Electric Field Assisted Assembly of Functionalized Quantum Dots into Multiple Layer Thin Films

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ABSTRACT

A CMOS electronic microarray device was used to carry out assisted self-assembly of quantum dots into multilayer structures. CMOS electronic microarrays produce reconfigurable DC electric fields that allow DNA, proteins and other charged molecules to be rapidly transported from the bulk solution and addressed to any activated site on the array surface. Such a device was now used to carry out rapid highly parallel assisted self-assembly of biotin and streptavidin derivatized quantum dots into multilayer structures. Nanoparticle addressing could be carried out in 15 seconds or less, and was monitored by changes in fluorescence as each quantum dot layer was deposited. Some final multilayered 3D nanostructures were examined by SEM.

Keywords: self-assembly, quantum dots, nanoparticles, nanofabrication, electronic microarray

INTRODUCTION

Considerable efforts are being carried out on the development of self-assembly processes for creating higher order structures from nanoscale components [1-6]. To this end both passive and active types of Layer-by-Layer (LBL) self-assembly processes have been used to make three dimensional layered structures which can have macroscopic x-y dimensions [7-18]. In cases where patterned structures are desired, the substrate material is generally pre-patterned using masking and a photolithographic process [19, 20]. Other approaches to patterning include the use of optically patterned ITO films and active deposition of the nanoparticles [21, 22]. To date, limitations of both passive LBL and active assembly processes provide considerable incentive to continue the development of better paradigms for nanofabrication. Over the past decade electronic microarray devices, produced by a top-down photolithography process, have been developed for DNA diagnostic applications. These electronic microarray devices which produce reconfigurable electric fields on their surfaces are first used to address and bind negatively charged biotinylated DNA molecules to selected test-sites on the microarray. Samples containing unknown DNA sequences are now applied to the array, and the target DNA sequences are then rapidly transported and selectively hybridized to the DNA sequences bound at the specific test-sites [23-31]. These devices are thus able to direct and accelerate the self-assembly or "bottom-up" process of DNA hybridization occurring on the microarray. In addition to the directed transport and addressing of biomolecules, the ability of electronic microarrays to carry out the rapid patterned deposition of charged nanoparticles was also demonstrated early in the development of the technology [24]. Ultimately, electronic microarrays have been used to carry out transport, addressing and selective binding of a variety of charged biomolecules such as DNA, RNA, biotin/streptavidin, and antibodies [34]; nanoparticles [24, 32-34]; cells [35] and even 20 micron sized light emitting diode (LED) semiconductor devices [36-40]. A first important feature of electronic microarrays is the permeation layer. This porous hydrogel structure overlying the electrodes allows relatively high DC electric field strengths to be used for rapid electrophoretic transport of molecules and nanostructures, while protecting the more sensitive DNA, proteins, or nanostructures from the adverse effects of the electrolysis products generated at the electrodes [23-31]. A second feature of electronic array devices is that they may be designed in a wide variety of shapes and sizes. Arrays have been fabricated in sizes from 2 mm x 2 mm to over 2.5 cm x 2.5 cm, with 25 to 10,000 electrodes and with electrode structures which range in size from 10 microns to several millimeters. A third feature is that sophisticated CMOS control elements can be integrated into the underlying silicon structure of electronic microarrays which allows precise control of currents and voltages to each of the individual microelectrodes on the array [41].

METHODS

Nanoparticle layering experiments were carried out using a 400 site CMOS microarray device (Nanogen, San Diego,

CA). This microarray device is able to independently output currents to each of the 400 different electrodes (54 micron diameter, in 25 columns by 16 rows) at up to 1 µA at 5 volts. Surrounding the 400 test-site microelectrodes are four large counter electrodes which encompass the inner electrode array (Figure 1).

