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PARALLEL NANOMETER SCALE FABRICATION

Final Report

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ABSTRACT

Our approach to nanotechnology stresses parallel (as opposed to serial) processing and self-assembly techniques and we have demonstrated a basic parallel nanofabrication process that will enable a wide variety of nanometer-scale structures to be made. The process of nanometer molecular lithography employs two-dimensional biomolecular crystals as patterning elements in the parallel fabrication of structures on the 1-10 nm length scale. We have further demonstrated the fabrication of composite biomolecular/solid state heterostructures of nanometer dimension (*nanoheterostructures*). We are presently pursuing central issues in the development of nanotechnology such as the understanding and control of fluctuations and structural variations as well as applications of our nanofabrication process. An example of the latter is the formation of porous silicon having monodisperse arrays of silicon 'quantum wires' to elucidate the role of quantum confinement in the phenomenon of luminescent silicon.

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In the report that follows we will evaluate progress in our research activities under the three headings: Pattern Transfer to Smooth Substrates, Pattern Development, and Mask Removal.

I. PATTERN TRANSFER TO SMOOTH SUBSTRATES

First Demonstration

We have recently demonstrated that a nanostructured metal oxide screen fabricated as shown in Figure 1 can act as a mask for the pattern transfer of a periodic array of holes to the underlying substrate [2]. In this study the stoichiometry of the metal oxide was determined by spectroscopic ellipsometry to be $\text{TiO}_{1.9}$ and for the ensuing discussion we will denote the titanium oxide film as TiO_x . The AFM image before FAB milling in Figure 1a shows that, as deposited, the TiO_x thin film is flat and of uniform thickness off-S-layer and exhibits a periodic thickness variation and surface height modulation on-S-layer. The AFM surface contour plot of Figure 1b, taken on the line indicated in Figure 1a, shows the on-S-layer modulation amplitude is ~ 3 nm and the peak on-S-layer height is ~ 6 nm above the graphite plane. This is less than the thickness reported from freeze-dried samples and may be attributable to shrinkage owing to air-drying of the S-layer sheets used in these particular experiments [1]. The after-milling image, Figure 2a, shows that the TiO_x thin film on-S-layer is modified by the FAB milling, forming a mesh composed of periodic arrays of 10 nm holes. Off S-layer, random holes appear on the graphite substrate, likely the result of localized contamination on the otherwise atomically smooth graphite surface. The after-milling AFM image shows that the holes penetrate both the TiO_x film and the graphite substrate, both on and off-S-layer. In fact, there is considerable erosion of the carbon layer. The AFM profile of Figure 2b, taken on the line in Figure 2a, shows that after FAB milling the protein layer is collapsed somewhat, possibly by shallow implantation of the Ar atoms, to a measured thickness of ~ 4 nm. The off-S-layer holes are as deep as 4.5 nm below the graphite surface. The on-S-layer holes, as measured from the graphite surface, are etched ~ 1.5 nm into the carbon. The difference between the on-S-layer and off-S-layer hole depths, ~ 3 nm, may be attributed to the additional height of the protein structures which protrude into the pores on-S-layer [2]. This "hole punching" is not observed in milled, bare HOPG, although slight (~ 2 Å rms) surface roughening is found, similar to that observed by Eklund et al. [3].

The off-S-layer presence of the TiO_x film after milling combined with the erosion of the graphite at the holes show that the 3.5 nm thick TiO_x is effectively acting as a mask for the FAB milling of carbon. It appears that the process of hole formation in the TiO_x film occurs by heterogeneous nucleation and growth, wherein holes open under FAB only at nucleation sites (perhaps thin spots in the TiO_x). On-S-layer this process is controlled, since the S-layer produces in the deposited TiO_x a periodic array of nucleation sites leading to a periodic array of holes. Once a hole is formed, continued milling erodes the carbon and deposits it near the hole edge.

Evidence for this can be obtained by quantitative analysis of hole profiles. Structure of individual holes is more easily measured off-S-layer because each hole is isolated from the others. Hole profiles were directly measured by AFM. The inset of Figure 3 shows a scale profile of a 7.5 nm deep hole. Volumes were calculated by numerical integration from the AFM raw data files of off-S-layer holes. In Figure 3, RV, the annular ring volume (excess volume above the milled TiO_x surface plane) is plotted against CV+TV, the total volume removed (volume missing below the TiO_x surface

plane) for a number of different hole sizes. The values for RV lie close to the CV+TV line, indicating that the excess volume of material deposited around the hole circumference is close to the total excess volume of material (both TiO_x and C) removed from the hole itself. The convolution of the finite tip radius on the AFM with a small hole profile could cause the measured hole depths to be anomalously low [4]. Then, for smaller holes, RV would be larger than CV+TV, an effect which is, in fact, not seen in Figure 3.

