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**NANOPARTICLE SOLUTIONS FOR PRINTED ELECTRONICS
APPLICATIONS**

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Final Report**

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14. ABSTRACT This project had a technological focus on the development of silicon nanoparticle based electronic devices. The level of uniformity and control of the essential electronic, structural, mechanical, and thermal properties was only possible with a thorough understanding of the nanomaterial properties, the complex microstructure of the printed composite, and the physical processes governing charge, and energy transport. Significant progress was made towards all 4 long-term study goals of the project: the internal and surface structure of the nanoparticles and their influence on charge transport; agglomeration and clustering of nanoparticles; the microstructure of the printed composite and multiscale modeling of the transport of charge and energy; and the prediction of the properties and the input of this knowledge into the design of electronic devices. This project was highly collaborative with a significant investment in human capacity development. It was therefore integrated into and complemented projects funded the USAID Higher Education Development US-Africa Initiative, the UCT Vice Chancellors's Strategic Initiative and the commercial development by UCT's spin-out company PST Sensors. These were complemented by temperature dependent electrical characterizatio					
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Abstract

This project had a technological focus on the development of silicon nanoparticle based electronic devices. The level of uniformity and control of the essential electronic, structural, mechanical, and thermal properties was only possible with a thorough understanding of the nanomaterial properties, the complex microstructure of the printed composite, and the physical processes governing charge, and energy transport. Significant progress was made towards all 4 long-term study goals of the project: the internal and surface structure of the nanoparticles and their influence on charge transport; agglomeration and clustering of nanoparticles; the microstructure of the printed composite and multiscale modeling of the transport of charge and energy; and the prediction of the properties and the input of this knowledge into the design of electronic devices. This project was highly collaborative with a significant investment in human capacity development. It was therefore integrated into and complemented projects funded the USAID Higher Education Development US-Africa Initiative, the UCT Vice Chancellors's Strategic Initiative and the commercial development by UCT's spin-out company PST Sensors. These were complemented by temperature dependent electrical characterization, providing input to charge transport, which led to the development of the first new type of transistor functionality in 65 years.

Project Overview

Printed electronics is an emerging technology that offers many significant advantages in processing simplicity, and possible form factors, over conventional thin film technology. These advantages are most significant in large area and flexible applications, such as integrated sensors and photovoltaics, where high temperature processing cannot be applied, and which take full advantage of emergent properties of the two classes of materials used. Printable, or solution processable, semiconductors fall into two broad classes: soluble conducting polymers, such as the polythiophenes, and inorganic nanoparticle based inks. The focus of this project was the latter, with which the University of Cape Town has had several notable successes, including the demonstration of fully printed silicon field effect transistors, through a strategy of underpinning development and innovation with basic research into the properties of both the printed semiconductor materials and their nanoparticle and colloidal precursors. Without this basic knowledge, further development and the achievement of technological innovation is not possible.

This project was designed to be highly collaborative, in that it required the expertise and infrastructural resources of both partners, as well as a significant investment in human capacity development. It was therefore integrated into and complemented projects funded by the USAID Higher Education Development US-Africa Initiative, the University of Cape Town's Vice-Chancellors' Strategic Fund, the SA National Research Foundation and various commercial projects of PST Sensors.

The technological focus of the project was on the development of silicon nanoparticle based sensors and photovoltaics, as well as other large area devices, which can only be achieved by printing and coating techniques. Besides photovoltaic modules and low resolution transistor arrays, specific targeted applications originally include optical, thermal and mechanical sensors (2D strain gauges), and eventually actuators, in which a *single* device occupies a large area and is conformable with its environment. However, this level of

uniformity and control of the essential electronic, structural, mechanical, and thermal properties is only possible with a thorough understanding of the nanomaterial properties, the complex microstructure of the printed composite, and the physical processes governing charge, and energy transport in the layer. Hence, during the project the focus was shifted towards temperature sensors and photovoltaics, and their supporting components and materials. Other end-use applications are being considered on a needs basis as determined by enquires to PST Sensors, which are beyond its immediate scope of expertise and capacity. Two such recent (post-project close-down) examples are: printable diodes to prevent cross-talk pressure sensor arrays; and electrically readable humidity sensors.

