

X-Ray Structure Analysis of Ultra-Thin Silver Films on the (0001) Surface of the Topological Insulator Bi_2Se_3

Sumalay Roy, Andrey Polyakov, Katayoon Mohseni, and Holger L. Meyerheim*

Using surface X-ray diffraction we have studied the atomic structure of ultra-thin silver films deposited in the one monolayer thickness-regime on the (0001) surface of the Topological Insulator Bi_2Se_3 . Depending on the preparation of the substrate surface, different interface structures are formed. For sputter-annealed single crystalline Bi_2Se_3 (0001) silver atoms substitute bismuth atoms within the first quintuple layer and simultaneously reside in surface hollow sites. When silver is deposited on a substrate grown by molecular beam epitaxy and which was only annealed prior to silver deposition, only adsorption in surface hollow sites is observed. Neither intercalation into the van der Waals gap nor its vertical expansion is observed in any case. An expansion induced appearance of surface states can be excluded.

Topological insulators (TIs) have attracted intense interest owing to their fascinating properties. While insulators in the bulk, they host a topologically protected surface state (TSS) at the surface which is robust against perturbations as long as time reversal symmetry is preserved. A large variety of studies, both experimental and theoretical have been carried out to investigate the effect of adsorption of magnetic and non-magnetic foreign species on the electronic structure of TIs. Due to its large band gap of the order of 0.3 eV, Bi_2Se_3 represents a prototype of a TI, and after several years of research it can be concluded that the (0001) surface Bi_2Se_3 can be regarded as highly reactive against adsorption, at least as long as the sample surface is kept at a temperature above 160 K. For instance, recent quantitative surface-structure determinations of in-situ deposited films in the sub-monolayer range have revealed that d-transition metal ions like gold, chromium, manganese or iron substitute bismuth atoms within the first quintuple layer (QL), while alkali atoms like cesium or hydrogen atoms replace top-layer selenium atoms.^[1–4]

Already several years ago, the effect of alkali adsorption^[5–7] and several other species^[3,8–12] on the electronic structure of the TI and its TSS have been investigated. It was found that the TSS is stable while an adsorbate induced shift of the energetic

position of the Dirac point is induced. Most importantly, the appearance of new Rashba-split surface states has been identified. This was attributed to downward band bending leading to a confinement of the conduction electrons by a surface potential well. Another interpretation was suggested involving a strong expansion of the van der Waals (vdW) gap.^[13] This requires the expansion by at least 10–20% which might be conceivable by intercalation of large atoms or molecules. In this context, recent angle-resolved photoemission experiments on sub-monolayer to monolayer amounts of silver deposited on $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.7}\text{Se}_{1.3}$ were interpreted in this way, also referring to previous experimental^[14] and theoretical^[15,16] work. Based on scanning tunneling microscopy (STM), Ye et al.^[14] propose massive silver intercalation into the vdW gap thereby leading to a detachment of the top QL and a relocation of the TSS charge density to the space beneath the top QL and the concomitant appearance of the parabolic and M-shaped states.

In order to analyze the evolution of the Ag/ Bi_2Se_3 (0001) interface formation we have carried out a detailed surface X-ray diffraction (SXR) analysis. SXR has been recently successfully applied to study the geometric structure of pristine and adsorbate covered Bi_2Se_3 (0001)^[1,2,17,18] and is an ideal tool to study the interface structure of buried interfaces.

