

molecule in the simplest case. For polymer semiconductors, typical molecular weights range from 1,000 to 100,000 g/mol.³ Due to the statistical nature of the exact points of initiation and termination of chain extension, the details of which vary by synthetic strategy, the length of each individual polymer in a batch is not identical,⁴ which in turn results in a distribution of polymer chain lengths – and hence, molecular weights, termed polydispersity.⁴ Copolymers, which are composed of two or more chemically dissimilar monomers, can also have compositional heterogeneity depending on the relative reactivity of the monomers. Changes in the instantaneous copolymer composition during chain extension will depend strongly on reaction kinetics under the polymerization conditions, and can result in a varying local composition along the polymer backbone.⁵ Furthermore, for polymers made from asymmetric monomers, like for poly(3-hexylthiophene), P3HT, the direction with which the monomer unit is added during chain extension is an additional source of variability within and among polymer chains that can ultimately affect the local order along each chain. For the specific case of P3HT, where the alkyl chain introduces asymmetry to the thiophene unit, if the monomer units are all added so that the alkyl chains all face the same direction, the polymer is regioregular; if the monomer units are added without an overall directionality to the alkyl chains, the polymer is regio-irregular.⁶ Molecular semiconductors, on the other hand, are precisely synthesized and identical species can be selectively purified. Thus, these species have well-defined molecular weights that are typically on the order of 100 to 1,000 g/mol. However, akin to the issue of regioregularity with polymers, some molecular semiconductors are susceptible to isomerism, which is the tendency for two molecules to have the same chemical composition but different organization of bonds, depending on the synthesis scheme employed.^{7,8} These differences in the molecular weights, polydispersities, and chemical disorder of molecular and polymer semiconductors influence how they each assemble in the solid state.

Seeded Content – **How Semiconductors Work- HowStuffWorks**
<http://electronics.howstuffworks.com/diode.htm/printable>

Semiconductors have had a monumental impact on our society. You find semiconductors at the heart of [microprocessor chips](#) as well as transistors. Anything that's computerized or uses [radio waves](#) depends on semiconductors.

Today, most semiconductor chips and transistors are created with silicon. You may have heard expressions like "Silicon Valley" and the "silicon economy," and that's why -- silicon is the heart of any electronic device.

A diode is the simplest possible semiconductor device, and is therefore an excellent beginning point if you want to understand how semiconductors work. In this article, you'll learn what a semiconductor is, how doping works and how a diode can be created using semiconductors. But first, let's take a close look at silicon.

Silicon is a very common element -- for example, it is the main element in sand and quartz. If you look "silicon" up in the [periodic table](#), you will find that it sits next to aluminum, below carbon and above germanium.

Silicon sits next to aluminum and below carbon in the periodic table.

Carbon, silicon and germanium (germanium, like silicon, is also a semiconductor) have a unique property in their electron structure -- each has four electrons in its outer orbital. This allows them to form nice crystals. The four electrons form perfect covalent bonds with four neighboring [atoms](#), creating a lattice. In carbon, we know the crystalline form as [diamond](#). In silicon, the crystalline form is a silvery, metallic-looking substance.

In a silicon lattice, all silicon atoms bond perfectly to four neighbors, leaving no free electrons to conduct electric current. This makes a silicon crystal an insulator rather than a conductor.

Metals tend to be good conductors of electricity because they usually have "free electrons" that can move easily between atoms, and electricity involves the flow of electrons. While silicon crystals look metallic, they are not, in fact, metals. All of the outer electrons in a silicon crystal are involved in perfect covalent bonds, so they can't move around. A pure silicon crystal is nearly an insulator -- very little electricity will flow through it.

But you can change all this through a process called doping. **Doping Silicon**

You can change the behavior of silicon and turn it into a conductor by doping it. In doping, you mix a small amount of an impurity into the silicon crystal.

There are two types of impurities:

- N-type - In N-type doping, [phosphorus](#) or [arsenic](#) is added to the silicon in small quantities. Phosphorus and arsenic each have five outer electrons, so they're out of place when they get into the silicon lattice. The fifth electron has nothing to bond to, so it's free to move around. It takes only a very small quantity of the impurity to create enough free electrons to allow an electric current to flow through the silicon. N-type silicon is a good conductor. Electrons have a negative charge, hence the name N-type.
- P-type - In P-type doping, [boron](#) or [gallium](#) is the dopant. Boron and gallium each have only three outer electrons. When mixed into the silicon lattice, they form "holes" in the lattice where a silicon electron has nothing to bond to. The absence of an electron creates the effect of a positive charge, hence the name P-type. Holes can conduct current. A hole happily accepts an electron from a neighbor, moving the hole over a space. P-type silicon is a good conductor.

A minute amount of either N-type or P-type doping turns a silicon crystal from a good insulator into a viable (but not great) conductor -- hence the name "semiconductor."

