Showcasing the work on MOCVD-grown, epitaxial Sb$_2$Te$_3$ thin films presented by Prof. Stephan Schulz, Faculty of Chemistry, University of Duisburg-Essen and Center for Nanointegration Duisburg Essen (CENIDE).

Title: Deposition of topological insulator Sb$_2$Te$_3$ films by an MOCVD process

Smooth Sb$_2$Te$_3$ films were layer-by-layer grown on c-oriented Al$_2$O$_3$ substrates using Et$_2$Te$_2$ and i-Pr$_3$Sb. The high quality films allowed for the first time the measurement of the topological surface state for MOCVD grown Sb$_2$Te$_3$ by ARPES.

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Deposition of topological insulator Sb$_2$Te$_3$ films by an MOCVD process

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Layered Sb$_2$Te$_3$ films were grown by a MOCVD process on Al$_2$O$_3$(0001) substrates at 400 °C by use of i-Pr$_5$Sb and Et$_2$Te$_2$ and characterized by SEM, AFM, XRD, EDX and Auger spectroscopy. The electrical sheet resistivity was measured in the range of 4 to 400 K, showing a monotonic increase with increasing temperature. The valence band structure probed by angle-resolved photoemission shows the detailed dispersions of the bulk valence band and the topological surface state of a quality no less than for optimized bulk single crystals. The surface state dispersion gives a Dirac point roughly 30 meV above the Fermi level leading to hole doping and the presence of bulk valence states at the Fermi energy.

Sb$_2$Te$_3$ thin films were prepared in the past by microwave heating,$^{12,13}$ vapour phase transport,$^{14-21}$ vapour–liquid–solid growth,$^{22,23}$ atomic layer epitaxy,$^{24}$ electrochemical deposition,$^{25-31}$ DC and RF sputtering,$^{32,33}$ and molecular beam epitaxy (MBE).$^{34,35}$ Unfortunately, these processes very often only produced polycrystalline or highly faceted Sb$_2$Te$_3$ films, which additionally often suffered from high antisite concentrations, which typically result in a strong shift of the Fermi energy.

Metal organic chemical vapour deposition (MOCVD) is a promising technical alternative, which has been shown to produce crystalline Sb$_2$Te$_3$ films.$^{36-44}$ In MOCVD processes, trialkylstibines SbR$_3$ (R = Me, Et) and dialkyltellanes TeR$_2$ (R = Et, i-Pr, t-Bu) are typically used as molecular precursors.$^{45}$ Unfortunately, these precursors often require high pyrolysis temperatures, forcing the incorporation of impurities such as carbon into the material film. Therefore, there is a strong demand for alternative metal organic precursors. Single-source precursors are promising candidates for low-temperature deposition processes.$^{46}$ We recently demonstrated that (Et$_2$Sb)$_2$Te can be used as an MOCVD precursor for the synthesis of highly stoichiometric Sb$_2$Te$_3$ films with very low antisite defect concentrations at temperatures as low as 200 °C,” while O’Brien et al. and Chivers et al. deposited Sb$_2$Te$_3$ films in the temperature range from 375 to 475 °C using Sb[(TePi-Pr$_2$)$_2$N]$_3$ in an aerosol-assisted chemical vapour deposition (AACVD) process.$^{48}$ Unfortunately, the Sb$_2$Te$_3$ films obtained with both precursors were rather polycrystalline, consisting of hexagonal Sb$_2$Te$_3$ nanolayers. In the case of the (Et$_2$Sb)$_2$Te precursor, the low substrate temperature (200 °C) limited the diffusion mobility of the deposited Sb and Te atoms, hence avoiding the formation of a flat film. In contrast, higher substrate temperatures yielded flat Sb$_2$Te$_3$ films, but these were contaminated by elemental antimony.

