Chemical patterning for the highly specific and programmed assembly of nanostructures

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We have developed a new chemical patterning technique based on standard lithography-based processes to assemble nanostructures on surfaces with extraordinarily high selectivity. This patterning process is used to create patterns of aminosilane molecular layers surrounded by highly inert poly (ethylene glycol) (PEG) molecules. While the aminosilane regions facilitate nanostructure assembly, the PEG coating prevents adsorption of molecules and nanostructures, thereby priming the semiconductor substrate for the highly localized and programmed assembly of nanostructures. We demonstrate the power and versatility of this manufacturing process by building multilayered structures of gold nanoparticles attached to molecules of DNA onto the aminosilane patterns, with *zero* nanocrystal adsorption onto the surrounding PEG regions. The highly specific surface chemistry developed here can be used in conjunction with standard microfabrication and emerging nanofabrication technology to seamlessly integrate various nanostructures with semiconductor electronics. © *2005 American Vacuum Society.* [DOI: 10.1116/1.1990159]

I. INTRODUCTION

Lithography and etch-based top-down fabrication techniques are currently employed to manufacture micro/nanoscale devices and systems, which find extensive use in applications ranging from electronics to photonics to MEMS and so on. The sizes of critical functional elements (e.g., MOSFETs and semiconductor lasers) in these systems have shrunk down dramatically over the last few decades, resulting in tremendous improvements in cost and performance. However, it is also well known that fundamental limits of device physics (e.g., power dissipation, electron tunneling, etc.) will be reached soon, beyond which current technology will be unable to deliver enhanced device performance. Nanoscale building blocks such as nanowires,[1] carbon nanotubes,[2] and quantum dots[3] are relatively new materials in which quantum confinement effects result in fundamentally new physics. Their use in devices and systems offer the promise of new functionality, enhanced performance and possibly lower cost, which could greatly impact various technological applications.

In order to manufacture devices with nanoscale building blocks it is necessary to assemble them at specific locations on a substrate (such as a semiconductor chip) so that device location and functionality are well defined. For instance, Collins *et al.*[4] have demonstrated field-effect transistors based on carbon nanotubes that deliver superior performance, with the nanotube positioned such that both ends are in good electronic contact with the source and drain electrodes. As another example, Klein *et al.*[5] have fabricated a single electron transistor using a quantum dot precisely located between two tunneling barriers in which Coulomb blockade and gating effects were demonstrated. These and other recently developed nanostructure-based devices illustrate the importance of being able to precisely control the location of nanostructures to achieve the desired functionality. In addition, the fabrication process for making such devices and systems should be scalable for high-volume manufacturing for the technology to be practical. While self-assembly of molecular layers and nanostructures on different substrates has been demonstrated, what is ideally needed is a *hybrid manufacturing paradigm*, which brings together the spatial precision and mass production capabilities of lithography with the bottom-up nature of programmed molecular assembly in order to realize the above-mentioned goals. In essence, any high-throughput fabrication process involving devices and structures based on nanoscale materials should satisfy the following criteria: (a) it should be fully compatible with current and emerging lithography techniques; (b) it should be based on the programmed assembly of nanostructures; (c) the nanostructures should assemble on substrates at predetermined locations, with absolutely no nanostructure

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adsorption on undesired locations of the surface.

One of the most versatile approaches involves creating lithographically patterned regions of molecular layers on substrates, which serve as scaffolds for the programmed assembly of nanostructures and functional molecules. Of course, a key requirement of such a process is that nanostructures assemble only on the functional patterns and not in the regions of the substrate surrounding the patterns, since otherwise, random structures would be created at unwanted locations of the substrate. Different research groups have investigated variations of this concept mainly on substrates containing gold films deposited on silicon or glass. Clark *et al.*[6] used microcontact printing to create patterns of negatively charged alkanethiol monolayers (the negative charge arises from carboxyl groups) surrounded by oligo (ethylene glycol) (OEG) terminated alkanethiols on a gold coated surface to selectively and alternately assemble multilayered structures of poly-cations and poly-anions. An interesting aspect of the process is that by using different salt concentrations for polyelectrolyte deposition the assembly could either be performed on the negatively charged portions or the OEG regions of the surface. Musick *et al.*[7] also created binary molecular patterns on gold coated chips using microcontact printing with positively charged groups surrounded by negatively charged alkanethiols. (It should be noted that the positive charges come from amine chemical groups and the negative charges from carboxyl groups.) They used this patterned surface to build multilayers of gold nanocrystals on the positively charged parts of the chip, with adjacent layers of nanocrystals connected by the molecule mercaptoethylamine, both ends of which have strong affinity for gold. Due to the negative charge of the carboxyl groups around the amine groups, nanoparticle assembly was expected to be much lower on the carboxyl-coated parts of the chip. While this does turn out to be true, the nonspecific adsorption is still too high for this process to be of practical use in nanoscale fabrication.

