Simultaneous Quantization of Bulk Conduction and Valence States through Adsorption of Nonmagnetic Impurities on Bi_2Se_3

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Exposing the (111) surface of the topological insulator Bi_2Se_3 to carbon monoxide results in strong shifts of the features observed in angle-resolved photoemission. The behavior is very similar to an often reported ‘‘aging’’ effect of the surface, and it is concluded that this aging is most likely due to the adsorption of rest gas molecules. The spectral changes are also similar to those recently reported in connection with the adsorption of the magnetic adatom Fe. All spectral changes can be explained by a simultaneous confinement of the conduction band and valence band states. This is possible only because of the unusual bulk electronic structure of Bi_2Se_3. The valence band quantization leads to spectral features which resemble those of a band gap opening at the Dirac point.

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The existence of stable, topologically protected metallic states on the surfaces of certain bulk insulators, combined with the many special properties of these surface states, is currently generating considerable interest in condensed matter physics [1,2]. One remarkable property is the spin texture of the surface states which prevents backscattering [3,4] such that the surface state electrons do not suffer localization by weak disorder [5,6] and one-dimensional edge states do not undergo any scattering [7]. However, these restrictions hold only as long as time-reversal symmetry is preserved, such that the introduction of a magnetic field or magnetic impurities should strongly alter the situation.

Angle-resolved photoemission spectroscopy (ARPES) is an ideal tool to study the metallic states on topological insulators as it is surface-sensitive and can give detailed information about the spectral function. ARPES experiments have, for instance, shown that topological insulators indeed support surface states with a Dirac-cone-like dispersion and a Fermi surface topology consistent with theoretical predictions [8,9]. Adding spin resolution has verified that the surface states have the expected spin texture [10,11]. The first material experimentally shown to be a topological insulator in this way was a disordered Bi-Sb alloy, but more recently most experiments have been performed on the prototypical materials Bi_2Se_3 and Bi_2Te_3, which have a simpler electronic structure (a single Dirac cone) and a substantially larger bulk band gap [9,12,13].

There are a number of important unresolved issues linked to the basic electronic structure of these materials. The first is an ‘‘aging’’ effect which typically takes place over several hours after obtaining a fresh surface by cleaving the crystals [11,14]. The aging manifests itself as an increasing downward bending of the bands and the eventual appearance of quantized two-dimensional states in the conduction band [15]. The origin of the effect is unclear, but a surface relaxation has been discussed as a possible reason [9,11].

Another open question is the effect of surface or bulk impurities on the surface electronic structure. Especially interesting are magnetic impurities, since these are expected to break time-reversal symmetry, thus opening channels for backscattering and localization of the electrons in the topological state. They can also give rise to a distinct spectroscopic signature which is an opening of a gap at the Dirac point (DP) of the topological state, i.e., the transition from massless to massive fermions. Such gap openings have indeed been observed for both bulk and surface impurities [16,17]. For nonmagnetic impurities, on the other hand, one would naively expect a mere doping effect and an increase of defect scattering, but distinct spectral changes in the vicinity of the DP have also been predicted recently [18].

In this Letter, we show that these two issues are closely related. The adsorption of carbon monoxide, a nonmagnetic molecule commonly present in the rest gas of a vacuum recipient, can induce a drastic modification of the surface electronic structure. It gives rise to a strong downward band bending, leading to the appearance of quantized conduction band (CB) states, a behavior very similar to the aforementioned aging effect. For strong band bending, not only the CB states but also the valence band (VB) states become quantized. This effect of *simultaneous* quantization in CB and VB is not known from any other semiconductor surface and can be explained by the unusual valence electronic structure of Bi_2Se_3. The quantization of the valence states in the vicinity of the DP can resemble a gap opening, and the spectral appearance of the CO-induced changes is very similar to that brought about by Fe adsorption [17].

ARPES experiments were performed on *in situ* cleaved single crystals of Bi_2Se_3 at the ASTRID synchrotron radiation facility. The bulk crystals were doped with calcium in order to bring the bulk Fermi level into the gap, very close to the surface state DP [19]. Photoemission spectra were measured with an angular resolution of 0.13° and a combined energy resolution better than 15 meV. Spectra were taken along the $\bar{K}\,\bar{\Gamma}\,\bar{K}$ azimuthal direction. The sample temperature was 65 K. CO was dosed at a partial pressure of 8×10^{-9} mbar while taking photoemission spectra until saturation was reached. The data shown for the CO uptake and the photon energy scan are merely a subset from much more extensive data sets. These complete data sets are provided as movies in the Supplemental Materials [20], along with more information on the adsorption process.

