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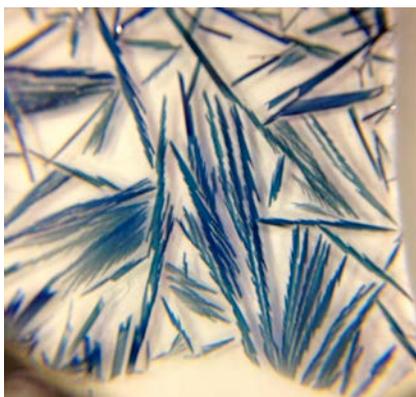
Organic Thin-Film Transistors and TIPS-Pentacene

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ABSTRACT



TIPS-Pentacene, an organic semiconductor characterized by its good electronic properties, solubility, and stability, is used primarily in organic thin-film transistors (OTFT). This research seeks to create an OTFT by crafting a stencil, depositing the source and drain onto a substrate's surface, and processing TIPS-Pentacene onto the channel between them. In addition, if time permits, the electronic properties of several OTFTs will be compared to determine how to optimize their production.

Introduction

One of the most important developments of the past century, the transistor has revolutionized and become an integral part in the development of various electronics because of its ability to amplify and switch electronic signals on and off. To this day, the most important part of a transistor is the semi-conductive material, typically amorphous or crystalline silicon, which regulates the flow of electrons and, therefore, charge.

Recent research, however, expands the repertoire of semiconducting materials to include certain organic molecules¹. Such organic semiconductors are superior to their inorganic counterparts in that they are cheaper to manufacture, cheaper to process on a substrate, lighter weight, and significantly more flexible.

Despite these appealing characteristics of organics, transistors are defined by two integral characteristics: the carrier mobility (the ease by which a charge moves from the source to the drain in response to an electric field) and the on/off ratio (the current across the source and drain

when a voltage is applied divided by the current when no voltage is applied). For instance, carrier mobilities of $0.1 \text{ cm}^2/\text{Vs}$ and on/off ratios of 10^6 are required to drive the circuits in liquid-crystal displays¹.

In an ideal case of the former where the distance between the source and drain is comparable to the size of the molecule, the definition of carrier mobility simplifies to resonance across a conjugated molecule, which allows for charge to move from one terminal to the next. Such an ideality is possible in the case of polymers, but, for small organic semiconductors, a charge must "hop" from one molecule to the next.

Unfortunately, optimal charge transfer requires HOMO overlap of molecular orbitals², which is complicated by

1. Katz, H. E; Bao, Z. The Physical Chemistry of Organic Field-Effect Transistors. *J. Phys. Chem. B.* **1999**, *104*, (4), 671—678.
2. Oliver, Y. Charge Transport in Organic Conjugated Materials: From the Molecular Picture to the Macroscopic Properties. Ph.D. Thesis, Academie Universitaire Wallonie Bruxelles, France. 2008.

electron-electron repulsion between such orbitals. Take, for instance, pentacene, a small organic molecule shown in Figure 1. Though the molecule was one of the first examined organic-semiconducting materials¹, study of the crystal structure and molecular orbitals of the molecule shows very poor overlap between HOMO orbitals, as it forms a herringbone crystal structure in which each acene backbone is positioned nearly perpendicular to its neighbor as shown in Figure 2. In other words, the potential carrier mobility of pentacene is largely wasted because of the poor overlap between HOMO orbitals.

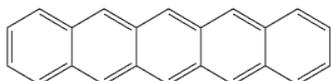


Figure 1. The above molecule is pentacene, one of the first organic semiconductors.

But this is not the only problem with pentacene: the molecule is insoluble in many common organic solvents, thereby complicating its deposition onto a substrate and increasing the cost of processing; when in solution, pentacene is subject to photo-dimerization³, which decreases the carrier mobility as conjugation is lost to the newly formed bridge; and, even in the solid phase, pentacene can react with oxygen⁴ to, once more, lose its conjugation to the newly formed bond.

