Ion beam induced micro-structuring of polymeric surfaces

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Ion beam induced micro-structuring of polymeric surfaces

PROEFSCHRIFT

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Summary

Ion beam induced micro-structuring of polymeric surfaces

The objective of this research is to present novel methods for fabricating patterns with micro and nano-scale features on homo-polymer substrates and polymer blend films. Top–down (irradiations through patterned openings over large areas) and bottom–up (local rearrangements of substrate properties) approaches were combined to introduce nano/micrometer length scale features spanning over large areas (few mm²) of the substrates. Ion projection lithography technique was used to create specific local interactions in different substrates viz. cross-linking in the case of uniaxially stretched homo-polymer substrates and pre-patterned substrates with varying surface energies for thin polymer blend films.

The irradiation of polystyrene (PS) surfaces with ion beams led to pronounced chemical and physical modifications, when the ions were scattered at the polymer chains. The local mechanical properties of the PS surface layers could be tailored (as measured by Young’s modulus) by changing the ion doses and ion species (with different masses). By annealing pre-stretched irradiated PS near the glass transition temperature, surface wrinkling occurred only in the irradiated areas. The moduli obtained from rippling periodicities and elastic model assumptions were in the range between 8 to 800 MPa and characterized the irradiated PS as rubber-like. From that, the network density and the molar mass of entanglement were quantified. Results confirm that even for non-discrete layered systems, a consistent elastic description can be applied and relevant polymer parameters can be derived from the measurements of surface ripple periodicities.

In the case of guided polymer blend phase separation, the gold layer coated silicon substrates were bombarded with focused ion beams (FIB) to sputter away Au grains in the irradiated regions and expose silicon oxide surface underneath, thereby creating pre-patterns of relatively hydrophobic (Au) / hydrophilic (silicon oxide) regions. In the pre-patterned regions, the spin-coated films consisting of immiscible PS and PtBA (poly-tert-butyl acrylate) blend exhibited phase separation induced by the underlying pre-patterns and formed two distinct ordered morphologies with periodicities much smaller than that of the pre-patterns. The effects of varying periodicities of the pre-patterned structures, pre-pattern geometries (viz. 1-D arrays of stripes and spaces and 2-D arrays of squares), blending ratios and spin-coating parameters on the resulting morphologies were investigated. Observed affinities of PS and PtBA towards Au and silicon oxide surfaces respectively were explained in terms of work of adhesions from the wetting analysis.

Thus, ion beam pre-patterning has been successfully combined with two different bottom-up approaches to fabricate micro/nano length scale patterns on polymeric substrates. Presented patterning combinations can provide a platform for developing commercial applications such as diffraction gratings, micro-sensors, environmental sensors and scaffolds for cell/tissue adhesions in biological studies.
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Chapter 1

Opening words

1.1 Why Nano-patterning?

The development of new techniques for fabrication of smaller and denser structures has interested material scientists and physicists world-wide since early 20th century. As smaller products consume less energy and are easier to use and carry, miniaturization has gained industrial importance. Nanotechnology refers to the creation and application of nanometer-scale objects i.e. structures with at least one lateral dimension between the size of an individual atom and approximately 100 nm (e.g. in semiconductor circuits). Nano-patterning is the branch of nanotechnology, which deals with the development of fabrication processes for such structures. Miniaturization technology has been driven tremendously by the semiconductor industry: the smallest and most complicated devices ever engineered are the silicon based integrated circuits.¹ Most prominent patterning techniques used in semiconductor industries are the lithography techniques realizing patterns of dense micro/nano scale features as components of a functional chip. Within the framework of advancing miniaturization, in recent times, semiconductor industries have been facing a new set of issues associated with decreasing length scales in particular in silicon based nanoelectronic devices². Issues related to fabrication processes can be divided into two main groups:

1) Physical¹: Resolution of photolithography is limited by diffraction effects³ and ever shorter wavelength light sources have to be used (industries are currently using 193 nm immersion lithography, Extreme ultra-violet (EUV) lithography at 14 nm is currently in development); electron beam lithography suffers from charging effects and scattering of electrons results in resolution limiting proximity effects⁴.

2) Economic: Tremendous growth of equipment cost associated with progress in resolution.

¹Foot-note 1: An overview of conventional and non-conventional patterning techniques is presented in appendix I.
Hence attempts are being made to implement evolutionary improvements which can extend the lifetime of established fabrication equipments and processes as far as possible. In parallel, alternative next generation patterning techniques are developed, amongst them ion beam patterning is a prominent example. Ion beam patterning\textsuperscript{5,6} provides patterning practically not limited by diffraction phenomena (at least for existing demands of 32 nm and near future 22 nm feature resolutions) and relatively low proximity and charging effects (higher energy imparted by the incident ion in the substrate per induced charge compared to e-beam lithography). But at this stage, equipment costs for ion beam patterning facilities still prohibit its establishment for industrial applications. This technique is under ongoing development to increase its functionality and reduce the costs.

Besides advances in top-down lithography techniques, material scientists have found growing interest in novel bottom-up patterning approaches for microfabrication. These methods provide cost effective techniques of patterning new materials such as polymer blends, tissues, and block co-polymers. Furthermore attempts are being made to combine the top-down and bottom-up approaches. This thesis focuses on two of such promising combinations involving polymeric materials. Instead of focusing on smallest possible structure formations, focus has been on understanding the processes driving these micro-structure formations in both cases. In the following, the concepts of each of the patterning techniques viz. ion beam patterning as top down and chemically and mechanically driven bottom-up patterning techniques are introduced.
1.2 Ion beam induced patterning

Ion beam patterning is potentially the next generation patterning technique because of its distinct advantages over currently used techniques. Most importantly, as ion beams have de Broglie wavelengths in the sub-nanometer range they can pattern devices with very small feature sizes (less than 20 nm). Other advantages include the possibility of generating high aspect ratio features and three dimensional patterned devices with depth of focus up to 500 µm. The ion beam when interacting with matter follows an almost straight path. Secondary electrons induced by the primary ion beam have low energy and therefore limited range, resulting in minimal proximity effects. The trajectory of an irradiated ion in a resist material is dependent on the interaction with both the atomic electrons and nuclei in the material. For most of its path, the probability that an ion interacts with an electron is a few orders of magnitude larger than for nuclear scattering and nuclear collisions have little effect on the trajectories. Because of the high mismatch in mass between the ions and the material’s electrons (even for the lightest positively charged ion i.e. proton, \( m_p/m_e \approx 1800 \)), ion collisions with electrons do not result in any significant deviation in the trajectory of a proton from a straight-line path. Whereas in e-beam writing, the primary interaction between the electron beam and the resist material is that of electron/electron collisions, which results in large-angle multiple scattering of the electron beam and the classic ‘pear-shaped’ ionization volume around the point of entry into the material. As an example, simulated travel paths of focused 50 KeV electron beam (typical operating energy range for e-beams) irradiated in the resist poly-methyl methacrylate (PMMA) is shown to penetrate up to a depth of 40 µm with a 20 µm spread in the beam (See Fig. 1.1). For comparison, simulated travel-paths of protons (lightest positively charged ions) are also presented which clearly show less scattering. Here ions are irradiated at very high energy of 2 MeV (typical operating energy range for light ions). Therefore, in the case of ion beams, proximity effects leading to line broadening are greatly reduced. Even more than e-beam patterning, ion

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Footnote 2: Brief review on the physical background behind ion-solid interactions and the computational models used for their simulations is presented in appendix II.
beam patterning offers direct writing and fabrication possibilities. State of the art for all
the conventional patterning techniques along with ion beam patterning is presented in
table 1.1.

Fig 1.1: Comparison of proximity effects occurring at irradiation of 2MeV ion
beams (left) and 50 KeV (typical energy range used for e-beams) e-beams in PMMA
resist. Red lines show simulated travel-paths of incident ions within the PMMA
whereas blue lines show simulated travel paths of incident electrons. Less scattering
occurs for ions compared to electrons (from respective points of incidences at the
PMMA surface) along the depth of the substrate. (For details see reference 11)
<table>
<thead>
<tr>
<th>Patterning technique</th>
<th>Demonstrated Resolution until 2009[nm]</th>
<th>Depth of Focus</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-Optical</td>
<td>157</td>
<td>~300 nm</td>
<td>cost effective</td>
<td>Resolution diffraction limited, High NA lenses needed: low DOF, therefore only suitable for planar substrates</td>
</tr>
<tr>
<td>EUV</td>
<td>35</td>
<td>~500 Nm</td>
<td>high resolution</td>
<td>Reflective mask required, high defect densities, mainly suitable for planar substrates, high vacuum required</td>
</tr>
<tr>
<td>X-ray</td>
<td>25</td>
<td>~500 nm</td>
<td>high resolution &amp; reproducibility, negligible diffractions, no high vacuum</td>
<td>Cost intensive, needs complicated masks with features as small as final features.</td>
</tr>
<tr>
<td>E-beam</td>
<td>&lt;25</td>
<td>~10 µm</td>
<td>very high resolution, high DOF, limited resist-less direct patterning possible</td>
<td>Substrate charging, Back scattering electrons leading to proximity effects, high vacuum required, cost intensive</td>
</tr>
<tr>
<td>Ion beam (Focused and Projection)</td>
<td>&lt;25</td>
<td>~500 µm</td>
<td>very high resolution, easy 3D feature formations, high DOF, almost no proximity &amp; back scattering effects, resist-less direct patterning &amp; variety of interactions.</td>
<td>High vacuum required, cost intensive</td>
</tr>
</tbody>
</table>

Table 1.1: State of the art of conventional and next generation lithography techniques
**Ion beam patterning tools**

In contrast to techniques involving photons (visible light, UV light, and X-rays), ions can induce structural modifications in the substrate, allowing a greater variety of surface modifications and their properties such as solubility, refractive index, optical absorption and chemical structure e.g. cross-linking of polymer surface layers. By choosing ion species, acceleration energy and ion fluence for each given substrate, different effects like sputtering\textsuperscript{12}, milling\textsuperscript{13}, and ion beam induced intermixing\textsuperscript{14} can be achieved. Substrate material removal during sputtering and milling can even be enhanced by introducing chemically reactive gases\textsuperscript{15}.

Ions are generated by exciting the electron shells of an atom or molecule so that one or more electrons are ejected from the shell structure. In typical ion sources for patterning tools, a constant or radio-frequency electric field is applied to a low pressure gas of the atoms to be ionized. Protons which are the simplest positive ions (nuclei of hydrogen atoms) but also atomic and molecular ions with wide range of charges and masses can be created. Single or multi-charge ions are generated depending on the strength of the electric field. Positively charged ions are extracted from the source and are shaped into a broad beam by a condenser ion optics containing a diverging electrostatic lens. The ions are further accelerated in electric fields to give them the kinetic energy required for the intended interactions with the substrate atoms. The accelerated ion beams are steered and focused using both magnetic and electrostatic fields so that the ions are transported over long distances and finally bombarded on the substrates\textsuperscript{16}. Spatial modulation of ion fluence on the substrate surface can be defined by different approaches; mask based ion beam projection tools and mask-less scanning focused ion beam tools.

**1.2.1 Ion beam projection tools**

In ion beam projection tools, a broad ion beam is projected on the substrate after passing a thin membrane (mask) with desired patterns of openings. The major advantage of ion beam projection is that an entire substrate can be exposed to the ion beam in a single operation because masks are covering relatively large areas.
(exposure fields can be even further increased using step and repeat techniques). This allows quick fabrication of large numbers of two dimensional features, making the process desirable for mass production. Projection systems consisting of electrostatic/electromagnetic lenses can de-magnify the pattern defined in the mask before the beam reaches the substrate and reduce dimensions of the features actually patterned on the substrate. Fig 1.2 shows a schematic and a photograph of a tool which was used in this research. In this way, the masks can be fabricated with dimensions many times larger than the final feature size on the substrate. However, mask fabrication may become very complex and expensive.

Fig 1.2: Schematic of ion projection lithography technique and photograph of Ion Projection Lithography (IPL) tool situated at Bratislava, Slovakia (Courtesy: Biont Ltd, Bratislava, Slovakia)
1.2.2 Focused ion beam (FIB) tools

In focused ion beam tools, the ion beam is focused to a very small spot diameter and the beam is scanned using electrostatic or magnetic fields across the surface of the sample to create the desired pattern. The minimum feature size is determined primarily by the diameter of the focused ion beam on the sample surface. The advantage of FIB is the flexibility, as changes in the pattern can be realized by the control software and not by changing a mask as in the previous case. FIB being a sequential process, is slow and not suitable for high-volume production. As of now, FIB patterning is primarily utilized for fabricating specialized or prototype devices. Another application of FIB technique is the repair of single small faults in expensive large-scale structures such as masks for X-ray lithography. FIB assisted with chemical vapor precursors allows convenient deposition and formation of 3-D structures that are complicated to fabricate with other existing technologies\(^1\)

1.2.3 Projection mask-less patterning (PMLP) tool

A proof–of-concept PMLP tool is one of the most advanced ion beam tools combining the advantages of projection tools with the ones of ion scanning tools [year: 2009] (Developed by IMS Nanofabrication AG, Vienna, Austria as a partner in CHARPAN consortium, an integrated project supported by the European Commission, Contract No: IP 515803-2). PMLP offers de-magnification of patterns of ion beams through mask openings by a factor as high as 200\(^1\)\(^8\). Smallest features of 15 nm dimensions have been fabricated by this technique\(^1\)\(^9\). Instead of using a fixed mask, PMLP is based on a programmable aperture plate system (APS) with possibilities of generating ~40,000 addressable ion beams. APS consists of an aperture plate and a blanking plate. Thousands of beam-lets of micrometer size diameters are formed by the openings in the aperture plate. The beam-lets pass through larger openings in the blanking plate and are demagnified by ion beam projection optics, consisting of three
electrostatic lenses with two crossovers, providing demagnification by a factor of 200. Deflection (ground and blanking) electrodes are placed adjacent to the openings in the blanking plate. If a blanking electrode is powered through the electronics integrated in the blanking plate, an ion beam-let passing through is slightly deflected and is filtered out at a stopping plate near a beam crossover in the projection optics (see fig 1.3).

Fig 1.3: Schematic of the PMPL tool (courtesy: IMS Vienna, Austria, See references 18 and 19)

1.3 Bottom-up patterning techniques

Material scientists have approached ‘physical’ and ‘economic’ problems associated with top-down patterning techniques discussed in the above. A novel approach has been adopted – by bottom-up patterning of novel materials like carbon nanotubes, nanowires, and polymers as an alternative to pure top-down approaches which are still exclusively used for industrial silicon based micro- and/or nano- systems. Bottom-up patterning or self-assembly is defined as a process in which the organization or the assembly into desired structures occurs through local rearrangement phenomena. These phenomena can be either enhanced through physical or chemical processes or even be assisted by molecular selectivity and specificity\(^{20}\). These materials have the potential
to facilitate the fabrication of smaller components composed of just tens or hundreds of molecules\textsuperscript{21,22}. As bottom-up patterning is based on the intrinsic material properties leading to material re-arrangements driven by local forces, problems encountered by previously mentioned patterning techniques can potentially be avoided. Fabrication costs could potentially be much lower as advanced infrastructures (e.g. light source, vacuum chambers) are not required. But applications of such novel materials for end products need to be researched further before mass productions in industries can be implemented. Many novel strategies to fabricate such materials are being developed\textsuperscript{23}, but only those methods that are easy to implement, cheap to perform, and highly reproducible will be favored for mass production. Two commonly discussed strategies are mechanically driven bottom-up pattern formations and chemical bottom-up pattern formations.

1.3.1 Mechanically driven bottom-up pattern formation

Mechanically driven bottom-up patterning technique provides arrangement of surface layers into useful conformations/patterns on account of variations in mechanical properties such as Young’s moduli and Poisson’s ratios. One of the variants of such a bottom-up patterning technique is polymer surface structuring provided by buckling instability\textsuperscript{24-27} (see fig 1.4). Buckling instabilities of surfaces can be observed in 2-layer or multilayer structures when stress is applied to the entire sample but the contributing layers have different mechanical properties. Buckling instabilities often occur in the form of surface ripples having a defined periodicity and height. This substrate structuring technique can be used for developing applications such as environmental sensors\textsuperscript{28}, diffraction gratings\textsuperscript{29}, and substrates for studying cell growth mechanisms\textsuperscript{30}.
1.3.2 Chemically driven Bottom-up pattern formation

Chemically driven bottom-up patterning techniques provide arrangement of single-molecules or group of molecules (e.g. polymer chains, DNA strands, micelles) by local chemical interactions into useful conformations/patterns. It is based on material systems that show ordering and pattern formation through self-assembly processes such as block co-polymers (see fig 1.5), polymer blends, biological cells and tissues. Self-assembly is also a process in which defects can be rejected because of thermodynamic reasons, and therefore the accuracy of features in the patterned regions is relatively high. Self-assembly of molecules and micro/nano-clusters can be accomplished with numerous and different mechanisms such as surface forces, direct chemical interactions and biomolecule-mediated self assembly techniques.
Fig 1.5: Height mode AFM image (1.5 µm × 1.5 µm) of polystyrene-block-poly (4-vinylpyridine) (PS-b-P4VP) film spin-coated on silicon substrate. The film shows P4VP dots regularly arranged in a continuous PS matrix. (For details see reference 31)

1.4 Combination of top down and bottom up techniques

Bottom-up techniques can provide patterning of nano-structured substrates. A main drawback however is that the patterning is coherent only on short length scales (arrangement of few tens of molecules or domains) e.g. - phase separated morphologies exhibited by block-copolymer films on homogeneous surfaces. Controlling the lateral organization and stability of these short length scale structures over large areas (few mm² or larger) is important for the industrial applications of such nano-structured materials. To meet these requirements, attempts have been made to combine top-down approaches easily inducing long range order like photolithography, electron beam (e-beam) lithography, X-ray lithography, and chemical patterning by micro-contact printing, with bottom-up techniques ³⁸,³⁹.
1.4.1 Ion beam induced pre-patterns guiding bottom up processes

In all the studies presenting polymer surface structuring using buckling instabilities, either mechanical properties of the entire surfaces were modified or unstructured stiff layers were deposited on top of the pre-stressed substrates. But, desired tailoring of mechanical properties of the surface layers together with control of their lateral dimensions and thicknesses has not yet been achieved. However, ion beam patterning can provide the control over lateral dimensions and thicknesses of the surface layers. Furthermore, ion beam patterning as a top down approach in a combination with mechanical bottom up patterning is particularly advantageous as ion beams can induce mechanical modifications in the polymer substrate with the desired variation and control, which is difficult to achieve with other top-down approaches. By varying the ion doses and species, tuning of modifications in mechanical properties of the surface layers should be possible.

Most of the studies related to pre-pattern induced phase separation of polymer blends or block co-polymers films, involve top-down strategies using chemical modifications\textsuperscript{40-42} (e.g. monolayer depositions by micro-contact printing). In recent studies (December 2009), J. Boneberg investigated morphologies of Poly-Styrene (PS)/Poly-Vinyl Pyrolydone (PVP) blend films (see fig 1.6) on pre-patterned substrates\textsuperscript{43}. These pre-patterning techniques involve chemical solvents, complicated procedures and have limitations in achieving complex geometries and smaller feature sizes. Hence, adoption of such top-down (chemical based) and bottom combination for mass production in industries may not be desirable in this form.
Fig 1.6: De-mixing of two immiscible polymers (PVP/PS) out of a ternary system with tetra-hydrofuran (THF) as solvent for different relative humidities and atmospheres on chemically pre-patterned substrates (For details see reference 43). Scale bars in all the images correspond to 4 µm.

Some attempts were made to introduce other top-down pre-patterning techniques such as photo-lithography\textsuperscript{44}, E-beam induced pre-patterning\textsuperscript{45,46} and a novel technique: scanning probe lithography\textsuperscript{47} in combination with bottom-up phase separation of blend/block copolymer films. But these top-down techniques also experience ‘physical’ and ‘economic’ limitations as explained previously. Scanning probe lithography does not experience the physical problems, but it is a very slow process as it is a serial process. Application of ion beam induced single-step patterning as a top-down approach in this combination should be advantageous as it avoids ‘physical’ limitations (at least compared to the present limits of previous patterning techniques). Moreover, organic solvents and complex process-steps will not be required with ion beam patterning. It may enable fabrication of large number features (with ion projection lithography) in one step of irradiation, making it suitable for high throughput rate requirements. This technique will be even more desirable with the advent of advanced machines such as the PMLP\textsuperscript{18,19} tool which will provide fabrication with programmable geometries (mask-less fabrications), very high resolution (down to 15 nm size features) and large area coverage (with laser-interferometer controlled high-precision vacuum stages).
1.5 Thesis objective

The objective of the thesis is to present novel methods for fabricating patterns with micro and nano-scale features in polymer materials using combinations of top-down and mechanical and chemical bottom-up patterning techniques. Ion beam pre-patterning is used for top-down pre-patterning in both the cases for the reasons explained previously. Ion beam irradiation is provided through mask openings and also using an FIB to induce interactions with substrates resulting in pre-patterns. These pre-patterned substrates are then further structured by inducing local self-rearrangements in polymeric surface layers. Two different ion-substrate interaction mechanisms followed by mechanical or chemical bottom-up patterning surface rearrangements are chosen.

In the first approach, ion beam induced locally modulated cross-linking of the uniaxially stretched PS substrates is combined with mechanical bottom-up patterning in the form of buckling instabilities in these cross-linked PS layers. In contrast to previous studies (references 24-27), cross-linked layers are fabricated by ion beams monolithically (i.e. within one material) with control over their lateral dimensions and thicknesses. Ion beams also provide possibilities of tuning the mechanical and chemical properties (Young’s modulus and cross-linking densities) of the stiff cross-linked surface layers by varying ion doses and species. Such tuning enables fabrication of ripple structures with periodicities ranging from few microns to 250 nm. The results suggest that the superficial elastic properties of polymers can locally be tuned via cross-linking over a large range by irradiation with ions of different species and energies. Moreover, a detailed analysis of the structure-formation process within the created structures is presented which can lead to new methods for the estimation of mechanical parameters sampled in very small volumes such as Poisson’s ratio, Young’s moduli, cross-link network densities etc. This is of particular interest because characterization of thin patterned polymer layers by conventional methods like nano-indentation is very cumbersome and may prove erroneous because of the visco-elastic nature of the polymeric materials.
In the second approach, ion beam induced sputtering is utilized to fabricate substrates with Au/SiOx patterns i.e. with spatially modulated surface properties. In contrast to the studies with other pre-patterning techniques as described in the literature (references 40-43), sputtering Au layers with ion beams for fabrication of such pre-patterns provides possibilities of more complex designs and as a non-contact method it is more suited for mass-fabrication. The ion beam pre-patterned substrates are spin-coated with thin polymer blend films, which undergo pre-pattern guided phase separation leading to locally ordered morphologies (a form of chemical bottom-up patterning). The formation of these morphologies has been analyzed not only phenomenologically but also quantitatively (in terms of work of adhesion calculations). Wetting experiments necessary for this quantitative analysis are shown to be an effective tool for the assessment of the adhesive properties of polymeric surfaces.

1.6 Potential applications

PS substrates with surface patterns of modified properties (cross-linked) can be used for developing environmental sensors e.g. organic molecules detectors. It was shown that cross-linked PS swells to a lesser extent (in volume) compared to non-cross linked PS when exposed to same solvent. The contrast in swelling behaviors of PS regions cross-linked by plasma treatment compared to non-irradiated (and hence non-cross-linked) PS regions in the presence of different organic solvents can be utilized to fabricate micro-vessels. Fabrication of such micro-vessels on extruded PS irradiated with plasma through TEM grid openings (and subsequent solvent treatment) has already been reported by K. Graf\textsuperscript{48} (see fig 1.7).
Ion beam irradiations instead of plasma through TEM grids can provide fabrication of micro-vessels with higher complexity, more precision and smaller geometries. These micro-vessels may act as micro-reactors for studying nano-crystal development or cell growth studies for pharmaceutical applications. Moreover, stress relaxations in ion beam cross-linked surface regions can introduce ripple formation leading to increased surface roughness. Such variations of surface properties can be exploited for providing catching centers of biological cells or tissues on the surfaces\textsuperscript{49,50}. Further, in the case of the PS substrates with surface layers of uniform thickness and cross-linking density, both tunable by ion beam irradiation, perfectly parallel ripples could be achievable. Such substrates may act as diffraction gratings, light out-coupling\textsuperscript{51} for organic LEDs especially if fabricated using transparent materials like poly-methyl methacrylate (PMMA) or poly-carbonate (PC).

