University of Missouri-University of the Western Cape
Linkage Program 2017 Report

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Objective of Visit

The objective of the visit was to initiate a research project on hybrid photodetectors. While my research group at the University of Missouri, Columbia (MU) has been involved with mainly polymer (organic) based materials for electronics over the last decade, the use of hybrid materials (using both inorganic and organic semiconductors) has the potential of enhancing device capabilities in terms of efficiency and cost. The growth of inorganic semiconductor and metal nanostructures with unique characterization capabilities at the University of Western Cape (UWC) has added an important dimension to our project. Along with the research project, I was also involved with teaching part of the course for the Nanoscience Master's program*: Electronic Structure and Excitations in Nanomaterials*. This course was team taught by Prof. Carsten Ullrich (MU), who visited UWC during the same period, and me.

Specific objectives of the research visit included:

(a) Characterization of polymer ferroelectric films using state-of-the-art electron microscopy facility at UWC.
(b) Synthesis of nano-patterned ZnO films for hybrid photodetectors (in MU).
(c) Characterization of ZnO films using x-ray photoelectron spectroscopy at the National Metrology Institute of South Africa (NMISA) in Pretoria.
(d) Planning of a new project involving organic-inorganic hybrid perovskite materials for exploring fundamental electronic and magnetic properties, and their application in solar cells.

Accomplished Work - Research

(a) *Polymer ferroelectrics in organic field-effect transistors*.

As an on-going research project (funded by the National Science Foundation (NSF) – ECCS 1305642), we are exploring charge transport mechanisms in organic field-effect transistors (FETs). These transistors utilize a gate dielectric layer and an organic polymer (semiconducting layer). We have been using polymer ferroelectric dielectrics in organic FETs to understand the role of polarization in charge transport properties. An advantage of ferroelectric dielectrics such as poly (vinylidene fluoride-tri-fluoroethylene) (PVDF-TrFE) is that its dielectric constant (κ) may be tuned by a factor of five from 100 K to its ferroelectric-paraelectric phase transition temperature at ~ 130 °C. Temperature-dependent transport measurements from polymer ferroelectric organic FETs reveal that the nature of transport changes as the organic semiconductor layer is varied –metallic (band-like) to hopping transport is observed, depending on the nature of trap states in the organic semiconducting layer. This has been published in some of our recent works.[1-3]

Since the dipole moment can be aligned (poling) in ferroelectric dielectrics by an external electric field, our on-going works involves poling the dielectric layer in vertical and horizontal directions and to observe its impact on transistor properties. The electrical properties of FETs improve significantly when the dipoles in the ferroelectric layer are aligned in a perpendicular direction. By applying a horizontal field, the transistor properties deteriorate, and again by changing the external electric field to the vertical direction, the transistor properties are recovered.

By modulating the dipole moment in the ferroelectric layer by an external electric field, we thus have a tuning knob for improving switching times in organic FETs. Along with the changes in the transport properties, it is important to know the exact microstructure of the ferroelectric dielectric layer. The ferroelectric film is characterized by micron/nano scale domains (which determine the net dipole moment). The state-of-the-art electron microscopy (EM) facility at UWC was used to image these domains. Dr. Franscious Cummings, a senior scientist and lecturer at the EM core facility in UWC helped us with these measurements. Fig. 1 shows a schematic of the poling process in the ferroelectric (PVDF-TrFE) film. After vertical poling (left), the same film was poled in a horizontal direction (right). Fig. 2 shows the scanning electron microscope (SEM) images of an unpoled, vertically poled, and lateral poling of the vertically poled ferroelectric film. These images were taken at UWC.

