Nanopatterning Using the Smectic Phase of Rod-Like Polymers as a Template

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Nanopatterning is the process of fabricating nanostructures across the surface of a substrate. It can be fabricated utilizing the layer-like pattern of smectic phase formed by a rod-like polymer polysilane mixed with a spherical particle, tetraalkylsilane. The polymer mixture exhibits stable liquid crystal properties, specifically a smectic phase with layered molecular arrangements. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) are used to analyze the resulting nanostructures. Fourier transform analysis of the AFM images indicate a periodic spacing of 39.3 nm before dry etching and 41.3 nm after dry etching, suggesting a minor expansion of the smectic layers caused by the plasma etching process. The observed shift in periodicity and the decrease in image clarity after etching can be attributed to slight distortions in the layered structure. Despite these changes, the overall layer-like arrangement of the smectic phase is maintained, confirming the polymer mixture's ability to form a robust smectic phase that remains stable even after dry etching. This demonstrates the effectiveness of using rod-like polymers for creating detailed nanoscale patterns.
Key words: Nanopatterning, Smectic phase, Polymers, AFM, SEM

1. INTRODUCTION

Polymers are large molecules made up of repeating subunits (monomers) which are connected to a chain by covalent bonds. This process is called polymerization. Commonly, polymers possess high molecular weights and flexibility [1].

In everyday life, four states of matter are observable: solid, liquid, gas and plasma. In addition to these states of matter some materials exhibit additional states of matter under specific conditions [2]. One of these materials are liquid crystals. Liquid crystals are substances that exhibit properties of liquids and crystalline solids. They are able to flow like liquids, but still maintain some degree of molecular order and orientation like crystals do. Typically, they are rod-shaped molecules (disc shaped are also observed [3]) which can align in various ordered arrangements, but still are able to move and flow [4].

Liquid Crystals with rod-shaped molecules exhibit additional phases – among them the smectic phase – in which their anisotropic molecules show a high degree of order. This results in different phase-dependent physical properties [5]. In the smectic phase, the molecules of the liquid crystal are arranged in layers with positional and orientational order. Typically, this can be observed if the temperature is below the temperature during which they form the so-called nematic phase [6].

A Polymer which exhibits such liquids crystal phases is polysilane. Its organic structure has a silicon backbone (main chain) i.e. it consists of repeating units of silicon atoms. These atoms are bonded to organic side chains with organic substituents [7]. Its molecules have a rod-like shape (calamitic molecules) and thus, polysilane can form the liquid crystal phases. Additionally, the polysilane used in this study has a narrow molecular weight distribution (Mw/Mn = 1.17) and a high molecular weight (Mw = 125,600).

Nanopatterning is the process of fabricating nanostructures across the surface of a substrate [8]. It is expected when using a stripe-like phase-separation structure formed by a mixture of a rod-like polymer (polysilane) and a small compound (tetraalkylsilane) that can be regarded as spherical [9]. The depletion effect, an entropic interaction, plays a key role in forming this structure by segregating and selectively storing the spherical particles between the layers of the smectic phase formed by the rod-like particles, thereby stabilizing the layered structure [10].

This structure can be observed using atomic force microscopy (AFM) and scanning electron microscopy (SEM). AFM is a technique used to analyze micro/nanostructured coatings, offering high-resolution imaging and the ability to study surface properties in various environments for obtaining topography and properties of coatings [11]. SEM is a technique that uses an electron beam to examine a material's surface, where interactions between the beam and the specimen generate signals that form an image, with backscattered electrons providing compositional and topographic information [12].

Here a mixture of a rod-like polymer (polysilane) and a small compound (tetraalkylsilane) is used for nanopatterning. The goal is to create detailed nanostructures of the layer-like arrangement of the smectic phase, with these patterns examined through AFM and SEM.

2. MATERIALS

A chloroform solution (1.5 mg/mL) of a mixed sample of a rod-like polymer Polysilane (Mw = 125,600, Mw/Mn =1.17) and a small compound, tetraalkylsilane (20wt%), which can be regarded as spherical, is used to perform nanopatterning. The chloroform solution thereby serves as solvent to dissolve the two particles. The substrates are 10x10 mm silicon wafers and to perform a process called dry etching (see: 3. Methods) methane tetrafluoride (CF4) is used.

3. METHODS

Figure 1 shows a flow-chart of the experimental process, detailing the sequence of procedures performed during the experiment. Figure 2 shows a molecular representation of the nanopatterning process happening during the different steps of figure 1.

