Controllable magnetic doping of the surface state of a topological insulator

T. Schlenk,1 M. Bianchi,2 M. Koleini,3 A. Eich,1 O. Pietzsch,1 T. O. Wehling,3,4 T. Frauenheim,3 A. Balatsky,5,6 J.-L. Mi,7 B. B. Iversen,7 J. Wiebe,1‡ A. A. Khajetoorians,1‡ Ph. Hofmann,2 and R. Wiesendanger1

1Institute for Applied Physics, Universität Hamburg, D-20355 Hamburg, Germany
2Department of Physics and Astronomy, Interdisciplinary Nanoscience Center, Aarhus University, 8000 Aarhus C, Denmark
3Bremen Center for Computational Materials Science, University of Bremen, D-28359 Bremen, Germany
4Institute for Theoretical Physics, Bremen University, D-28359 Bremen, Germany
5Theoretical Division and Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
6Nordic Institute for Theoretical Physics (NORDITA), S-106 91 Stockholm, Sweden
7Center for Materials Crystallography, Department of Chemistry, Interdisciplinary Nanoscience Center, Aarhus University, 8000 Aarhus C, Denmark

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A combined experimental and theoretical study of doping individual Fe atoms into Bi$_2$Se$_3$ is presented. It is shown through a scanning tunneling microscopy study that single Fe atoms initially located at hollow sites on top of the surface (adatoms) can be incorporated into subsurface layers by thermally-activated diffusion. Angle-resolved photoemission spectroscopy in combination with ab-initio calculations suggest that the doping behavior changes from electron donation for the Fe adatom to neutral or electron acceptance for Fe incorporated into substitutional Bi sites. According to first principles calculations within density functional theory, these Fe substitutional impurities retain a large magnetic moment thus presenting an alternative scheme for magnetically doping the topological surface state. For both types of Fe doping, we see no indication of a gap at the Dirac point.

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Three-dimensional topological insulators (3D TIs) have a gapped bulk band structure but a spin-orbit interaction induced band inversion leads to the existence of a metallic topological surface state (TSS). The TSS can exhibit a Dirac-like dispersion which is protected by time-reversal symmetry, resulting in unique properties such as spin-momentum locking and prohibited backscattering [1, 2]. Nevertheless, defect scattering is possible for a two-dimensional TSS and scattering by magnetic impurities is of particular interest, as these can break time-reversal symmetry in the system. This may affect the topological protection and could potentially open a gap in the topological protected band connection at the surface [3–6].

Two experimental approaches have been utilized to introduce magnetic impurities in 3D TIs, namely bulk magnetic doping in crystals or thin films [5, 7–10], and in-situ surface doping via adsorption of impurities on pristine topological insulators [5, 11, 12]. Surface doping can be easier to control experimentally and has the additional advantage that the bulk material remains a TI, something that is not necessarily the case for too high concentrations of bulk dopants [7]. Angle-resolved photoemission spectroscopy (ARPES) measurements of magnetically-doped Bi-chalcogenide samples prepared in both manners exhibit a feature near the DP which resembles a gap [5, 6, 8]. For the surface-doped case, however, it turned out that similar features can be generated by doping with non-magnetic impurities [13]. Indeed, an apparent gap opening can be caused via the adsorbate-induced strong band bending near the surface [14, 15]. More recently, gaps in bulk magnetically doped thin Bi$_2$Se$_3$ films have been observed [8] resulting in a spin reorientation of the TSS. Finally, it has been shown that potential disorder induced by charged bulk defects hinders a clear analysis of faint effects due to the breaking of time-reversal symmetry on the scattering of the TSS electrons [16]. Therefore, a method where neutral magnetic impurities can be introduced into the surface and magnetically interact with the TSS, while only weakly perturbing the band structure, is highly desirable.