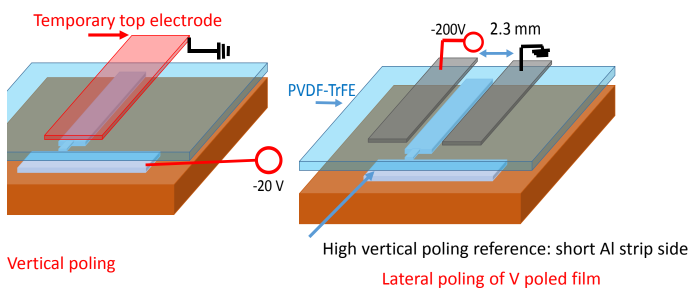
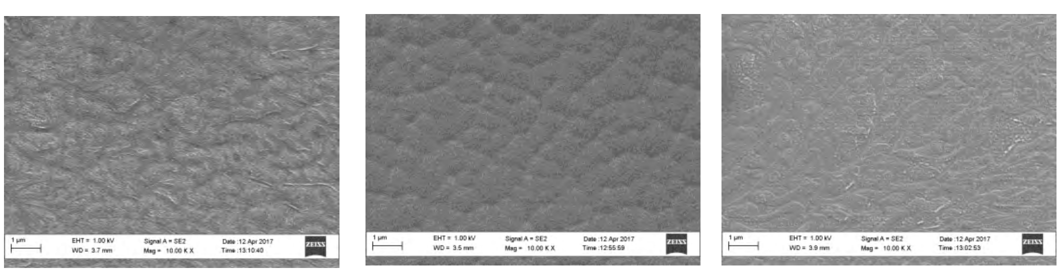


Fig. 1: Schematic of the poling process in the ferroelectric film



unpoled

Vertically poled

Laterally poled
(after V poling)

Fig. 2: (Left to right) SEM images of unpoled, vertically poled, and after lateral poling of a vertically poled film. These images were measured at the EM core facility at UWC.

The images above clearly show the changes in the domain features as a function of poling. With these images we can finally correlate our electrical properties of the transistors to the microstructure of the dielectric layer. We are in the process of preparing a manuscript with the UWC scientists as co-authors.

(b) & (c) Synthesis and characterization of nano-patterned ZnO films for hybrid photodetectors

Our main focus with the UWC collaboration has been on hybrid (inorganic-organic semiconductor) structures in efficient photodetectors. Initial work has been performed in MU where nano-patterned ZnO films have been explored in near-infrared (IR) photodetectors. ZnO, a non-toxic and an environmentally friendly metal-oxide semiconductor, is advantageous over other inorganic semiconductors since sol-gel chemistry may be used to synthesize high quality films with nano-patterning. We have come up with our own synthesis conditions for ZnO, and in conjunction with a research collaboration (at IISc, Bangalore), we have successfully demonstrated efficient near-IR photodetectors. This work has been recently published.[4] The structure of these photodetectors is: ITO/ZnO/polymer/Au.

In our next phase we are working with Dr. Theo Muller in adding ZnO and other nanoparticles to our nanopatterned ZnO films. Very recently Drs. Arendse and Muller in UWC have obtained a state-of-the-art plasma-enhanced/hot wire chemical vapor deposition (CVD) system. It is one its kind in Africa; even in the US there are only very few such systems. During my visit, the first test run of the system was carried out. Graduate students working with Dr. Muller are now working on the synthesis of semiconducting nanoparticles. In the next few months, we envisage using these nanostructures in our photodetector devices.

In our recent work on hybrid photodetectors [4], we found that oxygen plasma treatment of the ZnO layer significantly enhances the efficiency of photodetectors. However, at this point we do not know the exact mechanism as to how the oxygen atoms interact with the ZnO lattice. X-ray photoemission (XPS) spectroscopy is a powerful tool for understanding such interactions. Unfortunately, MU does not have such a system. Dr. Muller is well connected to NMISA in Pretoria, where a state-of-the-art XPS system is being currently installed. Unfortunately, there was a slight delay in installing this system and we had to re-schedule some of our planed experiments. In the next few weeks, will send our samples to Dr. Muller, and in collaboration with NMISA, XPS experiments will soon be performed.

(d) *Planning of a new project involving organic-inorganic hybrid perovskite materials for exploring fundamental electronic and magnetic properties, and their application in solar cells*.