The experiments were carried out in situ by using an ultra-high-vacuum (UHV) z-axis diffractometer at the Max-Planck-Institute in Halle using a microfocus X-ray source (Cu- K_α) and a two-dimensional (2D) pixel detector (Pilatus 100k). Integrated X-ray reflection intensities were collected along the (integer) order crystal truncation rods (CTRs) under total reflection (incidence angle = 0.3 deg.). Symbols in **Figure 1** represent experimental structure factor intensities, $|F|^2$, which were derived from the integrated intensities, $I_{\text{obs}} \propto |F|^2$, after correcting for instrumental factors.^[19,20] The CTRs arise due to the truncation of the bulk crystal and their intensity can be calculated analytically.^[21,22] The third reflection index, $L = q_z/c^*$ is a continuous parameter. Here, q_z and c^* represent the momentum transfer normal to the surface and reciprocal lattice unit, respectively. The structure analysis is based on the interference between the scattering amplitude of the substrate (F_{CTR}) with that of the adlayer (F_{AD}): $|F|^2 = |F_{\text{CTR}} + F_{\text{AD}} \times \exp[i\phi]|^2$, where the phase factor formally accounts for the registry between adlayer and substrate.

Silver was deposited from a well degassed electron beam evaporator on two different samples, namely (a): an MBE grown

Dr. S. Roy, Dr. A. Polyakov, Dr. K. Mohseni, Dr. H. L. Meyerheim
 Max-Planck-Institut für Mikrostrukturphysik Halle
 Weinberg 2, D-06120 Halle, Germany
 E-mail: holger.meyerheim@mpi-halle.mpg.de

Dr. S. Roy
 Department of Physics and Astrophysics
 University of Delhi
 Delhi-110007, India

DOI: 10.1002/pssr.201800138

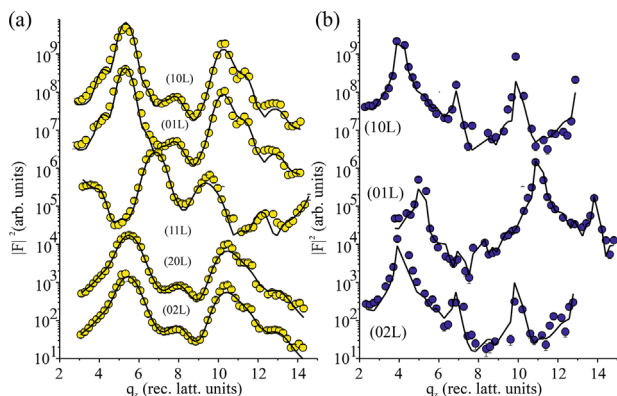


Figure 1. Experimental (symbols) and calculated (lines) structure factor intensities, $|F|^2$ along several CTR's for silver on the MBE grown film (a) and the single crystal (b). Curves are shifted for clarity.

(0001) oriented Bi_2Se_3 film of about 13 nm thickness and (b) on a Bi_2Se_3 (0001) single crystal. The structures of the pristine samples were studied in previous publications.^[17,18] In the following we refer to these as “MBE” and “single crystal” (SC), respectively. The SC substrate was prepared by mild Ar-ion sputtering ($E_{\text{kin}} = 500$ eV) followed by annealing at about 480 °C, while the MBE substrate was only heated up to about 250 to 300 °C in order to reduce the amount of water contamination on the surface. Owing to the low film thickness, no sputtering or annealing above the 400–450 °C temperature regime is possible without destroying the film or its complete evaporation. The amount of silver was estimated by Auger electron spectroscopy (AES) and ex posteriori by the analysis which is sensitive to the coherent fraction of adsorbed silver.

Selenium and bismuth atoms occupy only high symmetry sites (1a, 1b, and 1c) in the plane group $p3m$ leaving only the z-position as a free parameter per layer in addition to the Debye parameter ($B = 8\pi^2 U$) representing thermal and static disorder with U being the mean squared displacement amplitude.^[23] This considerably facilitates the fit problem. Silver atoms were placed in different amounts on different sites of the substrate and the vertical positions were simultaneously refined by least squares fitting of the calculated structure factor intensities $|F_{\text{calc}}|^2$ to the $|F_{\text{obs}}|^2$ using the program “Prometheus”.^[24] In Figure 1 the $|F_{\text{calc}}|^2$ are plotted as solid lines, which follow the experimental data in detail. The fit quality is quantified by the un-weighted residuum (R_u),¹ which is equal to 0.18 for the MBE and the SC sample. We note that in the case of the MBE sample, twinning of the film has to be considered,^[18] that is, there is an incoherent superposition of two 60° oriented domains.

