Research activities:

The following research activities are going on in Dr. Barnali Ghosh's group . The work involved starting from growth of materials (0D, 1D , 2D) using different methods, their characterization and details study of their physical properties.

Barnali Ghosh's Group has strong collaboration with Prof AKR's group. BG group is also involved in Technology development work through Technical Research centre (TRC) project of centre (https://newweb.bose.res.in/departments/TRC/Members.jsp) With the group of Prof. A.K. Raychaudhuri and Dr. Manik Pradhan, BG is also involved in development of breathe analysis as a tool for disease detection. This activity is a part of the TRC project. BG is also involved in the development of pollutant gas sensor related programme in TRC.

BG group research activities are mainly focused around 5 major themes:

- **(a) Phase stability and co-existence of competing phases in magnetic nanowires in context of manganite nanowires.**
- **(b) Physics and Technology with single nanowire devices**
- **(c) Nucleation site and interface controlled growth of complex and binary oxide nanowires and nanotubes by solvo-thermal and Pulsed Laser Deposition.**
- **(d) Use of nanowire based films and arrays for high sensitivity and selectivity gas sensors.**
- **(e) Growth of high performance thin film transistors (TFT) and physical property study**

(a) Phase stability and co-existence of competing phases in magnetic nanowires in context of manganite nanowires

Nanowires, because of their unique one-dimensional like structural characteristics and size effects, exhibit many novel physical properties, that are different from their bulk counterparts.

During past two decades much effort has been made to synthesize and characterize 1D nanostructure of manganites in the form of NW, tube, rods etc. The issues related to control of size, shape, structure, composition, homogeneity and growth kinetics of the perovskite oxide manganite NWs are still remained unexplored. In addition to these issues, how the size reduction to one dimension affects (with large aspect ratio structure) the crystallographic, magnetic, transport and other physical properties of NWs of manganite compared to bulk has been less investigated. In this work, we mainly focus on these issues and the underlying physics behind this.

This work led to definite results because we were able to grow high quality single crystalline manganite NWs. We mainly focus on the rational synthesis, growth mechanism, and detailed characterization of ensemble of NWs as well as single NW level of manganite ($La_{1-x}A_xMnO_3$; A

= Ca, Sr; x = 0.3 and 0.5). We have investigated how the crystallographic and magnetic structures (obtained from ND measurement) evolve on size reduction to 1D (with large aspect ratio structure) and how it affects the electrical, magnetic and other physical properties.

Magnetization measurement on half doped manganite nanowire shows several magnetic transitions which are different from bulk. Understanding of magnetic transitions done using several experiments like magneto caloric study, Neutron diffraction study, which shows the presence of phase coexistence of magnetic phases (antiferromagnetic and ferromagnetic).As the experiments are carried out on ensemble of nanowires, question may arise whether the phase coexistence observed in nanowires is due to size dispersion. To answer this question, instead of ensemble of nanowires, noise spectroscopy study of single nanowire (<50 nm) level is done to demonstrate how the noise spectroscopy can explain the magnetic transitions and phase separation.Field dependent as well as temperature dependent noise spectroscopy study was done on a single nano-wire to avoid the problems of size dispersion with the specific aim of corroborating the magnetic phase transitions as well as phase co-existence at a single NW level. Experiments with single nanowires; mainly on fabrication of single nanowire based devices, using different lithographic techniques.

<u>In the work the main challenges have been taken those are:</u>

1) **<u>We have shown innovation on hydrothermal growth ,</u>** so that one can tailor shape and size of nanostructures with controlled composition and stoichiometry by tuning the growth parameters in hydrothermal synthesis.

2) Electron Energy Loss Spectroscopy (EELS) and Energy Filtered Transmission Electron Microscopy (EFTEM) study for rigorous elemental analysis to validate the quality of the NW, single crystallinity, estimation of valency of transition metals, like Mn. Such rigorous elemental characterization was not done before on manganite nanocrystals, especially on NWs.

