

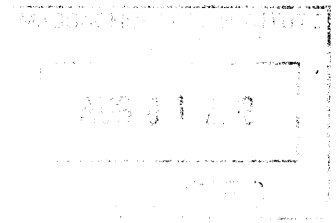
Design and Construction of Instruments for Exciton Diffusion Characterization and for Patterning of Thin Films

by

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B.S. Electrical Engineering (2010)
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ARCHIVES



Submitted to the Department of Electrical Engineering and Computer
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Abstract

In this thesis the instruments explore two main aspects of organic optoelectronic devices. One instrument characterizes exciton diffusion and the other patterns organic thin films. Exciton diffusion characteristics are important to study in organic materials because excitons mediate the transport of energy. In this work, a fluorescence microscope is designed and built in order to image directly the triplet exciton diffusion in organic crystals.

Patterning of organic thin films in industry is done by fine-metal masks, which are fragile and do not scale with substrate size. The second instrument is the first fully functional prototype for a new type of dry lithography technique invented in our research group which addresses the scalability and compatibility problems of past patterning methods. The proof-of-concept instrument replaces the traditional fine metal mask patterning method by patterning a sublimable mask with a micro-stamp.

Thesis Supervisor: Marc A. Baldo

Title: Associate Professor of Electrical Engineering

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I would like to first thank my advisor, Marc Baldo who taught me that passion is all that counts when it comes to research. I would also like to thank the Center of Excitonics as they provided with funding for me and my research. The instruments could not have been constructed without Cathy Bourgeois, who provided all of my administrative support. I would like to thank Matthias Bahlke for teaching me vacuum systems and for his support during long hours in the lab. Daniel Ashall for his help in designing the CAD files for the chamber. Nick Thompson for taking the time to teach me the essentials of material science. Priya Jadhav for helping me in 6.701 and for helping with my first project. Jiye Lee for helping with the growth of crystals and microscope setup. Amador Velazquez and Paul Azunre for interesting discussions about life. Carmel Rotschild and Carlijn Mulder for showing me how to conduct experiments and Phil Reusswig for his safety tips. Lastly, I would like to thank my family for all their support over the years.

My love and this thesis are dedicated to Khalea, whose positive energy and companionship helped grind out my last years in MIT.

Contents

1	Background	11
1.1	Organic Semiconductor Devices	11
I	Direct Imaging of Exciton Diffusion	15
2	Exciton Diffusion	17
2.1	Indirect Measurement methods	17
3	Fluorescence Microscope	19
3.1	Exciton Relaxation	19
3.2	Equipment Setup	21
3.3	Exciton Diffusion Measurement	23
4	Conclusion	25
II	Mask-less Patterning of Organic Materials	26
5	Patterning Organics	27
5.1	Thermal Evaporation	28
5.2	Embossing Micro-stamp techniques	29
6	Patterning Instrument	31
6.1	Sublimable Mask Process flow	32

6.2	Chamber Design	33
6.2.1	Carbon Dioxide Gas Delivery method	37
6.2.2	Substrate design	37
6.2.3	Stamping Apparatus	38
6.3	Results	39
7	Conclusion	41

List of Figures

1-1	Graphic Description of an Exciton. [2]	12
1-2	Example of an OLED. [6]	12
1-3	Example of a shadowmask. [15]	13
2-1	Molecular structure of Tetracene. [10]	18
3-1	Positions of the first excited singlet and triplet levels found in a typical molecule.	20
3-2	Exciton Diffusion mechanism: singlet is created by excitation light, singlet splits into two triplets, triplets diffuse through the crystal, then the triplets collide to form a singlet, then the singlet relaxes to emit the photon. [13]	20
3-3	Image of cells through fluorescence microscopy. [14]	21
3-4	Schematic of fluorescence microscopy.	22
3-5	Actual constructed fluorescence microscope.	23
3-6	Delayed Fluorescence in AB plane axis of Tetracene crystal [13]	24
3-7	Delayed Fluorescence in C plane axis of Tetracene crystal [13]	24
3-8	Cross-section of the fluorescence: spreading of spot size at later times. [13]	24
5-1	Image of a typical vacuum thermal evaporation setup using a shadow mask to pattern the material. [18]	29
5-2	Image of a typical embossing micro-stamp process. [19]	30

6-1	3D CAD Drawing of Constructed Instrument.	32
6-2	Sublimable Mask Process. [20]	33
6-3	Micro-stamp patterning the dry ice. [20]	33
6-4	A. Complete chamber B. Front Door without door handles C. Back Panel: Cryo Pump Placement	35
6-5	The two sides of the chamber with the corresponding item locations	35
6-6	A. Top view of chamber. B. Bottom view of chamber: thermal evapo- rators location	36
6-7	Door Mechanism Design for ease of use.	36
6-8	2-axis Stamping Mechanism in Vacuum Chamber.	38
6-9	Patterned Dry Ice and Patterned Pixels [20]	39

Chapter 1

Background

The past decade has been witness to new types of semiconductor devices which utilize organic materials. These organic materials are held together by weak van der Waals bonds which allow the devices to be created without the painstaking growth requirements of conventional silicon devices. Unlike silicon devices where the structure is highly ordered, these devices exploit short range order to enable devices to be created at potentially low-cost processes. Given the flexibility of organic materials in terms of molecular design and synthesis, it is possible to tune the physical properties and material structures to meet the requirements of the given application.

1.1 Organic Semiconductor Devices

Silicon devices dominate the electronics we use today. The relative abundance of silicon and large investment in its manufacturing infrastructure has enabled silicon to be the de facto material for many of the components that drive our digital revolution. Organic electronics with their low electron mobilities are not suitable for transistors and other computation devices. The intermolecular overlap of the van der Waals bonds generally limit charge transport mobilities to less than $10 \text{ cm}^2/Vs$ at room temperature.[1] However, organics are superior in terms of coupling the interactions of light and electrical signals because of excitons.

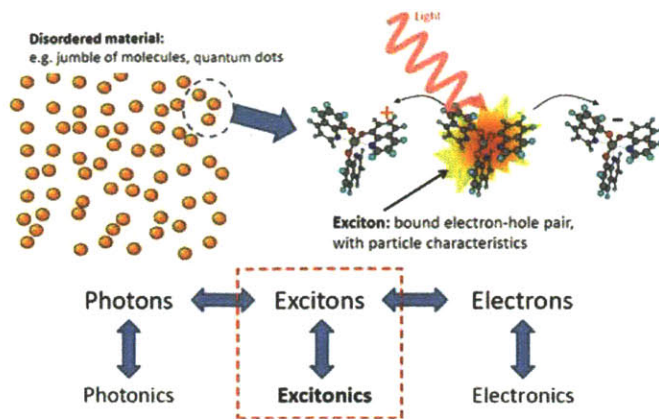


Figure 1-1: Graphic Description of an Exciton. [2]

Excitons are bound pairs of electrons and holes which are able to mediate the absorption and emission of photons.[2]

Therefore, these excitons are an excellent medium in which light can be generated and absorbed. Excitonic devices have been used in the development of many opto-electronic devices such as organic photovoltaics [3] and organic light emitting diodes [4].

