Nanoscale Patterning Using UV Light Pulsed Laser

T. K. Subramaniam

Department of Science and Humanities (Physics), Sri Sairam Engineering College, Chennai, India

Email address
subramaniam.phy@sairam.edu.in

Citation

Abstract
Nanoscale patterning means nanoscale fabrication using preferably the top-down lithography technique. Polymers' are nanoscopic materials and they have unique properties that have characteristic length scales in the nanometer range. The goal of nanoscience is to control the assembly of solid materials by its growth, removal, or etching at an extremely high spatial atomic resolution to that of a single atom. Several methods are already available to produce nanoscale patterns on a polymer substrate but the novelty of my method is to use a laser of short wavelength, preferably an ultraviolet radiation to shine on a 'self assembled' polymer. In doing so, the sample is expected to undergo a chemical attachment. One can expect covalent or ionic bonding to take place as the case may be with the polymer, and that depends on the type of polymer that we choose for our application. In going from a self assembly to a chemical attachment there will not be any degradation of the pattern. A carefully prepared monopolymer on a 'substrate' called a main polymer or a bulk acts as a 'stamp' carrying a nanoscale pattern made out of 'self assembly' process.[1] A photon induced reaction will bring about possibilities of chemically attached nanoscale patterns. A (Scanning Tunneling Microscope) STM investigation should reveal typical atomic resolution.

1. Introduction
Nano science has been making a paradigm shift across science and engineering in almost all disciplines of science. It has stimulated and inspired innovation both in teaching and in research for the development of large scale nano-manufacturing. The main goal of nano scale science is to control the assembly of solid materials by its growth, removal or etching in extremely high spatial atomic resolution to that of a single atom. Nano scale patterning corresponds to nano scale fabrication using the top-down lithography technique. For nanofabrication to be practical it must be based on large-scale molecular self-assembly and this self assembly should take place over a wide area to secure the molecules to the surface through strong bonds, preferably covalent or ionic bonds.

2. History of Lithography
The term ‘lithography’ is taken from the Greek language meaning ‘Stone Writing’. An example of a lithograph is ‘Escher Print’, invented by Alois Senefelder in 1798. There, an image was painted onto a limestone with grease and the stone was dipped in ‘ink’. The grease would retain the ink while the rest of the stone would repel it. This stone was then pressed onto a piece of paper to create a print. Lithography is used to make semiconductor chips. The ‘stone’ is the ‘silicon’ from which chips are made. The silicon is written upon by irradiation with a light source through a mask (like a stencil), to make a particular pattern. This pattern is then etched into the surface using a chemical developer. The...
radiation changes the reactivity of the silicon to the developer. The smallest width of the pattern that is obtainable through lithography is limited by the wavelength of the light used. So far, only visible light has been used for semiconductor manufacturing. In order to make the ‘chips’ below the current standards, it will be necessary to use smaller wavelengths. There are several types of lithography, namely, electron beam lithography which uses a stream of electrons instead of light to produce a pattern with a resolution of 10 nm, but is not suited for mass production; Nano imprint lithography invented by George Whitesides at the Harvard University Laboratory[2], to produce ‘nano scale patterns’. A company in the USA now uses this technique called as Flash Imprint Lithography (S-FIL) to produce this pattern in the semiconductors processing. Another technique is the “Dip Pen Nanolithography” and a company founded by Chad Mirkin, uses this technique to probe the tip of an Atomic Force Microscope (AFM). This technique has potential applications in electronics for drawing very small circuits or in creating very small arrays used in biochemical assays. Richard Feynman imagined a top-down process in which miniature tools were used to make even smaller tools and then these tools, in turn, used to make even smaller tools, until we reached a stage where tools could be employed to move atoms around, one at a time[3].

3. Concept of Self Assembly

In equilibrium, when there are no relevant external forces, self-organization proceeds to the energetic minimum. In the presence of external forces and fields, one can observe dynamic self assembly. The structure which is formed depends on the amount of energy we inject into the system and when it is stopped, the system falls apart. Thus, these structures are adaptive, and architectures that mutate to adapt to a new environment. Static self assembly has different aims. It is intended to create a complex architecture like high surface area for sensing, high strength for protective coatings, low dielectric constant for optical cladding, low thermal conductivity for thermo electrics, and mechanical flexibility for electronic paper. Thus the two main families of self assembly, namely static self assembly and the dynamic self assembly further subdivide into co-assembly, hierarchical self assembly, and directed self assembly. We can summarize self assembly as ‘apparently spontaneous self-organization of objects’; it arises as a system and strives to find minimal free energy [4].

