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Nanopatterning from the Gas Phase: High Resolution Soft Lithographic Patterning of Organosilane Thin Films

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A general methodology for nanopatterning organosilane thin films directly from vapor phase precursors is presented. Aminosilane line patterns with a width of ~200 nm in an area of 1 cm^2 were fabricated on silicon substrates by diffusion of aminosilane vapor through the open channels of PDMS stamps bonded to a substrate. The patterned thin films were characterized by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Patterns were initially formed at the three-phase boundary lines between substrate, PDMS mold, and vapor by exploiting the fact that vapors condense preferentially in geometrically restricted areas with a concave shape compared to flat surfaces. The lateral resolution of the formed patterns is about 1 order of magnitude smaller than the feature sizes of the PDMS stamp. Prolonged exposure to the precursor vapor resulted in micrometer-sized patterns with similar features and dimensions as the stamp. This methodology provides an easy and low cost parallel fabrication route of functional organosilane nanoscale patterns of arbitrary shape and composition from micrometer-size patterned stamps.

Introduction

Patterned self-assembled monolayers (SAMs) or thin films of organosilane molecules can be used to modify the surface chemical properties at specific locations.[1] For example, patterned SAMs and multilayer films can provide hydrophilicity, hydrophobicity, or a desired chemical functionality on specific locations on the substrate during device fabrication.[1] They have also been employed in nanofabrication technology as etch resist[2] and as templates for electroless deposition[3] and site selective immobilization of different materials such as nanoparticles,[4] polymers,[4] and biomolecules.[5] Patterned organosilane SAMs or thin films can therefore be used for nanofabrication of electronics, data storage devices, MEMS, and biological sensors. The very small size and the chemical stability of the organosilane molecules enable them as a very powerful material for high resolution nanopatterning.[1]

Electron beam lithography,[2,6,7] focused ion beam lithography,[7] photolithography,[8] scanning probe lithographic methods,[9,10] microcontact printing,[11] and nanoimprint lithography[4] are the most widely used serial and parallel patterning methods for organosilane thin films and SAMs. Serial techniques based on electron and ion beams can be used for high resolution nanopatterning either by using a polymer resist or directly modifying/destroying the SAM or thin film upon irradiation. The processing times are relatively long, and the cost of fabrication and maintenance are considerable.[12] Photolithography gives good results in standard clean room fabrication processes and yields resolutions up to the diffraction limit of the wavelength of light used for patterning the photoresists.[12] Scanning probe lithography can also be used for patterning up to sub-10 nm resolution. The processing time for scanning probe pattern generation is high compared to parallel methods. Microcontact printing (μCP) using a soft poly(dimethylsiloxane) (PDMS) stamp is a versatile approach due to its parallel nature, speed, and low cost to generate massively patterned substrates. However, the resolution of μCP is limited due to the noticeable effect of diffusion of ink on the substrate at higher resolutions.[11] Nanoimprint lithography (NIL) is a successful tool for patterning nanoscale patterning of SAMs. NIL is a fast parallel patterning method. It does require elevated pressures and temperatures during the processing, and a residual layer is present after the imprint has been made.[4]

Here we propose a new single step method to pattern organosilane molecules on silicon substrates directly from the vapor phase using a PDMS stamp as template. The approach belongs to the family of soft-lithography techniques, since it makes use of a polymeric mold in conformal contact with a substrate for replicating the features of a master structure.[13] Our technique enables the effective fabrication of organosilane patterns on large surface areas. The patterns have a high resolution, down to 200 nm, and a high packing density. A special feature of our methodology is that the resolution of the formed patterns is about 1 order of magnitude higher than the features of the

