CONTROLLED PART-TO-SUBSTRATE MICRO-ASSEMBLY VIA ELECTROCHEMICAL MODULATION OF SURFACE ENERGY

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ABSTRACT

A process designed for repeated parallel micro-assembly has been achieved by controlling the hydrophobicity of the binding sites between micro-parts and substrates. Active assembly sites consist of hydrophobic surfaces made of alkanethiol-coated gold, while inactive sites are clean, hydrophilic gold surfaces. Electrochemical reduction of the alkanethiolate monolayer on substrates with addressable binding sites returns the selected sites to their inactive, hydrophilic state. The parts are attracted, aligned, and anchored to the binding sites by a heat curable lubricant in an aqueous environment. The entire sequence is then repeated with a different set of active binding sites and parts. A two-batch assembly process is described in this paper. Principles for establishing electrical connections using electroplating are also demonstrated and discussed. This process forms the basis for a general technique to batch-assemble complex microstructures from simple components.

Keywords: self-assembly, micro-assembly, hydrophobic, surface modulation.

INTRODUCTION

Recent developments in micro electro mechanical systems (MEMS) research offer the prospects to produce complex systems with a wide range of functionalities (mechanical, electrical, optical, chemical, *etc.*). Monolithic integration of such systems is often limited by the poor compatibility between their fabrication processes. Recently, a number of techniques have been developed to assemble components into complex systems [1-6]. Conventional "pick and place" serial assembly methods [2] use miniaturized robots and tools for organizing parts. Such serial assembly strategies are rather limited when a large number of parts must be assembled, due to the large number of required manipulators. In order to accomplish efficient micro-assembly, two classes of parallel assembly approaches have emerged: deterministic and stochastic. In the first class, assembly is achieved by transferring microstructures between aligned wafers [3]. In stochastic parallel micro-assembly, parts are assembled in a random manner, and a large number of parts are supplied to the process in order to obtain good yield. Various driving forces have been employed for stochastic assembly. Yeh and Smith developed a process to assemble trapezoidal micro-components into complementary holes in substrates using fluidic flow and gravitation [4]. Srinivasan *et al.* adopted the surface tension driven assembly technique first described by Whitesides and coworkers [5] to assemble microscopic parts onto silicon and quartz substrates [6]. This approach has accomplished massively parallel assembly of equal micro parts with sub-micrometer precision.

In this paper, a new multi-step parallel micro-assembly technique is presented. As in [6], the driving force for the assembly is surface tension. By controlling the hydrophobicity of the binding sites the process can be repeated and multiple batches of micro-components can be organized onto desired sites on a single substrate. Electroplating is explored as a post assembly process to establish electrical connections for active components such as surface mount light emitting diodes (LEDs).

PRINCIPLE AND APPROACH

Figure 1 illustrates the schematic flow of our microassembly approach. Substrate and parts are fabricated with exposed clean hydrophilic gold patterns. When both the parts and substrate are soaked in ethanolic alkanethiol solution, a hydrophobic alkanethiolate self-assembled monolayer (SAM) is formed on gold patterns. This is the result of adsorption of alkanethiol organosulfur compounds on noble metals such as gold. The remaining areas on the substrate remain hydrophilic. The ability to electrochemically desorb alkanethiolate SAM from gold [7,8], *i.e.*, $CH_3(CH_2)_nSAu + e^- \rightarrow Au + CH_3(CH_2)_nS^-$ provides *in-situ* control of hydrophobicity. Thus, assembly can be controlled to occur only at sites without SAM desorption. The hydrophilic gold sites on the substrate can be reserved for future assembly. By repeating the SAM adsorption and assembly process, another batch of micro-components can be assembled in those regions.