Guided phase separation of polymer blend films on surface energy modulated substrates such as SiOx/Au pre-patterns may provide an alternative to an imprint or micro-contact master with the ability of introducing complex structures. The spin-coated and patterned blend films can be peeled off or transferred to other desired surfaces from the pre-patterned substrates (see fig 1.8).
Patterns of polymers (PS and PtBA in this case) with different chemical properties can be used for sensing the presence of organic solvents e.g. when PS and PtBA are exposed to methanol, PtBA dissolves readily in methanol, but PS is completely insoluble. Hence in the presence of methanol vapors (or liquid), PtBA aggregates will swell (or dissolve in the liquid) leaving behind PS matrix unaffected. Such selective responses of the patterned polymers to different organic solvents can be used for developing organic solvent detectors. Volumetric changes of smaller and patterned aggregates (~ 50-100 nm diameters) because of swelling effects can be tracked easily compared to continuous PtBA films. Amongst PS and PtBA polymers, PtBA exhibits photochemistry (conversion of acrylate group to functional acid group by exposure to UV light). Patterned PS/PtBA films (while keeping PS matrix or dissolving it in its selective solvent: Cyclohexane) may act as starting substrates for performing such photochemistry and further development to fabricate patterns of anchoring points with specific functional groups (a probable development scheme is presented in fig 1.9). Such patterns may find applications in pharmaceutical industries for capturing specific enzymes and cells. Faster and detailed understanding of the cells/enzymes requires patterned surfaces to generate cell responses with minimum background effects. Existing patterning techniques employed for patterning anchoring points (references 53-55) involve micro contact printing, e-beam lithography and complex chemicals. The presented technique offers advantages over these patterning techniques (discussed previously) and involves simpler
chemical route for patterning the anchoring points. Moreover, multi-component polymer films with controlled morphologies obtained by using top-down techniques have been already utilized in different fields, ranging from bioactive patterns\(^{56}\), lithographic templates\(^{57}\) to polymer electronics\(^{58}\).

**Fig 1.9**: Schematic presenting development of the platforms with patterned anchoring points, starting with patterned PS/PtBA blend films.
1.7 Thesis Outline

The thesis is organized as follows. In chapters 2 and 3, experiments related to the irradiation of polymer substrates with ion beams are described. These ion irradiations lead to pronounced chemical and physical modifications in the polymer chains. The local mechanical properties of the polystyrene (PS) surface layers are studied (as measured by Young’s modulus) at varying ion species and doses for different substrates. Surface rippling on pre-stretched irradiated PS annealed near the glass transition temperatures occurring in irradiated areas only are investigated and explained with an elastic model. From that, the network density and the molar mass of entanglement quantification is derived. In chapter 4 and 5, experiments for achieving guided polymer blend phase separation are described. The gold layer coated silicon substrates are bombarded with focused ion beams (FIB) to sputter away Au grains in the irradiated regions and expose silicon oxide surface underneath, thereby creating pre-patterns of relatively hydrophobic (Au) / hydrophilic (silicon oxide) regions. The substrates are spin-coated with thin polymer blend films of poly-styrene (PS) and poly-tert-butyl acrylate (PtBA). Within the pre-patterned regions of the spin-coated films, distinct and ordered morphologies with periodicities much smaller than that of the pre-patterns are observed. The film topographies recorded with AFM are analyzed in details with other surface characterization methods. The influence of varying periodicities of the pre-patterned structures and spin-coating parameters is investigated. Surface tensions of both polymers are resolved into their acidic, basic and electrodynamic Lifshitz-vander Waals (combination of dipole and dispersive) interactions. Further, the surface tension components are utilized to estimate work of adhesions that each of the polymers makes with the different substrate surfaces (silicon oxide and gold). In chapter 6 conclusions are drawn on how the ion beam induced patterning technique combined with local material rearrangements can be a powerful approach for nano-patterning and also for studying the related physical/chemical effects of material transformation.
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Chapter 2

Polystyrene surfaces – structure formations

2.1 Introduction

The buckling instability phenomenon has been widely used in the development of surfaces on different systems e.g. thin metal film deposited on the polydimethylsiloxane (PDMS) substrate, plasma treated PDMS film on the untreated PDMS bulk. This type of surface structuring was suggested to be useful for diffraction gratings, for optical sensors and for the roughening of textile fibers. Additionally, it was demonstrated to work as a testing platform to determine the mechanical properties of polymeric thin films without need for expensive test equipment. Young’s modulus of thin PS films deposited on the PDMS substrates has been calculated by exploiting the relationship between the periodicities of the ripples on the thin PS films and film thickness, Poisson’s ratios of the film and PDMS and the young’s modulus of the PDMS. Recently, the rippling concept was used to determine the mechanical properties of polyelectrolyte multilayer. But in all these cases, thin layers were either deposited or fabricated by modifications over the entire surfaces.

In this chapter, the concept of buckling instability at polymer surface layers is explored, which are locally irradiated by ions, to pattern polymer surfaces with structures of micro and nano-meter length scales. Because of this monolithic fabrication, the transition in mechanical properties of the cross-linked layers to those of the bulk soft substrate is continuous in contrast to the previous studies on buckling instabilities induced in two layered structures with distinct mechanical properties. Moreover, the surface layers are cross-linked or modified only in certain regions of the surfaces to form patterns by controlling the spatial resolution of the irradiated ion beams through mask applications.

Footnote 3: Results presented in this chapter are published as following journal publications:
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openings. The PS substrates are pre-stressed uniaxially by stretching them at temperatures close to the glass transition temperature of PS and cooling down to room temperature in stretched conformations. Ion irradiations induce cross-linking in the surface layers of the pre-stressed PS substrates as explained in detail in the next section. The cross-linked layer thickness and cross-linking densities are varied by varying ion species (He⁺, Ar⁺, Xe⁺) and irradiation doses for different substrates. Thickness of the cross-linked surface layers are estimated using TRIM code of the SRIM software package. The pre-stressed irradiated substrates are annealed above glass transition temperature of PS to release the stresses inducing buckling instability and uniaxially oriented ripple structures (in a direction perpendicular to the stretching direction) are formed in the irradiated regions. After every experimental step, substrate topographies are recorded with AFM (in tapping mode). The recorded AFM images are analyzed to measure ripple periodicities, estimate mechanical properties and deduce conclusions related to surface modifications.

2.2 Theory

2.2.1 Poisson’s ratio and Young’s modulus

Poisson’s ratio (ν) is defined as the ratio of the relative contraction strain, or transverse strain (normal to the applied load) to the relative extension strain or axial strain (in the direction of the applied load).\(^8\)

\[
\nu = -\frac{\epsilon_{\text{transverse}}}{\epsilon_{\text{axial}}} 
\]

On the molecular level, Poisson’s effect is caused by slight movements between molecules and the stretching of molecular bonds within the material lattice to accommodate stress. When the bonds elongate in the stress direction, they shorten in the other direction. This behavior multiplied millions of times throughout the material is what drives the phenomenon. The Poisson’s ratio of a stable material can not be less than -1 and can not exceed 0.5 due to the requirement that the elastic modulus, the shear modulus and the bulk modulus have positive values. A perfectly incompressible material
deforming elastically at small strains would have a Poisson’s ratio of exactly 0.5. Rubber is nearly incompressible and so has a Poisson’s ratio of nearly 0.5.

Young’s modulus \(E\) is defined as the ratio of stress to the corresponding strain when the material behaves elastically. Young’s modulus is represented by the slope of initial straight segment of the stress-strain diagram,

\[
E = \frac{\Delta S}{\Delta \varepsilon}
\]

Young’s modulus is a measure of stiffness with the same units as stress (Pascals). In the case of polymers, Young’s modulus strongly depends upon temperature, strain rate molar mass and poly-disparity etc. Especially variations in temperature around the glass transition temperature \(T_g\) influence the Young’s modulus values to a large extent.

### 2.2.2 Buckling instability in multi–layered structures

The phenomenon of buckling instability for an elastic surface layer attached to a softer bulk substrate material (see fig.2.1) can be explained as follows. If a compressive force parallel to the surface on the skin layer and the interface between skin layer and bulk material exceeds a critical value, ripples appear on the skin. The ripple periodicity depends on the material properties of the skin and the bulk material (their Poisson ratio and elastic modulus) and the thickness of the skin, but is independent of the applied stress and strain.\(^9\) The quantitative relationship between the measured ripple periodicity, \(R_p\), induced by the buckling instability and the Young’s modulus of the buckled layer in the surface \((E_s)\) is given by\(^10\)

\[
E_s = 3E_b \frac{1-v_s^2}{1-v_b^2} \left( \frac{R_p}{2\pi h} \right)^3 \tag{1}
\]

Where \(v_b\) and \(E_b\) are Poisson’s ratio and Young’s modulus of the bulk substrate and \(v_s\) and \(h\) are the Poisson’s ratio and thickness of the rippled surface layer, respectively.\(^4\) Equation (1) does not describe the amplitude of the ripples, which depends on the compressive force.

\(^{IV}\) Footnote 4: Derivation of equation (1) on the basis of Biot’s theory is presented in appendix III.
2.2.3 Ion projection direct cross-linking

A new technique for providing a uniform cross-linked layer/s on a soft bulk polymer substrate in a monolithic fashion i.e. by cross-linking only the surface layer to change its mechanical properties compared to rest of the bulk substrate (in contrast to two layered structures where stiff thin layer is deposited on the soft substrate externally) has been developed. Ion Projection Direct Cross-Linking (IPDC)\textsuperscript{11} was used to locally cross-link skin layers of stretched polymer substrates on the sub-µm scale laterally and from few nanometers to hundreds of micrometers along the depth of the targets. When an ion beam is exposing a polymer surface, the accelerated projectile ions transfer their kinetic energies to the carbon and hydrogen atoms of the polymer chains in the targets surface layers while advancing through them. If the transferred energy is higher than the binding energies of C-C and C-H bonds in the polymer chains, carbon and hydrogen atoms are displaced from their original positions leaving behind carbon and hydrogen vacancies in the skin-layers. The vacancies being highly reactive undergo re-combinations amongst themselves resulting in cross-linked skin-layers (fig 2.2). The
cross-linked layer thicknesses and the cross-link network densities depend upon the ion species, ion dose and the acceleration energy of the projectiles.

![Fig 2.2: Schematic re-presentation of ion projection direct cross-linking (IPDC)](image)

2.2.4 Atomic force microscopy (AFM)

The underlying principle of AFM is that the interactions between the end of a probe tip that is mounted on a cantilever and the sample surface results in a response in the cantilever, notably a deflection\(^\text{12}\). A tip is attached to a cantilever, which can be moved over a solid surface in \((x, y)\) direction and perpendicular to the sample surface in \(z\) – direction. A laser beam is reflected from the back side of the cantilever onto a position sensitive detector (PSD). Wherever a force is acting on the tip, either attractive or
repulsive, a deflection is measured. There are different modes to perform the measurement: tapping and contact mode. In contact mode, the cantilever is scanned along the substrate keeping it always in contact with the surface at a pre-defined force (stress). While scanning, the feed back loop system records the variations in this pre-defined force (stress) in the cantilever caused by the variations in topography of the substrate and compensates to maintain the pre-determined value. Theses force compensation values are used to generate the topography maps. In tapping mode, the cantilever vibrates in proximity of the substrate slightly tapping the surface while scanning. In contrast to the force (stress) in the case of contact mode, vibration amplitude of the cantilever is maintained by the feed loop system at a constant value as explained in details in the following section.

**Topography contrast in tapping mode**

In tapping mode, the vibration characteristics of the cantilever are used. The mechanical resonance frequency of the cantilever is determined by its dimensions and its material properties. The resonance frequency is related to the cantilever spring constant. The resonance is located by oscillating the cantilever with various frequencies and measuring the rms response\textsuperscript{13}. For imaging, the cantilever is oscillated and scanned across the sample surface at or near its resonance frequency with amplitudes ranging typically from 20nm to 100nm. The tip slightly “taps” on the sample surface during scanning, contacting the surface at the bottom of its swing. The feedback loop maintains constant oscillation amplitude as a constant RMS of the oscillation signal acquired by the split photodiode detector by controlling the z height of the cantilever. The vertical z position of the scanner at each (x, y) data point is stored by the computer at which a constant "set point" amplitude is obtained and hence a topographic image of the sample surface is recorded. By maintaining constant oscillation amplitude, a constant tip-sample interaction is maintained during imaging. Tapping mode is generally considered to be less damaging to soft surfaces such as polymers and to the samples with poor substrate adhesion like nano-tubes or DNA on silicon.
Phase contrast in tapping mode

Tapping mode AFM can also be used to map tip–surface interactions. While feedback loop forces the amplitude of the cantilever oscillation to remain constant using a lock-in amplifier, it is possible to measure the phase difference between the driving oscillation and the detected cantilever oscillation and a phase difference map can be obtained. An increase in the phase difference arises from a stronger tip–sample interaction creating contrast in the phase map. Phase contrast images obtained from heterogeneous samples by tapping mode can be exploited to image variations of elastic, visco-elastic and adhesion properties etc.

**Fig 2.3: AFM in tapping mode** - A laser beam is deflected by the backside of the cantilever and the deflection is detected by a split photodiode. The excitation frequency is chosen externally with a modulation unit, which drives the excitation piezo. A lock-in amplifier analyses phase and amplitude of the cantilever oscillation. The amplitude is used as the feedback signal for the probe-sample distance control. (For details, see references 13, 14)
2.3 Experimental

2.3.1 Fabrication of polymer substrates

Polystyrene (PS) powder (Mw = $2.6 \times 10^5$ g mol$^{-1}$, PDI = 1.07) was synthesized in-house by anionic polymerization and annealed in a 60 mm $\times$ 10 mm pressing mold (PW 40 EH Paul-OttoWeber Maschinen- und Apparatebau GmbH, Germany). Two Kapton® foils of the same dimensions were placed on both sides of the mold cavity to avoid the direct contact of the molten PS with the metal surfaces of the mold. This way smooth polymer surfaces with a root-mean-square (rms) roughness of $\sim$ 2 nm were obtained. The PS powder was annealed at 160°C ($T_g \approx$ 100°C) in air for 1 hr. After that, the molten PS was pressed at 20 kN into substrates and then cooled down to room temperature in 90 min. PS substrates with different thicknesses varying from 2 mm to 4 mm were obtained by varying the amount of the PS powder. Afterwards, each substrate was fixed with a clamp in an Extensometer (Instron 6022, Instron Deutschland GmbH, Germany) and heated to 100°C, the glass temperature of PS (step 1 in fig 2.4).

After that the PS substrate was clipped with a second clamp in a distance of 3 cm below the first one and stretched at a constant speed of 0.5 mm-min$^{-1}$ to the desired stretching ratio of 200% ($\equiv$ length of the substrate after stretching, divided by its original length in %). After stretching, the clamped substrate was slowly cooled down in air to 50°C in 2 hrs and then within 1 min. to room temperature. Such a substrate was divided into smaller pieces of 10 mm $\times$ 6-7 mm. Here, only those pieces from the central areas of the stretched substrate were used (step 2 in fig 2.4). The RMS roughness values for the substrates were $\sim$ 6.3 nm.
2.3.2 Ion Beam Irradiation

The surfaces of the polymer substrates were modified by means of Ion Projection Direct Cross-Linking within locally defined areas at a lateral resolution of less than 100 nm. A grid mask with an array of square-shaped openings of 265 µm x 265 µm was inserted into the beam. Ions passing through the mask openings are projected perpendicular onto the target surface with a demagnification of 8.3 at 73 KeV. Thus, the stretched PS substrates were irradiated in the pattern of an array of square-shaped areas of 32 µm × 32 µm each. Different ion species (He⁺, Ar⁺, Xe⁺) were used (step 3 in fig 2.4). The ion current was set constant and monitored with a Faraday cup within a measurement error of ~ 5% percent and the ion fluence was varied from $10^{13}$ ions-cm$^{-2}$ to $4.0 \times 10^{15}$ ions-cm$^{-2}$ by exposure times between 5 s and about 34 min. To further reduce the penetration depth of projectiles in the polymer a 25 nm thick sacrificial Au layer
evaporated before Xe$^+$ ion irradiation covered the surface in some experiments. This Au layer was removed after irradiation using gold etchant (KI + I$_2$ + H$_2$O in 4:1:40 proportion). Afterwards, the irradiated PS substrates were annealed in vacuum (< 1 mbar) at 110°C for 1 hr and cooled down to room temperature within 2-3 min (step 4 in fig 2.4).

2.3.3 Characterization by AFM, ATR-FTIR and SEM

The substrate topography was recorded before and after annealing with atomic force microscope, SFM (D3100 connected to a Nanoscope IV- controller, Veeco Instruments, Santa Barbara, CA/USA), in tapping mode. We used silicon cantilevers (Olympus OMCL AC 160 TS-W2) with a nominal resonance frequency of 300 kHz, a spring constant of 42 N m$^{-1}$, a tip height of 11 µm and a tip radius of < 10nm. A first order flatten filter was applied to the raw data. The Fourier transform infrared (FTIR) measurements were performed with a Nicolet MAGNA-IR 850 spectrometer in a single-reflection ATR setup (Spectra-Tech Foundation Endurance, Thermo Fisher Scientific, Waltham, Maine, USA) that utilizes a composite diamond crystal sampling surface with a ZnSe focusing element. The spectra were background corrected. The scanning electron microscopy (SEM) images (LEO 1530 Gemini, Carl Zeiss SMT AG, Oberkochen, Germany) were recorded at 2kV. To avoid charging of the sample 10 nm of gold was sputtered on one side of the PS sample at a rate of 0.3 nm·s$^{-1}$ prior to imaging.
2.4 Results

2.4.1 Simulations of ion scattering in polymer surfaces

Monte Carlo (MC) simulations of the different ions (He\textsuperscript{+}, Ar\textsuperscript{+}, Xe\textsuperscript{+}) interacting with the PS substrate were performed, using TRIM code from the software package freely accessible from the internet (SRIM ≡ Stopping Range of Ions in Matter, version SRIM-2006\textsuperscript{18}). The parameters for PS (viz. elemental composition and atomic density) were taken from the SRIM database. For each projectile the cascading collision events and atomic displacements were recorded along with distribution of resulting C and H vacancies created along the target depth. For each vacancy distribution profile, 2000 projectiles trajectories were simulated each having an initial energy of 73 KeV and analyzed to estimate the cross-linked layer thicknesses as explained below.

2.4.2 Determination of cross-linked layer thickness

During the scattering of the ions, H- and C-vacancies are generated in the PS substrate from C-H and C-C bonds (Fig. 2.5a), which leave highly reactive radicals leading to a modification of the PS within a skin layer of a certain depth. The depth distributions of H vacancies in PS obtained from simulations (Xe\textsuperscript{+}, Ar\textsuperscript{+} and He\textsuperscript{+}) are plotted in Fig. 2.5b.
Fig 2.5: (a) Schematic representation of H-vacancy generation in the polymer chains owing to ion beam irradiation. H-vacancies re-combine to form a cross-linked layer at the surface with thickness $h$. (b) Hydrogen- (lower plots) and total (upper plots) vacancy density versus target depth for irradiation of PS substrates with 73 KeV Xe$^+$-ions as simulated with SRIM. The distributions for He$^+$ irradiations are multiplied with factor 10 for better visibility. (c) Derivatives of (b) for the determination of the thickness of the modified PS from the point of maximum slope (≡ minimum in derivative). The hatched areas for He$^+$ exemplarily illustrate the definition of the position of the interface (see text).
The simulation reveals that both, the H- and C-vacancy density pass through a local maximum. It represents the depth, where the maximum chemical modification occurs, which is not representative for the layer thickness \( h \). In the derivation of eq. 1 an abrupt interface between the stiff skin layer and the soft bulk substrate is assumed. In order to determine an effective interface depth also in the case of the more gradual transition from skin layer to bulk for the case of ion beam cross-linking a suitable definition has to be established. Analogous to the abrupt interface depth it can be defined as the point of inflection, where the highest change in the vacancy density occurs. This point is determined from the minimum of the derivative of the H- and C-vacancy density (Fig. 2.5c). The corresponding depth represents an effective layer thickness with respect to the PS surface (at depth = 0). This definition of the layer thickness ensures that the hatched areas left and right from the point of inflection are equal in accordance with the thermodynamic definition of an interface\(^{19}\), as shown exemplarily in fig. 2.5b for He\(^+\). This way, a layer thickness \( h \) of \( \sim 66 \) nm was obtained for the exposure to Xe\(^+\)-ions. For He\(^+\) there are two inflection points, leading actually to a three layered system for which Eq. (1) is not valid anymore. The three layers as presented by the simulation results can be explained on the basis of scattering of lighter He\(^+\) ions in PS bulk substrate in directions lateral to the irradiation direction along the thickness of substrate. Being smaller in size compared to Xe\(^+\) and Ar\(^+\) ions, He\(^+\) ions scatter more and penetrate much dipper in the PS substrate creating collision cascades and hence the H- and C- vacancies with varying distributions. Therefore, the analysis is simplified by considering the deeper inflection point only. The simulation results are also analyzed to quantify the cross-linked network densities and critical molar mass between the cross-links as explained in more detail in the next chapter.
2.4.3 Proof of cross-linking and validity of TRIM simulations

To prove that the PS skin layer was cross-linked by the irradiation with ions, a PS substrate was exposed with Ar\(^+\)-ions at a high ion fluence of \(10^{15}\) ions/cm\(^2\) and afterwards dipped into toluene, a good solvent for not crosslinked PS (Fig. 2.6a). An insoluble crumpled skin layer of PS remained after solvent treatment. From scanning electron microscopy (SEM) a thickness of \(\sim 100\) nm was obtained for the insoluble part (Fig. 2.6b). MC simulations for chosen irradiation conditions revealed an interface depth of \(\sim 63\) nm if the point of inflection is taken as in fig. 2.6b & c. However, part of the polymer may become insoluble when cross-linked at all, even at very low cross-link density and thus vacancy density. Therefore, to judge on the validity of the TRIM simulations, the total thickness of the ion-exposed and damaged layer has to be taken into account. This thickness was obtained from the depth where the vacancy density approaches 0 and representing the maximum penetration depth of the ions. For the above ions the maximum penetration depth obtained from TRIM simulations was \(\sim 105\) nm and therefore in excellent agreement with the experimental result from SEM which supports validity of the TRIM simulations. Such estimation of the total affected depth of the PS substrate because of Ar\(^+\) irradiations also agrees with findings in the literature, where 12 different simulation tools were compared\(^{20,21}\). Since the simulations neglected sputter-etching of the PS surface by the incident ions, this effect was determined experimentally with AFM for all samples. It was found to be below 15% of the simulated layer thickness.
Fig 2.6: Microscopy image of a gold-covered, Ar+ -irradiated PS substrate of 1 cm × 1 cm (30 KeV, 10^{15} ions/cm^2), dipped into toluene (a). The visible crumpled part is insoluble in the solvent and proves that this part of the PS substrate was cross-linked by the irradiation with the ions. (b) SEM image of the crumbled part. The corrected thickness of the lamella is ~ 100 nm (subtraction of gold layer). (c) Simulation of the H- (lower plot) and total (upper plot) vacancy densities for the conditions of the experiment in (a) and (b). As for fig. c), the minimum of the derivative of the vacancy density was analyzed (inset) to get a thickness of the cross-linked layer of ~ 63 nm (dashed line). A thickness of ~ 105 nm is obtained if that depth is taken where the vacancy densities approach 0 (dashed line on the right, inset).
Additionally, ATR-FTIR measurements were performed on the original and irradiated PS substrates (fig. 2.7). The irradiated PS surface showed mainly the same peaks as the original PS surface but with lower intensity, resulting in negative peaks in the difference spectrum, as for the C-H stretching bands in the range of 4000-2500 cm\(^{-1}\) and the vibration and bending modes in the range of 700-1600 cm\(^{-1}\). This was observed earlier for cross-linked PS (by other methods) and reflects the chemical modification of the surface by the ions\(^{22}\). Considerable change was the appearance of a broad O-H band between 3000 and 3700 cm\(^{-1}\) after irradiation. This is accompanied by an increase in hydrophilicity of the PS surface, which is completely wetted after the deposition of a water droplet. This typical behavior occurs after the exposure of PS to reactive ions and is caused by superficial oxidation\(^{23}\). A further hint for the oxidation of the PS surface was the broad peak at \(~\)1700 cm\(^{-1}\). It is indicative of ketonic groups which typically occur in PS upon exposure to argon ions\(^{24}\). In addition, a direct proof of cross-links in the sample is impossible here as well. The band at 706 cm\(^{-1}\), which was supposed to be related to cross-linking\(^{25}\), is at the limit of our spectrometer.

