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Photovoltaic Self-Assembly (LDRD 149212)

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Photovoltaic Self Assembly

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Abstract

This late-start LDRD was focused on the application of chemical principles of self-assembly on the ordering and placement of photovoltaic cells in a module. The drive for this chemical-based self-assembly stems from the escalating prices in the “pick-and-place” technology currently used in the MEMS industries as the size of chips decreases. The chemical self-assembly principles are well-known on a molecular scale in other material science systems but to date had not been applied to the assembly of cells in a photovoltaic array or module. We explored several types of chemical-based self-assembly techniques, including gold-thiol interactions, liquid polymer binding, and hydrophobic-hydrophilic interactions designed to array both Si and GaAs PV chips onto a substrate. Additional research was focused on the modification of PV cells in an effort to gain control over the facial directionality of the cells in a solvent-based environment. Despite being a small footprint research project worked on for only a short time, the technical results and scientific accomplishments were significant and could prove to be enabling technology in the disruptive advancement of the microelectronic photovoltaics industry.

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One of the authors (CAS) would like to thank Eric Branson (Org. 01815) for helpful discussions with the superhydrophobic/hydrophilic patterning, Andrew Collord for preparation of the templates for the masks and the Direct Write Lab for the use of their equipment. CAS would also like to thank Anton Filatov (Org. 01749-2) for many valuable discussions, for his pattern design and development, and for running the assembly experiments in his lab and for photographs and movies of the process. The authors would also like to thank Greg Nielson and Murat Okandan (Org. 01749-2) for helpful discussions and for generous access to the micro-PV cells. As well, the authors acknowledge the key role played by Jeff Nelson in getting this project started and funded, and we appreciate as well his continued interest in this topic.

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Nomenclature

DOE	Department of Energy
SNL	Sandia National Laboratories
PV	Photovoltaic
SAM	Self-assembled monolayer
LDRD	Laboratory Directed Research Development
Si	Silicon
GaAsP	Galium Arsenide Phosphide
mM	millimolar
nm	Nanometer
μm	Micrometer or micron
SEM	Scanning Electron Microscopy
SU-8	Epoxy-based photoresist

Photovoltaic Self-Assembly

Executive Summary

The goal of this LDRD project is to develop a new chemical-based means of assembling photovoltaic (PV) chips onto a module. The current state-of-the-art process for chip assembly is the “pick-and-place” mechanical method of physically placing each chip to a specific location on the substrate. While this process works very well for larger chips, it is known that as the chip size decreases both the difficulty and cost of handling these smaller chips, using pick-and-place technology significantly increases. As the PV industry becomes a serious contender globally in influencing the world’s energy source as a leader in renewable energy, in doing so it has and continues to move towards smaller, thinner, and more efficient cells and arrays. Thus to help realize these smaller, more efficient arrays we are interested in exploring a range of chemical approaches to facilitate and drive the specific assembly of micro PV-cells onto a substrate. At the same time, we hope to gain control over the specific face orientation of the cell via surface modification. It is worth noting that the self-assembly techniques explored here operate over a range of length scales, from nano- to micrometer, thus creating an environment where assembly can occur over both long and short interaction lengths.

Significant goals and milestones accomplished over the course of this late-start LDRD include:

- **Gold-dithiol interactions in the assembly of parts from nanospheres to 250 micron cells.** Surrogate gold-coated wafers modified with a dithiol self-assembled monolayer (SAM) demonstrated the ability to permanently bind gold parts over a range of sizes. Gold-thiol interactions are well-known to interact with one another and extensive research has been reported in the literature; however, this is the first time such interactions have been used in the assembly of small parts.
- **Liquid polymer coating in selective assembly of die.** The selective coating of hydrophobically-modified areas on a substrate with a hydrophobic polymer followed by the directed addition of parts modified with a hydrophobic SAM resulted in their fast and selective self-assembly.
- **Superhydrophobic/hydrophilic patterning of substrates, in conjunction with evaporative alignment, has been shown as a viable technique for assembling micron-sized PV cells into ordered arrays.** This method uses water as the solvent with the assembly times being short (minutes) and should be scalable to large arrays.
- **Specific face modification of gold-GaAs cells and subsequent facial control in a mixed solvent system.** Taking advantage of the different chemical makeup of the two faces of the PV cells (gold on one side, GaAs (or Si) as the other) enabled selective modification of one surface by

rendering its properties drastically dissimilar to the other. When placed in a mixed solvent system, e.g., water-toluene, the cells flipped preferentially, ensuring the hydrophobic side of the cell was directed into the non-polar organic toluene.

The concept of using molecular forces to assemble microscale objects has been clearly demonstrated in this late-start LDRD project. The results from this work indicate that it is feasible (using combinations of chemistries) to place micron-sized PV chips at predetermined locations on a substrate and in the proper facial orientation. From a manufacturing standpoint and from an energy efficiency perspective, micro-PV chips will in the future go down in size and thickness, at which point the use of mechanical pick-and-place technology becomes impractical due to economics and the fragility of the parts. The results from this LDRD study, using chemical-assisted self-assembly, is clearly a very attractive alternative technology to examine further. As an added benefit, this method of placement/assembly is applicable towards other small, micron-sized objects and should be easily scalable to large arrays. This project holds tremendous potential going forward as a future long-term LDRD project. Much more work towards the refinement of the recently developed chemistries and techniques is necessary to go to the next stage large-scale assembly and optimization.

