

Nanoscale Patterning of Organic and Metallic Features on Semiconductors via Self-Assembly of Soft Materials

Jillian M. Buriak, Masato Aizawa, Yinghong Qiao and Dong Wang, National Institute for Nanotechnology, and the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

Abstract

Nanostructured materials continue to be the focus of intense research due to their promise of innumerable practical applications as well as advancing the fundamental understanding of these intriguing materials. In particular, the need for metallic and organic features of increasingly smaller size regimes has imposed stringent demands upon chemists to produce a variety of highly functional materials with reduced dimensions. The successful realization of arrayed nanosensor and nanoelectrode production, molecular electronics, ultra large scale integration (ULSI) device fabrication, and nanoelectromechanical systems (NEMS) will require unparalleled precision and control of geometry, aspect ratio, surface morphology, deposition rate, and substrate adhesion without sacrificing throughput or cost effectiveness. While much effort has been expended towards the synthesis of nanoscale structures, one of the most challenging aspects for the nanoscale materials community is the question of how to 'wire in' these functional elements with the real world. In this talk, we will describe recent work towards the interfacing of nanoscale patterns of organic molecular and metallic structures with semiconductor surfaces such as silicon, germanium, gallium arsenide and indium phosphide. We have developed a repertoire of chemical reactivities on semiconductor interfaces, and are now patterning them through straightforward and efficient, highly parallel patterning strategies via self-assembly of soft polymer materials. The self-assembled materials direct transport of reagents to the semiconductor so that the reaction takes place in a spatially defined manner, with precise control over the quantity of reagent delivered. Even mixtures of reagents can be 'sorted out' by these interfaces to produce nanoscale (~10 nm) domains of different chemical functionalities, simultaneously. We will describe these and related approaches towards precise patterning of semiconductor surfaces, entirely via wet-chemical processes that are compatible with existing fabrication strategies.

Introduction

There is a great deal of interest in patterning semiconducting surfaces for integration of electronically active nanoscale materials and organic molecules, to make hybrid, highly functional devices.¹ The need for control over surface and interfacial characteristics, morphology of interfaced metallic nanostructures (both shape and size), and efficient, reliable and controllable reaction conditions to generate organic monolayers for molecular electronics are a few of the requirements that must be addressed.² Much work remains, however, in terms of the efficient patterning and utilization of these structures with the goal of preparing higher order architectures and devices for technologically relevant applications.

Use of scanning probe instruments like atomic force microscopy (AFM) and scanning tunneling microscopy (STM) to pattern on the nanoscale is an area of rapidly growing interest because of its high precision and sub 100 nm accuracy.³ Balancing the exactness of the technique is the fact that it is a serial process, a factor that may not be problematic for certain specific niche applications. For large scale processing, however, the power of self-assembly to direct patterning of interconnects on semiconductor surfaces has a strong allure.⁴ In this paper, we will describe the use of electroless deposition to produce metallic features on silicon, germanium, gallium arsenide, and indium phosphide. The metallic structures are patterned on the surfaces first via AFM (serial process),⁵ and then shown to be compatible with a self-assembling, parallel process that is capable of patterning surfaces with features measured in ~5-10 nm, but over a centimeter range.⁶

Electroless Deposition

Industry is moving increasingly towards wet chemical processing of metallic features on semiconductor interfaces.⁷ Electroless deposition is particularly attractive since it is efficient, conformal, controllable, and inexpensive. The electroless deposition referred to here is galvanic displacement, in which the reducing electrons arise from the semiconductor onto which the metal is deposited.⁸ The resulting process is simply a dipping procedure of the wafer into the metal salt solution of choice. If the metal is sufficiently oxidizing (generally a $E^0 > 0.00$ V versus SHE), then the reaction is spontaneous. This approach leads to deposition of metal nanoparticles, films, or complex three-dimensional architectures.⁹

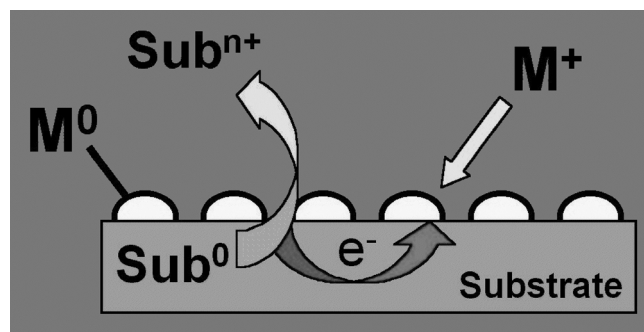


Figure 1. Schematic outline of electroless deposition on semiconductors.