The structure models derived on the best fits are schematically shown in Figure 2. Large (grey) and small (red) spheres represent bismuth and selenium atoms, respectively. The Figure only shows the topmost quintuple layer and the first vdW gap, deeper parts of the structure were found to be bulk-like with no significant

relaxations. Silver atoms are represented as blue spheres. There is a distinct difference between the structures:

- (i) For the MBE sample we find that silver atoms occupy both threefold hollow sites on the surface. These sites are labelled as “fcc” and “hcp” owing to the resemblance of the stacking in densely packed metal structures with “fcc” and “hcp” being a site above the third layer selenium and the second layer bismuth atom, respectively. The occupancy of the two sites lies in the 60% range, that is the layer filling is far from being complete. This might be attributed to steric reasons considering the fact that the closest Ag–Ag distance in neighboring hollow sites is equal to 2.39 Å while the distance in bulk silver is equal to 2.88 Å. However, one should keep in mind that the effective atomic radius strongly depends on the coordination number and it shrinks by as much as 10–15% when the coordination number is reduced from 12 to 4.^[25,26] Thus, the formation of a dense silver overlayer -albeit with a large number of defects- appears as a reasonable model.

The relaxation of the vertical position yields a Ag–Se distance of 3.23 and 3.32 Å for the fcc and the hcp site, respectively. The difference of about 0.1 Å is not considered as significant. We can compare the Ag–Se bond distance with those in bulk AgBiSe_2 investigated by S.Geller and J.H. Wernick^[27] who for the trigonal phase find values between 2.81 and 2.86 Å, while the sum of the atomic radii yields 2.75 Å with ($r_{\text{Ag}} = 1.60$ Å, $r_{\text{Se}} = 1.15$ Å according to Slater^[28]). Thus, we can conclude that the bonding of the silver to the selenium atoms is rather weak. Nevertheless there is an effect on the back-bonding of the selenium atoms to the second layer bismuth atoms. This is manifested by a significantly enhanced expansion of the top layer spacing (d_{12}) by +26% as compared to the bulk value (1.587 Å).^[18] Such an expansion of d_{12} in Bi_2Se_3 is not uncommon and has been observed in a number of recent studies, such as, for example for Cs adsorption on MBE grown Bi_2Se_3 (0001) (+24%)^[4] and even for carbon-doped pristine Bi_2Se_3 (0001)(+11%).^[17] The uncertainty for the determination of the d_j within the first QL is estimated to be ± 3 percentage points, i.e. for the MBE sample the deeper layers can be considered as unrelaxed. Finally, there is no evidence for any intercalation of silver into the vdW gap to within the accuracy of about 10% of a monolayer as discussed in more detail in the following.

Figure 3 shows a contour plot of the goodness of fit (GOF)² versus the occupancy factors of silver residing in the hcp and the vdW gap site. The global minimum is at about 60% for the hcp site occupancy and at 0% for the vdW site occupancy. Any increase of the latter increases the GOF. From the variation of the GOF we estimate an uncertainty of about 10% for the occupancy factors.

- (ii) For the SC sample the structure is distinctly different. Both bismuth layers are alloyed by about 30% with silver, while only the hcp surface site is occupied. Simultaneously, some fraction of bismuth is also located at the surface fcc site, possibly by bismuth atoms released by the Ag–Bi alloying.

¹ $R_u = \frac{\sum |F_{\text{obs}}| - |F_{\text{calc}}|}{\sum |F_{\text{obs}}|}$ are the experimental and calculated structure factors, respectively. The summation runs over all datapoints.

² $\text{GOF} = \sqrt{1/(N - P) \cdot \sum [(I_{\text{obs}} - I_{\text{calc}})^2 / \sigma^2]}$, with $I = |F|$, σ = standard deviations of the data points, N = number of data points, P = number of parameters.