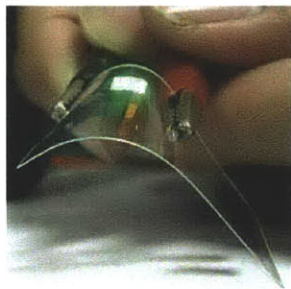


Figure 1-2: Example of an OLED. [6]

The instruments constructed in this thesis were built for exciton diffusion measurements and patterning for organic light emitting diodes. The fluorescence microscope created in this thesis, will allow these devices to be characterized by measuring the diffusion lengths of the excitons. Thereby allowing different configuration of materials to be tested to find the longest diffusion lengths.

The second instrument constructed deals with the patterning of OLEDs. In industry, people are using shadowmasks to pattern which does not scale with substrate size. As you increase the pattern area, the shadowmasks bend because of their thinness and become misaligned for the pixels. Industry is looking for alternative ways to pattern these devices. The tool constructed in this thesis is a prototype of a sublimable mask process that requires no shadow mask to pattern devices. A more detail account of the process will be explained in Chapter six.

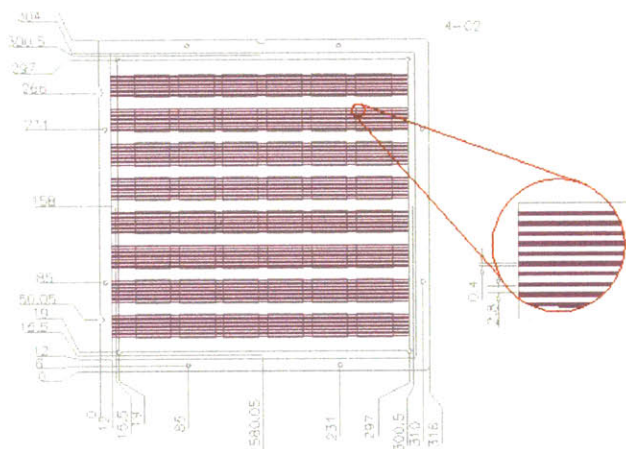


Figure 1-3: Example of a shadowmask. [15]

There are two parts to this thesis. In the first part, the construction of a fluorescence microscope is discussed in order to directly measure the exciton diffusion of devices. In the second part, the construction of a thermal evaporator equipped with a mask-less patterning method is discussed.

Chapter two discusses exciton diffusion in organic crystals and the indirect methods of measuring the diffusion.

Chapter three describes the construction of the fluorescence microscope and the direct measurement of the exciton diffusion.

Chapter four summarizes the results and concludes the discussions of this part.

Chapter five introduces current patterning techniques for organics, comparing the advantages and disadvantages of the mask-less technique discussed in section 6.1 .

Embossing techniques are also discussed as they play an important role in the new patterning method.

Chapter six describes the process flow for the patterning method. The design and construction of the working prototype are also discussed.

Chapter seven concludes the second part while discussing future additions to the prototype that would help the patterning technology mature into a feasible manufacturing capability.

Part I

Direct Imaging of Exciton Diffusion

Chapter 2

Exciton Diffusion

In organic optoelectronic devices a key parameter that controls the transfer of electrical energy to optical energy is the exciton. Exciton diffusion is especially important in devices like organic photovoltaics because it allows the optical energy to be carried through the exciton to a charge transfer site where the charge can be extracted. [8]

An organic crystal is a good starting point for exciton diffusion measurements because their structure can be determined. Mobilities of holes and electrons are highest in organic crystals and should therefore yield high exciton transport properties. In this work a Tetracene crystal was chosen because of its transport properties. In Tetracene there are two different excitons created at the point of excitation a singlet and a triplet exciton. A singlet has a decay rate of about 9 nano seconds while the triplet decay rate is much longer up to hundreds of microseconds. [1] Therefore, in the discussion below the triplet diffusion length is what is being measured since it has a lifetime that is long enough to diffuse.

2.1 Indirect Measurement methods

Many of the literature values of diffusion lengths vary because they are done indirectly. Diffusion lengths in anthracene crystals have been measured by studying the time dependence of the delayed fluorescence due to a varying distribution of excitation

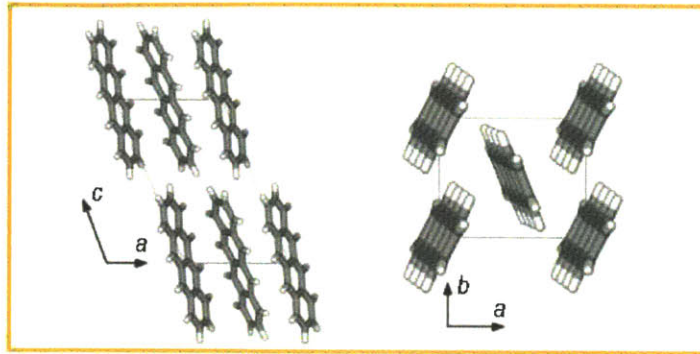


Figure 2-1: Molecular structure of Tetracene. [10]

light. [11] Another common method for measuring the triple diffusion indirectly is by examining the polarization and wavelength dependent photo-conductivity of the crystal. [12] In this case the photo-conductivity can be related to the diffusion lengths because the exciton dissociation at the surface of the crystals can contribute to the photo-conductivity. Unfortunately, none of these methods are able to directly capture the diffusion length of the exciton. In these experiments many other parameters have to be taken into account obscuring the true diffusion length. As a result, in the literature the diffusion lengths of a particular type of crystal can vary as much as 10 microns. In this thesis, a fluorescence microscope is constructed to help alleviate this problem of accuracy, as shown in the sections below.

Chapter 3

Fluorescence Microscope

3.1 Exciton Relaxation

In order to better understand how a fluorescence microscope helps in the direct measurement of the exciton diffusion. First, we have to understand how one is able to measure the location of the exciton. The exciton, fundamentally an excited electron and hole pair cannot be seen optically as it does not emit any light. By using the Born-Oppenheimer approximation one can simplify the energy levels of the molecules into two states; a ground state and an excited state. When an exciton is created either by injection of charge or by optical excitation, the electron jumps into the excited state. Given the allowed and disallowed electronic transitions according to spin; a singlet or triplet exciton can be created. When the electron relaxes it emits a photon to release the energy so that it can be brought to the ground state. The decay of excited singlet states is allowed therefore is it fairly rapid in the range of nanoseconds. This relaxation is called fluorescence. A triplet state decay is weakly allowed prescribed to certain second order effects that mix the singlet and triplet states, causing a relaxation in the range of microseconds. This relaxation is called phosphorescence. As shown in Figure 3-1.