1 Introduction

With strengths in microsystems technology, Sandia and DOE have significant interests in the manufacture of improved individual photovoltaic (PV) cells, as well as the assembly of these PV cells into more efficient and effective arrays. The broad uses of these PV cells range from commercial to military applications. The current state of the art method for chip assembly is the “pick and place” mechanical method of physically placing each chip where it is supposed to be located on a substrate. While pick and place is an effective placement process for current PV chips given their relatively large size, this technology is unable to keep abreast of the advancements in PV cell manufacture and the production of smaller PV cells. As a result pick-and-place technology suffers due to increased difficulty in handling PV cells, including cell fracturing, all leading to significantly higher costs of placement for each cell as the size decreases. Therefore, fast and versatile assembly of massive numbers of these PV cells by methods other than machine handling and movement is desired.

Our objective in this project was to investigate using chemical principles of “self-assembly” to order PV chips onto a Si-based or GaAsP-based substrate. These chemical self-assembly principles are well-known in other systems such as materials science, but have been applied only in a limited fashion in assembling PV cells. The overarching issue with all of the self-assembly techniques suggested was: is the strength and force of molecular scale interactions sufficient to assemble and bond parts on the micro scale? We were able to explore this question and provide several viable methods to providing a high-throughput, cost-effective arraying technology for current and next generation PV cells.

This report describes the efforts from the end of March 2010 to the end of September 2010 that were funded by a late-start Laboratory Directed Research and Development (LDRD) project to investigate the use of chemical principles in the self assembly of parts of a range of length scales onto a surface. Three milestones were completed by 10/01/10: a) demonstrate the ability of dithiols in the binding of gold parts to a surface; b) use hydrophobic patterning to align and assemble photovoltaic cells; and c) use polymeric techniques in the assembly of photovoltaic cells and other small parts. In addition control over the facial orientation of die was achieved by selective surface modification. Technical advances have been submitted for three key areas of this LDRD project:

“Microscale self assembly through hydrophobic/hydrophilic patterns” – SD# 11730,
“Method for Utilizing Gas Bubbles to Orient Micro-Scale Parts” – SD# 11753,
“Gold-Dithiol Assembly of Parts from Nanospheres to PV cells” – SD# 11806.

2 Results and Discussion

2.1 Gold-Thiol Based Self-Assembly

The use of gold-thiol interactions in the assembly of small parts including PV cells onto a gold substrate was identified as a possible means of chemical-based assembly. Historically, thiols are known to have very strong and favorable interactions with gold in the formation of self-assembled monolayers (SAM), as has been well-documented in a large body of literature.^{1,2} It is these strong covalent bonds, on the order of 400 kcal/mol, and the resulting organized SAM that lend stability to the assembly and bonding of gold parts, including cells, onto a gold substrate. The cartoon shown in Figure 2.1.1 illustrates the assembly between gold and a dithiol.

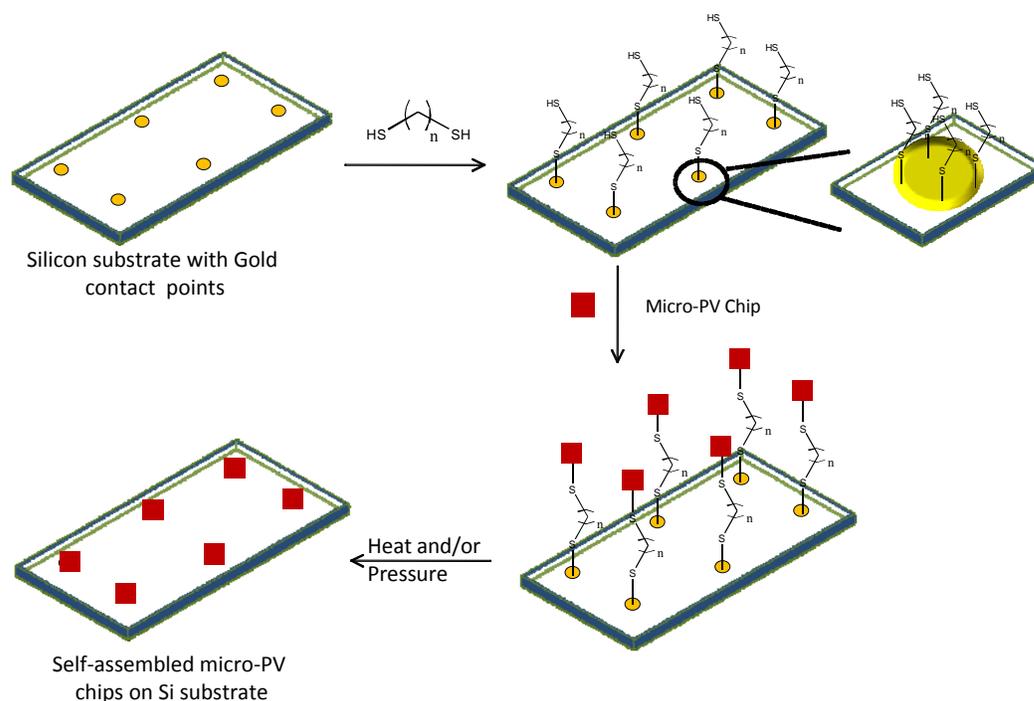


Figure 2.1.1 Cartoon illustrating the chemical based assembly process of PV chips onto gold patterned silicon wafer via dithiol SAM's.

