Atom-vacancy hopping in ultra-high vacuum at room temperature in SrTiO₃ (001)

Rasheed Atif

Received: 9 October 2020 / Accepted: 9 December 2020 / Published online: 16 January 2021
© The Author(s) 2021

Abstract
The diffusion at atomic scale is of considerable interest as one of the critical processes in growth and evaporation as well as a probe of the forces at an atomically flat reconstructed surface. This atomic-scale migration is critical to investigate in strontium titanate (SrTiO₃) as it possesses the same status in oxide electronics as does silicon in ordinary electronics based on elemental semiconductors. Here we show that (001) terminated SrTiO₃ reconstructed surface is atomically unstable enough to allow atom-vacancy hopping at room temperature. In this work, SrTiO₃ (001) single crystal (7×2×0.5 mm) was sputtered (0.5 keV, 2.5 µA, 10 min) and annealed multiple times in ultra-high vacuum (UHV) and imaged using scanning tunneling microscope (STM). A relatively unstable surface was observed at low-temperature annealing and tip–surface interactions caused dislocation of mass at the surface. Both square and zig-zag nanolines were observed with atomic resolution where an atom-vacancy hopping was observed in a square diline while imaging at room temperature. The hopping was ceased when sample was annealed at higher temperature and a more compact network of nanolines was achieved.

Graphic abstract

Keywords  Atom-vacancy hopping · STM · UHV · Room temperature · Nanolines · SrTiO₃ (001)

© Springer
1 Introduction

Comprehension of atomic-scale migration would help us to understand mass transport and shape changes in nanocrystals [1]. As diffusion plays a critical role in phase transformations, atomic-scale migration would allow us to better tune materials for the desired electronic applications. One of the factors that strongly influence diffusion is defects. For example, a point defect, such as vacancy, can pull atoms that have been evaporated from a metal rod by acting as a tiny heterogeneous nucleus site. The study of defects on perovskite surfaces has many potential applications, such as nuclear waste disposal, centers of chemical reactions, geology, and solid-state devices [2].

A knowledge of the composition, structure, and migration pathways of point defects is vital in understanding how an oxide will react to nuclear radiations. Another important parameter which is hard to measure experimentally is threshold displacement energy which is the energy required to permanently displace an atom from its lattice site to form a point defect [3]. This creation of point defects changes the chemical environment and creates new charge states influencing both chemical and environmental properties [4].

Perovskites, such as SrTiO$_3$ (with cubic symmetry $Pm3m - O_3^1$), can accommodate a wide variety of chemical compositions and atomic defects [3]. Of significant importance are the point defects, especially vacancies, which can play an important role for the electronic properties of SrTiO$_3$ [5]. When oxygen vacancies are generated, insulating SrTiO$_3$ becomes conductive and makes STM imaging possible [6]. Surfaces of SrTiO$_3$ with a high concentration of defects are very reactive concerning, e.g., the adsorption of O$_2$, H$_2$O and H$_2$ [1]. Defect-related band gap states are thought to play a decisive role in the catalytic reactions [7]. For compound systems, formation energy of vacancies depends on the atomic chemical potentials. In addition, formation energy of charged defects also vary with the electron chemical potential, i.e., Fermi energy [5]. The generation of vacancies introduces extra levels in the band gap and causes structural relaxations of the ions surrounding the vacancies. The distances from each vacancy to neighboring ions before and after relaxation vary which can cause localized variations in chemical and electronic proper [5].

As diffusion is a thermally activated process, atomic-scale migration occurs easily at elevated temperatures. High-temperature STM observed the nanolines status nascenti by taking successive STM images at temperatures of 825 °C, and showed the formation of stable nucleation centers and their subsequent growth [8]. Nanolines are technologically important as they can be used as templates for nanoscale patterning of molecules or nanoparticles [9, 10]. Auger spectroscopy showed the nanoline surfaces to be Ti$_4^+$ rich [11]. UHV annealing causes surface segregation, giving rise to nanoline decorated surfaces. The continuation of this process results in the formation of islands of anatase TiO$_2$ [12, 13]. However, would room temperature provide enough conducive environment for diffusion to occur? To answer this question, we investigate a reconstructed surface of SrTiO$_3$ using scanning tunneling microscope (STM).

