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NANOMANUFACTURING TECHNOLOGIES: ADVANCES AND OPPORTUNITIES

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Nanotechnologies have attracted wide interests and evolved rapidly in the past two decades. They are expected to have transformative impacts on the health, environment, energy, and many other aspects of our society. However, their applications so far are severely hindered by the lack of matured and affordable manufacturing technologies to realize systems in large scales where millions of nanoscale elements are assembled to form commercial products. In this paper, we give a brief overview of the current status of different nanomanufacturing technologies, including top-down approaches such as scanning probe lithography, focused beam, soft and nanoimprint lithography, as well as bottom-up approaches such as vapor deposition and dip-pen nanolithography. Those methods were developed for materials such as carbon, silicon, and polymers in various industries. We analyze the future opportunities and challenges of these technologies.

Keywords: nanotechnology; nanomanufacturing

Introduction

Nanotechnology is the understanding and control of matter at dimensions between 1 and 100 nanometers. Materials at these scales usually exhibit unique characteristics and can provide significant technical and economic advancement with novel applications. In the domain of energy, foreseen applications include, solid-state lighting, low-power display, fuel cells, hydrogen storage, battery materials, solar power, catalysis, etc. In the domain of environment, nanotechnologies can revolutionize sensing, remediation, emission reduction, membrane separations, coating, radioactive waste containment, etc. The importance of nanotechnology has been recognized by governments. In the U.S., a national nanotechnology initiative (NNI) that coordinates federal nanoscale research and development activities among different agencies was established in 2001. Since then, more than 8.3 billion dollars has been invested on nanotechnology.

Although promising, most nanotechnology research only focuses on dozens to a few hundred particles or molecules. To realize large-scale devices and commercializable products, massive assembly techniques with high-volume high-rate output are needed. This poses a great challenge to the nanomanufacturing research community. In this paper, we summarize a survey study of current nanomanufacturing techniques.

The review paper authored by Xia et al. (1999) and two recently published books edited by Busnaina (2007) and Tseng (2008), which contain papers from nanomanufacturing researchers around the world, may serve as good initial references for nanomanufacturing techniques, even though these reviews are not exhaustive. In general, nanomanufacturing techniques are classified as either top-down or bottom-up. In the top-down approaches, materials are removed with low volumes and sizes down to the scale of dozens of nanometers. In the bottom-up approaches, materials are assembled under the guidance of nano-scale templates, either physically or chemically. Some of those techniques are inherited and extended from the traditional semiconductor manufacturing techniques, such as nanoimprint lithography and vapor deposition, since semiconductor is one of the major driving forces for nanomanufacturing.

The objective of this paper is to give an overview of various nanofabrication techniques that are relatively well developed and promising for commercialization in the near future. The methods are introduced in such a way that readers can have an overall picture of existing nanofabrication capabilities. More details and variations of these methods can be found in listed references. In the remainder of the paper, top-down and bottom-up approaches are described in Sections 2 and 3 respectively. In Section 4, we discuss the advantages and disadvantages of these methods, as well as the future of nanomanufacturing.

Top-Down Approaches

Most top-down nano-fabrications are for surface patterning. By patterning local surface regions of a solid substrate with nanoscale features, the substrate has the ability to recognize specific nanostructures. For instance, when the substrate is placed in a solution, millions of nanostructures can self-assemble in parallel. Some patterning methods are developed to write nanoscale features, others are to replicate. The well developed patterning methods include scanning probe lithography, focused beam lithography, soft lithography, and nanoimprint lithography.

Scanning probe lithography

The scanning probe lithography (SPL) techniques (Tseng et al., 2005) are mechanical approaches to realize patterning. Typically small (<50nm) tips or probes are used to scan near the surface of a sample. Although scanning probes were originally designed for imaging purposes, they can also be used to perform sophisticated lithography. The tips can be used to alter the structure of materials. Different configurations have been developed, such as scanning tunneling microscope (STM) (Binnig and Rohrer, 1985), atomic force microscope (AFM) (Binnig et al., 1986), and scanning electrochemical microscope (SECM) (Bard et al., 1989). Particularly, STM and AFM lithographies can provide nanometer resolutions and have been widely used.