![ATR-FTIR spectra of an Ar\(^+\)-irradiated PS substrate (10\(^{15}\) ions/cm\(^2\)) and of the original PS surface and their difference spectrum.](image)

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2.4.4 Polystyrene surfaces after irradiations

Here, the results of irradiation experiments on the PS substrates are explained mainly in the form of AFM images recorded in tapping mode. 200% stretched PS substrates were irradiated through the mask with Xe$^+$ ions accelerated to 73 KeV. The AFM image of the PS substrate irradiated with lower Xe$^+$-ion doses ($10^{13}$ and $2.0 \times 10^{13}$ ions/cm$^2$) shows that square shaped areas appear with a distinct contrast only in phase mode (fig. 2.8a).

![AFM images of the 200% stretched PS substrate after irradiation with a Xe$^+$ ion dose of $10^{13}$ ions/cm$^2$](image)

Fig 2.8: AFM images of the 200% stretched PS substrate after irradiation with a Xe$^+$ ion dose of $10^{13}$ ions/cm$^2$ (a) phase mode image (inset: height mode). (b) Square shapes of the irradiated areas changed to rhombic shapes after annealing the substrates at 110°C for 1 hr. in vacuum and (c) zoom-in scan into the rippled area.
It can be concluded that the PS substrate is exposed to the Xe\textsuperscript{+}-ions through the openings of the mask without pronounced etching (fig. 2.8a-Inset). The phase mode image shows that the irradiated areas are stiffer indicating that the polymer is cross-linked locally. After annealing at 110°C in vacuum for 1 hour, irradiated areas appeared with rhombic shapes with an average lower diagonal length of 21.6 µm and an average side length of 34.5 µm (fig 2.8b). Ripples appeared in the irradiated areas (fig 2.8c). They were almost uniaxial and were orientated perpendicular to the stretching direction with periodicity of 900 ± 183 nm. The periodicity of the ripples was determined from the linear height profile along stretching direction over the entire image. The numbers of peaks appearing were counted and the ratio of horizontal distance and the number of peaks gave the periodicity. The shape of the irradiated areas changed from square to rhombus after annealing because of the contraction in the opposite direction of stretching and expansion perpendicular to it. Annealing the PS substrates above the glass transition temperature causes the orientated polymer chains in the bulk to relax, release the stress induced during stretching and loose their orientation. The locally cross-linked stiff layers at the PS surface can not relax and the stiff surface layer buckles to form the orientated ripples.

For the PS substrates irradiated with higher Xe\textsuperscript{+} dose of 2.0 \times 10^{14} ions/cm\textsuperscript{2}, a height difference of 10 nm between the irradiated and non-irradiated PS surface could be measured as square-shaped micro-wells of 32 µm × 32 µm (not shown). Similar changes in the shape of the irradiated areas from squares to rhombi along with almost uniaxially orientated ripples perpendicular to the stretching direction in the irradiated areas occurred after annealing as explained previously. In this case, ripples have a periodicity of 1.5 ± 0.1 µm. Similar irradiation experiments were performed with lighter Ar\textsuperscript{+} and He\textsuperscript{+} ions (atomic mass of 39.94 amu and 4.003 amu respectively). The motivation behind these experiments was to increase the penetration depths by using lighter projectiles for irradiation. The acceleration energy of the ions was kept constant as 73 KeV. During Ar\textsuperscript{+} and He\textsuperscript{+} ions irradiation, the mask was oriented parallel to the stretching direction of the PS substrate so as to irradiate the array of the square shaped areas on the PS substrate with two opposite sides of each square parallel to the stretching direction. After annealing, the PS substrates contracted in a counter direction and
expanded in an orthogonal direction to the stretching direction, as shown for previous experiments (fig 2.9).

Fig 2.9: AFM images of 200% stretched PS substrates irradiated with an Ar\(^+\)- ion dose of \(10^{14}\) ions/cm\(^2\) (a) before annealing (vertical scale: 600 nm) and (b) after annealing at 110°C for 1 hr. in vacuum (vertical scale: 2.5 µm). (c) AFM image of the annealed PS substrate irradiated with an Ar\(^+\)- ion dose of \(2 \times 10^{13}\) ions/cm\(^2\) (vertical scale: 2.5 µm). d) AFM image of the annealed PS substrate irradiated with He\(^+\)- ion dose of \(10^{14}\) ions/cm\(^2\) (vertical scale: 2.5 µm). The arrows in the top-left corner of the images indicate the stretching direction.

The square geometry (approximate side of 32.5 µm) of the irradiated areas (fig 2.9a) change to the rectangular geometry with sides of 41 µm x 21 µm (fig 2.9c)
because of the shrinkage in the substrate in counter direction to the stretching direction. Similar changes in the shape of the irradiated areas are observed after annealing in the case of He$^+$-ion irradiation (fig 2.9d). Thus, by varying only the orientation of the mask with respect to the stretching direction of the PS substrate, different structures viz. rhombi in the case of Xe$^+$ ion irradiation and rectangles in the case of Ar$^+$-ion and He$^+$-ion irradiation were generated on the PS substrates after annealing.

### 2.4.5 Xe$^+$ ion irradiations through Au capping

A further reduction of the penetration depth of the projectiles was achieved by evaporation of a 25 nm thick sacrificial Au layer on top of the PS sample. For the Xe$^+$ ion dose of $10^{13}$ ions/cm$^2$, after removing the Au layer and annealing the sample we observed a decreased ripple periodicity of $250 \pm 40$ nm (Fig 2.10). By extrapolating the trend ripple periodicities around 100 nm might be feasible with the current IPDC method with reduced cross-linked layer thicknesses.

![AFM images of the 200% stretched PS substrate after irradiation through 25 nm Au capping with a Xe$^+$ ion dose of $10^{13}$ ions/cm$^2$. Au layer was removed by (KI$_2$ + I$_2$ + H$_2$O) solution after ion irradiation. (a) Square shapes of the irradiated areas changed to rhombic shapes after annealing the substrates at 110°C for 1 hr. in vacuum and (b) zoom-in scan into the rippled area.](image-url)
2.4.6 Sources of imperfections

Even though ripples were observed to be uniaxially oriented in a direction perpendicular to the stretching direction, some imperfections were observed in their orientations (fig 2.8-2.10). These imperfections may have occurred due to slight variations in clamping the substrates while stretching. It is important to note that the PS substrates were fabricated by cast molding amorphous PS polymer powder which does not exhibit any crystallinity and hence any ordered character. Hence stress orientation is mainly dependent on the stretching direction. Another source of imperfections may originate from increased surface roughness (RMS roughness of ~ 6 nm) which is induced during cooling down the substrates to room temperature in air after stretching which was performed at 100ºC in atmospheric conditions. The substrates were clamped during stretching and cooled down rapidly to freeze in the stresses. Rapid cooling in air may have induced high roughness which subsequently may have introduced imperfections in orientation of the ripple structures. The cross-linked surface layers were fabricated monolithically on the pre-stressed PS substrates by ion beams which penetrated the substrates much deeper than the cross-linked layer thicknesses as estimated by TRIM code simulations. Interaction of the accelerated ions with PS chains along the depth of the substrates is a statistical process. After ions have travelled deeper into the substrate and lost most of their kinetic energies, interactions may not be uniform laterally. Specially with lower ion doses irradiated on the substrates (as in the presented research), non uniformity of the ion-PS chain interactions might be even more pronounced at these depths of the PS substrates, which may lead to varying cross-linking densities laterally. Even if the cross-linking densities might be much lesser at depths below the estimated cross-linked layer thicknesses, the accelerated ions would have modified the substrates and their mechanical properties to a varying degree (with decreasing acceleration energies of ions because of collision cascades) along their penetration depths. Such abrupt transitions in mechanical properties of the cross-linked layers (below the cross-linked layer thinness estimated by TRIM simulations till the penetration depths of the ions) might have induced imperfections in the orientation of the rippled structures. These imperfections may be improved by irradiating the soft substrates with heavier ions as
such ions will induce thinner cross-linked layers with more uniform densities and smaller overall penetration depths.

In all the presented experiments compressive force was exerted by annealing the pre-stressed PS substrates at 110ºC (above glass transition temperature of PS) and releasing the stress. During pre-stressing step, the stretching ratio of 200 % was kept constant; hence the resulting compressive force also remained the same. Most probably, variations in ripple amplitudes may have been observed by varying the stretching ratios and the subsequent compressive forces which triggered the buckling instability in the cross-linked surface layers.

2.5 Conclusions

Locally structured PS substrates have been successfully fabricated using a two step process of the ion beam direct cross-linking followed by the relaxation of the orientated polymer chains by annealing the substrates above glass transition temperature. Surfaces of stretched polystyrene (PS) were locally cross-linked by irradiation with ions of different mass (He⁺, Ar⁺, Xe⁺) using a mask with square openings. As determined from Monte-Carlo simulations, the thickness of the ion beam modified layer decreases with the mass of the ion and is between ~60 nm and ~1 µm. By annealing above the glass temperature, rippling within the irradiated areas occurred. Ripple periodicities have been estimated quantitatively by analysis of the AFM images. Dependence of the ripple periodicities on different ion species and doses will be described in next chapter. Structures with ripple periodicities down to 250 nm were fabricated. Even though ripples were oriented uniaxially in a direction perpendicular to the stretching direction of the substrates, some imperfections were observed in their organization locally. These imperfections can be reduced by irradiating the soft substrates with heavier ions to induce thinner cross-linked layers with more uniform densities. Surface roughness, stretching ratios and local variations in the induced stresses need to be controlled for improving the ripple orientations and uniformity (in their periodicities and amplitudes).
Possible applications of this technique can be seen in the development of environmental sensors such as organic solvent detectors by using locally different swelling behavior of the PS surface layers because of cross-linking (explained in chapter 1). Such variation in swelling behavior because of local changes in the molecular structures offers the possibility of releasing specific chemical compounds e.g. pharmaceuticals. The control of the three-dimensional topology of soft surfaces is desirable for the fabrication of a variety of micro- and nano-functional devices such as micro-vessels (explained in chapter 1), components for phonon filters or chemical reactors, or to control the surface roughness for on-demand wettability. The rippled structures can also be used for micro/nano-fluidic systems with capillary transport through micro-channels or micro-fluidics consisting of a rippled capillary wicking path in contrast to conventional rectangular tubes. Rippled surfaces with controlled ripple amplitudes and periodicities can be used as a tunable phase grating for coherent beam intensities, light out couplings for organic LEDs.
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Chapter 3

Polystyrene surfaces – determination of mechanical properties

3.1 Introduction

In the previous chapter, concept of buckling instability induced in PS surface layers was explored. In this chapter, the results are analyzed further to estimate some of the basic mechanical and molecular properties of the polymer substrates. Recalling the mathematical expression for buckling instability –

\[ E_s = 3E_b \frac{1 - v_b^2}{1 - v_b^2} \left( \frac{R_p}{2\pi h} \right)^3 \] ................. (1)

\( v_b \) and \( E_b \) for the bulk PS substrate can be obtained from literature. The AFM images of the rippled surfaces are analyzed to give a measure for ripple periodicities. Based on these values of \( R_p \) and \( h \) (from TRIM simulations), \( E_s \) values for the cross-linked PS layers are estimated. From the detailed analysis of Carbon and Hydrogen vacancy distributions simulated by TRIM, an estimate for the cross-linked network density and molar mass between the cross-links is derived as well. The results show that well-known surface rippling theory can be employed to derive relevant physical parameters of such non-discrete layered polymer systems without need of a costly chemical analysis.\(^v\)

\(^v\) Foot note 5: Results presented in this chapter are published as following journal publication:

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3.2 Theory

3.2.1 Glass transition temperature

Glass transition temperature ($T_g$) is the temperature at which amorphous solids like polymers become brittle on cooling, or soft on heating. At sufficiently lower temperatures than $T_g$, polymers will be hard, brittle material with a modulus greater than 1 GPa. This is the glassy region. In the glassy region, the available thermal energy is insufficient to allow rotation around single bonds in the polymer backbone, and movements of large-scale (about 50 consecutive chain atoms) segments of macromolecules cannot take place. When such a material is stressed, it can respond by deforming in a non recoverable or in an elastic manner. The mechanism whereby the imposed stress is absorbed irreversibly involves the flow of sections of macromolecules in the solid specimen. In the case of elastic response, which is characteristic for amorphous polymers, the components can not flow passing each other. As the temperature is raised the thermal agitation becomes sufficient for segmental movement and the brittle glassy polymer begins to behave in a leathery fashion. This allows polymer chains to slide past each other when the force is applied. Hence the Young’s modulus of amorphous polymers goes on decreasing with increasing temperature with a typical sharp decrease of about 3 orders of magnitude (GPa to MPa) over a temperature range of about 10-15° C in the glass-to-rubber transition region.\footnote{1}

3.2.2 Cross-linked network density and molar mass between the cross-links

When polymer chains are connected to each other through chemical bonds (covalent or ionic) they are called cross-linked. A qualitative change in properties of polymers can be achieved by coupling all the polymer chains of a sample together, thereby building up a three-dimensional network. The properties of cross-linked polymers depend on the cross-linking density and the functionality of the junction units.\footnote{2} When the polymer chains are linked together by cross-links, they loose some of their ability to move as individual polymer chains. Cross-linking inhibits close packing of the
polymer chains, preventing the formation of crystalline regions. The restricted molecular mobility of a cross-linked structure limits the extension of the polymer material under loading. Cross-links can be formed by chemical reactions that are initiated by heat, pressure or radiation. In thermoplastic materials such as Polystyrene, cross-linking can be induced by exposure to irradiations such as electron beam exposure, gamma-radiation or UV light.

Fig 3.1: Polymer chains in different conformations

The average cross-link density, $\rho_{c,s}$, and the molar mass between the cross-links, $M_{c,s}$, can be estimated as follows\textsuperscript{3,4}

$$M_{c,s} = \frac{3\rho_s RT}{E_s} \quad \text{.................} (2)$$

$$\rho_{c,s} = \frac{3\rho_g N_A}{\rho_r RT \cdot E_s} = \frac{N_A}{RT \cdot E_s} \quad \text{..........................} (3)$$

Where, $\rho_r$ and $\rho_g$ are the densities of the polymer in the rubber and the glassy state, respectively, $N_A$ is the Avogadro number, $R$ the gas constant, and $T$ the temperature. Equations (2) and (3) were derived to characterize elastomeric materials such as polymer chains in a cross-linked network which exhibit entropy-driven elasticity. When the chains between the cross-links are stretched, their entropy is reduced by a large margin because there are fewer conformations available. Therefore, there is a restoring
force, which causes the polymer chains to return to equilibrium or unstretched state (such as a high entropy random coil configuration), once the external force is removed.

3.3 Experimental

Detailed experimental procedure for fabricating patterned ripple-structures on the locally cross-linked PS substrates is explained in chapter 2. The recoded AFM images (in tapping mode) of the rippled surfaces (at randomly chosen five different locations) are analyzed for the measurement of the ripple periodicities (see chapter 2, page 40). For Poisson’s ratio calculations on the non-irradiated substrates, four different substrates were also annealed at 110 °C and their dimensions were recorded before and after annealing. For the estimation of cross-linked thicknesses, C and H vacancy distributions created by ion beam irradiations, TRIM code simulations were performed using inflection points as explained in chapter 2. The measured ripple periodicities and cross-linked layer thicknesses were utilized to estimated Young’s moduli of cross-linked PS layers using equation (1). Furthermore, cross-linked network densities and molar mass of cross-links for the PS substrates were estimated using the C and H vacancy distribution data generated from the TRIM simulations and the estimated Young’s moduli of the PS substrates using equations (2) and (3).
3.4 Results

3.4.1 Determination of Poisson’s ratio

As described in chapter 2, when the Xe\(^+\)-irradiated \((10^{13} \text{ ions-cm}^{-2})\) PS substrates were annealed at 110°C in vacuum for 1 hour, the PS substrates contracted opposite to the direction of stretching and expanded in a direction perpendicular to it. Therefore, the irradiated areas appeared as rhombi with an average lower diagonal length of 21.6 \(\mu\text{m}\), a longer diagonal of 65.5 \(\mu\text{m}\), and a side length of 34.5 \(\mu\text{m}\) (Fig. 3.2b). In addition, ripples appeared in the irradiated areas (Fig. 3.2c). They were almost uniaxial and orientated perpendicular to the stretching direction with a periodicity of 900 ± 183 nm. (These results are already presented in Chapter 2 (fig 2.8), but represented here for further explanations of Poisson’s ratio calculations.)

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**Fig 3.2:** AFM images of a 200% stretched PS substrate after irradiation with a Xe\(^+\) ion fluence of \(10^{13} \text{ ions-cm}^{-2}\) (a) phase mode image (inset: height mode; bar: 10 \(\mu\text{m}\)), (b) change of the irradiated areas from square- to rhombic shaped after annealing the substrates at 110°C for 1 hr in vacuum and (c) zoom-in scan into the rippled area.
From the change in shape, Poisson’s ratio $s$ of the rippled skin layer can be calculated according to $\nu_s = -\varepsilon_t/\varepsilon_a$, where $\varepsilon_t = (w - w_0) / w_0 = \Delta w / w_0$ and $\varepsilon_a = (l - l_0) / l_0 = \Delta l / l_0$, which are the transverse and axial strains, respectively. They represent relative changes of the width $w$ or the length $l$ of the irradiation field structure with respect to its original width or length. In the presented experiments the original lengths were those after annealing, i.e. after relaxation of the substrate (with rhombic shape of irradiated regions). Thus, $w_0 = 65.0 \, \mu m$ and $l_0 = 21.6 \, \mu m$. Since the surface was topologically structured in the direction of $l_0$, the true length $l_{0,c}$ following the amplitude of the ripples is $23.7 \, \mu m$. In the stretched case the corresponding lengths were $w = l = \sqrt{2} \times 32.0 \, \mu m = 45.3 \, \mu m$ owing to the quadratic shape. Thus, the Poisson ratio of the $\text{Xe}^+$-irradiated material is $\nu_s = -\frac{(45.3 \, \mu m - 65.0 \, \mu m)}{(45.3 \, \mu m - 23.7 \, \mu m)} \cdot \frac{23.7 \, \mu m}{65.0 \, \mu m} = 0.333 \pm 0.05$. The same analysis can be performed for the dimensions of the whole PS substrate to get the bulk value $\nu_b$ of non-irradiated PS. From stretching four different PS substrates to a length of 200% an average Poisson ratio of $0.309 \pm 0.030$ was obtained. Within the limits of confidence both data are comparable with the values of 0.334 for bulk PS and 0.38 for cross-linked PS at room temperature, respectively\textsuperscript{5,6}. The value for the irradiated area tends to be higher, which supports that it is more rubber-like, as it can be expected for cross-linked PS.

It is important to highlight two simplifications assumed for the estimation of Poisson’s ratio values which are stated below:

1) Monolithic fabrication of the substrates may not allow complete relaxation of the induced stresses in both, counter direction to that of stretching and also transverse direction to the stretching, as assumed for Poisson’s ratio estimation. In particular, relaxation in transverse direction is not decoupled from the bulk material as ripples are not formed in a direction parallel to stretching.

2) The measured lengths and the resulting Poisson ratio values are reported to be the ones at room temperature since all the lengths were measured at room temperature. But the actual relaxation processes occurred mainly at elevated temperature (110ºC) and the volume changes because of cooling were neglected (being very small).
Since the rippling occurs during annealing close to the glass transition of PS, where Poisson’s ratio is 0.5, this value is taken for the further analysis based on Eq. 1.\(^7\)

### 3.4.2 Determination of Young’s modulus

Estimations for cross-linked layer thicknesses using TRIM simulations are explained in details in the previous chapter. A cross-linked layer thickness, \(h\) of \(\sim 66\) nm was obtained for the exposure to \(\text{Xe}^+\)-ions. This led to a calculated Young’s modulus of \(E_s = 30E_b\) in the rippled areas (using eq. 1), with a ripple periodicity of 0.9 \(\mu\)m and a Poisson’s ratio of 0.5 for the modified areas and bulk PS. The significant increase of Young’s modulus in the irradiated areas with respect to the one of bulk PS indicated that the surface becomes locally stiffer. Furthermore, it confirmed again the cross-linking in the surface.\(^8\) To estimate an absolute value for \(E_s\), \(E_b\) had to be taken at the actual temperature of the rippling, i.e. at 383 K. This temperature is above the glass transition of PS, where Young’s modulus sharply decreases owing to the full segmental mobility of the polymer chains. At temperatures above the glass transition, an elastic regime, the so-called rubber plateau, occurs, which is characterized by a dynamic shear modulus, \(G_N^0\) (ratio of shear stress to the shear strain). It offers the possibility to calculate \(E_b\) at the rippling temperature according to \(E_b = 2\ G_N^0\ (1 + v_b)\).\(^9\) With \(v_b = 0.5\) and \(G_N^0 = 0.16\) MPa, we obtained \(E_b = 0.48\) MPa and \(E_s = 14.5\) MPa. This value provides \(G_N^0 = E_s/3 = 4.8\) MPa for the irradiated PS parts. A similar value of 2.6 MPa was found in literature for chemically cross-linked PS\(^{10}\). The results are summarized in the table 3.1.

<table>
<thead>
<tr>
<th>Modulus [MPA] at 110º C</th>
<th>Irradiated PS</th>
<th>Non-irradiated PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear ((G_N^0))</td>
<td>4.8</td>
<td>0.16</td>
</tr>
<tr>
<td>Young’s ((E))</td>
<td>14.5</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Table 3.1: Estimated moduli of the PS substrates
3.4.3 Determination of cross-linked network density and molar mass of cross-links

Using the estimated data for the irradiated PS and equations (2) and (3), it is possible to estimate a direct measure of the structural modification in the irradiated areas of PS in terms of average cross-link density, $\rho_{c,s}$, and the molar mass between the cross-links, $M_{c,s}$. For calculations, densities $\rho_r = \rho_g = 1.02$ g cm$^{-3}$ were used, which is the density of bulk PS at the glass temperature$^{11,12}$. Calculations yielded $M_{c,s} = 671 \pm 407$ g·mol$^{-1}$ and $\rho_{c,s} = 0.92 \pm 0.56$ cross-links·nm$^{-3}$. Hereby the uncertainties were mainly owing to the broad distribution of the ripple distances. The value of $\rho_{c,s}$ suggests that the irradiated areas exhibit a cross-link density comparable to that of chemically cross-linked PS in the order of up to 0.4 cross-links nm$^{-3}$.$^{13,14}$

In the case of ion beam induced cross-linking the cross-link density can be related to the density of vacancies $\rho_{H,C}$, that can be calculated from the above TRIM simulations according to,

$$I \ast \int_{x=0}^{x=h} n_{H,C}(x)dx = \rho_{H,C} \text{ molar}$$

$I$ is the ion fluence and $n_{H,C}(x)$ the number of vacancies per depth $x$ and ion, (as plotted in Fig. 2.5, chapter 2). Thus, the integral provides the absolute number of vacancies a single ion is generating in the modified PS layer of thickness $h$. The latter value is given by the assumption that the layer thickness is defined by the maximum slope in the function $n_{H,C}(x)$. For Xe$^+$ ions ($h = 66$ nm) and an ion fluence of $10^{13}$ ions·cm$^{-2}$, $\rho_H = 0.69$ H-vacancies·nm$^{-3}$ is obtained. In a similar way, the total density of vacancies including C(carbon)-vacancies is determined as 1.18 vacancies nm$^{-3}$. This value obtained by the above consideration is in excellent agreement with the cross-link density of $\rho_{c,s} = 0.92 \pm 0.56$ cross-links·nm$^{-3}$ calculated from the experiment. This comparison confirms again that the vacancies (both C and H), generated by the impacting ions, actually lead to cross-linking of the PS surface. Furthermore, it can be concluded that the irradiated areas in the polymer surface can be characterized in terms of structural polymer parameters by analyzing the rippling distance. Good agreement between the cross-linking density derived from the elastic mechanical properties and the vacancy density derived from ion
collision simulations indicate that the mechanical properties of an ion-irradiated PS surface can be described successfully with Eq. (1). Thus, the locally modified areas in PS behave elastically during annealing. This conclusion is also supported by the value of critical rippling stress, which is given by

$$\sigma_r = \frac{3}{36} \frac{9E_bE}{(1-\nu^2)(1-\nu_b^2)}$$ ........................ (5)

With the mechanical parameters that were discussed above, $\sigma_r$ of 1.84 MPa was obtained. This is lower than the maximum yield stress of ~ 4 MPa for PS. Therefore, rippling occurs prior to plastic deformation and thus can be described with an elastic theory.