0.5 wt% niobium (Nb)-doped epi-polished SrTiO$_3$ (201) sample was supplied by PI-KEM Ltd, UK. As stoichiometric SrTiO$_3$ has 3.2 eV band gap and is electrically insulating with an empty d band and a work function of 4.2 eV [14], extrinsic n-type electron doping with Nb$^{5+}$ on a Ti$^{4+}$ site was necessary to reduce resistivity. Sample $2m$ that rendered the sample electrically conducting and generated tunneling current for STM imaging [15] demonstrated that SrTiO$_3$ has filled valence bands derived from oxygen 2p orbitals and empty conduction bands derived from titanium 3d orbitals. The Fermi level of SrTiO$_3$ is located close to the conduction band bottom and it is easy to induce conductivity by cation substitution at a fairly low carrier density of about $10^{18}$ cm$^{-3}$ [16]. As grain boundaries and defects can influence the reconstruction mechanism, a single crystal of dimensions $7 \times 2 \times 0.5$ mm was used in this study.

The sample was sonicate-cleaned in methanol and acetone and then transferred into JEOL JSTM-4500 s system operating at $10^{-8}$ Pa. The sample was degassed at 600 °C through resistive direct current heating to ensure minimal surface contamination. After degassing, the sample was sputtered with incidence angle of 45° for 10 min with Ar$^+$ ions of 0.5 keV energy and ion current of 2.5 μA. Ar-ion bombardment causes an irreversible change in the surface structure, stoichiometry, creates Ti$^{4+}$ and Sr$^{2+}$ vacancies, and electron energy distribution [17–19]. As sputtering generates a rough surface, to get an atomically flat surface, the sample was annealed multiple times in UHV.

The sample was imaged using the STM model JSTM-4500s. Various parts of the STM are shown and labeled in the supporting information. The STM comprised of three chambers: imaging chamber, a treatment chamber, and an exchange chamber. Both treatment and imaging chambers had a base pressure of $10^{-9}$ Pa created with the help of ion pumps and titanium sublimation pumps (TSP). STM scanner was calibrated with the use of the well-known Si (111)-(7×7) reconstruction. Images were obtained in constant current topography mode, and the sample was biased positively with respect to the tip, thus tunneling occurred into the empty states of the sample. A tungsten (W) tip was used that was prepared by electrochemical etching of a tungsten wire (diameter 0.3 mm) in a 2 mol/L NaOH solution. Above
750 °C, sample temperatures were measured through a viewport using a Leeds and Northrup disappearing filament optical pyrometer. ImageJ, Gwyddion, and WSxM software were used to improve image contrast and to measure morphological features. The signal-to-noise ratio of the STM images was enhanced by multiple frame averaging using SmartAlign software [20, 21]. Any peculiar results obtained in this study were attempted to be explained based on established theory and experimental observations.

Although both SrO and TiO$_2$ terminations are thermodynamically feasible, all known SrTiO$_3$ surface reconstructions are TiO$_2$ rich [22, 23]. Similar structure was observed after sputtering and annealing whose termination is schematically shown in Fig. 1. As step height was only 0.4 nm (equal to lattice constant), it indicates that surface was only TiO$_2$ terminated as a step height of 0.2 nm would exist had surface comprised of both TiO$_2$ and SrO terminations.

When surface of SrTiO$_3$ (001) was sputtered with Ar$^+$ ions and annealed at 820 °C for 30 min, terraces covered in nanoline started to appear. Figure 2 shows two images of the surface with image (a) being 10 min older than image (b). The difference in images is prominent as highlighted in white and yellow squares. The regions in white squares show that the terrace is trying to convert its end to sharp edges. The phenomenon occurring in yellow squares is more prominent. A chunk of material existing in the form of a protrusion in terrace had vanished after 10 min. The dislocation of the material at the surface by STM tip due to tip–surface