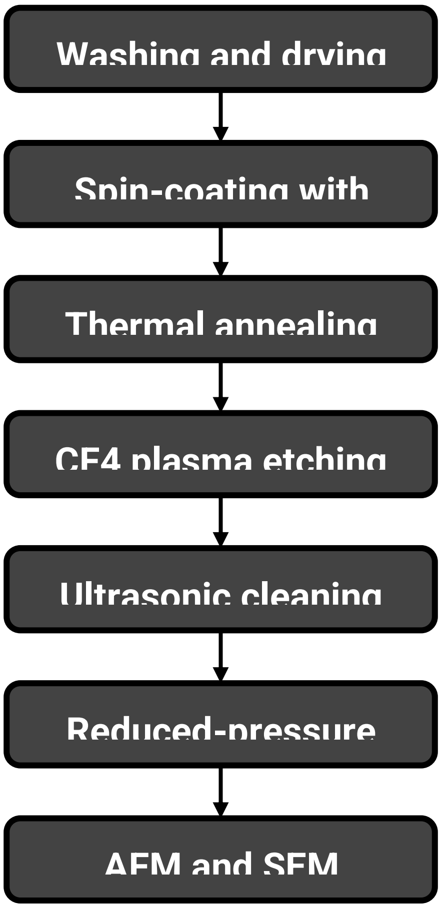

Fig. 1. Flow-chart of the experimental process, detailing the sequence of procedures performed during the experiment. Note that for comparative purposes AFM and SEM also were conducted before removing the polymer mixture from the substrate.

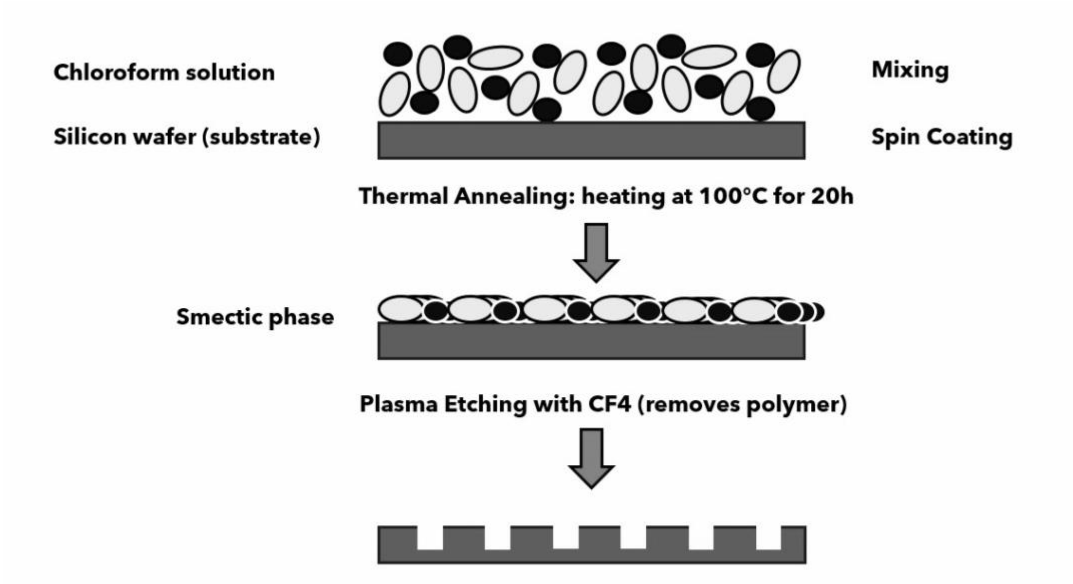

Fig. 2 A molecular representation of the nanopatterning process.

At first, silicon wafers are washed and dried to remove any impurities that might interfere with the patterning process. Then, the chloroform solution with polysilane and tetraalkylsilane is applied to the surface of the silicon wafer using spin coating. During this process the wafer is rapidly spinned to spread the solution evenly across its surface.

After applying the solution, the wafers are heated at 100°C for 20 hours. This process, called thermal annealing, allows the molecules to arrange themselves into stable layers, with the spherical molecules of tetraalkylsilane settling into the spaces between the layers of polysilane which forms the smectic phase.

To compare the pattern on the silicon wafers while the polymer mixture is still on the substrate with the pattern on the silicon wafers after removing the polymer mixture, AFM and SEM are performed also before removing the polymer mixture from the substrate. To remove the polymer mixture from the silicon wafers, CF4 plasma etching for one minute is used. Plasma etching involves bombarding the surface with a plasma (a highly energetic state of matter) to remove specific layers of material [13]. CF4 (methane tetrafluoride) is a gas used in this process to etch away material where needed.

After etching, the silicon wafers are cleaned using chloroform and ultrasound to remove any remaining polysilane. This leaves behind a pattern on the silicon surface that mimics the layered structure of the original mixture.

Finally, the patterned surface is observed using AFM and SEM. These techniques allow seeing the surface at a very high resolution, confirming that the pattern had been successfully transferred.

4. RESULTS

The SEM images before and after dry etching provided only a poor resolution. Thus, only the information provided by the AFM observation is used to describe the results. Figure 3 shows AFM images before (left) as well as after dry etching (right), including the cross-sectional profiles and their Fourier transformation.

