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Viewpoint Paper

Liquid deposition approaches to self-assembled periodic nanomasks

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Abstract—The fabrication of two-dimensional high-aspect-ratio nanostructures is becoming an important area of research for its technological implications, for example in photonics, fluidics and microelectronics. Nanopatterned layers prepared by liquid deposition methods and bottom-up approaches are emerging as good candidates due to the diversity of their structures and the fact that they can be applied to large surfaces. We discuss the recent developments of self-assembled nanomasks and how they can be exploited for efficient pattern transfer on silicon.

Keywords: Nanomask; Etching; Self-assembly; Liquid deposition; Nanopattern

1. Introduction

Surface nanostructuration, or nanopatterning, represents a growing domain in science and technology since miniaturizing objects down to the nanoscale can lead to an exponential increase in device efficiency. The improved performance has raised considerable demand for small-scale structures, pushing the feature size and spatial resolution down to sub-100 nm length scales for applications including nanoelectronics, optics, nanofluidics, sensing, analysis, energy harvesting and storage. Processing of nanopatterned surfaces can be accomplished by "top-down" techniques that consist of creating nanostructures by controlled cutting of supported bulk solids, often achieved by selective local chemical etching through a mask (lithography) or using ultrathin particle single beams (focused ion beam, electron beam lithography). Lithographic techniques offer the possibility of obtaining complex architectures with tight control over pattern regularity. A conventional lithographic process is based on a chemical change to a sensitive resist induced by a laser, particle bombardment (electrons, ions, protons) or X-ray radiation. However, resolution of conventional photolithography is limited by light diffraction through the mask, and single beam techniques face the challenges of high fabrication costs, low throughput and templates lacking durability when the size and periodicity are scaled down. Alternative approaches that allow fabrication of robust, high-resolution lithographic nanomasks over large surfaces are essential for developing technologies compatible with industrial production requirements. A promising alternative is the bottom-up approach that consists of the controlled nanosegregation, assembly of nanobulding blocks (NBBs) or dynamic supramolecular templating to form nanostructured materials over large areas. The NBBs can be either molecules or nano-objects, such as molecular precursors, block copolymer micelles, nanoparticles or clusters, which form a wide range of nano- and mesoscopic structures, with different chemical compositions, shapes and functionalities [1,2]. In order to be self-assembled onto a surface, the NBBs are usually dispersed in solution and then applied to a substrate by liquid deposition. In this category we can include block copolymer self-assembly, micelles and colloidal packing. This strategy allows the simple preparation of large surfaces patterned with sub-100 nm periodical assemblies, overcoming the scale-up and resolution limits of most lithographic methods. Once deposited onto a substrate, those patterns bearing periodic physical and/or chemical heterogeneities can be exploited as nanomasks to transfer the motifs of the pattern to the substrate material. The general concept is illustrated in Figure 1. The fabrication of the self-assembled nanomasks requires the combined control over the chemistry of the initial solution (containing the NBBs) and the associated liquid deposition process. The transfer through the

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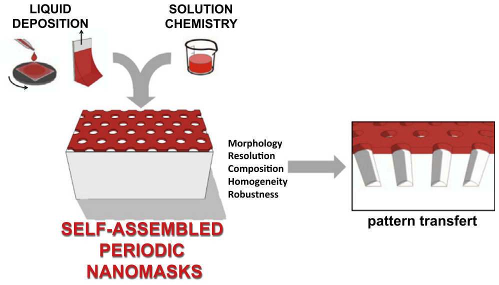

Figure 1. The general strategy to prepare self-assembled nanomasks.