---

**Fig. 1**  a, b SrTiO$_3$ (001) unit cell and TiO$_2$-terminated surface achieved after sputtering and annealing

**Fig. 2**  a, b SrTiO$_3$ (001) surface after being sputtered (0.5 keV, 2.5 µA, 10 min) and annealed at 820 °C for 30 min; $V_s$ = 2 V, $I_t$ = 0.2 nA. Image b was taken 10 min after image a.
interactions is a well-known fact; however, it hints that the sample’s surface is relatively “soft”. When sample was further annealed at 850 °C for 30 min, the whole surface was covered with two types of dilines: zig-zag and square, as shown in Fig. 3. The description of the dilines is available in the literature [22] and will not be repeated here. During imaging, an atom vacancy was found hopping between two position as shown in Fig. 4. The video can be downloaded using the following link: https://www.dropbox.com/s/32s5t2atz2gq489/1.%20SrTiO3%20atom%20hopping.avi?dl=0.

Fig. 3  a, b SrTiO$_3$ (001) sample after being annealed at 850 °C for 30 min; $V_s=2$ V, $I_t=0.2$ nA. The surface in a is predominantly covered in square dilines while b shows a zig-zag diline.

Fig. 4  a, b STM images showing atom-vacancy hopping is feasible on the SrTiO$_3$ (001) reconstructed surface at room temperature under UHV conditions; $V_s=2$ V, $I_t=0.2$ nA.
In an image of 30 nm × 30 nm, there are four instances of atom-vacancy hopping out of 380 surface atoms in dilines. The atom-vacancy hopping is only unilateral along close-packed <110> directions. This room temperature hopping is an example of an athermal surface diffusion that results either through an electronic mechanism or by direct knock-on of a surface atom [24]. For athermal processes, electron can cause electronic transitions which become converted into atomic motion leading to surface diffusion [25] for which various models have been proposed [26–29]. When sample was further annealed at 900 °C for 30 min, the dilines transformed into an equidistant, compact and stable network of nanolines as shown in Fig. 5. These nanolines have two domains that are perpendicular to each other. Although dilines, trilines, and tetralines have been commonly reported in the literature [8, 30], this kind of equidistant and compact networks of nanolines has been seldom reported. No surface mobility was observed even for prolonged period of time. When sample was further annealed at 950 °C terraces with right angle edges were observed as shown in Fig. 6. The nanolines at right angle can still be observed; however, no atom-vacancy hopping could be observed in this compact network of nanolines. There were two main orientations of observed nanolines: <100> and <010>. This right angle between nanolines stems from the reconstruction underneath the nanolines. It has been shown that reconstruction underneath the nanolines is c(4 × 2) [22]. Auger electron spectroscopy (AES) showed that the dilines are more Ti rich than cleaved surfaced and double-layer TiO₂-reconstructed structures such as c(4 × 2) [11].

These results suggest that SrTiO₃ surface is atomically mobile when annealed at low temperatures (≤ 850 °C). A compact and immobile surface results from high-temperature annealing. Since oxygen and strontium defects are more mobile than Ti defects [3], and neutral SrO Schottky defects are known to be low-energy defects in SrTiO₃ [5], one should expect the observed hopping is of SrO. While it is in principle possible for the reconstruction to be SrO rich, the only confirmed SrTiO₃ (001) surface structures are TiO₂ rich [31]. TiO₂ has inclination of coming out of perovskite oxides. When LaAlO₃ is deposited on SrTiO₃, TiO₂...
2D nano-mesh spontaneously detaches from the original SrTiO$_3$ surface and then recrystallizes on top of AlO$_2$ layer of LaAlO$_3$ [32]. It has been shown that each spot of the diline observed by STM corresponds to the convolution of the electronic states from 4 Ti atoms and 7.5 oxygen atoms [33]. The charge obtained for the ions in the bulk of SrTiO$_3$ are $Q_{Ti} = 1.35$, $Q_{O_2^-} = 1.44$, and $Q_{O} = -0.96$ [34, 35]. The values suggest that the Ti–O bond has a large part of covalent character and due to this strong bond, Ti–O diffuses as a unit. Therefore, the observed hopping is of either anatase TiO$_2$ or TiO$_x$ where $x$ can be smaller than 2 as oxygen is lost from SrTiO$_3$ surface upon annealing. Small particles of TiO$_x$ are known to diffuse across the surface of metals supported on TiO$_2$ (110) [36, 37].