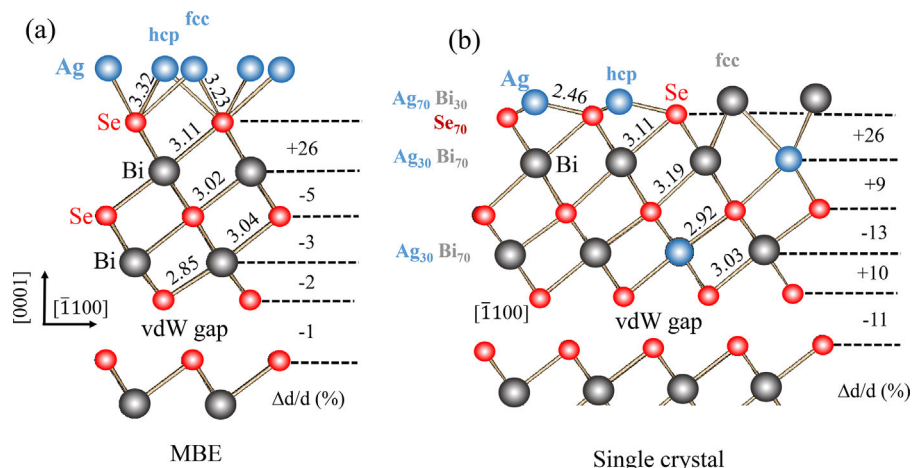


Figure 2. SXR D derived structure model of the Ag/Bi₂Se₃ (0001) interface for silver on the MBE grown film (a) and for silver grown on sputter-annealed single crystalline Bi₂Se₃ (0001) (b). Numbers indicate interatomic distances in Ångström units. Relaxations relative to bulk are given in percent on the right.

The Ag–Se distance is equal to 2.46 Å indicating a much stronger bond as compared to the MBE sample. This might be related to the fact that here no dense silver layer is formed and that the remaining hcp-site silver atoms form a stronger bond to selenium. As a result of the complicated structure including two alloyed layers, the pattern of inter-layer relaxations is also considerably more complex for which a (+, −, +, …) sequence is observed. The near surface structure of the SC sample resembles a disordered form of the trigonal bulk AgBiSe₂ phase.^[27] The latter is characterized by an ordered layer sequence (...Ag–Se–Bi–Se–Ag–Bi...), albeit without a vdW gap.

In summary, we have presented a SXR D analysis of the Ag/Bi₂Se₃ (0001) interface formation and find different structures depending on whether the sample surface was treated by sputter annealing or not. In the first case the surface is reactive and deposition of silver at room temperature leads to

the formation of a Ag–Bi alloy within the topmost quintuple layer while for the second (MBE) sample, a silver overlayer is formed which weakly interacts with the substrate. The differences in the reactivity of the two surface is attributed to the creation of defects by sputtering, which is not uncommon and has been observed in similar cases.^[4,29] In no case we observe intercalation of silver into the vdW gap site. Thus, the observation of Rashba-split surface states seems not to be related to the gap expansion, rather to the adsorbate induced band bending.

Acknowledgements

This work is supported by the Deutsche Forschungsgemeinschaft (DFG) through priority program SPP 1666 (Topological insulators). We thank A. Ernst, M.M. Otrokov, and E.V. Chulkov for helpful discussions. The authors also thank M.B. Babanly, K.A. Kokh for supplying the bulk single crystal samples, Gregor Mussler for the MBE grown samples. We also thank Frank Weiss for technical support.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

silver, surface X-ray diffraction, topological insulators

Received: March 20, 2018

Published online:

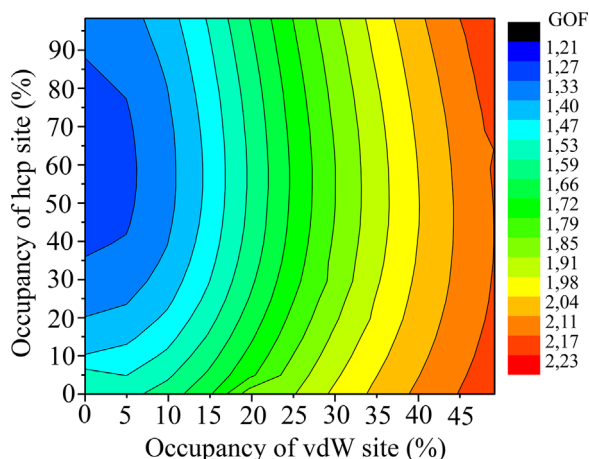


Figure 3. Contour plot of goodness of fit (GOF) versus occupancy of the hcp and the vdW gap site. One contour level corresponds to an increase of 5% relative to the best fit (GOF = 1.21). The vdW gap site is not occupied by silver to within the experimental sensitivity of about 10%.

[1] A. Polyakov, H. L. Meyerheim, E. D. Crozier, R. A. Gordon, K. Mohseni, S. Roy, A. Ernst, M. G. Vergniory, X. Zubizarreta, M. M. Otrokov, E. V. Chulkov, J. Kirschner, *Phys. Rev. B* **2015**, 92, 045423.