Atomic Force Microscopy (AFM) Tip-Mediated Nanolithography

Stemming from fundamental scanning probe experiments focused on exploring polymer tribology, static plowing lithography has

only recently been utilized as a viable fabrication process. In this facile yet effective method, an atomic force microscope probe is employed to mechanically “plow” away spatially defined regions of a target substrate with extremely high lateral resolution. We have demonstrated the use of static plowing lithography to rapidly prepare metallic nanostructures of varying geometric configuration with considerable ease and reproducibility.⁵ This process is accomplished in four fundamental operations as outlined in Figure 2: (1) application of a thin photoresist onto a semiconductor substrate, (2) utilization of an atomic force microscope tip to “plow” away patterns/domains of the resist, thereby exposing defined regions of the underlying semiconductor substrate, (3) immersion of the substrate into a dilute metal salt [such as $\text{HAuCl}_4(\text{aq})$], where electroless deposition proceeds onto the areas of semiconductor no longer concealed by the resist and (4) final removal of all resist via a solvent rinse. The resulting metallic structures were subsequently characterized utilizing atomic force microscopy (AFM) and scanning electron microscopy (SEM). This process takes minutes to complete, is carried out entirely under ambient conditions (in air, humidity unimportant), and requires only standard commercial apparatus. Actual AFM images of this process on germanium wafer, Ge(111), coated with its native oxide, resulting in gold lines and features, are shown in Figure 3.

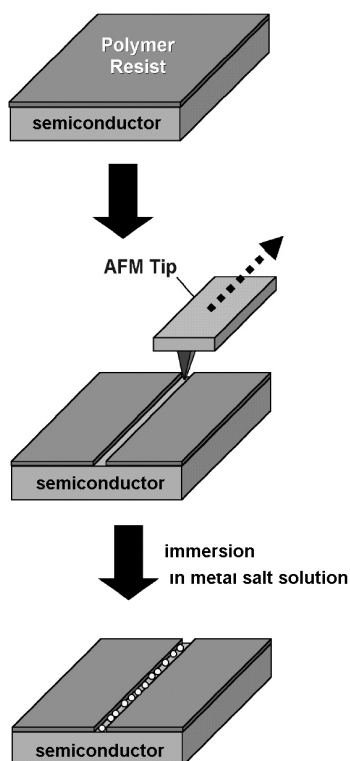


Figure 2. Nanolithography on a photoresist spin-coated onto a semiconductor wafer. An AFM tip scribes through the soft polymer, exposing the underlying semiconductor. Immersion of the wafer to a metal salt solution (gold, silver, palladium ions, for example), results in spontaneous metal deposition only in the exposed regions.

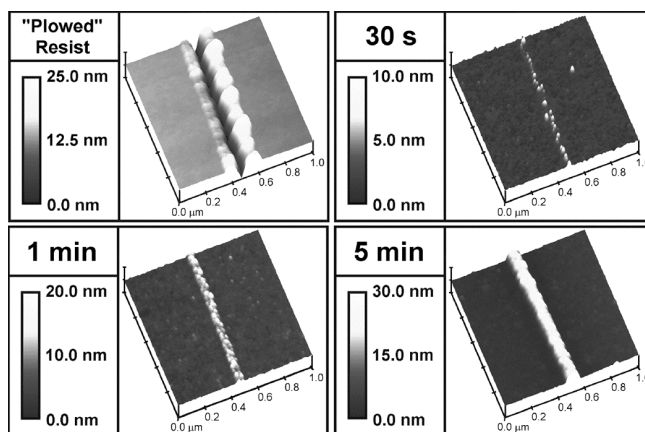


Figure 3. AFM images of different steps of the process on a Ge(111) surface. Top left: plowing through a Shipley 1805 photoresist (20 nm thickness). Top right: 30 s immersion in a gold chloride solution, and removal of the photoresist produce a line of gold nanoparticles. Bottom figures: Longer immersion times in gold chloride lead to continuous linear gold features.

Block Copolymer Mediated Patterning of Nanoscale Features on Semiconductor Wafers - Si, Ge, InP, GaAs

Block copolymers have been known for quite some time to self-assemble into nanoscale structures, but recent interest by workers at IBM demonstrating their compatibility with existing silicon-based fabrication processes has focused attention on these materials by the semiconductor community. Block copolymers are extremely versatile, and have been used as nanoreactors to prepare isolated nanostructures, as reactive ion etch masks, as a patterned hydrophobic/hydrophilic organic interface on which polymerization and sol-gel chemistry has been carried out, and others. Here we describe block copolymer templating of semiconductor surface chemistry, using the block copolymer to direct chemical reactions with the surface in a spatially defined manner.⁶ The chemistries accessible through this approach include interfacing of organic molecules, metal nanoparticle synthesis, biological molecule coupling, and others. The block copolymers are commercially available, and so this approach is highly accessible.