The EELS facility was developed by me in the centre as Central equipment facility added to HRTEM.

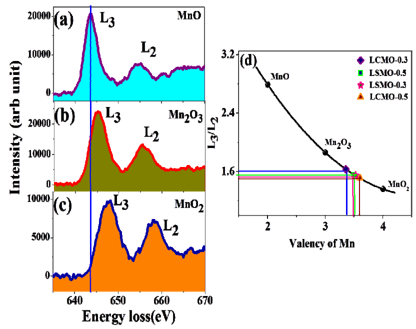

Fig2. The EELS spectra of (a) MnO, (b) Mn_2O_3 and (c) MnO_2 respectively, showing manganese L_3, L_2 lines. (d) Intensity ratio of L_3 and L_2 lines of different Mn oxide compounds as a function of their known valence. Mn valence of grown nanowires can be estimated from the curve. J Nanomaterials, 162315, (2013)

b)Physics and Technology with single nanowire devices

Single NW devices: Nano-fabrication

The lithographic facilities in the clean room was used for optical lithography, electron beam lithography (EBL) and focused ion beam (FIB) lithography to integrate sub- 100nm nanowire of materials produced by bottom-up approach like chemical route or physical/chemical vapour deposition to a single nanowire device connected to 2 or 4 probes. For attaching nanowires to prefabricated contact pads for optoelectronic or electronic measurements in addition to EBL –lift off, FIB or Focused electron beam deposited metals (Pt or W) are also used. Finally transport measurement on Single Nanowire was done.

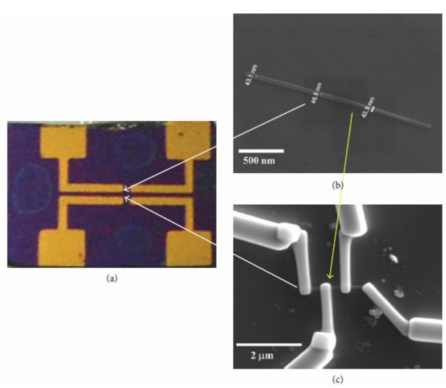

Fig 3.“ Growth and Physical Property Study of Single Nanowire (diameter ~45nm) of Half Doped Manganite” , J Nanomaterials, 162315, 2013

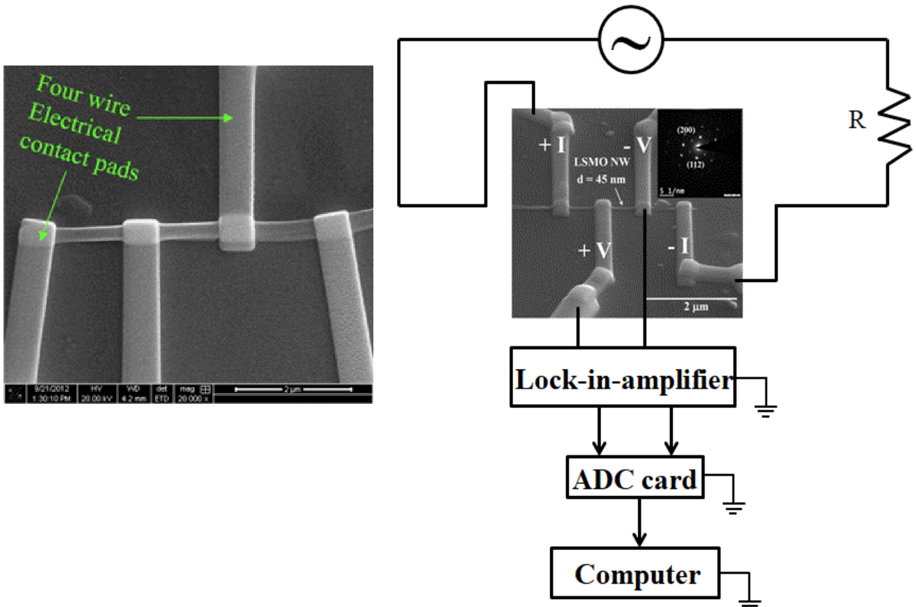

Fig4.$La_{0.5}Sr_{0.5}MnO_3$ nanowire (45nm diameter) length connected with Pt deposited Pt leads

“Low-frequency resistance fluctuations in a single nanowire (diameter 45nm) of a complex oxide and its relation to magnetic transitions and phase separation” Appl. Phys. Letts 105, 073117, (2014).

