ABSTRACT

Surface patterning is important in many areas of research and technology. In the recent two decades, a number of lithographic techniques have been developed, enabling the creation of surface micropatterns with sub micrometer-level resolution. It is possible to create well-controlled topographical or chemical micropatterns using conventional lithographic techniques for microfabrication. There are an increasing number of applications that require for simultaneous control of surface features at the nano- and microscales, driving the creation of innovative, economically viable microfabrication techniques that can incorporate topographical and chemical micropatterning. Due to their tremendous diversity in terms of chemical composition, characteristics, and processing methods, patterned polymer films are becoming ever more significant in relation to an increasing variety of applications. Microelectronics, optics, and biomedicine are just a few of the industries where polymer coatings are used.

Dewetting can be also used as one of the patterning techniques. Dewetting is a common occurrence, such as when a water coating breaks down into individual droplets on a Teflon-coated pan or a filthy window pane. Thin liquid film dewetting results from the instability of the liquid film on the solid surface and is dependent on the interaction of attractive intermolecular forces with unfavourable surface interactions. Droplets form as a result of self-organization and pattern formation during dewetting. Due to the growing usage of thin polymer films as coatings, lubricants, adhesives, membranes, and biological coatings, etc., there have been extensive investigations on the dynamics of instabilities and structure formation in these films. Dewetting and instability are undesirable in the majority of these applications. However, in some other cases it can lead to the formation of various useful and interesting features. It can also be used to create patterns on a meso and nano-scale over a wide area. On a flat,

homogeneous surface, dewetting begins with the nucleation of randomly located holes at a specific mean spacing. These holes expand and consolidate over time, resulting in randomly distributed polymer droplets. The initial thickness and the interfacial tension of the polymer film determine average diameter and mean separation of dewetted structures.

In the present work, patterns are produced by dewetting various 1D and 2D polymer structures such as thin films and electrospun nanofibers and these dewetted structures can be utilized in various applications such as organic field transistors, electronic devices and biological application such as cellular patterning. Further, the characteristic length-scale parameters such as droplet size and mean spacing is tuned by various techniques such as varying the dewetting mixture composition and by modifying the wettability properties of the substrates. Also, more ordered and aligned structures are produced by dewetting of nanofibers.

In the first chapter of the thesis, we systematically examine how the water to solvent ratio in a dewetting mixture affects the length scales of instability. Previously, only one composition of water-solvent dewetting mixture was tried but here we had varied the dewetting mixture composition. Here, the dewetting mixture was prepared by adding water to the solvent mixture (MEK and acetone) in different proportions, where water fraction is varied between 5% and 75%. It is determined how the amount of water in the dewetting mixture affects the instability wavelength (λ) and droplet diameter (d). As the water concentration is increased from 5% to 65% in the dewetting mixture, it is observed that the instability wavelength (λ) for 50 nm thick PS film is decreasing from approximately 17 to 7 µm. Similarly, the droplet diameter has decreased from 2.4 to 1.3 µm on increasing the water percentage. This is considerably smaller than the instability wavelength in air, which for the identical PS film is close to 50 µm. The mechanism of the observed change in the length scale is presented, and the solubility of PS in the dewetting mixture is also explored.

In the second chapter of the thesis, we present a straightforward technique for modifying the lengthscales of self-organized dewetting of polystyrene thin films by varying the extent of silane grafting on the substrate. By exposing glass substrates to varying concentrations of OTS vapour in a controlled, low-pressure environment, self-assembled monolayers (SAM) of octadecyltrichlorosilane (OTS) were deposited onto the substrates. When the duration of time exposed to the OTS vapours was increased from a few minutes to several hours, measurements of the water contact angles on the treated glass surfaces showed that the contact angles could be constantly increased from 40^o to 70^o. On the modified glass substrates, polystyrene (PS) thin films were spin coated, and water-solvent mixture induced dewetting of the PS thin films was done; the dewetting kinetics depended on the spreadability of water on the surface. By increasing the amount of OTS exposure, we noticed a decrease in the length scales of dewetting, notably the droplet size (d) and instability wavelength (λ). While the droplet diameter (d) reduced from 2.5 to 1.6 μm, the wavelength (λ) for a 50 nm thick PS film decreased from 12 to 4 μm.

In the last chapter, we had discussed the dewetting of electrospinned nanofibers. The dewetting of thin films lead to random structures. The randomness of the dewetted structures restricts this method's potential as a soft patterning technique in several applications. To impose a long-range order in the dewetted structures, a number of ways have been investigated. Various works had been done on physico-chemically structured surfaces and it was found that more ordered assemblies can be formed over such surfaces. Here we use one easy way to align droplets where instead of 2D structures we do dewetting on 1 D structures i.e., nanofibers. To get more number density of droplets and more aligned droplets we had switched from film configuration to fibre configuration. We have also done its comparison with Rayleigh-Plateau's instability model.

It has been found that the length scale of dewetting decreased with an increase in the water fraction in the dewetting mixture due to the faster kinetics of the hole-growth. Also, by just varying the amount of OTS grafting on the substrate, a three-fold reduction in wavelength and a two-fold reduction in droplet diameter were obtained. These techniques can be used as an additional way to control the droplet size that was obtained after dewetting. Finally, summary and overall conclusions based on the achievements are presented in the thesis.