Module1: Introduction to Patterned Surfaces and Their Applications

Lecture 1: Introduction to Patterned Surfaces and Their Applications

Welcome to the course on “Instability and Patterning of Thin Polymer films”! As the name suggests this course deals with two apparently distinct topics: “patterning” and “instability”. However as the course progresses we will see that two aspects are rather closely related. Once we understand the basic aspects of “Patterning” and also what is meant by “Instability”, we will realize how spontaneous instability in an ultra thin film can be utilized to make meso and nano scale patterns. The course is highly interdisciplinary and would build concepts by incorporating critical fundamental knowledge of Physics, Chemistry, Polymers and Material Science on a Chemical Engineering platform. Broadly, the course content will be as follows:

1. Extended Introduction:
    - What are Patterns?
    - What type of Patterns: Meso and Nano Patterns
    - Introduction to Instability
2. Application of Patterned Surfaces and Films
3. Some Basic Concepts:
    - Surface Tension; Young’s Equation; Dispersion Forces; Young Laplace Equation;
    - Surfactant Molecules and Critical Micelle Formation
4. Patterning Techniques:
    - Different Meso Scale Patterning Approaches
    - Brief Introduction to Photolithography
    - Discussion on Soft Lithography
        - Nano Imprint Lithography
        - Capillary Force Lithography
        - Micro Molding in Capillaries
        - Micro Contact Printing etc.
    - Brief mention of the other Patterning methods

We start our discussion by understanding what patterns are. Then we extend our understanding to meso scale patterns and structures, and focus on what exactly distinguishes the meso and the nano scale from the bulk. We then briefly talk about the different type of instability we are going to discuss. Then we cite some major applications of meso patterned surfaces.

1.1 What are patterns?

Patters are regular array of objects or entities. The elements of a pattern repeat itself in a predictable manner. Patterns can be both natural and artificial, can be seen in both living and inanimate worlds, and can be seen at all length scales. For example, regular orders can be seen in

Nebula or Galaxy where the length scale of ordering is in light years and on the other hand they can be seen in the way molecules or atoms are arranged inside a lattice in the length scale of few angstroms. There are many examples of patterned objects which we come across in our living world too which include zebra stripes, honeycomb etc. These patterns can be of various types as well, such as optical, structural etc. In this course, we will however discuss on the patterns at submicron and meso length scales. We all understand that 1 nm = 10^{-9} m. In our context the meso scale stretches from few nm to few hundreds of nm, which means that we are not talking about the molecular dimensions, but we are also far lower than bulk. This length scales is interesting as it bridges the molecular and the macroscopic worlds and often simultaneous signatures of both the regimes can be seen over this regime, often giving rise to exciting phenomena like quantum size effects (QSEs), single electron tunneling (SET), Coulomb blockade etc., which are not realized either in macroscopic or molecular regimes. Many unique properties in this regime arise out of the action of inter molecular forces, such as the van der Waal's force, the signature of which is absent in the macro scale, or in bulk materials. Additionally, in this regime the surface to volume ratio is significant and therefore the surface effects are very significant. Additionally, we talk about a length scale where the signature of inter molecular forces are present. Thus our discussion starts with an in depth understanding about the origin and nature of surface tension and its consequence on a surface, particularly a liquid surface. We discuss about the pressure imbalance across a curved surface in mechanical equilibrium and introduce the concept of Laplace pressure. At this point I will also introduce the concept of **equilibrium contact angle** that a stationary liquid drop makes on a flat solid surface. We will also learn what is meant by **contact angle hysteresis** (**CAH**) and how to identify if a surface is **superhydrophobic** or not based on the magnitude of equilibrium contact angle and CAH.

At this point we highlight that topographically patterned polymer films and surfaces, with sub micron and nanometer scale resolutions are important to a host of scientific and technological areas like components of molecular electronics, plastic or organic electronics, organic light emitting diodes (*OLED*), optoelectronic devices, photodiodes, thin film transistors (*TFT*), solar cells, biological sensors, microfluidics, smart and super adhesives, fabrication of surfaces with gradient and self cleaning properties, Micro Electro Mechanical System (*MEMS*) and *NEMS* devices, data storage media, confined chemistry applications, lab on a chip devices, surfaces for nano-biotechnology applications like single molecule enzymology, proteomic or genomic arrays, photodiode arrays for sub retinal implant in bionic eye, patterned substrates for probing of cell behavior, including stem cell scaffolds for tissue engineering, DNA stretching etc. For most of these applications and other similar bulk nano applications, as well as studies involving phenomena like structural color, super hydrophobicity [etc. rapid prototyping of surfaces with the pattern extending over large areas (~ cm^2) are necessary. The success and utility of many of the applications listed above depend on the availability of simple, robust yet cost effective meso fabrication technique. In this course we will get introduced to some of these techniques which are capable of producing well ordered surface patterns having sub micron resolution on surfaces polymers as well as other soft materials like gels etc. These methods fall in the broad category of "Soft Lithography" which we will discuss in this course in significant details. However, it is important to remember that Soft Lithography is a developing area (first research activities started around 1995) and therefore one must constantly upgrade oneself about the developments by tracking the recent research papers published in journals.