Size induced magnetic phases in half doped manganite nanowires of $La_{0.5}Sr_{0.5}MnO_3$: a neutron diffraction study
Subarna Datta, S D Kaushik, V Siruguri, Amit Kumar, S M Yusuf and **Barnali Ghosh**
J. Phys. D: Appl. Phys. ***50*** *425003, (2017)*

Manganite ($La_{1-x}A_xMnO_3$; A = Sr, Ca) nanowires with adaptable stoichiometry grown by hydrothermal method: understanding of growth mechanism using spatially resolved techniques, Subarna Datta, Ankita Ghatak. and **Barnali Ghosh**
J Mater Sci ***51*** *9679. (2016)*

Size dependence in magnetic memory, relaxation and interaction of $La_{0.67}Sr_{0.33}MnO_3$, Nilotpal Ghosh , Subarna Datta and **Barnali Ghosh**
Journal of Magnetism and Magnetic Materials, ***382*** *277 (2015)*

Low-frequency resistance fluctuations in a single nanowire (diameter 45nm) of a complex oxide and its relation to magnetic transitions and phase separation
Subarna Datta, Sudeshna Samanta, **Barnali Ghosh**, and A. K. Raychaudhuri,
*Applied Physics Letters **105**, 073117 (2014)*

Effect of size reduction in the structural and magnetic order in $LaMnO_{3+\delta}$ ($\delta \approx 0.03$) nano crystals: a neutron diffraction study
Barnali Ghosh, V. Siruguri, A.K. Raychaudhuri and Tapan Chatterji
*J. Phys. Condens. Matter **26** 025603 (2014)*

Inverse Magnetocaloric and Exchange Bias Effects in Single Crystalline $La_{0.5}Sr_{0.5}MnO_3$ Nanowires by, Sayan Chandra, Anis Biswas, Subarna Datta, **Barnali Ghosh**, Arup Raychaudhuri, Hariharan Srikanth*, **Nanotechnology 24** 505712 (2013).*

Universality in the entropy change for the inverse magnetocaloric effect, Anis Biswas, Sayan Chandra, Tapas Samanta, **Barnali Ghosh**, Subarna Datta, M. H. Phan, A. K. Raychaudhuri, I. Das, and H. Srikanth Phys, Rev B. **87**, 134420 (2013)

Stability of charge and orbital order in half-doped $Y_{0.5}Ca_{0.5}MnO_3$ nanocrystallites, Putul Malla Chowdhury**,** **Barnali Ghosh**, A. K. Raychaudhuri, S. D. Kaushik , V. Siruguri, J. Nanoparticle Res., Volume 15, issue 4 ,1585, 2013.

Growth and Physical property study of single nanowire (diameter ~45nm) of half doped Manganite, Subarna Datta, Sayan Chandra, Sudeshna Samanta, K. Das, H. Srikanth, **Barnali Ghosh**, *Journal of Nanomaterials*, vol. 2013, Article ID 162315 6 pages, 2013. doi:10.1155/2013/162315

Some of the work has been done using synchrotron Facility at KEK , Japan, Neutron beam line Facilities at i) Dhruba, BARC, ii) ILL, Grenoble, France and iii) Heinz Maier-Leibnitz Zentrum, Munich.

(c)**Nucleation site and interface controlled growth of complex and binary oxide nanowires and nanotubes by solvo-thermal and Pulsed Laser Deposition**.