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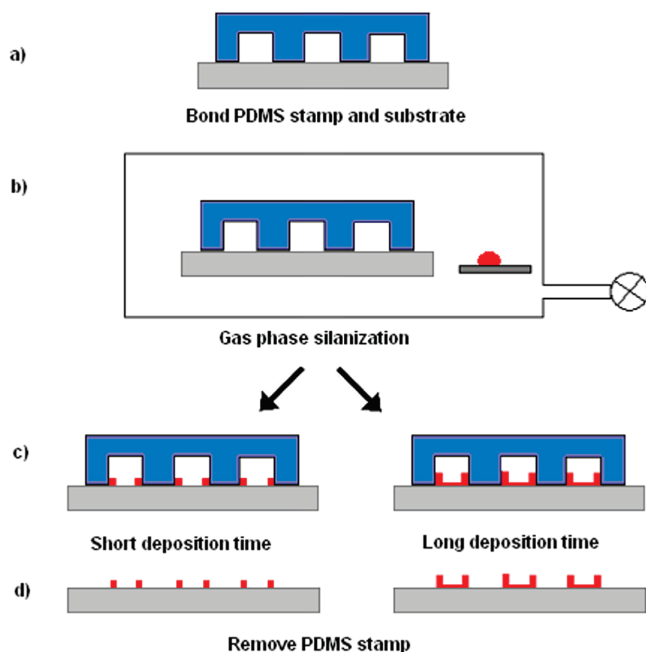

Figure 1. Procedure of direct gas phase patterning of organosilane thin films using a PDMS stamp template. (a) Reversible bonding of PDMS stamp to substrate. (b) Deposition of organosilane in desiccator. (c) Removal of substrate and stamp from desiccator after exposure. (d) Removal of stamp from substrate.

PDMS stamp with which the pattern is generated. The reason is that precursor deposition takes place primarily in areas that are very near to the triple phase contact lines between the substrate, PDMS mold, and organosilane vapor, that is, in those areas that have a sharp concave shape. The schematic diagram of the patterning process is shown in Figure 1. A patterned PDMS stamp is pressed against a pretreated silicon substrate. A connected channel structure is formed between the stamp and substrate, with openings to the ambient on the vertical sides of the stamp. The open channel pattern is then exposed to an organosilane saturated environment in an evacuated desiccator. The silane molecules diffuse into the channels via the openings and react with the exposed regions of the substrate. The regions in conformal contact with the PDMS stamp are protected from the organosilane molecules. Depending on the time of exposure to vapor, two different modes of pattern generation are possible with this technique. When the substrate is exposed to vapor for a limited period of time, patterns are formed only in the regions where the edges of the protruding regions of the PDMS stamp are in contact. When the substrate is exposed for a longer period of time, the flat areas of the substrate are also covered by reactive organosilane molecules.

Experimental Section

Preparation of PDMS Stamps. PDMS and curing agent (Sylgard 184) were purchased from Dow Corning Corporation and mixed in a ratio 8:1 and poured over the micro/nanopatterned silicon master (created by photolithography or e-beam lithography). The PDMS was cured at a temperature of 70 °C for 48 h. After curing, the PDMS stamps were removed from the master and cut into pieces of desired size and stored in absolute ethanol for 15 days before use. Every 5 days, the PDMS stamps were taken out of the ethanol, washed with ethanol, and stored again in fresh ethanol. This treatment reduced the amount of unreacted PDMS oligomers in the stamp which might otherwise contaminate the substrate during the patterning process. After this treatment, the PDMS stamps were dried at 90 °C for 3 h to remove any trace of ethanol prior to use.

Preparation of Silicon Substrates. P-Type silicon substrates cleaned with piranha solution (a mixture of H_2O_2 and H_2SO_4 in 1:3 volume ratio) were used in the experiments. The substrates were then washed several times with deionized water and stored in deionized water. Prior to use, the substrates were blow-dried in a nitrogen stream.

Fabrication of Organosilane Patterns. (3-Aminopropyl)-triethoxysilane (APTES, 98% pure) was purchased from Sigma Aldrich and used in the experiments as received. The dried PDMS stamps with micro/nanopatterned features were gently pressed against silicon substrates facing the patterned side of the stamp against the polished side of the silicon substrate. The PDMS stamp made conformal contact with the substrate via attractive van der Waals forces. Substrates with a bonded PDMS stamp were transferred to a desiccator. A drop of aminosilane precursor was placed in the desiccator. After evacuation of the atmosphere by a mechanical pump to 100 mbar, the desiccator was closed and an organosilane vapor-saturated environment formed inside it. The substrates were exposed to the organosilane environment for a time period of 3−12 h. The substrates were taken out from the desiccator and washed with absolute ethanol followed by deionized water and then stored for further analysis.