In this project, experimentation began using both surrogate substrates (gold deposited on silicon wafers) and cells, in the form of gold and silver nanoparticles as a means to demonstrate chemical based self-assembly. As a starting point and a means to demonstrate chemical based self-assembly, both surrogate substrates (gold deposited on silicon wafers) and cells (gold and silver nanoparticles) were utilized. Initial efforts focused on these surrogates for two reasons. Firstly, nanoparticles were used in place of cells as it was suspected that the large difference in scale, from molecular sizes in the SAM to macro- with the PV cells, could be a prohibitive factor in enabling chemical based self-assembly. Demonstrating assembly using nanoparticles would give merit to

this chemical-based assembly and testimony that this method of assembly is feasible, serving as the premise in moving to larger-sized parts. The second reason for using surrogates is to cut down in cost and waste of the patterned substrates in the early, exploratory stages of research.

Dithiol monolayers were formed by an immersion technique. Piranha-cleaned substrates were immersed in a 1mM solution of hexadecane dithiol for 8 hours before being removed, rinsed thoroughly, and dried under a stream of nitrogen. Substrates were then immersed in an aqueous solution containing either gold or silver nanoparticles (20 nm diameter) for 12 hours. Once removed, the surfaces were rinsed thoroughly with deionized water and dried. Having demonstrated surrogate substrate modification, gold patterned substrates were modified with dithiol in an identical manner to the surrogate substrates. Here, only the gold contact points were modified with the dithiol and the surrounding silicon areas remained unmodified. Results of this chemical-based assembly of nanoparticles onto both surrogate and gold-patterned wafers proved highly successful, as can be seen in the images shown in Figure 2.1.2 below.³

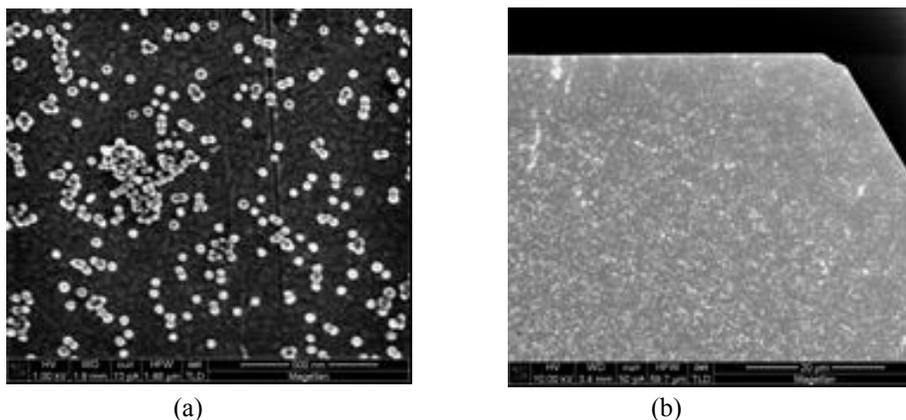


Figure 2.1.2 SEM images of self assembly of nanoparticles onto dithiol modified gold surfaces. Self-assembly of silver nanoparticles onto surrogate gold substrate (a). Gold contact point on a silicon wafer (dark region). Nanoparticles assembled only on the gold surface as can be seen by the bright speckles on the gold (b).

Given the success of assembly using nanoparticles, a larger, commercially-available gold powder (40 μm) was used in place of the nanoparticles. The same techniques as described above for dithiol SAM formation and particle assembly were used. As evidenced by the SEM image in Figure 2.1.3 the strength of the dithiol bonds proved sufficient to bind and fix the gold powder in place even after being thoroughly washed.

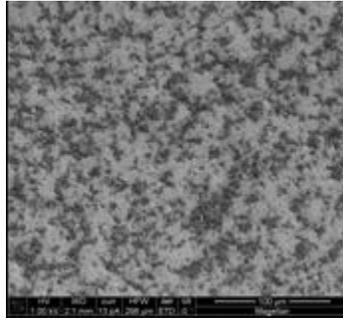


Figure 2.1.3 SEM images of self-assembly of gold powder (40 μm) onto dithiol-modified gold surfaces.

Finally, efforts moved towards the assembly of gold-backed GaAs PV cells onto gold substrates. Both cells and substrate were cleaned using a piranha solution, ensuring all surfaces were clean of organics. Surrogate substrates were immersed in a 1mM dithiol solution for 8 hours, rinsed thoroughly, and dried. Piranha-cleaned cells were pipetted onto the surface in a minimal amount of ethanol. Preliminary experiments were conducted to analyze the effects of solvent volume, experiments in which the cells were dispensed onto the substrate and the ability to assemble with correct orientation was observed. It was found that large volumes of solvent resulted in the cells being able to float randomly around the container. Ideal conditions would call for the substrate to be held in a container the exact size of the substrate and for a minimal volume of solvent to be used in dispensing the of the cells. These ideal conditions were followed as closely as possible, however, results from these experiments were mixed. It was observed that once cells were aligned with the correct face down they remained bound to the surface of the substrate via the dithiol bond after rinsing in ethanol and drying under a stream of nitrogen. However, issues arose with the control of the facial orientation of the cells. As the cells were being dispensed using a pipette their orientation on hitting the substrate was totally random since the cells were being ejected under pressure and in a turbulent environment with no opportunity to orient. The only means of allowing alignment to occur was by aspiration using the pipette, which also gave mixed results. It is believed that the cells would preferentially orient with the gold side down given the affinity of gold for thiols; however, if no opportunity exists for the alignment of cells it is impossible for them to flip to the correct orientation. The SEM image in Figure 2.1.4 shows gold-GaAs cells bound a gold surrogate surface. It can be seen that one of the cells is oriented with the incorrect face, the gold face pointing up as can be seen by the bright color relative to the dull sides of the GaAs.