While patterning molecular layers on gold-coated substrates is relatively straightforward as seen from the above examples, it is certainly more useful as well as challenging to create binary molecular patterns (i.e., patterns of one functional molecule surrounded by regions coated with another molecule) on silicon surfaces. This offers the possibility of integration with standard electronic fabrication technology, as opposed to on gold, which is incompatible with VLSI. Though it is relatively straightforward to build monolayers (through vapor phase deposition) or multilayers (through solution phase deposition) of various silanes, there have been fewer instances and applications of surfaces patterned with silane molecules, with a few notable exceptions.[8–10] Xia *et al.*[8] demonstrated the microcontact printing of one type of alkylsilane on silicon substrates to define the molecular patterns, followed by deposition of another alkylsilane to create binary microscale patterns. The main drawback of this technique is its incompatibility with standard microfabrication technology. Krüger *et al.*[9] developed a technique to fabricate patterns of aminosilane (a positively charged molecule) surrounded by regions of octadecylsilane (a hydrophobic molecule) using a combination of photolithography and vapor/solution phase silanization. These substrates were used to self-assemble negatively charged microspheres onto the aminosilane patterns through electrostatic forces. It should be noted, though, that despite the hydrophobic nature of the octadecylsilane on silicon region surrounding the aminosilane patterns, there was substantial amount of nonspecific adsorption. Most recently, Pallandre *et al.*[10] used electron beam lithography to create PMMA patterns and functionalized regions not covered by PMMA with one type of silane molecule in by vapor phase deposition. After dissolution of the PMMA resist, the remaining portions of the silicon surface were functionalized with another silane molecule, also using vapor phase deposition, to create binary nanopatterned surfaces. The usefulness of this process was illustrated by assembling polyelectrolyte multilayers on the nanoscale patterns, despite the fact that nonspecific adsorption occurred to a measurable extent on undesired locations of the substrate.

The most important limitation of any of the above manufacturing methods is that they do not satisfy the third of the three fundamental criteria for nanostructure-based manufacturing processes mentioned above. In other words, the bottleneck has always been performing programmed nanostructure assembly without the nanostructures getting adsorbed onto undesired regions of the patterned substrate. In a recent publication[12] we proposed and demonstrated the use of poly (ethylene glycol) or PEG molecular coatings on silicon to completely block nonspecific adsorption of nanoparticles. These experiments involved coating of silicon regions of a substrate containing gold patterns with highly inert PEG layers and subsequently programming the assembly of gold nanoparticles onto the gold patterns. The latter technique of assembling gold nanoparticles is based on previous work done by Mirkin *et al.*[11] where, the highly specific attractive interaction between two strands of complementary DNA molecules is used to guide the self-assembly process. In this programmed assembly technique DNA molecules of a known sequence of bases are attached to one set of nanoparticles, while the complementary DNA molecule is attached to a second set of nanoparticles. When these two sets of particles are mixed they attract and bind (a process called hybridization) to each other due to the highly specific Watson-Crick base-pairing forces of the DNA molecules. Our work, which combined this programmed nanoparticle assembly with PEG-based lithographic patterning, demonstrated that the inertness of the PEG layer is so high that it completely prevents the adsorption of all gold nanoparticles, with the nanoparticle assembly occurring only on the gold patterns. To the best of our knowledge, such extraordinary specificity as seen with PEG layers has not been achieved with any other molecular coating, thus providing a route to highly localized and coded assembly of nanomaterials.