An exciton can also release a photon when it collides with other excitons forming high-energy states that can relax by releasing photons and phonons. In this work,

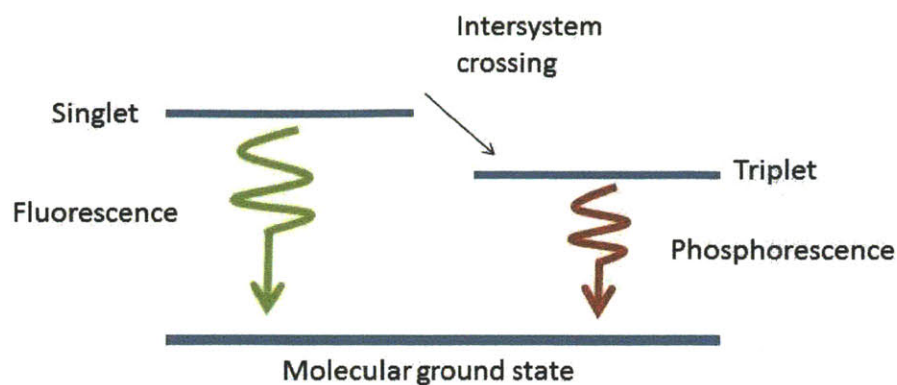


Figure 3-1: Positions of the first excited singlet and triplet levels found in a typical molecule.

the diffusion of the exciton is measured by looking at the triplet-triplet annihilation and imaging the fluorescence of the relaxing singlet exciton. As shown in Figure 3-2.

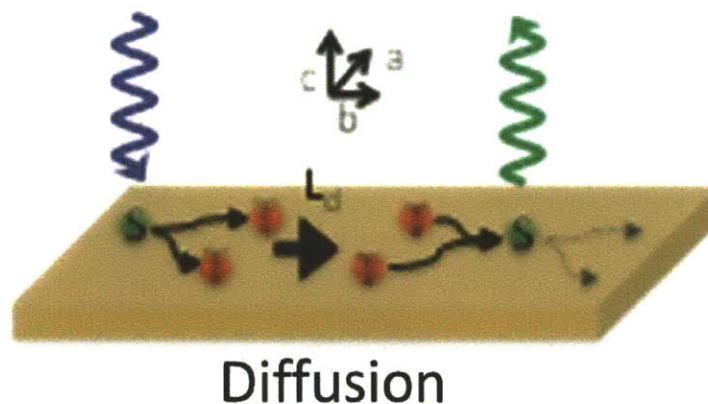


Figure 3-2: Exciton Diffusion mechanism: singlet is created by excitation light, singlet splits into two triplets, triplets diffuse through the crystal, then the triplets collide to form a singlet, then the singlet relaxes to emit the photon. [13]

A fluorescence microscope is typically used in biological applications, where dyes are mixed in different areas of the transparent organism. By exploiting the fluorescence of the dyes one can then image the specimen which otherwise would be transparent to white light. As can be seen in Figure 3-3.

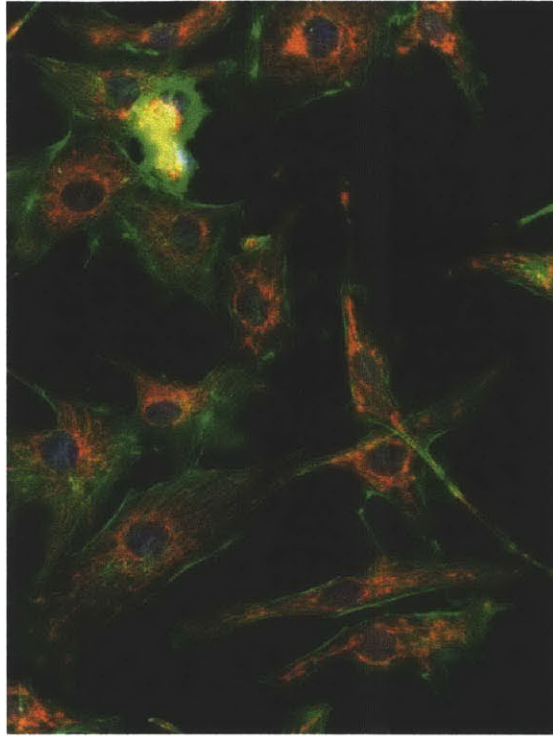


Figure 3-3: Image of cells through fluorescence microscopy. [14]

The key idea of the microscope is that the illuminated light is absorbed by the specimen and the fluorescence emitted by the sample is red-shifted to allow the image sensor to only look at the light emitted from the sample. This is the basis of how the exciton diffusion is measured, by direct imaging of the fluorescence.

3.2 Equipment Setup

The microscope is made up of the following components.

- * Solid-state laser beam: 350 nm wavelength, Spectra Physics.
- * Dichroic mirror: Reflective if below 400 nm, Transparent if above 450 nm.
- * UV-Transparent microscope Objective
- * Sample holder

* Focusing Lens

* CCD Camera (Q imaging)

A pulsed laser beam is delivered normal to the surface of the Tetracene crystal, by first reflecting off the dichroic mirror then being focused by the objective to a spot size of about a micron in diameter. Then delayed fluorescence is captured by the objective and passes through the dichroic mirror which focuses the rays using the focusing lens into the CCD camera. The resolution of the image was 0.63 micrometer per pixel. A schematic of this process is shown in Figure 3-4. The actual microscope set-up is also shown in Figure 3-5.