Technical Program

The goals of the project were to investigate using a variety of advanced techniques available to all partners:

1. The internal and surface structure of the nanoparticles, their dependence on the synthesis parameters, and their influence on charge transport and electronic properties;
2. Agglomeration and clustering of nanoparticles in both the dry phase and when incorporated with a liquid vehicle in an ink, and its eventual correlation with rheological properties, printability, and electrical characteristics of the final printed nanocomposite;
3. The microstructure of the printed composite and the multiscale modeling of the transport of charge and energy; and finally
4. The prediction of the overall properties and the input of this knowledge into the design of light and temperature sensitive devices.

Characterization of particle structure and agglomeration relied heavily on the small angle scattering techniques, performed mainly at the Advanced Photon Source at Argonne National Laboratory, but also at the HIFR and SNS neutron facilities at Oak Ridge National Laboratory, and built on the substantial expertise in analysis and modeling built up by the Beaucage group in Cincinnati. These results were supported by electron microscopy, and tomography, performed at three sites in South Africa, Nanogune in Spain, and lately using the TEAM 0.5 at NCEM, Lawrence Berkeley National Laboratory. After the end of the project an extended size scale was obtained by including dynamic light scattering, using a system developed during the project. Similar techniques were applied to the study of the printed layers, with the addition of FIB sectioning of the printed layers, and optical profilometry to study surface structure. The structural characterisation was complemented by temperature and magnetic field dependent electrical characterization, and electrical impedance spectroscopy to provide the input to multiscale charge transport models. The combination of basic electrical characterization with SAXS and microscopy methods was successfully applied to obtain a first correlation of the internal structure and electronic properties with the flow properties of the ink-substrate system.

The production of inks and the printing of semiconductor materials and devices, using a semi-automatic screen printing press, were performed exclusively in-house. In formulating the inks, attention will be paid equally to the achievement of the required flow characteristics and the functional properties of the dry layer. Besides the “standard” acrylic-based silicon ink used by PST Sensors in its temperature sensors other formulations, containing highly doped p-type and n-type silicon nanoparticles and using different binder-solvent systems, were investigated. These included both insulating and semiconducting polymers, specifically PEDOT:PSS, to print hybrid nanocomposite electronic materials. In addition to semiconducting systems, conducting (Ag, Pd, Ni, C, and Cu) and insulating nanoparticles (titania, silica) were investigated in the production of complementary inks for complex

devices. These were either obtained commercially in nanoparticle form from different suppliers or milled from commercially obtained feedstock.

With the exception of initial tests of material systems for third generation photovoltaics, all devices were fabricated on either paper or polymer film (PET) substrates. For specific characterisation techniques, layers were also deposited on borosilicate glass and silicon wafers. In the photovoltaic program, hybrid inorganic-organic semiconductor combinations were tested by printing PEDOT:PSS and silicon nanoparticle inks on highly doped silicon wafers. Similarly photochemical cells were initially fabricated by deposition of nanoparticle systems on ITO coated glass, but this was subsequently replaced by a printing a translucent conducting layer onto PET film.

Besides sensors and photovoltaic cells, other components which were printed included diodes (as the base system for solar cells and as rectifiers), capacitors (both as a test of insulators and conductors, and as reactive circuit elements), resistors, inductors, and transistor structures. Both multilayer and planar, with interdigitated top or bottom contacts, architectures were investigated. In the former, attention had to be focussed on delamination and punch-through arising from incompatibility between the materials in the different layers.

