Nanofabrication – European Research Labs Apply Dip Pen Nanolithography

Dip Pen Nanolithography® (DPN®) came to light as a novel research tool back in 1999 with a paper in Science from the a group at Northwestern University in the USA (1). Like many new technologies, the early development work was dedicated to understanding the fundamental strengths and weaknesses of the technique. Once DPN spread to other labs with more diverse research interests, DPN become an important tool that is now being used to solve some long-standing problems regarding nanoscale device fabrication. This paper will highlight some of these solutions by looking at three European research labs.

> ***"There are several different lithography techniques available for research, each with its own specialty or benefit."***

Author Details:

Tom Warwick
General Manager,
Sales and Applications
NanoInk, Inc.
8025 Lamon Avenue
Skokie, IL 60077, USA
Email: twarwick@nanoink.net

SO WHAT IS DPN?

Dip Pen Nanolithography (DPN) is an established method of nanofabrication in which materials are deposited onto a surface via a sharp tip. Molecules are typically transferred from the tip to the surface through a water meniscus which forms in ambient conditions as the tip nears the surface.

DPN enables controlled deposition of a variety of nanoscale materials onto many different substrates. The vehicle for deposition can include pyramidal scanning probe microscope tips, hollow tips, and even tips on thermally actuated cantilevers. Recent advances have demonstrated scalability of the technique with arrays of tips leading to true massive parallelisation with up to 55,000 tips.

The controlled transfer of a molecular 'ink' from a coated nanoscale tip to a substrate was described and initially developed by a research group at Northwestern University led by Professor Chad Mirkin. Analogous to the macro technique of a quill pen, these authors introduced the term Dip-Pen Nanolithography or DPN to describe their work.

Figure 1. Schematic of DPN technology.

There are several different lithography techniques available for research, each with its own specialty or benefit. The versatility of Dip Pen Nanolithography offers a number of benefits over other techniques, making it a leading method of nanofabrication. These have been summarized in *Table 1*.

Table 1. The benefits of DPN

- Resolution: feature sizes as small as 50nm may be routinely created
- Precision: automated nanoscale registry to create or image features
- Material flexibility: wide range of inks can be deposited onto a variety of different surfaces
- Approaches: top down & bottom up, direct write with the ability to change patterns on the fly
- Speed: achieved with scalability using multiple probe arrays
- Affordable: low start up and running costs compared to other lithographies
- Multiplexing: multiple ink deposition is possible onto the same substrate
- Operation in ambient conditions: no need for UHV or clean room operation
- Optimised performance: uses dedicated instrumentation & MEMS devices designed for DPN

INSTRUMENTATION ADVANCES

The early days of DPN use took place in labs using SPM systems. The first papers reported the deposition of inks, predominantly alkane thiols, onto surfaces such as gold and glass. Commercial software which enabled users to develop and control inking protocols including the temperature and humidity for the experiment was released in around 2000. Dedicated instrumentation arrived in 2002 with a family of tools called NSCRIPTOR®, (NanoInk, Inc, Skokie, USA). User driven developments have been integrated into the latest systems which are being found in laboratories the world over.

There are two approaches. The first system provides the ability to scale up processes that have been developed on the DPN research platforms. The NLP2000 is the first dedicated benchtop nanofabrication lithographic platform built in a simple and affordable manner so virtually anyone can use it. Patterns from nano- to micron-sized features can be created using of a wide variety of materials from metal nano-particles to biomolecules. Researchers are able to rapidly design and create custom engineered and functionalised surfaces, using DPN to transfer minute amounts of materials (molecular quantities) over a large, environmentally controlled work area (40mm x 40mm). With a dynamic range of deposited feature sizes ranging from sub-100 nm to over 10 microns, the NLP2000 System provides an easy-to-use pathway to the world of nanofabrication.

Figure 2. Benchtop nanofabrication with the NLP2000

The second system is a top level benchtop research platform, the DPN5000 system. This enables dedicated DPN experiments based on a fully functional commercial scanning probe microscope (SPM) system. Leveraging these scanning probe capabilities, the system is optimised for both nanolithography and subsequent image acquisition.

It is a complete package solution, including a PC, instrument controllers, air table, and environmental chamber. Going far beyond a standard atomic force microscope, this turnkey approach uniquely applies NanoInk's MEMS offerings (1D and 2D probe arrays, microfluidic inkwells & Active Pens™) to provide the critical features necessary for accurate and reproducible DPN experimentation.

