

## Differentiation of Surface and Bulk Conductivities via Four-probe Spectroscopy

Saban M. Hus<sup>1</sup>, Corentin Durand<sup>1</sup>, X.-G. Zhang<sup>1,2</sup>, Chuanxu Ma<sup>1</sup>, Michael A. McGuire<sup>1</sup>, Yang Xu<sup>3</sup>, Helin Cao<sup>3</sup>, Ireneusz Miotkowski<sup>3</sup>, Yong P. Chen<sup>3</sup> and An-Ping Li<sup>1</sup>

<sup>1</sup> Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

<sup>2</sup> Department of Physics, University of Florida, Gainesville, FL 32611, USA

<sup>3</sup> Department of Physics and Astronomy, Purdue University, West Lafayette, IN 47907, USA

A large number of materials have localized electronic states present on their surfaces. Understanding and controlling the electronic properties of these states does not only constitute the foundations of surface science but also the modern electronic devices. Being studied with mature surface analytic techniques like STM and ARPES, local electronic properties of surface states can be characterized very well. However, little is known about the electron transport through these 2D surface states which can present completely different characteristics than the transport through the underlying 3D bulk. During the last decade however, the demand for understanding the transport through surface states increased significantly due to constantly decreasing size of microelectronic devices and discovery of new materials like topological insulators (TIs) and other 2D layered materials with surface states hosting new and interesting transport properties.

The main obstacle to study the transport through these surface states is the difficulty to separate them from the accompanying and usually overwhelming transport through bulk states. The only way to increase the surface sensitivity of a transport measurement is to use very small contact spacing. Recently, development of four-probe STM enabled such smaller contact spacing. And four-probe spectroscopy measurements where a large set of conductance vs. probe spacing data is collected, gave us a first glimpse of electron transport through surfaces [1-5].

The common practice in the conductivity studies with the four-probe spectroscopy measurements is to assume two decoupled conduction channels corresponding to the 2D conductance of surface states and the 3D conductance of bulk volume [2], as schematically shown in Fig. 1a. By definition this approximation assumes that the carriers can be injected to the bulk only at contact points. This is a very naïve approach particularly when the conduction through these channels are comparable. We developed a new method to account for not only the surface states and bulk conduction mechanisms but also the interaction between them [6]. By solving the simultaneous current continuity equations for both 2D and 3D, and allowing cross “channel” current at every point along the surface, as illustrated in Fig. 1b, we can derive a scaling relation of measured resistance with respect to varying inter-probe spacing:

$$R = \frac{1}{2\pi} \rho_{2D} \ln \left[ \frac{\left(g + \frac{s_{14}}{s_{12}}\right) \times \left(g + \frac{s_{14}}{s_{34}}\right)}{\left(g + \frac{s_{14}}{s_{13}}\right) \times \left(g + \frac{s_{14}}{s_{24}}\right)} \right] = \rho_{2D} \times X_g$$

Where,  $\rho_{2D}$  is the surface resistivity,  $s_{ij}$  is the distances between the probes  $i$  and  $j$ ; and  $g = \frac{\rho_{2D}}{\rho_{3D}} s_{14}$  is a dimensionless parameter which gives an estimation of the ratio between the contributions from the 2D surface and the 3D bulk to the total resistance. The relationship between  $R$  and  $X_g$  is linear only for the correct value of  $g$  which is determined by tuning  $g$  to obtain a linear plot.

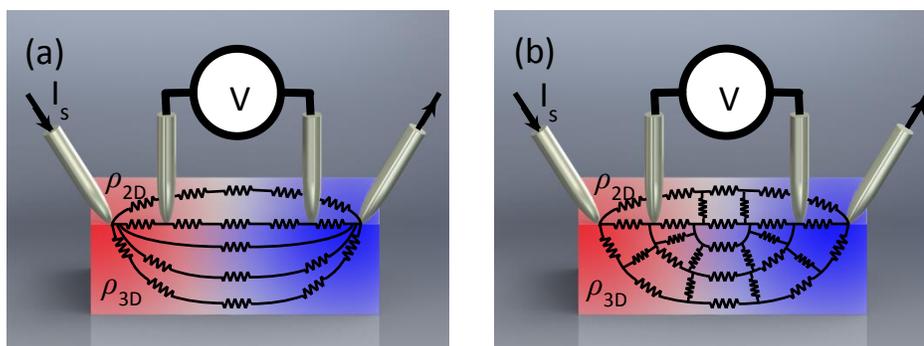
Experiments are performed in a cryogenic 4-probe STM under Ultra High Vacuum (UHV) environment [4]. On the surface, the 4 STM tips are arranged in a collinear configuration. To obtain a complete set of measurements, the voltage probes are moved step by step toward the center of the investigated area, while the positions of the outer source probes are kept fixed.

Control measurements on cleaved  $\text{Bi}_2\text{Se}_3$  surface and on epitaxial graphene grown on an insulating substrate of SiC validate the 3D and 2D limits of the model respectively. Measurements on the freshly cleaved surface of  $\text{Bi}_2\text{Te}_2\text{Se}$  at 82 K show that when  $s_{14}$  is set to  $46.6 \mu\text{m}$ , 2% of conductance is via 2D channel on this TI material. Quantitative character of the new method also enabled us to measure the aging effects of residual gases on the surface conductance of  $\text{Bi}_2\text{Te}_2\text{Se}$ . After 5 days of exposure to a residual pressure in the  $1 \times 10^{-9}$  Torr range, the surface conductivity of the sample is enhanced by about 20%. The reason behind this enhancement can be understood via STS measurements on the same sample which show that the carrier concentration of the surface increases by aging.

The newly developed transport spectroscopy method which considers both the 2D and 3D conduction channels and their interactions gives a quantitative way to differentiate them and can be used to understand the myriad of phenomena in 3D TI materials and the 2D to 3D crossover of conductance in other complex systems such as correlated electron systems [7, 8].

#### References:

- [1] Ph Hofmann and JW Wells, *J. Phys.: Condens. Matter* **21** (2009), p. 013003.
- [2] S Hasegawa *et al.*, *Surf. Rev. Lett.* **10** (2003), p. 963.
- [3] A-P Li *et al.*, *Adv. Funct. Mater.* **23** (2013), p. 2509.
- [4] TH Kim, *et al.*, *Rev. Sci. Instrum.* **78** (2007), p. 123701.
- [5] KW Clark, *et al.*, *ACS Nano* **7** (2013), p. 7956.
- [6] C Durand *et al.*, Manuscript submitted for publication.
- [7] TH Kim, *et al.*, *Proc. Natl. Acad. Sci. USA* **107** (2010), p. 5272.
- [8] This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. MAM acknowledges support from the DOE Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. The  $\text{Bi}_2\text{Te}_2\text{Se}$  crystal growth and characterization at Purdue was supported by DARPA MESO program (Grant N66001-11-1-4107).



**Figure 1.** Schematic of four-probe transport measurement on a dual system made of a surface overlaying a semi-infinite bulk. (a) The two components are represented as two decoupled parallel channels in a conventional model. (b) The system is represented by a generally inhomogeneous resistor network with leakage current paths at every point between the surface and the bulk.