In the current article, we show that the PEG-based assembly technique developed above may be extended to silicon surfaces without the need for gold, thereby making the chemical patterning process much more versatile than our

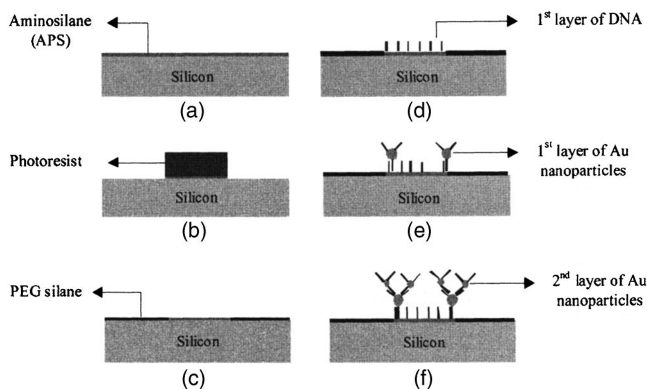

FIG. 1. (a) Vapor deposition of APS on the Si substrate. (b) Patterning of the photoresist film by photolithography and then using oxygen plasma to remove the APS from the regions not protected by the photoresist. (c) Functionalization of the surrounding Si substrate by PEG-silane and removal of the photoresist covering amine-terminated patterns. (d) Selective assembly of single-stranded thiolated DNA on APS patterns. (e) Assembly of first layer of DNA-1conjugated Au nanoparticles on APS patterns. (f) Assembly of second layer of nanoparticles on the first nanoparticle layer.

previous work. Figure 1 shows the process flow. To demonstrate the effectiveness of this surface chemistry technique, we assemble multilayer structures of DNA-conjugated gold nanoparticles on these patterned substrates and show that the assembly process is specific down to a single nanoparticle level. The compatibility of our fabrication process with standard semiconductor processes makes the integration of novel nanostructure-based functional devices with standard electronics a very real possibility in the near future.

II. EXPERIMENT

A. Materials and reagents

4 in. *N*-type silicon wafers and a vacuum pump were purchased from the Berkeley Microfabrication Laboratory. A Wheaton Dry-Seal® desiccator (150 mm diameter) was purchased from Wheaton Science Products. 3-Aminopropyltri methoxysilane (APS) and 2-[methoxy(polyethyleneoxy) propyl]trimethoxysilane (henceforth referred to as PEG silane, which has between 12 and 18 CH_2O or ethleneoxy groups) were purchased from Gelest, Inc. (Morrisville, PA). Gold nanocrystals, 10 nm (nominal) and 15 nm (nominal) in diameter, were purchased from Ted Pella, Inc. (Redding, CA) bis(*p*-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt (henceforth referred to as phosphine) was purchased from Cardinal Industries (Milwaukee, WI). Complementary DNA molecules were purchased from Integrated DNA Technologies (Coralville, IA) in powder form. The names and base sequences of the complementary DNA molecules are as follows (note that the first 20 bases do not hybridize):

Substrate Oligo:
5'- SH-C6-TTTTTTTTTTTTTTTTTTTTAATATTGATAAGGAT

NC Oligo:
5'-SH-C6- TTTTTTTTTTTTTTTTTTTTATCCTTATCAATATT

B. Synthesis of DNA-conjugated gold nanoparticles

All experimental details regarding the attachment of complementary DNA molecules to gold nanoparticles are presented in our recently published work.[12] Briefly, highly concentrated solutions of both the DNA molecules as well as gold nanoparticles are prepared. The gold nanoparticles are made highly negatively charged through the addition of the phosphine molecule in order to prevent them from precipitating at such high concentrations. DNA molecules are then added to the nanoparticle solution and the reaction between the gold and sulfur groups is allowed to proceed for a few days before removing excess, unattached DNA molecules though centrifugation. Sodium chloride is then added to this solution of DNA-conjugated nanoparticles in order to facilitate the reaction between complementary DNA molecules during the self-assembly process. It should be noted that the addition of DNA molecules makes the gold nanoparticles even more negative and prevents them from precipitation during the addition of sodium chloride.[11]

C. Vapor phase deposition and lithographic patterning of APS

The process sequence for chemical patterning is outlined in Fig. 1 (molecular layers are not drawn to scale). Before vapor phase deposition of aminosilane on the wafer, the wafer was partly diced and reversibly bonded using photoresist to a handle wafer. This was done in order to make it suitable for reaction with gold nanocrystal solutions (which are available only in small volumes such as a hundreds of microliters) and also to perform imaging using the high resolution field emission scanning electron microscope (FE-SEM), which is capable of handling only very small substrates (4 mm $\times 5$ mm maximum size).

