Investigation of magnetoresistance and localization behavior in nanobulk assembly of Bi$_2$Te$_3$

R.Venkatesh, S. Shanmukharao Samatham, and V.Ganesan

Low Temperature Laboratory, UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 001, M.P, India

E-mail: rvenkatesh@csr.res.in

Abstract. Magnetoresistance (MR) measurements are used to investigate the topological nature of nanobulk assembly of two dimensional (2D) Bi$_2$Te$_3$ nanoflakes prepared by microwave assisted solvothermal reactions. Average edge to edge length of individual hexagonal nanoflakes is found to be of ~3-4 microns as demonstrated by SEM micrographs. Nanobulk assemblies prepared out of this 2D nanoflakes exhibit rhombohedral structure and have a high surface to volume ratio that is advantageous for probing the signatures of surface states through bulk measurements. At low temperatures, magnetic field dependent MR measurements demonstrate a clear positive MR with a prominent dip below ±1T. Significant changes happening in magnetic field dependent MR measurements are analyzed and discussed in the light of Weak anti localization (WAL) effect arising likely from surface states in nanobulk Bi$_2$Te$_3$ materials which on proper optimization can open up a new gateway for large scale application of these topological insulating materials in NEMS and MEMS technology.

1. Introduction
The topologically protected gapless edge/surface states in Topological insulators (TI) along with their bulk states is being investigated rigorously for the past few years through various measurement probes for nanoelectronics and thermoelectric applications[1]. Many of the reported TI materials are either single crystals or nanowires [2, 3]. Few reports are available regarding the investigation of surface states in TI thinfilms grown by molecular beam epitaxy [4] and significantly low amount of literature is available for polycrystalline thinfilms [5]. Dissipation-less electronic transport arising in surface states of these TI materials are detected through Shubnikov - de Haas oscillations (SDH) at high magnetic field - low temperatures and by the WAL/WL effects at low magnetic field - low temperatures [6]. In this work, we are reporting the signature of surface states with detailed MR measurements in nanobulk assembly of two dimensional Bi$_2$Te$_3$ nanoflakes. These materials on optimization assures the possibility of large scale application in NEMS/MEMS technology. Interesting behavior observed in MR measurements at low temperatures are discussed and presented in the light of 3D WAL arising likely from the hybridization of surface states in intrinsic nanopores formed on the surface of flakes.

2. Experimental details
Two dimensional Bi$_2$Te$_3$ nanoflakes were prepared by microwave assisted wet chemical synthesis [7]. In a typical synthesis, analytical grade BiCl$_3$, Telluric acid (Te(OH)$_3$), Thioglycolic acid, 1,5 Pentanediol, were used without any further purification. The microwave reactions were carried out in...
microwave oven (1250 W). The black precipitate of nano flakes obtained finally is centrifuged and washed several times in ethanol, acetone and finally stored in acetone. These nanoflakes were dried in room temperature and were cold pelletized followed by vacuum annealing at 200°C. SEM images and chemical composition analysis using EDS measurements were performed with JEOL SEM EDS instrument. Atomic force microscope (AFM) images of nanoflakes were obtained using nanoscopeE AFM in contact mode. MR measurements were performed in Quantum design made PPMS in 12T/1.8K range.

3. Results and Analysis
Powder Xray diffraction (PXRD) pattern of Bi$_2$Te$_3$ (figure1) shows that it crystallizes in rhombohedral structure with $A_3m$ space group with no observable evidence for secondary phase. This is in accordance with the reported literature [8]. SEM image of Bi$_2$Te$_3$ nanoflakes as shown in figure 2 demonstrates the surface morphology of cluster of flakes. The white rod like structure seen above the flake is the C axis growth which on giving more microwave doses can develop into a three dimensional spherical nanoparticle. The flake size and morphology can be systematically varied by increasing the dosage of microwave given to the sample. Chemical composition as analyzed from EDS analysis confirmed that the Bismuth and tellurium exists in the ratio of 2:3. Temperature dependence of resistance for Bi$_2$Te$_3$ in various applied magnetic field is shown in figure 3. Resistivity measurements were carried out in ~0.5mm thin rectangular pellet using linear four probe method. R vs T at zero applied magnetic field and upto 10T shows a metallic behavior from 2 to 300K. On application of magnetic field a negative MR is observed upto a magnetic field of 0.5T which becomes positive MR from 0.5 to 10T as shown in the inset of figure 3. Magnetic field dependence of resistance for Bi$_2$Te$_3$ is as shown in figure 4. It indicates a positive MR in all the measured temperatures. A parabolic behavior is observed in R vs. H down to a temperature of 8K. Below that temperature a pronounced dip appears around 0T as shown for 5K in figure 4 which broadens significantly at further lower temperatures. At 1.8K the dip broadens upto a magnetic field of ±1T as shown in figure 4. The interesting features observed in MR measurements of Bi$_2$Te$_3$ are analyzed and discussed in the forthcoming section.

4. Discussion
Two dimensional single crystalline [9] nanoflakes of Bi$_2$Te$_3$ with very high surface to volume ratio is advantageous for probing the signatures of surface states through various measurements. In the present work, these 2D nanoflakes with negligible thickness when compared to their surface area are put together by cold pressing and annealed in vacuum at 200°C. This annealed sample shows a metallic behavior (fig 3) in all the applied magnetic field which is in contrast to the semiconducting nature observed in transport measurements of single flake [10].