One of the possible reasons for this hopping could be electronic charge transfer from oxygen to titanium [4]. The nanolines are mainly composed of anatase TiO$_2$, and $s$ orbitals of Ti in TiO$_2$ does not possess valence electrons. An interatomic Auger process requires two electrons for 3p hole decay [27]. These two electrons come from oxygen as it acts as a donor site by releasing two electrons thereby forming an oxygen vacancy $O^{2-}_{vac}$ [38]. These oxygen vacancies do not only impart electrical conductivity to SrTiO$_3$, but also cause to form various surface reconstructions. Isolated defect energies in SrTiO$_3$ are calculated according to a modified Mott–Littleton method [39] as embodied in the general utility lattice program (GULP) [40]. The average enthalpy for forming an oxygen vacancy with two conduction band electrons is $5.76 \pm 0.20$ eV [41]. Oxygen vacancies migrate via a slightly curved pathway between oxygen nearest neighbor sites. Displaced oxygen atoms collide directly with nearby oxygen atoms, favoring the formation of oxygen Frenkel pairs through replacement sequences. Oxygen favors a split-interstitial configuration in one dimension (normal to Ti bonds in the vicinity), with two atoms sharing a single lattice site [3]. $O^{2-}_{vac}$ vacancy importance increases in the oxygen 2$p$ band cause localized magnetism [42]. If oxygen sitting at the surface releases two electrons, then that oxygen will be electrically neutral and likely to desorb [27]. However, TiO$_x$ vacancy complex is not entirely suppressed by oxygen desorption/adsorption [41]. The released pair of electrons will delocalize within the partial wedge created by the positively charged layer of surface vacancies [43].

Successive changes in charge state lead to motion of the point defects through the lattice [24]. In a similar compound, the oxygen vacancies in barium titanate (BaTiO$_3$) are either partially [44] or fully [45] doubly ionized at temperatures $\geq 800$ °C. The oxygen vacancy levels in SrTiO$_3$ are very close to the conduction band and can bring the resistivity down even at low temperatures [46]. In pure SrTiO$_3$, matter transport proceeds through diffusion of oxygen vacancies created by Schottky defects, as reported by Paladino et al. [47]. Similar results were reported by Kingery et al. [48], Yamaji [49], and Walters and Grace [50]. The oxygen vacancies created under reductive environment (UHV) can be quenched upon cooling to room temperature, and while they remain doubly ionized, to very low temperatures [41]. Paladino et al. [47] have investigated oxygen self-diffusion in single crystal SrTiO$_3$ in the temperature range of 825–1525 °C. Based on the oxidation process and oxygen self-diffusion, Paladino [51] concluded that an oxygen vacancy defect model fits well for the SrTiO$_3$. The diffusion of ionized species can be explored to tune the quantity of states in the topological insulators [52]. In addition, given that titanium dioxide surfaces [53] are the preferred material for developing photocatalytic applications, mobility of TiO$_x$ at room temperature reported here may provide new means for developing technologies in photocatalysis.

2 Conclusions

Atom-vacancy hopping is possible in SrTiO$_3$ (001) in ultra-high vacuum at room temperature. Such hopping can be used to produce functional materials via defect engineering. The hopping was only observed in square diline and not in any other type of nanoline. A low-temperature annealing (≤ 850 °C) is more suitable to produce a surface that is mobile at atomic scale. Annealing at higher temperatures yielded a more compact and stable network of nanolines.

Acknowledgements The author would like to thank the Department of Materials, University of Oxford, UK, for the provision of research facilities and Oxford-Sir Anwar Pervez research scholarship for financial assistance.