We therefore became interested in suitable Sb- and Te-precursors for the MOCVD deposition at temperatures between
350 and 400 °C and report herein on the MOCVD deposition of Sb₂Te₃ films using i-Pr₃Sb as the Sb-source and Et₂Te₂ as the Te-source. Both precursors are stable liquids at ambient temperature with a good volatility. i-Pr₃Sb has been used in the past for the CVD-deposition of GeSb₂Te₄ phase change materials,⁴⁹–⁵¹ whereas Et₂Te₂ has not been used as a CVD precursor, to date. To the best of our knowledge, dimethyl ditellane Me₂Te₂ is the only ditellane that has been used as a MOCVD-precursor, to date,⁵²,⁵³ but it suffers from a relatively low vapour pressure. We carefully investigated the distinctive role of different substrates and substrate temperatures on the growth of the antimony telluride films, which were analyzed by energy dispersive X-ray analysis (EDX) and Auger spectroscopy, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Moreover, the electrical resistance of these films was determined by a Physical Property Measurement System (PPMS) in the range of 4 to 400 K and angle-resolved photoemission spectroscopy (ARPES) experiments revealed that the surface electronic structure presents a slightly hole-doped Dirac cone with photon-energy dependent photoemission intensity and a more surface localized surface state at higher binding energy. The measured doping level of the Dirac cone indicates that bulk valence states are present at the Fermi energy where they dominate the transport properties.

**Experimental section**

**Materials**

i-Pr₃Sb and Et₂Te₂ were prepared by literature methods.⁴⁴,⁵⁵

**MOCVD deposition**

MOCVD studies were performed in a cold-wall high-vacuum MOCVD reactor.⁴⁷ Sb₂Te₃ films were deposited on either Si(100) or Al₂O₃(0001) substrates at a working pressure of 10 mbar within 15 minutes. Si(100) substrates were previously degreased with acetone, treated with hydrofluoric acid and heated to 500 °C at 10⁻³ mbar for 1 hour in the reactor. Al₂O₃(0001) substrates were degreased with acetone and cleaned with a 3 : 1 mixture of sulphuric acid and phosphoric acid before use. The precursors were loaded into bubblers attached to the MOCVD-reactor under inert conditions (Ar) and the bubbler temperature was set to −5 °C (i-Pr₃Sb) and 20 °C (Et₂Te₂) throughout the experiment. Argon was used as the carrier gas (40 sccm Et₂Te₂, 5 sccm i-Pr₃Sb) and the precursor flow was controlled by use of a mass flow controller (MKS Instruments). After the film deposition was finished, the system was cooled to ambient temperature within 30 minutes under vacuum.

**DSC analysis**

A DSC 200 Phox (Netzsch Gerätebau) was used for differential scanning calorimetry (DSC) analysis.

**X-ray analysis**

XRD patterns were obtained using a Bruker D8 Advance powder diffractometer with Cu Kα radiation (λ: 1.5418 Å).

**Surface-analysis**

The surface morphology of the Sb₂Te₃-film was investigated by AFM using an AFM Veeco diınnova and by SEM using a Jeol JSM 6510 equipped with an energy dispersive X-ray spectroscopy (EDX) device (Bruker Quantax 400). A cross-sectional sample of the Sb₂Te₃ film was prepared by using a Jeol Cross-Section Polisher (IB-09010CP).

**Auger spectroscopy**

SAM/AES studies were carried out on a Perkin Elmer PHI 660 Scanning Auger Microprobe System.

**Photoelectron spectroscopy**

Angle-resolved photoelectron spectroscopy (ARPES) was performed with linearly polarized synchrotron radiation (s + p) at the UE112-PGM2a undulator beamline of BESSY II using a Scienta R8000 hemispherical electron energy analyzer. The samples were transferred in air and the surface was prepared in situ by sputtering for 1 h at 1.5 keV at 1.2 × 10⁻⁵ mbar Ar pressure followed by 30 min annealing at 230 °C. ARPES was subsequently performed in a base pressure of 2 × 10⁻¹⁰ mbar at ambient temperature.

**Results and discussion**

Ditellanes R₃Te₂ are promising low-temperature Te precursors for MOCVD deposition due to their low thermal stability. Me₂Te₂, whose decomposition temperature is ≈ 100 °C lower compared to that of Me₃Te, has been successfully used by Kisker et al. for the growth of CdTe films at 250 °C.⁵⁶ Moreover, ditellanes are easily accessible by reaction of Na₂Te₂ with alkyl halides in liquid ammonia or other standard reactions.⁵⁷–⁵⁹ The thermal properties of Et₂Te₂ and i-Pr₃Sb were investigated by DSC to identify suitable substrate temperatures for the MOCVD process. The decomposition temperature of i-Pr₃Sb (255 °C) is significantly lower compared to that of Et₂Te₂ (310 °C) and Me₂Te₂ (370 °C), which are typically used for the MOCVD process (Fig. 1). Et₂Te₂ starts to disproportionate at 150 °C with subsequent formation of elemental tellurium and Et₂Te, which then decomposes at higher temperature (260 °C) as is shown by comparing the DSC curves of Et₂Te₂ (Fig. 2, black curve) and of pure Et₂Te (Fig. 2, red curve).

