The Impact of Crystal Morphology on the Opto-Electronic Properties of Amorphous and Organic Crystalline Materials

Written by

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Abstract

Organic aggregates and transparent amorphous metals are transforming opto-electronic devices such as highly efficiency solar cells and flexible displays. We present a fundamental optical study of how local morphology critically impacts the device performance of both stacked, conjugated organics and In-Ga-Zn-O (IGZO) transparent metallic materials. Derivatives of anthradithiophene (ADT): ADT-TES-F, ADT-TDMS-F, and ADT-TSBS-F were investigated through polarization-dependent optical absorption spectroscopy. While each ADT derivative has a different intermolecular stacking morphology, the intramolecular physics is dominated by their identical conjugated ring structure. We show that the morphology-dependent dipole-moment orientation drastically changes the electronic excited states, through mapping the absorption spectra anisotropy with respect to polarization.

Photocells ideally need transparent metals to efficiently harvest the charges created. We present a method of extracting the band gap and Fermi energies for amorphous metals and semiconductors. To determine the Fermi energy and defect bands in such materials we developed a novel simulation code to fit data obtained from a spectroscopic technique called Photo Excited Charge Collection Spectroscopy (PECCS). We applied this technique to amorphous In-Ga-Zn-O (IGZO) transistors, however due to IP protection, we present the procedure through analysis on a simulated device. When applied to a real IGZO device, the code gave realistic values (on the order of eV) for the Fermi energy and optical band gap (Within 0.2 eV).

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1 Introduction

Atomic stacking and disorder play a major role in the electronic behavior of both crystalline and amorphous systems [1]. Structure governs phenomena that underlie many technologies today. For example, the optical effect of bi-refringence in wave plates is determined by the symmetries of the crystal unit cell. The next generation of the transistors and solar cells will require advanced structural and molecular engineering, and silicon based devices have hit engineering barriers. Organic and amorphous semiconductors can push past those barriers. Fluorinated anthradithiophene (ADT) derivatives are a class of organic semiconductors with tunable crystal structure [2]. Different structures are created by attaching different side groups to the core ADT molecule. In particular, these side groups do not affect the isolated molecules opto-electronic properties, thus total structural control is possible. The stacking structure guides the excited state electron distributions in these materials, which governs charge transfer. Thus such structural control leads to control over the electron dynamics in the system. However, in many systems, the effect of intermolecular interactions on the electronic states is not totally understood. A question that remains is how structural differences affect charge transfer and intermolecular interactions, which are very important considerations when building any photovoltaic device. We present a study on how morphological differences impact the optical and electronic properties of two classes of materials: Anthradithiophene derivatives and In-Ga-Zn-O (IGZO). Specifically, we studied the polarization dependent optical properties of the derivatives ADT-TES-F, ADT-TSBS-F, and ADT-TDMS-F. Their different side functional groups cause different stacking structures when crystallized, whose resulting optical behavior can be can be understood under a quantum mechanical coupling model for molecular aggregates, via approximating the system as a mix of H or J aggregate stacking. These different stacking geometries are reflected in their polarization dependent absorption spectra.

The crystallinity of IGZO can be controlled by anneal temperatures and other post processing techniques [3]. Thus IGZO is another exciting new material with structural control for the next generation of devices. Future work with Apple inc may investigate how crystallinity affects the density of states (DOS) of electron traps in IGZO. In this work, we show how both the density of states and the intrinsic Fermi level of many materials can be estimated via a novel simulation code. The Fermi level is a key parameter for understanding charge flow in a device. This work's method is promising and presents a new way to study amorphous systems. All the work herein has been applied to IGZO transistors, but due to IP protection, we only present analysis on simulated devices which are qualitatively characteristic of amorphous based transistors.

2 Organic Photovoltaics

This work is a study of Anthradithiophene (ADT) and three different functional derivatives. The molecule is shown in Figure 1. ADT has a stacking structure determined by which functional groups are present off the core of the molecule. Different functional groups create different derivatives, such as ADT-TES-F and ADT-TSBS-F. Those derivatives all have the same core molecular structure, shown in figure 1. Thus in solution, when intermolecular interactions can be ignored, their optical properties are approximately the same [2]. But when these molecules crystallize, the side groups cause different intermolecular interactions and thus different structures. The difference in packing structure between derivatives causes different crystal electronic structure, and therefore optical properties. ADT-TES-F and ADT-TSBS-F exhibit 2D π -stacking and 1D sandwich-herringbone crystal stacking respectively [4]. The resulting structures can be decomposed into a mix of face to face(H

aggregate) or head to tail (J aggregate) oriented molecules, shown in figure 2. The structure of ADT-TDMS-F is such that it behaves J-like [5].