- [2] R. Shokri, H. L. Meyerheim, S. Roy, K. Mohseni, A. Ernst, M. M. Otrokov, E. V. Chulkov, J. Kirschner, *Phys. Rev. B* **2015**, *91*, 205430.
- [3] A. Polyakov, C. Tusche, M. Ellguth, E. D. Crozier, K. Mohseni, M. M. Otrokov, X. Zubizarreta, M. G. Vergniory, M. Geilhufe, E. V. Chulkov, A. Ernst, H. L. Meyerheim, S. S. P. Parkin, *Phys. Rev. B* **2017**, *95*, 180202.
- [4] M. M. Otrokov, A. Ernst, K. Mohseni, H. Fulara, S. Roy, G. R. Castro, J. Rubio-Zuazo, A. G. Ryabishchenkova, K. A. Kokh, O. E. Tereshchenko, Z. S. Aliev, M. B. Babanly, E. V. Chulkov, H. L. Meyerheim, S. S. P. Parkin, *Phys. Rev. B* **2017**, *95*, 205429.
- [5] P. D. C. King, R. C. Hatch, M. Bianchi, R. Ovsyannikov, C. Lupulescu, G. Landolt, B. Slomski, J. H. Dil, D. Guan, J. L. Mi, E. D. L. Rienks, J. Fink, A. Lindblad, S. Svensson, S. Bao, G. Balakrishnan, B. B. Iversen, J. Osterwalder, W. Eberhardt, F. Baumberger, P. Hofmann, *Phys. Rev. Lett.* **2011**, *107*, 096802.
- [6] T. Valla, Z. H. Pan, D. Gardner, Y. S. Lee, S. Chu, *Phys. Rev. Lett.* **2012**, *108*, 117601.
- [7] M. Bianchi, R. C. Hatch, Z. Li, P. Hofmann, F. Song, J. Mi, B. B. Iversen, Z. M. Abd El-Fattah, P. Loeptien, L. Zhou, A. A. Khajetoorians, J. Wiebe, R. Wiesendanger, J. W. Wells, *ACS Nano* **2012**, *6*, 7009.
- [8] D. Hsieh, Y. Xia, D. Qian, L. Wray, J. H. Dil, F. Meier, J. Osterwalder, L. Patthey, J. G. Checkelsky, N. P. Ong, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, M. Z. Hasan, *Nature* **2009**, *460*, 1101.
- [9] H. M. Benia, C. Lin, K. Kern, C. R. Ast, *Phys. Rev. Lett.* **2011**, *107*, 177602.
- [10] M. Bianchi, R. C. Hatch, J. Mi, B. B. Iversen, P. Hofmann, *Phys. Rev. Lett.* **2011**, *107*, 086802.
- [11] L. A. Wray, S. Y. Xu, Y. Xia, D. Hsieh, A. V. Fedorov, Y. S. Hor, R. J. Cava, A. Bansil, H. Lin, M. Z. Hasan, *Nat. Phys.* **2011**, *7*, 32.
- [12] M. R. Scholz, J. Sánchez-Barriga, D. Marchenko, A. Varykhalov, A. Volykhov, L. V. Yashina, O. Rader, *Phys. Rev. Lett.* **2012**, *108*, 256810.
- [13] S. V. Eremeev, M. G. Vergniory, T. V. Menshchikova, A. A. Shaposhnikov, E. V. Chulkov, *New J. Phys.* **2012**, *14*, 113030.
- [14] M. Ye, S. V. Eremeev, K. Kuroda, M. Nakatake, S. Kim, Y. Yamada, E. E. Krasovskii, E. V. Chulkov, M. Arita, H. Miyahara, T. Maegawa, K. Okamoto, K. Miyamoto, T. Okuda, K. Shimada, H. Namatame, M. Taniguchi, Y. Ueda, A. Kimura, arXiv:1112.5869, **2011**.
- [15] M. M. Otrokov, S. D. Borisova, V. Chis, M. G. Vergniory, S. V. Eremeev, V. M. Kuznetsov, E. V. Chulkov, *JETP Lett.* **2012**, *96*, 714.
- [16] M. A. Gosalvez, M. M. Otrokov, N. Ferrando, A. G. Ryabishchenkova, A. Ayuela, P. M. Echenique, E. V. Chulkov, arXiv:1402.5920, **2014**.
- [17] S. Roy, H. L. Meyerheim, A. Ernst, K. Mohseni, C. Tusche, M. G. Vergniory, T. V. Menshchikova, M. M. Otrokov, A. G. Ryabishchenkova, Z. S. Aliev, M. B. Babanly, K. A. Kokh, O. E. Tereshchenko, E. V. Chulkov, J. Schneider, J. Kirschner, *Phys. Rev. Lett.* **2014**, *113*, 116802.
- [18] S. Roy, H. L. Meyerheim, K. Mohseni, A. Ernst, M. M. Otrokov, M. G. Vergniory, G. Mussler, J. Kampmeier, D. Grützmacher, C. Tusche, J. Schneider, E. V. Chulkov, J. Kirschner, *Phys. Rev. B* **2014**, *90*, 155456.
- [19] C. Schamper, H. L. Meyerheim, W. Moritz, *J. Appl. Crystallogr.* **1993**, *26*, 687.
- [20] E. Vlieg, *J. Appl. Crystallogr.* **1997**, *30*, 532.
- [21] I. Robinson, *Phys. Rev. B* **1986**, *33*, 3830.
- [22] H. Meyerheim, W. Moritz, *Appl. Phys. A* **1998**, *67*, 645.
- [23] M. J. Buerger, *Kristallographie. Eine Einführung in die geometrische und röntgenographische Kristallkunde*, Walter de Gruyter Verlag, Berlin **1977**.
- [24] U. H. Zucker, E. Perenthaler, W. F. Kuhs, R. Bachmann, H. Schulz, *J. Appl. Crystallogr.* **1983**, *16*, 358.
- [25] R. D. Shannon, C. T. Prewitt, *Acta Crystallogr. B* **1969**, *25*, 925.
- [26] R. D. Shannon, *Acta Crystallogr. A* **1976**, *32*, 751.
- [27] S. Geller, J. H. Wernick, *Acta Crystallogr.* **1959**, *12*, 46.
- [28] J. C. Slater, *J. Chem. Phys.* **1964**, *41*, 3199.
- [29] H. L. Meyerheim, U. Döbler, A. Puschmann, *Phys. Rev. B* **1991**, *44*, 5738.