nanomask is done either by dry or wet chemical etching processes. The pattern transfer to a silicon substrate is particularly appealing to both academics and industry since the development of two-dimensional (2-D) periodic arrays of silicon-based nano-objects (pillars, wells, wires) is crucial for the fabrication of highly efficient devices. Precise control over the dimensions, distribution and orientation of the silicon nanostructures is needed since these parameters affect their physical properties considerably. The structural parameters of the device thus depend on the characteristics of the initial nanomask and its faithful replication within the Si substrate. In order to be appealing for industrial production, the ideal nanomask must meet several requirements. (i) The structure of the patterns and their resolution must be controlled in terms of morphology, periodicity and aspect ratio. (ii) The composition of the nanomask should be a robust barrier against aggressive etching processes. (iii) The nanomask preparation method must be simple, fast and homogeneous over a large surface. The effectiveness of a nanomask is thus strongly dependent on the chemistry of the NBBs in solution and on the deposition process. The aim of this article is to provide an overview of the recent trends and perspectives in the development of various periodic self-assembled nanomasks that allow pattern transfer and the fabrication of 2-D silicon periodical nanostructures. The different aspects concerning the liquid deposition techniques and the general methods of nanopatterning by the bottom-up approach are described in Sections 2 and 3, respectively. Some examples of how these patterns are designed and adapted for pattern transfer on silicon are discussed in Section 4. We will not cover the entire body of literature regarding liquid deposition of nanomasks, though we will highlight research that we find especially important, particularly with regards to dip coating.

2. Liquid deposition/the dip-coating technique

The nanomasks are usually applied as thin films to the substrate by liquid deposition processes such as spin coating, dip coating and drop casting. Despite the fact that these techniques are well known and easy to apply, the deposition and eventual self-assembly of the NBBs is a complex multistep mechanism that involves homogeneous wetting of the substrate, evaporation of the volatile species and dynamic evolution of the physico-chemical characteristics (concentration, viscosity, solvent polarity, temperature). The combined effects of all evaporation-governing parameters can be controlled and contribute to the quality of the mask in terms of thickness, nano-ordering and long-range homogeneity. Spin coating is widely used at the laboratory scale in most microfabrication processes and for the deposition of organic layers such as block copolymers. However, the evaporation takes place very quickly and a large amount of the mother solution is lost while spinning the substrate. In contrast, dip coating is a technique that allows a high degree of control during evaporation and can be applied to a large surface without wasting the mother solution. In dip coating, schematically shown in Figure 2 (a), the substrate is dipped into the solution and withdrawn at a constant speed. After evaporation of the solvent, a layer of non-volatile species is obtained above the drying line. This technique is particularly suitable for deposition of sol–gel-based materials [3], and is widely used to deposit biomolecules, polymers or metal nanoparticles [4–7]. In addition, dip coating was recently exploited to prepare block copolymer layers with tailored morphology just by tuning the withdrawal speed without any post-annealing steps [8,9].

The withdrawal speed of the substrate and the evaporation conditions, adjusted by the atmosphere composition and the applied temperature, are the two factors that allow the tuning of the film thickness and quality from a given solution. Figure 2(b) displays the typical log–log evolution of the thickness vs. the withdrawal speed [10]. Two opposite deposition regimes dominate at low and high speeds respectively. These coexist and counterbalance one another at intermediate speeds to create a minimum in thickness. The so-called draining regime, following the Landau–Levich model, applies at speeds above 1 mm s^{-1} for ethanol-based solutions. The same solution can be processed in the capillary regime at speeds below 0.1 mm s^{-1}, where the deposition is governed by the simultaneous capillary rising and evaporation of the solvent at the triple line. The deposition speed and, thus, the final thickness in the capillary regime is directly dependent on the evaporation rate. Increasing the atmospheric temperature induces faster deposition in the capillary regime due to a faster evaporation rate. Capillary deposition can also be used to prepare optical-quality films from aqueous solutions, as water surface tension decreases with increasing temperature [11]. The intermediate regime is thus located between 0.1 and 1 mm s^{-1}, where the minimal thickness is obtained. The dilution of the initial solution leads to a decrease in the final thickness that is roughly similar in both regimes. The high degree of control associated with the dip-coating technique enables the precise

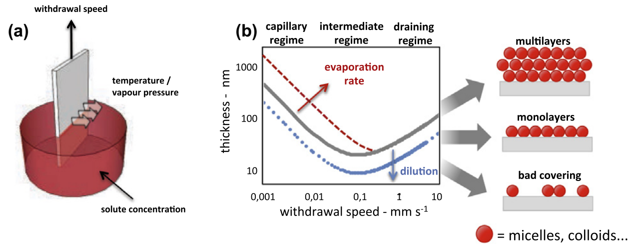

Figure 2. (a) Illustration of the dip-coating process; (b) typical log–log plot of the thickness as a function of the withdrawal speed.