Technical Physics Letters, 2022, Vol. 48, No. 12

06

Electronic structure of ultrathin Cs/Bi_2Se_3 interfaces

© G.V. Benemanskaya[1], S.N. Timoshnev[2]

[1] Ioffe Institute, St. Petersburg, Russia
[2] Alferov University, St. Petersburg, Russia
E-mail: timoshnev@mail.ru

Received April 27, 2022
Revised October 24, 2022
Accepted October 25, 2022

The electronic structure of ultrathin Cs/Bi_2Se_3 interfaces has been studied by photoelectron spectroscopy using synchrotron radiation. The experiments were carried out *in situ* in ultrahigh vacuum with submonolayer Cs coverages on Bi_2Se_3 samples. It was found that the adsorption of Cs causes changes in the core level spectra of Bi $4f$, Bi $5d$, Se $3d$. It has been established that Cs atoms are adsorbed predominantly on Bi atoms in the upper surface layer. The states of the valence band were studied for a clean Bi_2Se_3 surface and for the Cs/Bi_2Se_3 interface. Near the Fermi level, 2D topological states have been found. Two induced surface states appear in the region of the valence band upon adsorption of Cs.

Keywords: topological insulators, electronic structure, ultrathin interfaces, photoelectron spectroscopy.

DOI: 10.21883/TPL.2022.12.54951.19236

At present, there exists a promising new class of substances with topologically protected surface electronic states, namely, the so-called topological insulators (TI) exhibiting unique electronic properties [1]. TIs are characterized by an insulating bulk and conductive surface due to a strong spin-orbit interaction and emergence of spin-split surface states with a continuous spectrum forming the Dirac cone. Using TIs in high−tech industries, it is possible to create innovative electronic, spintronic and magnetoelectric devices [2]. However, transport through the topological states may be limited by the electron−phonon and other interactions. Therefore, it is important to reveal how the topological states vary due to, for instance, deformation, adsorption and intercalation. To ensure efficient practical application of TIs, it is necessary to study in detail the surface properties and electronic structure, as well as their resistance to external impacts. Bi_2Se_3 is a prominent representative of TIs and has a pronounced laminated structure formed as a set of quint-layers Se−Bi−Se−Bi−Se with the ion-covalent bond. The quints are coupled via weak Van der Waals forces. TI Bi_2Se_3 has been studied in many aspects both theoretically and experimentally [3,4]. Modification of the TI electronic structure due to adsorption of metal atoms was studied in [5–9]. In [5], adsorption of rubidium on Bi_2Se_3 was investigated. It was found out that the Rb adsorption results in a strong downward bending of bands and shift of the Bi and Se core level lines by 0.4 eV toward higher binding energies. Nevertheless, many aspects of interactions taking place during formation of interfaces still remain unstudied.

In this work, electronic structures of the Bi_2Se_3 TI and Cs/Bi_2Se_3 interface were studied by photoelectron spectroscopy based on synchrotron radiation. Photoelectron spectroscopy is a powerful technique for studying electronic characteristics and obtaining the most complete information on the material band structure. The technique distinguishing feature is high sensitivity to the surface chemical states.

The photoemission studies were performed at the RGL−station of the BESSY II synchrotron (Berlin, Germany). The photon energy ranged from 72 to 900 eV. The experiments were performed *in situ* in ultrahigh vacuum of $5 \cdot 10^{-10}$ Torr at room temperature. Photoelectrons were detected in the surface−normal direction, the exciting beam impinged on the sample surface at the angle of 45°. The total energy resolution was 50 meV. The Bi_2Se_3 sample was grown by the modified Bridgeman method described in detail in [10]. The samples were pre-annealed at ~ 650 K. Measurements of the photoemission spectrum at the excitation energy of 900 eV did not reveal the existence of the oxygen O $1s$ core level, nevertheless, an insignificant amount of carbon C $1s$ was fixed. The atomically pure cesium was sputtered step by step onto the clean sample surface from a standard source. Notice that one monolayer (ML) is defined as a single complete layer of Cs atoms, and in the case of a singular surface is equivalent to $\sim 6.25 \cdot 10^{14}$ atoms/cm^2. The extent of the submonolayer coating was estimated also via the decrease in photoemission intensity of the Bi $4f$ core level.