Figure 1: Molecular structure of ADT and the various derivatives, R is one of the side groups: TES, TSBS, or TDMS, shown on the right hand side. The dipole moment for the S1 set of transitions is along the short axis of the molecule, i.e. points from R to R. [4]

The isolated molecule's absorption spectra is in large part determined by its core molecular structure[6]. When the molecules are interacting in a crystal lattice however, their side groups determine the electronic structure of the crystal. Fig. 2 (d) and (e) show the calculated spectra of the same molecule placed in H and J aggregate crystal structure. Particularly, H or J refers to the orientation of the dipole moments for certain electronic transitions. In Fig. 1 the dipole moment for the S1 set of transitions (S1a and S1b) transitions is along the short axis of the molecule, from R to R. In Fig. 2, note that H aggregates have a S1a/S1b ratio less than one, and for J aggregates the ratio is greater than 1. In ADT-TES-F and the other derivatives, the crystal structure has a mix of H and J dipole orientations. Figure 2 (d) shows an idealization of HJ mixing. Therefore, we expect that the optical absorption can be decomposed into the independent parts deriving from H or J aggregation. Informally, we could say the following about the absorption spectra of a mixed system:

$$A(\omega) = aA_J(\omega) + bA_H(\omega) \tag{1}$$

Where a and b are undetermined coefficients, ω the transition frequency, A_J and A_H are the absorption contributions due to the J and H stacking respectively. In this work we present polarization dependent optical absorption spectra of ADT derivatives, to resolve the H and J parts of their optical behavior. In the future, we hope to use these spectra to estimate the H and J exciton bandwidth term W for all three structures. Excitons are electron-hole (electron and electron vacancy) pairs that are formed when an electron is excited in the system. Exciton separation, i.e. separating the bound positive and negative charges, is the key to current harvesting in solar cells [2]. W is a measure of the intermolecular coupling of excitons, and thus is crucially important for understanding charge transfer and separation in a system.

2.1 Background

This section is a brief overview of what polarization dependent absorption spectra tell us about a system described by H and J aggregates. The theory of H and J aggregates is built upon the assumption that all the molecular excited states are harmonic oscillators characterized identically by frequency ω_0 and displaced vertically from eachother by $E = \lambda^2 \omega_0$ (See figure 3 for a diagram). Both λ^2 , the Huang-Rhys factor, and ω_0 are obtained from a fit to the absorption spectra of the molecules while



Figure 2: The different packing structures of the anthradithiophene derivatives. The pure H (side to side) and pure J (head to tail) transition dipole moment arrangements are shown in sub figures (b) through (d) with associated packing structures directly above in (a). The ADT derivatives in this work have structures which are mixes of the pure H or J aggregates. (e) and (f) show the calculated absorption spectra of a pure H and J aggregate system shown in blue, with photoemission spectra shown in red. The grey trace is not relevant to this work. The inset shows the corresponding identical spectra for both molecules (H or J). Sub figures (a) through (d) are adapted from [2], and subfigures (e) and (f) are adapted from Spano [6].

they are dissolved in solution [7], which will be discussed further in the peak ratio analysis section. In H and J aggregate systems, we use standard pertubation theory to build the aggregate Hamiltonian $H_{agg} = H_0 + H_{ex}$ [7]. The zeroth order Hamiltonian H_0 consists of the energies along the diagonal (in a matrix representation) of the local non vibrational states of each molecule in the aggregate. The pertubation Hamiltonian H_{ex} can be written as [6]:

$$H_{ex} = \sum_{m,n} J_{mn} |m\rangle \langle n| \tag{2}$$

Where $|m\rangle$ represents the 0th order electronic excitation of the m^{th} molecule, and J_{mn} parameterizes the exciton coupling between the m^{th} and n^{th} molecules [6]. In the nearest neighbor approximation only states $|m\rangle$ and $|m \pm 1\rangle$ are considered, in which case $J_{mn} = J_{12} \equiv J_0$. As in Fig. 2, H and J aggregates have oppositely signed nearest neighbor excitonic coupling constants J_0 [2]. The width of the exciton band is related to J_0 through $W = |4J_0|$ [7], i.e. W is an equivalent way to characterize the interaction between neighboring molecules. The absorption spectrum can be written as [7]

$$A(\omega) = \frac{1}{N\mu^2} \sum_{i} |\langle G|\hat{\mu}|\psi^i\rangle|^2 L_i(\omega)$$
(3)

