Optical Addressing of Polymer Beads for Chip-Based Systems

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Conventional methods that emerged from microelectronics are now used for fabrication of lab-on-a-chip devices for applications in chemical and biological studies. Sample localization and arraying within these devices are desired for high throughput screening applications. We developed a novel optical addressing scheme in an electrochemical system to localize polymer beads (0.8-10 µm in diameter) on various semiconductor substrates with a nonlithographic pattern transfer concept. Optical microbeam that is directed on the substrate creates an active local electrode area with a certain charge that is defined by the solid-liquid interface characteristics. This localized charge attracts the oppositely charged objects within electrolyte solution, which helps to form desired object pattern. By using a multi-beam system or illumination through a mask a relatively large object arrays can be formed for high throughput chemical or biological applications.

**Keywords:** optical addressing, lab-on-a-chip, high throughput, and miniaturization

1. **INTRODUCTION**

Chemical and biological lab-on-a-chip systems are in rapid progress toward a high degree of functionality and integration\(^1\)\(^-\)\(^4\). For high throughput screening applications, a massively parallel object arrays within these chip systems are a necessity. The standard fabrication process used by the semiconductor industry, which involves electron beam 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 \(^5\text{-}^8\). However, active and individual patterning of objects is not feasible with these techniques or will require extensive fabrication.

In this paper, a novel optical addressing technique is presented that 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. This is an off-chip method that does not require any fabrication. This technique is based on the optical properties of materials; photoconducting properties of semiconductors and photosensitive polymers are investigated to be used as photosensitive electrodes for optical addressing of polymer beads. In addition, the effects of substrate selection and intensity of light on the patterning efficiency are also discussed. Since localization can be applied to such a wide range of miniaturized laboratory processes, nonlithographic optical addressing can be used as an enabling technology for lab-on-a-chip systems with applications in chemistry and biology.

2. MATERIALS AND METHODS

2.1 Optical Addressing System

Fig. 1 schematically depicts of 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 photosensitive substrate such as a semiconductor, absorption of 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.

Figure 1. Schematic drawing of optically assisted assembly system. Objects are driven to localized high electric fields as a result of illumination.

2.2 Photosensitive Electrode Selection

Semiconductors and some polymers are known to be photosensitive. Substrate selection varies for different chemical or biological applications. Fig 2(a) illustrates the electrical behavior of several semiconductors: GaAs, InP, pn-silicon, nn+silicon in the absence of illumination.
Figure 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.

Fig. 2(b) illustrates the electrical behavior of InP, pn-silicon and nn+ silicon substrates at the 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. GaAs is also very corrosive in the electrochemical environment. InP has excellent diode characteristics, however it is quite expensive and also a very corrosive substrate. Therefore, silicon is determined to be the perfect substrate and it is also known as bio-compatible.

The specific type of silicon electrode chosen is also very important. The final choice 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 photo diode characteristics, which satisfies the requirements for our purpose.
However, in the $\text{nn}^+/\text{Deionized water}/\text{Indium Tin Oxide}$ photo-electro-chemical system, there is a net dark current that could be significant for the non-specific assembly of objects without directed light on the surface. To solve this potential problem, a photo-conducting polymer was spin coated over a silicon substrate.

![I-V behaviour of photoconductive polymer coated electrochemical cell](image)

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

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 preventing undesired patterning of objects over the substrate and therefore it could improve the patterning efficiency appreciably.
3. THEORY

In an electrochemical system like 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 solid-liquid interface characteristics and its effect on the overall performance of the system are discussed elsewhere \textsuperscript{9,10}. Here, we focus on the effect of illumination and intensity of illumination on the photoconductivity of the system and hence on the optical patterning efficiency.