This work provides information about synthesis and physical property study of metal binary oxide nanostructures (e.g WO_3, TiO_2). Binary (metal) oxide nanostructure created much more attention in last 4-5 decades due to its versatile nanostructure and different synthesis techniques, which may able to control/modify its physical properties. In recent time research works on metal binary oxide nanostructures are carried out to develop highly crystalline nanostructured devices with better performance/applications and to achieve this synthesis techniques has been tuned or modified. The main motivation of this thesis work involve growth of vertically aligned nanowires in physical vapour deposition technique (like, Pulse Laser Deposition (PLD) technique), which is a non trivial technique for growth of 1D kind structure. Moreover, it also involves the growth of nanorods/nanoflowers kind structure in laser assisted wet chemistry technique and porous 1D nanostructures by hydrothermal (wet chemistry) method by tuning the growth parameters and techniques. Further, the physics behind the growth of these nanostructures has been investigated by cross sectional interface physics study which involves spatially resolved tools for sample preparation and microstructural analysis in details. In this thesis, analysis also carried out to investigate the effect of different shape and morphology of metal binary oxide on the physical properties like opto-electrical, gas transport. Opto-electrical property in the binary oxides under study showed significant change due to surface morphology change. The transport/binary of gas through 1D porous binary oxide nanostructure was analyzed using high precision laser spectroscopy technique to provide information about the selectivity of gas transport and mechanism behind the phenomena.

Few other important works:

1.Growth of vertically aligned NWs using PLD:

a) Use of **Pulsed laser deposition technique** that leads to growth of vertically aligned array of large aspect ratio nanostructures (nanotubes and nanotubes) of metal oxides, which is a non-trivial route of growth of nanostructures other than thin film.

***b)* Making of Cross-sectional sample for understanding of growth mechanism**

Cross-section of Nanowire/ substrate interface was done using Focused ion beam lithography (FIB), dual beam system.

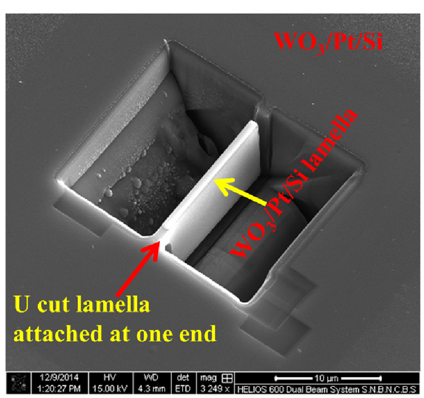

Figure 5: *Cross sectional TEM lamella preparation of vertically aligned WO_3/Pt/Si sample using ion beam lithography (Helios dual beam system)*

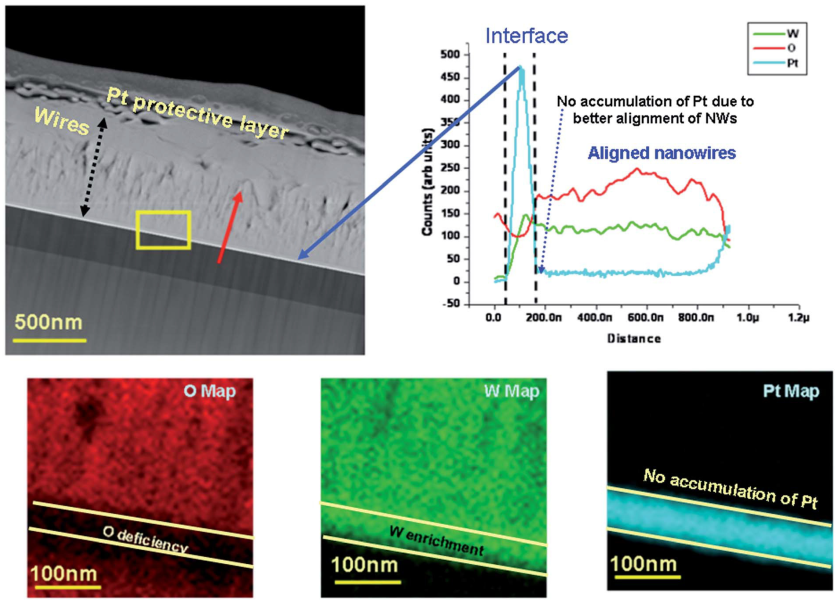

Fig 6. STEM-EDS line scan and area mapping of the aligned WO_3 nanowires grown at 200 mJ using PLD showing the overall uniformity in the chemical composition of the wire along with modified Pt layer due to diffusion of W and O. RSC Adv., 2016, 6, 31705

