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We have pursued experiments to produce a two-dimensional array of crystalline Si(c-Si) quantum dots surrounded by a hydrogenated amorphous Si(a-Si:H) matrix. The quantum dots are to be defined laterally on the silicon surface using our protein crystal masking technique. We have investigated two methods for impressing the quantum dot array into the silicon substrate. In the first approach we used our protein crystal/metal oxide mask to create an array of 10 nm Pd dots and tried annealing parameters to crystallize a-Si under these Pd dots without having the crystallized dots coalesce. In our second approach we used low energy electron enhanced etching (LE4) to extend the surface nanostructuring of silicon deeper into the bulk. This was followed by removal of the TiO_2/protein crystal mask and the subsequent creation of a self-assembled, free-standing, ordered nano-array of metal clusters. We have also used LE4 as an alternative to ion beam milling as a means of pattern transfer. We have found that samples which experienced only LE4 produced pattern transfer of comparable or better fidelity than samples which had been ion milled prior to LE4. Also, we have found a way to fabricate the 'inverse' pattern in the surface nanostructuring of silicon. The inverse pattern consists of an array of *isolated* metal dots which form an hexagonal lattice with lattice constant 20 nm.

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Introduction

We have been pursuing the creation of quantum dot arrays fabricated in crystalline silicon. We wish to produce a two-dimensional array of crystalline Si(c-Si) quantum dots or boxes surrounded by a hydrogenated amorphous Si(a-Si:H) matrix. The quantum dots are to be defined spatially using the protein crystal masking technique described in our research grant and which we now briefly summarize. This nanofabrication technique is implemented using two-dimensional crystalline protein monolayers which are deposited on a substrate, metal shadowed at oblique incidence with an ultrathin (~1 nm) titanium film, and then ion milled at normal incidence. During milling the metal film is reconfigured through a combination of sputtering and surface diffusion leaving a periodically nanostructured, ultrathin metal(oxide) film. Moreover, we have found that this nanostructured screen acts as a mask for the pattern transfer of a periodic array of holes or etch pits to the underlying substrate, which in the present case is silicon.

Constrained Crystallization

Over the course of this effort we have concentrated on two approaches. Our initial attempts were based on the results of Liu and Fonash (Appl. Phys. Lett. 55,660 (1989)) who found that a-Si:H, when coated with a thin (<100Å) layer of palladium, crystallized to cubic Si at temperatures several hundred degrees lower than that required for uncoated a-Si:H. Our goal was to use our protein crystal/metal oxide mask to create an array of 10 nm Pd dots with a 20 nm lattice constant and to find annealing parameters so that we crystallize the Si under these Pd dots without having the crystallized dots grow together. In initial experiments in this direction we.used e-beam lithography to create an array of 1 μm Pd squares separated by 1 μm. To create this array of 1 μm squares, we spun on 4% 950k PMMA onto our substrates (100Å a-Si:H on sapphire) at 5000 rpm for 30 seconds and cured at 160°C for two hours. We then thermally evaporated 150Å of Al onto the PMMA to prevent charging in the SEM. The pattern was designed using DesignCad 2-D and written using a Philips SEM501. The x-y scan coils and beam blanking were controlled with a Nanometer Pattern Generation System from J. C. Nabity Lithography Systems using a DT2823 board from Data Translation, Inc. We dissolved the Al in a NaOH solution and the pattern was developed by soaking in MIBK/IPA (1:3) for 60 seconds and then rinsing with IPA for 30 seconds. We then deposited 20Å of Pd at normal incidence using e-beam evaporation. We annealed these samples for 10 minutes at various temperatures. At 550°C, the Si crystallized beneath the Pd without bridging together. In fact, the crystallization was confined to approximately less than 0.1 μm (100 nm). At 600°C, the crystallized areas beneath the Pd began to bridge together.

Following this we began an investigation of annealing times and temperatures based on these results but using the protein crystal masks. This requires that palladium catalyzed, selective Si crystallization (and hole bridging) be controlled on the 10 nm length scale. This constraint of the crystallization appears to be the major technical problem to be solved in this approach. The a-Si:H beneath the Pd dots must crystallize completely, but at the same time, the crystallization must not extend beyond the Pd dots. The two parameters that are available for controlling this crystallization are annealing time and temperature. To date we have examined nanopatterned samples which were annealed for 10 minutes at temperatures between 500°C and 600°C in increments of 25°C. Pd-coated a-Si:H samples (not nanopatterned) were annealed in parallel and used as controls. At this time no photoluminescence has been observed. It should be noted that every luminescence measurement was plagued by scattered light that appeared in the final

spectra as either yellow or red peaks. The extraneous nature of these peaks can be readily verified and this problem is being addressed.

Low Energy Electron Enhanced Etching (LE4)

In our second approach to the parallel fabrication of a c-Si quantum dot array we have used the new etching method of low energy electron enhanced etching (LE4) to extend the surface nanostructuring of silicon (accomplished with our biologically derived patterning templates) deeper into the bulk. To assay the extent of LE4 Si etching we *removed* the mask and XPS measurements were performed which show that the TiO_2 was completely removed within the sensitivity of XPS. AFM imaging of the bare silicon showed arrays of holes having the hexagonal symmetry and lattice constant of the protein crystal template and hole depths which exceeded those found on Si patterned with protein crystal/metal oxide masks and ion milling but no LE4 processing. We then performed a novel 'metal staining' experiment in which 12Å of Ti was electron beam evaporated at normal incidence onto the sample in an attempt to enhance the constrast of the patterned Si. The result of this experiment was that arrays of TiO_2 islands were formed and these arrays display the same hexagonal symmetry and lattice constant of the protein crystal used for patterning the surface. This can be explained by the fact that Ti can diffuse large distances on passivated surfaces until it finds a defect site. Our post-LE4 surfaces appear to have both defect sites and passivated areas and Ti adsorbed to the surface migrates to the defect sites (where etching has occurred) rather than the weaker bonding sites in the passivated regions. Once a few Ti atoms are adsorbed at defects, they act as nucleation sites for ensuing adsorption of Ti. Thus, these experiments have shown that patterning a substrate with the (naturally self-assembled) protein crystal mask can induce self-assembly of an ensuing free-standing, ordered nano-array of metal clusters *subsequent* to mask removal.