Where ω is the angular frequency of the incident light, μ is the magnitude of the net molecular transition dipole moment along the axis in consideration [7], N is the number of molecules in the system, $|G\rangle$ is the zeroth order ground state (sum of purely electronic and vacuum vibrational ground states[8]) and $|\psi^i\rangle$ is the i^{th} eigenstate of the Hamiltonian H_{agg} with energy characterized by ω_i [6]. $\hat{\mu} = \sum_{n=i} \mu_n^i (|g\rangle \langle n| + |n\rangle \langle g|)$. μ_n^i is the transition dipole moment of molecule n, and $|g\rangle$ is the purely electronic ground state. [8]. The transition dipole moments of a chain of molecules are arranged according to H or J as in Fig. 2 (b) through (d). The line width function $L_i(\omega)$ (e.g. Lorentzian or Guassian) characterizes the line shape and location of the i^{th} transition [8]. Diagonilizing H_{agg} gives the eigenstates $|\psi^i\rangle$ [6] and thereby the exciton coupling $W = |4J_0|$ is intrinsically involved in the absorption spectrum, and can be obtained from fitting equation 3 to the absorption spectra.

Furthermore, one should obtain two different values of W corresponding to the H and J absorption $A_J(\omega)$ and $A_H(\omega)$.



Figure 3: The nuclear potential wells that represent the ground (S_0) and excited states (S_1) of an organic photovoltaic like ADT. The *i* to *j* transition is characterized by ω_{i-j} , with interband energy levels determined by ω_{vib} . The Huang-Rhys factor's affect on the energy levels of the excited state S_1 is indicated. Figure from [9].

2.2 Theory

This section introduces the underlying theory of the experiments in this investigation. This work involves many different optical measurements, and therefore a broad set of analysis techniques. In ADT-TES-F, the crystal grains can be large (100 micron) but contain many domains of a single structural orientation, which are typically each less than 10 microns in length [10]. Moreover, these different domains are often at angles to each other, as shown in Fig. 4. Thus light polarized along a single axis relative to a crystal flake, is exciting many crystal domains at many different angles with respect to the polarization. Thus high spatial resolution is required to to examine these small domains and thereby polarization response along a single axis. We collected transmission and reflection data by wide field imaging of the sample through a microscope at different illumination wavelengths, which granted sub-micron spatial resolution. The system has a spectral range from 300 nm to 1000 nm, with single nm spectral resolution. The system consists of a monochromatic tunable light source coupled to a microscope via a fiber optic cable, diagrammed in Fig. 8. Two different illumination geometries are possible, either transmissive or reflective. Illuminating the sample underneath allows direct measurement of the transmittance, and illuminating from above allows us to measure differential reflection. We introduce those two methods in the following sections.

2.2.1 Transmission and Reflection

Differential reflection is the simultaneous measurement of reflected light from two key places on a sample; The sample itself, and an area of substrate. Light intensity recorded from the sample are hereafter referred to as I_{sample} and from the substrate as I_{sub} . For materials with a low absorbance, i.e. incident light is absorbed very little, we can use a first order approximation. The approximation is shown in Fig. 5, in which case $\Delta R/R$ is proportional to the transmittance. In the realm of low reflection from the sample, the absorbance A can be approximated by $A = -log_{10}(T)$, where T is the transmittance ($0 \le T \le 1$). Differential reflection is defined in equation 4, with quantities illustrated



Figure 4: Diagram of one crystal of ADT-TES-F (outer boundary), while in fact the crystal contains many domains of different dipole orientations with respect to eachother. The dipole moments are dependent on the stacking orientation. Figure from Grimm [4]

in Fig. 5. Dark intensities are already accounted for in the experimental method through a calibration file, so they are ignored in the calculations that follow.

$$\frac{\Delta R}{R} = \frac{I_{sample} - I_{sub}}{I_{sub}} \tag{4}$$

$$=\frac{I_{sample}}{I_{sub}} - 1 \tag{5}$$



First order approximation

Figure 5: Diagram of the reflected light rays present in differential reflection measurements. The first order approximation is that the sample does not have any effect on the incoming light, only on the outgoing reflected ray from the substrate. Despite this being a rough approximation, the $\Delta R/R$ spectrum for ADT-TES-F does yield a similar spectra to transmission. See Figures 10 and 11

