

Optical Addressing of Polymer Beads in Microdevices

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Integrated 'lab-on-a-chip' devices that utilize microfabrication tools are emerging for chemical and biological applications. Facile, robust sample manipulation within these devices will be particularly important for realizing the potential to perform many assays in parallel. Often, biomolecules are manipulated by derivatization to larger 'carrier beads'; therefore, we have developed a novel optical addressing scheme to localize polymer beads (0.8–10 μm in diameter) on an unpatterned semiconductor surface. This approach utilizes an optical microbeam that is directed on the substrate to create an active 'virtual' electrode. The localized charge is defined by the characteristics of the solid-liquid interface in the electrochemical system and serves to attract oppositely charged objects within the solution. Furthermore, to improve patterning efficiency and resolution, a photosensitive polymer coating is used on semiconductor substrates to minimize undesired effects of the dark current. Thus, illumination through a mask or use of multiple beams enables a nonlithographic, dynamic pattern transfer to a uniform substrate. In the future, this approach may be useful for 'off-chip', sterile manipulation of arrays of 'carrier beads' for high-throughput applications.

1. Introduction

Chemical and biological lab-on-a-chip systems are rapidly progressing toward a high degree of functionality and integration.^(1–4) For high throughput screening applications, massively parallel object arrays within these chip systems are essential. The standard fabrication process used by the semiconductor industry, which involves electron beam

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lithography for formation of desired patterns on a set of masks, can be used for formation of arrays of certain materials on a chip. However, for applications in biology or biochemistry, new technological ingredients must be added to meet requirements such as fluidic environment, low power and bio-compatibility. Recently, a number of lithographic patterning techniques have been developed for localization of organic objects such as live cells.⁽⁵⁻⁸⁾ However, active and individual patterning of objects is not feasible with these techniques or will require extensive fabrication. Recently, Hayward *et al.* have shown the assembly of colloidal crystals on indium tin oxide anodic substrates under applied UV-light over a period of 2.5 h.⁽⁹⁾ This technique may not be applicable to biological applications due to potential damage to cells or proteins with UV-light absorption. On the other hand, an individually addressable electrode array has been developed by Cheng *et al.* to form DNA arrays on a chip.⁽¹⁰⁾ However, active manipulation of objects in this technique is unlikely and potential limitation with the number of interconnects restricts the size of the working array. Another approach by Chiu *et al.* tolerates pattern deposition of cells and proteins onto surfaces by using three-dimensional microfluidic systems.⁽¹¹⁾ In this case, dynamic patterning of objects cannot be achieved. Another example proposed by Odde and Renn has shown the laser-guided direct writing of cells.⁽¹²⁾ In this method, optical forces are used to manipulate, guide and write the cells. Due to the serial nature of this method it is not applicable to high-throughput applications.

In this paper, a novel optical addressing technique is presented. This technique allows "active" and "nonlithographic" pattern transfer of polymer beads (0.8–10 μm in diameter) as model ingredients or cells in an electrochemical system for applications in chemistry and biology. For instance, illuminating specific regions of a planar electrode (photoconductor or photosensitive polymer) allows surface charging only in the illuminated areas, thus attracting oppositely charged particles to the illuminated regions. This provides an "off-chip" manipulation and patterning of objects without any lithographic fabrication. Similarly, "off-chip" use of this technique can provide a sterile and controlled environment for sensitive biological samples and thus, it can be employed as an enabling technology for lab-on-a-chip systems with applications both in chemistry and biology. In addition, dynamic patterning of objects can offer continuous manipulation and transport of objects within a lab-on-a-chip system. Here, photoconducting properties of various substrates including semiconductors and photosensitive polymers are investigated to form virtual electrodes for optical addressing of polymer beads. Then, the effects of the type of substrate and intensity of the light on the patterning efficiency are discussed. Finally, the potential effects of the dark current on the patterning efficiency and minimization of the dark current with a photosensitive polymer coating on semiconductor substrates are emphasized.

