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Nanoscale materials patterning and engineering by atomic force microscopy nanolithography

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Abstract

This review article aims to provide an updated and comprehensive description on the development of atomic force microscopy (AFM) nanolithography for structuring and fabrication at the nanometer scale. The many AFM nanolithographic techniques are classified into two general groups of force-assisted and bias-assisted nanolithography on the basis of their mechanistic and operational principles. Force-assisted AFM nanolithography includes mechanical indentation and plowing, thermomechanical writing, manipulation and dip-pen nanolithography. Bias-assisted AFM nanolithography encompasses probe anodic oxidation, field evaporation, electrochemical deposition and modification, electrical cutting and nicking, electrostatic deformation and electro-hydrodynamic nanofluidic motion, nanoexplosion and shock wave generation, and charge deposition and manipulation. The experimental procedures, pattern formation mechanisms, characteristics, and functionality of nanostructures and nanodevices fabricated by AFM nanolithography are reviewed. The capabilities of AFM nanolithography in patterning a large family of materials ranging from single atoms and molecules to large biological networks are presented. Emphasis is given to AFM nanolithographic techniques such as dip-pen nanolithography, probe anodic oxidation, etc. due to the rapid progress and wide applications of these techniques.

Keywords: Atomic force microscopy; Scanning force microscopy; Nanolithography; Atomic force microscopy nanolithography; Dip-pen nanolithography; Anodic oxidation

1. Introduction

Nanotechnology encompasses many processes that are important in the fabrication of integrated circuits, memory devices, display units, biochips and biosensors. One of the key processes in nanofabrication is the creation and construction of functional units in the size regime of less than 100 nm. Two approaches namely top-down and bottom-up, have been used to categorize the generation of nanostructures. The top-down approach applies various

Abbreviations: AFM, atomic force microscopy; cAFM, conductive atomic force microscopy; CNT, carbon nanotube; 2DEG, two-dimensional electron gas; DPN, dip-pen nanolithography; EDPN, electrochemical dip-pen nanolithography; F–N, Fowler–Nordheim; HMDS, hexamethyldisilazane; *I–V*, current–voltage; MHA, 16-mercaptohexadecanoic acid; NC-AFM, non-contact atomic force microscopy; NTS, 18-nonadecenyltrichlorosilane; ODT, 1-octadecanethiol; OTS, octadecyltrichlorosilane; PEO, polyethyleneoxide; PMMA, polymethyl methacrylate; PS, polystyrene; PVK, polyvinyl carbazole; SAM, self-assembled monolayer; SEM, scanning electron microscope; STM, scanning tunneling microscopy; T_g, glass transition temperature; TMS, trimethylsilyl

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lithographical techniques to create nanoscale patterns from a featureless bulk starting material, while the bottom-up route often uses the interactions of molecules and colloidal particles to assemble two- and three-dimensional structures. The conventional techniques for nanofabrication are based on various lithographical methods in the top-down approach. Typical examples include photolithography [1,2], electron beam lithography [3,4] and focused ion beam lithography [5,6], and are widely implemented in semiconductor manufacturing. However, the applicability of these techniques is often limited by their high capital and operating cost, multiple-step processes, and poor accessibility. Several newly developed methods appear to be flexible alternatives for nanoscale patterning and fabrication, such as nano-imprint lithography [7–9], soft lithography [10], and atomic force microscopy (AFM) nanolithography [11,12]. These novel methods have the potential to be future low-cost techniques for nanoscale pattern formation and replication.

Among these newer techniques, AFM nanolithography has shown itself to be a unique tool for materials structuring and patterning with nanometer precision. AFM was invented in 1986 for use as a microscope to directly image the surface morphology with atomic and molecular resolution [13]. The morphological image of a surface is obtained by recording and regulating the forces felt by a probe as it scans the surface. AFM can be used to study both insulating and conducting materials, and can be operated in liquid, air or vacuum. The working principle of AFM nanolithography is based on the interaction between the probe and substrate. The typical radius of curvature of the probe is 20–60 nm, and the probe–substrate separation in close contact condition is <1 nm. When suitable forces are exerted, and/or external fields applied, the probe can induce various physical and chemical processes on the substrate surface. Consequently, localized nanostructures are generated through physical modifications and/or chemical reactions of the surface materials. AFM nanolithography possesses the versatility to pattern a wide range of materials including metals, semiconductors, polymers and biological molecules in different media. Due to its nanoscale positioning and imaging capability, AFM nanolithography is uniquely able to create site-specific and localized functional structures. Moreover, the morphological and physical properties of patterns formed can be immediately characterized with AFM by integrating additional measurement modules. This combined fabrication and characterization function in AFM nanolithography allows convenient *in situ* and in-line pattern creation and characterization.

Numerous AFM-based lithographic techniques have been developed in the last two decades. Generally, these techniques can be classified into two groups in terms of their operational principles: (i) force-assisted AFM nanolithography; (ii) bias-assisted AFM nanolithography (see Fig. 1). In force-assisted AFM nanolithography, a large force is applied to the tip for pattern fabrication, and the tip–surface interaction is mainly mechanical. Typical methods in this category include mechanical indentation and plowing [14], thermomechanical writing [15], nanomanipulation [16], and dip-pen nanolithography (DPN) [17]. During force-assisted nanolithography, forces larger than those used for AFM imaging are loaded onto the tip. The initially featureless surface is then patterned by mechanically scratching, pulling, or pushing the surface atoms and molecules with the probe. In DPN, instead of manipulating the existing molecules on the surfaces, the tip is used as a nanoscale pen to directly deposit collections of ink materials onto the substrate to define a functional structure. As for bias-assisted AFM nanolithography, the AFM tip is biased to create a localized electric field in the regime of 10^8 V/m to 10^{10} V/m, and the tip acts as a nanoscale electrode for current injection or collection. Under such a high localized field, electrostatic, electrochemical, field emission, dielectric breakdown and explosive gas discharge processes can be initiated to facilitate pattern formation. Depending on the magnitude of tip bias and substrate materials, the application of tip voltage can lead to anodic oxidation [12],

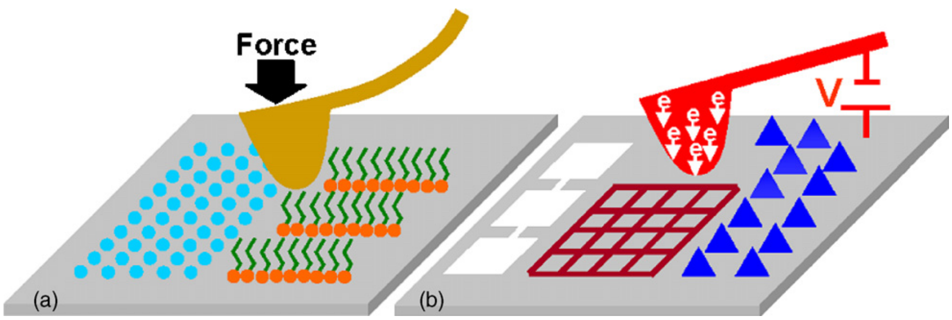

Fig. 1. (a) Force-assisted and (b) bias-assisted AFM nanolithography.