Vapor phase was preferred for silanization reaction since the wafers were bonded using photoresist, which is readily soluble in organic solvents such as ethanol used for liquid-phase silanization reactions. For vapor phase silanization, the wafer was placed in a vacuum desiccator along with 2 vials of APS solution, 100 μl each and the pressure was reduced to approximately 27 in. Hg below atmosphere using a vacuum pump. The process was allowed to occur for 1 h at the end of which, the silane vials were taken out and the physisorbed layer of APS was removed by applying vacuum to the desiccator again. The wafer was cleaned in toluene to further wash the non-specifically adsorbed silane and baked at 120 °C to remove traces of solvents. After spin-coating photoresist, photolithographic patterning was performed using a Karl Suss MA6 Mask Aligner and the wafer was developed using standard resist developer solutions to remove exposed photoresist. The wafer was then baked for 5 min at 120 °C to harden the patterned photoresist and broken into

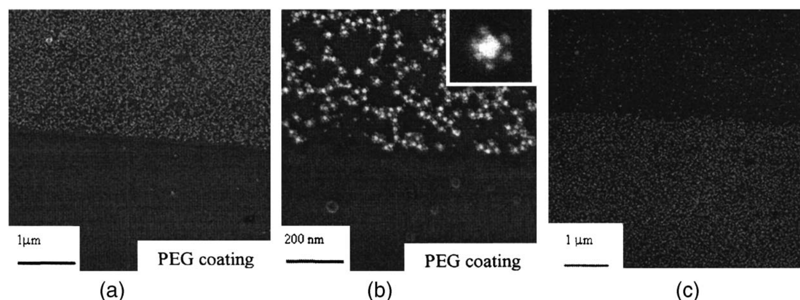

FIG. 2. (a) Two layers of gold nanocrystals assembled on silicon surfaces connected via complementary strands of single-stranded DNA, with APS patterns surrounded by a PEG coating. (b) Magnified view of the image of in (a). The inset on the top right corner of shows a zoomed-in view of a satellite structure of two layers of gold nanoparticles. (c) Gold nanoparticles assembled on APS patterns surrounded by bare silicon, with substantial nonspecific adsorption occurring on silicon.

smaller chips. From this stage onwards all processing was performed at the chip level rather than with wafers.

D. Coating of SiO_2 regions of patterned chips with PEG

The chips with the patterns of APS protected by photoresist were placed in Technics® Plasma Etcher and exposed to O_2 plasma (100 W for 1 min, at a pressure of 0.04 Torr) both to "descum" after the resist development process as well as to remove the APS layer surrounding the resist patterns. In order to ensure that the SiO_2 surface surrounding the photoresist was absolutely clean, patterned substrates were dipped in a 5:1 buffered hydrofluoric acid (hydrofluoric acid buffered with ammonium fluoride at pH=5.3) solution for approximately 20 s to remove the native oxide. The chips were washed in deionized water and dried before being placed in a clean and O_2 gas rich atmosphere (in the Technics® Plasma Etcher at 0.75 Torr pressure) for 2 h to allow the native oxide to grow back. The chips were cleaned with O_2 plasma in the same chamber (100 W for 1 min at a pressure of 0.04 Torr) to make the SiO_2 surface hydrophilic and baked at 120 °C to remove traces of moisture. In conjunction with the latter step, a solution of PEG silane in toluene was prepared as follows, based on the protocol developed by Papra *et al.*[13] PEG silane and concentrated hydrochloric acid (HCl) were mixed in toluene in a freshly cleaned glass beaker with 100 μl PEG and 40 μl HCl present in 50 μl of toluene. The beaker was then placed in a sonicator for 10 min after which, its contents were transferred to another clean glass beaker. The dry chips were placed in the PEG-toluene solution immediately after the O_2 plasma cleaning process for approximately 1 h. This was followed by washing the chips once in toluene, once in acetone to remove the photoresist, once in ethanol and finally in deionized water, with each wash 2 min duration. It should be noted that the photoresist does not get dissolved in toluene during the PEG silanization process despite the fact that it dissolves in most other organic solvents. At this stage, each chip had aminosilane patterns on it that were surrounded by an inert coating of PEG molecules.