2. Materials and Methods

2.1 Optical addressing system

Figure 1 schematically depicts the proposed optical addressing unit. In the figure, spheres represent the objects to be integrated over the substrate by optical addressing. After shining a laser on a photo-sensitive substrate such as a semiconductor, absorption of

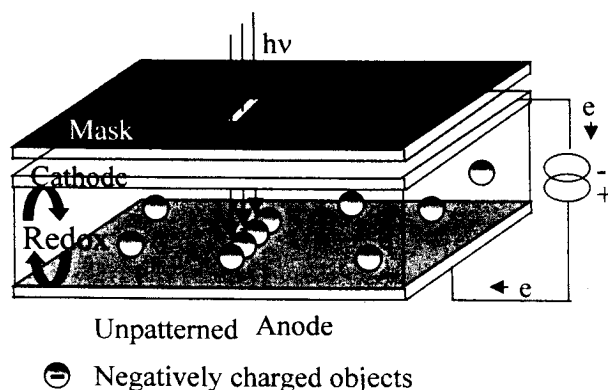


Fig. 1. Schematic drawing of optically assisted assembly system. Objects are driven to a highly charge localized region as a result of illumination.

photons in the semiconductor creates electrons and holes, giving rise to both minority and majority carrier photo-induced currents. Electrons and holes will be separated by the electric field present at the liquid and solid interface. Holes will move toward the surface and electrons will move into the substrate depending upon the characteristics of the solid-liquid junction. Specifically, excess positive charge at the surface is available to attract the negatively charged ions or objects inside the solution.

Primarily, an n-type silicon substrate (Ma-Com Inc.) is used as an anode and indium tin oxide deposited quartz substrate (Delta Technologies Inc.) is used as a transparent cathode to enable light penetration. In addition, a 0.5×0.5 cm² reaction chamber is machined in a 1-mm-thick silicon rubber spacer (Polysciences Inc.). In a similar system as that shown in Fig. 1 polymer beads (Bangs Laboratories Inc.) with $0.87 \mu\text{m}$ diameter are assembled by 650 nm diode laser (Coherent Inc.) illumination. Different kinds of photo-sensitive anodic substrates can be used in this system. Effects of anodic substrate selection on the object assembly are discussed further in the following section.

2.2 Photosensitive electrode selection

Different substrates may be adopted for diverse chemical or biological applications. Here, we studied a number of semiconductor and polymer substrates. Figure 2(a) illustrates the electrical behavior of several semiconductors: GaAs (Ma-Com Inc.), InP (Wafer Tech Products), pn-silicon, nn+silicon in the absence of illumination.

Figure 2(b) illustrates the electrical behavior of InP, pn-silicon and nn+ silicon substrates on a microscale. All the measurements are conducted using deionized water as the electrolyte solution and indium tin oxide as the cathode electrode. The surface area of the contact is 25 mm² in all cases. Substrates are evaluated by several criteria: cost, corrosion and dark current. GaAs is eliminated due to the observed high dark current. Besides, GaAs is very corrosive in the electrochemical environment. InP has excellent diode characteristics (low dark current), however it is expensive and also a very corrosive substrate. Therefore, silicon is determined to be the substrate of choice and besides, it is also known to be as bio-compatible.

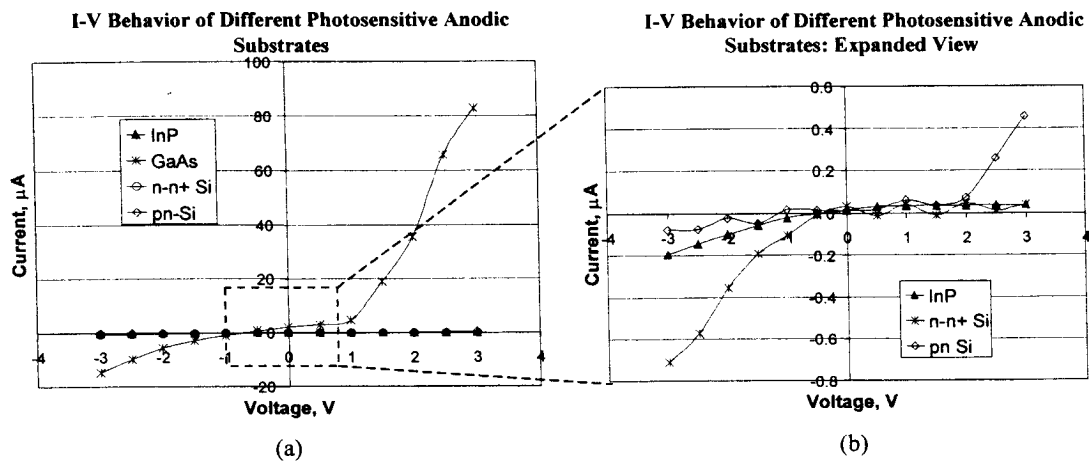


Fig. 2. (a) Current versus voltage behavior of GaAs, InP, pn-silicon and nn+ silicon anodic system in the dark, (b) current versus voltage behavior InP, pn-silicon and nn+ silicon anodic system in the dark. Notice differences in scale.