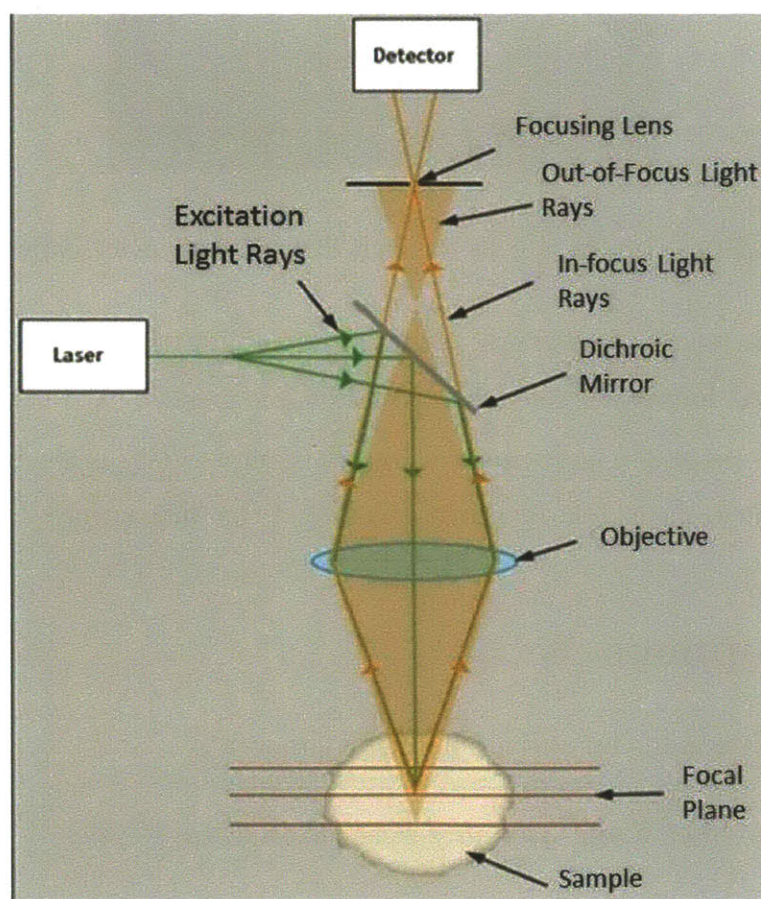


Figure 3-4: Schematic of fluorescence microscopy.

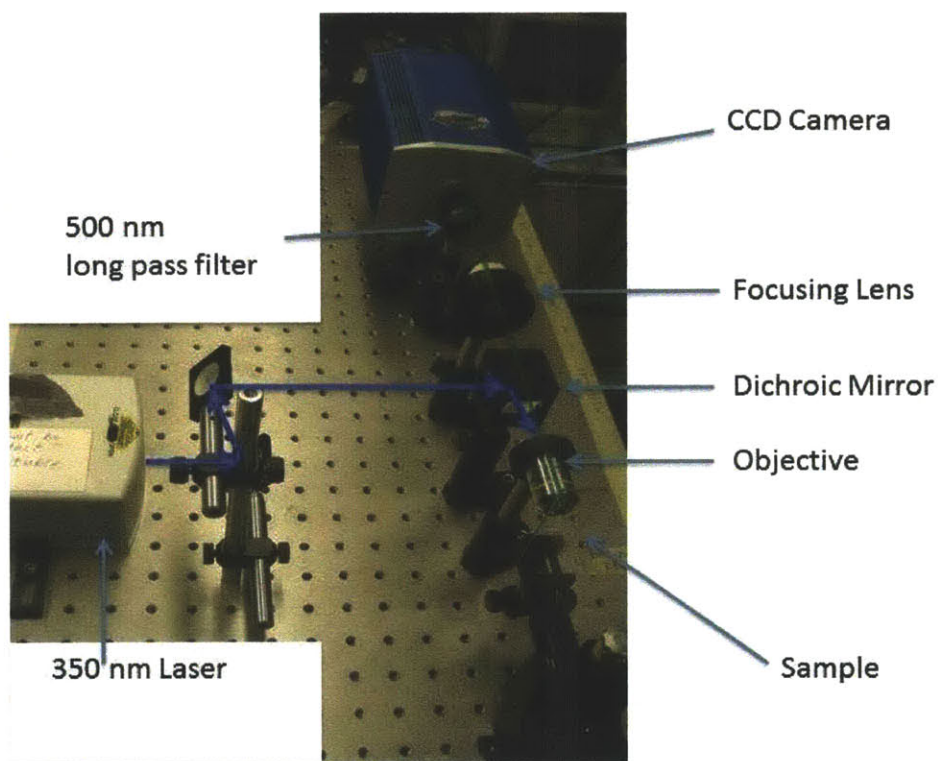


Figure 3-5: Actual constructed fluorescence microscope.

3.3 Exciton Diffusion Measurement

The Tetracene crystal was measured at two different planes. This was to investigate which axis of the crystal would yield the highest diffusion length. The laser excitation spot was pulsed and the CCD camera would capture the image at later times. This allowed the diffusion profile to be imaged dependent on the initial excitation. Figure 3-6 and 3-7 show the instantaneous spot along with the delayed images. The diffusion profile is seen in Figure 3-8, which results in a diffusion length of about 5 microns.



Figure 3-6: Delayed Fluorescence in AB plane axis of Tetracene crystal [13]

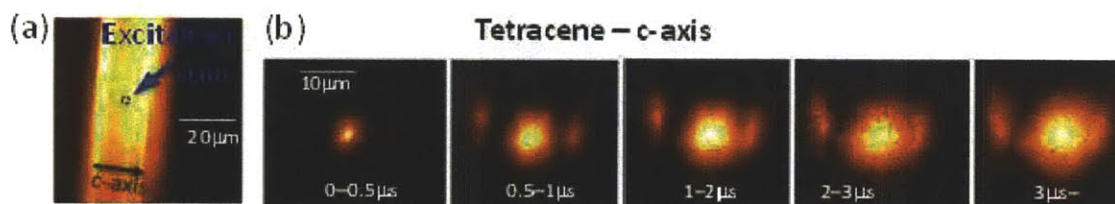


Figure 3-7: Delayed Fluorescence in C plane axis of Tetracene crystal [13]

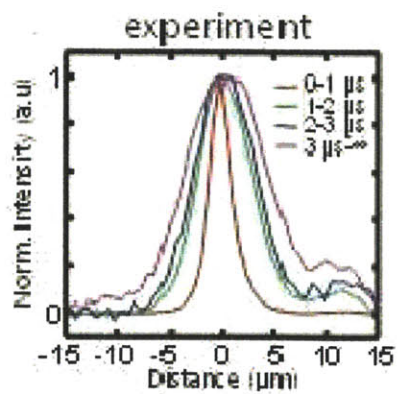


Figure 3-8: Cross-section of the fluorescence: spreading of spot size at later times. [13]

Chapter 4

Conclusion

The instrument constructed was able to effectively measure the exciton diffusion directly. By borrowing the techniques used in studying biological specimen, a diffusion length of about 5 micrometers was measured. Considering that the C plane and AB plane had similar spot profiles, this should suggest that optical wave-guiding and self-absorption are also playing a role in the transport of energy. This is because the C plane diffusion length in Tetracene should be considerably less according to theoretical calculation.

The next steps are to study other types of crystals and to verify actual triplet diffusion. Transient measurements with a streak camera can lead to studies of self-absorption. Organic semiconductor devices that can benefit from long diffusion lengths could also be studied.