N-type and P-type silicon are not that amazing by themselves; but when you put them together, you get some very interesting behavior at the junction. That's what happens in a diode.

A diode is the simplest possible semiconductor device. A diode allows current to flow in one direction but not the other. You may have seen turnstiles at a stadium or a subway station that let people go through in only one direction. A diode is a one-way turnstile for electrons.

When you put N-type and P-type silicon together as shown in this diagram, you get a very interesting phenomenon that gives a diode its unique properties.

Even though N-type silicon by itself is a conductor, and P-type silicon by itself is also a conductor, the combination shown in the diagram does not conduct any electricity. The negative electrons in the N-type silicon get attracted to the positive terminal of the [battery](#). The positive holes in the P-type silicon get attracted to the negative terminal of the battery. No current flows across the junction because the holes and the electrons are each moving in the wrong direction.

If you flip the battery around, the diode conducts electricity just fine. The free electrons in the N-type silicon are repelled by the negative terminal of the battery. The holes in the P-type silicon are repelled by the positive terminal. At the junction between the N-type and P-type silicon, holes and free electrons meet. The electrons fill the holes. Those holes and free electrons cease to exist, and new holes and electrons spring up to take their place. The effect is that current flows through the junction.

In the next section we'll look at the uses for diodes and transistors. **Diodes and Transistors**

A device that blocks current in one direction while letting current flow in another direction is called a diode. Diodes can be used in a number of ways. For example, a device that uses batteries often contains a diode that protects the device if you insert the batteries backward. The diode simply blocks any current from leaving the battery if it is reversed -- this protects the sensitive electronics in the device.

A semiconductor diode's behavior is not perfect, as shown in this graph:

When reverse-biased, an ideal diode would block all current. A real diode lets perhaps 10 [microamps](#) through -- not a lot, but still not perfect. And if you apply enough reverse [voltage](#) (V), the junction breaks down and lets current through. Usually, the breakdown voltage is a lot more voltage than the circuit will ever see, so it is irrelevant.

When forward-biased, there is a small amount of voltage necessary to get the diode going. In silicon, this voltage is about 0.7 volts. This voltage is needed to start the hole-electron combination process at the junction.

Another monumental technology that's related to the diode is the transistor. Transistors and diodes have a lot in common. Transistors

A transistor is created by using three layers rather than the two layers used in a diode. You can create either an NPN or a PNP sandwich. A transistor can act as a switch or an amplifier.

A transistor looks like two diodes back-to-back. You'd imagine that no current could flow through a transistor because back-to-back diodes would block current both ways. And this is true. However, when you apply a small current to the center layer of the sandwich, a much larger current can flow through the sandwich as a whole. This gives a transistor its switching behavior. A small current can turn a larger current on and off.

A silicon chip is a piece of silicon that can hold thousands of transistors. With transistors acting as switches, you can create [Boolean gates](#), and with Boolean gates you can create [microprocessor chips](#).

The natural progression from silicon to doped silicon to transistors to chips is what has made microprocessors and other electronic devices so inexpensive and ubiquitous in today's society. The fundamental principles are surprisingly simple. The miracle is the constant refinement of those principles to the point where, today, tens of millions of transistors can be inexpensively formed onto a single chip.

substrate, and molecule-solvent interactions to form structures that we desire, rather than accepting the often kinetically-trapped structures that are formed given the deposition conditions.

1.5 Non-planar Organic Semiconductors

In this thesis, we have elucidated the chemistry-processing-structure-function relationships of contorted hexabenzocoronene, cHBC, a non-planar molecular semiconductor whose chemical structure is shown in Figure 1.3. Two proton environments are present on the molecule, labeled as the α and β positions in Figure 1.3. Due to steric interactions between hydrogens at the β position on neighboring aromatic rings, circled in Figure 1.3, the outer aromatic rings of cHBC are bent out-of-plane from the core, giving rise to the molecule's non-planar geometry. This non-planarity frustrates molecular assembly, leading to films with no long-range order upon thermal evaporation onto substrates. The lack of long-range order in thermally-evaporated cHBC films makes this system an excellent candidate for post-deposition processing. Planar conjugated molecules are more commonly investigated as organic semiconductors because their flat structure allows for close intermolecular packing and hence considerable π -overlap. However, fullerene derivatives are an excellent counterexample as they have a spherical shape and yet are consistently one of the most widely used and best performing materials for organic solar cells. Indeed, interest in non-planar molecules has grown significantly in the organic electronics community within the past several years as the potential benefits of non-planarity become apparent.^{38,39} Specifically, non-planar molecules provide a wider array of potential intermolecular interactions with other molecules than planar counterparts, which may yield improved intermolecular charge transport.⁴⁰

well.^{46,47} Taking advantage of such geometrical matching, the Nuckolls Group has demonstrated power conversion efficiencies as high as 2.41% in solar cells with solubilized cHBC derivatives as the electron donor and fullerene derivatives as the electron acceptor.^{46,47}