Characterization. The patterned organosilane thin films were characterized using atomic force microscopy (AFM, Dimension D3100 Nanoscope IVa controller, Veeco Instruments) for surface morphology and X-ray photoelectron spectroscopy (XPS, Quanta SXM scanning electron microprobe, Physical Electronics) for surface chemical information.

Results and Discussion

Figures 2 and 3 show tapping mode AFM height and phase images of patterned aminosilanes on silicon wafers after deposition for 3 and 12 h, respectively. The PDMS stamp used for patterning the organosilane lines in Figure 2 has a line width of 1 μm and a spacing of 1.3 μm in an area of 1 cm^2. The width of organosilane line patterns is approximately 200 nm and the height is ∼7 nm. The phase image indicates that the areas in between the aminosilane lines did not contain noticeable amounts of aminosilane. The organosilane molecules entered the PDMS channels through the openings located on the side walls of the stamp. The effective diameter d of APTES is smaller than 0.8 nm, and the vapor pressure at 293 K is 2 Pa.[14] With a background pressure $p \sim$ 10 kPa inside the desiccator, the mean free path $\lambda = k_BT/(\sqrt{2}\pi d^2 p)$ (k_B is the Boltzmann constant, and T is the temperature) of APTES in the gas phase is of the order of 200 nm. This is almost 1 order of magnitude smaller than the dimensions of the channels. Therefore, the predominant mechanism of gas transport inside the channels is bulk diffusion. The molecules then deposited on the substrates, forming covalent bonds with the OH terminated silicon surface. Upon exposure to ambient air, the alkoxy-functional organosilane molecules react with water vapor by sol−gel hydrolysis and condensation into a polymerized network. Interestingly, the AFM data clearly show that patterns are generated that have much smaller dimensions than the original PDMS stamp template.

Figure 3 shows micropatterns of condensed γ-aminopropyl silane after deposition for 12 h. The PDMS stamps shown had a line width and spacing of approximately 4 μm in an area of 1 cm^2. The thick lines at the edges of the line confirm that the molecules

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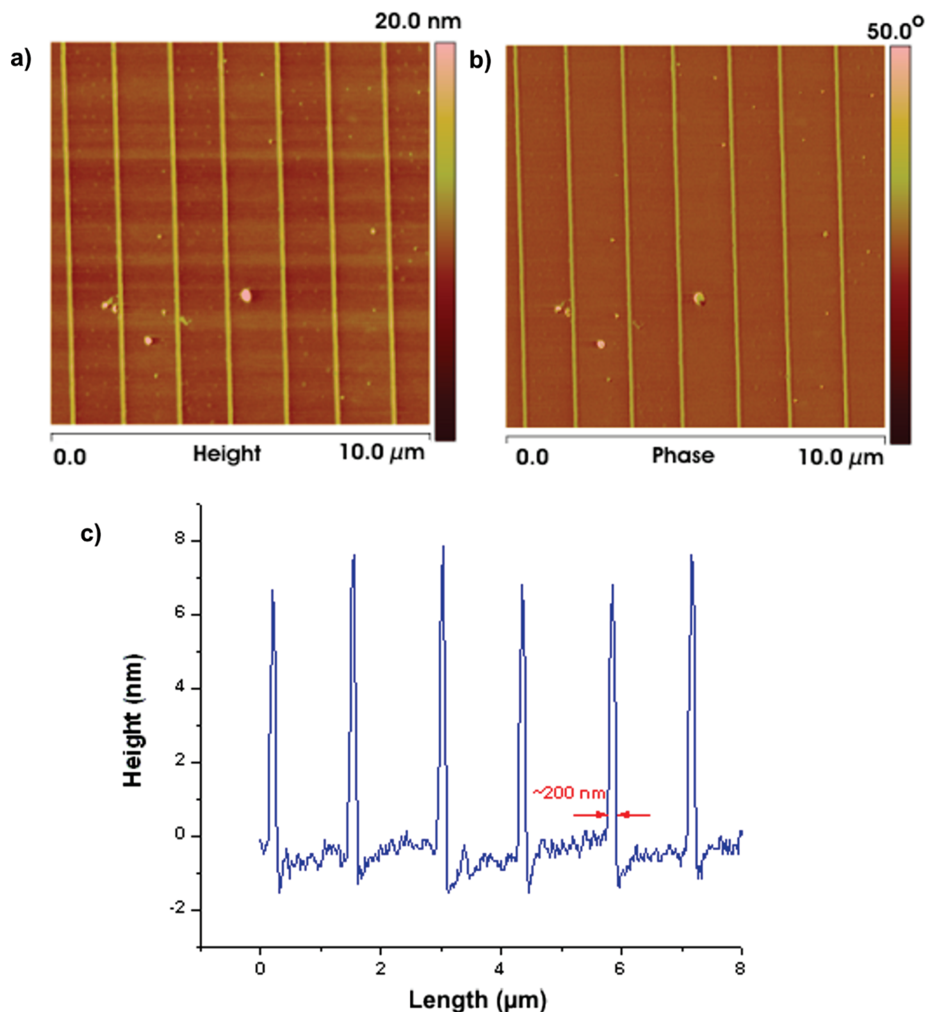