Figure 1 shows the evolution of the surface electronic structure as the crystal is exposed to CO. We first discuss the changes near the Fermi level and in the CB. Immediately after cleaving the sample, the DP is very close to the Fermi level at a binding energy of 46(5) meV. This uptake experiment was started about an hour after the cleave, and the DP had moved to a binding energy of 102(5) meV [see Fig. 1(a)]. Still, only the topological state is present at the Fermi surface. As the CO coverage increases, the DP moves rapidly to higher binding energies, indicative of an increasing band bending near the surface. Further states emerge at the Fermi level and move to higher binding energies [see Figs. 1(b) and 1(c)]. These states have been shown to be quantized subbands of the CB [15]. For a sufficiently strong band bending (or potential gradient), these quantum well states (QWS) show a considerable Rashba splitting [21]. The quantization effect can be simulated by assuming a Schottky model for the space charge region near the surface. The degree of band bending can then be determined by requiring the model to reproduce the number and approximate binding energies of the QWS that are in fact observed. The details of this calculation are available in the Supplemental Materials [20]. The resulting potential and the calculated QWS in the conduction band are given in Fig. 2(a).

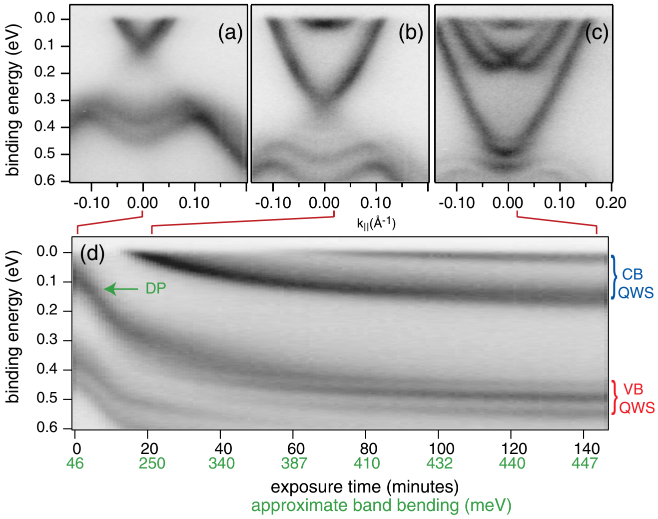

FIG. 1 (color online). ARPES spectra taken during the exposure of the surface to carbon monoxide ($h\nu = 16$ eV). (a)–(c) Photoemission intensity for different exposures as a function of binding energy and k vector parallel to the surface (dark corresponds to high intensity). (d) Cut through the center of the entire series of such images, illustrating the development of the different states with exposure time. The states marked in (d) are the conduction band and valence band quantum well states (CB QWS and VB QWS) as well as the Dirac point of the topological surface state (DP) [20].

The VB region is also affected by the CO adsorption. Immediately after cleaving, a single M-shaped state is observable in this region, but after a short time two such states can be identified, as in Fig. 1(a). The state with the higher binding energy has been assigned to a surface state in a projected band gap below the upper VB [for a band structure projection, see Fig. 2(b)] [15]. The state with the lower binding energy and the similar, well-separated features which appear for a higher CO coverage all fall in the energy region of the projected valence band. Below, we will argue that these are QWS formed in the VB. Figure 3 shows a high-coverage data set over a wider energy range and with better statistics. Because of the prominent QWS superimposed with the topological state, it is difficult to determine the exact position of the DP. Extrapolating the topological state's dispersion from low binding energy to high binding energy suggests that the DP falls somewhere between VB QWS. This is also consistent with the coverage-dependent positions of states shown in Fig. 1(d).