2) Surface morphology induced photo response in WO_3 Nanowires

Photoresponse behaviour of Tungsten trioxide (WO3) films of different surface morphology, grown by using pulsed laser deposition (PLD) has been studied. It has been observed that photoresponse is greatly modified in two different films because of two different surface morphologies. *Appl. Phys. Lett,* ***104****, 232107 (2014).*

3) Transport of gases through WO_3 nanostructures:

One of the more recent applications of oxide nanostructures is the diffusion and transport of a gas in long aspect ratio nanowires and tubes that leads to isotope selectivity which appears to be guided by physical processes that arise when gas flows through such nanostructures (like WO_3) and not due to chemical activities and often thought before, the work has been filed a patent (ref patent 1). One extramural funding has been obtained based on the patent work from SERB, India (EMR/2017/001990)

1) Patent: Advancement in methodology and system to Control Isotopic Fractionations in Carbon Containing Gases, Indian Patent Filed No. 201731017087, May, 2017.

Study of surface chemistry and microstructure of TiO_2 nanostructures on Pt(111)/Si wafer and FTO glass substrates: A comparative approach
Samik Roy Moulik, Ankita Ghatak, **Barnali Ghosh**
Surface Science, 651, 175–181 (2016)

Pulsed laser assisted growth of aligned nanowires of WO3: role of interface with substrate,
Ankita Ghatak, Samik Roy Moulik and **Barnali Ghosh**
*RSC Advances., **6** 31705 (2016)*

Photoresponse in thin films of WO3 grown by pulsed laser deposition
Samik Roy Moulik, Sudeshna Samanta, and **Barnali Ghosh** *Applied Physics Letters **104** 232107 (2014)*

Evidence of Isotope Selective Diffusion of Ambient CO_2Gas in WO3 Nanostructures

Samik Roy Moulik, Abhijit Maity, Prasenjit Chakraborty, Manik Pradhan, and Barnali Ghosh
J. Phys. Chem. C 2019, 123, 2573−2578

(b) Use of nanowire based films and arrays for high sensitivity and selectivity gas sensors of perovskite halides and metal oxide heterojunctions.

During the period under review, I have started to work in a new area. This is the area of very high sensitivity gas sensing using nanowire films and arrays. This research although done as a part of TRC project, it grew into a major research activity because of exciting new results and also the ideas involved. 2 of my students (SRF) who are registered with Calcutta University are working in this area.

This work principally started with the objective to make room temperature (unheated) gas sensors that can reach sensitivity better than 1ppm for gases that are used in disease diagnosis by breath analysis. While for this work focus was on to make sensors with electrical read out, we also have invented sensors where NH_3 gas can be detected by visual change and it is tested to be used in industrial sectors where NH_3 leaks may occur (Fig 7).

The work led to development of visual color change sensor for NH_3 (with a sensitivity of 10ppm) where the senor (which is a perovskite halide coated paper) consists of a nanowire film of the senor material. The paper is initially black in color and it changes to yellow on exposure to NH_3 gas. The sensor has been developed as a product “Ammo-watch” (patented) which is shown below. It is a wearable visual color change based sensor.
After obtaining publication of the patent, the work has been submitted for publication and is in advanced stage of reviewing.[1]

Ammonia sensor with electrical readouts has also been patented with better than 1ppm sensitivity

.