Fig. 1 presents photoemission spectra measured in the vicinity of the valence band for the Bi_2Se_3 sample and ultrathin Cs/Bi_2Se_3 interface in the case of the Cs coating 1 ML thick at the excitation energy $h\nu = 72$ eV. The background was subtracted by the Shirley method. The effect of the sample charging was not observed because Bi_2Se_3 is high−conductive. The valence band ranges from 0 to 6 eV. Study [11] showed that the valence band consists mainly of the partial state densities of Bi $6p$ and Se $4p$. The obtained experimental data exhibit two clearly pronounced features in the valence state region. One of them is located in the low-energy range at ~ 1.3 eV; the greatest contribution to

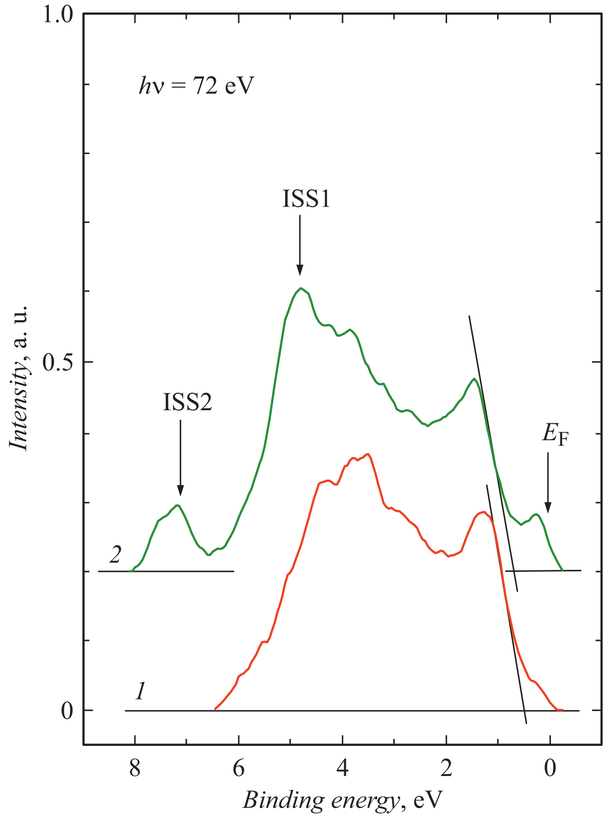

Figure 1. Photoemission spectra in the vicinity of the valence band for a pure Bi_2Se_3 sample (*1*) and Cs/Bi_2Se_3 interface (*2*) in the case of the Cs coating 1 ML thick. The excitation energy is $h\nu = 72$ eV.

it may be made by the Se 4*p* orbital. The other feature (at ∼ 4 eV) reflects mainly the contribution of the Bi 6*p* orbitals. The position of the valence band maximum E_{VBM} was determined by liner approximation of the leading edge of the valence band spectrum. The E_{VBM} position was found at the energy 0.45 eV lower than Fermi level E_{F} for the pure Bi_2Se_3 surface. Taking into account that the Bi_2Se_3 band gap is 0.3 eV [12], it was established that the Fermi level is located in the conduction band 0.15 eV higher than the conduction band minimum. This agrees with the results presented in [13]. Near the Fermi level there are topological surface states. Adsorption of Cs results in the valence-band spectrum shift by 0.25 eV towards higher binding energies. In the spectra obtained at the energies of ∼ 5 and ∼ 7 eV, two surface states induced by the Cs adsorption were revealed: ISS1 and ISS2, respectively. In addition, the strong downward band bending causes occupation of the conduction band bulk by doped states near E_{F} (Fig. 1, curve *2*). The reason for the band bending is the charge transfer between the adsorbed cesium layer and Bi_2Se_3 surface, which causes creation of a surface dipole.

Fig. 2 presents photoemission spectra of the Bi 4*f* core level obtained for the pure Bi_2Se_3 surface (curve *1*) and ultrathin Cs/Bi_2Se_3 interface in the case of a monolayer Cs coating (curve *2*). There are observed two pronounced peaks corresponding to spin-orbit split components Bi $4f_{7/2}$ and Bi $4f_{5/2}$. Positions of core-level peaks of Bi $4f_{7/2}$ (binding energy 157.9 eV) and Bi $4f_{5/2}$ (binding energy 163.2 eV) were determined. In addition, the Bi 4*f* core level photoemission spectrum exhibits a small contribution of the Se 3*p* core level; this agrees with the data of [13]. The peak full width at half height (FWHM) is 0.64 eV for both Bi $4f_{7/2}$ and Bi $4f_{5/2}$. The Cs adsorption leads to the shift of the Bi 4*f* core level lines by 0.25 eV towards higher binding energies and also to the FWHM increase to 0.70 eV for both Bi $4f_{7/2}$ and Bi $4f_{5/2}$. The shift of the Bi 4*f* core level is consistent with an analogous shift of the valence band spectrum. Besides this shift, a reduction in the main level intensities is observed.

