DEPENDENCE OF TiO₂ FILM SIZE AND SHAPE FOR LIGHT ACTIVATED FLOW CONTROL IN MICROCHANNELS

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ABSTRACT

The surface charge of Titanium Dioxide (TiO₂) can be varied with light to control the electroosmotic flow velocity in microchannels. The use and limitations of TiO₂ films inside microfluidic channels to control both local and bulk flows are explored. Different patterns of TiO₂ can be fabricated over which the surface charge can be modulated. Both modeling and experimental results are presented. In channels containing long patterns, bubble formation was observed due to electrochemical reactions. A threshold potential drop for bubble generation varied from 700 V for a 2.5 cm long film to 1000 V for a 0.5 cm film.

INTRODUCTION

Modulation of local velocity in electroosmotic flow driven systems is useful in applications like mixing at low Reynolds number and improving resolution in capillary electrophoresis. Other workers have reported the use of radial fields to influence the local velocity [1], [2]. However, this is limited by fringing effects [3]. Recently, we have reported active control of the zeta potential with light using TiO₂ films [4].

TiO₂ is a direct semiconductor, and its surface charge can be modulated by irradiating the interface with light of appropriate wavelength. Patterns of TiO₂ can be fabricated giving a definite region over which the surface charge can be controlled. Pattern geometry is limited by electrochemical reactions occurring on the film. Here we describe preliminary experimental and computational work to characterize the parameter space of light modulated zeta potential control.

BACKGROUND

Irradiating a direct semiconductor forms electron-hole pairs (Figure 1) that can then undergo oxidation, reduction or recombination reactions. The relative rates of these reactions determine the nature and magnitude of change in the surface charge. Since such changes can be affected dynamically, the electroosmotic flow velocity can be actively modulated.

Based on this concept, Bard and coworkers [5] have shown that the velocity of TiO₂ particles is affected by irradiation with UV light. Motivated by their work and the fact that TiO₂ is robust in aqueous solutions, we have used TiO₂ films in our study. Preliminary results [4] showing both bulk and local flow control with TiO₂ patterns have been demonstrated. In previous work, the bulk velocity was measured using current monitoring techniques in the presence and absence of UV irradiation in different buffer solutions. The change in the velocity was seen to vary with pH. The largest velocity change was at pH 4.7 with smaller changes observed at higher and lower pH values. To modulate the local flow, staggered patches

of TiO₂ (500 μ m square) were patterned in the microchannel. Upon irradiation with UV light, bending of the flow towards the pattern was observed (Figure 2). The limitations imposed by the

Figure 1 An electron hole pair is formed upon irradiation of a direct semiconductor. The change in the surface charge depends on the relative rates of the oxidation, reduction and recombination reactions.

electrochemical reactions and flow fields on the size and continuity of the pattern are reported in this paper.

MODEL STUDIES

Figure 2 Flow bending towards the pattern (shown as black squares) due to UV irradiation [4]

Effect of the Pattern length on Electrochemical reactions

A TiO₂ film can be prepared from the oxidation of Ti. Incomplete oxidation results in a Ti/TiO₂ interface. The films can be modeled along with the electrolyte and electrical double layer at the interface as a combination of resistors and capacitors. For the experimental conditions used here, a simple resistive model is proposed (Figure 3). When there is a defect in the TiO₂ film or when the film is contaminated (i.e. not a perfect insulator), the resistance R_{TiO_2} is lowered and some current flows through the Ti/TiO₂ layer. This creates a potential drop across the film. This is a function of the length of the film. When this drop is large enough, electrochemical reactions can occur resulting in the generation of bubbles and, in some cases, degradation of the film.

Figure 3 Simplified circuit model equivalent for fluid filled channels with TiO_2 films.

Effect of Pattern Geometry on Flow Field A computational grid was generated on a $2000\ \mu\text{m}$ long section of the channel ($1000\ \mu\text{m}$ wide x $20\ \mu\text{m}$ deep), and the velocity field in this domain was computed numerically with the CFD-ACE package (CFD, Research Corporation). An infinite channel was modeled by enforcing periodic boundary conditions at the inlet and exit of the computational domain; i.e. by requiring the velocities and the pressure profile to be identical at the inlet and exit. A flow of mean velocity $5400\ \mu\text{m/s}$ was created in the channel by maintaining a pressure difference (ΔP) between the inlet and the exit. Varying ΔP controls the net flow rate through the channel. No-slip boundary conditions were assumed on all channel walls. To simulate the TiO_2 patterns a wall velocity of $242\ \mu\text{m/s}$ (obtained from bulk flow experiments) was assumed on the bottom side of the channel. Two patterns, one with staggered $500\ \mu\text{m}$ square patches and the other with a meandering continuous strip were studied (Figure 4). The wall velocity on all other parts of the channel was assumed to be zero.