At this point one also needs to understand that though we have mentioned host of areas which utilize patterned substrates, the biggest user of patterning is some other Industry. It may appear as a surprise, but yes, the biggest user of surface patterning is the micro electronic industry. In fact the phenomenal progress that one has witnessed in the field of micro electronics in terms of development of new gadgets (personal computers, laptops, tablets etc.) as well as higher storage capacity (high capacity Terra byte hard discs, Blue Ray Disks, Pen Drives) or faster processors with higher clock speed are all attributed to the progress in the area of surface patterning, which allows packaging of more number of P – N junctions on a Integrated Circuit (IC) Chip. All this has become possible due to the patterning technique called "Photo Lithography". This is one technique that is widely used in industry and is seeing rapid progress. In order to understand any patterning methodology, it therefore becomes important to have some idea about Photolithography. However, before we star discussing the patterning methods, we would like to highlight that present-day technology has three distinct approaches to offer for mesoscale patterning. The popular two amongst the three are: (1) The top-down methods that include various types of lithography and the serial writing methods; (2) the "bottom-up" self–assembly (SA) techniques where individual components assemble in a desired fashion to form structures; and (3) a third alternative that is based on self-organization, where a highly confined and unstable object such as a thin film spontaneously changes shape to form a more complex arrangement. The third approach is gaining significance as neither bottom-up nor top-down patterning techniques by themselves are capable of achieving structural control at the molecular and mesoscopic level combined with macroscopic addressability, and which can be addressed in a self organization based technique. This is the approach that relies on spontaneous or external field mediated instability in ultra thin films due to action of inter-molecular, interfacial and other types of meso scale forces. In the past several decades a rich convergence on insight on patterns has evolved from a wide range of scientific disciplines, including biology, chemistry, computer science, mathematics and physics. It is now understood that many natural mechanism, irrespective of their size and length scale follow a similar mechanism of formation called self organization. Self organization refers to a wide range of processes in both living and non living systems. The organization is based on the local interaction between the constituent of the system. The constituents can vary from being molecules right up to macroscopic objects. Formation of surfactant micelles is a classic example of self organization. Most natural processes emerge towards minimization of the free energy of the system, which acts as the driving force for such self organization.

Our discussion in the context of thin film instability will focus on this very recent approach of self organization mediated patterning of polymer films and surfaces. In order to understand the underlying physics that governs the morphological evolution in a highly confined thin polymer film, we need to understand the precise nature of interfacial interactions. This includes discussion on effective Hamaker constant and understanding stability from the stand point of free energy minimization. Once we understand these critical concepts, we then move on to understand a special class of instability that is spontaneous rupture and dewetting of an ultra thin liquid film. Dewetting is a very commonly observed phenomena and is responsible for the painful dry eye syndrome due to the rupture of the corneal tear film. The same phenomenon is also responsible for loss of effective functionality of various types of coatings. We look at the physics that is associated with spontaneous rupture and dewetting of an ultra thin polymer film. Then we learn the various stages of dewetting of a thin polymer films. We subsequently show how the phenomenon, which is undesirable from the stand point of a coating can be effectively utilized for fabrication of meso scale patterns, with suitable templating strategies. Some of these templates might be fabricated by top down soft lithography techniques discussed before. Thus we essentially introduce the concept of combined top down and self organized patterning, that is capable of multi functional hierarchical meso scale patterns which are difficult to fabricate by the top down methods only! We would also introduce some other types of instabilities, which include contact instability in an ultra thin elastic film, external filed (such as an electric field or thermal gradient) induced patterning of a thin film, contact line instability in an evaporating/ drying droplet etc. We will understand the method of electrohydrynamic lithography (EHD), which applies an electric field across a thin film in a capacitor geometry to generate variety of exotic structures, by tailoring process parameters like filed strength, film thickness etc. At this point we will understand the concept of "beyond the master" patterning, where novel methods based on careful control of process parameters allow fabrication of structures which are not only a mere negative or positive replica of the stamp. We will also briefly talk about the instability and morphological evolution in polymer blends and polymer bilayer thin films. Finally, we will discuss how exotic surfaces such as one with a gradient topography or gradient wettability can be fabricated by some of the methods discussed in the course.

Once we understand how to make the patterns, either based on the top down lithography techniques or based on the self organization based approaches, we now face a new question. How to examine the morphology of these structures? Well, we typically use the “microscope” for viewing something that is small. However, it is important to remember that an “optical” microscope uses visible light to illuminate a sample and therefore the resolution is limited by the wavelength of light. One can go to smaller wavelength electrons and can use a “Scanning electron Microscope” (SEM) to resolve the structures. However, there is another specialized microscopy technique that has become extremely popular over the past few years and has almost become an integral part of materials science research. This microscope is known as an “Atomic Force Microscope” (AFM) which was invented as an extension of the Scanning Tunneling Microscope (STM) in mid 80’s. We will discuss the basic operating principles of an AFM in some what details. Not only an AFM is an important tool for visualizing the type of structures that can be fabricated by the methods discussed in the course, but the fundamental operation of an AFM is also based on atomic and molecular level interactions, which makes the study rather relevant to this course.