In STM, a voltage bias is applied between the sharp tip and an electrically conductive surface (typically metals and semiconductors) as illustrated in Fig. 1. The distance between the tip and sample is only a few atomic diameters, and the transport of electrons occurs due to the tunneling effect. Based on the measured tunneling current when scanning through the sample surface, the distance can be determined at the atomic resolution. The STM needs a vacuum environment to ensure the accuracy of measurement. When used for fabrication purpose, by applying a higher voltage, chemical properties of the sample surface can be modified locally. For example, a Si surface can be locally oxidized under an open-air ambient condition with the electric field desorbing hydrogen passivation (Dagata et al., 1990). STM can be used for direct material deposition by which the metal or semiconductor coated tip acts as a miniature emission source in a vacuum environment (Rauscher et al., 1997; Fujita et al., 2003). Selective material removals with STM have also been demonstrated by thermal decomposition at high temperatures (Li et al., 1999), by electrochemical etching under various chemical solutions (Kaneshiro and Okumura, 1997), or even without the presence of chemical solutions by directly drilling holes (Lebreton and Wang, 1998). By applying low-voltage tunneling pulse, single atoms on sample surfaces can be extracted and deposited to different locations (Eigler and Schweizer, 1990; Hla et al., 2003).

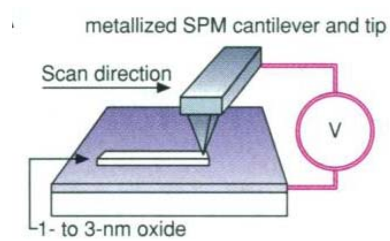

Fig. 1. Scanned Tunneling Microscopy lithography (Dagata, 1995)

The AFM is similar to an STM, except that the tunneling tip is replaced by an atomic scale force sensor known as cantilever to measure the attractive or repulsive forces between the tip and sample. The operation of AFM is less restrictive than that of STM. It can be operated in a room temperature for any kind of materials without the vacuum environment requirement. AFM has a higher scanning speed but a lower resolution than STM. Similar to STM lithography, a voltage can be applied between the non-contact AFM tip and sample so that the sample surface can be patterned by resist exposure (Wilder et al., 1998), local oxidation (Keyser et al., 2000), and material deposition (Lee et al., 2004). By heating up the AFM tip to 170ºC with electrical pulses, the substrate surface can also be modified to achieve thermomechanical writing (Mamin, 1996). The AFM tip can also be employed for mechanical patterning by applying a certain amount of force to ‘scratch’ the substrate surface, including metals, semiconductors, or soft materials (Notargiacomo et al., 1999). Various materials and techniques have been chosen to increase the life time of probes and prevent substrate damage.

The obvious advantage of SPL techniques is high resolution or accuracy. They are capable of creating features at the atomic level. However, they do not provide high-throughput fabrication, even though research has been done to increase the speed by modifying tips and increasing resonance frequencies with piezoelectric elements. It is likely that the SPL techniques are more suitable for rapid tooling to produce masters or masks.

Focused beam lithography

Focused beam lithography is the process of scanning a beam of electrons or ions across the resist surface and generate patterns by selectively exposing and removing the resist. This can be done on a modified electron microscope. In electron beam (e-beam) lithography, a high-energy electron beam is used to form patterned nanostructures in an electron-sensitive resist film such as polymethylmethacrylate (PMMA) with sub-10 nm resolution. For instance, e-beam can be used to build 3~4 nm electrode gaps with properly chosen dose and developing time (Liu et al., 2002). Moreover, high energy e-beam can also be used for material deposition (Mitsuishi et al., 2003; van Dorp et al., 2005).