Without simultaneously measuring both the transmitted and reflected beams, we cannot extract the real absorption spectrum (as A = 100% - (%T + %R)), where %T and %R are the percent of light transmitted and reflected respectively. The previous equation holds only for very thick and atomically thin materials where we can ignore interference effects. If interference effects are present, then T must be amended by performing $T \mapsto T/(1-R)$ [11]. But if the approximation in Fig. 5 holds, then we can derive the relation between $\Delta R/R$ and transmittance as follows.

$$\frac{\Delta R}{R} = \frac{I_{sample}}{I_{sub}} - 1 \approx \frac{I_{sub}T_{sample}}{I_{sub}} - 1 = T_{sample} - 1 \tag{6}$$

As we shall see ADT-TES-F has non negligible reflectance R, thus the T and $\frac{\Delta R}{R}$ do not compare exactly, as seen in Figures 10 and 11. However, peak locations and anisotropy are preserved, which shows the approximation holds loosely. Thus $\Delta R/R$ spectrum is useful in confirming polarization dependent anisotropy and the location of peaks seen in a T spectrum.

2.2.2 Transmission

To measure the transmittance of the sample, the transmitted intensity through the sample and the substrate are measured. First, the illumination source is set below the microscope stage, illuminating the sample from beneath, which projects an image onto a camera above. The camera then records an image of the sample at each wavelength. The image is just a spatially resolved transmission intensity map at each wavelength. We extract the intensities from the desired regions and substrate simultaneously at each frame. In the following calculation, the intensities of the sample is called $I_{sample+sub}$, as the light passing through the sample also passes through the substrate, and I_{sub} for the substrate signal. We assume the reflection is only weakly wavelength dependent, and the magnitude of reflected light is much smaller than that absorbed. I_{inc} is the incident intensity, T_{sample} is the transmittance of the sample and T_{sub} is the transmittance of the substrate. It is implicit that all the quantities below are functions of the wavelength λ .

$$\frac{I_{sample+sub}}{I_{sub}} = \frac{T_{sample}T_{sub}I_{inc}}{I_{inc}T_{sub}} = T_{sample} \tag{7}$$

Thus dividing the intensities at each wavelength of two regions in the image gives the transmittance $T(\lambda)$ of the sample.

2.2.3 Polarized Transmission and Reflection

A transmission or differential reflection spectrum is obtained through a three step process. The sample is first illuminated at a single wavelength under a microscope, and the image of the illuminated sample is recorded by a CCD. That process is repeated for every wavelength that falls within the scan range, for example between 300 nm and 1100 nm. That process creates a stack of frames, or movie. We then which take a total intensity count of the sample and substrate region in each frame, thereby obtaining $I_{sample}(\lambda)$ and $I_{sub}(\lambda)$, i.e. intensities as a function of wavelength (because each frame corresponds to a single wavelength). The analysis for differential reflection or transmission then gives us a spectrum. Finally, we repeat and measure a T or $\Delta R/R$ spectrum at every polarization angle.

2.2.4 Translator Circuit

Previously, the camera was set to record while the light source stepped through each wavelength freely. The light source uses a monochromator to switch wavelengths, and it takes between 20 and 50 milliseconds for the monochromator to step 1 nm in wavelength. The switching time fluctuates depending on the monochromator's current position. The length of time that the light source spent at each wavelength, and the exposure time on the camera were set so that one camera frame corresponded to a single wavelength of light incident on the sample. However in practice this did not work well. The camera often recorded a frame while the light source was switching wavelengths, which caused a lot of noise, and worse, we didn't know exactly what wavelength of light each frame corresponded to. My solution was to electrically couple the timing of the lightsource and the camera. We found a signal that was only active when the light source was switching wavelengths, and then we built a circuit which enables the signal to trigger the camera to record a frame. The translator circuit

reads when the light source is switching wavelengths and outputs a square wave pulse at 3.8V high and 0 V low. This signal was tailored so that it triggers the camera, a Princeton EMCCD, to record a picture of the sample at every wavelength of light in the scan. Furthermore, we built a 40 ms delay between when the lightsource switches wavelengths and when the translator circuit sends out the camera trigger. That delay is long enough to let the monochromator settle at a stable wavelength, before the camera records a frame. The implementation of this circuit has greatly reduced noise. More importantly, we now know exactly which wavelength corresponds to which frame, and can therefore extract absorption data precisely. The circuit is diagrammed in Fig. 6.



Figure 6: Translator circuit diagram. The system is in essence three parts married together: a 555 timer, a low pass filter, and then an active gain circuit.

