Barrier-free subsurface incorporation of 3d metal atoms into Bi(111) films

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(Received 11 December 2014; revised manuscript received 1 May 2015; published 27 May 2015)

By combining scanning tunneling microscopy with density functional theory it is shown that the Bi(111) surface provides a well-defined incorporation site in the first bilayer that traps highly coordinating atoms such as transition metals (TMs) or noble metals. All deposited atoms assume exactly the same specific sevenfold coordinated subsurface interstitial site while the surface topography remains nearly unchanged. Notably, 3d TMs show a barrier-free incorporation. The observed surface modification by barrier-free suborption helps to suppress aggregation in clusters. It allows a tuning of the electronic properties not only for the pure Bi(111) surface, but may also be observed for topological insulators formed by substrate-stabilized Bi bilayers.

DOI: 10.1103/PhysRevB.91.195441 PACS number(s): 68.43.Fg, 68.37.Ef, 68.43.Bc, 73.20.—r

I. INTRODUCTION

Materials with spin-polarized two-dimensional (2D) surface states arising from the Rashba effect and topological insulators are of large potential interest for spintronic or dissipationless devices. Among the special properties of such systems are the suppression of backscattering, the existence of spin-polarized currents, and the topological protection of the surface state. Besides bismuth chalcogenides such as Bi2Se3 and Bi2Te3, also Bi bulk is a well-known model system for materials with strongly spin-split surface states [1–6]. Application of these novel material systems, however, requires the controlled tuning of properties such as band gap, carrier density, or doping level by electronic or morphological manipulation [7–11]. Often the electron transport in 2D surface electron systems is strongly influenced by individual scatterers, e.g., single atoms or molecules [7,8,12]. Unintentional defects such as step edges or impurities frequently show pronounced scattering patterns in scanning tunneling microscopy (STM) [7,13–19]. In contrast to these uncontrolled surface modifications, the deposition of single atoms at the surface, usually followed by thermally activated in-diffusion, allows for intentional doping of the near-surface region. Such controlled modification was recently reported for Bi2Se3 and Bi2Te3 compound films [18,20,21]. Depending on deposition temperature and subsequent annealing, Fe atoms occupy, however, various different metastable interstitial or substitutional sites [20].

In this work, we apply a similar approach to high-quality (111) bismuth films and demonstrate the incorporation of individual impurity atoms into highly specific, well-defined subsurface interstitial sites: Combining STM and density functional theory (DFT), we show that the first Bi bilayer traps transition metal (TM) or noble metal atoms in exactly the same highly coordinated interstitial site. Moreover, 3d TMs such as Fe, Co, and Ni show a barrier-free incorporation. No thermal activation is required. Even at temperature below 10 K, the deposited atoms occupy always the same sevenfold coordinated subsurface site. The neighboring Bi atoms relax towards the interstitial impurity atom, but do not protrude and, thus, the surface remains structurally almost unchanged. This contrasts with typical adsorption, surface alloying, or surface reconstruction phenomena. In the following, we will refer to this special kind of surface modification as subsorption. It allows for the preparation of nominally undoped systems with metallic and even ferromagnetic electronic states, where backscattering is still suppressed by Rashba splitting. The barrier-free subsorption is not restricted to pure Bi(111) surfaces, but may also be found in the case of Bi(111) bilayer islands and substrate-stabilized Bi bilayers [19,22–26].

II. EXPERIMENTAL DETAILS

Ultrastable low-temperature scanning tunneling microscopy (LT-STM) was used to image and identify Friedel-like electronic scattering patterns as fingerprints for foreign atoms in a suborption site. All experiments were performed under ultrahigh-vacuum (UHV) conditions. The preparation chamber had a base pressure below 2 × 10−10 mbar. The measurements were performed using a LT-STM in a bath cryostat at a pressure below the detection limit of 10−13 mbar and a base temperature of 5 K. Virtual Bi(111) substrates were grown on Si samples cut from an As-doped Si(111) wafer with a miscut below 0.1° and a resistivity of 0.004 Ω cm at room temperature. All samples were degassed in the load lock for 12 h at a temperature of 600 °C prior to transfer into UHV. A short flash annealing cycle up to 1200 °C was performed to remove the native oxide resulting in a clear (7 × 7) reconstruction on Si(111). Afterwards Bi was deposited by evaporation from a ceramic crucible heated by a tantalum filament. Bi(111) films were prepared by deposition of 20 nm of Bi at a sample temperature of 80 K, followed by an additional annealing step for 30 min at 200 °C [27]. This preparation results in an atomically smooth surface with