Focused ion beam (FIB) lithography (Phaneuf, 1999) is another high-resolution patterning method where ion beam is used. It has been used in semiconductor industry mainly for mask repairing, device modification and analysis. Compared to e-beam, FIB has a higher resist exposure sensitivity, and it has negligible ion scattering in the resist and low backscattering in the substrate. Since the momentum of ions is directly transferred to the atoms at the sample surface and sub-surface, high-energy ions tend to damage the sample surface. Therefore FIB can be used as the precise ion milling tool (Tseng, 2004; Cabrini et al., 2005). With the scanned area simultaneously exposed to reactive gas molecules, such as chlorine, FIB can be used for gas-assisted etching (Young et al., 1993; Lee and Kuo, 2008) with higher selectivity and faster rate than sputtering. FIB can also be used for induced material deposition (Sadki et al., 2004).

Soft lithography

Soft lithographies (Xia and Whitesides, 1998; Rogers and Nuzzo, 2005) are techniques to fabricate or replicate structures by stamps, molds, and conformable photomasks made from elastomeric materials, most notably polydimethylsiloxane (PDMS). The earliest soft-lithographic method (Xia and Whitesides, 1998) represents a form of contact printing that uses a high-resolution elastomeric stamp with a chemical ink capable of forming a self-assembled monolayer (SAM) on a target substrate. This monolayer can guide material deposition on or removal from the substrate to yield patterns. The interest lies in its ability to form structures with dimensions deep into the submicron length scales using some ordinary chemical laboratory apparatus without expensive facilities.

In the two-step process, the elastomeric elements are first derived by masters, which have well-defined structures of resist and can be fabricated precisely by techniques such as AFM lithography. Then, the elastomeric elements are used to pattern features. With optimized elastomeric materials, this process can produce relief with nanometer depths and width. Both molecular and solid inks can be used for stamping. In solid case, chemically tailored surfaces with interfacial ‘glue’ and ‘release’ layers help control the transfer of ink from stamps to substrates.

Instead of stamps or molds, recently PDMS elements were used as optical components for patterning structures in photosensitive polymer (Jeon et al., 2004). The PDMS elements function as phase masks, create intensive distributions of ultraviolet (UV) light to cure photopolymer, and help build 3D porous structures.

Nanoimprint lithography

Nanoimprint lithography (NIL) (Sotomayor Torres et al., 2003; Guo, 2004) is able to replicate sub-10 nm patterns with high throughput. Different from the soft lithography, NIL uses a hard mold (e.g. Si, SiO_2, and SiC) that contains nanoscale features to emboss into polymer materials and cast on the substrate under controlled temperature and pressure conditions, which can be further transferred through the resist layer via etching processes. Since its inception, NIL has attracted much attention and been applied in various materials such as organic light-emitting diodes (OLED) (Wang et al., 1999), photonic crystals (Belotti et al., 2006), biological sensors (Hoff et al., 2004; Truskett et al., 2006), and others. Recent research is also on seeking new materials, such as metallic glasses (Kumar et al., 2009), to improve the durability of molds.

Bottom-Up Approaches

In bottom-up approaches, nanoscale structures are synthesized by self-assembly with physical or chemical guidance. Self-assembly is a parallel process in nature. However, it is more difficult to achieve controllable high precision compared to the top-down approaches.

Chemical and physical vapor deposition

Chemical vapor deposition (CVD) (Choy, 2003) is a relatively matured coating process which involves the dissociation and chemical reactions of gaseous reactants in an activated (heat, light, plasma) environment, followed by the formation of a stable solid product. It has been widely used in ceramic and semiconductor industry. A CVD process involves chemical reactions in the gas phase, on the substrate surface, chemisorption and desorption. For nanoscale structures, CVD has been used to grow arrays of carbon nanotubes (Pan et al., 1999; Lee et al., 1999) and ZnO nanowires (Pung et al., 2008) on substrates. Several variants of CVD have been developed, such as electrostatic spray assisted vapor deposition (ESAVD), combustion chemical vapor deposition (CCVD), metalorganic chemical vapor deposition (MOCVD), and aerosol assisted chemical vapor deposition (AACVD), to use more environmentally friendly precursors and facilitate chemical reactions. Recently, it was demonstrated that complex 3D nanostructures can be fabricated by CVD induced by focused ion beams (Matsui et al., 2005).