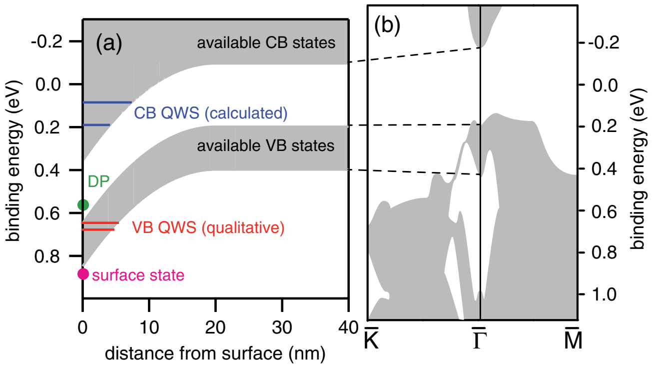

FIG. 2 (color online). (a) Semiquantitative model for the quantum confinement of the CB and VB states. The band bending corresponds to the value for the full coverage in Fig. 1. The width of the space charge layer has been estimated by requiring the presence of two calculated and occupied quantum well states in the CB with similar binding energies as observed experimentally. The position of the quantum-confined states in the VB is merely a qualitative sketch. (b) Projected band structure of Bi_2Se_3 adapted from Ref. [24], illustrating that the upper part of the VB is quite narrow (around 200 meV), such that the VB states can be confined for a band bending exceeding this value.

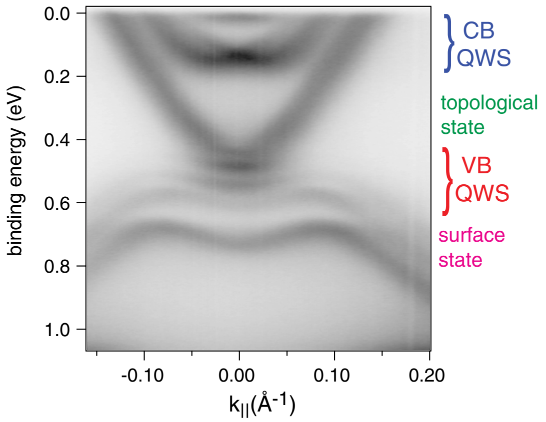

FIG. 3 (color online). Detailed ARPES spectrum of the valence band quantum well states for the full CO exposure reached in the end of the uptake in Fig. 1 ($h\nu = 16$ eV).

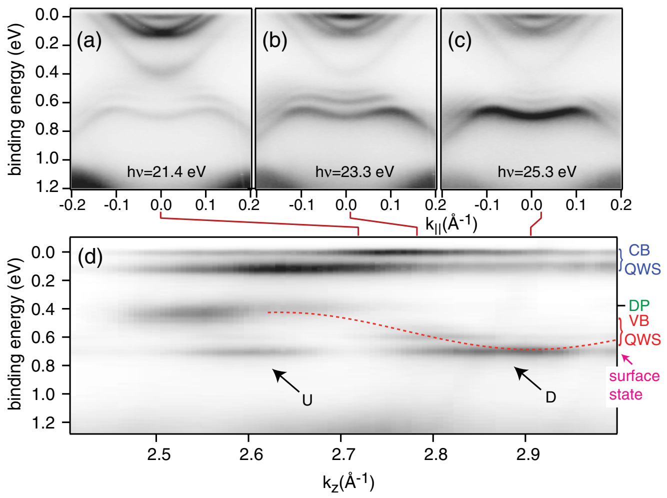

FIG. 4 (color online). Photon energy scan to probe the k_z dependence of the observed states. (a)–(c) Photoemission intensity for selected photon energies [20]. (d) Cut through the center of the entire series of such images, illustrating the dispersion of the states at normal emission. Neither the CB nor the VB QWS show any dispersion. The VB QWS closely track the dispersion of the VB which is observed in the absence of quantization, given here as a dashed line to guide the eye [15]. The branch marked D corresponds to the direct photoemission, while the branch marked U involves an umklapp process with a surface reciprocal lattice vector.

In the following, we argue that the M-shaped states in the VB do indeed arise from a quantization. Such a quantization is counterintuitive: While a downward band bending near the surface is expected to confine the CB states, an upward bending would be needed to confine the VB states [22,23], and thus a simultaneous confinement of both bands does not appear to be possible. Nevertheless, in the particular case of Bi_2Se_3, the simultaneous quantization of VB and CB states becomes possible because the top part of the VB exists only in a narrow energy region near the surface Brillouin zone center [13,24], as seen in the projected band structure in Fig. 2(b). The emergence of QWS in the VB can thus be understood as follows: The VB must undergo the same band bending as the CB, at least in the absence of effects like near-surface band shrinkage [25]. For a semiconductor with a wide VB, such a downward bending could not lead to the quantization of VB states. But for Bi_2Se_3 the total width of the upper VB is only around 200 meV [13,24]. This makes it possible to confine VB-derived states by the "rear side" of the conduction band, as indicated in Fig. 2(a). Unfortunately, it is not possible to calculate the energies of the VB quantum-confined states in the same simple manner as for the CB states, because the approximation of a constant effective mass breaks down [20].

