da Vinci's notebook

da Vinci's Notebook, vol. 3 (2011)

Dip-pen Nanolithography: An Overview Including Some Applications

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In nanofabrication, most techniques for creating nanoscale structures are based on lithographic techniques previously developed on a larger scale. However, these conventional techniques, such as photolithography, can be miniaturized only so far because of limitations such as optical diffraction and the cost of the complex equipment required (Ozin & Arsenault, 2005, Chapter 2). Fortunately, scanning probe microscopy (SPM), best known for its role in spectroscopy and imaging, has proven to be of great use in patterning nanostructures (Tseng, Notargiacomo, & Chen, 2005). There are many types of SPM-based lithographic techniques, which can be divided into those based on scanning tunnelling microscopy (STM) and those based on atomic force microscopy (AFM) (Tseng et al.). Of the techniques based on AFM, one technique with great potential for fabricating nanostructures is dip-pen nanolithography (Ginger, Zhang, & Mirkin, 2004).

Dip-pen nanolithography (DPN) is a "direct-write scanning-probe-based lithography" (Ginger et al., 2004, p. 31) that delivers molecular inks directly to a specific region of a target substrate using an AFM tip (Ginger et al.; Xie, Chung, Sow, & Wee, 2006). Unlike STM-based techniques that only function in a vacuum, DPN can be used in ambient lab conditions (Tseng et al., 2005). For optimal results, DPN is best carried out in an environment with controlled humidity (Ginger et al.). The 'inks' used in DPN form a monolayer on the substrate by chemically reacting with it (Ginger et al.). The ink-substrate combination is determined by the chemical and physical properties of each substance (Tseng et al.). Inks can range from organics, such as silanes, alkynes, thiols, and silazanes (e.g. 1-octadecane-thiol, or ODT) to inorganics, such as oxides, metals, and magnetic compounds (e.g. gold nanoparticles) to biomolecules such as peptides, DNA, and proteins (e.g. thioredoxin) (Salaita, Wang, & Mirkin, 2007; Xie et al.). Substrates include metals, semiconductors, insulators and self-assembled monolayers (SAMs) (Tseng et al.). Useful ink-substrate combinations include alkylthiols on gold, alkynes on silicon, DNA on silicon oxide, metal salts on germanium (Ginger et al.). This wide range of available ink-substrate combinations allows for a number of potential applications, as the surface chemistry of each combination is different, and the different combinations can be used to control different properties in the substrate — among them wettability, reactivity, and corrosion (Ozin & Arsenault, 2005, Chapter 2).

DPN was introduced in 1999, having been invented by Mirkin and coworkers (Xie et al., 2006). It was inspired by a persistent problem in AFM imaging: the formation of a water meniscus between the AFM tip and the sample, which influences the AFM image, especially at high resolutions (Piner, Zhu, Xu, Hong, & Mirkin, 1999). Mirkin's group found that water is either transported from the tip to the sample or from the sample to the tip, depending on the properties of each (Piner et al.). They found that in the former case, molecules could be transported from the AFM tip to the sample via the water (Piner et al.), a transfer that served as the basis for developing DPN. DPN was first demonstrated by writing with an alkanethiol ink (ODT) on a gold substrate (Piner et al.). The resulting pattern was indistinguishable from a bulk grown SAM, and had a stable crystalline structure (Salaita et al., 2007), showing that when SAMs are created with DPN, they are equally as functional as SAMs grown in bulk. The SAMs created with DPN, however, can be written in any arbitrary pattern (Ozin & Arsenault, 2005, Chapter 12). These patterns have potential applications in multiple fields, including optics, microelectronics, and cell biology (Ozin & Arsenault, 2005, Chapter 2).

DPN is carried out by coating an AFM tip with a thin film of ink molecules and bringing it close to the target substrate in a high humidity atmosphere. The process begins when the humidity of the air increases at a constant temperature and tip-substrate distance, causing a bead of water to condense and form a water meniscus that begins near the tip apex and spreads out (Xie et al., 2006). The water meniscus functions as a bridge, delivering small collections of ink molecules to the substrate (Ozin & Arsenault, 2005, Chapter 4). The size of the meniscus affects the size of the pattern created, with a smaller meniscus allowing for higher resolution in the

pattern (Xie et al.). If the meniscus is too small, it becomes unstable and fluctuates in shape, with fluctuations that are larger in magnitude than its average width (Xie et al.). Several factors that affect the size of the meniscus include the shape of the tip, humidity, wettability of the tip, tip-substrate distance, and temperature (Xie et al.). A sharper tip results in a smaller meniscus and better resolution. Decreased humidity, decreased tip wettability, increased tip-substrate distance and increased temperature will all lead to a decrease in meniscus size. As well, the movement of the tip controls the amount of ink deposited. The longer the AFM tip is kept stationary in contact with the surface, the wider the pattern gets (Ginger et al., 2004). When using DPN to pattern lines, using a slow scan rate results in relatively broad, fuzzy lines, while using a faster scan rate results in isolated dots and disconnected lines (Xie et al.). With careful control of meniscus size, chemical and physical properties of the ink and substrate, writing speed, and tip-substrate contact force, patterns as small as 10-15 nm can be created (Tseng et al., 2005).