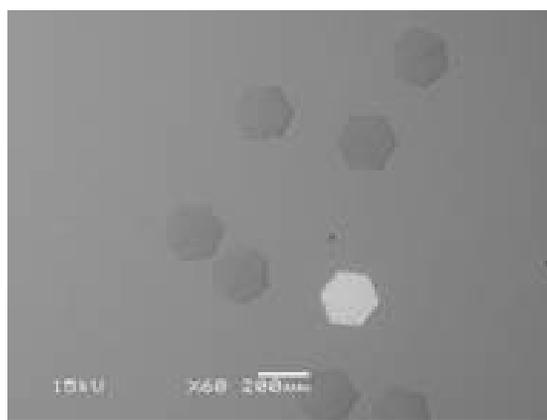


Figure 2.1.4 SEM image of 250 micron gold-GaAs cells on a gold coated silicon wafer. The image shows that 7 of the 8 cells are oriented with the desired face (gold) down and have bonded to the surface. One cell has settled with the undesired gold face up as can be seen by the lighter color.

In order for this technique to advance and hold promise as a viable means of self-assembly in the photovoltaic and microelectronics industries it is evident that control over the facial orientation of the parts must be achieved.

2.2 *Liquid Polymer Based Self Assembly*

Another chemical-based self-assembly technique investigated in this project was the use of polymers in both dictating the facial orientation and the binding of the cells to the surface. These polymers, referred to as liquid polymers, form a layer on the surface of hydrophobically-modified gold substrates driven by energy minimization. Once the cells are laying down on the surface they can be fixed in place by either thermal or chemical polymerization.

Experiments were carried out using surrogate gold-coated silicon wafers and an array of parts, from gold powder (40 μm) to gold-GaAs PV cells (250 μm). Gold-coated wafers were first modified using an aliphatic octadecanethiol molecule by immersion in 0.1 M solution for 24 hours, thus making them hydrophobic. The wafers were rinsed and dried. Modified wafers were then passed through a methacrylate solution floating on the surface of water and isolated in a cylinder to prevent contamination of the surrounding aqueous environment, as shown in Figure 2.2.1. Adhesion of the liquid polymer to the surface of the wafer is driven by energy minimization forces. The thermally-curable liquid polymer solution was prepared as follows: 85 wt.% *n*-dodecyl methacrylate, 14.5 wt.% triethylene glycol dimethacrylate, 0.5 wt.% benzoyl peroxide. The photo-curable version of this consisted of 96 wt.% *n*-dodecyl methacrylate, 2 wt.% 1,6-hexanediol diacrylate, and 2 wt.% photoinitiator.

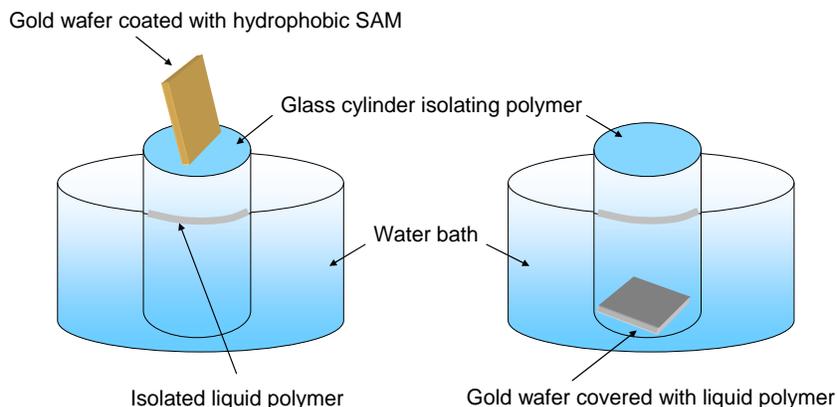


Figure 2.2.1 Cartoon of experimental setup for coating hydrophobically-coated gold wafer with liquid polymer.

It is necessary to isolate the polymer from the surrounding aqueous environment as any exposure of the liquid polymer-coated wafer to air or trace polymer solution would result in the displacement of the surface-bound polymer from the wafer. As the methacrylate polymer is very hydrophobic and immiscible with water, on passing a wafer modified with octadecanethiol (also hydrophobic) through the polymer and aqueous environment the polymer preferentially adheres to the surface of the wafer, again driven by energy minimization. The wafer is collected in a dish sitting at the bottom of the cylinder and is gently pulled aside, ensuring that at all times it remains submerged in water. If the wafer is either brought to the surface or comes in contact with a hydrophobic molecule on the surface, the polymer immediately migrates towards the molecule or the air-water interface, as this has a lower energy than the wafer surface. With the polymer-coated wafer submerged in water, parts that had also been modified with octadecanethiol were carefully pipetted onto the surface. The parts were modified by immersion in octadecanethiol 0.1 M ethanol solution for 24 hours. Again, driven by energy minimization the parts migrate to a lowest energy point, in this case, the surface of the wafer. In the case of the PV cells, only the gold side is modified with the hydrophobic molecule via the gold-thiol bond (thiols do not form bonds with GaAs) and a preferential facial assembly - gold side down – dominates, allowing hydrophobic surfaces to come in contact and thereby reach an energy minimization.