### 3.4.4 Influence of ion species and fluence

Same irradiation experiments as for Xe$^+$ were performed with lighter Ar$^+$ and He$^+$ ions at different ion fluences. The kinetic energy of the ions was kept constant at 73 KeV. The ripple distance $R_p$ was observed to be dependent on both, the ion fluence and the type of the ions. For a quantitative comparison, $R_p$ is plotted versus the ion fluence for all investigated ion species (fig 3.3).

![Fig 3.3: Periodicity of ripples, $R_p$, on a PS surface in dependence of the ion fluence after Xe$^+$, Ar$^+$ and He$^+$-ion irradiation and subsequent annealing. The dashed lines are guide to the eye.](image)
The ripple periodicities are in the range between 900 nm and 21 µm for ion fluences between $10^{13}$ and $2 \times 10^{15}$ ions-cm$^{-2}$. It increases with the ion fluence and decreases with the mass of the ion. For a given atomic structure of the target, heavier ions (with bigger sizes) undergo more number of collisions with target atoms along their penetration path and lose their acceleration energies at a higher rate. This results in smaller penetration depths and in the given case of PS substrates, thinner cross-linked layers. In contrast, lighter ions (with smaller sizes) collide with less number of target atoms loosing less acceleration energy, and can penetrate deeper into the target. Hence lighter ions end up with higher penetration depths and for the PS substrates, thicker cross-linked layers. As generation of the collision cascades because of the ion irradiations is a statistical and collective effect, increasing ion fluence also increases their effective penetration depths and generate thicker cross-linked layers (for PS substrates). Ripple periodicity being inversely proportional to the cross-linked layer thickness (eq.1), decreasing periodicities were observed with increasing mass of the ion with same irradiation doses. Because of the statistical nature of the collision events, higher ion doses and longer penetration depths in the case of lighter ions (e.g. He$^+$) generate thick cross-linked layers with non uniform cross-linking densities. These non-uniformities in the cross-linked layers result in ripples with periodicities spanning over long range as observed in the form of large error bars. (Other sources of errors are already discussed in details in chapter 2, section: sources of imperfections.)

The results suggest that the rippling distance can be controlled over two orders of magnitude. With Eqs. (1) and (3), Young’s moduli and the cross-link densities were calculated, respectively (Fig. 3.4). As for the layer thickness $h$, the data is taken from the simulations (as plotted in Fig. 2.5, chapter 2). It is determined from the point of inflection on the H- and C-vacancy density distribution curves along the PS target depths. This point is determined from the minimum of the derivative of the H- and C-vacancy density (Fig. 2.5c, chapter 2).
As expected, both, Young’s moduli and the cross-link densities in the irradiated areas increase with the ion fluence and the mass of the ion. They are in the range of 8 - 880 MPa, which characterizes the irradiated PS as a rubber\textsuperscript{17}. The cross-link density is 0.5 - 55.5 cross-links-nm\textsuperscript{-3}, respectively, and equal or larger compared to usual chemically cross-linked PS\textsuperscript{18,19}. The cross-link densities perfectly match the density of vacancies, indicated as hatched boxes in Fig. 3.4. The lower edges of the hatched boxes represent the density of H-vacancies, the upper one the total density of vacancies including the C-vacancies. Since the most data points are close to the bottom of the hatched boxes, the cross-links are mainly generated by H-vacancies or it indicates that not all vacancies that are generated lead to cross-linking. The close relation between the density of H-vacancies and cross-link density is chemically reasonable since carbon radicals from C-H bonds enhance cross-linking without degradation of the polymer.
Good agreement between the network density, obtained from the analysis of the ripple distance, and the density of H-vacancies, obtained from simulations, confirms that cross-linking is a major process in the polymer upon ion irradiation at 73 KeV. Therefore, fits to the double-logarithmic plotted data reveal a slope of nearly 1 within the limits of confidence, i.e. the cross-link density and Young’s modulus depend linearly on the ion fluence. A linear plot of the experiment (inset of Fig. 3.4) shows that the ion mass and fluence determine the accessible range of Young’s moduli. As a consequence, the mechanical properties of the PS surface can be controlled more accurately with lighter ions owing to the weaker dependence on the ion fluence. In contrast, bigger local changes in the mechanical properties can be generated more conveniently with heavier ions with fluences that are easily realized in experiments. Hereby, the change of the ion species leads to different depths of the modified polymer layers. To decouple the layer thickness from the mechanical properties, the polymer can be covered by a sacrificial gold layer prior to ion exposure which is removed chemically before annealing.

![Network molar mass, $M_{c,s}$, versus ion fluence for irradiation with Xe$^+$, Ar$^+$, and He$^+$-ions (double-logarithmic). $M_{c,s}$ was calculated using Eq. (3) as described in the text. The dashed lines are linear fits.](image)
Beside the cross-link density, the network molar mass, $M_{c,s}$ (molar mass between the cross-links) is another important polymer parameter that can be determined from rippling (Eq. 3). Since it is inversely proportional to the cross-link density, it decreases with the ion fluence and the mass of the ion. $M_{c,s}$ is in the range of 10 - 1000 g·mol$^{-1}$. This is 1-3 orders of magnitude lower than the entanglement molar mass of $\sim 19$kDa for bulk PS and corresponds to 20 or less chain atoms between the cross-links (fig 3.5). Thus the irradiated areas of PS are densely cross-linked$^{23,24}$.

3.5 Conclusions

The irradiation of PS surfaces with ion beams led to pronounced chemical and physical modifications, when the ions were scattered at the PS chains. By annealing pre-stretched irradiated PS near the glass transition temperature, surface rippling occurs in the irradiated areas only, which can be described with an elastic model. The results showed that by changing the ion fluence and the mass of the ion, the local mechanical properties of a polystyrene surface layer could be tailored, as measured by Young’s modulus. The moduli obtained from rippling periodicities and elastic model assumptions were in the range between 8 and 800 MPa at the glass transition and characterize the irradiated PS as rubber-like. From that, the network density and the molar mass of entanglement were quantified. The obtained network density equaled the density of hydrogen vacancies generated through the scattered ions. The obtained molar mass of entanglement revealed that the PS was densely cross-linked. These results suggest that the superficial elastic properties of polymers can locally be tuned via cross-linking over a large range by irradiation with ions.

Although the mechanical properties and stability of these submicrometer-thick films are paramount for their effective utilization, there are currently few options for measuring such properties in thin-film systems$^{25}$. Conventional mechanical testing techniques such as nano-indentation have proved to be successful in materials such as ceramics and some metals, but are challenged by soft materials like polymer thin films, especially those of submicrometre thickness, or which exhibit significant viscoelastic
behaviour.\textsuperscript{26} Scanning probe microscopy has been used to measure the moduli of polymer films, but uncertainty in the tip size and/or contact areas often limit the accuracy of these types of measurements\textsuperscript{27,28}. The presented technique may find applications in characterizing mechanical properties of thin films of materials with complex visco-elastic nature.
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Chapter 4

PS: PtBA blend films - substructure formations

4.1 Introduction

The development of cost-effective and novel techniques for organizing soft materials like polymer blends in patterns with sub-micron length scales has found considerable technological interest\textsuperscript{1-4}. Material scientists world-wide have conducted investigations on utilizing inherent (or intrinsic) ability of polymer blends and block copolymers for segregation or phase separation to form sub-micron self-assembly patterns\textsuperscript{5-7}. The patterned polymer blend surfaces find applications such as functional elements in photonic, opto-electronic and other functional devices\textsuperscript{8,9}. In general, polymer blends are less miscible than low molecular weight mixtures and nearly every technical polymer blend exhibits phase separation. In the case of thin polymer blend films, phase separation is always dynamically coupled with preferential wetting of one or more components with the substrate and the air/vacuum interfaces\textsuperscript{10-12}. Even though self-assembly can establish a short-range order in polymer blend films, the induced patterns often lack long range coherence. This problem can be addressed by combining the self-assembly (with length scales of order of only a few tens of nanometers) with a top-down pre-patterning.\textsuperscript{13} But almost all the studies related to pattern induced phase separation of polymer blend/block co-polymer films involve pre-patterned surfaces fabricated by chemical modifications (e.g. monolayer depositions) of the substrates. These pre-patterning techniques involve chemical solvents, complicated procedures and have limitations in achieving complex geometries and smaller feature sizes. As explained in chapter 1, ion beam induced patterning offers fabrication of the pre-patterns while avoiding problems encountered with chemical pre-patterning and other top-down approaches. In this chapter, an ion beam technique for inducing pre-patterns guiding phase separation in the polymer blend films is presented.\textsuperscript{VI}

\textsuperscript{VI} Foot note 6: Results presented in this chapter are published as following journal publication:
1) Y. Karade, F. Madani-Grasset, R. Berger, V. Csiba, M. Rommel, A. Dietzel; Microelectronic Engineering; 2010; 87; 1569–1574
The top-down pre-patterning is achieved by a focused ion beam (FIB)\textsuperscript{14,15}. Such pre-patterned substrates consist of ‘relatively hydrophobic’ gold (non-polar i.e. neither acidic, nor basic but quite energetic) regions and hydrophilic silicon oxide (polar) regions. In the pre-patterned regions, spin-coated polymer blend films form two distinct and ordered morphologies. The influence of varying periodicities of the pre-patterned structures, pre-pattern geometries (1-D arrays of stripes and the 2-D arrays of squares) on the polymer blend phase separation is discussed. Furthermore, a mechanism for explaining this pre-pattern induced phase separation in polymer blend films is proposed.

4.2 Theory

4.2.1 Polymer blends

Polymer blend is a type of material in which two or more polymers are mixed together to create a new material with different physical properties\textsuperscript{16}. Formulating polymer blends consisting of chemically different polymers offers means to fabricate products with optimally tailored material properties\textsuperscript{17}. Additionally, polymer blend systems have been model systems in statistical physics for studying fundamental aspects of equilibrium/ non-equilibrium properties like phase diagrams, thermal composition fluctuations, conformational properties of the polymer chains, phase transition kinetics, dynamics of diffusion processes etc.\textsuperscript{18-21}. Many theoretical models have been established to explain physics behind phase separation of polymer components. But the model presented by Flory and Huggins on the basis of mean field approximations is most widely accepted.\textsuperscript{VII}

\textsuperscript{VII}Foot note 7: Flory-Huggins Theory for polymer blend phase separation is presented in Appendix IV.
4.2.2 Spinodal decomposition\textsuperscript{22,23}

Phase separation usually occurs by the mechanism of nucleation and growth. Spinodal decomposition, another mechanism for phase separation, is more common for polymer blends. Spinodal decomposition is a mechanism by which a solution of two or more components can separate into phases with distinctly different chemical compositions and physical properties. This mechanism differs from classical nucleation in that phase separation due to spinodal decomposition is much more subtle, and occurs uniformly throughout the material, not just at discrete nucleation sites. Since there is no thermodynamic barrier to the reaction inside of the spinodal region, the decomposition is determined solely by diffusion.

![Phase diagram showing spinodal decomposition](image)

**Fig 4.1: Phase diagram showing spinodal decomposition**

The upper section in the fig. 4.1 shows a one-phase region. The concave solid line marks the boundary between the one phase and the two-phase regions for the transition occurring by a binodal (nucleation and growth) mechanism. The dashed line represents the boundary between a binodal transition and a spinodal decomposition transition. The region enclosed by a dashed line constitutes a region in which phase transition by spinodal decomposition is the stable form. The two boundary lines coincide at only one point, $T_s$, i.e. upper critical solution temperature (UCST). The point $T_s$ corresponds to the
condition that the second derivative of the free energy with respect to composition equals to zero. If a point in the one phase region, say at A, with a composition given by AB is cooled suddenly to a temperature at B, then the phase transition would occur by spinodal decomposition alone resulting in phases corresponding to C and D as shown in the fig 4.1.

### 4.2.3 Solvent induced morphologies

Most challenges in studying solvent-induced patterns come from the difficulty in controlling the evaporation rate of the solvent. Because phase separation occurs during solvent evaporation, major changes in morphology happen at very short intervals of time while the composition of solvent quickly reduces at the evaporation front. In the case of thin polymer blend films, solvent evaporation rate can be controlled by spinning rate, but is not linear with time and is also strongly influenced by environment, such as relative humidity. Also, solubility differences of different blend components profoundly complicate the problem in thin blend films. Parameters influencing spin-cast morphologies can be categorized as blend compositions, polymer-polymer and polymer-substrate interfacial tensions, molecular weight and solubility of polymer components in solution, solvent evaporation rate and overall film thickness, although it is very difficult to systematically decouple the influences.

### 4.3 Experimental

#### 4.3.1 Silicon wafer cleaning and Au sputter deposition

Silicon wafers with the following characteristics: 4 inches in diameter, resistivity = 1 to 20 ohm-cm, thickness = 500 to 550 µm, emerging plane's indices are {100} were purchased from Westec Technologies, Netherlands. The wafers were cut into small rectangular pieces (approximately 15 mm × 20 mm) and baked in a furnace at around 500°C with a flow of (di)oxygen-rich gas in order to grow a 125nm thick and uniform silicon dioxide layer. The Si fragments were blown dry with oxygen-free N₂ and then treated with a piranha mixture (7 parts of 98 % sulfuric acid and 3 parts of hydrogen
peroxide; both chemicals 99.999% pure, purchased from VWR, Netherlands) to remove any adsorbed organic contamination (airborne mainly) as well as to cause the silicon oxide outermost surface to exhibit a large amount of strongly adsorbing and hydrophilic silanol sites (Si-OH groups). After piranha treatment, the substrates were thoroughly rinsed with milli-Q water (resistivity = 18.2 MΩ cm) (and then systematically stored in a milli-Q water bath to avoid further contaminations) Later, the substrates were coated with an ultra-thin gold (Au) film by sputter deposition (Turbo sputter coater k575X dual, Emitech Ltd., UK, settings: current of 65 mA for 15 s at 7e-3 mbar). The hydrophilicity of the Au-coated substrates was determined by contact angle measurements with de-ionized (DI) water as probe liquid using OCA 30, a video-based semi-automatic contact angle meter from DataPhysics Instruments Gmbh, Germany.

4.3.2 Phase shifting interferometry (PSI) using PLu 2300, Sensofar

PSI is an intensity-sensitive surface topography measuring technique that is fast, accurate, precise with sensitivity in height of the sub-nanometer order and reproducible. The instrument is a PLu 2300 by Sensofar-Tech (Spain), it uses a monochromatic light source that emits at $\lambda = 470$ nm. To compensate for the lack of flatness of the interferometer’s internal mirror and improve the system’s accuracy, a system error measurement was made with a certified flatness standard (CVD SiC reference flat, flatness = 0.011\(\lambda\), rms = 0.54Å by Rohm & Haas). A surface step at the film edge is used to estimate the thickness of a film, unlike ellipsometry or spectral reflectance. The field of view being considered must have uniform reflectivity for the measurement to be accurate. Silicon, silicon dioxide and gold have different optical constants and hence reflectivity, and hence an over-layer is needed to even them out. Therefore, the silicon pieces, partially covered with thin (150 µm in thickness) glass cover slips, were first sputter-coated with ultra-thin Au layers (fig 4.2a) at generator currents of 65, 75 and 85 mA for varying sputter deposition times of 5 to 15 seconds; then, the cover slips were removed carefully (fig 4.2b) and the samples were sputter-coated once more so that the entire surface area was covered in a thicker gold layer of nominal uniform thickness (fig 4.2c) close to 60 nm for the measurements. Note that the
cross-section clearly shows that the step is not vertical (fig 4.2d) due to the ‘shadowing effect’ caused by the thick glass cover slip four orders of magnitude thicker than the gold layers considered.

![Schematic and surface map](image)

**Fig 4.2: a through c: Schematic presenting substrate preparation for thin Au layer thickness measurement by PSI. d) PSI 3D surface map of the gold film step with a cross-section across the step (A-A’).**

### 4.3.3 Substrate pre-patterning

Pre-patterning of Au films was performed by pure physical sputtering using a FEI 800 (single beam) focused ion beam system (FIB) whose beam consists of Ga⁺ ions (travelling) at 30 KeV. VIII A moderate beam current of 70 pA with a nominal beam diameter of approximately 25 nm was chosen to enable the patterning of sub-micron features at the same time allowing for moderate patterning times. A dwell time (i.e., the time the beam remains at one pixel during the rastering process) of 1µs was used and the distance between each rastering pixel was about 11.25 nm. As gold films typically can not be removed homogeneously by FIB processing due to their polycrystalline nature and cluster formation during the sputter removal process, the total

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VIII Foot note 8: Experiments for pre-patterning the substrates by ion projection lithography techniques are presented in appendix V.
patterning time was adapted to almost completely remove the gold whilst minimizing the sputtering of the underlying SiOx layer. As will also be discussed in Appendix V, for this application not the ion dose alone is sufficient but also the local ion irradiation rate which determines occurrence of favorable sputtering and unfavorable deposition effects. After pre-patterning, the substrates were kept immersed in toluene baths. Then the substrates were ultra-sonicated twice in freshly filtered toluene (99.999% pure, purchased from VWR, Netherlands) baths and dried under N₂ jets prior to spin-coating the polymer blend solutions.

4.3.4 Polymer blend solutions and spin-coating

Polystyrene (PS : \( -\text{CH}_2-\text{CH}_3 \)) powder \( (M_w = 1.4 \times 10^4 \text{ g/mol}, \text{polydispersity index (PDI) = 1.07}) \) was synthesised in-house by anionic polymerization and poly-tert butyl acrylate (PtBA : \( -\text{CH}_2-\text{OC(CH}_3\text{)}_3 \)) powder \( (M_w = 2.1 \times 10^4 \text{ g/mol, PDI = 1.08}) \) was purchased from Polymer Source Ltd., Canada. Toluene being a good solvent for both of these polymers, PS and PtBA chains attain conformations with radii of gyration \( (R_g) \) of 18.9 nm and 21.3 nm when dissolved in toluene, respectively. Solutions with varying blending ratios (by weight) were prepared by varying the concentrations of PS and PtBA powders in toluene. The irradiated substrates were spin-coated with the above-mentioned solutions of PS: PtBA blends (in toluene) at speeds ranging from 2000 to 8000 rpm for 1 min, which resulted in the fabrication of thin polymer blend films. Films were also spin-coated on some non-irradiated substrates (with and without Au layer deposition) to study the blend film morphologies on the continuous silicon oxide as well as gold surfaces.

4.3.5 Substrate scanning with AFM

The film morphologies were measured by scanning force microscopy (XE instruments, Korea), in intermittent contact mode. Silicon cantilevers (Olympus OMCL AC 160 TS-W2) were used with a nominal resonance frequency of 300 kHz, a spring constant of 42 N/m and a tip radius smaller than 10nm. A best-fit plane was removed
from the raw data. For imaging, the cantilever was oscillated and scanned across the sample surface at or near its resonance frequency with constant ‘set point’ amplitude. Phase contrast images were also recorded to establish variations of elastic, visco-elastic and adhesion properties.

4.4 Results

4.4.1 Au layer sputter deposition

SiOx wafer pieces were sputter deposited with thin gold layers. Generator current and deposition times were varied for different depositions to vary the gold layer thicknesses and uniformity. The Au layer thicknesses were measured by phase shifting interferometry (see fig 4.2). It was observed that 15 seconds of sputter deposition at 65 mA of generator current yielded the desired 5 nm thick Au layers. The average film thickness determined over 20 cross-sections was (5.4 ± 0.5) nm. These settings were used for sputter-deposition of ultra-thin Au layers on all subsequent samples. The sputter deposited Au layers were further characterized to estimate surface roughness and wetting properties by AFM and contact angle measurements, respectively. AFM scans show fairly smooth surfaces with RMS roughness of 0.5 nm. The advancing contact angle made by de-ionized water drop with the Au coated substrate was recorded to be 88 ±0.5° (fig 4.3) compared to piranha treated silicon surfaces (i.e. surfaces with uniform SiOx layer) with contact angle of 0° with de-ionized water.

Fig 4.3: Contact angle measurement of an advancing drop of de-ionized water on 5 nm thick Au layer coated silicon substrate. Run number represents instance when the contact angle is recorded with a time lag of approximately 60 milliseconds between two consecutive runs. (Contact angle measurement Procedure is explained in details in chapter 5, section 5.3.3).
4.4.2 Pre-patterned substrates

Fig 4.4: AFM maps of FIB-irradiated substrates. a & c: Topographic maps: silicon oxide squares and stripes, respectively after being irradiated (step heights of 5-8 nm). b & d: Phase maps corresponding to a) and c) respectively that show variations in surface mechanical properties confirming the presence of two distinct surface materials making up a pattern consisting of Au and SiOx regions.

In the FIB-exposed regions of the substrates, the surface appears significantly rougher than in non-exposed regions. Au grains were sputtered away by the incident ions and the buried thermally grown silicon oxide was exposed again. Step heights of 5 to 8 nm were measured at the randomly chosen cross-sectional positions in the AFM topographic images (fig 4.4a & c). The corresponding phase images (fig 4.4b & d, respectively) also confirm the existence of a pre-pattern that consists of surfaces with different mechanical/adhesion properties with a phase difference of approximately 25°.
Pre-patterned substrates with 1-D arrays of stripes and 2-D arrays of squares were fabricated. The widths of the stripes and squares and the spacing between these features were varied from 2 \( \mu m \) to 0.5 \( \mu m \) for different arrays.

### 4.4.3 Polymer blend films on 1-D arrays of lines and stripes

The pre-patterned substrates were spin-coated with PS:PtBA blend solutions in toluene (1-3 % by weight) with varying blending ratios to form thin blend films. It was observed that only PS-rich blend films phase-separate into sub-structures that correlate to the pre-pattern geometries. AFM topographic maps of PS-rich (blending ratio of 7:3) blend films in the pre-patterned areas are shown in fig 4.5a-c. The blend film morphologies across the Au stripes were influenced by the adjacent SiOx stripes and the widths of both Au and SiOx stripes.

For the PS: PtBA films spin-coated from a solution with a blending ratio of 7:3, a 3 % (by wt.) concentration at rotational speed of 4000 rpm and decreasing stripe width from 2 \( \mu m \) down to 0.5 \( \mu m \), the sizes of the PtBA aggregates were measured to be \((930 \pm 40) \, nm\), \((750 \pm 40) \, nm\) and \((190 \pm 20) \, nm\) (see fig 4.5 a-c). The smaller aggregates, which are most probably lower molar mass chains of PtBA powder (PDI for PtBA is 1.07) or some unknown chemical impurities remaining only on the upper skin layers of PS matrix, were neglected in determining the aggregate size variations. For the pre-patterns with 2 \( \mu m \) wide stripes, approximately two PtBA aggregates are observed across one Au stripe. Also, these aggregates tend to be located near the Au-SiOx interface (fig 4.5 a), most probably owing to the affinity of the carbonyl groups of the PtBA chains towards the silanol sites of the silicon oxide outermost surface. In the case of pre-patterns with narrower stripes, especially for 0.5 \( \mu m \), the PtBA aggregates tend to line up at the center of the Au stripes (fig 4.5c). Furthermore, the number of PtBA aggregates along and within the Au stripe increases with decreasing stripe width. The average number of PtBA aggregates per 10\( \mu m \) of Au stripe was counted to be 5, 6 and 16 for 2, 1 and 0.5 \( \mu m \) wide stripes, respectively.
Fig 4.5: a, b, c) AFM topographic maps of PS: PtBA blend films spin coated on 1-D pre-patterns of silicon oxide and Au stripes of 2 µm, 1 µm and 0.5 µm in width, respectively (blending ratio of 7:3; film thickness of 120 nm; from 3 % blend solution at 4000 rpm).

Several PS: PtBA blend films in the pre-patterned regions with same blending ratio of 7:3, but with varying concentrations of 1 to 3 % (by wt.) and rotational speeds of 2000 to 4000 rpm were fabricated to vary the film thicknesses between 50 nm to 120 nm and reveled similar statistics as in the previous case related to average PtBA aggregate sizes and their number density as summarized in fig 4.6. For thinner films, the variations in PtBA aggregate sizes, irregularities in their number densities and spacing
along the Au stripes (especially for 0.5 µm wide Au stripes) are higher compared to the thicker films.

**Fig 4.6**: a) Averaged PtBA aggregate sizes & b) number of PtBA aggregates per 10 µm stripe length in dependence of the Au stripe widths for blend films (PS:PtBA blending ratio of 7:3 for all) with varying thicknesses of 50 to 120 nm.

