Instability of the topological surface state in Bi$_2$Se$_3$ upon deposition of gold

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Momentum-resolved photoemission spectroscopy indicates the instability of the Dirac surface state upon deposition of gold on the (0001) surface of the topological insulator Bi$_2$Se$_3$. Based on the structure model derived from extended x-ray absorption fine structure experiments showing that gold atoms substitute bismuth atoms, first-principles calculations provide evidence that a gap appears due to hybridization of the surface state with gold d states near the Fermi level. Our findings provide insights into the mechanisms affecting the stability of the surface state.

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Topological protection of the Dirac electrons at the three-dimensional (3D) topological insulator (TI) surface caused enormous interest in these materials as potential candidates for spintronics [1,2]. This remarkable property guarantees the absence of time-reversal symmetry breaking perturbations, regardless of the surface quality. The only condition that has to be set is the absence of time-reversal symmetry breaking perturbations, for instance, an out-of-plane ferromagnetism. Since the property includes the absence of elastic backscattering, there is no indication of the surface quality. The only condition that can be imposed is the absence of time-reversal symmetry breaking perturbations, for instance, an out-of-plane ferromagnetism. Therefore, since the very discovery of three-dimensional TIs, considerable experimental effort has been devoted to the confirmation of the topological protection.

The striking evidence of the property includes the absence of elastic backscattering on disordered or defected surfaces [3–6], the existence of well-defined Dirac states at the thallium-based 3D TI surfaces exhibiting complex morphology [7,8], and the tolerance of the topological states to the in-plane [9,10] or, possibly, noncollinear [11] magnetic moments.

The property of the topological protection is intimately related to the topological surface state (TSS) integrity. In particular, time-reversal symmetry leads to a crossing of the surface states at the two-dimensional (2D) Brillouin zone center. To gap out the Dirac point (DP) an effective mass term has to be taken into account, e.g., by applying a magnetic field in the z direction [12–17]. Otherwise, both experimentally and theoretically, the DP and TSS were found to be robust upon deposition of various adsorbates [18–21] and overlayers [22–24]. However, recently, it has been found that the TSS can be destroyed by strain in the vicinity of grain boundaries on the surface of epitaxial Bi$_2$Se$_3$(0001) thin films [25] and in Pb$_1-x$Sn$_x$Te [26]. More recently, for the bulk alloy (Bi$_{1-x}$Mn$_x$)$_2$Se$_3$, the influence of Mn-induced ferromagnetic order was excluded from being responsible for the formation of the 100 meV band gap [27]. It was argued that the system remains topologically nontrivial while in-gap resonance states of $d$ symmetry are involved in the gap opening [27]. This view is supported by theoretical studies suggesting the formation of impurity (vacancy) resonance states near the DP [28–30], located in the bulk or in the near-surface region. These resonance states hybridize with the TSS, which is destroyed and the DP is energetically split. As pointed out in Ref. [30], the topological protection of the TSS is only valid for two-dimensional backscattering but there is no protection against scattering by bulk states, which may originate from nonmagnetic and magnetic impurities.

Since the experiment in Ref. [27] only dealt with bulk alloys it remains an open question whether the disruption of the TSS also occurs in the case of a surface alloy prepared by in situ deposition of (sub)monolayer amounts of an adsorbate on a TI surface. As was already proven, a topological surface state is generated by the electronic structure of the bulk and is mainly located in the two first quintuple layers (QLs) [1]. Therefore, one cannot exclude that the TSS in the experiment in Ref. [27] is destroyed due to substantial changes in the structural or electronic properties of the whole sample. In addition, the magnetic nature of the band gap opening was not fully ruled out: Mn can form clusters with nonzero magnetization. Also, each Mn atom possesses a magnetic moment, which can strongly interact with the free-electron gas. Such an electron-magnon interaction can also induce the band gap opening [31].
In order to elucidate the mechanism by which the TSS is modified by doping with an impurity, we have carried out a combined experimental and theoretical study to investigate the effect of a prototype nonmagnetic surface alloy such as gold on the (0001) surface of a Bi$_2$Se$_3$ single crystal, in the following written as (Bi$_{1-x}$Au$_x$)$_2$Se$_3$. The structure analysis by extended x-ray absorption fine structure (EXAFS) experiments provides evidence that gold atoms deposited at a $T = 160$ K substrate temperature substitute bismuth atoms within the near-surface regime. Simultaneously, photoemission experiments carried out at 0.3, 0.5, and 1 monolayer (ML) coverage indicate the opening of a gap at the DP of the TSS even at a coverage of 0.3 ML equivalent to $x = 0.15$. Here, and in the following, we refer to 1 ML as $6.74 \times 10^{14}$ atoms/cm$^2$, i.e., one adatom per surface atom. Ab initio calculations based on the model structure show that the modification of the TSS already begins between $x = 0.0125$ and 0.0375. They perfectly reproduce the experimental spectral function recorded by photoemission. We conclude that impurity states of $d$ symmetry located within the topmost QL are responsible for the gap opening. Our results provide experimental and theoretical proof that even nonmagnetic surface impurities create resonance states near the DP, involving scattering by bulklike states [28–30].