Fig. 3 presents photoemission spectra of the Se 3*d* core level obtained for a pure Bi_3Se_3 surface (curve *1*) and Cs/Bi_2Se_3 interface in the case of a monolayer Cs coating (curve *2*). Similarly to the Bi 4*f* core level, the Se 3*d* core level is well describable by a doublet of the Se $3d_{5/2}$ and Se $3d_{3/2}$ lines at the binding energies of 53.2 and 54.0 eV, respectively. Decomposition of the spectra was performed using Gaussian functions. The Se $3d_{5/2}$ FWHM is 0.60 eV, while that of Se $3d_{3/2}$ is 0.64 eV; the FWHM values do not change upon the cesium sputtering. Adsorption of Cs results in the shift of the Se core level spectrum by 0.25 eV towards higher binding energies. This shift is consistent with

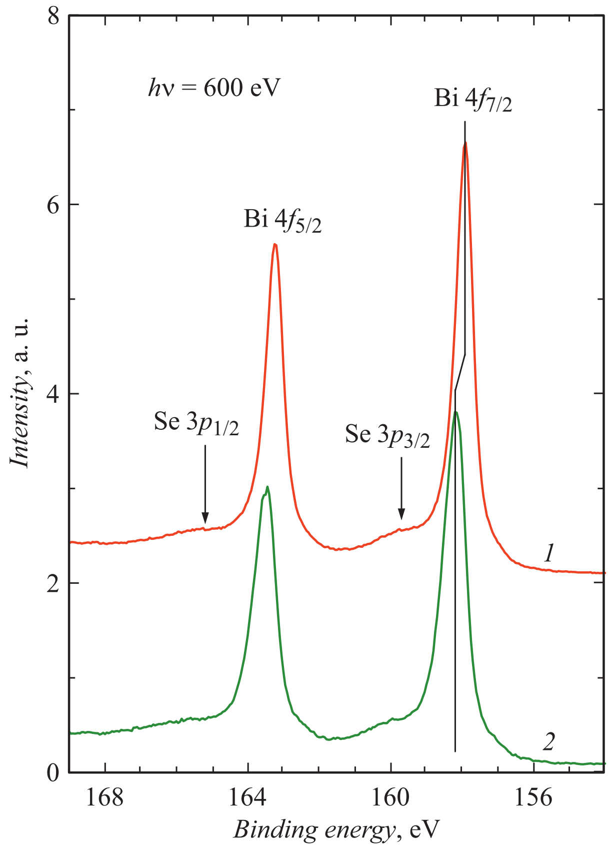

Figure 2. Photoemission spectra of the Bi 4*f* core level for a pure Bi_2Se_3 sample (*1*) and Cs/Bi_2Se_3 interface (*2*) in the case of the Cs coating 1 ML thick. The excitation energy is $h\nu = 600$ eV.

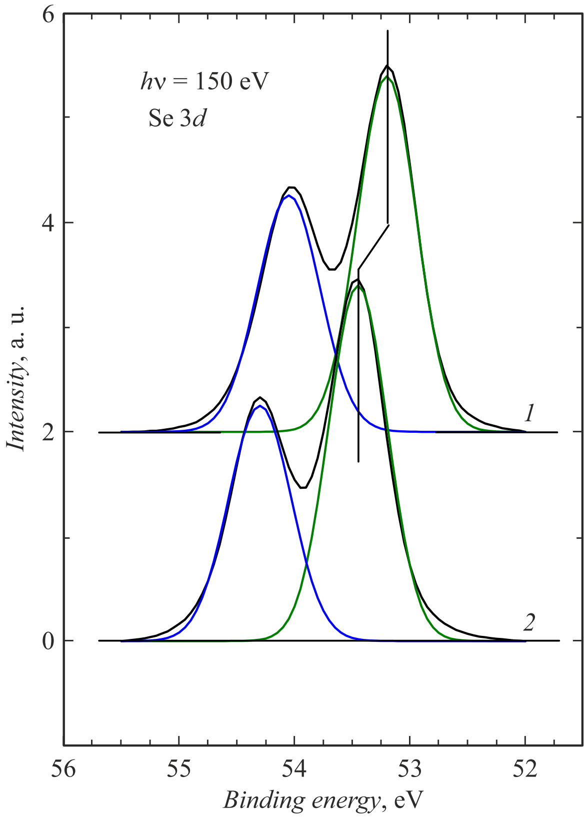

Figure 3. Photoemission spectra of the Se 3*d* core level for a pure Bi$_2$Se$_3$ sample (*1*) and Cs/Bi$_2$Se$_3$ interface (*2*) in the case of the Cs coating 1 ML thick. The excitation energy is $h\nu = 150\,\mathrm{eV}$.

analogous shifts of the valence band spectrum and Bi 4*f* core level spectrum. Since the shift is of the electrostatic character, positions of the Bi 4*f* and Se 3*d* core level peaks change identically. Except for this shift, the shape of the Se 3*d* ground level remains almost unvaried. Based on the results of the core level spectra analysis, we can conclude that Cs atoms efficiently interact also with bismuth atoms in the second layer. It is possible to assume that this occurs when selenium atoms are replaced with cesium atoms and when there are selenium vacancies in the upper layer. For instance, paper [8] has demonstrated that location of Cs atoms in Se vacancies is energetically favorable.