In the assembly step, a hydrocarbon-based lubricant is spread on the substrate before it is immersed in water. The lubricant, which wets only the hydrophobic patterns in water, reduces friction, increases the capillary forces, and thus produces alignment between parts and substrate (Figure 1d). Detailed information about the multi-batch micro-assembly process is described in the following experimental section.
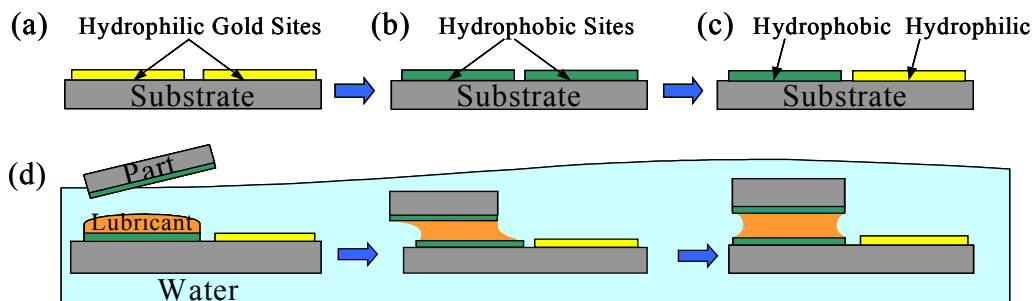
Figure 1. *Schematics of assembly steps: (a) Substrate with electrically isolated regions of gold sites. (b) SAM adsorption on all gold patterns. (c) Selective SAM desorption by cyclic voltammetry (CV). On the right regions, SAM is removed from the gold pattern by electrochemical modulation. (d) Lubricant spread and assembly.*

EXPERIMENTAL

Substrates and Parts Preparation

The substrate is prepared by sputtering 1100Å TiW/Au on a 3″ (100) Si wafer with a thermal oxidation layer of approximately 4000Å. The wafer is patterned with electrically isolated gold stripes in a lift-off process. Then a passivation layer of spin-on glass (SOG) (311, Honeywell) is patterned by photolithography and reactive ion etching (RIE) until gold squares (1 by 1mm) on the stripes are exposed (Figure 2a,b). Sputtered silicon nitride and silicon dioxide have been shown to be compatible for our microassembly process. Square test parts (1 by 1mm) are fabricated by dicing 3″ (100) Si wafers with sputtered Cr/Au as thick as 1100Å (Figure 2).
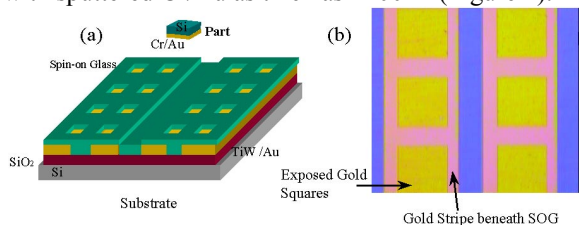

Figure 2. *Fabricated part and substrate (a) Cross-section of part and substrate. (b) Top view of a fabricated substrate.*

Alkanethiolate SAMs are deposited on exposed gold by soaking the substrates and the parts in 1mM ethanolic alkanethiol solution for two to twenty-four hours. The substrate is cleaned by O_2 plasma for two minutes before being immersed into the ethanolic alkanethiol solution.

SAM Desorption Characterization and Optimization

Reductive desorption of SAMs is performed in a conventional three-electrode electrochemical cell (Figure 3). The counter electrode is a platinum mesh. A saturated calomel electrode (SCE) is used as the reference electrode. The working electrodes are test samples. The electrolyte is 0.5 M aqueous KOH solution. Cyclic voltammetry (*i.e.*, the repeated scanning of the working electrode potential) was performed to both characterize

and to desorb SAMs from electrode surfaces [8]. In all cases, the potential window for the cyclic voltammetry (CV) was from 0 V to –1.4 V *vs.* SCE. Characterization scan rates were 100 mV/s for the characterization experiments, and approximately 70 mV/s for the desorption of SAMs from actual patterned substrates.
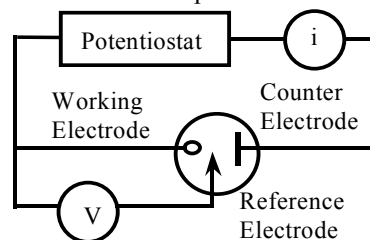

Figure 3. *Three-electrode electrochemical cell setup.*

To find the optimal alkanethiol forming stable SAMs with reasonable desorption times, reductive desorption of different alkanethiolate SAMs, C_3H_8S, $C_8H_{18}S$, $C_{12}H_{26}S$ and $C_{18}H_{38}S$ (Aldrich), was characterized. Cyclic voltammograms (CVs) obtained from Au (111) textured thin films on mica [9] were used for characterization. The negative current peaks on the CVs in the potential range from –1.1 to –1.4 V (Figure 4a-c) indicate the reductive desorption of alkanethiolate SAMs from the surfaces. The peaks become smaller with decreasing coverage of SAMs on the gold surface. Desorption is complete when the peak is no longer visible in the CV. The reduced alkanethiol dissolves into the electrolyte. Re-adsorption is unlikely to affect the surface hydrophobicity because the reduced alkanethiol is satisfied electronically (*i.e.,* it no longer forms chemical bonds with the gold), and because of its low solution concentration.

