Science at the Sharp End: Recent Advances in Tip-based Nanolithography for the Fabrication and Modification of Plasmonic Structures and Sensors

Robert J. Stokes, Robert M. Marchmont, Alexander Smetana

NanoInk Inc., 8025 Lamon Avenue, Skokie, IL, USA
rstokes@nanoink.net

Abstract

Dip Pen Nanolithography is an established method of nanofabrication in which materials are deposited onto a surface via a sharp tip.[1] Dip Pen Nanolithography (DPN) can be employed both as a rapid fabrication technique for nanophotonic materials and as an effective means to directly deposit localised functional chemistry into the same structures with nm precision. Nanophotonic materials hold great promise for a wide range of applications. However, the selective modification and functionalisation of such structures in many cases remains a challenge.

Recent advances in DPN methods has resulted in the ability to directly print relevant materials, including proteins and DNA, on to a variety of structures under ambient conditions. Most approaches fall into two general cases. In the first case, solid inks, typically alkane thiols onto gold, transported via a water meniscus are capable of producing very ordered structures with high resolution (10's nm). In some cases these chemical patterns are utilized as chemical templates for the assembly of a secondary material or to provide functionality for bioconjugation (e.g. through simple EDC coupling). The advantage of this method is high registration accuracy and small features sizes that can be achieved (due to slow ink diffusion coefficients of ~0.1 $\mu m^2.s^{-1}$ and tip-surface actuation times ~100 milliseconds). If greater chemical complexity is required then the direct deposition of up to 48 liquid materials can be achieved via the use of microfluidic devices coupled to recent advances in writer pen design, using these systems complex multicomponent patterns can be written over cm^2 areas with ease. In general, the feature sizes using liquids are determined by dwell time and surface chemistry. The relative advantages and trade offs in these two methods will be presented and discussed in context of recent examples.

Recent examples in biosensing will be presented. In particular, biosensors based on surface enhanced Raman scattering (SERS) and localized surface plasmon resonance (LSPR) can benefit greatly from methods whereby the capture biological moiety can be localized within the area providing the greatest enhancement of response.[2] The practicalities of building biosensors such as aligning into microfluidic structures will be presented in addition to recent commercial applications in diagnostics and screening from small sample volumes (tear fluid, tumor lysates, dried blood spots). Several DPN techniques have also proven useful technique in the rapid iteration of photonic structures. Molecular inks, such as alkane thiols, allow the rapid fabrication of very small features (~15 nm) with nanoscale registry. These patterns can be used as etch resists in one or more steps to produce a wide range of structures. All of the techniques presented are easily scalable over cm^2 areas using 2D print arrays of cantilevers and, more recently, polymer pens comprising several million tips.

References

[1] R. D. Piner, J. Zhu, F. Xu, S. Hong, C.A. Mirkin, *Science*, 283, (1999), 661.

[2] R. J Stokes, J. A. Dougan, D. Graham Chem. Commun. (2008), 5734.

Figures

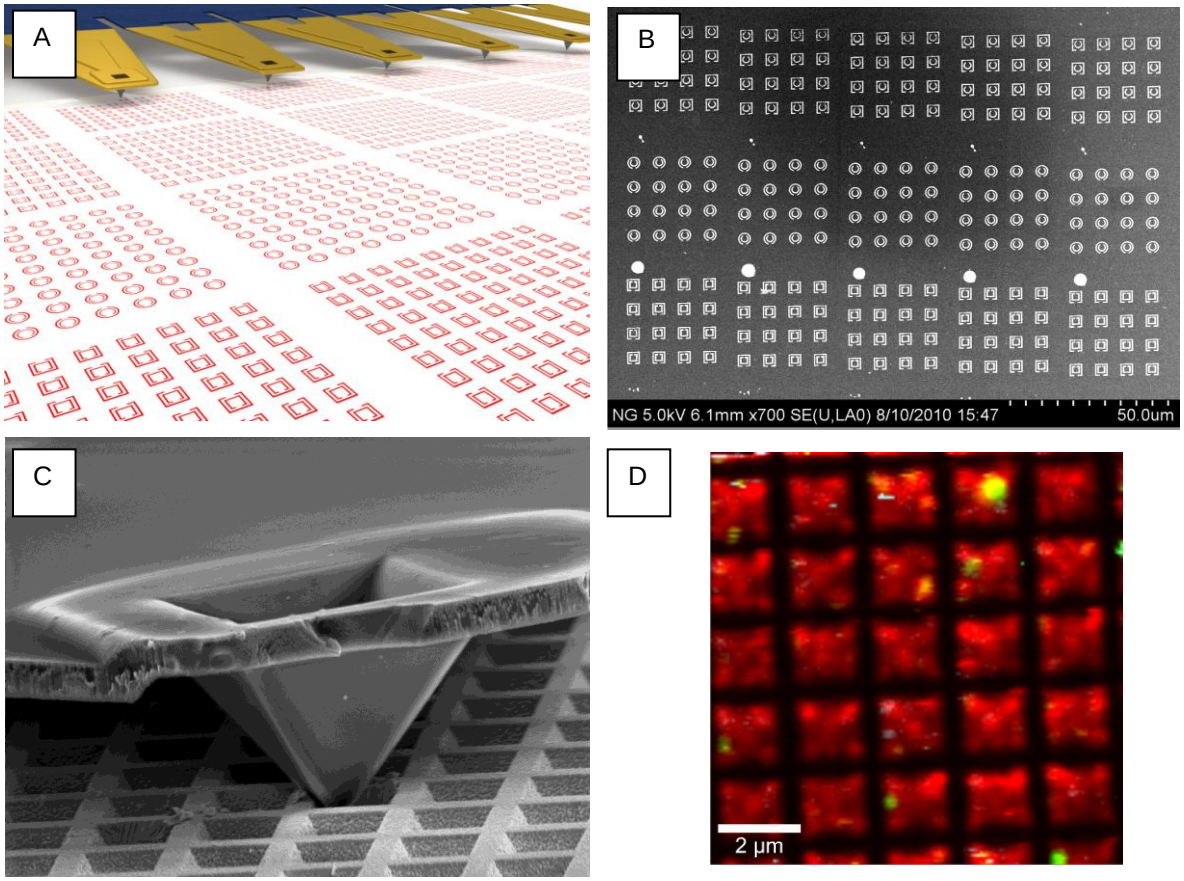

Figure: A: Illustration of 1D multipen patterning by DPN B: Scanning electron micrograph of split ring oscillator devices fabricated by etching from DPN resist. C: SEM showing DPN tip interaction with nanophotonic structure. D: Confocal scanning Raman image of Surface Enhanced Raman Spectroscopy (SERS) surface, functionalized with dye-labeled DNA.