Part II

**Mask-less Patterning of Organic
Materials**

Chapter 5

Patterning Organics

Organics cannot be patterned with conventional lithography because of the solvents involved. Therefore, there are three main alternatives that are being developed to pattern organic devices. The most successful method is shadow mask patterning. In this method the organic is deposited using thermal evaporation where the organic material is heated in a boat in a vacuum atmosphere. The low pressure allows the organic to travel relatively unobstructed and can be patterned by a shadow mask that sits just above the substrate. [15] The disadvantages of this method is its inability to scale with the substrate and a reliance on a batch-based approach. Even with these drawbacks, this is the method that is used in industry. The second method of patterning is a stamping technique. This is usually called soft lithography and typically uses a patterned elastomer to transfer a single layer of material to its substrate. [16] Its limitations are the contamination issues involved and the adhesion of the organic material to the elastomer. The third method that is being explored is a modification to inkjet printing. One example is a technique called organic vapor phase deposition where the print head actually becomes a source of the organic vapor and by careful control of the head, micro patterns can be printed on a substrate. [17] The disadvantage of this technique is a need for parallel heads and organic material compatibility.

The instrument constructed in this thesis uses a completely different technique than previously used. The method is most similar to the shadow mask method as

it uses a thermal evaporator but is different because instead of the shadow mask a sublimable resist is used to pattern the organics. The sublimable resist can be patterned many ways but the most energy efficient is by soft lithography (embossing micro-stamp). The complete method will be explained in Section 6.1 but it is useful to first understand two main aspects of the process: the thermal evaporation and embossing micro-stamp.

5.1 Thermal Evaporation

Thermal evaporation is currently the only method used in industry that allows for large substrates to be coated with a very precise thickness of organics, down to a couple of Angstroms. Usually low pressures are used to minimize the contamination and maximize the mean free path of the organic evaporated, pressures range from high vacuum (10^{-6}) Torr to ultra high vacuum (10^{-9}) Torr. The technique uses metal or ceramic boats that are heated by running a high current through them. This in turn causes the organic in the metal or ceramic boats to evaporate upwards where the substrate is usually located. Since the pressure is very low, the mean free path of the vapor of the organics is very high causing the particles to travel in a relatively straight line from the source boat. A quartz crystal monitor is typically used to measure the thickness of the evaporated material. The crystal monitor vibrates at a specific frequency and can detect minute changes in its mass as organic is evaporated on it. A tooling factor is typically used to match the thickness read on the crystal monitor to the thickness of the substrate. A schematic of a typical evaporator is shown in Figure 5-1.

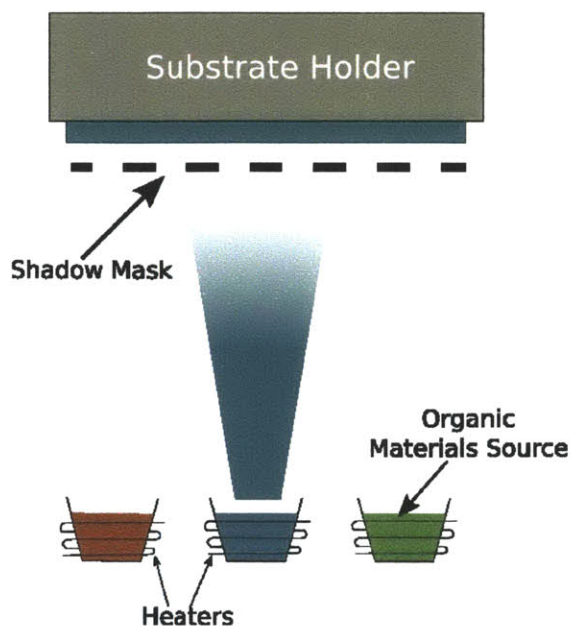


Figure 5-1: Image of a typical vacuum thermal evaporation setup using a shadow mask to pattern the material. [18]

5.2 Embossing Micro-stamp techniques

Embossing micro-stamp techniques work like printing presses, where the contact of the stamp can transfer a pattern to the substrate except that the scales are in micrometers instead of centimetres. Stamps are typically made up of a patterned elastomer, which can be made with a master stamp. Polydimethylsiloxane(PDMS) is the most common elastomer used because of its cost and ease of use. The most important factor is the rigidity of the stamp and the ability to conform to the substrate in order to transfer the desired patterned. The rigidity is needed to make sure the pattern is the same as the stamp and the ability to conform is needed to make consistent contact for even patterning. Although these can be formidable challenges, the micro-stamp techniques have advantages in large scale manufacturing because it is conceivable that a roll-to-roll micro stamp could be developed to mimic the fast throughput of printing presses. A typical micro-stamp configuration is showed in Figure 5-2.

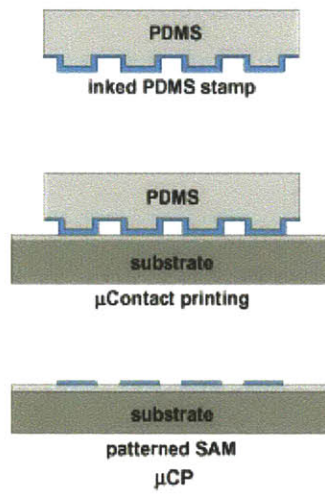


Figure 5-2: Image of a typical embossing micro-stamp process. [19]

Chapter 6

Patterning Instrument

The instrument constructed combines the method of thermal evaporation with that of soft lithography. A vacuum chamber with thermal sources is equipped with a custom micro stamp system. The process will be explained in detail in Section 6.1. In addition to the vacuum chamber, a glove box filled with nitrogen gas was designed and purchased. This is because organics are incompatible with oxygen and water. The glovebox was constructed so that the chamber would mate to it to preserve the nitrogen environment. The glove box was constructed and purchased from LC Tech Inc. A 3D model of the complete instrument is shown below in Figure 6-1.

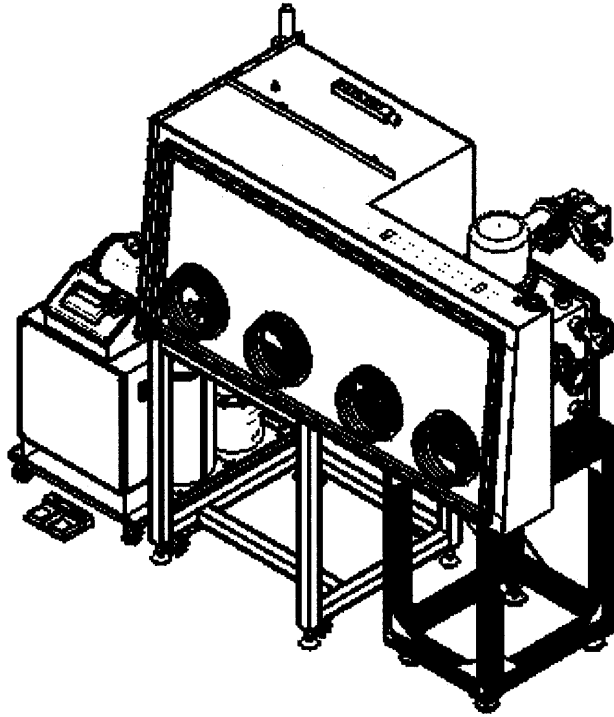
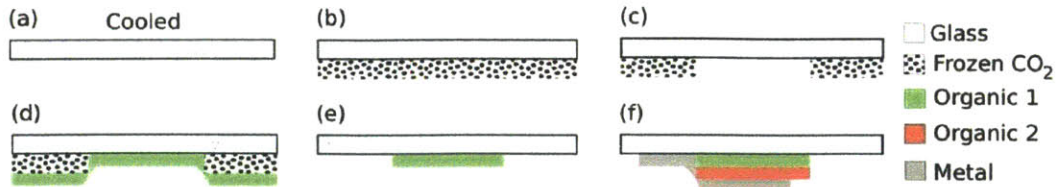


Figure 6-1: 3D CAD Drawing of Constructed Instrument.