Funding Funding was provided by Oxford Research Fund.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included under Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. S. Ferrer, G.A. Somorjai, UPS and XPS studies of the chemisorption of O$_2$, H$_2$ AND H$_2$O on reduced and stoichiometric SrTiO$_3$(111) surfaces; the effects of illumination. Surf. Sci. 94, 41–56 (1980). https://doi.org/10.1016/0039-6028(80)90155-7
2. G. Ayrault, G. Ehrlich, Surface self-diffusion on an ice crystal: an atomic view. J. Chem. Phys. 60, 281–294 (1974). https://doi.org/10.1063/1.1680781

3. B.S. Thomas, N.A. Marks, B.D. Begg, Defects and threshold displacement energies in SrTiO3 perovskite using atomistic computer simulations. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms. 254, 211–218 (2007). https://doi.org/10.1016/j.nimb.2006.11.069

4. B. Cord, R. Courths, Electronic study of SrTiO3(001) surfaces by photoemission. Surf. Sci. 162, 34–38 (1985). https://doi.org/10.1016/0039-6028(85)90782-6

5. T. Tanaka, K. Matsunaga, Y. Ikuhara, T. Yamamoto, First-principles study on structures and energetics of intrinsic vacancies in SrTiO3. Phys. Rev. B Condens. Matter Phys. 68, 1–8 (2003). https://doi.org/10.1103/PhysRevB.68.205213

6. T. Higuchi, T. Tsukamoto, N. Sata, M. Ishigame, Y. Tezuka, S. Shin, Electronic structure of p-type SrTiO3 by photoemission spectroscopy. Phys. Rev. B 57, 6978–6983 (1998). https://doi.org/10.1103/PhysRevB.57.6978

7. T. Wolfram, F.J. Morin, A model for surface states and catalysis on d-band perovskites. Appl. Phys. 8, 125–141 (1975). https://doi.org/10.1007/BF02459733

8. H.L. Marsh, D.S. Deak, F. Silly, A.I. Kirkland, M.R. Castell, Hot STM of nanostructure dynamics on SrTiO3(001). Nanotechnology. 17, 3543–3548 (2006). https://doi.org/10.1088/0957-4484/17/14/031

9. D.S. Deak, F. Silly, K. Poryfakis, M.R. Castell, Template ordered open-grid arrays of paired endothelial fullerenes. J. Am. Chem. Soc. 128, 13976–13977 (2006). https://doi.org/10.1021/ja0634369

10. D.S. Deak, F. Silly, K. Poryfakis, M.R. Castell, Controlled surface ordering of endothelial fullerenes with a SrTiO3 template. Nanotechnology 18, 075301 (2007). https://doi.org/10.1088/0957-4484/18/7/075301

11. D.S. Deak, F. Silly, D.T. Newell, M.R. Castell, Ordering of TiO2-based nanostructures on SrTiO3(001) surfaces. J. Phys. Chem. B. 110, 9246–9251 (2006). https://doi.org/10.1021/jp054954x

12. F. Silly, M.R. Castell, Formation of single-domain nanotube TiO2(001)-1×1(4x) islands on SrTiO3(001) after thermal annealing. Appl. Phys. Lett. 85, 3223–3225 (2000). https://doi.org/10.1063/1.1267177

13. M.S.J. Marshall, M.R. Castell, Shape transformation of epitaxial islands during strained layer growth: nanotube TiO2(001) on SrTiO3(001). Phys. Rev. Lett. 102, 146102 (2009). https://doi.org/10.1103/PhysRevLett.102.146102

14. Y.W. Chung, W.B. Wassall, Surface spectroscopy studies of the SrTiO3 (100) surface and platinum-SrTiO3 (100) interface. Phys. Rev. B 20, 3458–3461 (1979). https://doi.org/10.1103/PhysRevB.20.3458

15. A.H. Kahn, A.J. Lekkerkerker, Electronic energy bands in strontium titanate. Phys. Rev. 135, A1321–A1325 (1964). https://doi.org/10.1103/PhysRev.135.A1321

16. O.N. Teo, P.W. Chapman, Electron mobility in semiconducting strontium titanate. Phys. Rev. 155, 796–802 (1967). https://doi.org/10.1103/PhysRev.155.796

17. J. Lopez, A. Somorjai, Temperature-dependent surface structure, composition, and electronic properties of the clean SrTiO3(111) crystal face: low-energy-electron diffraction, Auger-electron spectroscopy, electron energy loss, and ultraviolet-photoelectron spectroscopy studies. Phys. Rev. B 17, 4942–4950 (1978). https://doi.org/10.1103/PhysRevB.17.4942