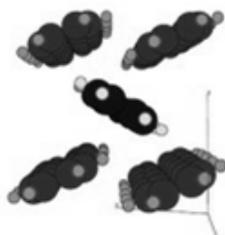


Figure 2. The herringbone crystal structure of pentacene⁵.

Though some might abandon pentacene for these complications and seek a new, more ideal semiconducting material, the Anthony group realized these three problems are interconnected and can be largely remedied by substitution on the central ring⁶. For instance, if triisopropylsilylethynyl acetylene is added to pentacene, the resulting molecule is known as TIPS-Pentacene (Figure 3). By substituting onto pentacene, the isopropyl groups greatly increase the solubility of the molecule in organic solutions, the rate of photo-oxidation is decreased because the reaction must be concerted as opposed to radical or zwitterionic⁵, the large functional group decreases the favorability of most dimerizations³, and, most importantly, the carrier mobility greatly increases⁷.

This final change is worth exploring in more detail. Recall the herringbone crystal structure of pentacene. Because the TIPS groups are so large, the crystal structure of the molecule becomes largely characterized by its functional groups. That is, by adding these large TIPS groups onto pentacene, the crystal structure flattens out because the functional groups mandate the crystal structure and the acene backbones begin to stack on top of one another. This, however, does not necessarily mean HOMO overlap is maximized, as the orbitals, once again, repel. However, by changing the groups attached to the silicon, one can tweak the crystal structure of the molecule and, therefore, change the overlap of the acene backbone until optimal overlap is obtained.

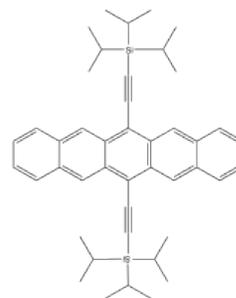


Figure 3. Molecular structure of TIPS-Pentacene or 6,13-Bis(triisopropylsilylethynyl)pentacene.

It should be mentioned, however, the overlap of HOMO orbitals for TIPS-Pentacene is not optimized but rather quite good. For instance, certain molecules synthesized by the Anthony group such as Allyl-DIPS or IP-DIPS⁷ have significantly better carrier mobility. Regardless, TIPS-Pentacene marked the turning point in the field of organic thin-film transistors as the molecule is easily synthesized in good yield, stable in normal conditions, and exhibits carrier mobility comparable to and better than amorphous silicon^{1,7}.

- Zade, S. S.; Zamoschik, N.; Reddy, A. R.; Fridman-Marueli, G.; Sheberla, D.; Bendikov, M. Products and Mechanism of Acene Dimerization. A Computational Study. *J. Am. Chem. Soc.* **2011**, *133*, (128), 10803–10816.
- Fudickar, W.; Linker, T. Why Triple Bonds Protect Acenes from Oxidation and Decomposition. *J. Am. Chem. Soc.* **2012**, *134*, (36), 15071–15082.
- Park, S. K.; Mourey, D. A.; Han, J. I.; Anthony, J. E.; Jackson, T. N. Environmental and operational stability of solution-processed 6,13-bis(triisopropyl-silylethynyl) pentacene thin film transistors. *Org. Electron.* **2009**, *10*, (3), 486–490.
- Anthony, J. E. The Larger Acenes: Versatile Organic Semiconductors. *Angew. Chem. Int. Ed.* **2008**, *47*, (3), 452–483.
- Anthony, J.E.; Caldwell, G.A.; Clough, R.S.; Novack, J.C.; Payne, M.M.; Redinger, D.H.; Vogel, D.E. Silylethynyl Pentacene Compounds and Compositions and Methods of Making and Using the Same. US20110073813. April 13, 2011.

The main goal of this research with Dr. Anthony is to design and create an organic transistor. This includes processing the organic material onto a flexible, plastic substrate, optimizing and designing a rigid, reusable, stencil mask out of metal, and evaporating metals onto the substrate layer to be used as the source and drain.