2.2.5 Peak Ratio Analysis

Absorption peaks are really markers of a resonant energetic transition from the ground state to an excited state. Optical transitions are those transitions which occur via the absorption of a photon, i.e. the transfer of energy from the electromagnetic field to the molecules electrons. A transition from the ground state (0) of one nuclear state to the ground state of an excited nuclear state (0) is least energetic and most likely in rigid molecules [5] and is thus the lowest lying strongest peak in energy space. In non rigid molecules, an excitation tends to deform the molecule in real space, and thus that rule of thumb may not hold. Fig. 7 illustrates the ground to ground $(0 \rightarrow 0)$ transitions along with other prominent transitions, and how they show up in an absorption spectrum.

Intermolecular interactions, determined by structure, dictate the strength of photonic transitions in a crystal. Thus examining the absorption spectrum reveals many factors that determine the strength of interactions, as we will see below. Fitting the in solution absorption spectra of ADT to equation 8 below gives both Huang-Rhys (HR) factor λ^2 and the oscillator frequency ω_0 [8]. Conceptually, the area of each solution absorption peak (in energy space) is determined by λ^2 .

$$A_{mon} = \sum_{n} \frac{e^{-\lambda^2} \lambda^2}{n!} W_{LS}(\omega - \omega_{0-0})$$
(8)

Where W_{LS} are the Frank-Condon factors [8]. Armed with the HR factor and ω_0 we calculate the ratio of the absorption peaks for any two transitions to the ground state, $v_p \to 0$ and $v_t \to 0$, as below

[8]

$$\frac{A^{(v_p \to 0)\pm}}{A^{(v_t \to 0)\pm}} = \frac{1}{\lambda^2} \frac{1 - G(v_p : \lambda^2) e^{-\lambda^2} (\pm J_0) / \omega_0}{1 - G(v_t : \lambda^2) e^{-\lambda^2} (\pm J_0) / \omega_0}$$
(9)

The plus or minus of the transition indicates that it is either an H aggregate transition (+ as $+J_0 > 0$), or a J aggregate transition (where $-J_0 < 0$). This is where the exciton bandwidth W comes in, as could easily substitute $\pm J_0$ for $\pm W/4$. $G(v_t : \lambda^2)$ is the vibrational function, defined as [7]:

$$G(v_t : \lambda^2) = \sum_{n, n \neq v} \frac{\lambda^{2n}}{n!(n-v)} \text{ for } u, v \in 0, 1, 2...$$
(10)

Thus fitting equation 9 to measured peak intensity ratios will yield the parameters we desire. For example $\frac{A^{(0\to 0)+}}{A^{(1\to 0)+}}$ would yield values of J_0 (+ for H aggregates as J_0 >) and thereby the exciton coupling bandwidth $W = 4J_0$. This analysis is planned for future work.

For polarized electric fields, we have that $\hat{\mu} \mapsto \hat{\mu} \cdot \hat{j}$ in equation 3, where \hat{j} is the unit polarization vector of the incident light. Furthermore, $\sigma \mapsto \sigma_j$, i.e. the Gaussian width is now allowed to be dependent on the polarization \hat{j} . Because H and J stacking correspond to alignment of molecules along an axis, polarized light tuned to that angle can selectively excite either H or J stacking independently. Thus polarization dependent absorption spectra enable us to study H and J effects independently in mixed orientation systems, like the ADT derivatives in this work.

2.3 Methods

The Ostroverkhova lab at Oregon State University supplied the ADT samples. The ADT-TES-F and ADT-TSBS-F samples were deposited on a fused silica substrate with gold stripes laid on top for electrical contact. Adjacent crystals on the samples were scraped away so that only a single flake, roughly 50 micron long and 10 micron wide, remained. Fig. 9 shows the ADT-TES-F crystal studied. That crystal flake contained about 5 different crystal domains based on visual inspection. It is possible that there are multiple crystal domains layered on top of each other. We try to find regions of a crystal that are a single domain, such as the red outlined region in Fig. 9.