In this letter, we demonstrate a way to control the charge state of a magnetic impurity such that this is achieved. Scanning tunneling microscopy (STM) experiments illustrate that Fe atoms that are adsorbed on the surface (adatoms) diffuse into subsurface sites of Bi$_2$Se$_3$ upon thermal annealing. Such bulk doping via the surface can be realized for a large range of coverages. Complementary ARPES studies illustrate that annealing reduces the downwards band-bending, initially produced by Fe adatoms, and restores the DP near its initial location before Fe adsorption. These effects are seen regardless of the initial location of the DP, namely for both pristine (n-doped) and Ca-doped (nearly intrinsic) substrates. The difference in doping behavior of Fe adatoms compared to incorporated subsurface Fe atoms at different lattice sites is further studied by first principles calculations within density functional theory. The cal-
FIG. 1: Constant current STM images of differently prepared samples of Fe on Bi$_2$Se$_3$ ($I_t = 50$pA, $V_b = 0.25$V (a-d), $V_b = 1$V (e).) (a) Cold deposited Fe ($\approx$ 1% of a ML) on pristine Bi$_2$Se$_3$. Inset: magnified view showing 8 individual Fe adatoms (10nm × 10nm, $V_b = −0.3$V, $I_t = 1$nA). (b), (c) Samples prepared as in (a) annealed to $T_A ≈ 260$ K and 370 K, respectively. (d) Cold deposited Fe (0.5% ML) on Ca-doped Bi$_2$Se$_3$. (e) Sample prepared as in (d) but with 6% ML Fe and annealed to $T_A ≈ 370$ K. (f) Number of Fe adatoms and subsurface Fe atoms relative to initial Fe adatom number as a function of $T_A$. Emergent clusters were not counted in the statistics.

culations reveal that the doping character changes from electron donor for Fe adatoms towards neutral for Fe incorporated into Bi substitutional sites consistent with the ARPES results. Such incorporated Fe atoms theoretically retain a large magnetic moment which is a prerequisite for modifying the TSS by breaking the time-reversal symmetry locally.

STM experiments were carried out in a multichamber UHV-system with a base pressure below 1 × 10$^{-10}$ mbar utilizing a home-built variable temperature scanning tunneling microscope (VT-STM) [17]. Annealed tungsten tips were used for all experiments and both tip and sample were cooled to $T = 30$ K. STM topography images were taken in constant current mode at a tunneling current $I_t$ with the bias voltage $V_b$ applied to the sample. ARPES measurements were performed at the SGM-3 beamline of the ASTRID synchrotron radiation facility [18] at a sample temperature of $T = 60$ K. The angular and combined energy resolutions were 0.13° and better than 15 meV, respectively. Spectra were obtained along the $\vec{K}−\vec{\Gamma}−\vec{K}$ azimuthal direction with a photon energy of $h\nu = 19.2$ eV. Pristine and Ca-doped Bi$_2$Se$_3$ single crystals were grown as described in refs. [14, 19]. In both experimental setups the Bi$_2$Se$_3$ samples were cleaved in situ at room temperature (RT) and immediately cooled to temperatures of $T \leq 150$ K. Fe was originally deposited onto the cold surface by e-beam evaporation resulting in a distribution of single Fe adatoms [20].

To achieve a theoretical description of the Fe/Bi$_2$Se$_3$ system, we have performed density functional theory calculations with the VASP code [21, 22], where we employed the GGA-PBE approximation to the exchange and correlation functional [23] and used plane wave basis sets with a kinetic energy cutoff of 20 Ry in combination with projector augmented-wave (PAW) pseudopotentials [24, 25]. We used a (3 × 3) supercell with two quintuple slabs which have been relaxed until the maximum force component of every atom was lower than 0.02 eV/Å. A (6 × 6) $k$-point grid has been employed to obtain the precise density of states (DOS).
different subsurface Fe defects [26].

FIG. 2: (a), (b) Atomically resolved STM images of two different subsurface Fe defects [\(I_t = 50\) pA, \(V_b = 1\) V (a), \(V_b = 0.25\) V (b)]. (c)-(h) Bias dependent constant current images of a subsurface Fe atom (red arrows), 3 Fe adatoms and a Se vacancy at \(V_b\) as indicated. \((I_t = 100\) pA, \(\Delta z = 35\) pm).