The SAM of propanethiol (C_3H_8S) does not form stable hydrophobic surfaces in these electrolytes. Therefore, propanethiol was ruled out as a choice for the assembly experiment. By comparing desorption time and stability of the different alkanethiolate SAMs, dodecanethiol

($C_{12}H_{26}S$) was chosen for the assembly experiments. The dodecanethiol forms stable hydrophobic SAMs on gold, and desorption of the SAMs takes approximately twenty minutes compared to six hours for octadec-anethiol ($C_{18}H_{38}S$). Desorption of dodecanethiolate ($C_{12}H_{26}S$) SAM on specific polycrystalline gold patterns of the Si substrate is shown in Figure 4d. The CV for desorption of SAMs from polycrystalline gold on a Si substrate has broader peaks, compared to CVs for desorption of SAMs from single crystalline gold on mica.
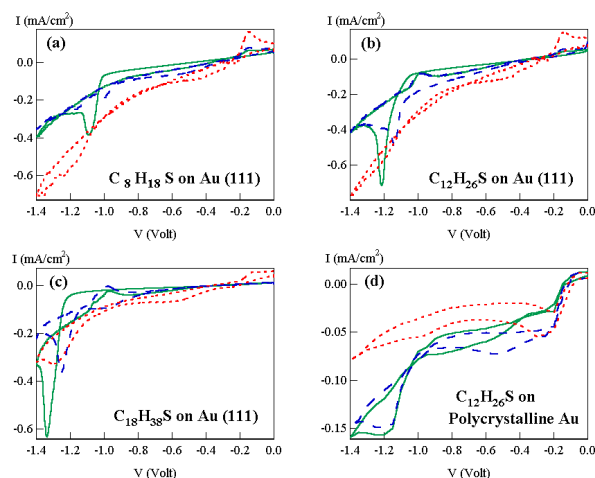

Figure 4. *CVs from desorption of n-alkanethiolate SAMs on Au. Solid and dashed curves in each figure are first and second CVs for desorption. Dotted curves are CVs from desorption after ten minutes in (a), fifteen minutes in (b), one hour and a half in (c) and twenty minutes in (d).*

Assembly Experiments
After desorption of SAMs from specific sites, the substrate was removed from the electrochemical bath, rinsed with DI water and dried with N_2. A hydrocarbon lubricant was spread on the whole substrate. The lubricant is heat-curable, and composed of 97wt.% triethyle-neglycol dimethacrylate (Sigma) as crosslinker, and 3wt.% benzoyl peroxide (Sigma) as thermal initiator. Then the substrate was immersed in water in a petri-dish. The lubricant wetted only the SAM-coated hydrophobic binding sites. The differences between the gold regions with and without SAM desorption are readily seen in Figure 5a. Then the parts were cleaned and added into the water in the container. The petri-dish was placed on an orbital shaker. With agitation, the assembly took place exclusively on the hydrophobic areas with lubricant. The lubricant, polymerized at 80°C for approximately half an hour, permanently bonded the parts to their sites (Figure 5b). The gold squares with SAM desorption on the substrate remained clean (Figure 5a). A second assembly step has been achieved by repeating the SAM formation and the assembly process on these clean binding sites (Figure 6).
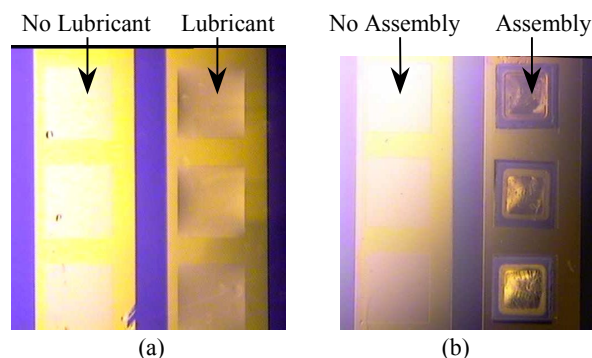