Results

The SAXS experiments at ANL and SANS experiments at ORNL, conducted on different nanoparticle layers, yielded important results on the influence of flow conditions on the particle network structure, leading to two publications on these data. Improved methods of data reconstruction for electron transmission and scanning electron tomography have been developed, with one paper published and two more being prepared for submission. In the final quarter of the project, it was possible to correlate three-dimensional structural information obtained from the tomograms with topological information obtained from SAXS to make inferences about the alignment of the particles and clusters in the printed layers. Both the nanoparticles and primary clusters are slightly prolate and appear to align vertically for high concentrations of particles. There was also a clear indication, subsequently confirmed by dynamic light scattering, that the primary particle clusters formed in the dry powder are maintained during ink processing. The data analysis continued after the end of the project and is being prepared for publication. Moreover, using the understanding gained from internal structural studies of printed layers using USAXS, it was possible to successfully interpret older surface studies performed in 2008 at the Advanced Light Source at Lawrence Berkley National Laboratory, which have now been submitted for publication.

Over the last two years, great progress has been made in understanding the mechanisms of charge transport in the printed silicon network, culminating in the PhD thesis of Batsirai Magunje, of which some details are included in paper published by Männl and Britton. As previously understood, the charge transport mechanism has been confirmed as a hopping through a percolation network of particles, with each junction having the electrical characteristics of a back-to-back combination of Zener diodes. Four activation energies have been associated with these junctions, three of which arise from band-bending and which apply to both electrons and holes, and one corresponding to an interfacial electron state. Subsequent to the completion of Dr Magunje's thesis, the model has been extended by Emmanuel Jonah to include capacitive couplings in incomplete networks. Early results show a good agreement with the network topology obtained from small angle scattering. Another direct consequence of the understanding of the charge transport mechanisms, was the ability to predict and model the properties of a new type of junctionless transistor, which functions as a double-throw switch. A patent for this device was filed in September 2012, and it has recently been published in AIP Advances. Between filing and scientific publication, PST Sensors launched a productized version at the Printed Electronics Europe Show in April 2013.

Early results of the applicability of different materials systems for third generation photovoltaics have been encouraging. The first successful demonstration of a hybrid system consisted of a PEDOT:PSS layer printed onto a high doped silicon wafer and overprinted with a silver top contact. This test structure had an effective efficiency, scaled to the open area, of 1% under AM1.5 illumination. However, this material system proved to be difficult to transfer directly to a fully printed structure, yielding efficiencies 5 orders of magnitude lower. A significant improvement was obtained by using a similar architecture to the photochemical cells, with the replacement of the liquid electrolyte with the semiconducting polymer. The final geometry chosen for further work consisted of transparent conducting contacts, one coated with a blend of silicon and titania nanoparticles, with the electrolyte or semiconducting polymer between. Unlike conventional photochemical cells, the cell under development does not contain a dye. Efficiencies for both systems are similar, at around the 0.1 % - 0.5% level for structures which have not yet been optimised.

The most successful capacitor and diode structures were three layer architectures consisting of planar top and bottom contacts, and an intermediate layer – silicon in a diode and insulator in a capacitor. For the diodes different materials were used for the two contacts, whereas the capacitor construction was symmetric. The best Schottky diode structures were obtained using an ink containing highly doped p-type silicon nanoparticles, although diode-like behaviour was observed for all types of silicon. The simplest and most cost-effective diodes were produced with silver and carbon contacts, printed with commercial inks, although in-house formulations and materials supplied by collaborators worked equally as well. There was no significant difference in performance between graphite, carbon nanotubes or graphene. High voltage diodes could also be produced using palladium nanoparticles for one of the particles. A provisional patent specification is currently in preparation for the diode technology, after which the results will be submitted for publication in the scientific literature.

Through PST Sensors, commercialisation of the temperature sensors is continuing at an increasing pace. In 2012 a consortium led by Thin Film Electronics ASA announced a prototype temperature indicating tag including this technology. In another customer-driven project, the NanoSciences Innovation Centre assisted PST Sensors in developing and characterizing a 256 element thermal sensing array on a quarter inch pitch. Also towards the end of the project the PI engaged in discussions with scientists at NASA JPL during the 2013 Flex Conference in Phoenix. Subsequently PST Sensors has been contracted by Xerox PARC to supply temperature sensors for phase II of JPL's printable spacecraft NAIAC project.

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