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The experimental observations strongly evidence that even without thermal activation all Co atoms are incorporated into the Bi film at identical subsurface sites without any morpho-

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III. COMPUTATIONAL METHOD
logical modification at the surface. In order to rationalize this surprising experimental finding, DFT total-energy calculations were performed. The QUANTUM ESPRESSO package [30] was used, employing the gradient-corrected PBE functional [31] for the description of the electron exchange and correlation. Relativistic effects are taken into account on different levels of theory: While for structure relaxation a scalar-relativistic description is found to be sufficient, spin-orbit coupling affects the details of the electronic structure considerably [5]. Hence, spectroscopic properties such as magnetic moments require multicomponent relativistic calculations [32,33] with noncollinear spin polarization. The latter is visualized by arrows in Figs. 2(b) and 2(c) for the calculated subsorption geometries I and II, respectively.

The Bi(111) surface is modeled by periodic supercells, which contain between 6 and 22 Bi bilayers [34] separated by 20 Å vacuum. The atoms in the bottom bilayer are kept fixed at their ideal bulk positions. All other atoms are freely relaxed. Numerically converged subsorption geometries are obtained using a 6 × 6 × 1 Brillouin zone sampling and require 6 Bi(111) bilayer slabs with a (4 × 4) translational symmetry. Hence, the Bi(111) surface structure contains 193 Bi atoms, including the impurity. The incorporation energy profiles are investigated by keeping the z coordinate of the adatom fixed. Its lateral position, as well as the Bi atoms within the three uppermost bilayers are freely relaxed. Migration barriers are calculated by explicitly determining the corresponding saddle points via the nudged elastic band (NEB) approach [35].

IV. RESULTS AND DISCUSSION

The resulting reaction paths are shown in Fig. 2(a). In principle, the adatoms could adsorb at the surface (i) singly coordinated on top of a Bi atom of the first Bi layer or (ii) in two different threefold coordinated positions. However, for all investigated TM atoms a subsorbate position within the first Bi bilayer is the most stable configuration [labeled I in Fig. 2(a)]. Here, similar to the CoSi2/Si(111) interface [36], the TM atoms are sevenfold coordinated: Six bonds are formed to the ligands within the first Bi bilayer. A seventh Bi atom from the second bilayer binds to the TM atom.

Interestingly, for the 3d transition metals the subsorbate incorporation in the first Bi bilayer turns out to be barrier free; i.e., no thermal activation is required. Only Sc shows a very weak, metastable minimum 0.48 Å above the surface separated by a very shallow barrier ΔE < 0.01 eV from the stable subsorbate configuration. The interstitial configuration I is by far (∼1.1 eV) more stable than any substitutional incorporation, but energetically nearly degenerate with the fivefold coordinated interlayer position II [cf. Fig. 2(a)] as well as further intralayer positions deeper below the surface. However, migration into subsurface sites beyond configuration II is hindered by energy barriers of about 0.7 eV (Co) to 0.9 eV (Fe). The lateral mobility is restricted as well, but remains more probable: A lateral movement via configuration II and back into the top bilayer [cf. arrow in Fig. 2(a)] requires activation energies below 0.5 eV, and should thus occur prior to in-diffusion into the bulk.

The computational finding that the 3d TMs are captured at specific high-symmetry, sevenfold coordinated positions within the uppermost Bi bilayer is further corroborated by the comparison of the measured STM images with simulations based on the Tersoff-Hamann approach [37]: Only for the high-symmetry configuration I we obtain agreement with the measured STM data [cf. Fig. 1(d1) and Fig. 2 showing Co as an example]. The three pronounced spots arise from $p$-like
TABLE I. Calculated adsorption and incorporation energies (exothermic, in eV, relative to the respective free atom, metastable minima in brackets) calculated for various third, fourth, and fifth row element adatoms at or into the Bi(111) surface. If existing, energy barriers $\Delta E$ for the incorporation into the first Bi layer are also given.