### 4.4.4 Intrinsic wavelengths by 2D Fast Fourier Transform

In order to understand the pre-pattern induced phase separation exhibited by the PS-rich blend films, FFT analysis of the AFM images of the blend films (spin-coated on continuous Au surfaces) was performed and their intrinsic wavelengths were estimated (see fig 4.7). FFT analysis is used to decompose an image into its sine and cosine components. The resulting intensities in frequency domains can be represented in the form of a power density spectrum (PSD). Similar to the most of the polymer blend films, the FFT of the PS:PtBA films on continuous Au layer deposited on silicon wafer show radially isotropic distribution. For a given pattern, a characteristic structure size or intrinsic wavelength ($\lambda_m$) is inversely proportional to the abscissa value that corresponds to a peak in the PSD plot. It is important to note that intrinsic wavelengths are not the inherent lengths or sizes of the single polymer chains of the polymer species making up the blend films but rather are somewhat larger material clusters. These material clusters are controlled by processing parameters such as drying time, temperature, polymer...
weight loading, solvent volatility etc. Whereas the polymer chain lengths are dependent on the parameters set during the synthesis of individual polymer species.

![Fig 4.7: a) AFM topographic image of PS: PtBA blend film (blending ratio of 7:3 for PS:PtBA) on continuous Au surface as spin-coated at 4000 rpm for 1 min using 3\% solution (by weight) in toluene. b) 2d-FFT image of (a). c) Power spectrum density (PSD) distributions in frequency domains obtained from the 2D FFT analysis of the AFM images of the blend films (blending ratio of 7:3 for PS:PtBA) spin coated on the Au surfaces from blend solutions in toluene at varying solution concentrations (by wt.) and rotational speeds to vary the film thicknesses. Peaks can be interpreted as intrinsic wavelengths of the decomposed films (right hand side Y axis for the red curve)
In the case of the PS-rich films, variations in the power density spectrum profiles with varying spin-coating parameters were observed (fig 4.7c). Several peaks stand out, notably the ones with abscissa values 0.2 µm⁻¹, 0.4 µm⁻¹, 0.6 µm⁻¹, 0.8 µm⁻¹ and 1.4 µm⁻¹ from the PSD spectrum representing the film spin coated from 3 % blend solution with 4000 rpm speed (fig 4.7c, black curve). These values correspond to multiple intrinsic wavelengths ranging from 0.8 µm to 5 µm. For the lower rotational speed of 2000 rpm, the film shows single peak (maximum) at 0.2 µm⁻¹ (fig 4.7c, red curve) corresponding to the internal wavelength of 5 µm. As for lower blend concentration of 2 %, spin coating at 4000 rpm speed produced blend film with two intrinsic wavelengths corresponding to peak maxima of 0.2 and 0.4 µm⁻¹ (fig 4.7c, green curve). PSD peak maxima and thicknesses recorded for varying spin-coating parameters (viz. blend concentration and rotational speed) are summarized in the table 4.1.

<table>
<thead>
<tr>
<th>Spin-coating parameters</th>
<th>Film thickness (nm)</th>
<th>Abscissa on the PSD plot that corresponds to the peak maxima (µm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 %, 2000 rpm</td>
<td>50</td>
<td>0.3, 0.5, 0.7</td>
</tr>
<tr>
<td>2 %, 2000 rpm</td>
<td>114</td>
<td>0.2, 0.4</td>
</tr>
<tr>
<td>2 %, 4000 rpm</td>
<td>84</td>
<td>0.2</td>
</tr>
<tr>
<td>3 %, 2000 rpm</td>
<td>216</td>
<td>0.2, 0.4</td>
</tr>
<tr>
<td>3 %, 4000 rpm</td>
<td>120</td>
<td>0.2, 0.4, 0.6, 0.8, 1.4</td>
</tr>
<tr>
<td>4 %, 8000 rpm</td>
<td>185</td>
<td>0.1, 0.2</td>
</tr>
</tbody>
</table>

**Table 4.1: Thickness and PSD variations for PS/PtBA blend films in dependence of spin-coating parameters**

In general, lower rotational speeds tend to produce thicker films with single or two significant intrinsic wavelengths. With higher rotational speeds, thin films with several intrinsic wavelengths are fabricated. This effect is observed most probably because at lower speeds toluene evaporates slowly giving more time to form bigger aggregates by merging of smaller ones. At higher rotational speeds, solvent evaporates rapidly, and smaller aggregates with distinct sizes remain and are frozen in resulting in films with more than one intrinsic wavelength.
For the phase separation of a polymer blend film to be driven by the presence of an underlying pre-pattern, its intrinsic wavelength should be comparable with the pre-pattern periodicity. In the case of PS:PtBA blend, only PS-rich films exhibited pre-pattern-guided phase separation. Blend films with higher PtBA concentrations, e.g. with blending ratio of 7:3 for PtBA: PS, were not characterized by a phase separation guided by the pre-patterns of our experiments. For as-deposited PtBA-rich films, intrinsic wavelengths were estimated to be more than 5 µm. Whereas in the case of PS-rich films, the intrinsic wavelength estimates ranged from 0.8 µm to 5 µm. The latter compare favorably with the pre-pattern periodicities ranging from 1 µm to 4 µm. These intrinsic wavelength values provide an argument as to why PS-rich films show pre-pattern-induced phase separation while PtBA-rich blend films do not.

4.4.5 2D-FFT of PS rich blend films on Au regions of pre-patterns

On all the Au-coated stripes (within the pre-patterns), the blend films form sub-structures of PtBA aggregates in the PS matrix, similar to those observed on un-patterned Au substrates (fig 4.7a). However, as revealed by their PSD spectra acquired from 2D FFT analysis (see fig 4.8 a-c) it was observed that the number of maxima in the PSD spectra decrease with decreasing Au strip widths. For comparison, the PSD spectrum of the film on continuous Au surface is also presented (fig 4.8d). It can be deduced that, the blend film attains morphologies characterized by lower number of intrinsic wavelengths on the Au stripes of the pre-patterns, compared to continuous Au surfaces. Moreover, blend film forms morphology with only one intrinsic wavelength for sufficiently narrow Au stripes (e.g. 0.5 µm wide), suppressing other intrinsic wavelengths, especially but not exclusively those larger than the stripe width. In fig 4.9, intrinsic wavelengths of the 120 nm thick blend films in the Au stripes (presented in fig 4.5a-c) of pre-patterns are presented. PtBA aggregate sizes tend to align with stripe width values, especially for narrower Au stripes where aggregate size is half of the stripe width.

Foot note 9: Influence of increased contrast in wetting properties of the surfaces forming the pre-patterns on the induced phase separation of the PS/PtBA blend films is presented in appendix VI.
Fig 4.8: a, b, c) PSD distributions in frequency domains obtained from the 2D FFT analysis of the AFM images of the blend films on the Au stripes of the pre-patterns with varying widths of 0.5 µm, 1 µm and 2 µm, respectively. (films with blending ratio of 7:3; film thickness of 120 nm; from 3 % blend solution at 4000 rpm, shown in fig 5 a-c). d) PSD spectrum of the AFM image of the blend film on continuous Au surface (with same spin-coating parameters as for a, b and c). Dashed lines in a) to c) indicate λm equal to the Au stripe widths in respective spectra. Intrinsic wavelengths higher than the stripe widths in pre-patterned regions cannot occur as indicated by the absence of peaks on left of the dashed lines in all the three spectra a) to c).

Fig 4.9: Intrinsic wavelengths in dependence of Au stripe widths as taken from the 2D FFT spectra (fig 4.8 a,b,c) for 120 nm thick PS rich blend film. Dashed area represents aggregates larger than the stripe width which cannot occur.
4.4.6 Polymer blend films on 2-D arrays of squares

In the case of 2-D pre-patterns with square arrays, phase separation well in accordance with the pre-patterns was observed. AFM topographic maps of PS-rich blend films in the pre-patterned areas are shown in fig 4.10 a-c. On all the Au-coated ligaments separating the silicon oxide squares (within the pre-patterns), the blend films form PS scaffolds with very less to almost no PtBA aggregates. Instead, the PtBA aggregates occupy the exposed silicon oxide squares of the pre-patterns.

Fig 4.10: a, b, c) AFM topographic maps of PS: PtBA blend films spin coated on 2-D pre-patterns of SiOx square arrays on Au surface with varying sides of 2 µm, 1 µm and 0.5 µm, respectively (blending ratio of 7:3; film thickness of 114 nm; from 2 % blend solution at 2000 rpm).
The size of the PtBA aggregates varied in accordance with the square sides of 2 µm to 0.5 µm (fig 4.10 a-c). It is important to highlight that these images are recorded from closely situated pre-patterned regions (approximately 500 µm apart) of the same film. PS: PtBA films with varying thicknesses but same blending ratio of 7:3 (similar to 1-D pre-patterns of stripes) were studied. The variations in PtBA aggregate sizes were observed to be reduced, even for thin films, in contrast to the films in the case of 1-D pre-patterns of stripes. The AFM topographic maps presented in fig 4.5 and 4.10 show that the components of the blends films did phase-separate under the influence of the pre-patterns. Even though the PtBA aggregates appear to follow a somewhat periodical arrangement within the Au stripes (fig 4.5), some imperfections are observed in their organization such as irregular spacing between aggregates along the stripes and their remaining variation in size, especially for pre-patterns with 0.5 µm wide lines and absence of PtBA aggregates on the certain regions of the Au stripes (e.g. fig 4.5c, lower left). One of the probable reasons for these imperfections is the non-uniform solution concentration throughout the fluid (toluene is a better solvent of PS than it is of PtBA) and an aggravation of this tendency due to toluene evaporation during the spin-coating process. Toluene evaporation might have caused local variations in the solution concentrations and subsequently variations in PtBA aggregate sizes. The short range order of these guided phase separations is improved by introducing 2-D pre-patterns of arrays of squares instead stripes (fig 4.10). There might also be some line edge roughness caused by the pre-patterns fabrication (FIB). These effects are more pronounced for smaller structures (0.5 µm wide lines or squares). Since it was attempted to fabricate pre-patterns with minimal step-heights of 5-8 nm to avoid the influence of heights of the pre-patterned structures on the blend film morphologies, sputtering doses were kept rather low. This might have left small residual Au islands in the irradiated regions. Au islands would disturb the surface energy homogeneity (in amplitude and in nature) in the SiOx regions, which finally might have disturbed the ordered character of the polymer blend film after pre-pattern-induced phase separation. Furthermore, presence of more than one intrinsic wavelength (fig 4.7c, PSDs for PS rich blend films) most probably due to not-so-perfectly mono-disperse polymer blend components, (with PDI's of 1.07 and 1.08 for PS and PtBA respectively), might have aggravated the PtBA aggregate size variations in the
pre-patterned regions. The absence of PtBA aggregates on certain regions of the Au stripes may be due to local variations in surface properties of the Au layer because deposition of airborne contamination or impurities during or after pre-pattern fabrication by FIB may have occurred and could not be completely removed even after cleaning the pre-patterned substrates thoroughly before spin-coating.

4.4.7 Probable mechanism

The probable mechanism responsible for this pattern formation can be explained with the schematic presented in fig 4.11. At the onset of the spin-coating process, polymer chains are dissolved in toluene and can move quite freely in a random manner as long as the solution is rather dilute (fig 4.11a), in other words their coils do not overlap. In the case of 1-D pre-patterns of stripe arrays, as the solvent rapidly evaporates, the PS and PtBA chains close to the boundary between Au and SiOx stripes move towards Au-coated and uncoated silicon oxide regions, respectively, owing to their affinities towards different surfaces (fig 4.11b). More affinity of PS towards Au compared to SiOx causes higher concentration of PS chains at the edges of the Au stripes (fig 4.11c). The increased amount of PS at the edges coming in from both neighboring SiOx regions displace the trapped PtBA chains inwards. In a frozen state, this gives rise to their ordered arrangement (fig 4.11d). Similarly, richer PtBA regions were formed at the edges of the silicon oxide stripes forcing the trapped PS chains into the middle of the stripes. In the case of 2-D pre-patterns of square arrays, the PS and PtBA chains close to the boundary between Au and SiOx edges move towards Au-coated and uncoated SiOx regions as explained previously. But the polymer chains have four edges of the squares to move across in contrast to two for the stripes (fig 4.11e). Besides, the exposed silicon oxide area with square arrays is less by half compared to stripe arrays in the pre-patterned regions. This causes almost complete movement of PS chains to the Au regions and PtBA chains to the SiOx regions with almost no trapping of the PtBA and PS chains in the Au and SiOx regions, respectively. In a frozen state, this gives rise to more ordered phase separation compared to stripe arrays (fig 4.11f).
Fig 4.11: Schematic of the conjectured mechanism explaining the pre-pattern-induced phase separation of PS/PtBA blend film: a) randomly moving PS and PtBA chains dissolved in toluene before spin-coating (chain lengths are out of scale). b) as toluene evaporates during spin-coating, polymer chains at two interfaces of each stripe move towards favored regions of the pre-pattern. c) at the last stages of spin-coating, banks of PS and PtBA chains are accumulated at the Au and SiOx edges d) PtBA chains trapped between PS banks form point-like aggregates and PS chains trapped between PtBA banks form linear features. e) for 2-D pre-patterns of square arrays, polymer chains move towards favored regions of the pre-pattern from four interfaces in contrast to two for the stripes. f) Increased room for chain movement causes almost complete segregation of the blend components resulting in PtBA aggregates in square arrays surrounded by PS matrix on the Au surface.
4.5 Conclusions

FIB induced pre-patterned substrates were used for fabricating thin polymer blend films with phase separated aggregates. In the case blend films on the 1-D pre-patterns of stripes, the size of the PtBA aggregates were influenced by the Au stripe widths because the Au stripe width imposes a certain maximum. This effect reduces the aggregate dispersity and enhances the degree of order. Also, within the pre-patterned Au stripes, PtBA aggregates seem to organize themselves along the stripes with certain periodicities. These periodicities are stripe width-dependent. In the case of 2-D pre-patterns with square arrays, almost complete movement of PS chains to the Au regions and PtBA chains to the SiOx regions of the pre-patterns are observed with almost no trapping of the PtBA and PS chains in the Au and SiOx regions, respectively. In general, for all the pre-patterns, the short range order of the phase separation is enhanced by reducing imperfections within the pre-patterns, avoiding substrate contaminations and optimizing blend film thicknesses (by varying spin-coating parameters such as solution concentrations, rotational speeds) etc. Also, polymer blend films which already segregate in a mono-disperse manner (represented in the form of unique and narrow peak in power density spectra resulting from 2D FFT analysis) will exhibit improved short range order. A careful selection of a polymer blend system which exhibits intrinsically mono-disperse segregation would be essential to achieve structures from phase separation much smaller than the pre-pattern geometries but regularly arranged within.

Ion beam induced pre-patterning technique provides possibilities of writing complex geometries. The pre-patterned substrates may act as template of contact master (an alternative to imprint or micro-contact master). Pre-patterned substrates may find applications as starting surfaces for micro optic surfaces without need of any further structuring and polymeric substrates with optical properties can be deposited spatially on such substrates. Charging of Au regions of the pre-patterned substrates may be beneficial in tuning spatial arrangement of electrolyte polymers and once deposited, such layers can be utilized further to perform local electrolytic depositions and local photochemistry (chapter 1, fig 1.9) of other polymers/surfactants or chemicals.
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Chapter 5

PS: PtBA blend films - surface free energy calculations

5.1 Introduction

The morphologies of thin polymer blend films are mainly influenced collectively by three factors viz. phase separation, wetting and dewetting. The influence of each of these factors can be resolved only if one can differentiate the dominant mechanism for each stage of morphology development. Naturally, transient and final morphology cannot be interpreted without understanding wetting phenomena which is associated with surface tensions of the polymer blend components and the substrates. But, surface tension of polymer components alone can not describe the wetting behavior of the films. Contributions of van der Waals forces, acid-base interactions etc. in the resulting surface tension values also need to be calculated. Along with surface tension components, estimation of work of adhesion between polymer - substrate and polymer - polymer interfaces (for blend films) can provide quantitative explanations for the resulting blend film morphologies.

In this chapter, estimations of different interactions making contributions to surface tensions of the polymer blend components, PS and PtBA are presented. For these calculations, the advancing contact angles that probe liquids make on a flat, chemically homogeneous and smooth solid polymer films are measured. Suitable set of three probe liquids with known three surface tension components has to be chosen for both the polymer films. With these, surface tensions of both polymers can then be resolved into their acidic, basic and electrodynamic Lifshitz-van der Waals (combination of dipole and dispersive) interactions. Further, these surface tension components can be utilized to estimate work of adhesions that each of the polymers make with the surfaces (SiOx and Au). These estimated works of adhesion values can provide quantitative

Footnote 10: A manuscript presenting the results in this chapter is in preparation for journal publication.
measures for the affinities of PS and PtBA chains towards Au and SiOx surfaces, respectively. These selective affinities of polymer chains towards different surfaces are responsible for and can explain different morphologies that PS/PtBA blend films exhibited on continuous SiOx and Au surfaces as well as on pre-patterned surfaces (data presented in chapter 4).

5.2 Theory

5.2.1 Polymer blend film morphologies

Fig. 5.1 shows a set of possible configurations of morphologies for phase-separating binary polymer blend films on a substrate. Assuming an asymmetric blend system such that the A-rich phase is preferred at the top free surface (interface to air), one can hypothesize six equilibrium morphologies: a) A- and B-rich phases completely wet the surface and substrate respectively, b) A-rich phase completely wets both the surface and substrate and the B-rich is located in the middle, c) A-rich completely wets the surface and B-rich partially wets the substrate, d) A-rich completely wets both surfaces and B-rich is broken as droplets, e) both A- and B-rich dewets from the substrate and f) A-rich partially wets the surface and B-rich completely wets the substrate. Among the

![A-rich and B-rich phases configurations](image)

Fig 5.1: Morphologies of thin film polymer blends (asymmetric blend system with A rich phase preferred at free surface to air compared to B rich phase) driven by interplay between phase separation, wetting and dewetting.
suggested possibilities, the bilayer structure as suggested in a) and a tri-layer structure suggested in b) are not likely to persist due to large interfacial layers between A and B phases (which is expensive in terms of total change in free energy of adhesion required).

In the case of symmetric blend systems, blend films acquire transient or metastable configurations. Two of the most probable metastable configurations are presented in fig 5.2. Columnar domains connecting surface and substrate can be formed when phase A partially wets the free surface and the substrate (fig 5.2a). This case is possible if the kinetics of phase separation is much faster than wetting. In the second case, a tri-layer like structure as drawn in fig 5.1 b can be formed when wetting kinetics dominates (fig 5.2b). This structure may rupture by dewetting or be kinetically stabilized.

Fig 5.2: Morphologies of thin film polymer blends (symmetric blend system). In b), positions of A and B rich phase may interchange.

Besides the morphologies presented in fig 5.1 & 5.2, various other transient morphologies are also possible for asymmetric blends due to kinetic competition among phase separation, wetting and dewetting. Here, dewetting implies breakup of film to achieve minimization of free energy of the system by reducing surface or interface energy. Apart from these physical parameters, technical parameters such as blending ratios, blend solution concentrations and film thicknesses also influence the transient morphologies attained by the blend films.
5.2.2 Young’s equation

In the case of solids, direct measurement of surface tension is not possible as they don’t deform easily (unlike liquid drops). Therefore, an indirect method involving measurement of advancing contact angle that a probe liquid makes on a flat, chemically homogeneous and smooth solid surface is commonly employed (fig 5.3). Young [1805] presented a mathematical description, well known as Young’s equation -

\[ \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \] ........................(1)

Where \( \gamma_{SV} \) is solid-vapor interface tension, \( \gamma_{SL} \) is solid-liquid interface tension, \( \gamma_{LV} \) is the liquid-vapor interface tension which can be measured by the sessile drop method and \( \theta \) is the Young’s contact angle, commonly measured as the advancing contact angle.

Fig 5.3: Schematic presenting Young’s equation

5.2.3 Advancing contact angle\(^3\) (\( \theta \))

The angle formed between the moving liquid interface and the solid surface at the line of three-phase contact (the contact line) is called dynamic contact angle. The experimentally observed dynamic angle is referred as either an advancing contact angle or a receding contact angle based on advancing (wetting) or receding (dewetting) interface. Since solid surfaces are often rough or chemically heterogeneous, even equilibrium contact angles may not be single-valued, but will depend on whether the interface has been advanced or recessed, a phenomenon known as contact angle hysteresis and reflects the degree of heterogeneity of the surface. On such surfaces,
wetting lines tend to pin, and when they do eventually move they do so in an unsteady way. Such factors complicate both the measurement and the interpretation of the contact angle. This is especially true on surfaces that react, swell or reorganize in some way on contact with the liquid.

5.2.4 Work of adhesion

In 1869, Dupre\(^3\) proposed the concept of work of adhesion \(W^a\), defined as the work necessary to separate two dissimilar materials into two portions in a reversible way. Vann Oss et. al.\(^4\) rephrased the concept by introducing the change in surface energy \(\Delta G\) and proposed following equation for the work of adhesion

\[
\Delta G^a_{ij} = \gamma_{ij} - \gamma_i - \gamma_j = -W^a_{ij} \quad \text{.........(2)}
\]

Where \(\Delta G^a_{ij}\) is the free energy change due to adhesion i.e. the energy needed to bring materials \(i\) and \(j\) into contact from infinity (in a vacuum). In the process two interfaces disappear (represented by two negative signs) and one is created (represented by positive sign). \(\gamma_{ij}\), \(\gamma_i\) and \(\gamma_j\) are interfacial tensions between materials \(i\) and \(j\), surface tension of material \(i\) and surface tension of material \(j\), respectively. Replacing material \(i\) by solid film, presented by \(S\), and material \(j\) by probe liquid, presented by \(L\), and introducing well known Young’s equation (1) in equation (2) we get -

\[
\Delta G^a_{SL} = \gamma_{LV}(1 + \cos \theta) \quad \text{...............(3)}
\]

5.2.5 Surface tension components

The underlying concept of this analysis is that in the case of liquid advancing on the solid surface the free energy change due to adhesion, \(\Delta G^a_{SL}\), can be expressed in terms of the surface tension contributions of the interacting bodies. With prolonged deliberation lasting over decades, generalized and most accepted expression
for the free energy change due to adhesion\textsuperscript{5,6} related to different interactions is presented as follows-

\[
\Delta G_{ij}^a = -2(\gamma_{iLW}^L \gamma_{jLW}^S)^{1/2} - 2(\gamma_i^+ \gamma_{ij}^-)^{1/2} - 2(\gamma_i^- \gamma_{ij}^+)^{1/2} \quad \ldots \ldots . (4)
\]

Where $\gamma_i^{LW}$ represents a component of the surface tension related to the electrodynamic Lifshitz-van der Waals interactions of the substance i (combines all the three van der Waals types of interactions, viz. dispersion, induction and polarization). $\gamma_i^+$ and $\gamma_i^-$ are the acidic (or H-bond donating) and basic (or H-bond accepting) components of the surface tension of substance i, respectively. Electron acceptor-electron donor, or polar, interactions are essentially asymmetrical and can only be satisfactorily treated by taking that asymmetry into account. The polar component of the free energy of interaction between materials i and j is expressed by last two terms of equation (4) to take into account the electron acceptor interaction of material i with the electron donor of material j, as well as the electron donor interaction of material i with the electron acceptor of material j\textsuperscript{7}.

Rewriting equation (4) for an interface between a solid surface S, and probe liquid L, and replacing the term for the free energy change due to adhesion by RHS of equation (3), we obtain a relationship between surface tension components of the solid-liquid pair with measurable quantities viz. $\gamma_{LV}$, the liquid-vapor interface tension (can be measured by the sessile drop method\textsuperscript{8}) and the advancing contact angle $\theta$. The re-written equation is presented as follows.

\[
\gamma_{LV}(1 + \cos \theta) = 2(\gamma_s^{LW} \gamma_{LW}^S)^{1/2} + 2(\gamma_s^+ \gamma_{L}^-)^{1/2} + 2(\gamma_s^- \gamma_{L}^+)^{1/2} \quad \ldots \ldots . (5)
\]

By choosing a suitable set of three probe liquids (presented as $L_1$, $L_2$ and $L_3$ respectively) with known surface tension components (presented as $\gamma_{Li}^{LW}$, $\gamma_{Li}^+$ and $\gamma_{Li}^-$ with i = 1, 2 and 3 respectively for the three probe liquids), their liquid-vapor interface tensions (presented as $\gamma_{LIV}$, $\gamma_{LIV}$, and $\gamma_{LIV}$ respectively) and measuring the advancing contact angles (presented as $\theta_{L1}$, $\theta_{L2}$ and $\theta_{L3}$ respectively) that these probe liquids make on a flat,
chemically homogeneous and smooth solid surface, a system of three equations (6), (7)
and (8) with three unknown surface tension components of the solid film material viz. 
\( \gamma_s^{LW}, \gamma_s^+ \) and \( \gamma_s^- \) can be formulated as follows.