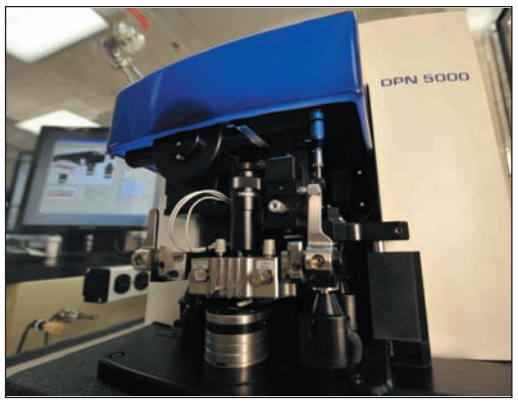

Figure 3. The research platform DPN5000

STARTING IN GERMANY, THE FORSCHUNGSZENTRUM KARLSRUHE – BIO APPLICATIONS

Having been the first European facility to use commercial Dip Pen Nanolithography technology in 2005, one of Germany's premier research institutes, the Forschungszentrum Karlsruhe (FZK), is now using these latest systems to meet the increased demand from a growing group of users. Located in the Nanomechanics Group of Professor Harald Fuchs, DPN is being used to drive practical applications in the fields of drug discovery, tissue engineering and the early detection of specific diseases. The Centre now offers open access to these instruments through the Karlsruhe NanoMicro Facility (KNMF).

The FZK have developed methods applying DPN for patterning with biological membrane lipids. Phospholipids are important biological molecules that self-assemble under physiological conditions to form the bilayer structure of biological membranes. However, available methods for generating phospholipid arrays on surfaces are severely limited in their lateral resolution. Based on non-covalent adhesion and humidity control of the liquid crystalline phase of the ink, it is possible to use phospholipids as a universal ink for DPN on a variety of substrates. Being able to produce 3D liposome-like structures on a surface allows model cells and membranes to be constructed. Taken further, DPN's unique multiplexing writing with different inks has provided the concept from which combinatorial nanostructure libraries of materials have been successfully developed.

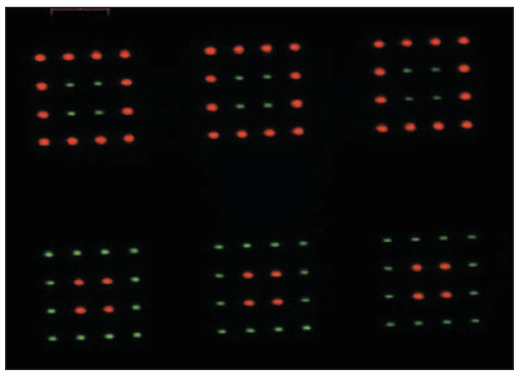

Figure 4. Fluorescent imaging of lipid patterns

The original platform for DPN was based on an atomic force microscope (AFM). However, for biological experiments, a rapid scale-up system is required to generate hundreds if not thousands of samples for testing to provide the required statistical approach of the biologist. A high powered imaging system was no longer required. This exemplifies the development of the NLP 2000 nanofabrication platform to provide an easy-to-use system with a vastly increased speed of output for the generation of huge phospholipid arrays.

Commenting on the new NLP platform capabilities, FZK's DPN group leader, Dr Steven Lenhert' said: "As expected, the NLP is an amazing piece of equipment that takes micro/nanoarraying to the next level. In just the first day, I had already made functional nanostructures with it that I believe would be impossible to make with any other existing fabrication method. We are still realising the possibilities it opens up, and I think it will really enable us and the growing DPN community to make some major scientific breakthroughs."

The head of the laboratory, Professor Fuchs, said "our lipid DPN project is funded by the DFG to manufacture and study model bio-membrane systems has opened the door to a better understanding of how the cell membrane functions and how this could lead to new ways of getting therapeutic drugs into cells. Using DPN and applying phospholipid inks has opened many potential applications for the technique include biochemical sensors, drug screening and delivery, tissue engineering and nanofabrication in general."

INORGANIC INKS ARE USED IN AACHEN

With an extensive background in the development of different routes for template assisted assembly of metal nanoparticles on solid supports, the Institute of Inorganic Chemistry (IAC) at the RWTH University of Aachen has recently taken delivery of NanoInk's flagship Dip Pen Nanolithography® (DPN®) research platform, the DPN 5000. This will be used to fabricate conducting nanostructures independently of any structure- guiding templates, and for this purpose it is much more flexible than any other lithography techniques, such as e-beam or EUV lithography.

As part of the Institute of Inorganic Chemistry, the group of Professor Ulrich Simon, chair of Inorganic Chemistry and Electrochemistry, focuses on the synthesis, characterisation and assembly of metal and semiconductor nanoparticles, nanostructures and biomolecular materials. Assembly at the nanometer scale on isolating and semiconducting surfaces will be facilitated by DPN. Research will investigate the interplay of microstructure and their electrical properties. In turn, this will complement the existing in-situ measuring system.

The main applications include the oriented deposition of gold nanoparticles; the writing of conducting metal structures of arbitrary shape; and the nanostructuring of metal oxides. Eventually, applications will include taking the microelectronic chip down to the nano scale, i.e. producing the smallest available transistor. There is also interest to study the electronic properties of biofunctionalised of nanoparticles.