Figure 2. γ-Aminopropylsilane based thin line patterns formed after a deposition time of 3 h. (a) AFM height image; (b) AFM phase image; and (c) distance−height line scan in a direction perpendicular to the line pattern.

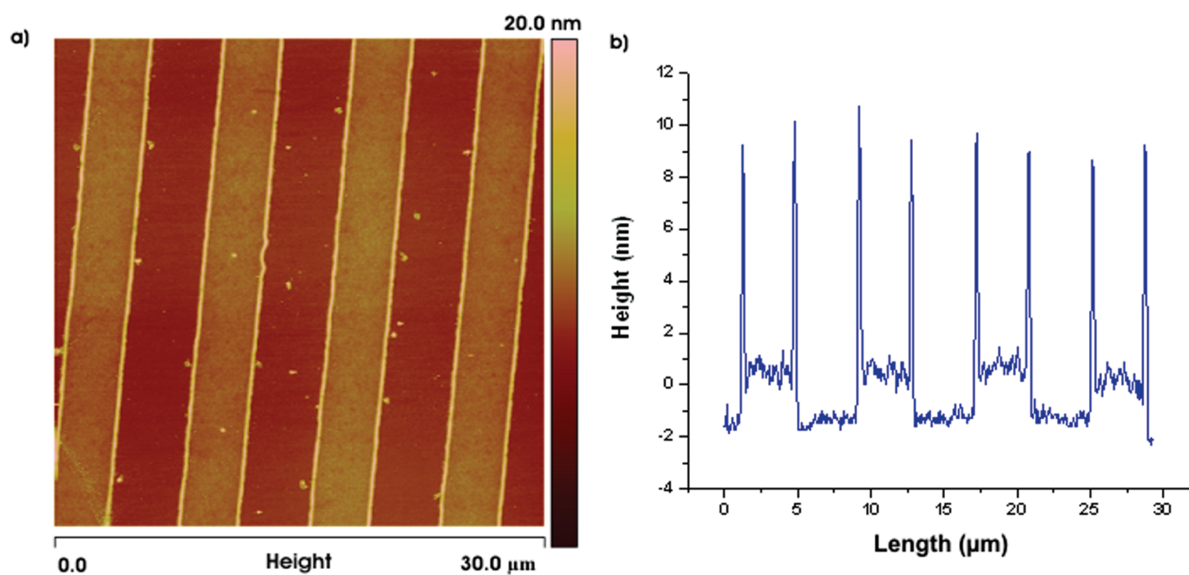

Figure 3. γ-Aminopropylsilane based line patterns formed after a deposition time of 12 h. (a) AFM height image and (b) distance−height line scan in a direction perpendicular to the line pattern.

deposited first at the PDMS−silicon−air triple phase boundary lines and then deposited in the region between the edges. The AFM height−distance plot shows that the thickness of the aminosilane thin film is approximately 3 nm in the central regions, with well-defined thicker edges of approximately 10 nm height and 200 nm width. The method bears some resemblance to the gas