With all parts in place either photo- or thermo-polymerization, depending on the initiator (thermal - benzoyl peroxide; photo - benzoin methyl ether) permanently binds the parts to the surface of the substrate. Figure 2.2.2 shows examples of the assembly of a variety of parts to the surface of gold-coated substrates using liquid polymer, parts that remain permanently held in place upon polymerization. Images were collected using a standard stereoscope with a mounted camera. Although preliminary results were promising, one persistent problem is the displacement of cells from their original site on polymerization. This shifting of cells is likely due to an excess of crosslinker in the polymer solution and should be resolved by controlling the monomer to crosslinker ratio.

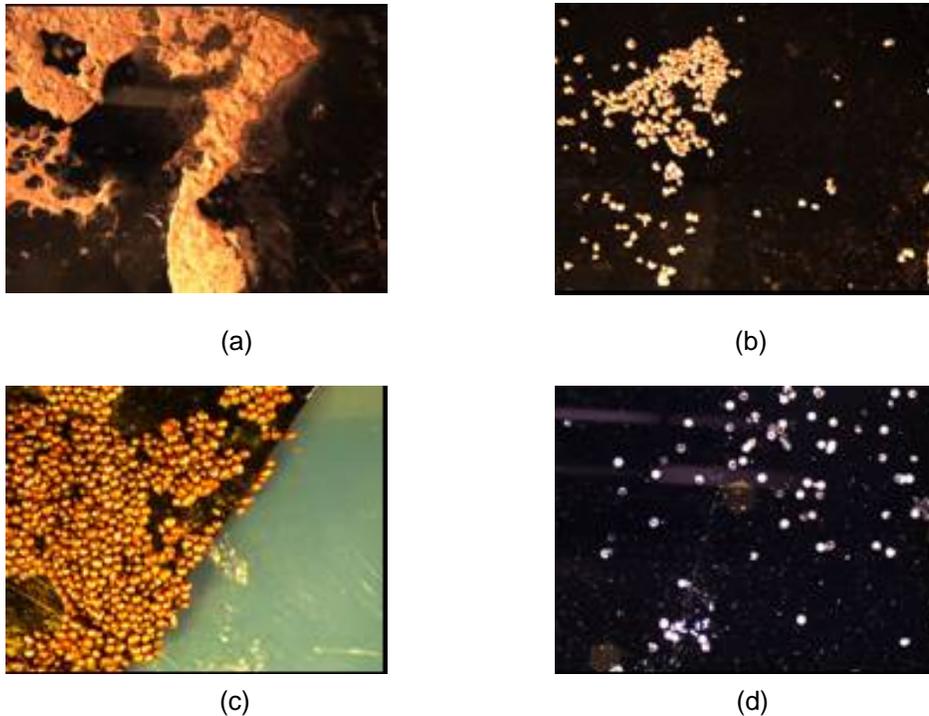


Figure 2.2.2 Microscope images taken at 1X of the assembly of parts by liquid polymer on to a hydrophobically-modified gold wafer. (a) Gold powder $<40\ \mu\text{m}$. (b) Gold particles $<850\ \mu\text{m}$. (c) Copper spheres $800\ \mu\text{m}$. (d) PV cells $250\ \mu\text{m}$

In moving forward with this chemical-based assembly technique, efforts will be focused on the fine-tuning of the experimental conditions, specifically the ratio of monomer to cross-linker, and in the case of thermal polymerization the temperature of polymerization and its effects on accuracy of cell placement.

2.3 *Micro-PV Placement Using Superhydrophobic-Hydrophilic Patterns*

Our technical approach to using evaporative alignment in water to organize cells into a designated array is based on a number of approaches that have been reported in the literature or are extensions to some of the current methodologies used in other systems.⁴⁻¹² This concept of micro-PV placement via superhydrophobic-hydrophilic patterns uses chemical surface modifications of the substrate to divide it into hydrophilic and hydrophobic regions. Upon the introduction of a thin film of water onto this substrate, followed by the slow removal of the water, the resulting substrate will have regions containing water (hydrophilic) and regions without water (hydrophobic). Now if this process is repeated and micro-PV chips are floated on the surface, upon removal of the water the chips should end up in the hydrophilic regions on the substrate.

This concept was initially demonstrated using a glass slide ($7.62\ \text{cm} \times 2.45\ \text{cm}$) that had been hydrophobically/hydrophilically patterned with $2\ \text{mm}$ wide hydrophilic lines separated by $2\ \text{mm}$ of hydrophobic space. The process for this patterning is shown in Figure 2.3.1 below.¹³

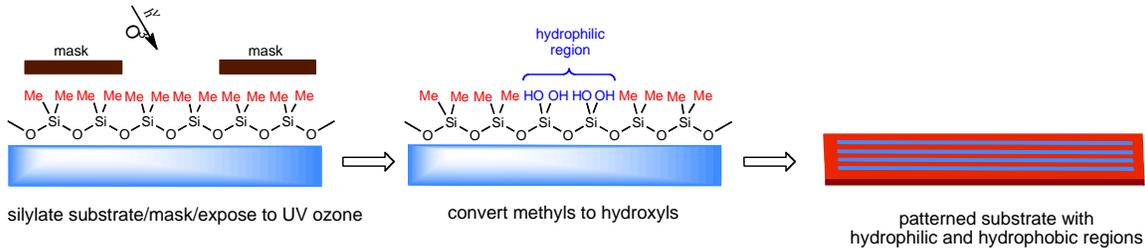


Figure 2.3.1 Schematic showing the steps to make a substrate with hydrophilic and hydrophobic patterns.