For solid film S & probe liquid L1:
\[
\gamma_{L1V}(1 + \cos \theta_{L1}) = 2(\gamma_s^{LW} \gamma_{L1}^{LW})^{1/2} + 2(\gamma_s^+ \gamma_{L1}^-)^{1/2} + 2(\gamma_s^- \gamma_{L1}^+)^{1/2} \ldots \ldots \ldots (6)
\]

For solid film S & probe liquid L2:
\[
\gamma_{L2V}(1 + \cos \theta_{L2}) = 2(\gamma_s^{LW} \gamma_{L2}^{LW})^{1/2} + 2(\gamma_s^+ \gamma_{L2}^-)^{1/2} + 2(\gamma_s^- \gamma_{L2}^+)^{1/2} \ldots \ldots \ldots (7)
\]

For solid film S & probe liquid L3:
\[
\gamma_{L3V}(1 + \cos \theta_{L3}) = 2(\gamma_s^{LW} \gamma_{L3}^{LW})^{1/2} + 2(\gamma_s^+ \gamma_{L3}^-)^{1/2} + 2(\gamma_s^- \gamma_{L3}^+)^{1/2} \ldots \ldots \ldots (8)
\]

From this system of three equations with three unknowns, surface tension components
\( (\gamma_s^{LW}, \gamma_s^+ \) and \( \gamma_s^- \) \) of the solid film can be estimated. In order to simplify the calculations,
three probe liquids with only one of the three acidic, basic and dispersive as dominant
interaction for each, respectively have to be chosen.

Rewriting RHS of the equation (4) for the surface tension components of
two solids such as a polymer film (presented as S1) spin-coated on solid substrate
(presented as S2) through its solution in solvent and equating to the RHS of equation (2),
work of adhesion between S1 and S2 materials can be estimated. It is important to
highlight that, these equations are applicable when the polymer chains are dissolved
completely in the solvent at the onset of spin-coating i.e. it’s a good solvent for the
polymer\(^9\), and the solvent wets the solid substrate at the onset of spin coating. In such
conditions, polymer chains can interact with the substrate material (while precipitating
out of the solution when the solvent evaporates during spin-coating) and exhibit
morphologies driven by their molecular affinities. The rewritten equation is as follows

\[
W_{S1S2}^a = 2(\gamma_{S1}^{LW} \gamma_{S2}^{LW})^{1/2} + 2(\gamma_{S1}^+ \gamma_{S2}^-)^{1/2} + 2(\gamma_{S1}^- \gamma_{S2}^+)^{1/2} \ldots \ldots \ldots (9)
\]
5.3 Experimental

5.3.1 Polymer blend films on continuous SiOx and Au surfaces

Silicon wafers with thermally grown SiOx layers (125 nm thick) were cleaned by piranha treatment and DI water. Some of the cleaned substrates were sputter deposited with thin Au layer (Procedures for piranha treatment and Au layer deposition are explained in chapter 4). Polystyrene powder (\(M_w = 1.4 \times 10^4\) g/mol, poly-dispersity index (PDI) = 1.07) was synthesized in-house by anionic polymerization and poly-tert butyl acrylate (PtBA) powder (\(M_w = 2.1 \times 10^4\) g/mol, PDI = 1.08) was purchased from Polymer Source Ltd., Canada. Solutions with varying blending ratios (by weight) were prepared by varying the concentrations of PS and PtBA powders in toluene. The substrates with continuous SiOx surfaces and Au surfaces were spin-coated with the above-mentioned solutions of PS: PtBA blends (in toluene) at speeds ranging from 2000 to 8000 rpm for 1 min.

5.3.2 Polymer films for advancing contact angle measurements

PS and PtBA powders were dissolved separately in toluene to form two different homo-polymer solutions (5 % by weight). The silicon substrates were spin-coated with the above-mentioned solutions at 2000 for 1 min, to form thick, homogeneous and smooth polymer films. The film topographies were measured by scanning force microscopy (XE instruments, Korea), in intermittent contact mode to record the film roughnesses.

5.3.3 Advancing contact angle measurements

Advancing contact angles formed by different probe liquids on different polymer films were measured using OCA 30, a video-based semi-automatic contact angle meter from DataPhysics Instruments GmbH, Germany. Very slow liquid flow rates of 0.6 \(\mu\)l/s were maintained to minimize the influence of liquid velocities on the contact angle measurements. Optical lens system of the instrument records the side-view image of the
probe liquid drop placed on the substrate. The system measures the angle made by the tangent drawn from the solid surface at the line of three-phase contact (the contact line) to the probe-liquid drop image as the contact angle. At the onset of the measurements, shape of the liquid drop changes with increasing liquid volume and hence the angle made by tangent also increases and it is known as the advancing contact angle. But the drop remains pinned at the solid surface without any change in its base diameter. When sufficiently high volume of the probe-liquid has been collected, the probe-liquid front starts advancing along the liquid-solid interface line, without changing advancing contact angle made by the liquid front same. The advancing contact angle values in the plateau regions of the measurements (with almost no change in contact angle for a significant change in the base diameter) are averaged and reported as the advancing contact angle made by the probe-liquid with the measured solid surface.

The measurements were performed with increasing volume of the probe-liquid and advancing contact angles were recorded after every 60 milliseconds and each measurement was reported as a ‘run’. For PS films probe liquids were di-ionised water, ethylene glycol and DMSO. PtBA films were probed with di-ionised water, DMSO and 1-bormo-naphthalene.

5.3.4 Surface tension components and work of adhesions estimations

The measured advancing contact angle values made by three different probe-liquids with PS and PtBA films along with the surface tension components and the liquid-vapor interface tensions of these probe-liquids (as reported in literature\textsuperscript{10,11}) were utilized to calculate surface tension components of the PS and PtBA films using equations (6), (7) and (8). The calculated surface tension component values of the PS and PtBA films and the surface tension component values of the Au and SiO\textsubscript{x} surfaces (as reported in literature\textsuperscript{12}) were utilized to estimate work of adhesion values for each of the polymers against Au and SiO\textsubscript{x} surfaces, respectively using equation (9) (four times for the four combinations viz. PS/Au, PS/SiO\textsubscript{x}, PtBA/Au and PtBA/SiO\textsubscript{x}). Finally, the
calculated works of adhesion values were utilized to interpret the morphologies exhibited by the blend films on these surfaces.

5.4 Results

5.4.1 Polymer blend films on continuous SiOx and gold surfaces

SiOx and Au layer coated substrates were spin coated with PS/PtBA blend solutions in toluene (1 % by weight) with varying blending ratios to form PS rich and PtBA rich blend films as shown in figure 5.4. Films with distinct morphologies are formed on different surfaces with same blending ratio (fig 5.4a & b). In the case of PS rich films on SiOx surfaces, a smooth film without internal aggregate structure is observed (fig 5.4a). In the case of PS rich blend films spin-coated on Au surfaces, PtBA aggregates are observed to be formed randomly scattered in a continuous PS matrix (fig 5.4b). The contrast in film morphologies on different surfaces, even when they are spin-coated with same parameters and blending ratio, is the result of different molecular interactions of PS and PtBA chains with Au and SiOx surfaces. These interactions are probed in terms of work of adhesions and presented in sections 5.4.3 and 5.4.4. Observed film morphologies are interpreted on the basis of work of adhesion (Wij) estimations in section 5.4.5.
Fig 5.4: AFM topographic images of PS: PtBA blend films as spin-coated at 2000 rpm for 1 min using 1% solution (by weight) in toluene: a) film with blending ratio of 7:3 for PS:PtBA on SiOx surface b) film with blending ratio of 7:3 for PS:PtBA on Au surface c) film with blending ratio of 7:3 for PS:PtBA, partially scratched with needle, on Au surface after methanol bath treatment. Section lines are shown in black (fig 5.4b), red and green (fig 5.4c).

5.4.2 Section analysis and selective solvent treatment

Various sections recorded across AFM images of the as spin-coated PS rich blend films show a step height of approximately 15 nm across the PtBA aggregates (fig 5.4b, fig 5.5: black section line and profile). To understand the film morphology along its thickness, the polymer blend film was scratched with a sharp tip needle of 20 µm diameter and the inorganic Au substrate beneath was exposed. Section analysis of the
AFM image of the film topography across the scratched region of the film revealed a film thickness of 50 nm. In order to establish the identity of different polymer components (PS and PtBA) observed on the film, selective solvent treatment was performed on this scratched spin-coated film surface.

### Fig 5.5: Section profiles at randomly chosen locations of the images

Section lines are shown in black (fig 5.4b) & red and green (fig 5.4c) and respective height profiles in same colors are shown here.

Between PS and PtBA, PtBA dissolves in methanol but it’s a poor solvent for PS. When the scratched film was immersed in methanol bath for 2 min, the corresponding step height across the PtBA aggregates increased to approximately 50 nm from 15 nm (fig 5.4c, fig 5.5: green section line and profile) clearly confirming the fact that, the matrix consists of PS chains and the PtBA chains form the aggregates which get dissolved in methanol selectively. Overall film morphology remains intact with same nominal film thickness of 50 nm across the scratched region (fig 5.4c, fig 5.5: red section line and profile). Comparison of step heights across PtBA aggregate regions recorded by the section analysis before and after methanol dissolution at different locations indicates that PtBA aggregates were formed as randomly segregated cylinders in a PS matrix with an average length of 35 nm (comparing step heights from fig 5 e: black and green section...
lines), reaching from surface almost to the inorganic substrate (Au surface) beneath. But the presence of an extremely thin layer of PS (~ 3 nm) in between PtBA aggregates and the Au surface as well as an extremely thin PS layer covering PtBA aggregates can not be ruled out completely.

The influence of varying spin coating parameters (viz. total blend concentration in toluene and rotation speeds) on the film morphologies spin-coated on Au surfaces was studied, keeping the blending ratio of 7:3 for PS: PtBA same. Variations in film thicknesses and the PtBA aggregate diameters with varying parameters were observed. Even for a given set of parameters, the diameters of the PtBA aggregates varied e.g. from 50 to 200 nm within a film (fig 5.4b). One of the probable reasons for these variations is the non-uniform evaporation of toluene during spin-coating. This might cause local variations in the solution concentrations resulting in variations in PtBA aggregate diameters. Secondly, not so perfectly mono-disperse polymer blend components, (with PDIs of 1.07 and 1.08 for PS and PtBA respectively) may have contributed to these PtBA aggregate diameter variations.

5.4.3 Advancing contact angles

Advancing contact angles of three probe liquids on smooth, homogeneous films of PS and PtBA spin-coated on silicon oxide substrates through 5 % solutions in toluene were measured. For PS films probe liquids were di-ionised water, 1-bromo-naphthalene and DMSO.
Fig 5.6: a, b, c) Contact angle measurements for PS films with different probe-liquids. d) AFM image of one of the PS films which were probed, showing very low roughness, spin coated on Si surface from 5% solution in toluene at 2000 rpm. Run number for a), b) and c) represents instance when the contact angle is recorded with a time lag of approximately 60 milliseconds between two consecutive runs.
The PtBA films were probed with di-ionised water, DMSO and diiodomethane.

![Graphs and images](image_url)

**Fig 5.7:** a, b, c) Contact angle measurements for PtBA films with different probe-liquids d) AFM image of one of the PtBA films which were probed, showing very low roughness, spin coated on Si surface from 5% solution in toluene at 2000 rpm. Run number for a), b) and c) represents instance when the contact angle is recorded with a time lag of approximately 60 milliseconds between two consecutive runs.

The advancing angle measurement for PtBA film with DI-water as a probe liquid showed advancing angles which varied between 85° to 95° and a saw-tooth profile of the curve was observed (fig 5.7b). These measurements suggest that DI water has a tendency to stick to the PtBA surface. It was observed that initially the apparent drop volume increases linearly, and advancing angle values increased up to 95.4 °. Suddenly, the drop front jumps to a new location as more liquid is supplied into the sessile drop.
The resulting contact angle decreased sharply from 95.4 ° to approximately 86°. As more liquid was supplied into the sessile drop, the contact angle increased again. Such slip/stick behavior could be due to non-inertness of the PtBA surface against DI-water. The mechanism behind this observed stick-slip behavior is not yet fully understood in the scientific community. For the presented analysis, contact angle values at the lower limits of the saw tooth profiles were considered to extract the required advancing angle. Advancing contact angles made by the different liquid fronts are summarized in table 5.1.

<table>
<thead>
<tr>
<th>Polymer Films</th>
<th>Measured advancing contact angles θ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DI water</td>
</tr>
<tr>
<td>PS</td>
<td>91.2 ± 1°</td>
</tr>
<tr>
<td>PtBA</td>
<td>86.4 ± 2°</td>
</tr>
</tbody>
</table>

Table 5.1: Contact angle measurements

5.4.4 Surface tension components and work of adhesions

The surface tension components for the liquids, Au and SiOx (as taken from literature) are summarized in table 5.2. Using the measured advancing contact angles and the data related to probe liquids in equations (6), (7) and (8), surface tension components for PS and PtBA were estimated and summarized in the table 5.2. Finally, the calculated surface tension components for polymers and substrates (taken from literature) were utilized to estimate work of adhesions for PS and PtBA with SiOx and Au surfaces (using equation (9)) as summarized in table 5.3.
### Surface tension components

<table>
<thead>
<tr>
<th>Probe liquids</th>
<th>Surface tension components ([\text{mJ/m}^2]) (^{(\text{from literature})^{10,11}})</th>
<th>Liquid -vapor interface tension (\gamma_{LV} \text{ [mJ/m}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\gamma_{LW}) (\gamma^+) (\gamma^-)</td>
<td></td>
</tr>
<tr>
<td>DI water</td>
<td>21.8  34.2  19.0</td>
<td>72.8</td>
</tr>
<tr>
<td>Di-iodomethane</td>
<td>50.8  0  0</td>
<td>50.8</td>
</tr>
<tr>
<td>DMSO</td>
<td>29.0  2.0  28.0</td>
<td>44.0</td>
</tr>
<tr>
<td>1-bromonaphthalene</td>
<td>43.5  0.0  0.0</td>
<td>44.4</td>
</tr>
</tbody>
</table>

### Substrates

<table>
<thead>
<tr>
<th>Substrates (^{(\text{from literature})^{12}})</th>
<th>Calculated values for polymers ([\text{mJ/m}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOx</td>
<td>35.0 ± 5.0  35.0 ± 4.0  383.0 ± 43</td>
</tr>
<tr>
<td>Au</td>
<td>39.33 ± 2  0.11 ± 0  7.91 ± 0</td>
</tr>
</tbody>
</table>

### Polymer films

<table>
<thead>
<tr>
<th>Polymer films</th>
<th>Calculated values for polymers ([\text{mJ/m}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>39.5 ± 2.4  0.63 ± 0.04  2.67 ± 0.15</td>
</tr>
<tr>
<td>PtBA</td>
<td>23.43 ± 2.0 0.06 ± 0.004  6.57 ± 0.5</td>
</tr>
</tbody>
</table>

**Table 5.2:** Surface tension components for PS and PtBA as determined by wetting analysis

<table>
<thead>
<tr>
<th>(W_{ij}^{a})</th>
<th>Work of adhesion ([\text{mJ/m}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>(W_{Au/PS}^{a})</td>
<td>63.8 ± 8</td>
</tr>
<tr>
<td>(W_{Au/PtBA}^{a})</td>
<td>84.2 ± 10</td>
</tr>
<tr>
<td>(W_{SiOx/PS}^{a})</td>
<td>146.6 ± 40</td>
</tr>
<tr>
<td>(W_{SiOx/PtBA}^{a})</td>
<td>160.5 ± 46</td>
</tr>
</tbody>
</table>

**Table 5.3:** Work of adhesions \(W_{ij}^{a}\) calculated from the surface tension components of the polymers and Au, SiOx surfaces
For SiOx surfaces, estimated values of $W_{SiOx/PS}^a$ and $W_{SiOx/PtBA}^a$ are $146.6 \pm 40$ mJ/m$^2$ and $160.5 \pm 46$ mJ/m$^2$, respectively. These $W_{ij}^a$ values indicate more affinity of PtBA chains towards SiOx surfaces compared to PS chains. For continuous Au surfaces, estimated $W_{Au/PS}^a$ and $W_{Au/PtBA}^a$ are $84.2 \pm 10$ mJ/m$^2$ and $63.8 \pm 8$ mJ/m$^2$, respectively. These $W_{ij}^a$ confirms more affinity of PS chains towards Au surfaces compared to PtBA chains.

5.4.5 Interpretation of polymer blend film morphologies

In the case of PS rich films on SiOx surfaces, no distinct morphology is observed in the surface analysis using AFM (fig 5.4a). It is important to note that, $W_{SiOx/PS}^a$ is only slightly lesser than $W_{SiOx/PtBA}^a$ which indicates that, in the case of SiOx surfaces, contrast in the affinities of PS and PtBA chains is lesser, with PtBA chains showing slightly more affinity. This analysis suggests that for SiOx surfaces, the film is formed according to the schematic suggested in left hand side of fig 5.8 (also see section 5.2.1). PtBA chains (as aggregates or films) are adsorbed directly on the SiOx surface owing to their more affinity towards SiOx compared to PS chains which cover the PtBA chains and rest of SiOx surface. This explains why at the surface probed by AFM, only a continuous PS layer is seen (fig 5.4a).

![Fig 5.8: Interpreted Morphologies of thin film PS:PtBA blend films (with excess of PS) on SiOx (left schematic) and Au (right schematic) surfaces on the basis of work of adhesion estimations.](image-url)
With decisively more affinity of PS chains towards Au surface compared to PtBA chains indicated by higher $W_{Au/PS}^{a}$ compared to $W_{Au/PtBA}^{a}$ the film is formed according to the schematic suggested in right hand side of fig 5.8 (also see section 5.2.1). In the case of PS rich blend films spin-coated on Au surfaces, PtBA aggregates are observed to be formed randomly scattered in a continuous PS matrix (fig 5.4b). Moreover, the PtBA aggregates are probably covered with very thin layer of PS chains. But, the presence of the PS layer in between Au and PtBA aggregates, as well as the PS layer covering the PtBA aggregates could not be confirmed by AFM analysis, most probably because these layers are extremely small (~ 3 nm) and hence could not be traced. Phase contrast images of the films in tapping mode were also not conclusive owing to very similar mechanical properties of the PS and PtBA materials. XPS analysis with depth profiling may provide experimental proofs for this suggested morphology structure, especially for the proposed upper PS layer covering the PtBA aggregates.

5.5 Conclusions

Surface tensions of both polymers (PS and PtBA) were resolved into their acidic, basic and electrodynamic Lifshitz-vander Waals (combination of dipole and dispersive) interactions. Further, the surface tension components were utilized to estimate work of adhesions that each of the polymers makes with the different substrate surfaces (SiOx and Au). These calculations provide quantitative arguments for the observed affinities of PS and PtBA towards Au and SiOx surfaces, respectively and provide explanations for the different morphologies exhibited by the blend films on different homogeneous substrates (shown in fig 5.4, fig 5.8) and pre-patterned heterogeneous substrates (shown in chapter 4). The estimated works of adhesion values for PS and PtBA with Au and SiOx surfaces provide quantitative arguments for the suggested mechanism for guided phase separation of the PS rich blend films in the pre-patterned regions. The quantitative analysis confirms that the chosen PS and PtBA blend system together with the pre-patterns of Au/SiOx regions are highly suitable for studying such pre-pattern induced phase separated blend film morphologies. Influence of increased contrast in wetting properties of the surfaces forming the pre-patterns on the induced phase
separation of the PS/PtBA blend films is presented in appendix VI. Such increased contrast is observed to be less favorable for guided phase separation.

Adhesion to solid surfaces can be desirable or undesirable depending on the context e.g. adhesion is desired in the case of paints, coatings, adhesives and fiber-matrix composites. Hence, study of surface tension components and subsequent work of adhesion calculations are important by industrial point of view. This interest is certainly due, in part, to the relatively modest cost of the wettability measurement. The experiments provide the dynamic contact angle (advancing or receding) as an experimental measurement responding very sensitively to minor modifications of the interfaces between solid, test liquid and vapor atmosphere. Consequently, wetting experiments are an effective tool for the assessment of the adhesive properties of polymer surfaces. Especially in the case of polymer blend thin films, such wetting analysis of different polymer blend components can be useful in predicting possible blend film morphologies on different surfaces.

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Chapter 6

Conclusions

Ion beam induced pre-patterning is shown as an effective technique for fabricating patterned polymeric substrates. The experimental results show two successful combinations of top-down patterning by ion beams with bottom-up organization of polymeric materials because of specific physical or chemical interactions induced by the ion beams with the materials. Two sets of ion-substrate interactions viz. 1) Ion projection direct cross-linking in PS substrates and 2) FIB sputtering of Au layers deposited on silicon wafers were implemented for top-down pre-patterning. These interactions were followed by, in the first case: ripple formations in cross-linked PS layers by inducing buckling instabilities; and in the second case: pre-pattern induced phase separation of PS/PtBA blend films. Both the cases were analyzed thoroughly for understanding the underlying physical/chemical processes behind these structure formations. The analysis provides a platform whereby these techniques can be applied to other materials, especially polymers for developing commercial applications.

6.1 Ion projection direct cross-linking (IPDC) and buckling instabilities

Locally structured PS substrates were fabricated using a two step process of the ion projection direct cross-linking followed by the relaxation of the orientated polymer chains by annealing the substrates above glass transition temperature. Surfaces of stretched polystyrene (PS) were locally cross-linked by irradiation with ions of different mass (He+, Ar+, Xe+) using a mask with square openings. By annealing above the glass temperature, rippling within the irradiated areas occurred. Periodicities of the ripples were observed to be strongly dependent on the penetration depths of the ion species and hence the cross-linked layer thicknesses. Even though ripples were oriented almost uniaxially, some imperfections were observed. These imperfections can be
reduced by optimizing ion doses and species. Analysis of the rippled substrates revealed that the irradiated areas in PS behave as described by an elastic model. The results show that by changing the ion fluence and the mass of the ion, the local mechanical properties of a polystyrene surface layer (typically 60 nm to 800 nm thick) can be tailored (measured by Young’s moduli). The moduli obtained from rippling periodicities and elastic model assumptions were in the range between 8 and 800 MPa at the glass transition and characterize the irradiated PS as rubber-like. From that, the network density and the molar mass of entanglement were quantified. These results suggest that the superficial elastic properties of polymers can locally be tuned via cross-linking over a large range by irradiation with ions.

Potential applications of this polymer substrate patterning technique can be seen in the development of organic solvent detectors, micro-vessels, substrates with rippled capillary wicking paths to study transport of the micro/nano-fluidic systems and tunable phase gratings for coherent beam intensities. Apart from these applications, presented analysis of the rippled structures may find applications in characterizing mechanical and chemical properties of thin material films and coatings with complex elastic properties.