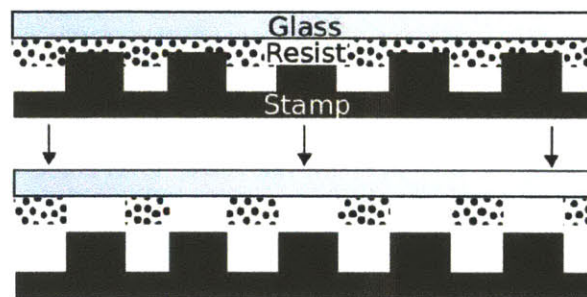
6.1 Sublimable Mask Process flow

The invented process that is prototyped in this thesis is described in this section. This process uses the same vacuum chamber and thermal evaporation techniques as the shadow mask method but instead of using a shadow mask, frozen carbon dioxide is used as a dry resist which is then patterned by a micro-stamp. The substrate is cooled in order to keep the CO_2 from subliming. After the dry ice is patterned, the thermal sources are fed with current which causes the organic to be deposited on the substrate and patterned dry ice. After the desired thickness is reached, the substrate is then heated to lift off the resist and leave a patterned organic layer. It is an inert process which just replaces the shadow mask but keeps the advantages of thermal evaporation. A detailed diagram of the process is shown in Figure 6-2. A schematic representation of the micro-stamp patterning the resist is also shown in Figure 6-3.



Simplified process flow for sublimation lithography using a frozen CO₂ resist (not to scale). (a) Cool substrate below 100K. (b) Freeze on thin film of CO₂. (c) Pattern CO₂ film using moderate local heating. (d) Deposit desired organic or metal thin film using thermal evaporation. (e) Warm substrate, sublime CO₂, and lift off unwanted material. (f) Repeat as necessary to complete device.

Figure 6-2: Sublimable Mask Process. [20]



Schematic representation of using a micro-featured stamp to define exposed area of a sublimable mask

Figure 6-3: Micro-stamp patterning the dry ice. [20]

6.2 Chamber Design

The vacuum chamber was made out of stainless steel. Stainless steel was chosen because it has a very low out-gas rate which aids in achieving a pressure of 10^{-7} Torr. Below is the list of components that were either machined or bought.

- * Stainless steel chamber: constructed by MIT Machine shop
- * Cryogenic pump: Low pressure pump to get to pressures of 10^{-7} Torr. Bought from CTI-CRYOGENICS.
- * Dry Rough Pump: High pressure pump to get to pressure of 10^{-3} torr.
- * Ionization Gauge: Measure low pressures down to 10^{-7} torr.

- * Convection Gauge: Measure high pressure down to 10^{-3} torr.
- * USB Connector Flange: for connectivity to the insitu microscope.
- * X-stage and Y stage micro motors: for use in manipulating the stamp.
- * Vent Connector: in order to vent the chamber to atmosphere pressure.
- * Quartz Crystal Monitor: to monitor organic layer thickness.
- * Liquid Nitrogen Feed-through: this is so that Liquid Nitrogen can be flowed into the substrate holder to cool it down to 77 Kelvin.
- * Mass flow controller: this is to control the CO_2 flow rate.
- * Viewport: ability to transfer laser light into chamber for interference thickness monitoring.
- * Electrical Feed-throughs: Heating capability, control of micro manipulators, temperature sensors.
- * K-cells: ceramic boats which are used as thermal evaporators to deposit the organic.
- * Door Mechanism: Allows chamber door to slide for ease of use made out of 80/20 material.

The figures below are the 3D CAD files designed for the construction of the chamber. Figures 6-4, 6-5, and 6-6 refer to the chamber. Figure 6-7 is the door mechanism design. The dimensions are in inches.

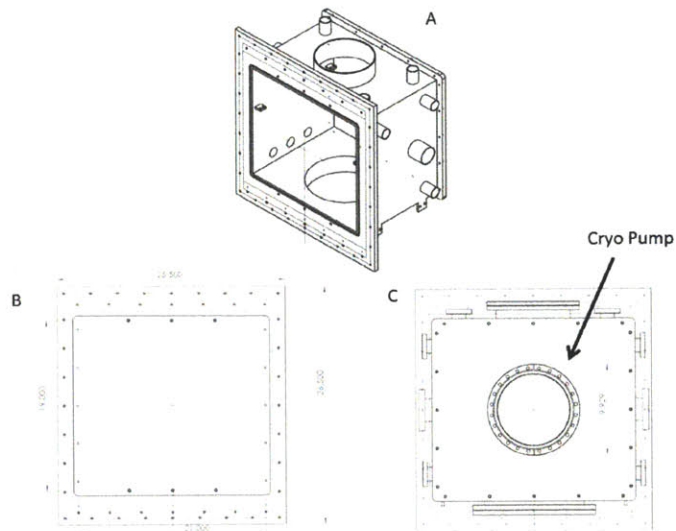


Figure 6-4: A. Complete chamber B. Front Door without door handles C. Back Panel: Cryo Pump Placement