EXAFS measurements were carried out at the Sector 20 insertion device beamline at the Advanced Photon Source (APS), Argonne National Laboratory (US) using the MBE1 end station equipped with standard surface analytical tools [32]. Two samples were investigated corresponding to a similar structure parameters have been derived. The structure model is discussed on the basis of Fig. 2, where the near-surface structure of Bi$_2$Se$_3$ including the first selenium shell, while peaks 2 and 3 are related to bismuth shells. For the present discussion we focus on the first shell, which was fitted in $R$ space using theoretical scattering amplitudes and phases. The fit results are listed in Table I. In detail, we find that the first peak corresponds to six selenium atoms in total, three of which are located at a distance of 2.45 Å and the other three at a distance of 2.65 Å ($E_i$). For $E_{\perp}$ geometry the distances can be viewed as identical. The structure parameters are compatible with a model in which gold atoms substitute bismuth atoms.

A comparison of the experimental first shell distances with those in the unrelaxed bulk ($R_0 = 2.87$ and 3.07 Å) indicates substantial local relaxations of the surrounding selenium atoms upon bismuth substitution. This situation closely resembles that of iron deposition on Bi$_2$Se$_3$(0001) [11], where very similar structure parameters have been derived.

The structure model is discussed on the basis of Fig. 2, where the near-surface structure of Bi$_2$Se$_3$ including the first QL is schematically shown. Large (blue) and small (red) spheres represent bismuth and selenium atoms, respectively.

| Pol. Shell | $R_0$ (Å) | $N$ | $R$ (Å) | $N^*$ | $\sigma^2$ (Å$^2$) | $\Delta E_0$ (eV) | $R_u$ |
|------------|-----------|----|---------|-------|------------------|----------------|------|
| Se1        | 2.87      | 3  | 2.45(3) | 3.04(*)| 0.004            | 2.6            | 4.9  |
| Se2        | 3.07      | 2  | 2.65(4) | 2.92(*)| 0.014            | 2.6            | 2.6  |
| Se1        | 2.87      | 3  | 2.44(3) | 2.92(*)| 0.004            | 3.3            | 2.3  |
| Se2        | 3.07      | 2  | 2.66(4) | 3.16(*)| 0.021            | 3.3            | 3.3  |
The Bi$_2$Se$_3$ crystal structure is characterized by an ABCBA
stack of van der Waals (vdW) bonded QLs each being com-
posed of a Se-Bi-Se-Bi-Se sequence of layers [34]. Possible
adsorption positions for gold are indicated and are labeled as
fcc (f), hcp (h), substitutional (S), interstitial (I), and octahedral
gap (O). The absence of any polarization dependence of the
first peak and its relation to a Au-Se bond length.

Spin-resolved photoemission experiments were carried out
using a momentum microscope (MM) [37] equipped with a 2D
imaging spin filter based on low-energy electron diffraction
at 1 ML Au/Ir(001) [38]. Sample preparation which closely
followed the procedure employed for the EXAFS experiments
and experimental details are reported in the Supplemental Material [39]. The photoemission spectra collected by the
MM for pristine and gold-covered Bi$_2$Se$_3$ (0001) are displayed
along the $\Gamma$-M-$\overline{\Gamma}$ direction in Figs. 3(a)–3(e), respectively.
In the case of the pristine Bi$_2$Se$_3$ sample [Fig. 3(a)], the DP
is located approximately 350 meV below $E_F$, resulting from
n doping by selenium vacancies. After deposition of 1 ML of
gold [Fig. 3(b)], the TSS is strongly broadened by the structural
disorder introduced by the randomly distributed gold atoms on
Bi sites.