Examples of this approach for metal electroless deposition are shown in Figure 5. Using a block polymer made up of a polystyrene and a polyvinylpyridine block, gold chloride transport through a self-assembled monolayer of this block copolymer occurs in a spatially defined manner, with nanoscale resolution. The spontaneous reduction of the gold(III) ions occurs instantly on both Si(100) and GaAs(100), leading to ordered arrays of nanoparticles firmly attached to the surface. We will describe results concerning linear patterns, templated by other block copolymer monolayer films on the surface.

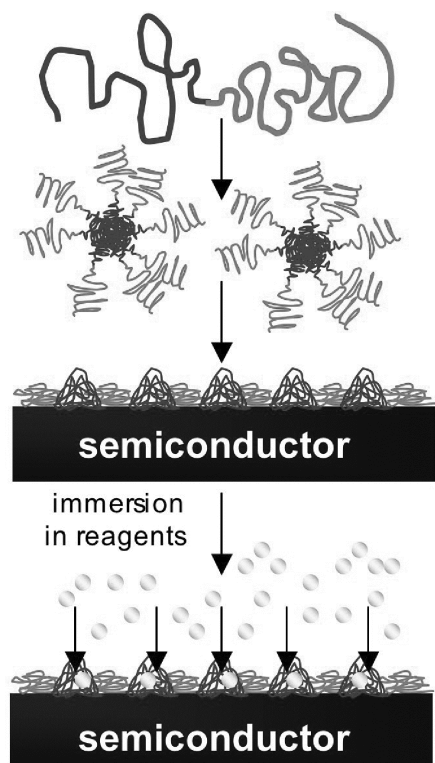


Figure 4. Outline of the block copolymer mediated surface chemistry. A polymer with 2 different blocks (top) self assembles into a nanoscale micelle structure that can be deposited, as a monolayer, on a semiconductor. This self-assembled film can then direct surface chemistry in a spatially defined manner.

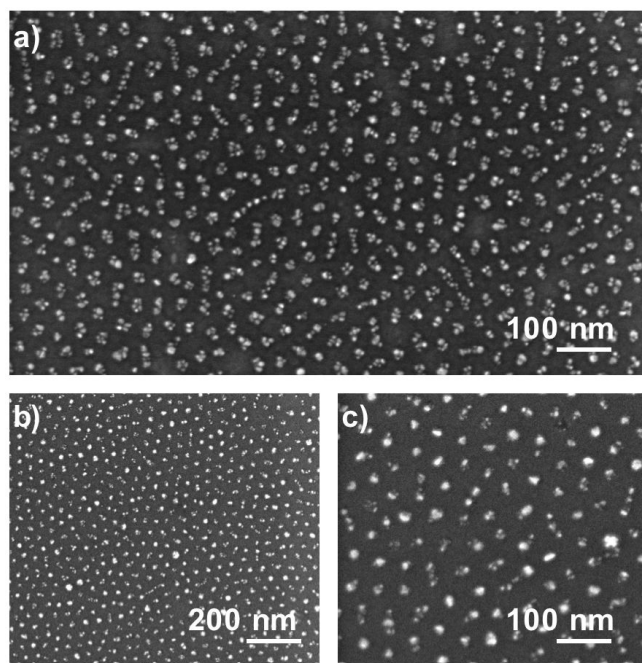


Figure 5. Scanning electron microscope (SEM) images of gold nanoparticles on a) GaAs(100), and b+c) Si(100), patterned via this simple and efficient block copolymer patterning approach.

Conclusions

The integration of soft polymeric materials with semiconductors such as silicon, germanium, gallium arsenide and indium phosphide can lead to highly patterned interfaces, with nanoscale precision. In one approach, AFM tip-mediated nanolithography through a thin photoresist can be utilized to produce linear patterns of metallic nanostructures of varying length, size and overall shape. The second approach utilizes the self-assembling nature of a group of polymeric materials called block copolymers. Block copolymers can self assemble into hexagonal close-packed array patterns, linear structures, and many others. We demonstrate how these materials can be harnessed to template surface chemistries on semiconductor surfaces for various technological applications.

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Author Biography

Jillian Buriak received her A.B. in chemistry from Harvard University in 1990, and her Ph.D. from the Université Louis Pasteur (France) in 1995. She completed a post-doc at The Scripps Research Institute in La Jolla CA, and was an assistant (1997-2001) and associate professor (2001-2003) in the Department of Chemistry at Purdue University, IN. In 2003, she left to become a founding scientist of Canada's new National Institute for Nanotechnology (NINT) where she is a full professor and Group Leader, and holds the Canada Research Chair of Inorganic and Nanoscale Materials.