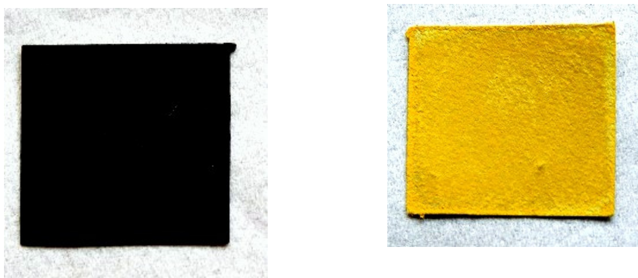

Fig 7.Color change response of the NH_3 Sensor: a) represents the original black colour of the unexposed film. b) Represents the yellow colour of the film in presence of NH_3 gas.

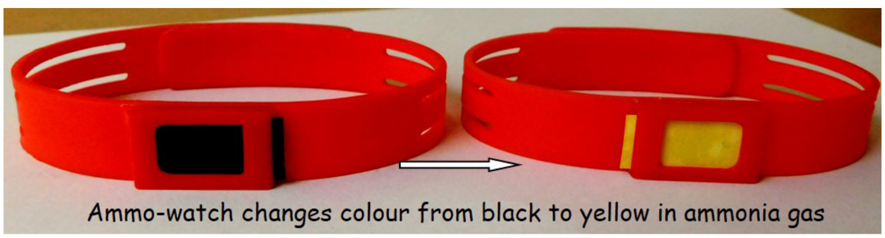

Fig 8 "Ammo-Watch"-Prototype of Ammonia Sensor:
"Wear it when you work in any environment prone to ammonia for your safety".

Patent1: Ammonia gas sensor and a method for manufacturing the same Indian Patent Filed No 201731000270 , Jan 2017.

Patent2. A paper based ammonia gas selective sensor with electrical read out and a method for manufacturing the same, Indian Patent Filed No 201831001993 A , Jan 2018.

Fast response paper based visual color change gas sensor for efficient ammonia detection at room temperature
Avisek Maity and Barnali Ghosh, Scientific Reports *(2018) 8:16851*

High sensitivity NH_3 gas sensor with electrical readout made on paper with perovskite halide as sensor material,
Avisek Maity, A. K. Raychaudhuri and Barnali Ghosh,
Scientific Reports | *(2019) 9:7777*

BG group also developed a Si nanowire-binary oxide based NO gas sensor[1] . The senor is an electrical read-out base sensor (patented) that works as an unheated sensor for NO gas and we are able to achieve a sensitivity of better than 0.5 ppm and is now being tested for its stability and reproducibility before it is taken up for translational activities. The sensitivity achieved (and its selectivity) makes it a good candidate for solid state non-invasive breath analysis work that I am doing along with my colleague Dr. Manik Pradhan [2,3].The ultra-high sensitivity NO sensor work is now being submitted after we have patented this.

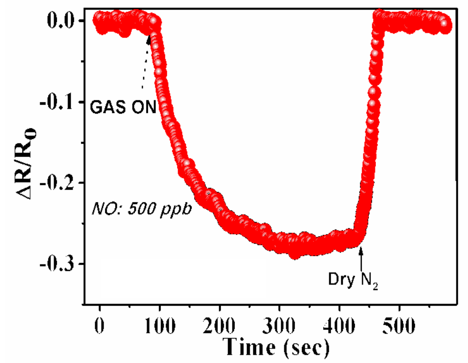

Fig 9: *Variation of $\Delta R/R_0$ with time under 0.5 ppm concentration of NO*

[1] **ZnO/Si nanowires heterojunction array based nitric Oxide (NO) gas sensor with noise limited detectivity approaching 10 ppb**
Chandan Samanta, Ankita Ghatak , A K Raychaudhuri and Barnali Ghosh,
Nanotechnology 30 (2019) 305501

[2]*J. Breath Res.* ***8*** *036001* **,** *(2014)*
[3]*J. Breath Res.* 8 016005 (2014)

Patent 1) A Gas-sensing system for selective detection of (Nitric Oxide) NO gas and a method for fabricating the same, *Indian Patent Filed No* 201731038036, Jan 2017.