EXPERIMENTAL

Fabrication A channel was etched on Pyrex 7740 wafers. Inside the channel, TiO_2 films of varying lengths (2.5 cm, 1 cm,

Figure 4 The TiO_2 patterns (shown as black blocks) that were modeled a) staggered patches b) meandering continuous strip

0.5 cm, 0.25 cm, $500\ \mu\text{m}$) were prepared by sputtering (DC magnetron, 1 kW) Ti followed by thermal oxidation ($450\ ^\circ\text{C}$ for 2 h). Polydimethylsiloxane (PDMS) slab with holes punched for the inlets was used as the top cover to seal the channels.

Procedure The electrolyte (50 mM Sodium Phosphate buffer at 4.7 pH) was degassed before the experiment. To facilitate filling

with the aqueous electrolyte, the PDMS was made hydrophilic by treating the channel with oxygen plasma. A DC potential was applied across the channel through Pt electrodes placed at the wells. The potential was incremented in steps of 100 V (range 100 V – 3000 V). The applied potential at which the bubbles

Figure 5: Channel designs with different size TiO_2 patterns (black). The channels were $1000\ \mu\text{m}$ wide, $20\ \mu\text{m}$ deep and 4 cm long. The length of the patterns is indicated in the figure.

first occur was recorded.

RESULTS AND DISCUSSION

Constraints due to electrochemical reactions We tested different pattern lengths over a range of voltages. Preliminary results show that above a certain applied potential, electrochemical reactions occur. This was observed to vary with the film length (Figure 6). From the simplified circuit model presented earlier, a potential drop is generated across the film. When this crosses a threshold, the film acts as an electrode for the electrochemical reactions. For a film of a given quality, the threshold is reached at lower applied potentials as the length increases. In previous studies of local flow control [4] with small $500\ \mu\text{m}$ patterns, no reactions were observed.

Figure 6 Applied potential at which the threshold potential is reached for the different film lengths

The possible electrochemical reactions occurring on the film are:

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The electrolysis of water (equation 3 and 5) results in evolution of bubbles (see Figure 7). Further oxidation of partially oxidized TiO_2 also results in bubble formation (equations 4 and 6). Once these regions are oxidized, the threshold potential for the electrolysis is increased. This is because the resistance of TiO_2 film (R_{TiO_2} in Figure 3) increases with continued (complete) oxidation. Salt deposition was observed on the film. This could be due to the consumption of the electrolyte.

Figure 7 Bubble evolution on the TiO_2 film due to electrochemical reactions

In all cases, bubble formation was observed. However, there was no apparent degradation of the TiO_2 film except at the edges, where the largest surface defects of the oxide film exist and adhesion to Pyrex maybe poor. However, earlier studies with films prepared by evaporation of Ti followed by electrochemical oxidation resulted in degradation of the film at lower applied potential (500 V). This could be due to lower resistance (R_{TiO_2}) due to defects or contamination

Influence of pattern geometry on flow fields

The computational models show that the presence of the pattern produces spanwise flow, both in the horizontal and vertical directions. Figures 8 and 9 show the velocity fields generated by the patterns. Flow in the horizontal direction is produced at the corners of the pattern. For the continuous strip geometry (Figure 8b) this sets up localized circulation of the fluid at the corners; whereas the patches (Figure 8a) produce a bending effect similar to that observed experimentally (Figure 2). The magnitude of the maximum horizontal velocity is almost double for the patches (see Table 1). The edges of the patterns normal to the streamwise flow direction produce vertical velocity fields (Figure 9). The magnitude of the velocity in this direction is greater for the patches.

Figure 8 Horizontal flow fields (at one half channel depth) generated by a) patch and b) continuous. The black regions indicate flow to the left while the white regions indicate flow to the right.

Figure 9 Vertical flow fields (at one half channel depth) generated by a) staggered patch geometry and b) continuous. The black regions indicate flow into the plane while the white regions indicate flow out of the plane.

Table 1 Maximum spanwise flow velocity generated by the pattern.

Geometry of the Pattern	Horizontal Velocity (um/s)	Vertical Velocity (um/s)
Continuous Strip	66	30
Patches	110	30

Design Criteria for Light Modulated Control

The simulation studies show that the edges and corners of the pattern generate flow in the vertical and horizontal directions respectively. By changing the pattern geometry, different types of effects can be produced for various applications. For example, by increasing the number of corners, localized flow can be produced which would help in mixing. If desired, the flow can be routed by placing the patterns appropriately (Figure 8a). Since the likelihood of the electrochemical reactions occurring depends on the length of the film, a long pattern can be designed by using smaller patches.

CONCLUSIONS

In order to control the electroosmotic flow using light, TiO_2 films can be patterned in the channels. Here, the effect of the geometry of the pattern was explored. A microchannel with different lengths of TiO_2 films was fabricated to study the limitations on the length of the patterns. We observed electrochemical reactions occurring on the TiO_2 films initiated at a threshold voltage. This varied as a function of the film length. A circuit model has been proposed to explain the reactions. CFD flow simulations show that the corner and edge of the pattern produces spanwise flow in the horizontal and vertical directions. These experimental and computational results provide a design space in which one can design geometries to achieve specific patterns of flow control. The use of light to turn the flow control on and off provides a simplified mechanism for both local and bulk electroosmotic flow control in microchannels.

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