To further investigate the impact of Fe doping on the TSS, ARPES measurements were performed. In Fig. 3 two series of ARPES measurements are shown for pristine (a-e) and Ca-doped (f-j) Bi$_2$Se$_3$ substrates, at different stages of the preparation procedure. After in-situ cleaving (a,f), subsequent iterations of cold Fe deposition (\(T \approx 150\) K) and annealing to \(T_A \approx 370\) K were performed with no cleaving in between. The amount of subsequently deposited Fe was increased for each iteration (1%, 2.5%, 5%, 10%). The ARPES data after each cold deposition but before subsequent annealing (Fig. 3 (b,d,g,i)) reveals a downward shift of the DP as compared to its energetic position before Fe deposition. We can thus conclude that Fe adatoms are donors inducing downwards band bending. Such band bending leads to the well known formation of quantum well states (QWS) [6, 11, 13, 19, 30] in both the conduction and the valence bands [13], where the conduction band QWS shows a clear Rashba splitting.

Surprisingly, after annealing to temperatures coinciding with STM observations of Fe diffusion into the subsurface region (Fig. 1(d)), the DP shifts back toward its initial position and the surface’s electronic band structure is reverted close to its initial state before Fe deposition (Fig. 3 (c,e,h,j)). Strikingly, after annealing, the QWS are nearly destroyed. In order to further analyze this behavior,fo the binding energy of the DP after each preparation step of the subsequent iterations has been extracted from the ARPES spectra and is plotted in Fig. 3(k) for the pristine and two Ca-doped substrates with different Ca concentrations. It reveals the aforementioned oscillation of the DP binding energy after each preparation step, i.e. an increase in the DP binding energy for cold
deposition of Fe, and a decrease after annealing the Fe covered sample. The gradual shifting of the DP toward higher binding energies is most likely the result of the well known aging effect of the Bi$_2$Se$_3$ surface [30]. In order to exclude the influence of rest gas physisorption at low temperature that would also lead to a downward band bending, the following test has been performed. The very same procedure of Fe deposition has been followed but keeping the shutter of the Fe evaporator closed and no appreciable change in the band bending has been observed after this simulated deposition. Our result is contrary to a recent ARPES study that concludes surface electron doping for Fe deposition at RT and hole doping for cold deposited Fe [12]. Taking into account the STM-observed thermally-induced subsurface diffusion of Fe adatoms (Fig. 1(f)), our sequence of ARPES experiments indicates, that substitutional Fe atoms are either neutral dopants or electron acceptors, while the Fe adatoms that are prepared by cold deposition are electron donors. In all of these cases the DP stays intact without the opening of a gap.

In order to determine the electronic and magnetic properties of the incorporated Fe atoms, we performed ab initio calculations. As shown in the ball and stick models in Fig. 4 (a-f), we considered pure Bi$_2$Se$_3$, as well as Fe on the two different hollow sites fcc (a) and hcp (b), Fe substituting Bi atoms in the 2$^{nd}$ (c) and 4$^{th}$ (d) subsurface layer, and Fe in two different interstitial sites (e,f) of the Bi$_2$Se$_3$ lattice. The calculated total density of states (DOS) for these different cases is illustrated in Fig. 4 (g). For pure Bi$_2$Se$_3$ (grey shaded), the onset of the valence band emerges at energies below the Fermi energy $E_F$ and the onset of the conduction band DOS for $E - E_F > 0.75$ eV. The minimum and gradual increase in the DOS within the bulk band gap ($E - E_F < 0.75$ eV) are due to the DP of the TSS. Compared to the DOS of the pure Bi$_2$Se$_3$, the Fe adatoms (green, yellow) or the Fe subsurface interstitials (cyan and purple) cause a shift of the bulk band gap and DP to a higher binding energy by $\Delta E \approx 0.5$ eV. This reproduces the electron doping behavior of the Fe adatoms, as observed by ARPES. Moreover, Fe atoms in Bi substitutional sites (red, blue) do not shift the bulk band gap and DP with respect to the pure Bi$_2$Se$_3$, indicating neutral doping for these impurities. Note here that the Fermi energy is always below the onset of the conduction band within the calculations, while in the experiment it is slightly shifted into the conduction band due to Se vacancy doping and aging effects. For a strong shift of the Fermi energy, the Fe atoms on Bi substitutional sites might become electron acceptors. These conclusions are consistent with the above interpretation of the STM and ARPES data, confirming that the thermally-induced subsurface Fe doping results in a preferential occupation of Bi substitutional sites, as already suggested by STM.