Experimental Details

Before depositing TIPS-Pentacene on a plastic substrate, it is first tested on glass slides that have been bathed in acetone and cleaned in a sonicator for fifteen minutes. The slides are then taken, a novoc border applied, and then, depending on the experiment, the plate is given an incline, the concentration of TIPS-Pentacene is varied, and the composition of the solvent is changed. In each case, however, the plate is covered with solution (usually about 10 drops delivered by a syringe).

To manufacture a stencil, or shadow mask, the source and drain dimensions are measured on a thin sheet of metal and then rectangular holes cut out with a knife. Once these holes are cut horizontally, a thin strip of copper wire is placed over the center of the rectangles going vertically, cutting them in to two equal-sized pieces, and secured with small pieces of tape carefully positioned to not cover up one of the cut-out holes.

Finally, with it produced, the stencil is wrapped tightly around a plastic substrate and the two held together using binder clamps and paper clips placed onto the corners of the stencil to ensure they are not blocking the holes in the stencil. This is then placed inside the chamber of an evaporator and hung above a tungsten filament that has been wrapped loosely with aluminum foil. The chamber is evacuated for about thirty minutes before the current is turned on, the tungsten filament begins to burn, and the aluminum deposits onto the substrate.

Results and Discussion

One of the easiest ways to deposit an organic material onto a surface is by dissolving the material in a solvent, depositing the solution onto the substrate's surface, and then allowing the solvent to evaporate. In the ideal case, the material is evenly distributed across the substrate with the intermolecular distance small enough to allow charges to hop from one molecule to the next.

Initial tests compared the effects of various solvents and solvent compositions on TIPS-Pentacene. The results of these tests are shown in Figure 4.

These tests show a variety of factors must be considered when finding an appropriate solvent for depositing the solution on a substrate. For instance, high boiling solvents like those used in Figures 4.3, 4.4, 4.5, and 4.6 promote good crystal growth and, therefore, a non-uniform distribution of organic material. Moreover, the increased time in solution promotes the growth of the photo-oxidized and photo-dimerized products. Notice, in Figure 4.1 and 4.2, that lower boiling solvents seem to

promote a more uniform distribution. This, of course, makes sense: in a solution, the molecules are evenly

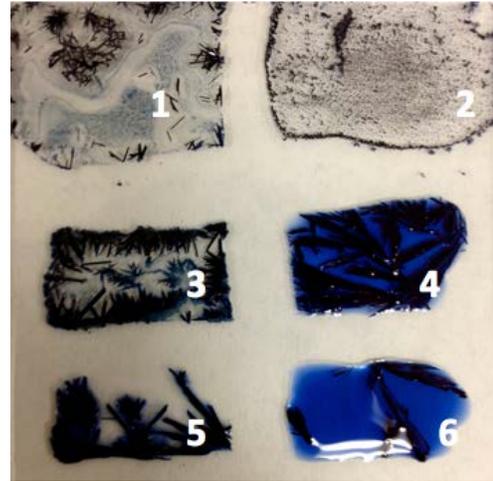


Figure 4. All trials shown above contain twenty milligrams of TIPS-Pentacene with the exception of plate six which has 40 milligrams. The solvent composition is as follows: (1) 80% heptane / 20% acetone, (2) pure heptane, (3) 80% chlorobenzene / 20% 1,2-dichlorobenzene, (4) 20% 1,2-dichlorobenzene / 80% hexadecane, (5) toluene, and (6) 20% hexadecane / 80% chlorobenzene.

distributed; so, if the solvent instantly evaporates away, the solvent molecules spread across a surface must, therefore, remain evenly distributed unless perturbed by some force. Thus, the closer a solvent is to this ideality, the better the expected uniformity.

Additional experiments, therefore, use lower boiling solvents like isopropyl alcohol (IPA). However, because IPA is a relatively poor solvent for TIPS-Pentacene, a small concentration of toluene is added. The results are shown in Figure 5 below.