(e)Growth of high performance thin film transistors (TFT) and physical property study

Fabrication of amorphous Indium Gallium Zinc Oxide thin film transistor on flexible substrate using a polymer electrolyte as gate dielectric:
BG group has fabricated a flexible thin film transistor (TFT) with relevant high performances indices using polymer electrolyte as gate dielectric and amorphous Indium Gallium Zinc Oxide (a-$InGaZn_2O_5$) as a channel on polyimide Kapton tape. Low temperature (≈100^O-120^O C) prepared amorphous Indium Gallium Zinc Oxide (a-IGZO) showed n- channel device characteristic and operated in enhancement mode with high saturation mobility of 42 cm^2/Vs, good ON/OFF ratio of ~10^5, low threshold voltage of ~ 0.7 V and low sub-threshold swing of ~ 175mV/decade. The improvements of the performance indices arise due to influence high value of specific gate capacitance of polymer electrolyte. The gate bias stress test of the flexible TFT showed the stable electrical characteristics.

Patent:
Flexible thin film transistor using eletrcic double layer as gate dielectric and a method of fabrication thereof
Inventors: Rishi Ram Ghimire,Chandan Samanta,Barnali Ghosh,Arup Kumar Raychaudhuri
patent no: 201731015268, Filed on 29/04/2017, published on: 09/6/2017

Publication:

. Fabrication of Amorphous Indium–Gallium– Zinc–Oxide Thin-Film Transistor on Flexible Substrate Using a Polymer Electrolyte as Gate Dielectric

Chandan Samanta, Rishi Ram Ghimire and **Barnali Ghosh**

IEEE Transactions on Electron Devices, ***65***, *2827-2832 (2018).*

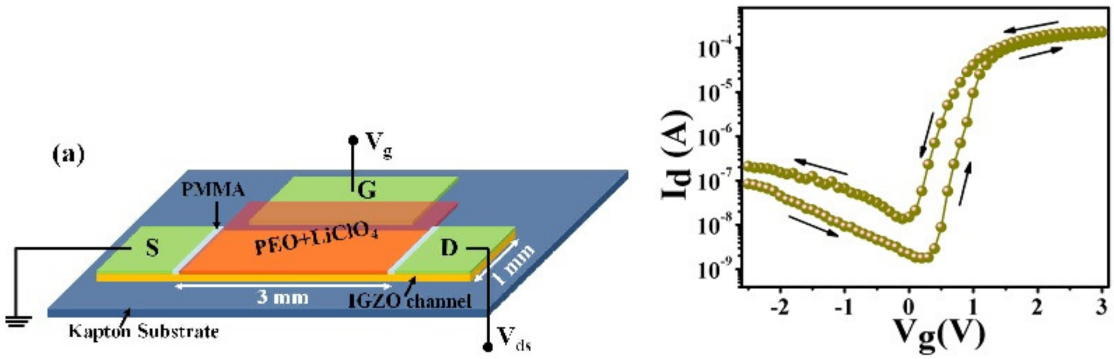

Fig1: a)A schematic of Flexible TFT composed of a kapton substrate, source, drain and gate Cr/Au electrode patterns, an amorphous IGZO semiconducting channel , b) Transfer characteristic curve (I_d vs V_g) at V_{ds} = 1V.

Major Resources used for Research work:

1) Central Facility instruments of S.N. Bose Centre under Technical Cell E-beam, Ion beam lithography Facility, at Helios Dual beam system at our Center, Cross-sectional TEM facility at our Centre
2) Neutron beam time facility at Dhruba, BARC, Mumbai, India
3) Neutron beam line at ILL, Grenoble, France
4) Neutron beam line, at Heinz Maier-Leibnitz Zentrum (MLZ), Lichtenbergstr, Garching, Germany
5) Synchrotron beam line at KEK ,Photon factory, Japan
6) SQUID facility UGC- DAE- CSR, Kolkata