One exciting application of DPN is its use in fabricating biological nanoarrays. Microarrays are chip-based systems of biomolecules, and are used to detect proteins, DNA and small molecules in a sample (Ginger et al., 2004). By using DPN to pattern these biomolecules directly, nanoarrays that are 10,000 to 100,000 times denser than typical microarrays can be created (Ginger et al.; Salaita et al., 2007). These extremely dense arrays can screen the same number of targets much faster and with a smaller array area than microarrays, which allows a much smaller sample to be used (Salaita et al.). Alternately, a much larger number of targets can be screened in a shorter period of time (Salaita et al.). Because the minimum area of the nanoarray is smaller, a target can be detected at much lower concentrations (Salaita et al.). One example of the use of nanoarrays is screening for the HIV-1 virus in a serum sample using anti-p24 antibody nanoarrays (Lee, Kim, Mirkin & Wolinsky, 2004).

Another application of DPN relating to biomolecules is DNA patterning. With DPN, DNA can be deposited directly onto a substrate where it can be used to assemble particles that are DNA-functionalized into nanoscale patterns (Ginger et al., 2004). When using indirect patterning methods to write multiple patterns with DNA, multiple steps are required for each pattern. Cross-contamination becomes highly possible (Ginger et al.). This cross-contamination can be avoided by using DPN to directly pattern DNA onto the substrate, allowing for greater accuracy (Ginger et al.). DNA is an excellent medium for forming patterns, and has a huge number of useful variations. While significant time and effort are required to prepare equipment and conditions for the direct patterning of DNA, those conditions can be reused with minimal change for any DNA variation (Ginger et al.). In general, DPN is an extremely useful technique for patterning soft materials because it doesn't damage the substrate by scraping, scratching or pulling it, and it doesn't require that the substrate be exposed to harsh solvents or irradiation (Salaita et al., 2007; Tseng et al., 2005).

While DPN has enormous potential as a tool in fields such as magnetic information storage, micro and nanoscale electronics, and photonics, it does have several limiting factors (Ginger et al., 2004). Firstly, DPN requires complicated, delicate equipment, primarily an atomic force microscope. Also, because it is so important that the AFM tip be sharp and in excellent condition, the life of each tip is short, necessitating frequent replacements (Tseng et al., 2005). Achieving reliable, reproducible results requires DPN being performed in an environment with controlled humidity. Changes in the humidity cause variations in the water meniscus between the tip and substrate, affecting the results (Ginger et al.). To obtain the best results, temperature, and tip-substrate distance also require careful control (Xie et al., 2006). On a positive note, DPN techniques can be learned quickly by any researcher who uses AFM (Ginger et al.), and dedicated DPN equipment is commercially available (NanoInk, 2010).

Overall, when managed properly, DPN is a technique with the potential to revolutionize nanoscience. It constitutes a tool to study the new properties of materials on a nanoscale (Salaita et al., 2007). Applications in a variety of fields exist, including microelectronics, optics, medicine, and biology (Ozin & Arsenault, 2005, Chapter 2; Salaita et al.). The field of DPN is expanding quickly because it is highly accessible, and is being studied by many labs (Ginger et al., 2004). DPN shows potential for many future applications.

REFERENCES

Ginger, D. S., Zhang, H., & Mirkin, C. A. (2004). The evolution of dip-pen nanolithography. *Angewandte Chemie International Edition*, *43*, 30-45. doi:10.1002/anie.200300608

Lee, K.-B., Kim, E.-Y., Mirkin, C. A., & Wolinsky, S. M. (2004). The use of nanoarrays for highly sensitive and selective detection of human immunodeficiency virus type 1 in plasma. *Nano Letters*, *4*, 1869-1872. doi:10.1021/nl049002y

NanoInk (2010). Nanofabrication instruments. Retrieved from http://www.nanoink.net/products-services.html

Ozin, G. A., & Arsenault, A. C. (2005). *Nanochemistry: A chemical approach to nanomaterials*. Cambridge, England: Royal Society of Chemistry.

Piner, R. D., Zhu, J., Xu, F., Hong, S., & Mirkin, C. A. (1999). "Dip-pen" nanolithography. *Science*, *283*, 661-663. doi:10.1126/science.283.5402.661

Salaita, K., Wang, Y., & Mirkin, C. A. (2007). Applications of dip-pen nanolithography. *Nature Nanotechnology*, *2*, 145-155. doi:10.1038/nnano.2007.39

Tseng, A. A., Notargiacomo, A., & Chen, T. P. (2005). Nanofabrication by scanning probe microscope lithography: A review. *Journal of Vacuum Science and Technology B*, *23*, 877-894. doi:10.1116/1.1926293

Xie, X. N., Chung, H. J., Sow, C. H., & Wee, A. T. S. (2006). Nanoscale materials patterning and engineering by atomic force microscopy nanolithography. *Materials Science and Engineering: R: Reports*, *54*(1-2), 1-48. doi:10.1016/j.mser.2006.10.001