Micro-PV cells ranging in sizes from 250 μm up to 0.5 mm were distributed on the surface of a film of water and the water was allowed to evaporate. Water troughs were created in the hydrophilic regions (see Figure 2.3.2.) Upon complete evaporation of the water the cells mostly deposited in the hydrophilic regions of the glass slide (see Figure 2.3.3.) This experiment demonstrated long-range movement over several centimeters of cells to confined tracks of dimensions 1 mm x 40 mm. Higher-resolution masks can produce more narrow lines or smaller arrays if desired. The cells are attached to the glass slide such that they are not easily dislodged with low-pressure airflow or brushing with a tissue. However the cells can be lifted off onto adhesive tape, which suggests the ability to transfer the cells to a pre-wired, flexible substrate.

For these initial experiments the cells did not close-pack due to their mismatching edges and the large water contact angle of the water trough due to the superhydrophobic coating on the substrate. The fact that the cells did not close-pack during these experiments is actually not critical for future assembly of these arrays. In addition, the faces of the micro-PV chips were not all oriented in the same direction (recall the cells have a top and a bottom). One of the methods that might be applicable to achieve facial orientation is the treatment of the micro-PV chips with a sol-gel solution to make that surface hydrophobic prior to release.¹⁴ If superhydrophobic treatment of the chips is performed before the release step, the cell should then have an air bubble formed on this treated surface once it is placed in an aqueous solution. This in turn should orient all the cells with the air bubble side up.

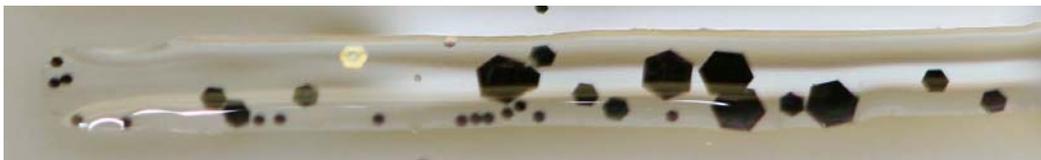


Figure 2.3.2 Various sizes of micro-PV cells floating in a hydrophilic trough on a glass slide.

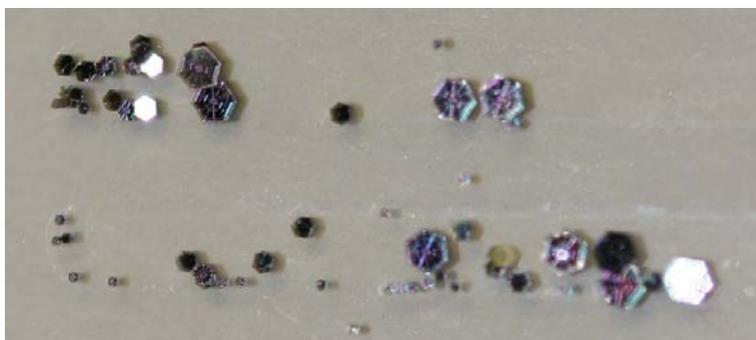


Figure 2.3.3 Micro-PV cells after drying remained in the hydrophilic regions of the glass slide.

These initial results of patterning a glass slide with simple lines of superhydrophobic and hydrophilic regions were promising. These results led us to extend this concept to other patterns. Anton Filatov (Org. 01749-1) prepared several computer-graphic generated patterns and an example can be seen in Figure 2.3.4 below.

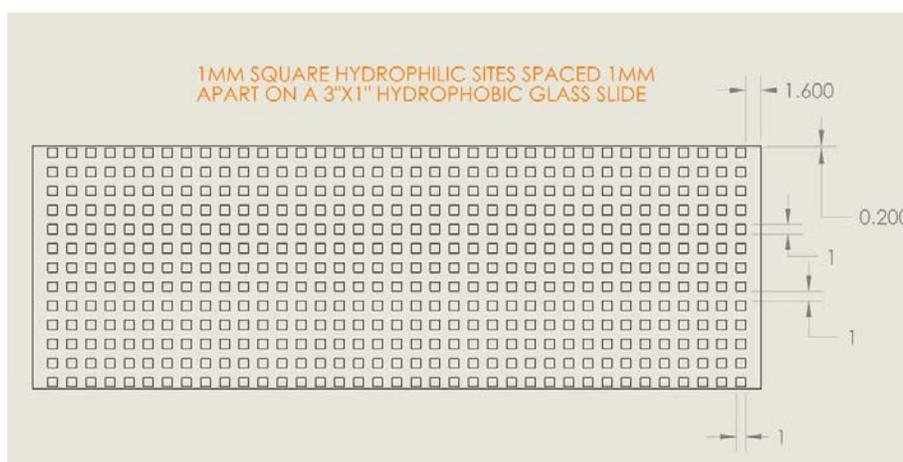


Figure 2.3.4 A 7.62 cm x 2.45 cm area with 1 mm squares spaced 1 mm apart (A. Filatov).

These patterns were used to make a patterned film of SU-8 on a quartz slide template, which was then used as a mask to prepare glass slides with hydrophilic square regions separated by a superhydrophobic surface. A typical glass slide after being patterned and wetted with water is shown in Figure 2.3.5 below. As with the original mask the hydrophilic squares are 1 mm x 1 mm in size separated from each other by 1 mm of superhydrophobic space.