Photoconductivity depends on the intensity of the light. Concentration of photoelectrons after the illumination within semiconductor is given below \textsuperscript{11}:

\[ n = \frac{\beta}{\sqrt{\gamma}} J, \]

where \( n \) is the concentration of photoelectrons, \( \beta \) and \( \gamma \) are proportionality factors, and \( J \) is the number of absorbed quanta. Eq. (1) shows that the concentration of photoelectrons, \( n \), that brings 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 showed that light can bring positive or negative effect on total current in the system under illumination \textsuperscript{11,12}. 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 gets 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 electrolyte.
4. RESULTS

4.1 Bead patterning on Silicon

For applications in which it is desirable to place a specific object at a specific location, optical addressing can be used. To demonstrate optical addressing, negatively charged polystyrene beads (0.87 µm in diameter) were suspended in DI-water in the electrochemical cell. Initially, the beads were randomly distributed over the substrate surface. A reverse bias voltage of 2.0 volts was applied across the cell, and a He-Ne laser (λ = 632nm) 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. Images in Fig.4 illustrate the fluorescence obtained from highly concentrated bead area with laser radiation. The details of this experiment are given elsewhere 10.

Figure 2. 0.87 µm diameter polystyrene spheres are localized optically trough a rectangular slit mask with a He-Ne laser (λ = 632nm) on a n type silicon substrate.
4.2 Bead patterning on Photopolymer

For the initial demonstration, 10 µm 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.

Figure 5. 10µm diameter polystyrene spheres are optically positioned on a silicon substrate that covered with a photoconducting polymer. Beads are attracted to lasers illuminated spot. The distribution of beads is randomized after turning of the lasers and reversing the applied bias.
A bias of 2.0 volts 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. Fig. 4 shows the results of this experiment. Image (1) gives 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 laser light on spot 1 is turned off. Image (4) shows the reversibility of optical patterning. In this case, 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 photo-conducting polymer coated substrates could be the potential choice for our optical patterning process. They also can 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.

### 4.3 Effect of light intensity on photoconduction

To investigate effect of light intensity on photoconduction of the system in Fig.1 a series of experiments are conducted by using $\text{nm+ silicon/ deionized water/ indium tin oxide}$ combination. Fig.6 (a) and (b) illustrates positive and negative effect of illumination intensity, respectively. Fig. 6(a) gives a common behavior of positive effect of illumination and also shows that photoconductivity of the semiconductor increases with higher intensity of light. On the other hand, with further increments in the intensity of illumination causes a drop in the photoconductivity of the system (Fig. 6(b)). This effect is discussed earlier in section 3. Adsorption of oxygen molecules at the anodic surface can be enhanced by illumination and be more pronounced at higher intensities. These adsorbed molecules can behave as a surface trapping centers, which can trap generated holes after illumination. In Fig. 6(b) 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 need to be analyzed prior to integration to a lab-on-a-chip system.

Figure 6. 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 adsorbed oxygen molecules on the surface of semiconductor behaves as a trapping center for photo generated carriers.

4. DISCUSSION

It is difficult to generate an active platform during assembly of individual or multiple objects. Our purpose in this paper is to develop an optical addressing technique that will enable active patterning of objects with nonlithographic means. This can enable random patterning of many kinds of objects on the same chip, which can require an enormous amount of fabrication or a very serial integration steps with other existing art.
A photosensitive substrate is selected based on specifications of system performance, and price and robustness. A n-n+ silicon substrate is selected and characterized in terms of photoconductivity. The n-n+silicon/deionized water/ITO system mimics a diode-like behavior. The major possible limitation in this technique is the high dark currents. But our photopolymer substrate is very promising and it showed very low dark current behavior. This specifically increases the contrast between the illuminated and dark regions in turn optical patterning efficiency can be improved.

Finally, polystyrene spheres 0.8 µm and 10 µm diameter in size are successfully positioned on silicon and photopolymer anodic substrates by using a 650 nm diode laser. These results show the feasibility of the process to be used for active patterning of a single or multiple objects or devices. During localization intensity of light can be important to attract or retract the objects from the surface. By adjusting the intensity of light molecule adsorption on the surface can be altered and hence it can change the assembly to disassembly simply by attracting or rejecting objects with a given charge. More detailed study needs to be done to characterize and improve the photocurrent efficiency of the solid-liquid interface by studying different combinations of solutions and substrates. While optically assisted assembly as objects move in the large local field region, they could cause shielding and scattering of laser light (it is more 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 object or objects near by can occur. Due to this potential problem, small objects such as molecules can be patterned optically, but it may not be applicable to larger size and reflective or absorbing objects or devices.
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