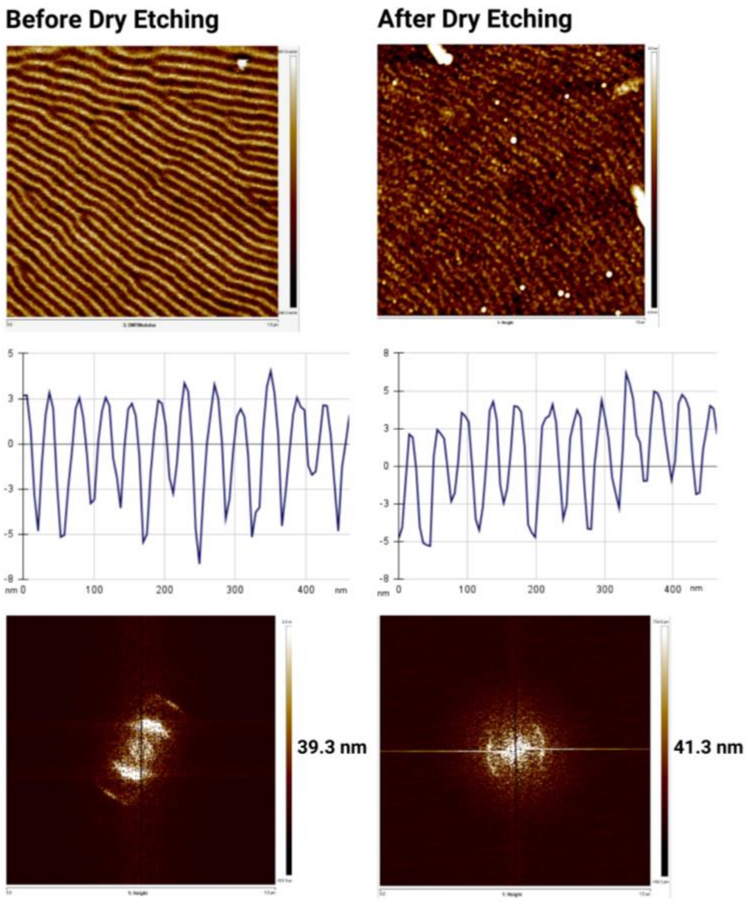

Fig. 3. AFM image, cross-sectional profile and Fourier transformation before (left) and after dry etching (right)

Before, as well as after dry etching, periodically repeating patterns are observable. Especially when looking at the AFM image before dry etching, a layer-like arrangement of molecules is visible. Lighter stripes correspond to the higher regions in the AFM image, which represent the liquid crystal layers. Darker (brown) stripes represent the lower regions, which are the spaces between the layers.

This shows that during thermal annealing the rod-like particles of the polysilane formed the smectic phase, thereby segregated from the spherical particles (tetraalkylsilane) which have been selectively stored between the layers of the rod-like particles. This stabilizes the layered structure.

This visual observation is supported by the cross-sectional profiles of the AFM images which show a periodic repetition of high and low areas in the image. Since the cross-sectional profiles before and after dry etching show the almost same repeating pattern, the transfer of the layered structure onto the surface of the silicon wafers was successful. Note that differences between the images / cross-sectional profiles before and after dry etching can be explained by the slight degradation of the pattern during the etching process, which may have caused minor distortions or changes in the dimensions of the layers. Despite these changes, the overall layered structure remains largely intact, indicating that the nanopatterning process was effective in transferring the smectic phase's arrangement onto the silicon wafer's surface.

The Fourier transform analysis of the AFM images reveals a periodic spacing of 39.3 nm before dry etching and 41.3 nm after dry etching. This slight increase in the periodicity can be attributed to the impact of the dry etching process on the layered structure. Specifically, the CF4 plasma etching may have caused a minor expansion or distortion of the smectic phase's layers. This effect could be due to the removal of material at different rates across the layers, leading to a slight relaxation or swelling of the structure. This also explains why the AFM image before dry etching appears sharper and more defined compared to the image after dry etching. Despite this small change in periodicity, the overall layered arrangement is preserved, indicating that the fundamental structure remains stable during and after the etching process.

5. CONCLUSION

The nanopatterning process using a mixture of polysilane and tetraalkylsilane successfully transferred the layered structure of the smectic phase onto the surface of silicon wafers. AFM and Fourier transform analyses confirmed the presence of a periodic pattern both before and after dry etching, with slight changes in the periodicity (39.3 nm before etching and 41.3 nm after etching) probably caused by minor distortions during the etching process. While the AFM images before etching displayed a sharper and more defined pattern, the overall layered arrangement remained largely intact after etching, demonstrating the stability and effectiveness of the nanopatterning technique. This observation indicates that the polymer mixture forms a stable smectic phase, which retains its structural integrity even after undergoing plasma etching, demonstrating its robustness in maintaining the layered order.

6. COPYRIGHT STATEMENT

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