1.6 Overview of Thesis

Different from prior work, we have explored cHBC and derivatives *not* functionalized with alkyl chains. While the reduced solubility of such cHBC derivatives has been previously viewed as an unattractive quality, here we demonstrate that by thermally evaporating cHBC and starting with amorphous films, we have yet greater tunability over the film structure *via* post-deposition processing. Specifically, we have studied how both post-deposition processing and chemical modification affect the structure and optoelectronic properties of cHBC thin films and ultimately, their performance in TFTs and OSCs. The thesis is divided into three sections according to these different approaches to tune thin-film properties. In the first section, we focus only on cHBC and explore post-deposition processing techniques to modify its film structure. In the second section, we functionalize cHBC *via* halogenation to tune its molecular conformation and optoelectronic properties. In the third section, we combine these two approaches to explore how chemical modification of cHBC affects the structure of films that are thermally and solvent-vapor annealed using a variety of solvents.

The first section, which focuses on post-deposition processing techniques in the parent cHBC compound only, consists of Chapters 4 and 5. In Chapter 4, we demonstrate that we can tune the out-of-plane orientation of cHBC molecules as they crystallize depending on the post-deposition processing technique applied: hexanes solvent-vapor annealing, thermal annealing or contact with a poly(dimethylsiloxane) stamp. We study the resulting film structure with each processing technique across a broad range of length

scales *via* optical and atomic force microscopies and synchrotron-based two-dimensional grazing-incidence X-ray diffraction (2D-GIXD). Given the multitude of techniques used to characterize the thin film structure, we are able to correlate the macroscopic morphologies observed with optical microscopy with the microstructure we deduce from 2D-GIXD. The elucidation of such relationships is valuable for rapid assessment of film structure as it provides an approximation of the molecular orientation without necessarily requiring synchrotron-based 2D-GIXD. Furthermore, we construct TFTs from these various films and correlate the degree of out-of-plane orientation with the mobilities of devices, which provide a measure for the efficiency of charge transport.

In Chapter 5, we explore post-deposition processing strategies by solvent-vapor annealing with tetrahydrofuran (THF) vapor and find that it induces crystallization of cHBC with a previously unreported crystal structure. Applying sequential thermal and THF-vapor annealing (and *vice versa*), we find that we can transform between crystal structures and create a processing map to guide access to different crystalline phases. Using this processing map, we can access cHBC films having different crystal structures yet the same preferred out-of-plane molecular orientation, or alternatively, we can access films having the same crystal structure yet different preferred out-of-plane molecular orientations. Accessing these combinations of crystal structures and out-of-plane orientations allows us to decouple the relative contribution of each on charge transport in TFTs.

Chemistry also provides a knob to tune the properties, and in the second section of this thesis (Chapters 6 and 7), we explore chemical modifications of cHBC as a means of tuning its optoelectronic and physical properties. While organic semiconductors are neither intrinsically hole- nor electron-transporting, the alignment of an organic semiconductor's energy levels with the work function of electrodes typically allows for one type of charge to be more easily injected or extracted than the other. The lowest unoccupied molecular orbital

(LUMO) energy level of most organic semiconductors tends to be relatively high, yielding more efficient hole (than electron) injection and extraction; we refer to such organic semiconductors as “electron donors.” Due to its energy level alignment with electrode materials, unsubstituted cHBC has only been used as an electron donor.

However, for OLEDs, OSCs, and logic circuits, organic semiconductors capable of transporting electrons *via* efficient electron injection and extraction are also needed. Such organic semiconductors are termed “electron acceptors” and require lower-lying energy levels for efficient electron injection into and extraction out of the LUMO to take place. Here, chemical modification provides an additional tuning knob to alter molecular properties. Modifying organic semiconductors with electron-withdrawing groups is a known strategy for lowering molecular energy levels, and in Chapter 6, we synthesize and characterize the optoelectronic properties of three series of halogenated cHBCs having either fluorines, chlorines, or a mixture of fluorines and chlorines decorating the periphery of the molecule. This systematic study allows us to derive quantitative relationships for the lowering of energy levels and decrease in the optical bandgap for each fluorine and chlorine substitution. We evaluate these derivatives as potential electron acceptors in OSCs and attain power conversion efficiencies up to 1.2%, marking the first demonstration of a cHBC derivative as an electron acceptor.

In exploring the halogenated cHBC derivatives discussed in Chapter 6, we found that some of the highly halogenated derivatives can adopt a second metastable molecular conformation due to intramolecular steric hindrance between substituents in the β positions of neighboring aromatic rings, circled in Figure 1.3.²⁷ In Chapter 7, we explore a series of cHBC derivatives with peripheral substitutions of increasing size in order to increase the degree of intramolecular steric hindrance. Using this series, we define the window in which the metastable molecular conformation is accessible using our synthesis pathway, and we

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