4. Experimental Method

I wish to consider ‘polymers’, since polymers can be considered among the first nanoscopic materials and many of their unique properties have characteristic length scales in the nanometer range. Polymer is defined as ‘….of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass’, as given or as accepted by IUPAC(International Union of Pure and Applied Chemistry). Firstly, I take a ‘bulk polymer’. This will act as a substrate. The silicon is taken and it is then made ‘hydrophobic’ with molecules like the Piranha solution which can be used to increase the surface density of reactive hydroxyl groups on the surface of silicon. The –OH groups can hydrolyze and subsequently form siloxane linkages (Si-O-Si) with organic silane molecules. Preparation of silicon surfaces for silanization involves the removal of surface contaminants. This can be achieved by using two methods, firstly, using UV-ozone and Piranha solution. Piranha solution in particular constitutes quite a harsh treatment that can potentially damage the integrity of the silicon surface. Piranha solution is used frequently in the microelectronics industry, e.g. to clean photo resist residue from silicon wafers. The other alternative method is the silicon treated with oxygen plasma and it is made ‘hydrophobic’ with molecules like the (CH3)3 SiCl, trimethylsilylchloride and the oxygen plasma will introduce silanol (Si-OH) groups on the surface of the silicon. Equilibrium will exist between neighboring silanols and water. The equilibrium is strongly dependent on temperature, humidity and pH. The concentration of silanols on the surface of silica can be modified in two ways: In the first method, it can be exposed to oxygen plasma or air plasma more, or by immersing the surface into a strong acid with Oxidizing characteristics (H2SO4 + H2O2), i.e., Piranha solution. These methods will break the -Si-O-Si- bonds, thereby increasing the concentration of silanols temporarily above the equilibrium level. In the second method it can be decreased to about 1 per 10 nm2 by heating silica to about 800°C. At such high temperatures, silanols will condense releasing water and forming a new -Si-O-Si- bridge. Silanols can be protonated or deprotonated strongly dependent on the pH of the environment. They not only determine the surface charge but also the surface reactivity; they react with chlorides or alkoxides and can be used to covalently attach any molecule to the surface of silica. Silanization reacts most of the surface reactivity and adhesion with the ‘polymer’ and it increases the accuracy of the ‘template’ replication. I will now bring in the ‘monolayer polymer’ or also called as a pre-polymer. A polymer of small molecular weight and manageable viscosity that is safely mixed with initiators, additives, and that can be set by further polymerization in aging process is a pre-polymer. This pre-polymer is then poured over the ‘main’ polymer. Care should be taken not to form bubbles which otherwise will get trapped in the pre-polymer. The ‘main’ polymer (bulk) then undergoes ‘curing’ which the pre-polymer molecules ‘cross-link’ or it creates a bond between the two (main and pre-polymer) forming two polymer chains. This will result in a final ‘stamp’ with rubber-like properties. This ‘stamp’ can be peeled off from the ‘bulk’ providing a very accurate free-standing replica of the ‘main’ and which can be used in a variety of ways to generate surface patterns also known as nanoscale patterns. Several methods are there for the utility of the process mentioned above. They are: a) Micro contact printing, b) Self-assembled monolayer, c) Micro-molding, and
d) Microlithography. So, the first process of creating a nano pattern using ‘self assembly’ method is accomplished.

My goal will be achieved by irradiating this ‘physisorbed’ species with UV light from a pulsed laser.[5] The prepared polymer should be kept at a low temperature (~77 Kelvin) and at an ultra high vacuum chamber (10 Torr) for this purpose. Due to physical interaction, the polymers will lose their high degree of order at higher temperatures. Now, a reaction is induced by a pulsed laser of λ=193 nm wavelength. By this action of the laser irradiation, we can expect covalent or ionic bonding to take place as the case may be, that depends on the type of polymer that we choose for our application. In going from a self assembly to a chemical attachment there should not be any degradation of the pattern. An entire set of ad-atoms circle will be filled and then reaction is initiated. The sample is then analyzed with the help of a Scanning Tunneling Microscope (STM) which will reveal a ‘unit cell’ surface after a typical atomic resolution.

5. Conclusion

Since the entire experiment should be done at a low temperature only a marginal rise in temperature is expected to take place (~5 Kelvin) due to UV photon interaction and it will not alter the thermal reaction significantly and so only single-photon reaction will be the main process. Thus a photon induced reaction of a self assembled monolayer of a ‘polymer’ on a bulk substrate suggests powerful possibilities of imprinting chemically attached nano scale patterns. The novelty of this method as compared to the already existing processes followed by Whitesides et.al is that the surface reaction can be classified as having a daughter-mediated dynamics. The ‘parent’ is the ‘bulk polymer’ and the daughter is the pre-polymer or the monolayer polymer. The daughter mediated mode of reaction or chemical imprinting finally results or takes place on a self assembled monolayer causing nano scale patterns because the surface chemical reaction involves ‘bulk or main polymer in which the adsorbate which is in its initial physisorbed state as mentioned by Ashcroft and Mermin[6], is directly attached to the surface of the atom to be imprinted, i.e., nano scale pattern on a monolayer polymer. There have been recent developments in the methods adopted to nano scale lithography technique as related to semiconductor applications, for example, In GaN etc., [7-10].

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References