More details are derived by spin-resolved spectra collected
for 0.3, 0.5, and 1 ML, as shown in Figs. 3(b)–3(e). Here,
the characteristic spin-momentum locking of the surface
state is observed. Gold deposition induces an upwards shift (p
doping) and, more importantly, an opening of the gap which
amounts to about 100 meV. The surface state dispersion is not
observed to continue into the energy range below the black
dashed lines where the two spin-polarized branches meet at
$k_x = 0$ [see Figs. 3(d) and 3(e)]. The experimental findings
are well reproduced by $ab\ initio$ calculations, as discussed in the
following.

First-principles calculations of Au/Bi$_2$Se$_3$(0001) model
gold induced modifications of the TSS. We used a self-
consistent full relativistic Green’s function method especially
designed for semi-infinite materials such as surfaces and
interfaces [40,41]. Alloying the bismuth layers with gold
was simulated within a coherent potential approximation as
implemented within the multiple scattering theory [42,43].
The structural information was adopted from the EXAFS
experiments (see Table I).

In order to trace the evolution of the TSS upon gold
congentration, the $k$-resolved spectral density was calculated
in the (Bi$_{1-x}$Au$_x$)$_2$Se$_3$ QL on the Bi$_2$Se$_3$(0001) surface for
the $\overline{K}$-$\Gamma$-$\overline{M}$ direction in the surface Brillouin zone (SBZ)
at concentrations $x = [0.0125, 0.0375, 0.0625, 0.125]$ [see
Figs. 4(a)–4(d), respectively]. In all these cases Au is assumed
to be homogeneously distributed over the Bi sites within

FIG. 3. (a), (b) Spin-integrated photoemission spectra of pristine and gold-covered Bi$_2$Se$_3$ using unpolarized He $\lambda$ radiation ($h\nu = 21.2$ eV).
(c)–(e) Spin-resolved spectra using $s$-polarized laser light ($h\nu = 6.0$ eV) collected for 0.3, 0.5, and 1.0 ML of gold. Dashed lines indicate
the opening of a gap in the surface state. Further details are provided in the Supplemental Material.
the first QL. The results are shown in Fig. 4, where the low, medium, and high spectral densities are represented by blue, white, and red color coding, respectively. At $x = 0.0125$ [see Fig. 4(a)], the spectral density is similar to that of the pristine Bi$_2$Se$_3$(0001) surface (not shown), but some broadening is seen in the vicinity of $E_F$, which is attributed to a gold resonance state.

The most important result is that gold substitution induces the formation of a gap of $\Delta E = 200$ meV, in good agreement with photoemission spectra. Within the gap regime the spectral density is considerably weakened due to the presence of a resonance state and because of band broadening induced by structural disorder. Furthermore, gold acts as a $p$ dopant, shifting the bands up in energy. Comparison of the calculated band structure of the pristine surface (not shown here) and the alloyed sample indicates an upward shift of the bands by approximately 330 meV (at $x = 0.5$).

Our study provides insight into the nonmagnetic impurity mediated modification of the TSS. Gold atoms deposited in the submonolayer to 1 ML range on Bi$_2$Se$_3$(0001) occupy substitutional bismuth sites as evidenced by EXAFS measurements. This goes in parallel with the dramatic weakening of the spectral density of the TSS, thus opening a gap as observed by photoemission. In accordance with first-principles calculations, gold in a bismuth substitutional site within the first QL creates a $d$-type resonant state near the $E_F$, which strongly hybridizes with the bands of the TI and substantially modifies its surface electronic structure. The surface alloy involving only the topmost QL is sufficient for the gap opening, which we attribute to the fact that the resonance state near $E_F$ is of $d$ symmetry. According to the model of Black-Schaffer and Balatsky [28–30], a bulk-surface interaction is a prerequisite for the opening of the gap, since the TSS is not protected by scattering processes involving bulk three-dimensional states.

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