E. Assembly of multilayers of gold nanocrystals on patterned chips

Standard covalent chemistry techniques[14] were employed to immobilize single-stranded thiolated DNA onto the APS patterns. Following this, the chips were placed in a solution of the thiolated single-stranded DNA named **Substrate Oligo** (DNA concentration=1micromole per liter or 1 μM), suspended in an aqueous buffer (phosphate buffer at 1 mole per liter or 1 M concentration, composed of potassium phosphate monobasic and potassium phosphate dibasic, pH ~ 7.0) for approximately 4–6 h and then washed according to standard techniques.[14] Following Chrisely *et al.*,[14] the chips were placed in a solution of high concentration of sodium chloride for approximately 6–8 h and washed to remove DNA attached electrostatically to the positively charged amine groups on the surface. The remaining steps for building multilayered assemblies of gold nanoparticles containing the complementary DNA molecules are exactly the same as in our recently published article.[12] Once the desired number of multilayers is assembled on the patterns, imaging is carried out using the scanning electron microscope. The work in this article deals with building only two layers of nanoparticles, as it is relatively straightforward to extend this principle to creating more than two particle layers.

F. Imaging the assemblies on the patterned chip

All images were obtained using a Hitachi S-5000 Field Emission SEM (FESEM) (Robert D. Ogg, Electron Microscopy Center, UC Berkeley), with the accelerating voltage set to 10 kV. The chips were first stuck to a double-sided sticky carbon tape and then mounted onto copper chips before imaging. The chips need to be completely dry before being imaged to achieve the best results.

III. RESULTS AND DISCUSSION

The results of nanoparticle assembly where the first layer of gold nanoparticles are 15 nm in diameter (nominal size as obtained from Ted Pella, Inc.) and the second layer with complementary oligonucleotides are 10 nm in diameter are presented in Fig. 2. Two different nanoparticle sizes are used to distinguish one layer from the other and in order to gauge the specificity of hybridization of complementary DNA mol-

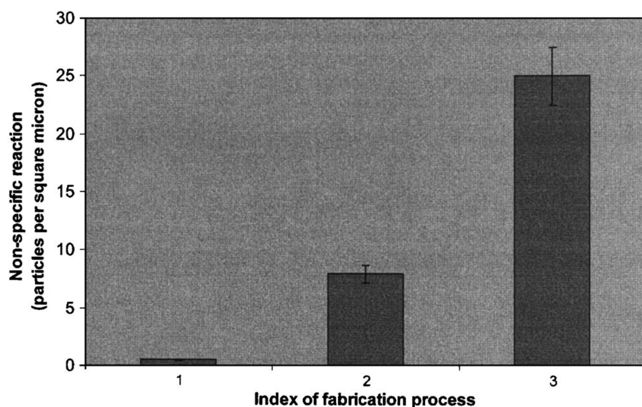

FIG. 3. Histogram for quantitative comparison of different chemical patterning techniques. Fabrication process index "1" refers to aminosilane/PEG patterning developed in this research, "2" refers to gold/OTS-based patterning (Ref. 16), and "3" refers to aminosilane/bare silicon patterning.