Figure 1: (a) Image of TiO_x coated on-S-layer and off-S-layer areas before FAB milling. The image shows both the two dimensional hexagonal lattice on-S-layer as well as smooth off-S-layer areas. The lattice parameter of 22 nm serves to indicate the scale length; (b) AFM cross-section profile of unmilled TiO_x coated S-layer along the line in Figure 5(a). The vertical height difference between the arrowheads is 6.1 nm

(a)

(b)

Figure 2: (a) Image of TiO_x coated on-S-layer and off-S-layer areas after FAB milling; (b) AFM cross-section profile of milled TiO_x coated S-layer along the line in Figure 6(a). The vertical distance between the leftmost set of arrowheads is 4 nm and the vertical distance between the rightmost set of arrowheads is 8 nm. The erosion of deep holes in the carbon is evident, as are the annular rings of material at the hole edges.

Figure 3: Annular ring volume, RV (o), and total removed volume, CV + TV (---), for holes of various sizes. The total removed volume, CV + TV, and annular ring volume, RV, are nearly the same for most holes. INSET: Scale diagram of a 7.5 nm deep hole showing the annular ring and Ti film.

Thus we have shown that a TiO_x film, although only 3.5 nm thick, can act, in the absence of random nucleation sites, as an effective mask material for FAB milling of HOPG.

Crystalline Silicon

Following the initial demonstration of pattern transfer to an HOPG substrate we are pursuing experiments to achieve pattern transfer to substrates of interest. One such material is silicon, owing, in part, to the great interest in the luminescent properties of porous silicon following the pioneering work of Canham in 1990 in which anodic etching of bulk silicon in hydrofluoric acid/ethanol solutions was shown to produce porous/luminescent silicon [5]. As of this writing there have been a plethora of experiments reported which have been interpreted to suggest quite different mechanisms to explain the observed phenomenon. Specifically, explanations include (i) quantum confinement in Si quantum wires, (ii) the formation of siloxene, (iii) chemisorbed molecules on the vast surface area provided by porous silicon, (iv) the formation of amorphous silicon, (v) some combination of the above. We are working toward the objective of using our metal oxide masks to define the initial positions of the etch sites on the silicon surface prior to the anodic etching of the silicon. The shallow etch pits in the silicon surface resulting from the FAB milling will be deepened either by anisotropic wet chemical etching or by dry etching via plasma or reactive ion etching. After deep initial pore locations are defined in the silicon surface, it is straightforward to remove the mask (protein crystal plus metal oxide) chemically using a titanium etchant (manuscript in preparation). Consequently, by periodic nanostructuring of the silicon surface prior to anodic etching, we will fabricate porous silicon with uniform pore diameters and uniform silicon 'column' diameters and thus produce a monodisperse array of silicon quantum wires. This will enable us to elucidate the role of quantum confinement in the phenomenon of luminescent silicon. Moreover, should quantum confinement be found to play a role in the observed luminescence, then the availability of crystalline, biomolecular patterning templates with a wide range of lattice constants may enable us to fabricate porous silicon with a spectrum of pore diameters and silicon 'column' diameters and thus to controllably tune the wavelength of the resulting luminescence. In addition, we note that the role of *periodic* nanostructuring on operative effects is unknown.

In our work to date on this project we have successfully addressed two major requirements for the patterning of macroscopic areas of silicon: (1) adhesion—monolayer coverage of the majority of the silicon substrate by the ~1 micron diameter protein crystals; and (2) sidedness—the cytoplasmic side (as opposed to the exoplasmic side) of the protein crystals must face up (that is, away from the substrate) in order to produce a satisfactory metal oxide mask and subsequent pattern transfer from the mask to the substrate. In fact, the solution to both these issues was neatly provided in one step by application of a suitably chosen silane coupling agent to the silicon surface prior to the deposition of the protein crystals. Glycidoxypopyltrimethoxysilane applied to the silicon surface provided excellent coverage over macroscopic areas. Figure 4a shows representative coverage (the region shown is limited only by the maximum scan size of the AFM scan head), and Figure 4b shows a higher magnification view of the metallized (but unmilled) patterning templates, that is, the metallized protein crystals. Moreover, the glycidoxypopyl silane coupler selectively binds to the carbohydrate moiety found only on the exoplasmic side of the protein crystals and thus ensures that the cytoplasmic side of the protein crystal is face up. Figure 5 shows a portion of a nanostructured titanium oxide mask formed on a (100) silicon substrate. The protruding hillocks are metal oxide-coated protein and the holes in the mask are hexagonally ordered with a lattice spacing of 20 nm.

The bottom most portion of the holes are etch pits which extend several nanometers into the silicon substrate which is directly beneath the metal oxide mask.

Figure 4: (a) Low magnification view of metallized (but unmilled) S-layer on a silanized Si substrate (scale bar = $1\mu\text{m}$); (b) Higher magnification view of (a) (scale bar = 250 nm).

Figure 5: AFM surface mode image, fourier filtered, of a portion of a nanostructured titanium oxide mask on a (100) silicon substrate.