6.1.1 Future scope

Further research related to IPDC of PS substrates should be focused on optimizing experimental parameters such as stretching ratios and ion doses on the ripple amplitudes. Studies for optimizing orientations of the ripples need to be performed so as to fabricate substrates suitable for developing industrial applications like diffraction gratings. Experiments for further reducing the ripple periodicities need to be performed by varying ion doses and different ion species. Availability of PMLP tool (see chapter 1) with higher demagnification factor and lower ion acceleration energies of 10 KeV may provide possibilities of structuring even smaller regions on the PS substrates and fabricating thinner cross-linked layers.
6.2 FIB pre-patterning and guided phase separation

FIB pre-patterned substrates consisting of silicon oxide and Au were used for spin-coating thin PS/PtBA blend films. In the pre-patterned regions, the PS-rich blend films formed two distinct and ordered morphologies. The influence of pre-pattern geometries (1-D arrays of stripes and the 2-D arrays of squares), varying periodicities of the pre-patterned structures, and spin-coating parameters (blending ratios and film thicknesses) were studied. For the PS-rich blend films on the 1-D pre-patterns of stripes, the sizes of the PtBA aggregates were influenced by the Au stripe widths. Intrinsic wavelengths (measured by 2D-FFT analysis) of the PS-rich blend films on the Au surfaces (in the pre-patterned regions as well as on continuous surfaces) confirm that film morphologies can be manipulated by the pre-pattern geometry (stripe widths). In the case of 2-D pre-patterns with square arrays, almost complete movement of PS chains to the Au regions and PtBA chains to the silicon oxide regions of the pre-patterns were observed. A phenomenological model was presented to explain the formation of ordered morphologies in the pre-patterns. Most significant parameter responsible for the specific morphologies, affinities of PS and PtBA towards Au and SiOx surfaces respectively, was quantified in terms of work of adhesions ($W_{ij}^a$). For SiOx surfaces, estimated values of $W_{SiOx/PS}^a$ and $W_{SiOx/PtBA}^a$ were 146.6 ± 40 mJ/m$^2$ and 160.5 ± 46mJ/m$^2$, respectively. For continuous Au surfaces, estimated $W_{Au/PS}^a$ and $W_{Au/PtBA}^a$ are 84.2 ± 10 mJ/m$^2$ and 63.8 ± 8 mJ/m$^2$, respectively. These $W_{ij}^a$ confirm more affinity of PS chains towards Au surfaces and more affinity of PtBA chains towards SiOx surfaces. For these estimations, surface tensions of both polymers (PS and PtBA) were resolved into their acidic, basic and electrodynamic Lifshitz-vander Waals (combination of dipole and dispersive) interactions. Wetting analysis (with advancing contact angle measurements and subsequent calculations) provides a strategy for estimating affinities of different polymers towards different substrates. Such analysis is important for developing stable coatings and other adhesion based applications.
Pre-patterned substrates may find applications as an alternative for micro contact master, substrate platform for fabricating micro optic surfaces. Charging of Au regions of the pre-patterned substrates may be beneficial in tuning spatial arrangement of electrolyte polymers and local electrolytic depositions of other polymers, surfactants or chemicals. Patterned polymer blend films can provide starting substrates for patterning functional groups as anchoring points for cells and enzymes. In addition to these probable applications, multi-component polymer thin films with controlled morphology have been already utilized in variety of devices, e.g. photo-voltaics, LEDs, FETs, and electronic circuits composed of polymer blends. The arrangement and size of domains in these patterned films have decisive impacts on performances of these devices.

6.2.1 Future scope

Pre-pattern induced phase separation of PS: PtBA blend films can be studied further with even more mono-disperse polymer blend components compared to the presented research. The FFT analysis showed PSD spectra of the PS:PtBA blend films with more than one intrinsic wavelength (chapter 4). Studies for further optimizing spin-coating parameters, different solvents for blend solutions should be performed to fabricate blend films ideally with one intrinsic wavelength, but in the sub-micron length scales. Such blend films are expected to exhibit morphologies in the pre-patterned regions with even smaller and more regular sub-structures. In the case of narrow Au stripes with widths of 0.5 µm, PtBA aggregates exhibited ordered arrangement along the length of the stripe even though patterning was performed only along the widths. These results can be further explored to study the influence of pre-pattern geometries to achieve more regular sub-structures. This would define a route towards extremely small, regular bottom up structures finely forced into long range order by course top down structures. Suitable blend systems and corresponding pre-patterned substrates can be chosen by performing wetting analysis and using work of adhesion estimations for different polymer/surface combinations. In addition, block co-polymer systems may be studied to achieve even smaller and regular sub-structures.
Appendix I

Nano-patterning techniques

A review of patterning techniques is presented to establish state of the art. Patterning silicon and non-silicon based devices can utilize conventional techniques such as photolithography, UV, X-ray, e-beam and ion beam lithography as well as non-conventional techniques like scanning probe lithography, dip-pen lithography, and soft lithography techniques like micro-contact printing, inkjet printing, rapid prototyping etc. At the end of the appendix, resolutions exhibited by the lithography techniques till 2009, their advantages and dis-advantages are summarized in table I.1.

I.1 Conventional lithography techniques

I.1.1 Optical lithography technique

Optical lithography\(^1\) is a photographic process by which a light-sensitive polymer, called a photoresist is exposed and developed to form 3D relief images on the substrate. In general, the ideal photoresist has the exact shape of the designed or intended pattern in the plane of the substrate, with vertical walls through the thickness of the resist. The final resist pattern has parts of the substrate covered with resist while the remaining parts are completely uncovered. The uncovered parts are subjected to subsequent pattern transfer mechanisms like etching, ion implantation etc.

The basic principle behind the operation of photoresist is the change in solubility of the resist in a developer upon exposure to light or other forms of radiation\(^2\). Contact and proximity lithography are the simplest methods of exposing a photoresist through a master pattern called a photo mask (fig I.1). Contact lithography offers
reasonably high resolution (down to about the wavelength of the radiation) but suffers from practical problems such as mask damage, and low yields making it unsustainable in most production environments. Proximity printing reduces mask damage by keeping the mask at a certain distance above the substrate (approx. 20 µm), but this deteriorates the achievable resolution significantly. For a mask-wafer gap of \( g \) and an exposure wavelength of \( \lambda \) this can be expressed\(^2\) as:

\[
resolution \sim (g \cdot \lambda)^{1/2} \quad \text{.......................... (1)}
\]

Because of the high defect densities associated with contact printing and the poor resolution of the proximity printing, the most common industrial method of exposure is projection lithography. In projection lithography, the image of the mask is projected on the substrate through a lens system. With huge improvements in computer aided lens designs, lens materials and manufacturing methods, almost perfect lens systems can be fabricated and the only distortions practically influencing the shape of the projected images are caused by the optical diffraction limits. The achievable resolution, defined as the size of the smallest feature that can be transferred with adequate control, is a result of two independent limitations: the smallest feature size that can be projected onto the wafer surface, and the resolving capability of the photoresist that is exposed by the projected image before being developed. From the projection side, resolution is determined by the wavelength of the imaging light (\( \lambda \)) and the numerical aperture (\( NA \)) of the projection lens and follows the Rayleigh resolution\(^2\) criterion:
\[ \text{resolution} = \frac{\lambda}{\text{NA}} \] ..............................(2)

All conventional photolithography techniques are limited by optical diffraction. Unlimited reduction of feature sizes is not possible with such a mask-based process: when the openings in the mask become smaller than or equal to half the wavelength of light, resulting structures will not be clearly defined as diffraction will disturb the patterns.\(^3\) Further disturbances occur if the substrate to be exposed is not planar i.e. if there are steps in which the resist is further from the mask than it is in other regions. Lithography systems have progressed from blue wavelengths (436 nm) to UV (365 nm) to deep-UV (248 nm) to today’s high-resolution wavelengths of 193 nm. The numerical apertures of available projection tools have risen from 0.16 to 0.93 NA systems (by 2006) producing features well under 100 nm size\(^4\). Moreover, novel variants of photolithography such as near field optics lithography\(^5\), near field scanning optical microscopy\(^6\) offer some success to circumvent the diffraction limit.

**Projection imperfections created by interference in the resist**

A problem associated with photo-resist exposure is the local occurrence of standing waves. Monochromatic light, when projected on the substrate, strikes the photoresist surface over a very limited range of angles and can therefore be approximated as plane waves. This light travels down through the photoresist and if the substrate is reflective, it is reflected back up through the resist. The incoming and reflected light waves interfere to form a standing wave pattern of high and low intensities along the photoresist depth causing a periodic ridge structure along the side walls of the resist features. As the pattern dimensions become smaller, these ridges can significantly affect the feature quality. These effects can be suppressed by coating the substrate with a thin absorbing layer called a bottom antireflective coating that reduces the reflectivity of the substrate as seen by the photoresist to much less than 1 %.
Depth of focus limitation

In addition to the diffraction limit, optical lithography is constrained by the achievable depth of focus. As previously discussed, in diffraction-limited optical systems, the resolvable line width is related to the numerical aperture (eq. 2). Hence, short wavelength and large numerical aperture need to be used to obtain narrow lines. However, the total depth of focus (DOF) of such a system is given by

\[ DOF \sim \frac{\lambda}{NA^2} \]  

Thus, steps taken to reduce the line widths result in very small depth of focus and hence demand extreme planarity of the wafer surface and thin resists.

I.1.2 Extreme ultraviolet (EUV) and X-ray lithography techniques

EUV lithography\(^8\) using wavelengths of 10 to 14 nm is a natural extension of optical projection lithography, as in principle, it only differs in terms of the wavelength. The technique is capable of printing sub-100 nm features while still maintaining a DOF of 0.5 \(\mu\)m or larger. But light at such wavelengths is strongly absorbed in almost all the materials. Consequently, imaging has to be carried out in vacuum and requires all optics, masks etc to be reflective rather than refractive. A major disadvantage is that very few techniques are available to produce suitable reflective coatings with acceptable very low defect densities.

X-ray lithography\(^9\) employs X-rays and allows high DOF values. In contrast to electron beam /ion beam lithography techniques, vacuum conditions are not required for X-ray lithography. Moreover, X-rays are not disturbed by low atomic
number (Z) particle contamination (dust). With low X-ray wavelengths of 10 Å or less, diffraction effects are negligible and proximity mask can be used to fabricate features of down to 50 nm sizes. But with no optics involved, only 1:1 shadow printing is possible. As no image reduction is possible, mask fabrication becomes very challenging.

I.1.3 Electron (e-) beam lithography

The fundamental constraints of diffraction limit and the standing waves in optical lithography techniques are bypassed with the advent of e-beam lithography technique. The basis of this technology is a finely focused electron beam (10 to 100 KeV) that is both scanned over a surface and blacked on and off under computer control. The electron beam exposes the resist where it strikes i.e., the electrons cross-link the molecules of the resist and thereby locally change its characteristics in such a way that subsequent development can either remove selectively the exposed part (positive resist) or remove the unexposed part (negative resist). Larger areas can be exposed by a precisely controlled step-wise movement of the substrate and repetition of the e-beam patterning.

E-beam technology has limitations due to the interactions of the resist materials with the electron beam, causing a charging effect, which restricts the achievable writing speeds with unavoidable discharging steps after certain time. A serious limitation for the resolution is the broadening of line-widths due to proximity effects\(^\text{11}\). Forward scattering of electrons in the resist leads to a broader spot diameter on the resist surface and back scattering of electrons from the substrate to the resist spreads the beam intensity over volumes in the proximity of the nominal beam position. This effect forms the ultimate limit for the minimum line width attainable by e-beam technique. DOF values (up to 10 µm are reported\(^\text{12}\)) are superior to optical lithography techniques, but still fall short of current industrial requirements. In addition, there are limitations resulting from imperfections of electron optics and mechanical and electronic for the scan area and scan rate. Also, very high vacuum is required making the apparatus more complex and expensive.
I.2 Non-conventional patterning techniques

Conventional lithography techniques (derived from optical and electron beam / ion beam techniques) are generally cost intensive and often unsuitable to handle the large variety of organic and biological systems available in nanotechnology\textsuperscript{13}. Also, there are many challenges to conventional lithographic techniques as they are approaching their fundamental size limits\textsuperscript{14}. These limitations have stimulated the research and development of alternative non conventional techniques viz. scanning probe based (e.g. scanning tunneling microscope lithography, dip pen lithography etc.), soft lithography (e.g. micro-contact printing, inkjet printing, rapid prototyping etc) techniques and bottom-up lithography techniques. Even though these methods are clearly interesting, and can lead to unique and interesting structures, currently there are some clear disadvantages: The ability of patterning alone is insufficient for successful application in advanced (nano) devices, since besides size and structure, control over position is also essential. Moreover, the ability to characterize the created structures and the feasibility of producing these structures on large areas is also important\textsuperscript{15}. Hence, most of the non-conventional patterning techniques are still in the development stage and not yet widely employed for mass-production of devices compared to the conventional techniques.

I.2.1 Scanning probe Lithography (SPL)

Scanning probe lithography is based on possibilities of conversion of a scanning force microscope set-up into a modification tool to achieve a variety of atomic and nanometer-scale modification approaches. Those approaches involve the interaction of a sharp probe with a local region of the substrate surface. Mechanical, thermal, electrostatic and chemical interactions, or several combinations among them, are currently exploited to modify surfaces at the nano-scale with probe microscopes. Some of the most interesting approaches are described below.
I.2.2 Scanning tunneling microscope lithography (STML)

STM\textsuperscript{16} uses a sharpened conducting probe tip with a bias voltage applied between the tip and the target substrate. When the tip is within the atomic range (approx. 1 nm) of the substrates, electrons from the sample begin to tunnel through the gap to the tip or vice versa, depending on the sign of the bias voltage. The exponential dependence of the distance between the tip and target to the tunneling current gives STM its remarkable sensitivity with sub angstrom precision vertically and sub nanometer resolution laterally. The induced tunneling current, which depends on topography and the local surface electronic properties, constitutes the STM image. The STML technique utilizes current coming through these probes for writing\textsuperscript{17-20}. STML does not suffer from electron back scattering and proximity effects because of the low electron energy as compared to conventional E-beam lithography. Furthermore, in some techniques, STML can be operated in ambient air, while E-beam lithography is always conducted under high vacuum conditions.

I.2.3 Physical probe lithography

Imaging of soft (organic) materials using atomic force microscope (AFM) in contact mode (with relatively hard tips and stiff cantilevers) may lead to surface damage. The concept of the controlled mechanical deformation of substrates using standard AFM tips can be transferred to almost any substrate. Mechanical patterning (force lithography) has successfully been applied to substrates and films of soft metals such as copper, gold, nickel, and silver\textsuperscript{21-24}. Besides the mechanically induced deformation of substrates and films, scanning probe techniques can also be used for the gentle movement of metallic\textsuperscript{25,26} or latex\textsuperscript{27} nano-particles into dimers, trimers, linear structures, and letters. The same method has also been applied for the local removal of parts of SAMs and Langmuir–Blodgett (LB) films\textsuperscript{28}. The limiting factor in creating
reproducible patterns is the stability of the tip itself, which is prone to deformation and contamination.

I.2.4 Dip-pen lithography (DPN)

DPN\textsuperscript{29} uses an AFM tip coated with a thin film of ink molecules such as alkanethiols that react with the substrate surface such as gold to write nano-scale patterns for lithography applications. When the tip is placed in a high-humidity atmosphere and is close to the Au substrate, a minute drop of water is naturally condensed between the AFM probe and the substrate. The drop of water acts as a bridge over which the ink molecules migrate from the tip to the gold surface where they are self assembled or anchored. The capillary transport from the probe towards the tip apex provides a resupply of new molecules for a continuous writing. The molecules and substrates are chosen in order to have chemical affinity and favor adhesion of the deposited film. A number of different ink materials have been successfully developed for DPN. These include inorganics, organics, biomolecules, and conducting polymers, which are also compatible with a variety of substrates such as metals, semiconductors, and functionalized surfaces.

I.3 Soft Lithography

Soft lithography is based on the use of a patterned elastomer as a stamp, mold or mask instead of rigid photo-mask\textsuperscript{30}. A master mold is first made by conventional lithographic techniques and an elastomeric stamp, most commonly made from polydimethylsiloxane (PDMS), is cast from this master mold. Soft lithography offers possibilities of patterning very small structures (down to 30 nm size) on non-planer substrates, unusual materials. Disadvantages include shrinkage of the masks during curing, swelling when subjected to non-polar solvents, thermal expansion and limited aspect ratios through sagging of the soft mask materials. Micro contact printing (µCP), micro-molding in capillaries (MIMIC), micro-transfer molding (µTM) etc. are some the most interesting soft lithography techniques and are described below.
I.3.1 Micro-contact Printing

Micro-contact printing is a process of transferring a material (ink) from the raised parts of the elastomeric stamp to the substrate when the two are in conformal contact. The ink, usually an alkyl-thiol, forms a self-assembled monolayer (SAM) on the surface of the substrates by covalent chemical reaction and this reaction is controlled spatially by the topography of the stamp\(^ {31-33}\). Once the master mold is made, this technique is not subject to diffraction or DOF limits. The deformability of the elastomer stamp allows printing even on rough surfaces. Micro-contact printing has some disadvantages with respect to fabrication of functional micro-devices. Physical properties of the elastomeric stamps (high coefficient of thermal expansion and low elastic modulus) make it difficult to achieve alignment of multiple lithography steps with accuracy less than 1 \(\mu\)m. Moreover, elastomeric stamps are not stable to many organic solvents at high temperatures.

I.3.2 Micro-transfer molding (\(\mu\)TM) and Micro-molding in capillaries (MIMIC)

In \(\mu\)TM the elastomer stamp is filled with a polymer precursor and the stamp is pushed against the substrate. The polymer in the stamp is cured and transferred to the substrate, and the stamp is peeled off\(^ {34}\). In MIMIC, the elastomer stamp is pushed against the substrate and the liquid polymer is applied to access the holes in the mold. The liquid winks into the cavities formed by the elastomer mold against the substrate\(^ {35}\). Once the polymer is cured, the stamp is removed. MIMIC has been used to fabricate plastic field effect transistors, Pt-Si diodes\(^ {36}\) etc.
In inkjet printing, a cylindrical jet of liquid is formed by forcing a fluid under pressure through an orifice. Surface tension forces create instabilities in the jet, causing it to break up into drops\textsuperscript{37,38}. By providing a single controlled-frequency disturbance, the jet can be forced to break up at precise time intervals into droplets of uniform diameter and velocity. The droplets can be charged by an electrostatic field during their breakup and deflected from a straight trajectory by a second electrostatic field. Charging the drops to different levels allows the drops to be deflected to one of the several locations on a substrate, or directly into a catcher or gutter for recycling or disposal. Inkjet printing can pattern few tens of micron size droplets at very high frequencies (typically 40 KHz). Patterning with inkjet printing is controlled by software and does not require masks or screens. It utilizes only the minimum amount of material necessary to perform required functions, reducing handling and cleanup costs. Apart from home/office printing, ink-jet printing has led to developments in many novel patterning applications such as rapid prototyping\textsuperscript{39}, electronics manufacturing\textsuperscript{40,41}, and photonics applications\textsuperscript{42}. 
<table>
<thead>
<tr>
<th>Non-conventional Lithography techniques</th>
<th>Demonstrated resolution until 2009 [nm]</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>STM lithography</td>
<td>&lt; 10 nm</td>
<td>Almost atomic scale writing, limited to no charging effect with low energy e-beam</td>
<td>Large writing time &amp; expensive set-ups required.</td>
</tr>
<tr>
<td>Physical Probe</td>
<td>~ 10 nm</td>
<td>Varity of local interactions on varying materials possible, cost effective</td>
<td>Prone to tip-damage and hence less reproducibility, large writing time</td>
</tr>
<tr>
<td>DPN</td>
<td>~ 10 nm</td>
<td>Local material depositions with bio materials like proteins, DNA etc, Relatively high writing speed</td>
<td>Effective mostly on planer substrates</td>
</tr>
<tr>
<td>Micro-contact</td>
<td>~ 100 nm</td>
<td>Easy, fast and low cost fabrication, Substrate with profiles can be accommodated.</td>
<td>Shrinkage and other deformations of masks, limited resolution</td>
</tr>
<tr>
<td>Micro-transfer/capillary</td>
<td>~ microns</td>
<td>High speed patterning, minimal ink-material usage</td>
<td>Limited resolution, limited print lifetime</td>
</tr>
</tbody>
</table>

Table I.1: State of the art of non-conventional lithography techniques

All the non-conventional lithography techniques discussed so far are resistless and provide direct substrate modifications through local interactions with the patterning tool. DPN is considered as an additive technique as it is mostly employed to locally deposit molecules on the substrates. Whereas, physical probe lithography is a subtractive technique.
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Appendix II

Ion-solid interactions & computational models

II.1 Ion-solid interactions

Ion beam induced patterning exploits interactions of accelerated positively charged ions and atoms of the substrate to be patterned. In this section, basic interactions occurring during irradiation events are explained. In the case of solid substrates, a number of mechanisms operate to slow the ion and dissipate its kinetic energy. The mechanisms can be subdivided as a) nuclear energy losses and b) electronic energy losses. Nuclear energy transfer occurs in discrete steps as the result of elastic collisions where energy is imparted from the nucleus of incident ion to the nucleus of target atom by momentum transfer. Electronic energy losses occur as the result of inelastic scattering events where the electrons of the ions interact with the electrons of the target atoms. The rate of ion energy loss per unit path length includes both nuclear and electronic energy losses. But most of the interactions responsible for patterning effects are associated with atomic displacements. As these displacements occur in energy ranges (typically > few KeV) which are dominated by nuclear energy losses, their description is sufficient for explaining various effects observed during patterning.¹

During elastic collisions, if the energy imparted to the target atom by the accelerated ion is more than the displacement energy ($E_{\text{disp}}$), the minimum energy required to knock a target atom far enough from its lattice or molecular site so that it will not return immediately, the target atom is ejected from its lattice site creating a vacancy. The ejected atom is also called recoil atom. A part of $E_{\text{disp}}$ is lost as lattice binding energy ($E_{\text{latt}}$), the minimum energy needed to remove an atom from a lattice site, leaving the recoil atom with energy $E_{\text{recoil}} = E_{\text{disp}} - E_{\text{latt}}$. If the recoiled atoms and the incident ion have energy, greater than $E_{\text{disp}}$, they both keep on penetrating deeper into the substrate, hitting other atoms, creating vacancies and thereby generating new recoil atoms. This phenomenon is known as collision cascade effect and forms the basis of all the ion beam...
induced patterning techniques (fig II.1). Collision cascade stops once energy of the incident ions or $E_{\text{recoil}}$ for recoiled atoms is below $E_{\text{disp}}$ and they remain into the substrate as interstitial atoms or foreign atoms (for amorphous substrates). Momentum and energy transfer during elastic collisions depend upon various factors such as acceleration energy of the incident ions, atomic size of the ions, atomic size of the target atoms/molecules and their atomic densities. Apart from these factors, the penetration depth of the ions also depends upon the angle of incidence with the substrate normal in the case of crystalline substrates. Although the definitions mentioned here refer to a single incident ion, ion beam induced processes involve collective effects of larger number of ions.

Fig II.1: Schematic diagram of ion-solid interactions.

II.2 Computational models

Ions irradiated onto a solid substrate can cause a wide range of phenomena, which can be divided into two main groups, namely processes taking place in the solid and processes at the solid–vacuum interface\(^2\). A number of factors determine which of the processes will dominate in each particular case, and they have to be carefully considered making sure no significant physical process has been left out. For such quantitative
analysis, various computational models (e.g. SRIM, TRIDYN) have been developed. Two well-known approaches have formed the basis of computational modeling of atomic collisions in solids, and have been applied to various phenomena arising during ion bombardment of surfaces, namely, the molecular dynamics (MD) and the binary collision approximation (BCA) methods. MD approach takes into account the simultaneous interaction between many particles in the solid, and is, undoubtedly, more accurate (e.g. TRIDYN). In addition, MD codes are suitable for the simulation of chemical reactions at surfaces, nucleation and growth processes as well as for the study of near-equilibrium atomistic processes such as stable defect formation, defect diffusion, etc. However, at sufficiently high energies of ions and cascade atoms, BCA is a more useful approach as it approximates the atomic collisions in solids by a sequence of binary collisions. The BCA models can be classified in two groups. One of the groups, represented by MARLOWE and alike, has the locations of the potential target atoms determined by a well-defined crystal structure. Stochastic methods play a role only in selecting the initial impact points of the bombarding particles on the surface, and in evaluating the thermal or chemical disorder. The other class of models includes structure-less, i.e. non-deterministic methods used to define both the impact parameters for the collisions and the flight distances. This class of models is referred to as Monte Carlo (MC) type of codes, and the best known programme in this class is TRIM code (Transport of Ions in Matter) which is a part of freely available software package on internet, SRIM (Scattering Range of Ions in Matter).