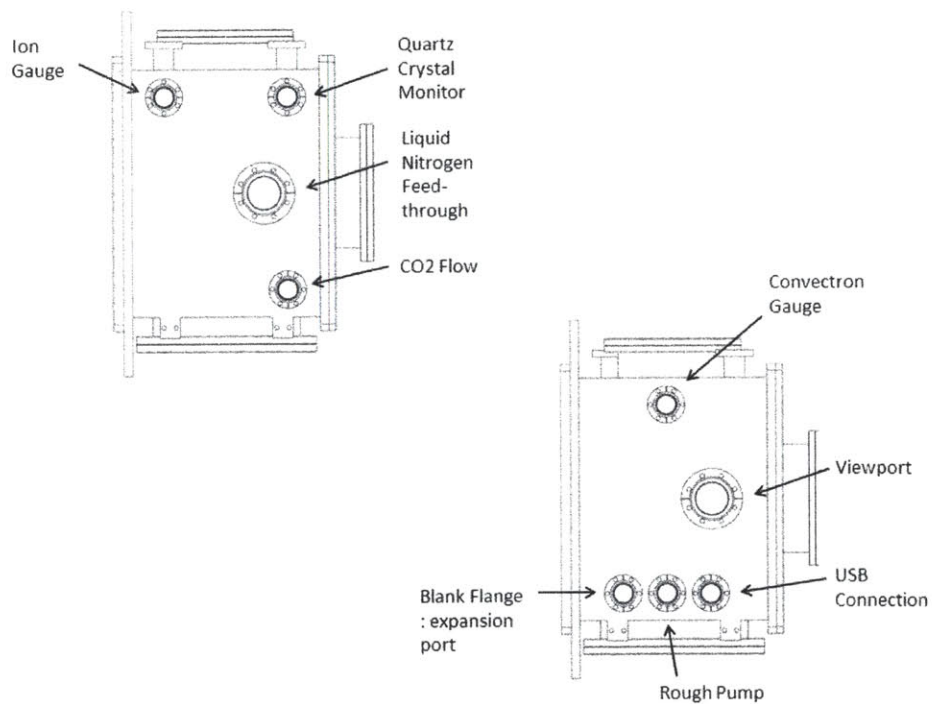


Figure 6-5: The two sides of the chamber with the corresponding item locations

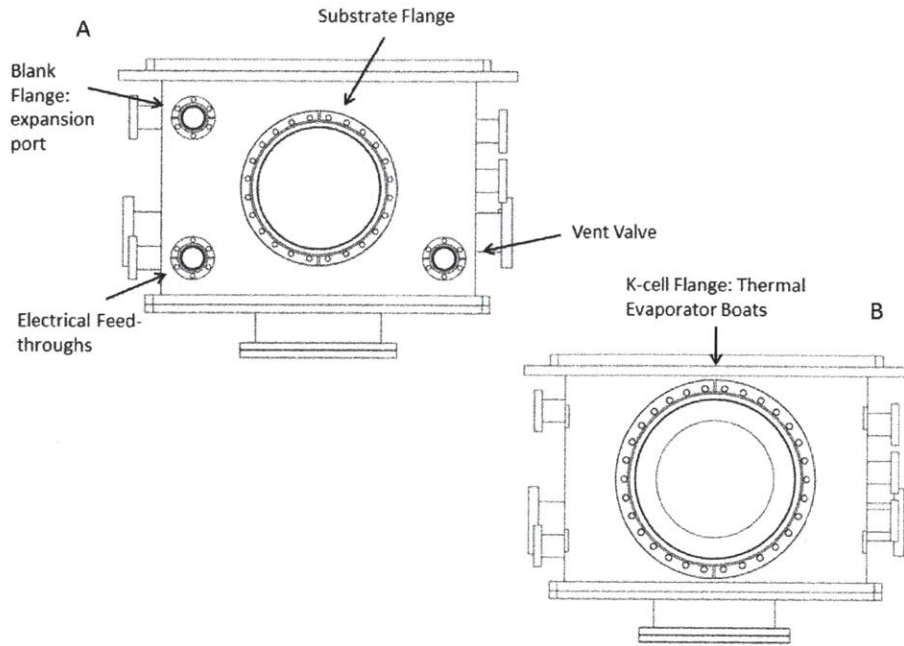


Figure 6-6: A. Top view of chamber. B. Bottom view of chamber: thermal evaporators location

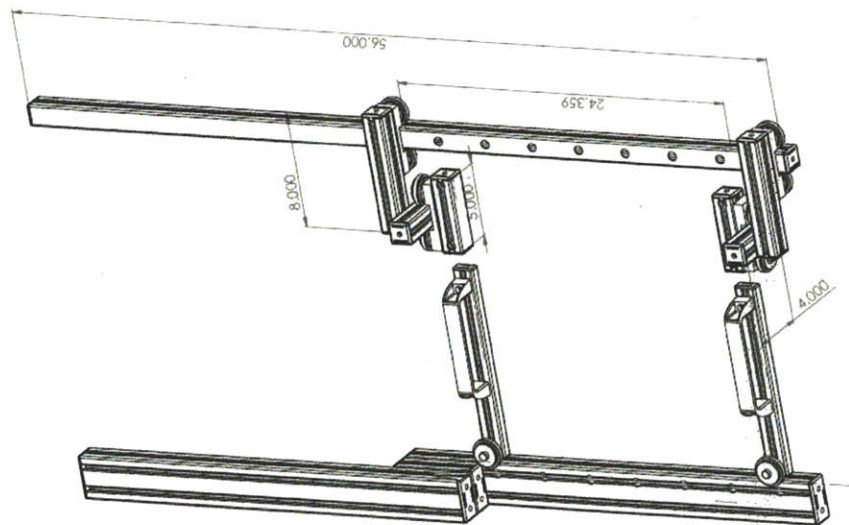


Figure 6-7: Door Mechanism Design for ease of use.

6.2.1 Carbon Dioxide Gas Delivery method

The CO_2 delivery system is important for this process because it controls the thickness of the carbon dioxide. Initially, experiments were done with a leak valve where we would monitor the convectron gauge to see what type of pressure was flowing in. Since this method, is not very repeatable and accurate, a mass flow controller was purchased. A Type 2179A Mass-Flow controller from MKS Instruments was used. It allowed a control range of 2 to 100 percent of 100 sccm flow. Once the gas flowed into the controller, the flow was measured, then it moved on to the control valve where according to the given output value would adjust so that the total flow rate was the same as the set point. The flow measurement is based on a differential heat transfer between different temperature sensing heater elements in the sensor tube. Thermal mass movement is converted to mass flow via the specific heat equation $\frac{dm}{dt} = \frac{C}{C_p}$; where $\frac{dm}{dt}$ is the mass flow, C is the heat capacity of the gas, and C_p is the specific heat of the gas.

6.2.2 Substrate design

Thermal conductivity in vacuum is very important if the substrate is to be cooled to 77 Kelvin. This is the temperature where the CO_2 would freeze to form a stable resist. In the beginning, a cryo pump was used as a cold head to cool down the substrate. Indium foil was used in between the interfaces of the copper plates to ensure good thermal contact. Since the goal of this instrument is to illustrate a scalable prototype of this mask-less process, a copper chuck cooled by liquid nitrogen was chosen as the final substrate design. A copper chuck was machined and fitted with a slot so that a copper tube that had liquid nitrogen flowing through it would fit. The copper tube was glued to the chuck using silver epoxy, preserving good thermal transfer. A flexible kapton heater was sandwiched between the sample and the chuck. This heater would turn on after the resist was patterned and organic film deposited. A change of a few degrees was all that was needed to sublime the dry ice resist.