18. Y.A. Zulueta, J.A. Dawson, Y. Leyet, F. Guerrero, J. Anglada-Rivera, M.T. Nguyen, The potential existence of mixed defect incorporation modes for rare-earth doped cubic BaTiO3 Phys.
investigation of metal-support interactions in Rh/TiO₂. J. Chem. Soc. Faraday Trans. 92, 2799–2809 (1996). https://doi.org/10.1039/FT969202799

37. S. Takatani, Y.W. Chung, Effect of high temperature reduction on the surface composition of and CO chemisorption on Ni/TiO₂. Appl. Surf. Sci. 19, 341–347 (1984). https://doi.org/10.1016/0169-4332(84)90071-0

38. L.C. Walters, R.E. Grace, Formation of point defects in strontium titanate. J. Phys. Chem. Solids. 28, 239–244 (1967). https://doi.org/10.1016/0022-3697(67)90015-4

39. N.F. Mott, M.J. Littleton, Conduction in polar crystals. I. Electrolytic conduction in solid salts. J. Chem. Soc. Faraday Trans. II. 34, 565–579 (1938)

40. J.D. Gale, A.L. Rohl, The general utility lattice program (GULP). Mol. Simul. 29, 291–341 (2003). https://doi.org/10.1080/0892702031000104887

41. H. Yamada, G.R. Miller, Point defects in reduced strontium titanate. J. Solid State Chem. 6, 169–177 (1973). https://doi.org/10.1016/0022-4596(73)90216-8

42. J. Mannhart, D.G. Schlom, Oxide interfaces—an opportunity for electronics. Science 327, 1607–1611 (2010)

43. A.F. Santander-Syro, O. Copie, T. Kondo, F. Fortuna, S. Pailhès, R. Weht, X.G. Qiu, F. Bertran, A. Nicolau, A. Taleb-Ibrahimi, P. Le Fèvre, G. Herranz, M. Bibes, N. Reyren, Y. Apertet, P. Lecoeur, A. Barthélémy, M.J. Rozenberg, Two-dimensional electron gas with universal subbands at the surface of SrTiO₃. Nature 469, 189–193 (2011). https://doi.org/10.1038/nature09720

44. S.A. Long, R.N. Blumenthal, Ti-Rich nonstoichiometric BaTiO₃: I. high-temperature electrical conductivity measurements. J. Am. Ceram. Soc. 54, 515–519 (1971)

45. N.G. Eror, D.M. Smyth, Nonstoichiometric disorder in single-crystalline BaTiO₃ at elevated temperatures. J. Solid State Chem. 24, 235–244 (1978). https://doi.org/10.1016/0022-4596(78)90015-4

46. H.P.R. Frederikse, W.R. Thurber, W.R. Hosler, Electronic transport in strontium titanate. Phys. Rev. 134, A442–A445 (1964). https://doi.org/10.1136/sti.31.1.31

47. A.E. Paladino, L.G. Rubin, J.S. Waugh, Oxygen ion diffusion in single crystal SrTiO₃. J. Phys. Chem. Solids. 26, 391–397 (1965). https://doi.org/10.1016/0022-3697(65)90168-X

48. W.D. Kingery, J. Pappis, M.E. Doty, D.C. Hill, Oxygen ion mobility in cubic Zr0.85Ca0.15O1.85. J. Am. Ceram. Soc. 42, 393–398 (1959)

49. A. Yamaji, Oxygen-ion diffusion in single-crystal and polycrystalline SrTiO₃. J. Am. Ceram. Soc. 58, 152–153 (1975)

50. L.C. Walters, R.E. Grace, Formation of point defects in strontium titanate. J. Phys. Chem. Solids. 28, 245–252 (1967). https://doi.org/10.1016/0022-3697(67)90115-1

51. A.E. Paladino, Oxidation kinetics of single-crystal SrTiO₃. Am. Ceram. Soc. 1965, 1964–1966 (1964)

52. D. Hsieh, Y. Xia, D. Qian, L. Wray, M. D. 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, A tunable topological insulator in the spin helical Dirac transport regime. Nature 460, N101–N05 (2009). https://doi.org/10.1038/nature08234

53. U. Diebold, The surface science of titanium dioxide. Surf. Sci. Rep. 48, 53–227 (2003)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.