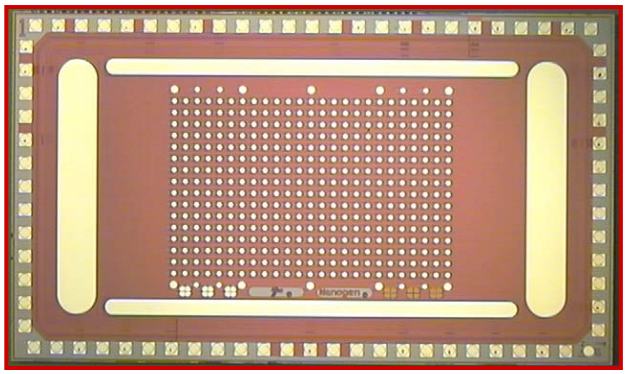

Figure 1 – The CMOS microarray (5mm x 7mm) with four hundred 54 micron test-site microelectrodes and four large perimeter counter electrodes used to produce electric field geometries that encompass the whole microarray surface area (~ 4mm x 6 mm).

The 400 site CMOS array is coated with a 10 µm thick polyacrylamide gel permeation layer which is impregnated with streptavidin. The CMOS microchip array is flip-chip bonded onto a ceramic platform, which then is mounted onto the CMOS controller system. The CMOS controller system is itself mounted under an epifluorescent microscope system with associated CCD camera and imaging system (Figure 2).

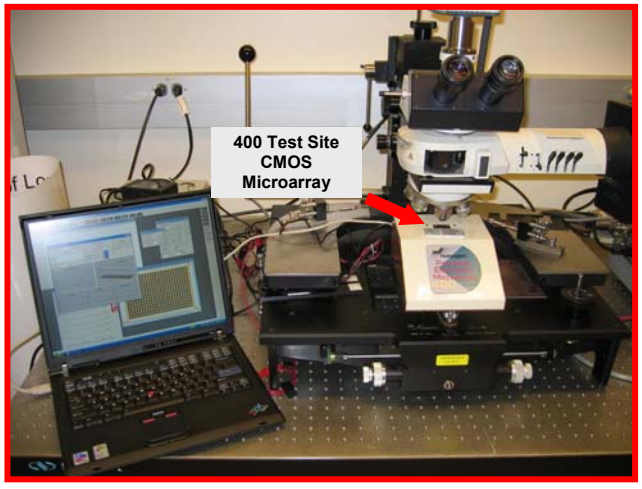

Figure 2 - CMOS controller system with fluorescent microscope imaging system.

This allows the nanoparticle addressing and deposition process to be monitored both electrically and optically in real time. The CMOS controller is run by a laptop computer. Standard procedures were developed to determine the optimal parameters for parallel 3D nanoparticle layering using the 400 site CMOS microarray. The array device was prepared by first washing it several times with ultra-purified water to remove a protective carbohydrate layer from the permeation layer. After washing, the permeation layer surface was reacted with a 20 µl of a 2 µM Biotin Dextran (Sigma B-9264) solution for 30 minutes. The array was then finally washed with a 100 mM L-Histidine solution. To determine optimal addressing (deposition) conditions, the microarray device was programmed to be activated in columns with currents varying from 0.025 µA to 0.4 µA in 0.025 µA increments. Since the quantum dots used in the experiments have a net negative charge, the electrodes at the desired addressing sites on the array were biased positive, and the larger counter electrodes on the perimeter of the device were biased negative. Generally, a group of alternating columns on the array would be activated in parallel at the different current levels and addressing times, while the intervening columns of electrodes were not activated and thus served as negative controls for the nanoparticle addressing and binding process. Array addressing was carried out using 10 µl of 100 mM L-Histidine buffer, containing from 1-10 nM of the derivatized quantum dots. The two types of derivatized quantum dots used in the nanoparticle layering experiments being described were red fluorescent quantum dots derivatized with biotin (Quantum Dot, Em 605 nm) and yellow-green fluorescent quantum dots derivatized with streptavidin (Quantum Dot, Em 565 nm). The biotin-streptavidin ligand binding reaction allows the two different types of fluorescent nanoparticles to be bound to each other, but nanoparticles of the same type do not bind to each other.