Finally, we calculated the magnetic spin moments of the Fe atoms in the different lattice sites as indicated in the legend of Fig. 4(g). For all defects, we find considerable magnetic moments $2.7 \mu_B < m_{Fe} < 3.5 \mu_B$ in the Fe $d$ shell. $m_{Fe}$ is largest for Fe substitutional defects, where Fe is nominally in a $3^+$ oxidation state. In contrast, Fe adatoms are clearly in a lower oxidation state as no Bi$^{3+}$

FIG. 3: Two series of ARPES measurements for pristine (a-e) and Ca-doped (f-j) Bi$_2$Se$_3$ samples after different Fe deposition and annealing steps. (a), (f) Initial spectra after in-situ cleaving. Subsequent cycles of cold deposition of Fe ($T \approx 150$K, % ML Fe as indicated and annealing at $T_A \approx 370$K followed. The DP extracted from the spectra is marked by a green and red horizontal line, respectively. (k) The resulting binding energy of the DP is plotted in dependence of the preparation step number for a pristine (circles) and two differently Ca-doped samples (up and down triangles). Preparation step number 0 indicates the freshly cleaved substrate without Fe, preparation step 1 (1%), 3 (2.5%), 5 (5%), 7 (10%), and 2, 4, 6, 8 subsequent annealing steps.
is missing. Thus, the reduced magnetic moments of Fe adatoms as compared to substitutional Fe atoms as well as the stronger tendency of Fe adatoms to donate further charge to the Bi$_2$Se$_3$ conduction band is well understandable. Fe substitutional atoms thus not only minimize the charge doping but also maximize the magnetic coupling to the Bi$_2$Se$_3$ host.

For a magnetism-induced modification of the TSS by Fe, the coupling of the Fe 3d magnetic moments to the Bi$_2$Se$_3$ host is decisive. It is therefore illustrative to analyze also the total spin magnetic moments $m_{\text{tot}}$ of the supercell. While the total magnetic moments $m_{\text{tot}}$ and $m_{\text{Fe}}$ are rather similar in the adatom case, $m_{\text{tot}}$ exceeds $m_{\text{Fe}}$ by $\sim 1.5 \mu_B$ in the case of Fe substitutionals. In the latter case a sizable magnetic moment is induced in the vicinity of Fe which indicates much stronger magnetic coupling between substitutional Fe atoms and the Bi$_2$Se$_3$ host than for adatoms.

In summary, it was demonstrated that, via low temperature deposition and moderate annealing, neutral magnetic moments can be introduced into the topmost layers of a prototypical TI, thus preserving the bulk electronic properties of the TI without causing significant band bending effects at the surface. In the investigated case of Fe on Bi$_2$Se$_3$, Fe acts as an electron donor when adsorbed on top of the surface at low temperature, but becomes neutral or an acceptor when substituted into a subsurface Bi site by thermally-activated diffusion. This allows for a study of the time-reversal symmetry breaking driven scattering of the TSS electrons by magnetic impurities.

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* Email: jwiebe@physnet.uni-hamburg.de
† Corresponding author: akhajeto@physnet.uni-hamburg.de

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