As mentioned earlier, the Physics Department in UWC now has a state-of-the-art thin film growth facility. Prof. Arendse is headed in a new direction of synthesizing organic-inorganic perovskite materials. These materials are very promising in solar cell applications and show power conversion efficiencies upward of 20%. CVD growth of perovskite films is at its infancy, and when successful, Prof. Arendse and his team will be at the forefront of such growth techniques for perovskite films. In addition to their application in solar cells, organic-inorganic perovskites provide a rich playground for exploring basic physical phenomena: presence of ferroelectricity, topological edge states, and spin-texture effect which are tunable with external perturbation.

In fall 2017, I will submit a proposal to the National Science Foundation on the tuning of the fundamental properties of perovskite using external perturbation. This proposal will be in collaboration with Prof. Arendse.

Teaching at UWC

The Master of Science (MSc) two-year degree in Nanoscience, a unique program in South Africa, is a collaborative initiative between UWC, University of Johannesburg (UJ), University of the Free State (UFS), the Nelson Mandela Metropolitan University (NMMU) and the Department of Science and Technology. It is spearheaded by UWC (and coordinated by Prof. Dirk Knoesen). The partnership between these institutions allows students from other campuses across South Africa to take courses at UWC. This year has been one of the largest enrollments in their MSc Nanoscience program. There are 11 students in the introductory year.

Prof. Carsten Ullrich and I team taught a course on "Electronic Structure and Excitations in Nanomaterials" over two weeks. The course was offered everyday day for two hours; I taught for one hour and Prof. Ullrich taught for another hour. The topics covered were as follows:

- **Overview of functional materials: crystal structure***
- Electronic band structure
- Introduction to the electronic many-body problem
- **Interaction of light and matter**
- **Optical constants, absorption measurements**
- Density-functional theory and modern computational materials science-I
- **Excitonic effects in optical spectra**
- Density-functional theory and modern computational materials science-II
- Time-dependent DFT and electronic excitations
- **Phonons and Raman scattering**
- Excitations in materials – excitons and plasmons
- **Carbon based nanostructures - fullerenes**
- Graphene
- **Plastic electronics – I**
- Topological insulators
- **Plastic electronics -II**

* in **bold** are the topics covered by Guha

The lectures were based on presentation style with in-class discussions. Students were assessed based on homework assignments and a short in-class test.

Other Research Visits in South Africa

We got the opportunity to visit other research facilities: The iThemba LABS in Cape Town and NMMU in Port Elizabeth. Research activities at the IThemba LABS are based on sub-atomic particle accelerators. It also has a strong focus on materials science related research. We got an in-depth tour of their research facilities.

The visit to NNMU in Port Elizabeth was organized by Prof. Arendse and the Nanoscience program. The electron microscopy facility at NNMU is a world-class research facility and is equipped with state-of-the-art electron microscopes. We profoundly thank Prof. Jan Neethling (Director of the high resolution microscopy center) and other faculty members of the physics department at NNMU for discussing their research activities and giving us a tour of their world-class research capabilities.

Value of the UM/UWC Exchange Program

At a personal level this exchange program has been extremely valuable. It has allowed me to embark on new research projects in the area of sustainable energy. As a Physics and Astronomy Department in MU, we only gain from this exchange program. The National Research Foundation (NRF) in South Africa has recently ranked UWC as the top-most Physics and Astronomy department in the country. In terms of materials science/nanoscience capabilities, MU and UWC have complementary scientific expertise and research capabilities. The new thin film growth capabilities at UWC is unique and opens several doors for researchers like me who are involved with device fabrication and characterization utilizing novel semiconducting and metallic films in electronic devices.

My current NSF funding will allow me to target special programs from US Agency for International Development (USAID) to support Partnerships for Enhanced Engagement in Research (PEER) in South Africa. The experience gained and preliminary data gathered as a result of the UMSAEP program is extremely beneficial for establishing joint research programs between my research group and the groups of Drs. Muller and Arendse. We envisage a more involved collaboration with NMISA and future student exchanges.

Acknowledgements

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Bibliography

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