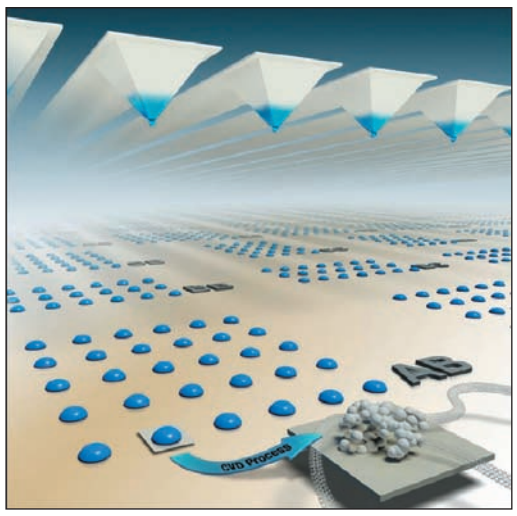

Figure 5. Graphic to illustrate the deposition of inorganic nanoparticles for growing of carbon nanotubes

In 2007, Professor Simon was a Visiting Professor at the International Institute of Nanotechnology, Northwestern University working with Professor Chad Mirkin. Excited now by having first-hand access to DPN in Aachen, he said: "Thanks to the generous financial support by the German research foundation as well as by RWTH Aachen University, we are now able to develop a new molecularly based approach to fabricate electrically functional nanostructures. This will have a huge impact on our efforts to apply such nanostructures in a technical or biological environment."

THE LINK TO PROVIDE NANOSCALE SOLUTIONS – THE UNIVERSITY OF STRATHCLYDE

The Centre for Molecular Nanometrology is based at the University of Strathclyde in Glasgow and is a collaboration of the Departments of Pure and Applied Chemistry, Physics and Applied Physics, with associated interdisciplinary groupings from across the Faculty of Science. Nano-metrology refers to the measurement of events on a nanoscale using novel physical techniques and chemical manipulations.

Nanometrology is part of the nanotechnology area that is not well established and is very much in the ascendancy. A distinctive grouping exists at Strathclyde that can advance the little explored and difficult field of measuring nm distances/structures in-situ, which lies at the heart of molecular biology and medicine, i.e. nanometrology.

Centre Director Duncan Graham is recognized for his work in the field of Surface Enhanced Raman Spectroscopy (SERS) and was an early adopter of DPN technology. His work required the ability to place nanoscale features onto existing microstructures. The main SERS substrate, Klarite®, is an array of gold-coated, microscale inverted pyramids designed to provide more consistent SERS data. Graham has demonstrated NanoInk's unique ability to precisely and controllably deposit materials to the individual pyramids. This combination of DPN and SERS is one of the few ways of extracting spectroscopic data from nanoscale patterns.

The demand for DPN within the group and from other collaborators has led to a marked expansion with the arrival of two new systems, the DPN5000 research platform and the NLP2000 bench-top nanofabrication system.

Strathclyde uses the DPN5000 to combine high resolution lithography with world class imaging capability will expand the group's already formidable nanotechnology toolkit and help Graham move towards in vivo imaging approaches based on functional nanoparticles and SERS analysis.

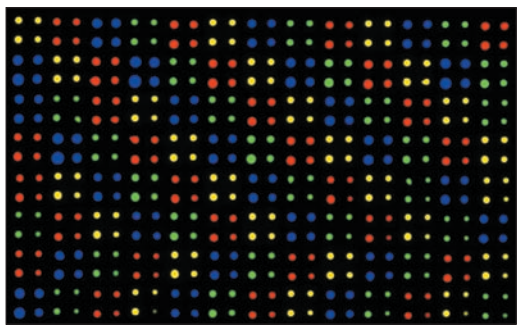

Figure 6. Multiplexed printing of four proteins using the NLP2000

Following the early successes with DPN, Graham's lab is now using the NLP 2000 to create large area nanoscale arrays of biomolecules, nanoparticles and SAM molecules. The team has shown that they can fabricate highly sensitive protein assays, ultimately leading to the development of new devices that could revolutionise the detection of cancer biomarkers.

LOOKING AHEAD

When one looks at the work of these three leading research laboratories, it is clear that DPN is now being used as a methodology to create solutions using both organic and inorganic nanomaterials. New work in the fields of polymers and photonics indicate that nanotechnology truly can provide the way forward for manufacturing in multiple disciplines worldwide.

No longer is nanofabrication a dream. It is clearly being demonstrated as a viable process on the bench scale ready for scaling up.

Acknowledgements

The author wishes to thank the research groups at Aachen, Karlsruhe and Strathclyde for their assistance in the preparation of this article.

References

[1] *'Dip-Pen' Nanolithography, R D Piner et al, Science 29 January 1999: Vol. 283. no. 5402, pp. 661 – 663 DOI: 10.1126/science.283.5402.661*

Trademarks