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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<tr>
<td>Top</td>
<td>(3.53)</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>First BL</td>
<td>4.24</td>
<td>5.34</td>
<td>5.92</td>
<td>6.10</td>
<td>5.86</td>
<td>5.48</td>
<td>5.20</td>
<td>4.80</td>
<td>4.01</td>
<td>(0.26)</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
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$\Delta E < 0.01$ means barrier-free incorporation, provided the lattice constant of the Bi bilayer (see Fig. 2) is related to a downwards relaxation of the second layer Bi atoms around the impurity. The topmost Bi atoms move laterally towards the impurity, but do essentially not vary their height; see inset I of Fig. 2. This agrees with the experimental observation that the topography of the surface remains unchanged.

3$d$ electrons are polarized by the second layer Bi atoms and the impurity atom relaxes further without barrier towards the preferred, highly coordinated subsorbate position I within the Bi bilayer (see Fig. 2). The Bi lattice itself experiences only minor strain upon incorporation: The Bi-Bi bonds around the subsorbate change their length by amounts ranging from 2% (for Sc) up to at most 6% (for Cr). This is mainly related to a downwards relaxation of the second layer Bi atoms around the impurity. The topmost Bi atoms move laterally towards the impurity, but do essentially not vary their height; see inset I of Fig. 2. This agrees with the experimental observation that the topography of the surface remains unchanged.

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4$d$/5$d$ TMs such as Pd and Pt also have partially filled $d$ shells, but tend to form longer bonds with Bi. While their incorporation in the first Bi bilayer is still favorable, they have to overcome energy barriers $\Delta E$ of up to 0.2 eV (see Table I). This also holds for the noble metals Ag and Au. Atoms without partially filled $d$ shell such as Zn, Bi, or Pb and even rather small atoms such as P and H cannot take advantage of the highly coordinated bonding position within the Bi bilayer. This position is either metastable or unstable for these atoms [cf. P and Bi in Fig. 2(a)] and they adsorb atop the surface.

That the barrier-free incorporation is actually a bond-length sensitive effect can also be seen by modifying the lateral lattice constant. This is of particular relevance for strained Bi(111) bilayer islands and substrate-stabilized Bi bilayers [22,23,19,24–26]. To obtain first estimates of how the atomic penetration will be influenced by strain, we perform additional total-energy calculations using single Bi(111) bilayers as a model systems. Thereby a barrier-free 3$d$ TM incorporation into the bilayer is predicted, provided they are not too strongly strained. In case of Co deposition, for example, barrier-free incorporation occurs for bilayer strain between $-5\%$ and $+8\%$. For larger compression the lateral distance between neighboring Bi atoms and for more tensile strain above $+8\%$ the distance between the two Bi layers becomes too small. Therefore, we expect also systems that contain single, substrate-stabilized Bi(111) bilayers to be susceptible to the barrier-free incorporation, provided the lattice constant of the substrate is close to that of the Bi(111) surface. Hexagonal BN ($-2\%$) or $\text{Bi}_2\text{Te}_3$ ($-5\%$), e.g., fulfill this requirement. For
Bi$_2$Se$_3$, however, causing 11% compressive strain, thermal activation is required for a subsurface in-diffusion into the Bi bilayer.

**V. SUMMARY**

In this work, it has been demonstrated that the Bi(111) surface provides a specific incorporation site within the first bilayer, which is attractive for highly coordinated transition and noble metal atoms. They are found to penetrate the surface in a well defined way, thereby causing no morphological changes at the surface. In contrast to thermally activated in-diffusion recently found for Bi$_2$Se$_3$ and Bi$_2$Te$_3$ compound films [18,20,21], the incorporation of 3d TM into Bi(111) films occurs barrier-free. No annealing step is required reducing the probability for lateral migration and unwanted aggregation of the TM atoms in clusters to a minimum. Hence, high doping concentration become possible, and each atom assumes a well-defined sevenfold coordinated interstitial position, providing a metallic near-surface state by only weakly perturbing the band structure. The observed surface modification by barrier-free suborption does not only allow for tuning the electronic properties of the Bi surfaces itself, but may also be applicable to topological insulators formed by substrate-stabilized Bi bilayers, provided the lattice constant of the substrate resembles within a few percent that of the Bi(111) surface; otherwise in-diffusion requires thermal activation.

**ACKNOWLEDGMENTS**

We acknowledge financial support by the DFG through SFB 616, SPP 1601, and PI238/31 as well as grants of high-performance computer time from the HLRS Stuttgart and the Paderborn PC². Research was carried out in part at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.