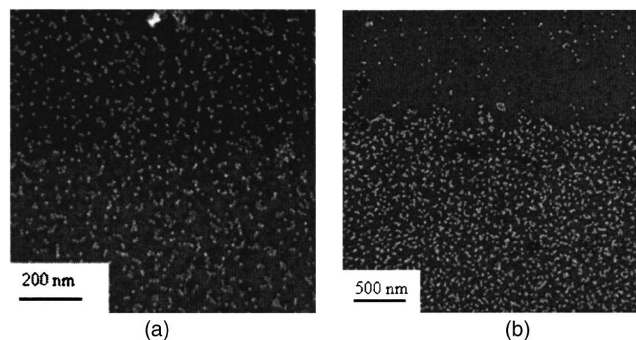

FIG. 4. (a) Assembly of DNA-functionalized gold nanoparticles on APS-patterned, PEG-passivated coated silicon substrates, with unclean native oxide used for the PEG coating process. The bottom half (slightly brighter region) is the PEG-coated surface, where a substantial amount of nonspecific adsorption is observed. (b) Nanoparticle assembly of APS/PEG patterned substrates when the PEG coating is exposed to normal atmospheric conditions for 2 h before performing nanoparticle assembly.

ecules. The most significant aspect of the assembly process, as seen in Fig. 2(a) and 2(b), is the almost complete absence of nonspecific adsorption on the PEG coated portions of the chip, with all nanoparticle assembly occurring exclusively on the aminosilane patterns. In contrast to this, nonspecific adsorption occurs on silicon surfaces where the APS patterns are not surrounded by PEG silane, as demonstrated by the results of a control experiment shown in Fig. 2(c). This extraordinary selectivity is on par with our recently published patterning technique[12] involving thin gold films on silicon substrates and has been found to be highly repeatable. Though several surface patterning techniques have been developed for use on both silicon and gold-coated surfaces (as outlined in the Introduction), none achieves the level of selectivity of the PEG-based method of surface passivation. Fluorosilanes[15] and octadecyltrimethoxysilane,[16] which stake a claim to be rather inert coatings, exhibit a substantial amount of adsorption of various molecules and nanostructures. A histogram quantitatively demonstrating the clear superiority of PEG coating in preventing nonspecific adsorption is presented in Fig. 3. It is seen that, while coating with long-chain hydrophobic silanes[16] does help in reducing nonspecific adsorption, the PEG completely eliminates it. The other important feature to be noted in Fig. 2 is the selectivity of the DNA hybridization process itself as evidenced by the formation of "satellite" structures of the 10 nm particles (the second layer) around the 15 nm particles assembled as the first layer, with very few 10 nm particles adsorbed onto the silicon region directly. Though results are presented only for two layers of nanoparticles, it is possible to assemble as many nanoparticle layers one on top of the other as required without any loss of specificity.

Despite the seeming simplicity and straightforward nature of this surface patterning technique, it was seen that several factors play an important role in achieving the high level of specificity demonstrated in the above images. The two most significant factors appear to be the cleanliness of the native oxide layer on which the PEG silane is coated and the duration for which the PEG layer is exposed to atmospheric conditions, rather than an aqueous solvent such as the potassium phosphate buffer employed in our experiments. (We are currently performing experiments to determine if the inertness of the PEG layer is preserved when chips are placed in an inert environment such as a nitrogen-filled glove box.)

To assess the importance of cleanliness of SiO_2 surface on which PEG is coated, an experiment comprising the following sequence was carried out after patterning the APS layer: (a) APS surrounding photoresist was etched away using oxygen plasma; (b) native oxide was *not* etched away and regrown; (c) chips were coated with PEG under a clean room environment. It was found that this procedure resulted in a nontrivial amount of nonspecific adsorption on the PEG coating, though, as expected, more particle assembly occurred on aminosilane patterns than on PEG, as seen in Fig. 4(a). A quantitative analysis of nonspecificity observed in these cases is presented in Fig. 5. It is seen that nonspecific adsorption on unclean native oxide drastically reduces the specificity of nanoparticle assembly and effectively negates the usefulness of the PEG coating. On the other hand, as outlined in the Experiment, when the existing native oxide was removed and new oxide allowed to grow and cleaned,