Sb₂Te₃ films were grown on polycrystalline Al₂O₃(0001) substrates at substrate temperatures between 350 and 400 °C using a home-made MOCVD cold-wall reactor and a deposition time of 15 minutes. An almost linear increasing growth rate with increasing substrate temperature was found in the temperature range from 350 °C to 400 °C, reaching 750 nm in 15 min at 400 °C. These findings point to a kinetically-controlled growth process, which we have also recently reported for the MOCVD deposition of Sb₂Te₃ films using (Et₂Sb)₂Te as a single source precursor.⁶⁰ The chemical composition (EDX) and the crystallinity (XRD) of the resulting Sb₂Te₃ films were not affected by the increasing substrate temperature, whereas the morphology of the Sb₂Te₃ films changed significantly. Sb₂Te₃ films deposited at 350 °C (Fig. 3a) and 375 °C (Fig. 3b) show a...
polycrystalline surface, most likely resulting from the low diffusion rates of adatoms as was observed with (Et3Sb)2Te. In contrast, very smooth Sb2Te3 films were obtained at 400 °C (Fig. 3c). The substrate material also has a distinguished influence on the film morphology since the deposition on Si(100) substrates at 400 °C only yielded polycrystalline Sb2Te3 films (Fig. 3d).

The substrate typically affects the morphology of the growing film. Epitaxial films are preferentially grown on substrates which exhibit a small lattice mismatch (<7%) in order to reduce the lattice strain (so-called hetero-epitaxy). However, since Sb2Te3 adopts a rhombohedral crystal structure, in which five monoatomic sheets in a sequence of Te–Sb–Te–Sb–Te are bonded in the c-axis direction, the Sb2Te3 films are always Te-terminated due to the weak van der Waals Te–Te bond. As a consequence, epitaxial V2VI3 films such as Sb2Te3, Bi2Se3 or Bi2Te3 have been grown on substrates with large lattice mismatches such as GaAs, Si[111] and Al2O3(0001), respectively, since the merely attached Sb2Te3 epilayers can achieve their own lattice parameters from the beginning of the growth. This growth mechanism is typically referred to as van der Waals epitaxy, which explains the formation of epitaxial Sb2Te3 films on Al2O3(0001). In contrast, Sb2Te3 films obtained on Si(100) always showed Sb2Te3 nanodisks on the Bi2Se3 substrate, whereas lower substrate temperatures gave Sb-deficient films due to the higher sticking coefficient of Te at low temperatures compared to that of Sb. Since the sticking coefficient of Te decreases at higher substrate temperatures, stoichiometric Sb2Te3 films were formed. However, Persiano et al. also reported on the MBE growth of stoichiometric Sb2Te3 films at a substrate temperature of 250 °C. Herein, we deposited highly stoichiometric Sb2Te3 films at 350 °C and at 400 °C. The film obtained at 400 °C is very flat, consisting of large Sb2Te3 flakes, whereas that obtained at 350 °C also showed hexagonal Sb2Te3 nanocrystals, which adopt orientations perpendicular to the film surface. The higher substrate temperature not only influences the decomposition kinetics of the precursor molecules, resulting in higher decomposition rates, but also affects the mobility of the adatoms, which increases with increasing substrate temperature, yielding larger Sb2Te3 nanoflakes. Moreover, the surface morphology (flatness) of the film improved with the increasing substrate temperature.

SEM (Fig. 4) and AFM micrographs (Fig. 5) of the Sb2Te3 film deposited on Al2O3(0001) substrates at 400 °C within 15 minutes prove the formation of smooth Sb2Te3 films over a large range (substrate dims. 10 × 10 mm). These results were confirmed by cross-sectional SEM microscopy (Fig. 5), showing a uniformly grown Sb2Te3 film of about 750 nm thickness.