The specific type of silicon electrode becomes an important parameter during optical addressing of objects. The final preference depends on the solid-liquid interface that is formed when silicon is in contact with the liquid as opposed to the steady state. pn-silicon, normally considered a conventional photodiode, reverses its behavior in solution due to the additional solid-liquid junction. Yet, a pn-silicon substrate exhibits diode behavior at the cathodic region, rather than the anodic electrode as desired. On the other hand, an nn⁺ silicon substrate in contact with liquid has photodiode characteristics, which satisfies the requirements for our purpose.

However, in the nn⁺ /deionized water/ indium tin oxide photo-electro-chemical system, there is a net dark current that could be significant for the nonspecific assembly of objects without directed light on the surface and thus could detrimentally affect the patterning efficiency and resolution. To solve this potential problem, a photo-conducting polymer was spin coated over a silicon substrate. The I-V behavior of such a system is shown in Fig. 3. The anodic dark current is suppressed and minimized significantly. This could help prevent undesired patterning of objects over the substrate and could therefore improve the patterning efficiency appreciably.

3. Theory

In an electrochemical system like that shown in Fig. 1, there is a potential drop at the solid-liquid interface due to electrostatic potential energy mismatch between the two. This can form an ohmic or diode-like junction. The details of the solid-liquid interface characteristics and its effect on the overall performance of the system are discussed elsewhere.^(13,14) Here, we focus on the effect of illumination and intensity of illumination on

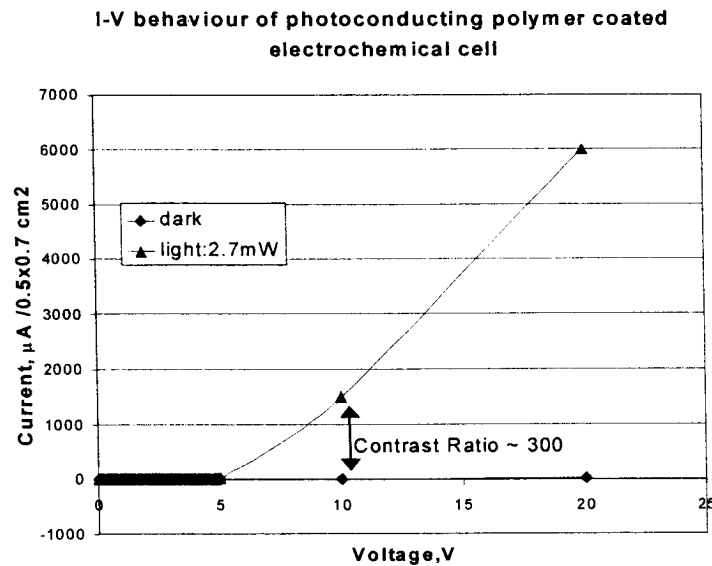


Fig. 3. I-V behavior of photoconducting polymer (poly vinyl carbazole (PVK) doped with hydrocarbons as the charge generator) spin coated silicon/deionized water/ ITO system.

the photoconductivity of the system and hence on the optical patterning efficiency.

Photoconductivity depends on the intensity of the light. The concentration of photoelectrons after the illumination within a semiconductor is given below⁽¹⁵⁾:

$$n = \sqrt{\frac{\beta}{\gamma} J}, \quad (1)$$

where n is the concentration of photoelectrons, β and γ are proportionality factors, and J is the number of absorbed quanta. Equation (1) shows that the concentration of photoelectrons, n , that results in photoconduction is directly proportional to the square root of the intensity of absorbed light. Therefore, total current after illumination can be expected to increase. Others have shown that light can bring about a positive or negative effect on the total current in the system under illumination.^(15,16) The latter is due to light-enhanced adsorption of molecules such as oxygen (a typical acceptor) or hydrogen (donor) on the surface of a semiconductor. When the surface adsorbs acceptors, it becomes charged negatively. The surface charge due to adsorption can either enhance or reduce the emission of electrons from the semiconductor. The adsorption of oxygen always produces an increase in the work function of the semiconductor, while the adsorption of hydrogen results in a decrease. This effect is also observed within our system when deionized water is used as the electrolyte.

4. Results

Previously, negatively charged polystyrene beads ($0.87\ \mu\text{m}$ in diameter) were localized on a silicon substrate with laser irradiation. The details of this experiment are given elsewhere.⁽¹⁴⁾ Here, the use of a photosensitive polymer coating on silicon substrates to minimize the dark current and thus to improve the patterning efficiency is presented.

