar since we see no detectable shift of the Fermi level of the sample with respect to the Fermi level of the spectrometer, which would be expected for a semiconducting sample with a grounded Ohmic back contact20 (see Fig. 3). This can happen if some volume of the sample under the light spot is charged because of very low interlayer conductivity while the surface of the crystal remains neutral due to good conductivity of the topmost layer, which may be a consequence of a topological protection of the surface states3 or formation at the surface of a two-dimensional electron gas.21

In summary, we observed the effect of photoemission-induced gating of the topological surface states on Cu$_0$Bi$_2$Se$_3$ which may stimulate the use of topological insulators in electronics.5,9 The observed enhancement of the effect by Cu intercalation shows the way to control it from the material side. While the peculiarities caused by the presence of the topologically protected surface states have to be understood, the very fact that the photovoltage effect has been observed directly for a compound in which the surface state dispersion can be measured in detail and controlled opens the opportunity to study the microscopic mechanisms of surface photovoltage effects on semiconducting surfaces and interfaces.

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