The AFM micrograph (Fig. 6) shows regular terraces of 1 nm height, which correspond to one quintuple layer of the layered tetradymite-type structure of Sb2Te3. These findings indicate a layered growth as was also observed in MBE-grown Sb2Te3 thin
$Sb_2Te_3$ crystallizes in the space group $R\bar{3}m-D_{3d}$ and forms a layered, rhombohedral crystal structure. It is built of anisotropic layers, in which five atomic planes are covalently bonded to the quintuple layer, that is roughly 1 nm thick and consists of five mono-atomic planes of Te(1)-Sb-Te(2)-Sb-Te(1) with 1 and 2 designating the different positions within the fivefold layer. The conventional unit cell includes three quintuple layers, which are bound by weak van der Waals forces.

The X-ray diffractogram (XRD) of the $Sb_2Te_3$ film deposited at 400 °C (Fig. 8) clearly proved the formation of highly crystalline $Sb_2Te_3$ films. All reflection peaks can be indexed on the basis of the structure of rhombohedral $Sb_2Te_3$. In addition, a small reflex of the $Al_2O_3(0001)$ substrate is visible at 41.6°. The peaks in the diffractogram correspond to (001) planes, pointing to a c-axis oriented growth as was previously reported for $Sb_2Te_3$ films grown by MBE, and MOCVD, respectively.

The chemical composition of the material film was analyzed by EDX analysis. Almost perfect $Sb_2Te_3$ films with the expected 40 : 60 (Sb : Te) molar ratios were found (standard deviation ±0.5 (Sb) and ±1.0 (Te)). Fig. 7 shows an $Sb_2Te_3$ film at an early stage of growth. The SEM image shows single plates which are not fully coalesced. The corresponding element mapping by scanning Auger electron microscopy (SAES) shows a homogeneous distribution of Sb and Te within the $Sb_2Te_3$ plates. In addition, some carbon impurities are located between the $Sb_2Te_3$ plates on the substrate surface.
We have characterized the band structure of the surface by photoelectron spectroscopy (PES) after transfer to the photoelectron spectrometer and in situ preparation. To the best of our knowledge, this is the first time that angle-resolved photoemission spectroscopy (ARPES) studies have been performed on MOCVD-grown Sb$_2$Te$_3$ thin films. The PE spectrum in Fig. 9 shows Sb and Te core-levels without any shifted components similar to that of Bi$_2$Se$_3$.\textsuperscript{71}

The overview ARPES spectra of the valence band in Fig. 10 show intense structures around 0.8 eV binding energy and more faint features near $E_F$ which are well discernible at 16 and 17 eV photon energy but not at 21 eV, where their photoemission intensity is weak due to final state effects. Fig. 11 shows, therefore, the range near $E_F$ for photon energies from 16 to 18 eV displaying the topological surface state. This surface state has previously been studied theoretically\textsuperscript{7} and in ARPES experiments at selected photon energies (21.2 eV),\textsuperscript{10,72} 55 eV,\textsuperscript{11} 8.44 and 24 eV,\textsuperscript{72} respectively.

While experiments on cleaved bulk samples led to the conclusion that the Fermi level does not cut the surface state,\textsuperscript{73} epitaxial Sb$_2$Te$_3$/Si(111) films observed slight hole doping (Dirac point = 100 meV above $E_F$) and, after deposition of 0.1 monolayer Cs, the undoped state with the Dirac point at $E_F$. The spin texture of the surface state has been probed by spin- and angle-resolved photoemission, and an additional, topologically protected, Rashba-split surface state was found.\textsuperscript{11} These results have been confirmed recently for epitaxial Sb$_2$Te$_3$/Si(111) films.\textsuperscript{72} In Fig. 10, this additional surface state is marked at 0.4–0.8 eV binding energy in the data taken at 21 eV photon energy. Due to its high binding energy, it does not contribute to transport. On the other hand it has been found to be much more surface localized than the topological surface state that forms the Dirac cone and its sharp, intense dispersing photoemission features here indicate the presence of a well ordered and stoichiometric surface.

