Chapter 15

Low-Cost Patterning of Ceramic Thin Films

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The patterning of ceramic thin films is of great interest for use in MEMS and other applications as discussed in the chapters by Maeda et al. and by Muralt and Baborowski. However, the complex chemistries of certain materials make the use of traditional photolithography techniques prohibitive. In this chapter, a number of low-cost, high throughput techniques for the patterning of ceramic thin films derived from chemical solution precursors, such as sol-gels and ceramic slurries, are presented. Most of these methods are derived from soft lithographic methods using elastomer molds, a method that is categorized as the next generation lithography in the chapter by Alexe et al. Two categories of techniques are discussed: first, the focus is on methods that rely on the principles of confinement within the physical features of the mold to define the pattern on the substrate surface. Then, subtractive patterning techniques that rely on transferring a pattern to a spin-cast large-area continuous thin film are described. Most techniques have been demonstrated with fidelities on the order of 100 nm; however, their inability to precisely register and align the patterns as part of a hierarchical fabrication scheme has hindered their commercial implementation thus far. This chapter has been updated from the original manuscript [1] to reflect the most recent available literature and complements the chapter by Baborowski on pattern formation by micromachining techniques.
1. Introduction

The advent of the electronic age has been the primary driving force for the development of thin film technologies for semiconductor applications, including techniques for the definition of submicrometer-scale patterns. A typical microfabrication process utilizes photolithography with photo-curable polymers to define patterns that are transferred to thin films of metal and semiconductor materials comprising the integrated circuit (IC) by wet or dry chemical etching. Many of these techniques have been transferred to materials with specialized properties for new engineering applications, such as microelectromechanical systems (MEMS) capable of sensing, actuation, information processing, optical waveguides, surface acoustic wave devices, and holographic memories. For example, Ozawa and Yao demonstrated the use of a photolithography lift-off process to pattern TiO$_2$ thin films with line widths as small as 1 µm. Similarly, Nashimoto et al. fabricated 5 µm wide (Pb,La)(Zr,Ti)O$_3$ waveguides by using wet chemical etching with HCl prior to heat treatment.

Unfortunately, the utility of applying conventional photolithography techniques to ceramics in general can be limited by the chemistry of the material. For instance, the integration of ferroelectric materials, such as lead zirconate titanate (PbZr$_x$Ti$_{1-x}$O$_3$, PZT), in electronic devices such as capacitors, transducers, pyroelectric devices, thermistors, and dielectrics is a field attracting considerable attention. However, traditional subtractive patterning steps are of limited utility to materials such as PZT because many of the solvents and acids used to etch silicon, such as HF, are not compatible with PZT. Instead, Reactive Ion Etching (RIE) must be used which is very costly due to the requirements of specialized equipment with controlled environments and waste control systems to minimize lead contamination.

During the past decade, a number of alternative techniques to traditional photolithography for patterning a variety of materials have been developed. The motivation for this work stems from four reasons: (1) lower cost and ease of use than the capital intensive equipment required for photolithography, (2) the ability to apply patterning techniques to new materials, (3) the potential to pattern large areas simultaneously, and (4) the ability to pattern on nanometer length scales that are not yet commercially produced by lithography. This chapter focuses on techniques developed to address the first three motivations. Specifically, we highlight the development of patterning methodologies on the submicrometer length scale that can be applied to a wide range of ceramic thin film materials. Patterning on smaller nanometer length scales is not our specific goal due to the propensity for many ferroelectric materials to lose particular properties that make them of interest for MEMS and other applications in the first place. For example, lead titanate may lose its piezoelectric properties in grains smaller than 20 nm although results contrary to this have also been reported.

Consistent with the objective of low cost processes, the discussion will be limited to methods that do not require large expenditures of capital equipment beyond what would be found in a basic microfabrication laboratory equipped for photolithography. As a result, our focus will be on materials that can be deposited and patterned using liquid precursors, such as sol-gels or colloidal suspensions. We will also further restrict our discussion by neglecting serial patterning techniques, such as ink-jet...