6.2.3 Stamping Apparatus

The stamp was made using SU-8 2150 photo-resist. It proved to be the most reliable stamp to sublime the dry ice. Other more conformal stamps need to be explored in order to overcome the yield problems. The actual stamping was performed using two motorized linear stages (Standa Ltd.) that allowed micron accuracy in a vacuum environment. A Dino-lite microscope was also attached to the 2 axis stamp mechanism to be able to look at the stamped region. The stamping mechanism was attached directly to the substrate holder to maximize accuracy. The Figure 6-8 shows this apparatus in the chamber.

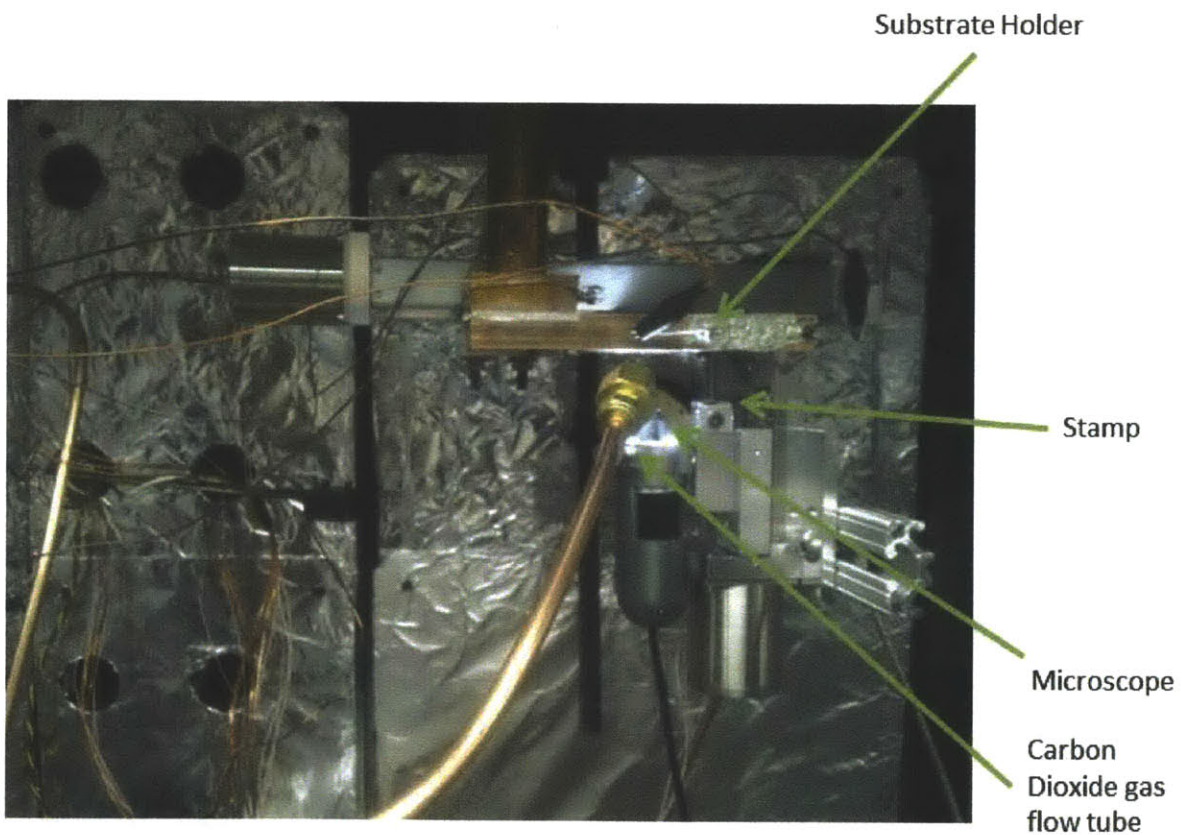
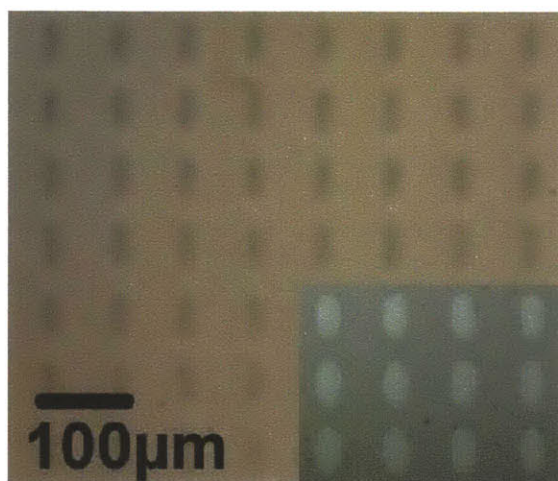


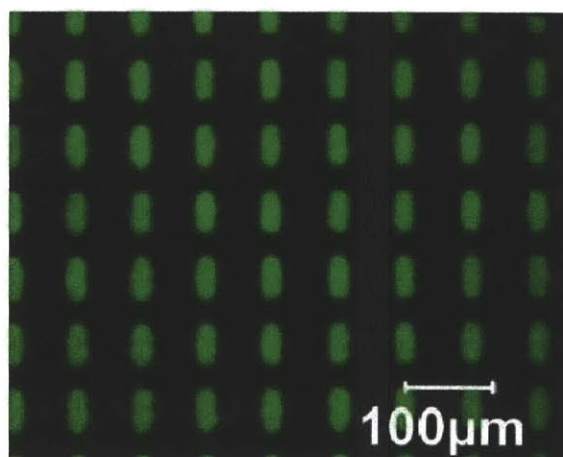
Figure 6-8: 2-axis Stamping Mechanism in Vacuum Chamber.

6.3 Results

The chamber was constructed and successfully mated with the glove box. A single color pattern was able to be demonstrated. Figure 6-9 shows the organic thin films patterned on the substrate.



Optical micrograph of a 78µm-pitch-patterned mask of carbon dioxide. The inset shows the AlQ₃ thin film after deposition and lift-off



Photoluminescence from a 78µm-pitch array of AlQ₃ pixels patterned using a sublimable mask of carbon dioxide.

Figure 6-9: Patterned Dry Ice and Patterned Pixels [20]

Chapter 7

Conclusion

The chamber was constructed and the stamping mechanism was able to accurately stamp the dry ice and produce green pixels. The yield of the process was still very low but given that this is the first prototype of the process it is understandable. This prototype effectively shows a proof-of-concept for a new type of manufacturing technique that might allow OLED displays to be made at a much lower cost. The next steps will be to attempt a two color patterning scheme. The ability to do two multiple color patterning is dependent on repeatability. Further design changes might have to be implemented in order to achieve micron repeatability. Eventually, a fully working OLED device should be demonstrated for this prototype to show the feasibility of this new manufacturing process. Looking at different stamp materials and designing a mini roll-to-roll system might further convince industry of the scalable advantage of this process. The ultimate limitations to this process are the ability to cool down a large substrate and the ability to match the high yield rates of a shadow mask process.

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