Changing the photon energy in ARPES allows us principally to vary the perpendicular component of the electron wave vector, $k_z$.\textsuperscript{74} In this way, we can distinguish three-dimensional dispersing features from two-dimensional features. The identical $E$ vs. $k_F$ dispersion in Fig. 11 proves the two-dimensional character. The intensity, however, is subject to the $k_z$-dependence of the parent bulk band structure, and this is seen at 18 eV as a shift of maximum intensity so that at 22 eV (not shown) the surface state is not discernible any longer. The intensity seen near the Fermi energy at 16 eV moves with increasing photon energy to lower binding energy and has crossed $E_F$ at 18 eV. This intensity stems directly from bulk valence band states which exist in the complete lower Dirac cone up to the Dirac point as is evident from, e.g., surface-projected bulk band calculations.\textsuperscript{11} Due to these states, the topological transport regime will require the Fermi level to be in the upper Dirac cone. The linear dispersion predicted by theory has been fitted to the data at 16.5 eV in Fig. 11. Extrapolation of the data yields a Fermi velocity of $(2.72 \pm 0.14) \times 10^5$ m s$^{-1}$, roughly in agreement with previous measurements from single crystals [(3.8 ± 0.2) $\times 10^5$ m s$^{-1}$] and density functional theory (3.2 $\times 10^5$ m s$^{-1}$),\textsuperscript{11} and a Dirac point $\approx$ 30 meV above $E_F$. The surface is, therefore, slightly hole doped. The calculation shows that bulk valence band states reach up to the Dirac point so that hole doping indicates that the Fermi level cuts through bulk valence band states rendering the transport bulk like.\textsuperscript{11}

Electrical measurements were performed with a PPMS-system (DynaCool QuantumDesign) using the standard...
Electronic Transport Option. By applying an alternate current of 1 mA with a frequency of 12.2 Hz and a sampling rate of 0.5 s⁻¹, the resistance was measured in the range of 4 to 400 K with a heating rate of 10 K min⁻¹. By making equally spaced 4-point contacts and choosing the contact spacing much larger than the film thickness, the sheet resistivity can be calculated by the following equation:  
\[ \rho = \frac{\pi V}{\ln 2 I} \]

\( I \) is the applied current at the outer contacts and \( V \) is the measured voltage drop between the inner contacts.

The measured sheet resistivity (Fig. 12) shows a metallic like behaviour with a dominating contribution of the carrier transport in the bulk, and a monotonic increase with increasing temperature as was previously observed for ALD-grown Sb₂Te₃ thin films. Here the sheet resistance increases by one order of magnitude (10×) over the temperature range from 2 to 400 K, whereas the resistance of the ALD film increased moderately by the factor of 1.5 over the same temperature range. The MOCVD films exhibit a higher carrier concentration (>10¹⁹ cm⁻³) correlated with intrinsic defects, most likely antisite defects as is common for Sb₂Te₃. Furthermore, we assume that the carrier concentration is nearly constant over the complete temperature range and the strong enhancement of the resistance over temperature is related to the reduction of the carrier mobility. Due to the high doping concentration the enhancement of the carrier concentration by thermal excitation of carriers over the bulk-bandgap is not observed by the resistance curve (Fig. 12) or has a negligible impact. In the case of ALD grown Sb₂Te₃ films a stabilisation of the resistance at least around 350 K has been reported.  

Conclusions

The layer-by-layer MOCVD deposition of highly crystalline Sb₂Te₃ films was achieved at substrate temperatures between 350 and 400 °C using i-Pr₃Sb and Et₃Te₂. Even though both precursors start to decompose at lower temperatures as was shown by DSC, higher temperatures are necessary in order to produce smooth and crystalline Sb₂Te₃ films. The film growth occurs under kinetic control, reaching deposition rates as high as 3 µm per hour at 400 °C. The electrical sheet resistivity was found to monotonically increase with increasing temperature. ARPES measurements for the first time showed the detailed dispersions of the bulk valence band and the topological surface state for MOCVD grown Sb₂Te₃ films with a quality no less than for optimized bulk single crystals. The surface state dispersion gives a Dirac point roughly 30 meV above the Fermi level leading to hole doping and the presence of bulk valence states at the Fermi energy. Additional Bi doping of the Sb₂Te₃ films is currently under investigation in order to further modify the valence band and the topological surface states.