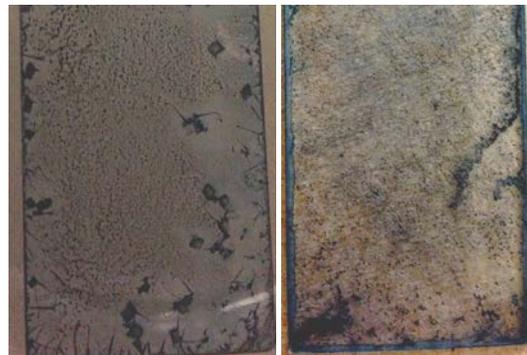


Figure 5. The effects of isopropyl alcohol and toluene for depositing TIPS-Pentacene on a glass substrate. The image on the left shows the effects of a 45% toluene / 55% IPA solution and that on the right for a 20% toluene / 80% IPA solution.

Notice the molecules of TIPS-Pentacene are more evenly distributed in Figure 5 than in Figure 4. This shows that switching to a more volatile solution does help distribute the TIPS-Pentacene molecules more uniformly. But notice each plate contains a border on which a greater concentration of TIPS-Pentacene molecules are deposited. This phenomenon is caused by a Marangoi flow⁸, that is a surface tension gradient forms between these two solvents. Though this might not seem like a major problem, having a larger concentration of TIPS-Pentacene on the perimeter of the plastic substrate is not only wasteful of semiconducting material that could be better placed between the source and drain but also allows the charge from the source to take multiple pathways that may not necessarily reach the drain in an optimized manner. For the purposes of this research, saturating the solution with TIPS-Pentacene largely ignores this problem. That is, although some will deposit along the border, a larger percentage will, nevertheless, be between the source and drain.

In addition to these results, tests run with an incline (one sheet of paper placed underneath one side of the plate) promote the formation of crystals and draw the solution toward the lower side of the plate. That is, in response to an incline, the solution moves toward the lower-energy side of the plate, causing more TIPS-Pentacene molecules to be closer together. And, when unperturbed, the molecules will come together making crystals.

After finding a suitable solvent mixture and optimizing the parameters necessary to promote uniform deposition of the solute, the next task is to design and produce a thin, rigid stencil to be used as a pattern onto which the source and drain are deposited. Typically, the distance between the source and drain, known as the channel, should be minimized but never zero. That is, a semiconductor must be able to be turned on and off in response to some bias from the gate. If the source and drain touch, however, the device is always on. In contrast, if the distance is too large, the device is essentially always off.

Using the methods described in the “Experimental Details” section, small rectangles are carefully measured onto and cut out of a metal sheet using a knife, and a 30 gauge copper wire (0.255 mm in diameter) placed directly in the center of the rectangle to serve as the channel length. A diagram of this is shown in Figure 6.

Once it is created, the stencil is used as a pattern on which the source and drain are deposited onto the substrate surface. That is, the stencil is placed in front of the substrate so that when the metal condenses onto the surface, it deposits in the shape mandated by the stencil and, therefore, creates a source and a drain separated by 0.255 millimeters.

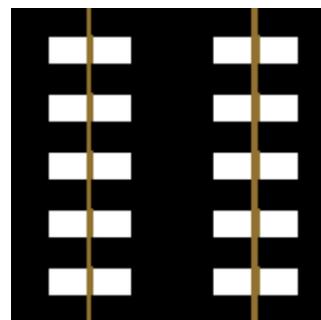


Figure 6. A diagram showing the shadow mask used in this experiment. Note the dark areas reflect the thin, metal sheet used, the white areas denote holes, and the brown areas represent the copper wire.

The metal is processed onto the substrate through vacuum deposition, a method in which a metal is sublimed under low pressures and high temperatures. When subliming metal, it is very important to remove oxygen from the chamber of the evaporator to reduce side reactions and increase the chance of the gas molecules being deposited on the substrate layer rather than the sides of the chamber.