Additionally, we have explored the use of LE4 as an *alternative* to ion beam milling as a means of pattern transfer. In the work described in the previous paragraph, we used LE4 to extend the surface nanostructuring of silicon deeper into the bulk but in all these experiments the pattern transfer was always initiated by ion milling prior to the use of LE4. We have now found that samples which experienced LE4 with no prior ion milling produced pattern transfer of comparable or better fidelity than samples which had been ion milled prior to LE4. Significantly, areas of the substrate covered only with titanium oxide but no S-layer protein crystals ("off-S-layer" areas) were extremely smooth compared to such areas on the samples which had been both ion milled and LE4'd. It appears that ion milling damages the titanium oxide mask in the off-S-layer areas and that such damage can be avoided by using LE4 alone.

We note that the DC plasma chamber used for LE4 has been reconfigured compared to previous experiments and in the new configuration the samples sit at a floating potential. The samples were LE4'd for 45 minutes in 100 mtorr of 100% H_2 at a current of 60 mA. As an indication of how non-damaging or 'gentle' the LE4 treatment is, a metallized sample is normally milled for only 12 minutes to achieve shallow pattern transfer to the substrate while in these experiments the samples were exposed to LE4 for 45 minutes, the mask itself remained very smooth (minimal damage), and the pattern transfer to the substrate appears to be at least as deep (although convolution of the AFM tip diameter with holes ~10 nm in diameter make this difficult to determine at present).

The evidence that LE4 can itself produce pattern transfer could be important in determining the best strategy for faithful pattern transfer with minimal fluctuations. We are now pursuing experiments to explore the optimal thickness of titanium oxide deposited prior to LE4 and the optimal shadowing angle for such deposition since removing the ion milling step in the pattern transfer protocol subjects these steps to reexamination. Moreover, we are also pursuing the

possibility use of bare, that is, unmetallized S-layer protein crystals as patterning masks in LE4 mediated pattern transfer.

Metal Dot Arrays

Finally, another research finding is that in the case of samples which *are* ion milled, we have found a way to fabricate the 'inverse' pattern in the surface nanostructuring of silicon. The 'inverse' pattern is easily described in relation to our basic processing protocol. Typically, the titanium metal, 12 Å as deposited, covers both the protein array and the pore sites between proteins which together define the protein crystal (lattice constant 20 nm). Subsequent to ion milling, the coating (which is now ~35 Å of titanium dioxide) is redistributed so that the substrate locations at the positions of the crystal pores are exposed. The remaining metal oxide covers the proteins only, forming a network of lines crossing at angles of 120°/60° as determined by the hexagonal lattice of the protein crystal.

We have now found that the deposition of 6 Å of titanium as measured *in vacuo* onto (100) silicon and which forms an oxide measured by atomic force microscopy to be 18 Å yields the opposite pattern when ion milled with parameters identical to the experiment described above. That is, the pattern consists of an array of *isolated* metal dots which form an hexagonal lattice with lattice constant 20 nm. It is now the uncoated area which is multiply-connected while in the 12 Å experiment it is the metal oxide coated area which is multiply-connected and the uncoated holes in the metal oxide overlayer form the hexagonal array of holes ('antidots'). It is this reciprocity in the pattern formation which results in the designation 'inverse' pattern. Our intention is to attempt to LE4 these arrays of metal dots on silicon in order to extend the surface nanostructuring deeper into the bulk. With such deeper, highly anisotropic initiation sites we will then anodically etch the silicon in order to produce controlled pore sizes and silicon column diameters.

FINAL REPORT

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7. List of manuscripts submitted or published under AFOSR sponsorship during this period, including journal references:

"Preparation of Self-Assembled Monolayers on Float Glass Using Trialkoxysilanes," D.M. Walba, C.A. Liberko, K. Douglas, S.D. Williams, A.F. Klittnick, and N.A. Clark, submitted to Chemistry of Materials.

"Biomimetic Approaches to Nanostructural Fabrication," Kenneth Douglas, in Biomimetic Approaches in Materials Science, p. 117, edited by Stephen Mann, VCH Publishers, New York, (1995).

"Silicon Quntum Dot Laser," K. Douglas, J. Pankove, and G. Moddell, US Patent Application Serial No. 08/473,523 filed 7 June 1995.

"Numerical Simulation of Nanopattern Formation from Protein Crystal Masks: Modeling by Curvature Dependent Ion Milling and Surface Self-Diffusion," Thomas A. Winningham, Zhong Zou, Ryan Weekley, Kenneth Douglas, Noel Clark, Bulletin of the American Physical Society 40, **1**, 27 (1995).

"Biologically Derived Nanometer-Scale Patterning on Chemically Modified Silicon Surfaces," B.W. Holland and K. Douglas, and N.A. Clark, in Mat. Res. Soc. Symp. Proc. 330, 121 (1994).

"Fabrication of 10 nm Holes on a 20 nm Hexagonal Lattice in Si (100)," T.A. Winningham, J.T. Moore, S.D. Williams, K. Douglas, D. Choutuv, J. D. Piper, K. P. Martin, H. P. Gillis, American Vacuum Society 41st National Symposium, p. 321, (1994).

8. Scientific personnel supported by this project and degrees awarded during this reporting period:

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