Atomic force microscope based nanofabrication of master pattern molds for use in soft lithography

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The authors have developed a technique that couples nanolithographic patterning using an atomic force microscope with the parallel patterning abilities of soft lithography. Master pattern generation is accomplished using local anodic oxidation as a mask pattern for anisotropic wet etching of Si(110). The resulting nanostructures are then used as master patterns for the molding of polymeric stamps to be used for microcontact printing of alkanethiols. Analysis of the resulting patterns demonstrates the validity of this method as a simple, effective, and low cost alternative to conduct and prototype nanoscale patterning in a parallel fashion. © 2007 American Institute of Physics

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Nanoscale patterning has emerged as an important research area due to its direct impact in areas of nanotechnology with applications in biosensing, immunological detection assay generation, and DNA templating. Soft lithography is a useful research prototyping technique to pattern organic and biological molecules on surfaces at the nanoscale. In soft lithography, polymeric materials are cast against rigid master patterns with relief structures on the order of 30 nm–500 μm. The initial development of soft lithography focused on a technique, now termed microcontact printing (μCP), in which a polydimethylsiloxane (PDMS) stamp with micron-scale protrusions was linked with an alkanethiol and used to pattern self-assembled monolayers (SAMs) on gold. Typically photolithography or e-beam lithography is employed to generate master patterns. We outline a technique through which master patterns for soft lithography are generated using atomic force microscope (AFM) based patterning followed by wet chemical etching to form high aspect ratio nanostructures that are then used as molds for the formation of polymeric stamps to pattern nanoscale alkanethiol SAMs on gold using μCP.

AFM based anodization nanolithography is a patterning technique in which a voltage bias between a conducting AFM tip and sample in the presence of a water meniscus generates a localized oxide layer. Current research focuses on determining the very nature through which this process occurs, including modeling and predicting the resulting oxide aspect ratio due to experimental parameters such as voltage, humidity, tip dwell time, and gaseous ambient environment. The result of such investigations demonstrates that anodization nanolithography on Si substrates can be used to control oxide features with spacing and width typically in the 10–150 nm range, which is attractive for nanoscale patterning. The feasibility of using dip-pen nanolithography to generate master patterns for soft lithography has been mentioned previously; however, the effectiveness and execution of such a method have yet to be demonstrated.

Thorough research on the anisotropic etching characteristics of Si(110) exists in the literature using wet chemical etching schemes of strong alkaline bases such as potassium hydroxide (KOH). This characteristic has been combined with AFM based anodization nanolithography to create nanostructures 50 nm wide and 300 nm tall. The crystal lattice structure of Si(110) enables the formation of high aspect ratio nanostructures, with etch rate selectivity S between {110} and {111} as high as 650:1. If the oxide mask is oriented along the [112] direction, KOH etching results in nanostructures with horizontal top planar (110) faces and vertical (111) sidewalls.

Substrates used in the experiments were cleaved from a 3 in. n-type phosphorous doped Si(110) wafer with a resistivity of 5–10 Ω·cm (Montco Silicon Technologies). The samples were cleaned in a solution of 70% H2SO4 and 30% H2O2 at 80 °C for 10 min to remove contamination. Samples were then dipped in buffered oxide etch (estimated to be 40% NH4F, 5% HF, and 55% H2O) for 30 s to remove the native oxide. The AFM cantilevers used are Si3N4 cantilevers that have a nominal force constant of 0.58 N/m (Veeco Metrology) and are tipside coated with 30 nm of evaporated Ti at 2 Å/s. In this work, anodization nanolithography is conducted in contact-mode AFM (CM-AFM) at 5 nN force setpoint using a custom AFM in a humidity controlled environment [5%–90% relative humidity (RH)]. Image measurements were made using IMAGEJ (NIH).

Figure 1 outlines the observed effects that humidity has on oxide linewidth and measured current during AFM based anodization nanolithography at 9 V tip-sample bias and...
0.5 μm/s translational velocity. The figure indicates that humidity regulation can be used to control resulting oxide linewidth as features vary from 91 to 175 nm over changes in relative humidity from 10% to 75%. Faradaic current is also monitored (6485 picoammeter, Keithley Instruments) and can be used as a means for quality control during lithography.11,12 Each data point for current and linewidth [full width at half maximum (FWHM)] is the average over the length of a 2 μm oxide line. Linear data trends are displayed to guide the eyes.