The nanoparticle addressing, binding and layering experiments were carried out as follows: (1) About 20 µl of a 10 nM solution of streptavidin quantum dots (green fluorescence) in 100 mM L-Histidine was placed on the microarray and the selected columns of electrodes were activated at the different current levels (0.025µA -0.4 µA), with addressing times of 5, 15 and 30 seconds. (2) The array was then immediately washed (manually) three times with 100 mM L-Histidine, which takes less than one minute. Epifluorescence (Em 565 nm) monitoring of the array was carried out during the process. (3) About 20 µl of a 10 nM solution of 40 nm biotin nanoparticles (red fluorescence) in 100 mM L-Histidine was placed on the array and selected electrodes were activated (currents form 0.025-0.4 µA, with addressing times of 5, 15 and 30 seconds). Epifluorescence (Em 605 nm) monitoring of the array was carried out during the process. (4) The array was then immediately washed three times with 100 mM L-Histidine. (5) Steps 1-4 were repeated to achieve desired number of nanoparticle layers, and epifluorescence (red and green) monitoring of the array was carried during the whole process. (6) The array was finally washed several times with deionized water to remove L-Histidine.

RESULTS

In order to determine optimal conditions for quantum dot nanoparticle layering, experiments were carried out with one, five, ten, fifteen and twenty addressing at 0.30 μA for 15 seconds. Figure 3 shows the fluorescent microscope imaging results for the quantum dot layering experiment

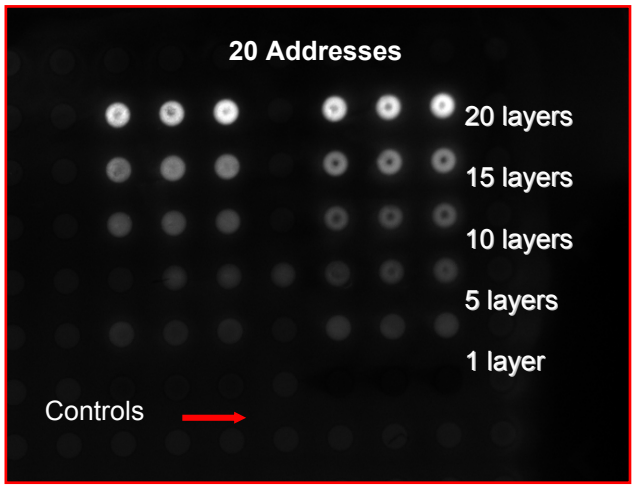

Figure 4 - Experiment showing one, five, ten, fifteen and twenty addressing with biotin and streptavidin quantum dots.

In order to show SEM images of quantum dot layering, some further experiments were carried out in which quantum dots were layered over an underlying layer of 40 nm nanoparticles. The SEM image of these multiple layers is shown in Figure 4.

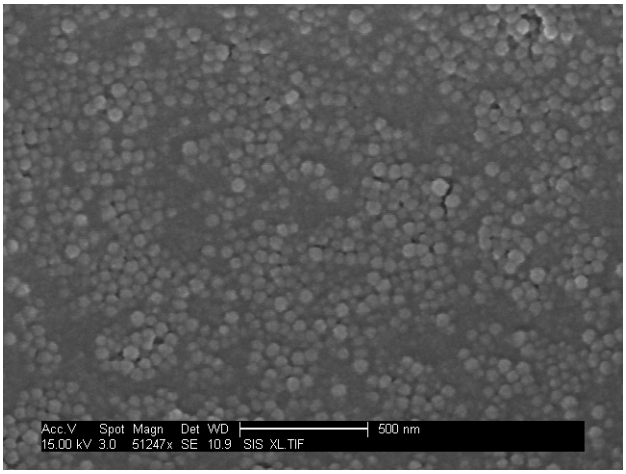

Figure 4 - SEM image of quantum dots overlaying 40 nm nanoparticles

We have shown that electric field assisted self-assembly of twenty multiple layer quantum dot structures could be carried out in a rapid and highly parallel format using a CMOS electronic microarray device. In this process, efficient nanoparticle addressing/deposition was achieved in 15 seconds or less. With a washing step of about 45 seconds, the total time for creating a nanoparticle layer was about one minute. Thus, the twenty layer nanopaticle structures could be completed in less than thirty minutes. The optimal electronic addressing window for creating high quality 3D layered structures appears to be at current levels in the 0.25uA to 0.40uA range. Overall, the use of a microelectronic array device for assisted self-assembly represents a unique example of combining "top-down" and "bottom-up" technologies into a potentially useful nanofabrication process. Such a process may be useful for the hierarchal assembly of integrated nano/micro/macrostructures for a variety of electronic, photonic, materials and other applications.

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