It should be noted that the QWS are truly quantum-confined CB and VB states, not surface states. In particular, they do not lie in a (projected) band gap but within the CB or VB. It is thus clear that no special topological significance can be assigned to the QWS, regardless of whether or not they are Rashba-split [21].

There are several experimental results underpinning the above interpretation of the VB features as QWS. The first is the absence of dispersion with k_z which is indicative of a state's two-dimensional nature. This can be directly accessed via a photon energy scan. We chose an energy range between 14 and 28.3 eV in which the dispersion of the VB is most clearly identified. The result of such a photon energy scan, taken for a slightly lower CO coverage than the maximum in Fig. 1, is given in Fig. 4. The k_z axis in (d) has been determined by using free electron final states. Details are given in Ref. [15], and Fig. 2 in this reference shows the corresponding scan for a smaller band bending and nonconfined VB states. The nondispersive character of the QWS is evident, but it is also interesting to note the energies at which the emission intensity from these states is resonantly enhanced. This happens at the same energies as the emission from the corresponding nonconfined states, either through direct photoemission (marked by a D in the figure) or via a surface umklapp process (marked by an U), clearly illustrating the origin of the QWS as being derived from the VB states with the corresponding energies.

The idea of VB confinement is further supported by the following consideration. According to the model laid out in Fig. 2, a necessary condition for the appearance of quantized VB sublevels is that the band bending is larger than the total width of the VB. The appearance of the quantized valence band features in Fig. 1(d) is indeed consistent with this, as they are observed only for a band bending larger than 250 meV or so. Note, however, that the states at the bottom of the valence band could already be confined for a smaller band bending. Indeed, this could form an alternative interpretation for the M-shaped state which is observed prior to CO adsorption and which has been interpreted as a surface state previously [15] and throughout this Letter so far. Given its proximity to the calculated band edge, an interpretation as a QWS for a very small band bending cannot be ruled out.

It is very interesting to compare our results to those obtained by the adsorption of Fe on the surface of Ca-doped Bi_2Se_3 [17]. The similarities are striking. In the CB very similar Rashba-split quantum well states are observed which are interpreted as additional surface states [17]. The VB shows a series of M-shaped features, very similar to what is reported here. The states are, however, not interpreted in the same way but rather in terms of a gap opening at the DP. In view of the present results, it appears that there is very little difference between nonmagnetic and magnetic impurities in these two cases, and both merely lead to doping and strong band bending. Note, however, that adsorbed Fe atoms are not necessarily magnetic in the first place. It would have to be confirmed that the Fe adatoms retain a significant magnetic moment after adsorption, and a band gap opening at the DP would be expected only for an ordering of the moments perpendicular to the surface [26].

As mentioned above, the precise position of the DP in the region of the VB QWS is not clear. It seems to be placed inside the regions of QWS, whereas it appears to be just outside the valence band region for the pristine surface [13,15]. This could have several reasons. One is that the DP is also degenerate with the VB top for the pristine surface and that this is merely hard to observe. A second is that the VB states that are degenerate with the DP or at even lower binding energies also become quantized. The wave function of such quantized states would not extend to the surface, leading to a small photoemission cross section, but they could still contribute to the spectra.

In summary, our results provide an interpretation of the multiple M-shaped features in the VB region of Bi_2Se_3 as QWS. The fact that such quantized states can exist in the case of a downward band bending is highly unusual and, to the best of our knowledge, a unique property of this, and probably similar, materials. The observed spectral changes, including an apparent "gap opening" at the DP, are very similar to those reported in the case of Fe adsorption on Bi_2Se_3 [17], raising the question if they are indeed due to the magnetic character of the impurity in the latter case. Finally, the facts that CO is common in the rest gas of a vacuum recipient and that it induces the strong band bending reported here suggest that the observed aging of several topological insulator surfaces is caused by adsorption and could possibly be avoided by a thin protective layer on the surface.

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