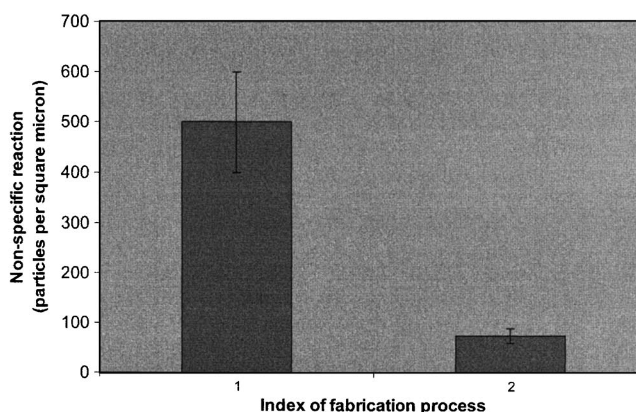

FIG. 5. Quantitative analysis of nonspecific adsorption on silicon substrates for the fabrication conditions in Fig. 4. Process index "1" is for Fig. 4(a) and index "2" for Fig. 4(b).

with the PEG silanization performed immediately in the clean room, the highly specific nanoparticle assembly, shown in Fig. 2, was achieved. Keeping the substrates clean before the PEG reaction was therefore key to obtaining exclusive assembly on the aminosilane patterns. While it is a well-known fact that unclean native oxide is not very conducive to the formation of silane coatings with the desired properties, it is a significant finding that despite performing oxygen plasma cleaning of the surrounding native oxide, it is absolutely necessary to etch off the native oxide and regrow it in order to achieve excellent PEG coatings.

In addition, the amount of time that elapses from the end of the PEG coating process to the start of DNA and nanoparticle assembly process was also a critical parameter. Substantial amount of nonspecific adsorption was observed, possibly due to deterioration of the PEG layer, when PEG-coated substrates were allowed to sit in ambient conditions for a few hours, before the assembly process was initiated. Figure 4(b) shows typical nonspecific adsorption that occurs when the PEG coated surface is exposed to the environment for two hours before nanoparticle assembly. This suggests that it is best to perform the nanoparticle assembly right after PEG silane is coated on the surrounding silicon. In all likelihood, the main reason for deterioration of selectivity of the PEG layer is due to the fact that PEG is a polyether that auto-oxidizes relatively rapidly in the presence of oxygen thereby making it chemically less resistant to adsorption of various molecules and structures, as mentioned in Ostuni *et al.*[17] Since PEG molecules of different lengths and configuration can be synthesized chemically, it would be of great interest to study if any other variants of the standard PEG can be synthesized that are more robust when exposed to atmospheric conditions. Such research will result in wider applicability of the surface chemistries and patterning techniques demonstrated in this article.

IV. CONCLUSIONS

We have developed a novel lithography-based manufacturing process for the programmed assembly of nanomaterials on semiconductor substrates. Borrowing from an observation in protein surface chemistry, where PEG groups are used to eliminate nonspecific adsorption,[18] we have demonstrated that the same principle may be applied to the assembly of nanostructures too, where the PEG effectively prevents the adsorption of nanostructures. Existing theoretical models[19] suggest that entropic forces are most likely responsible for the highly selective nature of the PEG coating and hold out the promise that PEG layers could also be used in systems containing other nanostructures such as nanowires, nanotubes, and other types of quantum dots. In addition the length of the PEG polymer chain and the surface density of the PEG molecules has also been proposed to play a crucial role in determining the level of nonspecific adsorption of nanometer scale structures and molecules.[20] Very long PEG chains are ideal for repelling relatively large structures, while very small molecules and structures can be effectively prevented from adsorbing through the use of highly dense PEG chains.[19] Further research in this area by way of using different nanostructures and different PEG molecules will throw light on the optimum conditions for highly specific programmed nanomaterial assembly on surfaces. In conclusion, unlike all other existing chemical patterning processes, our manufacturing technique satisfies all three criteria outlined in the Introduction for nanostructure-based manufacturing processes, since it incorporates lithography for mass production capabilities, involves programmed assembly of nanostructures, and provides extraordinarily high specificity for nanomaterial assembly. As our manufacturing method is fully compatible with standard microelectronic fabrication techniques it should enable the integration of chemically synthesized nanostructures with CMOS circuits in the future. While functional devices and circuits have not been demonstrated yet with this manufacturing process, the highly selective nanomaterial assembly demonstrated here is a significant first step in achieving the abovementioned integration.

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