Different computational approaches are summarized in table II.1. As interactions of ions beams (He+, Ar+, Xe+ and Ga+) accelerated at high energies (73 KeV) with different amorphous substrates such as polystyrene (PS) and thin metal layers (in amorphous form) are utilized to create various surface effects during this research work, TRIM code is used for quantitative analysis and overviewed briefly as in the next section.
Computational approaches for ion-solid interactions

<table>
<thead>
<tr>
<th>Features</th>
<th>Software packages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stochastic approach (Monte Carlo), Can assume crystalline or amorphous structures</td>
<td>TRIM (code from freeware software package SRIM)</td>
</tr>
<tr>
<td>Considers dynamic conditions, Suitable for studies involving defect formations, diffusion at higher irradiation doses, Needs more computation power</td>
<td>TRIDYN</td>
</tr>
</tbody>
</table>

Table II.1: computational approaches and corresponding software packages for simulating ion-solid interactions

II.2.1 TRIM code

TRIM is a group of programs which calculate the stopping and range of ions (10 eV - 2 GeV/amu) into the substrate using a quantum mechanical treatment of ion-atom collisions. This calculation is made very efficient by the use of statistical algorithms which allow the ion to make jumps between calculated collisions and then averaging the collision results over the intervening gap. The ions have long range interactions creating electron excitations such as plasmons (oscillations of free electron density against the fixed positive ions) within the substrate. These are accounted for by including a description of the collective electronic structure of the substrate and interatomic bond structure in the calculations. The charge state of the ion within the target is described using the concept of effective charge, which includes a velocity dependent charge state and long range screening due to the collective electron sea of the substrate. TRIM allows simulations of substrates made of compound materials with up to eight layers, each of different materials. It calculates both the final 3D distribution of the ions and also all kinetic phenomena associated with the ion's energy loss: substrate damage, sputtering, ionization, and phonon production. As an example, description of substrate damage calculations is explained.
**Detailed Calculation with Full Damage Cascades** - This option follows every recoiling atom until its energy drops below the lowest displacement energy of any target atom. Hence all the collisional damage to the substrate is analyzed. The results show the number of displacement collisions (indicating how many substrate atoms were set in motion in the cascade with energies above their displacement energy), number of vacancies generated in the substrate, number of interstitial atoms etc.

![Depth vs. Y-Axis](image1)

![Transverse View](image2)

**Fig II.2:** Example of TRIM recoil cascade calculations: Xe\(^+\) ions (73 KeV) irradiated on Polystyrene (PS) substrate. a) Calculated path of Xe\(^+\) ions (shown by red line) across the depth of the PS substrate and resulting cascade effect displacing C and H atoms (shown by green and blue lines respectively). b) Transverse view of the cascade shows effects caused because of the scattering of Xe\(^+\) ions in PS. c) Final atomic distributions in PS (C and H) along with Xe\(^+\) ions remaining as interstitials.
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Appendix III

Buckling instability: Biot’s theory

Fig III.1: Buckling instability phenomenon

Mechanical buckling instability of an elastic layer embedded in an elastic medium was considered by Biot\textsuperscript{1-3}. Here the stability of a surface layer is explained following Biot’s theory. The phenomenon is analyzed using logic similar to that introduced by Euler to describe the mechanical instability of a rod under compressive force. The upper surface of the coating is free, and its lower surface is adhered to the half-space as illustrated by Fig. III.1. The coordinate system is defined such that the $Y$ axis is perpendicular to the coating plane ($y = 0$). Compressive force is applied to the elastic layer along the $X$ axis. The shear stresses between the substrate and the coating are neglected.
Bending of an elastic layer on an elastic foundation is described by the following equation

$$\frac{EJ}{(1-v_s^2)} \frac{d^4y}{dx^4} + F \frac{d^2y}{dx^2} + ky = 0 \hspace{1cm} \text{………………(1)}$$

where $E_s$ is the Young’s modulus, $I = Wh^3/12$ is the second moment of area of the layer cross section about the axis of bending, $v_s$, $h$ and $W$ are the Poisson’s ratio, thickness and width of the surface layer, respectively. $y$ is the displacement of the layer. $F$ is the longitudinal compressive force in the layer.

The effect of the underlying half-space is represented by lateral load $k_y$ acting on the surface layer. According to Biot, the Winkler’s modulus of half-space, $k$ is

$$k = \frac{E_sW}{(1-v_b^2)} \frac{\pi}{R_p} \hspace{1cm} \text{………………(2)}$$

Where $v_b$ and $E_b$ are Poisson’s ratio and Young’s modulus of the bulk substrate and $R_p$ is the ripple periodicity, induced by the buckling instability. Equation 2 is valid for sinusoidal deflection of the surface layer.

$$y = A\sin\frac{2\pi x}{R_p} \hspace{1cm} \text{………………(3)}$$

The compressive force in the coating, $F$, is found by substituting Equations 2 and 3 into Equation 1

$$F = E_sJ \left( \frac{4\pi^2}{(1-v_s^2)R_p^2} + \frac{E_bW}{4\pi(1-v_b^2)E_sJ} \right) R_p \hspace{1cm} \text{………………(4)}$$

The function $F(R_p)$ is always higher than zero at any $R_p$. $F(R_p)$ has a minimum at some wavelength. If the load in the coating, $F$, is lower than the minimum $F^*$, the coating is stable. In contrast, if the load is higher than $F^*$, the coating is unstable and folds. At the minimum, the derivative $dF/dR_p$ is equal to zero. Differentiation gives the expression for the critical wavelength

$$R_p = 2\pi h \sqrt{\frac{(1-v_b^2)E_s}{3(1-v_s^2)E_b}} \hspace{1cm} \text{………………(5)}$$
Rearranging the equation (5) for Young’s modulus\(^5\) of the buckled layer in the surface
\((E_s)\), we get

\[
E_s = 3E_b \left( \frac{1 - v_s^2}{1 - v_b^2} \right) \left( \frac{R_p}{2\pi h} \right)^3
\]  

……………….. (6)

The critical buckling stress \(\sigma_r\), \((F^*/hW)\) is given by

\[
\sigma_r = \sqrt[3]{\frac{9 E_s E_b^2}{64(1 - v_s^2)(1 - v_b^2)}}
\]  

………………..(7)

Equations (5) and (6) predict the direct proportionality between the ripple periodicity \(R_p\) and the thickness \(h\) of the surface layer, and an increase in \(R_p\) with the decrease in bulk substrate rigidity. \(R_p\) remains independent of the applied compressive force as long as it is above \(F^*\). But more compressive force will deform the underlying soft substrate resulting into increased amplitude of the ripple structures and stretching of the ripples in a direction perpendicular to the compressive force. Above certain limit, increasing compressive force may induce cracks in the surface layer.

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Flory-Huggins theory for polymer blend phase separation

Flory-Huggins theory\textsuperscript{1-3}

To describe the immiscibility of polymer components in a blend, the free enthalpy of mixing $\Delta G_m$ is considered.

\[ \Delta G_m = \Delta H - T \Delta S \] .................(1)

Where, $\Delta G_m$ is the difference in free enthalpy of the mixed system and the two monocomponent systems. $\Delta H$ is the enthalpic and $T \Delta S$ the entropic contribution. The enthalpy $H$ of a mixture of two chemically different components (A, B) is different from the phase separated system because the mixture features more unfavorable A-B contacts compared to the phase separated situation. The chemical interaction of A-B contacts is not the same as A-A or B-B contacts and therefore, the chemical potential depends on the relative concentrations of A and B. The change in enthalpy is given by the following phenomenological expression.

\[ \Delta H = nk_b T \chi \phi_A \phi_B \] .................(2)

$n$ is the total number of monomers and $\Phi_A (= n_A / (n_A + n_B)$ $\&$ $\Phi_B (= n_B / (n_A + n_B)$ are the volume fractions of the two polymer species. $\chi$ is the phenomenological interaction parameter which describes the mean difference of interaction between monomers compared to identical monomers.

For the change in entropy the number of conformations of the system is considered to be

\[ \Omega = \frac{(n_A + n_B)!}{n_A!n_B!} \] .................(3)
This leads to the entropy
\[ S = k_B \ln \Omega = -n k_B (\Phi_A \ln \Phi_A + \Phi_B \ln \Phi_B) \] .........(4)

By transformation to the entropy of mixing
\[ \Delta S = -n k_B \left( \frac{\Phi_A}{N_A} \ln \Phi_A + \frac{\Phi_B}{N_B} \ln \Phi_B \right) \] ............(5)

With \( N_A \) & \( N_B \) being the degrees of polymerization.

The factors \( 1/N_A \) and \( 1/N_B \) show the strong influence of the length of polymers on their mixing behavior. It is responsible for the tendency of polymer blends to phase separate.

The complete expression for the free enthalpy of mixing is the Flory-Huggins relations for polymer mixtures and solutions.
\[ \Delta G_m = -n k_B T \left( \frac{\Phi_A}{N_A} \ln \Phi_A + \frac{\Phi_B}{N_B} \ln \Phi_B + \chi_{(-\Phi_A, \Phi_B, T)} \Phi_A \Phi_B \right) \] ............(6)

For a de-mixing blend, the plot of \( \Delta G_m \) versus the volume fraction \( \Phi \) of one of the two components shows two minima. The two minima mark the equilibrium compositions of the two co-existing phases. By lowering the interaction parameter or the degree of polymerization a variation of \( \Delta G_m \) with only one minimum can be obtained.

Fig IV.1: Free enthalpy of mixing versus the volume fraction of one of the components.
Even though Flory-Huggins theory accounts for upper critical solution temperature (UCST) behaviour, it fails to describe for the universal property of polymer solutions to phase separate on heating i.e. lower critical solution temperature\(^4\)-\(^5\) (LCST behaviour). Another approach based on equation-of –states\(^6\)-\(^7\) helps to explain this UCST behaviour. Also, FH theory employs a very simple mean field approximation that effectively ignores the details of the polymer chain connectivity, and therefore, can not distinguish between linear, star, branch, comb etc. polymer structures. Many other theories have been developed to explain polymer blend thermodynamics\(^8\)-\(^10\) to cover the drawbacks of Flory-Huggins model. In spite of these limitations, this model is still widely accepted.

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Appendix V

Pre-patterns by ion projection lithography

V.1 Introduction

As presented in chapter 4, the gold layer coated silicon substrates were bombarded with focused ion beams (FIB) to sputter away Au grains in the irradiated regions and expose silicon oxide surface underneath, thereby creating pre-patterns of relatively hydrophobic (Au) / hydrophilic (silicon oxide) regions. Ion projection lithography techniques were also attempted to fabricate such pre-patterned substrates. The major advantage of ion projection lithography is that an entire substrate can be exposed to the ion beam in a single operation because masks are covering relatively large areas, which can be further increased using step and repeat techniques. This allows quick fabrication of large number of two dimensional features, making the process desirable for mass production. Pre-pattern design transfers in accordance with the mask openings on the Au/SiOx surfaces are observed when the substrates are fabricated with projection lithography tools. As will be discussed in the following, the lower local ion irradiation rates associated with the parallel projection approach can lead to unfavorable deposition processes in particular if vacuum conditions are not satisfactory.

V.2 Experimental

V.2.1 Stencil mask design and fabrication

A stencil mask with desired array of openings (of lines and squares shapes) was designed at IMS, Stuttgart. The mask consisted of approximately 20 µm thick silicon membrane with the openings etched by e-beam in accordance with pre-defined pattern. Optical microscope images of the different sections of the stencil mask used for ion beam irradiations on different machines (IPL and MLT) are presented in fig V.1. Irradiated Ar⁺ ions are expected to sputter away Au layers deposited on the silicon substrates exposing silicon oxide surface in accordance with the line and square shaped openings of the mask.
The patterns were defined such that the same mask could be used on two different machines viz. IPL tool, an ion projection tool which operates with a demagnification factor of 8.3:1 and MLT tool, where ions passing through the mask openings are projected perpendicularly onto the target substrates without any demagnification (both situated in Biont Ltd, Bratislava, Slovakia). The pattern consisted of 5 sets of arrays of lines of widths 2µm to 0.5 µm and another 5 sets of arrays of squares with 2µm to 0.5 µm sides. In all the arrays, pitches of the arrays were kept equal to half widths of the respective features. As the mask was also set to be used on IPL machine, another two sets of arrays of lines and squares were etched on the mask with widths varying from 16 µm to 4 µm so that the features with desired dimensions of widths varying from 2µm to 0.5 µm were obtained on the substrates.

Fig V.1: Optical images of the stencil mask at different sections: a) arrays of lines and b) array of squares.
V.2.2 Silicon wafer cleaning and Au sputter deposition

All silicon substrates were cleaned with piranha solutions and later, the substrates were coated with an ultra-thin Au film (of approximately 5 nm) by sputter deposition. (Specifications for piranha treatment and Au deposition are mentioned in the ‘Experimental’ section of chapter 4).

V.2.3 TRIM simulations for calculating sputtering dose

TRIM simulations were performed to estimate the required Ar\(^+\) ion dose to achieve sputtering of Au layer during irradiations through mask openings. Surface atomic density of Au layer is calculated to be \(1.5 \times 10^{15}\) atoms/cm\(^2\) and atomic layer thickness of 0.25 nm. The IPL tool is operated at fixed pre-defined acceleration energy of 73 KeV and ion irradiation rate \(2 \times 10^{12}\) ions/cm\(^2\)-s. For the Ar\(^+\) ion beam with acceleration energy of 73 KeV, TRIM estimates sputtering coefficient (number of target atoms sputtered per irradiated ion) of 25 atoms/ion. Hence the required ion dose is estimated to be \(1.2 \times 10^{15}\) ions/ cm\(^2\) for sputtering away 5 nm (or 20 atomic mono-layers) Au layer through the mask openings with the irradiation time of 600 s. Taking into account surface roughness and underestimations of sputter yields predicted by TRIM, the substrates were irradiated for 40 minutes at the rate of \(2 \times 10^{12}\) ions/cm\(^2\)-s (four times more than the estimated time). The irradiations were performed through the stencil mask provided by IMS, Stuttgart as explained previously.

MLT tool with the 1:1 projection is operated at 22.5 KeV acceleration energy. For the Ar beam with acceleration energy of 22.5 KeV, TRIM estimates sputtering coefficient 8 atoms/ion. Hence the required ion dose is estimated to be \(3.79 \times 10^{15}\) ions/ cm\(^2\) for sputtering away 5 nm gold layer through the mask openings. Taking into account surface roughness and underestimations of sputter yields predicted by TRIM, the substrates were irradiated with an Ar\(^+\) ion dose of \(4 \times 10^{15}\) ions/ cm\(^2\) through the mask openings.
V.3 Results

Features in accordance with the design of mask openings were observed on the substrates after irradiations. The AFM images of one of the pre-patterned substrate after Ar\textsuperscript{+} beam irradiation on IPL tool is presented in fig V.2.

![AFM maps of Ar\textsuperscript{+}-irradiated substrate on IPL tool](image)

Fig V.2: AFM maps of Ar\textsuperscript{+}-irradiated substrate on IPL tool: a) Topographic map showing depositions in the irradiated regions. b) Phase map corresponding to a) that shows variations in surface mechanical properties confirming the presence of two distinct surface materials.

Regions exposed to the ion beams through the mask openings appeared rougher compared to the regions which were protected by the mask ligaments. In the irradiated region, depositions were observed (as concluded by the section analysis of the AFM image shown in fig V.2), instead of expected sputtering of the Au layers. Au layers of the regions protected by the mask ligaments remained intact. The depositions were most probably re-deposited Au particles or foreign particles from the walls of the vacuum chamber of the IPL tool. Repeated attempts of dissolving these depositions in various organic solvents viz. iso-propanol and toluene baths could not produce cleaned pre-patterned substrates which could be used for further experimental steps to study pre-pattern induced phase separation of polymer blend films. Similarly, substrates with redepositions instead of sputtering of Au layers were obtained, when the irradiations were performed on MLT tool.
Most probable reason for the observed re-deposition effect instead of sputtering is insufficient ion irradiation rates, even though irradiated ion doses were sufficiently high (as calculated by TRIM) and local variations in the vacuum conditions. Low ion irradiation rates meant less number of ions per unit time being bombarded at a given spot on the substrate reducing the probability of sputtering away the Au particles from the substrate. Moreover, knocked out Au particles in the vicinity of the substrates could have been re-deposited because of lesser vacuum than required to trap the sputtered Au particles. Hence, pre-patterning of the substrates was successfully performed only by pure physical sputtering using a FEI 800 (single beam) focused ion beam system (FIB) which operates with a very high irradiation rate and much better vacuum conditions.

V.4 Conclusions

It can be concluded from the results that, in principle ion projection lithography tools can provide faster pre-pattern transfers on the substrates. But the machines need to be optimized for their sputtering applications, especially in the case of amorphous layers like Au. For ion beam induced sputtering effect, along with estimated ion doses, higher ion irradiation rates are also required. Improved vacuum conditions to trap the sputtered particles may reduce the unfavorable ion beam induced deposition effect. However, the problems discussed are not of a fundamental nature and with further machine improvements this approach can provide a viable option for high throughput fabrication of pre-patterns.
Appendix VI

Polymer blend films on Silane/SiOx pre-patterns

VI.1 Introduction

In chapter 4 and 5 influence of molecular properties such as surface tensions (in their resolved components) of the polymers and substrates, work of adhesions and technical parameters viz. pre-pattern periodicities, polymer blend composition, film thicknesses, solvent volatility etc. on the morphologies attained by the PS/PtBA blend films undergoing pre-pattern induced guided phase separation has been studied. Pre-patterned substrates were fabricated consisting of ‘relatively hydrophobic’ gold regions separated by hydrophilic silicon oxide regions. ‘work of adhesion calculations’ presented in chapter 5 provided quantitative proofs for the observed affinities of PS and PtBA towards Au and SiOx surfaces, respectively and justified the choice of pre-patterns consisting Au/SiOx surfaces. Here, influence of even more increased contrast in wetting properties of the surfaces forming pre-patterns on the phase separation of the PS/PtBA blend films is investigated. Pre-patterned substrates consisting of Octadecyltrichlorosilane (OTS)/SiOx surfaces were fabricated. OTS being ‘more hydrophobic’ compared to gold which is only ‘relatively hydrophobic’, spin-coated blend films (with same parameters) attain different morphologies compared to those observed in chapter 4. A qualitative explanation for the observed morphologies is presented.

VI.2 Experimental

VI.2.1 Hydrophilisation of Si wafers

This step was performed as a pre-treatment for hydrophobisation of Si wafers. Si wafers were kept in the bath of ultra clean water, ammonium hydroxide and hydrogen peroxide (5: 1:1 by volume) at 80°C for 10 minutes and then cooled down to 50°C. Then, the mixture was half spilled and diluted with ultra clean water to half the initial concentration. The procedure was repeated 8 times. Finally the Si wafers were
cleaned in ultra clean water twice and then kept in ultrasonic bath of milli-Q water for 5 minutes.

**VI.2.2 Hydrophobisation of Si wafers**

The Si wafers were kept in a mixture of water and hydrochloric acid (36 – 38 %) with 1:1 volume ratio and ultrasonicated for 15 minutes. Hydrochloric acid was removed by eight times dilution with ultra clean water as explained above. The substrates were then treated in the ultrasonic baths of water-free methanol, methanol/chloroform (1:1) and just chloroform in a sequence for 5 minutes each. Then, the Si wafers were immersed in a mixture of decaline: tetrachlorocarbon: chloroform (7:2:1 volume ratio). OTS (1 % by volume) was added to this mixture and the substrates are placed with shining part upwards over night. Later, the substrates were placed in the ultrasonic baths of chloroform, methanol/chloroform (1:1) and methanol in the stated sequence, 5 minutes each. Finally, the hydrophobised substrates were cleaned in milli-Q water.

**VI.2.3 Substrate pre-patterning**

The hydrophobic substrates were irradiated with Argon ion (Ar⁺) beams through the mask openings to etch away the OTS layer from the exposed Si surfaces. Ion dose of \(3 \times 10^{14}\) ions/cm\(^2\) was chosen during irradiation for different samples, keeping the energy of the ions as 27.5 KeV. Thereby, Si wafers with pre-patterned hydrophilic/hydrophobic surfaces were generated. The open stencil mask (IPL-07) was provided by ISIT, Berlin and the irradiations were performed on MLT machine with 1:1 projection (with respect to mask opening dimensions) at Biont, Bratislava. Stencil mask consisted of array of openings with lines and spaces with widths varying from 2 μm to 0.125 μm and lengths of approximately 40 μm. Lines had discontinuities along the lengths resulting into arrow-shaped features with stacks of 9 lines and 8 spaces between them (Fig VI.1).
VI.2.4 Spin-coating and pattern development

Solutions of PS: PtBA blends with varying blending ratios (by weight) and concentrations in toluene were prepared as explained in chapter 4. The irradiated substrates were spin-coated with the above-mentioned solutions of PS: PtBA blends at 200 rpm for 10 minutes. Phase separation was triggered in the polymer blend films by exposure to toluene vapors which is a good solvent for both PS and PtBA. The influence of increasing toluene vapor exposure time on the varying blend film morphology was investigated.

VI.2.5 Characterization

Advancing and receding contact angle measurements were performed on the silanized substrates. The substrate topographies were recorded using white light microscopy and AFM (in taping mode) as explained previously in chapter 4.
VI.3 Results

VI.3.1 Silane coated Si wafers

Contact angle measurements performed on the silanised Si wafers show advancing and receding contact angles of 116° (± 0.2) and 100° (± 0.3) with distilled water drops at room temperature. The measurements were performed at three different (arbitrarily chosen) positions on the silanised silicon substrates. The values for contact angles clearly show hydrophobic nature of the silanised silicon substrates. AFM images of the silanised substrates show an average rms roughness value of 1.2 ± 0.3 nm. Very small pits randomly scattered on the substrates could be observed (fig VI.2) on otherwise smooth surfaces indicating uniform chemosorption of the OTS layers on the surfaces.

Fig VI.2: AFM topographic image of the silanised Si wafer

It is important to highlight that the advancing contact angles made by de-ionized water drop with the Au coated surface and cleaned silicon oxide surface were recorded to be 88 ±0.5° and 0°, respectively. Thus the pre-patterns consisting of OTS/SiOx offered more contrast in wetting properties compared to Au/SiOx pre-patterns studied in chapter 4.
VI.3.2 PS / PtBA blend films on pre-patterned substrates

After irradiations, pre-patterned substrates were spin coated with PS/PtBA blend solutions in toluene (1 % by weight) with varying blending ratios to form thin blend films. During spin coating, toluene could not wet continuous silanised surface of the substrate. Thin uniform films were formed only in the irradiated regions, most probably because the exposed SiOx regions acted as pinning-points to hold the toluene drops. In order to increase the toluene drop-substrate interaction time for uniform film formation, spin-coating parameters of low rotational speeds of 200 rpm for 10 minutes were chosen. AFM topographic maps of PS-rich (blending ratio of 7:3) blend film in the same pre-patterned region shown in fig VI.3a-c. Thin uniform film was formed only in the irradiated regions (fig VI.3a) without any pre-pattern induced phase separation. This film was incubated in toluene vapors. PS and PtBA chains performed lateral movements resulting in re-emergence of the pre-patterned features (as observed in the mask openings) after 60 s of incubation in toluene vapors (fig VI.3b). As opposed to the expected guided phase separation of PS and PtBA chains towards favored hydrophobic (OTS) and hydrophilic (SiOx) regions of the patterned areas, both the blend components were observed to move towards SiOx regions of the pre-pattern (fig VI.3b & c).

![AFM topographic maps of PS: PtBA blend film (blending ratio of 7:3; 1 % blend solution at 200 rpm) on OTS/SiOx pre-patterned substrate a) As spin-coated blend film b) film after 60 s incubation in toluene vapor & c) zoomed-in scan of (b).](image)

In contrast, blend films on Au/SiOx pre-patterned substrates (with exactly same blending ratio) showed pre-pattern induced phase separation immediately after the spin-coating as explained extensively in chapter 4.
VI.4 Conclusions

It can be concluded that pre-patterns consisting of OTS/SiOx regions can be successfully fabricated using chemo-sorption of OTS layers followed by ion beam irradiations. Ion projection lithography tools even with lower acceleration energies of ions and irradiation doses are sufficient for fabrication of such pre-patterns. Very low ion doses can create desired effects of removing OTS layers according to pre-designed openings of the mask, as OTS molecules are only chemosorbed on the SiOx surface and can be sputtered away with small ion doses. PS:PtBA blend films show morphologies in accordance with the design of OTS/SiOx regions of the pre-patterns. Results confirm that the contrast in wetting properties of the surfaces in the pre-patterns play a vital role in resulting pre-pattern induced phase separation of polymer blend films. In the case of OTS/SiOx pre-patterns, sharp contrast in wetting properties (as revealed by respective advancing contact angles of 116°/0°) forced both PS and PtBA chains towards SiOx regions of the pre-patterns. Blend film morphology was mainly driven by the contrast in wetting properties of the pre-pattern regions than by entropic phase separation of the blend components. But, such pre-patterned substrates with enhanced contrast in the wetting properties can be useful in studying phase separation of blend films or block-copolymers with more contrast in their surface energies. Hereby the wetting analysis on OTS layers to resolve its surface tension components and estimate the work of adhesions with different polymers can be useful for choosing suitable polymers.
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3) Guided phase separation of polymer blend thin films on ion beam-induced pre-patterned substrates

4) Polymer blend films on homogeneous and pre-patterned heterogeneous substrates: a two-fold experimental study of the molecular interactions resolving surface tension contributions for explaining the film morphologies
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