A minimum oxide mask thickness of 0.4–0.7 nm has been shown to be effective for anisotropic Si etching.13 Master pattern generation using anodization nanolithography was conducted at 10 V bias (oxide height ~2 nm), 0.5 μm/s, and 30% RH; these parameters were chosen as they are typical deposition parameters used for CM-AFM anodization nanolithography. Two mask patterns were generated that have lines spaced 500 and 350 nm, center to center, that are oriented in the [112] direction. After oxide mask deposition the samples were immersed in 40 wt % aqueous KOH at 45 °C for 30 s under ultrasonic agitation. Ultrasonic agitation during etching in KOH lowers roughness on the micron and millimeter scales.14 We have observed roughness on the order of 5 nm over 40×40 μm² with this method measured using AFM. Under these conditions, the etch rate of 44 wt % KOH on an unobstructed Si(110) surface is estimated to be 3.8 nm/s which yields an expected feature height of 113 nm.15 The two oxide mask patterns cover an area of 5 ×15 μm². To deposit the oxide mask over a larger area, counteract tip wear issues, or minimize oxide linewidth faster scan speeds (up to 0.13–0.5 mm/s for CM-AFM), alternative AFM modes of operation (intermittent contact-mode AFM) and high performance tips (carbon nanotube terminated) can be employed.16,17 Figure 2 depicts scanning electron microscope (SEM) images of the resulting nanostructures and AFM measurement yields an average feature height of 120 nm, which agrees well with predicted values. The prescribed pitches of 350 and 500 nm and resulting pitches of 356 and 503 nm (50 measurements, σ=5 nm) agree well and amount to a lateral pitch error of 1.7% for the 350 nm master and of 0.6% for the 500 nm master.

Commonly used PDMS material (Sylgard 184) for soft lithography applications is incapable of reliably patterning features below 1 μm primarily due to the low modulus of the cured PDMS (1–3 MPa depending on preparation).18 h-PDMS (~9 MPa) was developed to solve stability issues and composite stamps help alleviate the tendency towards stamp cracking.19 The master patterns of Fig. 2 form stamps with feature aspect ratios of 0.4 (500 nm master) and 0.6 (350 nm master), which are ideal for stamp stability during μCP.8

h-PDMS stamps were molded to the master patterns of Fig. 2 following procedures outlined in the literature.20 Au samples were prepared by coating a Si(100) wafer with 3 nm of Cr followed by 22 nm of Au. The stamp was used for μCP of 1 mM octadecanethiol (ODT) onto the Au substrates (30 s). Figure 3 depicts SEM images of ODT SAM patterns formed using h-PDMS stamps cast against the master patterns of Fig. 2. SEM imaging has been shown to be a viable method for imaging alkanethiolate SAMs on gold.21 Patternning was executed on a number of repeated printing attempts with no discernible degradation in pattern quality. Measurements were taken on the two printed SAM patterns shown in Fig. 3. Each measurement of width (black contrast, 109±18 nm for the 500 nm pattern and 96±12 nm for the 350 nm pattern), spacing (white contrast, 375±11 nm for the 500 nm pattern and 237±10 nm for the 350 nm pattern), and pitch (485±11 nm for the 500 nm pattern and 335±9 nm for the 350 nm pattern) is the result of 50 random measurements. There exists a noticeable 18 and 21 nm of pitch loss of the pattern (stamp) compared to the master.
For h-PDMS, the thermal expansion coefficient is reported as 0.450 nm/μm °C. The h-PDMS was cured at 80 °C, 56 °C above room temperature, and corresponds to an expected pitch contraction of 13 nm for the 500 nm stamp and of 9 nm for the 350 nm stamp. There also exists a measured decrease in feature width and corresponding increase in feature spacing noticed in both the 350 and 500 nm patterns. This is directly due to alkanethiol spreading during growth SEM. The depth of the relief structures is assumed to mirror the measured height as the SEM contrast outside the patterned area is identical to that between the raised features. Measurement analysis performed in Fig. 4 demonstrates good agreement between the planned and measured pitch (maximum difference of 3 nm) and highlights a minimum feature spacing of 25±3 nm. Below this spacing level it was found that the etch depth was uneven across the length and could indicate a critical limit for nanofabrication in this manner. Recent work focusing on decreasing the minimum feature dimensions of h-PDMS stamps molded to rigid master patterns demonstrated the generation of 40 nm feature widths with an aspect ratio (h/w) of 1.5. The authors hypothesize that smaller feature stamps could possibly be created using their designed methods as they were hindered by the inability to obtain master patterns with smaller feature sizes.

We have developed a method by which master patterns created using AFM based anodization nanolithography and wet chemical etching are used for soft lithographic patterning via μCP. We demonstrate that master patterns with pitches of 500 and 350 nm are used to form h-PDMS stamps that are subsequently used in μCP of alkanethiol SAMs down to feature dimensions of 96 nm. The fabrication of master pattern relief structures spaced 25 nm is highlighted, which is below the demonstrated limit for the critical dimension of polymeric stamp formation for soft lithography (40 nm). Master patterns generated using AFM based anodization nanolithography followed by wet chemical etching can aid in the exploration of the resolution limitations of stamp formation and patterning using soft lithographic techniques. This method provides for a simple, fast, cost-effective, and accessible alternative for master fabrication for soft lithographic stamp molding compared to more common methods such as electron beam lithography, ion beam milling, and photolithography. Due to the fast and simple generation of these master patterns, prototyping of new materials and processes concerning polymeric stamp formation for soft lithography can easily be investigated. The fabrication of such master patterns covering larger areas will be facilitated as parallel cantilever arrays become more commonplace in the research environment.

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