4.1 Bead patterning on photopolymer

For the initial demonstration, $10\text{-}\mu\text{m}$ -diameter negatively charged polystyrene beads were suspended in DI-water in the electrochemical cell which has a photoconducting polymer (poly vinyl carbazole (PVK) doped with hydrocarbons as the charge generator) spin coated over a silicon substrate as the anode. Initially, the beads were randomly distributed over the substrate surface. A bias of $2.0\ \text{V}$ was applied across the cell, and a He-Ne laser ($\lambda = 632\ \text{nm}$) was used to illuminate a small area on the silicon substrate. In this illuminated region, the generated photocurrent attracted the negatively charged beads towards the substrate. Figure 4 shows the results of this experiment. Image (1) gives the random distribution of beads during sedimentation. Image (2) represents two circular spots that were formed by shining the laser light on the substrate. Image (3) depicts the gathering of beads under constant laser light illumination on spot 2. Notice that during this period, the laser light on spot 1 is turned off. Image (4) shows the reversibility of optical

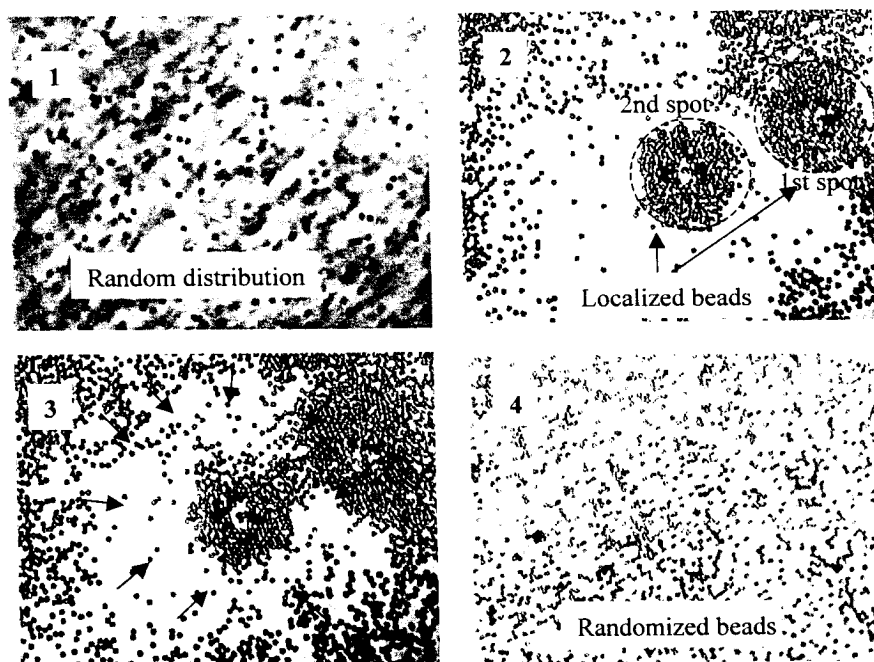


Fig. 4. $10\text{-}\mu\text{m}$ -diameter polystyrene spheres are optically positioned on a silicon substrate that is covered with a photoconducting polymer within 1 min. Beads are attracted to the laser illuminated spot. The distribution of beads is randomized after turning of the laser and reversing the applied bias in 2 min.

patterning. In this case, the laser light was turned off and a negative bias was applied to the substrate that is randomized in the distribution of beads. We believe that photoconducting polymer coated substrates could be the potential choice for our optical patterning process. They can also be used to pattern organic objects by directed light. Furthermore, polymers are cheaper and therefore the substrate is practically disposable. This is an important factor for many biological assays for preventing any possible cross-contamination or infection.

4.2 Effect of light intensity on photoconduction

To investigate the effect of the light intensity on photoconduction of the system in Fig. 1, a series of experiments are conducted by using the n-n+ silicon/deionized water/indium tin oxide combination. Figures 5(a) and 5(b) illustrate positive and negative effects of illumination intensity, respectively. Figure 5(a) depicts the common behavior of the positive effect of illumination and also shows that photoconductivity of the semiconductor increases with higher intensity of light. On the other hand, further increments in the intensity of illumination cause a drop in the photoconductivity of the system (Fig. 5(b)). This effect is discussed in section 3. Adsorption of oxygen molecules at the anodic surface can be enhanced by illumination and is more pronounced at higher intensities. These adsorbed molecules can behave as surface trapping centers, which can trap generated holes after illumination. In Fig. 5(b), the detrimental effect of higher intensities on the total system current supports the idea of oxygen adsorption on the silicon surface. For different substrates, this "turn-around" illumination intensity can be different and needs to be analyzed prior to integration to a lab-on-a-chip system.