Aluminum foil, rather than gold, is initially chosen for this role because of its low cost and boiling point. Unfortunately, depositing a uniform film of aluminum onto the substrate surface proved difficult. No matter what variables were changed—the location and distance of the substrate relative to the aluminum, the strength of the current, or the amount of aluminum wrapped around the tungsten wire—a uniform morphology cannot be obtained.

For instance, in the first example, because of the rigid nature of the evaporator used, the distance between the substrate and aluminum is essentially fixed. The location of the two can be changed, but, as expected, the best results are obtained when the substrate is directly overtop of the aluminum foil.

When changing the strength of the current flowing through the tungsten filament, if the current is turned on too high, the direction of deposition for the aluminum cannot be controlled and it deposits on the side walls of the evaporator. Therefore, applying the current and changing its magnitude slowly gives the best results.

Finally, increasing the amount of aluminum foil used causes the aluminum to melt around the tungsten wire and, therefore, not to deposit on the substrate. Moreover, the best results are obtained when the aluminum is rapped into a coil and lightly wound about the filament.

In addition to these problems, the gaseous aluminum molecules would sometimes go around the copper wire of

8. Li, Y.F.; Sheng, Y.J.; Tsao, H.K. Evaporation Stains: Suppressing the Coffee-Ring Effect by Contact Angle Hysteresis. *Langmuir*. **2013**, *29* (25), 7802–7811.

the stencil, thereby not creating a channel between the source and drain. To understand why this occurs, one must realize the copper wire is out of plane with the stencil by no more than 0.255 mm, a huge distance on the molecular level. The gaseous aluminum molecules, therefore, have an additional 0.255 mm to go after passing the tip of the copper wire before depositing on the substrate surface. In this time, the molecules can spread out and bridge the gap between the source and the drain. To fix this problem, one need only choose a smaller copper wire or, better yet, redesign the stencil so that everything is in plane.

Conclusion

Because it takes thirty minutes to evacuate the chamber before the aluminum is allowed to deposit and another ten to purge the chamber, fixing the issues with vacuum deposition proved to be a lengthy and strenuous process. These problems, in fact, were never fully resolved before the research project expired. Therefore, because not even a single transistor was created, the electronic properties are not measured.

Regardless of these shortcomings that show the difficulties with creating organic, semiconducting materials, the knowledge gained from this research shows how practical and how great the potential these devices have. For instance, depositing the organic material across the channel simply requires one to dissolve the material in solution, depositing that solution on the substrate surface, and then allowing the solvent to evaporate. From the results of this experiment, the 20% toluene / 80% IPA solution gave the best results in terms of uniform crystal morphology. It should be mentioned, however, that because the devices were not tested, one cannot say with certainty that this solution composition is the most ideal for dissolving TIPS-Pentacene. Therefore, additional research comparing the carrier mobilities and on/off ratios of various transistors created using different solvent compositions is required.

Moreover, the results of these experiments show using copper wire for the channel length is non-ideal because of the difficulty controlling the location in which gaseous aluminum molecules deposit on the substrate surface. This can be fixed by either redesigning the stencil or, better yet, purchasing a professionally made one in which the source and drain are distinct holes in the stencil.

This research may have not furthered the scientific community's understanding of organic semiconductors or how to better process them, but it has shown the difficulty early scientists had and shows how far their understanding has come since then. In fact, organic semiconductors are starting to take the place of their

inorganic counterparts in industry⁹ with TIPS-Pentacene still chosen as a standard. In time, perhaps another semiconducting material with good stability, good solubility, and better electronic properties will be developed further redefining the limits of organic semiconducting materials. But, until then, there is still much to learn to make organic transistors as common as inorganic ones.

9. Anthony, J. E. The Larger Acenes: Versatile Organic Semiconductors. *Angew. Chem. Int. Ed.* **2008**, *47*, (3), 452–483.