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Notes and references

1. R. Venkatasesubramanian, E. Siivola, T. Colpitts and B. O’Quinn, Nature, 2001, 413, 597.
2. T. C. Harman, P. J. Taylor, M. P. Walsh and B. E. LaForge, Science, 2002, 297, 2229.
3. D. Hsieh, Y. Xia, D. Qian, L. Wray, F. Meier, J. H. Dil, J. Osterwalder, L. Patthey, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava and M. Z. Hasan, Phys. Rev. Lett., 2009, 103, 146401.
4. H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang and S.-C. Zhang, Nat. Phys., 2009, 5, 438.
5. L. He, X. Kou and K. L. Wang, Phys. Status Solidi RRL, 2013, 7, 50.
6. J. J. Cha, K. J. Koski and Y. Cui, Phys. Status Solidi RRL, 2013, 7, 15.
7. J. Moore, Nat. Phys., 2009, 5, 378.
8. X.-L. Qi, R. Li, J. Zang and S.-C. Zhang, Science, 2009, 323, 1184.
9. H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang and S.-C. Zhang, Nat. Phys., 2009, 5, 438.
10. G. Wang, X. Zhu, J. Wen, X. Chen, K. He, L. Wang, X. Ma, Y. Liu, X. Dai, Z. Fang, J. Jia and Q. Xue, Nano Res., 2010, 3, 874.
11. C. Pauly, G. Bihlmayer, M. Liebmann, M. Grob, A. Georgi, D. Subramaniam, M. R. Scholz, J. Sánchez-Barriga, A. Varykhalov, S. Blügel, O. Rader and M. Morgenstern, Phys. Rev. B: Condens. Matter Mater. Phys., 2012, 86, 235106.
C. Pettenkofer and W. Jägermann, *J. Appl. Phys.*, 1994, 75, 7805.

63 Y. Takagaki, B. Jenichen, U. Jahn, M. Ramsteiner, K.-J. Friedland and J. Lähnemann, *Semicond. Sci. Technol.*, 2011, 26, 125009.

64 N. Periano, M. Winkler, Z. Aabdin, J. Koenig, H. Böttner and O. Eibl, *Phys. Status Solidi A*, 2012, 209, 289.

65 K. M. F. Shahil, M. Z. Hossain, V. Goyal and A. A. Balandin, *J. Appl. Phys.*, 2012, 111, 054305.

66 Y. Jiang, Y. Y. Sun, M. Chen, Y. Wang, Z. Li, C. Song, K. He, L. Wang, X. Chen, Q.-K. Xue, X. Ma and S. B. Zhang, *Phys. Rev. Lett.*, 2012, 108, 066809.

67 W. Richter, H. Köhler and C. R. Becker, *Phys. Status Solidi B*, 1977, 84, 619.

68 B. Aboulfarah, D. Sayah, A. Mzerd, A. Giani and A. Boyer, *Moroccan J. Condens. Matter*, 2000, 3, 76.

69 L. W. da Silva, M. Kaviany and C. Uher, *J. Appl. Phys.*, 2005, 97, 114903.

70 B. Huang, C. Lawrence, A. Gross, G.-S. Hwang, N. Ghafouri, S.-W. Lee, H. Kim, C.-P. Li, C. Uher, K. Najafi and M. Kaviany, *J. Appl. Phys.*, 2008, 104, 113710.

71 M. R. Scholz, J. Sánchez-Barriga, D. Marchenko, A. Varykhalov, A. Volykhov, L. V. Yashina and O. Rader, *Phys. Rev. Lett.*, 2012, 108, 256810.

72 L. Plucinski, A. Herdt, S. Fahrendorf, G. Bihlmayer, G. Mussler, S. Döring, J. Kampmeier, F. Matthes, D. E. Bürgler, D. Grützacher, S. Blügel and C. M. Schneider, *J. Appl. Phys.*, 2013, 113, 053706.

73 D. Hsieh, Y. Xia, D. Qian, L. Wray, F. Meier, J. H. Dil, J. Osterwalder, L. Patthey, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava and M. H. Hasan, *Phys. Rev. Lett.*, 2009, 103, 146401.

74 *Angle Resolved Photoemission*, ed. S. D. Kevan, Elsevier, Amsterdam, 1992.

75 F. M. Smits, *Bell Syst. Tech. J.*, 1958, 37, 371 (same as BT Monograph, 3894, Part 2).