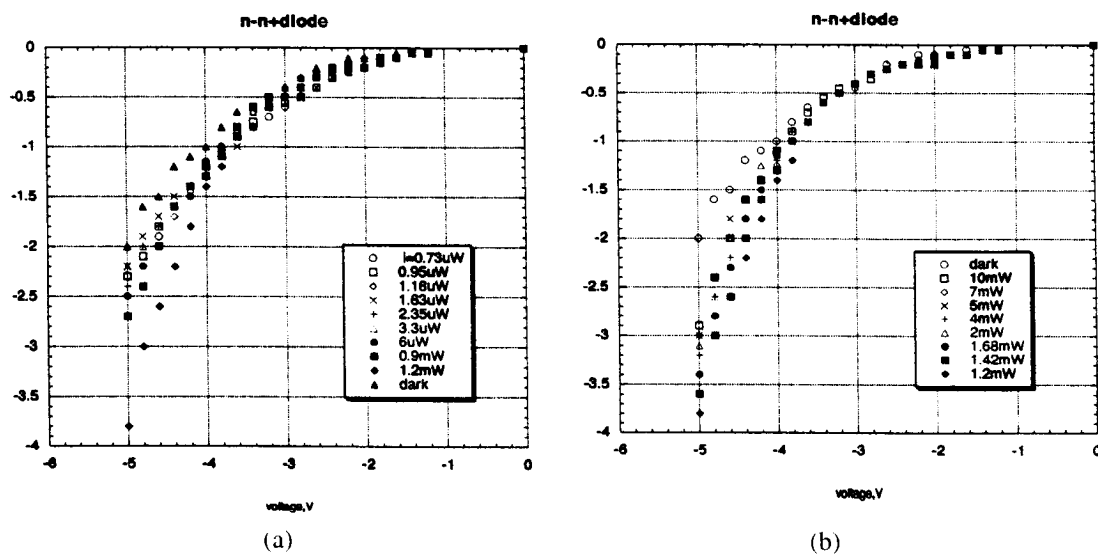


Fig. 5. Anodic total current of n-n+ silicon/deionized water/indium tin oxide system before and after illumination. (a) Positive and (b) negative effect of illumination and higher intensity of light on the photoconductivity of the system. We believe that the latter effect is due to the fact that adsorbed oxygen molecules on the surface of semiconductor behave as trapping centers for photo-generated carriers.

5. Discussion

It is difficult to generate an active platform during the assembly of individual or multiple objects. Our purpose in this study is to develop an optical addressing technique that will enable "off-chip", active patterning of objects with nonlithographic means. This can enable random patterning of many kinds of objects on the same chip, which may require an enormous amount of fabrication or highly serialized integration steps with other existing art.

A photosensitive substrate is selected based on the specifications of system performance, price, and robustness. An n-n+ silicon substrate is selected and characterized in terms of photoconductivity. The n-n+ silicon/deionized water/ITO system exhibits a diode-like behavior. The major possible limitation in this technique is the high dark current. As an alternative, a photopolymer-coated silicon substrate is used to minimize the effect of dark current significantly. This specifically increases the contrast between the illuminated and dark regions and, in turn optical patterning efficiency and resolution are improved.

Finally, polystyrene spheres 0.8 μm and 10 μm diameter in size are successfully positioned on silicon and photopolymer anodic substrates using a 650 nm diode laser. These results show the feasibility of using the process for active patterning of a single or multiple objects or devices. During localization, the intensity of light may be important in terms of attracting or retracting the objects from the surface. By adjusting the intensity of light, molecule adsorption on the surface can be altered and hence one can change the assembly to disassembly simply by attracting or rejecting objects with a given charge. More detailed study needs to be performed to characterize and improve the photocurrent efficiency of the solid-liquid interface by studying different combinations of solutions and substrates. While an optically assisted assembly as objects move in the large local field region, they could cause shielding and scattering of laser light (it is a greater problem with absorbing or reflecting objects or devices). As a consequence, a drop in the local field strength may be observed and therefore misalignment of an object or objects which are nearby can occur. Due to this potential limitation, small objects (< 20 μm) can be patterned with this technique, but it may not be applicable to larger sized and reflective or absorbing objects or devices.

In the future we would like to investigate the effects of object size and different optical characteristics (reflectivity or absorption) on assembly efficiency in more detail. We would also like to apply this technique to structure an "active" assembly of live cells for bioengineering applications.

Acknowledgements

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