Electronic structures of the pure Bi$_2$Se$_3$ sample and ultrathin Cs/Bi$_2$Se$_3$ interfaces were studied by photoelectron spectroscopy based on synchrotron radiation in the excitation energy range of 72−900 eV. In the study it was revealed that the Cs adsorption causes the ~ 0.25 eV shift towards higher binding energies of the valence band spectrum, as well as of the Bi 4*f* and Se 3*d* core level spectra. This may be assumed to be associated with the surface doping with Cs atoms. The shapes and intensities of the Se 3*d* core levels remained almost unvaried upon the Cs adsorption, while intensities of the Bi 4*f* core levels decreased substantially. It can be assumed that Cs is adsorbed predominantly on Bi atoms at Se sites in the uppermost layer. In addition, the valence band structure was determined for both the clean Bi$_2$Se$_3$ surface and Cs/Bi$_2$Se$_3$ interface at different excitation energies.

Acknowledgements

The authors are grateful to the Helmholtz-Zentrum Berlin for Materials and Energy for the opportunity to perform experiments at the BESSY II synchrotron and assistance during the experiments. The authors are also grateful to O.E. Tereshchenko for presenting the samples and M.N. Lapushkin for assistance in the experiment.

Conflict of interests

The authors declare that they have no conflict of interests.

References

[1] J. Moore, Nat. Phys., **5**, 378 (2009). DOI: 10.1038/nphys1294
[2] A.R. Mellnik, J.S. Lee, A. Richardella, J.L. Grab, P.J. Mintun, M.H. Fischer, A. Vaezi, A. Manchon, E.-A. Kim, N. Samarth, D.C. Ralph, Nature, **511**, 449 (2014). DOI: 10.1038/nature13534
[3] C.-T. Kuo, S.-C. Lin, J.-P. Rueff, Z. Chen, I. Aguilera, G. Bihlmayer, L. Plucinski, I.L. Graff, G. Conti, I.A. Vartanyants, C.M. Schneider, C.S. Fadley, Phys. Rev. B, **104** (24), 245105 (2021). DOI: 10.1103/PhysRevB.104.245105
[4] G. Tse, D. Yu, Comput. Condens. Matter, **4**, 59 (2015). DOI: 10.1016/j.cocom.2015.09.001
[5] M. Bianchi, R.C. Hatch, Z. Li, P. Hofmann, F. Song, J. Mi, B.B. Iversen, Z.M. Abd El-Fattah, P. Löptien, L. Zhou, A.A. Khajetoorians, J. Wiebe, R. Wiesendanger, J.W. Wells, ACS Nano, **6** (8), 7009 (2012). DOI: 10.1021/nn3021822
[6] A.G. Ryabishchenkova, M.M. Otrokov, V.M. Kuznetsov, E.V. Chulkov, JETP, **121** (3), 465 (2015). DOI: 10.1134/S1063776115090186.
[7] T. Valla, Z.-H. Pan, D. Gardner, Y.S. Lee, S. Chu, Phys. Rev. Lett., **108** (11), 117601 (2012). DOI: 10.1103/PhysRevLett.108.117601
[8] 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, **95** (20), 205429 (2017). DOI: 10.1103/PhysRevB.95.205429
[9] H. Zhu, W. Zhou, J.A. Yarmoff, Surf. Sci., **683**, 17 (2019). DOI: 10.1016/j.susc.2019.01.006
[10] O.O. Shvetsov, V.A. Kostarev, A. Kononov, V.A. Golyashov, K.A. Kokh, O.E. Tereshchenko, E.V. Deviatov, Europhys. Lett., **119** (5), 57009 (2017). DOI: 10.1209/0295-5075/119/57009
[11] D. Biswas, S. Thakur, G. Balakrishnan, K. Maiti, Sci. Rep., **5**, 17351 (2015). DOI: 10.1038/srep17351
[12] I.A. Nechaev, R.C. Hatch, M. Bianchi, D. Guan, C. Friedrich, I. Aguilera, J.L. Mi, B.B. Iversen, S. Blügel, Ph. Hofmann, E.V.Chulkov, Phys. Rev. B, **87** (12), 121111 (2013). DOI: 10.1103/PhysRevB.87.121111
[13] L.V. Yashina, J. Sánchez-Barriga, M.R. Scholz, A.A. Volykhov, A.P. Sirotina, V.S. Neudachina, M.E. Tamm, A. Varykhalov, D. Marchenko, G. Springholz, G. Bauer, A. Knop-Gericke, O. Rader, ACS Nano, **7** (6), 5181 (2013). DOI: 10.1021/nn400908b