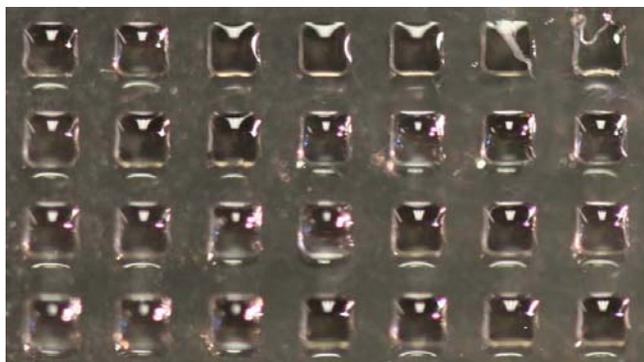


Figure 2.3.5 A close-up photograph of a portion of a superhydrophobic/hydrophilic patterned glass slide after being wetted with water. The hydrophilic squares are 1 mm x 1 mm in size separated from by 1 mm of superhydrophobic space.

These superhydrophobic/hydrophilic patterned slides were given to A. Filatov for testing. In these tests a glass slide was submerged under water and a large number of micro-PV chips (500 μm in size) were floated on the surface. The water was carefully removed at which point individual chips as well as clusters of chips came to rest on the hydrophilic regions. The result from one of these experiments is shown in Figure 2.3.6 below. Once the water had evaporated the chips adhered to the surface. These results demonstrate that hydrophilic/hydrophobic patterning is a viable method with which to orderly array chips onto a surface.¹⁵

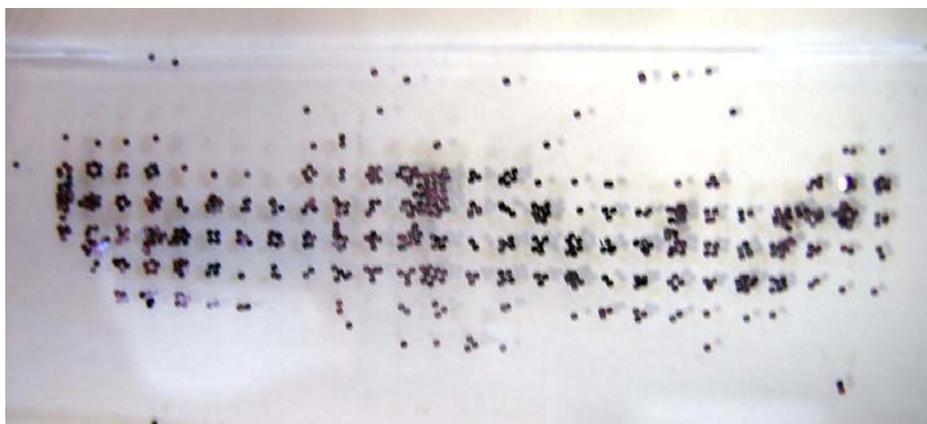


Figure 2.3.6 500 μm micro-PV silicon cells deposited on a glass (7.62 cm x 2.45 cm) patterned with 1 mm hydrophilic squares with 1 mm superhydrophobic spacing.

Micro-PV cell assembly has been demonstrated for the first time using superhydrophobic/hydrophilic patterning. The chemistry and techniques to achieve assembly are straightforward and seemingly amenable to large-scale processes. More work is required in order to achieve individual placement of the chips with no clustering. This most likely will require further refinement of the patterns (better size match agreement between cell size and hydrophilic region, higher resolution, more defined hydrophilic regions) and surfactant chemistry in order to lower the surface energy

of the cells (dispersants). Two Technical Advances have been submitted pertaining to superhydrophobic/hydrophilic patterning and coatings related to microscale assembly.

2.4 PV cell modification

The three previously described techniques all deal with the assembly and binding of parts on a substrate using chemical means, which is the main goal of this project. However, one key aspect, the initial facial control of the cells, was limiting the success of all of the assembly techniques. Having the correct facial orientation of cells would significantly increase the success rate in any one of the above described assembly techniques. A significant accomplishment realized through this LDRD work was the ability to modify PV cells and in doing so, gain control of the facial orientation in mixed solvent systems. By choice of modifier, the gold or GaAs face of the cell can be modified and depending on the end-group of the modifier, the surface could be rendered hydrophobic or hydrophilic.

In this project, modification of the gold face was achieved using a long hydrophobic thiol, octadecane thiol, and of the GaAs face using a hydrophobic silane, trichlorooctadecylsilane. Only one face of the PV cells was modified for any given experiment, thus giving both hydrophobic and hydrophilic faces to the cells, ideal for creating favorable orientation in a mixed solvent system. Modification of the gold face of PV cells began by cleaning the cells in a piranha solution, followed by a thorough rinsing and drying. Cells were then immersed in a solution of octadecanethiol in ethanol (0.01 M) for 24 hours. The cells were removed and rinsed and stored in methanol until needed. Modification of the GaAs surface of PV cells was carried out in a similar manner. Cells were cleaned in piranha solution and subsequently immersed in a solution of trichlorooctadecylsilane in toluene (0.1M) for 24 hours, resulting in the formation of a self-assembled monolayer. Cells were stored in toluene until required for use. The behavior of modified cells in single and mixed solvent systems was tested.

2.4.1 Octadecanethiol Modification of Gold Surface

Cells modified on the gold side with octadecanethiol showed no face selectivity in single solvent systems. Regardless of the solvent – water, ethanol, toluene, or methylene chloride – cells would sink to the bottom of the vial with a random facial orientation. It was concluded from this result that in order to obtain a facial preference both surface modification and a mixed solvent system are required.