Figure 5. *(a) A substrate with lubricant in water after selective SAM desorption. The SAM desorption has happened on the gold squares on the left column. Lubricant wets the gold squares without SAM desorption. (b) Thin 1mm^2 parts (fabricated by M. Cohn) were assembled and bonded only to gold patterns with adsorbed SAM on the right.*

By repeating SAM adsorption, selective desorption, and assembly, controlled micro-assembly is feasible in principle for a large number of batches. In the next section, the issue of establishing electrical connection between the assembled parts and substrate is discussed.
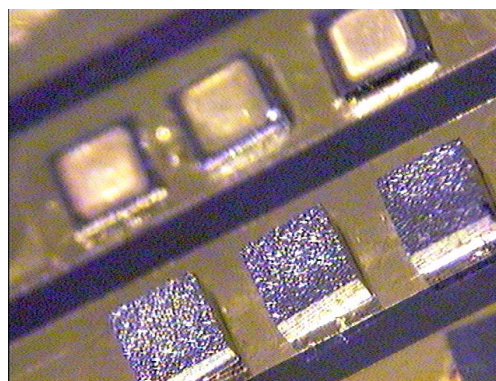

Figure 6. *Side view of two-batch controlled micro-assembly. Foreground: Second batch of 1mm^2 parts assembled (approximate 0.5mm thick; unpolished backside is visible). Background: First batch 1mm^2 thin parts assembled.*

CURRENT AND FUTURE WORK
Currently, we are investigating electroplating methods to establish electrical connections between assembled electrically active parts such as surface mount LEDs (Lumex) and the substrate. Figures 7a-c show a binding site design for a given LED, and electrically isolated seed sites for electroplating. To verify the feasibility of the electroplating process, we measure the gap between the assembled LED (Figure 7d) and the substrate to be approximately 20µm. An electroplated alloy on gold seeds is seen in Figure 7d.

Our future work includes: optimization of the electroplating process, improving the binding site designs [10], improvement of the assembly setup for better yield, and generalization of the assembly process for various micro-parts and substrates.
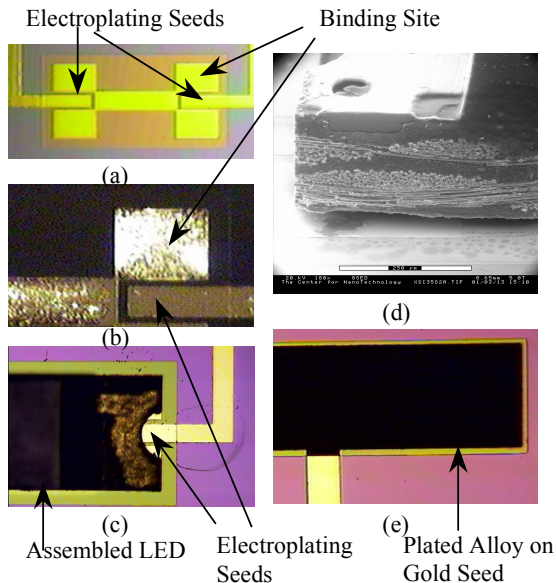

Figure 7. *(a) Binding site on the substrate with electroplating seed. (b) Plating seed with SAM desorption, without lubricant, compared to binding site wetted with lubricant. (c) Assembled LED on the binding site. (d) ESEM image of assembled LED (e) Alloy electro-plated on exposed gold.*

CONCLUSIONS

We have proposed a technique for repeated multi-batch parallel micro assembly via electrochemical modulation of surface hydrophobicity. Two-batch micro assembly has been successfully demonstrated. Presented were the principle, fabrication and assembly processes of this approach. Optimization of the desorption process was also accomplished, based on alkanethiolate SAM desorption characterization. With improvement of the assembly process and optimization of electroplating, it is anticipated that this technique can be applicable to a wide range of micro or nano components and materials, for the integration and packaging of complex systems.

ACKNOWLEDGEMENTS

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