![Figure 1. Powder XRD of Bi$_2$Te$_3$](image1)

![Figure 2. SEM image of cluster of 2D nanoflakes and white rods like structures are c-axis growth](image2)
This contradiction demonstrates that the annealing treatment in 200°C leads to the formation of more number of conducting channels due to the fusion of nanoflakes in a direction perpendicular to their surface area. Magnetic field dependence of MR at 50K is shown with red circles in figure 5. The solid line is the power law fit \[1\] for the equation

\[ \Delta R \propto |B|^\gamma \]

Where \( \Delta R \) is \( R(B) - R(0) \), \( B = \mu_0 H \) and \( \gamma \) is the power factor which determines the nature of MR as a function of applied magnetic field. The value of \( \gamma \) obtained from fitted curve is found to be 2.41 which can be satisfactorily approximated as \( \Delta R \propto B^2 \) which denotes the parabolic fit for \( R \) vs \( H \) at 50K. This parabolic fit indicates the classical MR exhibited by most of the metals due to Lorentz force. On reducing the temperature below 8K, a prominent dip started appearing nearer to the zero Tesla. A prominent cusp in magneto conductivity or a dip in MR is considered to be the significant signature of WAL especially in TI materials due to the presence of \( \pi \) Berry’s phase acquired by the surface states. Suppression of backscattering due to destructive quantum interference in Berry’s phase leads to this WAL. This feature is one of the valuable indications for the transport that is happening along the surface state. The value of \( \gamma \) is found to be 0.45 as inferred from the power law fit in the narrow region below ±3T at 1.8K. Interestingly, the value of \( \gamma \) is nearer to 0.5. The value of \( \gamma \) points out the presence of 3dimensional (3D) WAL [12] instead of expected 2D WAL in TI materials. In the literature, quantum percolation is a phenomenon proposed theoretically and realized experimentally [12] using 3DWAL in Bi\(_2\)Te\(_3\) sample. According to it, dot like structures are created artificially on the surface of TI materials which led to hybridization of 2D surface states along the walls of the dots. A detailed Transmission electron microscope (TEM) study [8] suggests that the Bi\(_2\)Te\(_3\) flakes prepared...
by microwave assisted solvothermal reactions have intrinsic natural nanopores of 5 nm along the surface of the flakes. These nanopores might be mimicking the artificially made percolation centers leading to the observed 3D WAL. The dip is not found in temperatures above 8 K and MR vs H is broadened considerably as shown at 50 K by the red symbol in figure 5. It can be attributed to the decrease in phase coherence at higher temperature as observed in many of the TI materials. [5]. Interestingly, γ obtained above ±3T using power law fit shows a value of 0.99 which shows that the obtained MR as a function of magnetic field is almost linear and it is very much beneficial for the MR device applications. The linearity in MR is consistent with the reported values in TI materials [11]. It can be attributed to the domination of dissipation-less 2D surface transport over the 3D bulk conductivity in low temperatures which might have modified the overall nature of MR at 1.8 K when compared to MR at 50 K. More measurements using various microprobes such as Hall- Effect as well as an analysis of high magnetic field MR in various magnetic field orientation is in progress which would be published else were.

5. Conclusions
In conclusion, we have probed the surface electrical transport properties of nanobulk assembly of Bi₂Te₃ nanoflakes using electrical resistivity and MR measurements which unambiguously support the signature of WAL at low temperature. Signature such as the prominent dip at low temperatures is attributed to be arising from the 3D WAL due to the intrinsic nanopores formed on the surface of the flakes which interrupt the 2D surface states in the form of percolation centers. This nanobulk assembly of TI materials is a promising candidate for spintronic /MR devices which on further optimization can open- up a new gateway for large scale application in NEMS and MEMS technology.

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References
[1] Hasan, Zahid M and Charles L Kane 2010 Rev. mod. phys. 82 3045.
[2] Qu D - X, Hor Y S, Xiong J, Cava, R J and Ong N P 2010 Science 329 821.
[3] Ning W, Hai Feng D, Feng yu K, Ji yong Y, Yuan H, Ming liang T, and Yuheng Z 2013 Scientific reports 3.
[4] He, Hong-T, Gan W, Tao Z, Jam-K, George KL W, Jian-Nong W, Hai-Z, Shun-Q, and Fu 2011 Phys. Rev. Lett. 106, 166805.
[5] Zhang, Yu H, Bao D H, SLi, Wang C X, and Yang G W 2012 Phys. Rev.B 86 075102.
[6] Pavlosiuk, Orest, Darius Kaczorowski, and Piotr Wiśniewski 2015 Scientific reports 5
[7] Mehta, Rutvik J., Zhang Y, Karthik C, Singh B, Siegel R W, Borca-Tasciuc T, and Ramanath G 2012 Nat. Mater. 11 233.
[8] Zhang, Yan liang, Rutvik M, Matthew B, Liang H, Ganpati R, and Theodorian B 2012 Appl. Phys. Lett. 100 193113.
[9] Mehta, Rutvik J., Zhang Y, Karthik C, Singh B, Siegel R W, Borca-Tasciuc T, and Ramanath G 2010 ACS nano 4 5055.
[10] Chiu S P and Lin J J 2013 Phys.Rev. B 87 0351221.
[11] Roy A, Samaresh G, Sushant S, Rik D, Tammooy P, Amritesh R, Hema C P, Luigi C, and Sanjay K. 2013 Appl. Phys. Lett. 102 163118.
[12] Song M., Chu J H, Zhou J, Tongay S, Liu K, Suh J, Chen H, Kang J S, Zou X. and You L. 2015 Nanotechnology 26 265301.