The same octadecanethiol cells were immersed in a water-toluene system. These are two immiscible liquids, with water being denser than toluene and therefore sitting at the bottom of the vial. When cells were pipetted into the liquids they immediately moved to the interface of the two liquids, taking up a hexagonal close-packed arrangement. The octadecanethiol gold-modified face of the cells pointed into the nonpolar hydrophobic toluene and the GaAs faced into the polar hydrophilic water. This is a clear example of the cells showing facial specificity of the hydrophobically-modified gold reaching close contact with the hydrophobic toluene.

In a water-methylene chloride system, again two immiscible solvents, the octadecanethiol-modified cells also displayed facial selectivity. Here, methylene chloride as the denser of the two solvents sits at the bottom of the vial with water floating on top. As with the water-toluene system, the cells oriented themselves with the gold surface pointed towards the hydrophobic methylene chloride and the GaAs facing the water. In this particular mixed solvent system, not all cells sat at the interface of the two solvents as some fell to the bottom of the vial. In water-toluene solution, the modified cells lay at the interface, being supported by water and held in contact with toluene. With methylene chloride-water, water floats on top being the lighter of the two solvents. Since the cells strive to have close contact with methylene chloride residing at the bottom of the vial, some cells fall towards the bottom. Water in this instance does not serve as a buoyant medium to bring the die into close proximity to the organic solvent; therefore, not all cells sit at the solvent interface. All cells are, however, directed with the gold-modified face directed in towards the organic methylene chloride. In a solvent system with excess water and a very limited volume of methylene chloride, modified PV cells are encapsulated in a small bubble with all of the octadecanethiol-modified gold faces directed into the hydrophobic methylene chloride and the GaAs faces into the hydrophilic water.

2.4.2 Trichlorooctadecylsilane Modification of GaAs Surface

GaAs cells modified with trichlorooctadecylsilane showed no facial selectivity in single solvent systems regardless of the solvent, as was observed with cells modified on the gold side. Facial preference and orientation was observed in the case of immiscible solvents.

In a water-toluene mixed solvent system, cells floated at the solvent interface with the GaAs face directed into the toluene. Here the gold is more hydrophilic than the C-18 silane modified GaAs, and so the gold face takes up a preferential orientation facing into water while the hydrophobically modified GaAs face is directed into toluene. A water-methylene chloride solvent system gave a very different result. As before, cells primarily fell to the bottom of the vial with little driving force to keep them floating at the interface of the solvents; however, no facial preference was observed for the modified cells. It is possible that all PV cells were not modified, which would give rise to mixed results. This may result from either from inadequate cleaning or immersion or because the strength of the silane-Ga bond is not as strong as a silane-Si bond. More work is required in this case to understand and resolve the issues at hand.

To summarize, we have successfully demonstrated the ability to selectively modify the surface of gold-GaAs cells such that their properties are very different from their original surface and from the unmodified, opposite surface of the cell. This technique gives excellent control in dictating the facial orientation of PV cells in mixed solvent systems such as water-toluene. In both surface modifications, limiting the volume of one solvent gives more discrete control over cell distribution. Such control should enable a rapid and accurate assembly of cells onto an array via chemical means.

3 Conclusion

The use of chemical forces to assist in the assembly and *placement* of micro-PV chips and surrogate objects (gold and silver nano- to micro-sized particles) onto substrates was one of the key technical developments achieved during this late-start LDRD. Different combinations of chemistry (sol-gel) and techniques (superhydrophobic/hydrophilic patterning) were used to place chips onto patterned arrays on a substrate. In addition, other chemical methods (dithiols and self assembled monolayers) were used to facially orient micro-PV chips in two-phase solvent systems. These methods directly impact Sandia and DOE missions in the area of microsystems technology as it pertains to the manufacture of improved individual photovoltaic (PV) cells. These methods pertain specifically to the assembly of these PV cells into more efficient and effective arrays. Overall, results from this LDRD have shown that the proposed concept of using chemically assisted assembly of micron-sized objects is clearly achievable. The chemistry involved in these processes is relatively straightforward and can be scaled to large arrays. Furthermore, it is entirely conceivable that these methods can be engineered to be continuous (for example roll-to-roll processing).

Specifically we have shown that by floating micro-PV chips (ranging in sizes from 250 μm to 1 mm) on water over a superhydrophobic-coated substrate with hydrophilic areas and then removing the water the chips are deposited in the hydrophilic regions. We have also demonstrated that using dithiols in conjunction with micro-PV chips (gold coated on one side) we are able to facially orient these chips at the boundary layer between a system consisting of water and an organic solvent. This technique allows for the positioning of one-sided gold-coated chips to be facing upward. Although yet to be demonstrated, taken together these two methods should allow for the placement and facial orientation of chips (gold-coated on one side) on a superhydrophobic/hydrophilic patterned substrate. These results are of significant interest to the Microsystems Enabled PV Group and would allow them to go forward with confidence to manufacture the more efficient smaller and thinner PV chips. The current technology of mechanical pick-and-place is not suitable for these smaller more fragile chips. The chemical assembly technology demonstrated in this LDRD can also be adapted to other systems that require the placement of micron-sized electronic components, mirrors or other MEMs devices in large arrays.

In summary, for this late-start LDRD we have achieved success in demonstrating that the chemical concepts of self-assembly, conventionally used for molecular-level interactions, can be used for the manipulation and placement of much larger objects onto substrates. These larger objects – PV cells – are currently placed into specified locations using “pick and place” technology, but the currently-used technology will not be appropriate as PV cells get smaller in size and more fragile. We believe there are many significant aspects of our research that will resonate with the outside scientific community and the PV groups and microsystems researchers within Sandia. As well, we believe that industrial PV manufacturers will also be interested in the advances in this work.

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