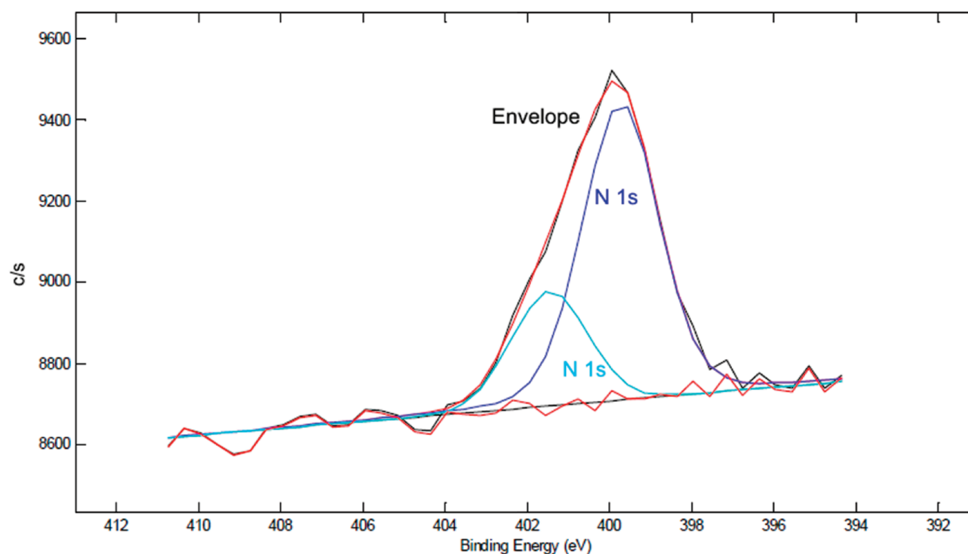

Figure 4. XPS N 1s spectrum of patterned γ-aminopropylsilane based lines from Figure 2. Peaks at 399.7 and 401.5 eV represent $-NH_2$ and $-NH_3^+$ groups, respectively.

transfer lithography process proposed by De la Rica et al.,[15] because it uses PDMS molds and gaseous aminosilanes as precursors, but there are some essential differences with our technology. It also bears resemblance to the solvent-assisted soft lithography method introduced recently by Shi et al.,[16] but our method uses gaseous precursors instead of liquid sols.

XPS experiments were done to validate the chemical identity of the patterns and confirm the presence of an aminosilane line structure. Figure 4 shows the XPS N 1s spectrum obtained on the thin line patterns of Figure 2. The data indicate a notable presence of nitrogen from the end functional groups of the condensed aminosilane molecules on the substrate. This confirms the deposition of an aminosilane network on the substrate and rules out the possibility that the lines are composed of PDMS oligomers that somehow segregated from the stamp. The asymmetry of the N 1s peak suggests that more than one type of nitrogen was present. The peak could be deconvoluted into two Gaussians, with peak positions at 399.7 and 401.5 eV. Most likely, these correspond to the amine end group ($-NH_2$) and the protonated amine end group (NH_3^+) of the patterned aminosilane thin film, respectively.

The AFM images in Figures 2 and 3 confirmed two modes of pattern generation, depending on the time of exposure of the substrate to the organosilane vapor. Short exposure led to pattern formation along lines where the silicon substrate was in contact with the edges of the protruding regions of the stamp. Upon increasing the exposure time, the molecules also condensed and assembled in the regions between the edges and filled all unmasked areas of the substrate surface. This means that the aminosilane molecules condense first along edges rather than homogeneously over the entire OH terminated silicon substrate. Although the process is not understood in microscopic detail, this type of preferential wetting is generally interpreted in terms of increased van der Waals interaction of vapors due to size confinement.[17] The edges of the protruding PDMS features in contact with the silicon substrate form very sharp concave corners. This geometry promotes the initial condensation of organosilanes compared to deposition on flat areas. Upon prolonged exposure, the organosilanes eventually also condense on flat surfaces, resulting in micrometer-sized organosilane patterns with a thickness of 10 nm.

Conclusions

In conclusion, we have presented a novel gas phase patterning technique using PDMS templates as a reliable method for nanopatterning organosilane thin films. Some aspects of this gas phase patterning procedure may make it more suitable for organosilane nanopatterning than soft lithographic techniques based on printing liquid precursors. The methodology does not depend on the application of a controlled pressure on the mold, so that stamp deformation is limited, and contact times are less critical. Second, gas phase deposition of organosilanes prevents aggregation of reactants prior to deposition and results in regular patterns of controlled thickness. The process had high fidelity, and high quality patterns were obtained over large surface areas. Further experiments to make materials using other organic and inorganic precursors are under way.

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