In addition to our work in progress on silicon substrates we are also engaged in experiments to transfer a nanostructured pattern to metal substrates. One reason for our interest is the compelling technological goal to develop a process for fabricating large arrays of interconnected nanometer-scale metal tunnel junctions for coulomb blockade or "single-electronics" applications. In very small normal metal tunnel junctions the change in potential due to a single electron on an electrode can cause a significant reduction in the tunneling rate. This phenomenon, also known as the coulomb blockade, provides the physical basis for a new class of electronic devices [6]. Although current devices at the 100 nm scale only operate well at low temperatures, when coulomb blockade devices are implemented at the molecular scale the coulomb energy associated with a single electron will become large, and operation in liquid nitrogen or even at room temperature is expected. To date we have succeeded in forming TiO_x masks and, concomitantly, nanostructured periodic arrays of etch pits on the surfaces of both noble metal (Pt) and metal oxide (Ta_2O_5) substrates. These results are analogous to those we have obtained with crystalline Si substrates. We are now exploring methods such as plasma etching and reactive ion etching to impress these patterns more deeply (several tens of nanometers) into the substrate. After doing this we will remove the mask (S-layer plus TiO_x) and use electron beam lithography to attach leads to nanostructured portions of the metal and perform a variety of electron transport measurements (e.g., measurement of the electron diffusion constant) in order to electronically characterize these parallel fabricated metal nanostructures.

II. PATTERN DEVELOPMENT

Microstructural Characteristics of Ultrathin Metal Films

We have used transmission electron microscopy (TEM) to evaluate the microstructural modification of a variety of ultrathin films (transition and noble metals) undergoing parallel molecular lithography [7]. Thin films of Ti, Ta, Pt, Pt/C, Pt/Ir, Pt/Ir/C, Va, Cr, Ni, Ag, Zr, and Nb show dramatic differences in their response to this method of nanotexturing. It was found that metals which deposited as amorphous or very fine grained layers and did not crystallize or grain coarsen during milling were the most likely to form uniform nanostructures. These included Ti, Ta, Nb, Zr and Cr.

An example of the disparity in the pattern creation in ultrathin films of different materials is presented in bright field electron micrographs in Figure 6. The dark field electron micrograph of the nickel oxide film shows that grain coarsening has occurred after milling and the electron beam diffraction pattern corroborates this showing sharper more well defined rings [12]. By contrast, the titanium dark field image shows no grain structure and the diffraction pattern is composed of diffuse, broad halos, the signature of a very fine grained (or amorphous) structure.

We note that the pattern formation shown in Figure 6 is not optimal because the S-layer templates were air-dried onto the substrates prior to metallization rather than dried in such a way as to limit plastic deformation, for example, by using critical point drying

Defects in Naturally Occurring Protein Crystals

We have studied fluctuation generation in the parallel nanofabrication process we have developed and have identified one source arising from fluctuations in the patterning template itself [8]. In the case of *Sulfolobus acidocaldarius*, for example, the symmetry of the S-layer arises from the hexagonal ordering of triads of dimers of S-layer protein (Figure 7). These proteins are held together by charge, not covalently. As the bacteria grows, additional S-layer protein is produced and added to the growing surface [9]. A sheet of protein having pure 6-fold symmetry cannot encase a volume [10]. Defect structures in *S. acidocaldarius* have been inferred from image analysis using high resolution TEM [11]. We have

Figure 6: TEM micrographs of nanostructures formed from (a) nickel (oxide) (Scale bar = 140 nm) and (b) titanium (oxide) (Scale bar = 150 nm). In both cases, the S-layer of *S. acidocaldarius* was shadowed with 12Å of metal and fast atom beam (FAB) milled for 20 seconds.

Figure 7: Atomic force microscope (AFM) image of cytoplasmic surface of S-layer of *Sulfolobus acidocaldarius* with has been air-dried and metallized. The triads (of dimers) of S-layer protein are clearly visible.

ourselves **directly imaged** twin boundaries in metallized S-layers from *Sulfolobus acidocaldarius* using atomic force microscopy (AFM) (Figure 8).

Figure 8: Atomic force microscope (AFM) image of cytoplasmic surface of S-layer of *Sulfolobus acidocaldarius* (air-dried and metallized) showing rotation twin boundary. The orientation of the triads of dimers changes at a twin boundary as shown. This image has been filtered using a Fast Fourier Transform to display more clearly the boundary.

III. MASK REMOVAL

We have succeeded in removing the masking material (S-layer plus TiOx) and in thus exposing the 'bare' nanostructured substrate (manuscript in preparation). This has been accomplished by treating the masked, nanostructured surface with a metal oxide etchant which removes both the metal oxide overlayer and the protein crystal to which it is adhered. We have used two different commercial etchants supplied by Transene Company, Inc. One of the etchants, type TFT, is a hydrofluoric acid based etch and the other, TFTN type, is a hydrochloric acid based etch. Samples are treated with the etchant for ~10' at 80 C and are then rinsed with distilled water and air dried. Analysis with x-ray photoelectron spectroscopy (XPS) confirmed preliminary results obtained with scanning tunneling microscopy (STM) and showed that the masking material was successfully removed.

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In addition, during this funding period our work has been featured in the following publications:

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