Physical vapor deposition (PVD) (Mattox, 1998; Singh and Wolfe, 2005) is a variety of surface coating methods in which materials are evaporated by electron beam, ion beam, plasma, or laser. As illustrated in Fig. 2, the evaporant material is vaporized with the supplied energy and solidified on the surface of substrate. Different from CVD, there are no chemical reactions involved in PVD. PVD processes usually require a high vacuum environment, both to allow the vapor to reach the substrate without reacting with other gas-phase atoms in the chamber, and to reduce the impurity of deposited films.

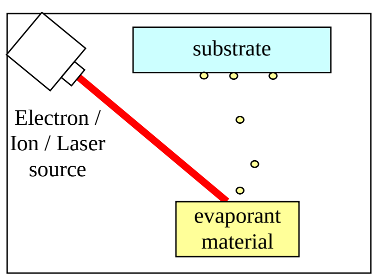

Fig. 2. A schematic diagram of PVD

Dip-pen nanolithography

Dip-pen nanolithography (DPN) is a scanning probe microscopy-based nanofabrication technique that uniquely combines direct-write soft-matter compatibility with the high resolution and registry of AFM (Salaita et al., 2007). It uses an ‘ink’-coated AFM tip to pattern a surface, as illustrated in Fig. 3. Unlike the SPL methods, DPN is a direct-write constructive lithography that allows for printing from scanning probe tips onto a surface with sub-50-nm resolution, and no premodification of the surface through energy delivery (such as ultraviolet, ion- or electron-beam irradiation, and non-polar solvents) is required prior to the material delivery process. It has been applied in building nanoarrays of biological molecules, studying localized surface reactions with enzymes, and creating chemical template for hierarchical assemblies.

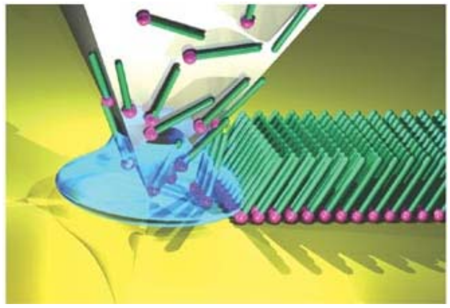

Fig. 3. A schematic diagram of the dip-pen nanolithography (Salaita et al., 2007)

To increase fabrication throughput, up to 55,000 DPN tips aligned in parallel, which can produce sophisticated surface patterns, has been demonstrated (Salaita et al., 2006). Another advantage of DPN is that because it uses an AFM tip to deposit organic molecules, one can take advantage of the high resolution of AFM to generate multiple ink patterns with different materials with good alignment (Hong et al., 1999).

Discussion and Summary

Among the different nanomanufacturing techniques, some have become matured and commercial equipment is available, such as AFM, FIB, CVD, and PVD. The nanotechnologies are being developed at a very rapid pace. It is foreseen that more manufacturing approaches will be commercially available in the coming decade. Particularly, nanoimprint lithography has gained much attention for potential high-throughput production since its inception in mid 1990s. As the extension of current semiconductor fabrication techniques, it can take advantage of existing facilities without significant changes.

Some of the key issues in nanomanufacturing include how to produce and use precursor materials, how to assemble and characterize precursors, how to design and integrate structures into devices and systems, as well as developing the corresponding instrumentation and equipment (Doumanidis, 2002). The major challenge for nanomanufacturing is still the issue of how to fabricate high-precision nanostructures with high-throughput rates. Tradeoffs are usually required for these two conflicting goals. It is obvious that the top-down and bottom-up approaches are both useful and complementary for each other. A combination of the two is required to produce future commercial nanoscale products. Another challenge for nanomanufacturing is how to fabricate 3D structures. Most of the existing techniques concentrate on 2D surface patterning. 3D fabrication techniques will bring much more opportunities of nanotechnology applications.

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