2.3.1 Transmission and Reflection

The methods and procedures used to collect transmission and $\Delta R/R$ spectrum are discussed in this section. Monochromatic light is coupled via a fiber optical cable from a Horiba Fluorolog to an Olympus BX50WI microscope. The Horiba Fluorolog contains a 500W Xenon arc lamp which filters white light into monochromatic light via a double monochromator. Both the illumination geometries are diagrammed in Fig. 8. In the reflective geometry, the light is focused by two aluminum spherical concave mirrors, and then is reflected down to the sample by a 50/50 silvered mirror. From there, the light is focused onto the sample by an Edmund Optics reflective 40x objective. The use of all reflective optics removes any chromatic aberration, which would distort images. In transmissive geometry, the light emerges from the fiber optic cable and is focused beneath and through the sample to the objective and camera. In both cases, a Princeton Instruments EMCCD (highly sensitive camera) sits atop the microscope and records the image of the sample. At each wavelength, an image of the sample is recorded thereby creating a movie (a stack of frames). The translator circuit synchronizes the Fluorolog and the EMCCD so that the EMCCD records only one frame at each wavelength in the scan. We extract spatial absorption data from each frame and thereby each wavelength, creating a transmission or reflection spectrum.



Figure 7: Qualitative absorption features of an organic molecule. Transitions are denoted above each corresponding peak seen in energy space (determined by ω). Figure 3 is reproduced to show the HJ model representations of the transitions.



Figure 8: Diagram of the system for collecting both transmission and reflection spectrum. The EMCCD would capture an image like Fig. 9 at each wavelength in the scan. The translator circuit is labeled TC and connects from the internal circuitry of the light source to the EMCCD.

Polarization 40°



Figure 9: 3 frames (intensity maps of transmission) at 40° , 90° and 140° polarization angles, at a constant wavelength of light (525 nm), for ADT-TES-F. The incident light polarization at 110° and 20° with respect to the crystal is shown in the center frame. The crystal domain is outlined in red, and the substrate used for subtraction in yellow. The substrate is glass (appears white) with gold fingers (black). The transmission of light through the crystal is highly dependent on the incident light polarization angle.

The resulting movie is one frame less than the number of wavelengths in the scan reported by the Fluorolog software. The movie is exported as a tiff file type, using the export utility in *LightField*. We use *ImageJ* to extract intensity data of a region from each frame of the tiff movie files, which is described next.

2.3.2 Data Analysis

For both transmission and reflection type scans, the analysis is the same. From the images of the sample at each wavelength, we select a region of the sample and the substrate, using the tool *Time Series Analyzer v3* for *ImageJ*. A region of an ADT-TES-F sample is shown in Fig. 9, with regions of substrate and crystal highlighted. The intensities of the crystal region and substrate region are calculated by *ImageJ* at each frame, and thereby at each wavelength. Thus we have an intensity spectrum of the light passing through (or reflecting off) the substrate and sample. From those intensities at each wavelength, we calculate either the transmission or differential reflection spectrum according to the procedures in section 2.2. Furthermore, we use *ImageJ* to record the size of the regions we selected, and then divide both $I_{sample}(\lambda)$ and $I_{sub}(\lambda)$ by the region areas so that the intensities are area normalized.

2.4 Results

Figures 10, 11, and 12 show the polarization dependence of the transmission spectra of ADT-TES-F, ADT-TSBS-F respectively. Figure 13 shows the transmission spectrum of ADT-TDMS-F, as the sample was too thick for polarization dependent measurements. ADT-TES-F exhibits large polarization dependence as the peak transmission intensity varies from 0.75 to 0.05 (fraction of incident light), see Fig. 11.TSBS-F shows minimal dependence, with transmission fluctuating from 0.7 to 0.55. Thus significant polarization dependence was only seen in the ADT-TES-F sample. Moreover, the ratio of the heights of the S1a peak to the S1b peak in the ADT-TES-F absorption spectra were calculated at each polarization angle and are shown in Fig. 14. Fig. 15 shows the polar representation of the same data in Fig. 14.



Figure 10: $\Delta R/R$ Spectrum of ADT-TES-F as a function of the polarization angle of the incident light. Reflection peaks are approximately proportional to transmission valleys (see differential reflection section) and therefore absorption peaks. The polarization is from 0° to 180° by 10° steps. The angle is measured with respect to the starting angle of polarization and via Figure 9. The S1br peak is located at 525 nm, and the S1ar peak is convoluted with the broad shoulder at B, but is located at 553 nm.

In the $\Delta R/R$ spectrum (Fig. 10, we see that the reflection peaks (corresponding to transmission valleys and therefore absorption peaks) denoted S1ar and S1br have different relative magnitudes depending on the polarization angle, just as in the transmission spectra. Near 20° S1ar has a lower reflection than S1br, while closer to 80° that ratio flips. The odd shaped shoulder, *B*, centered at 575 is of unknown origin, but it is not seen in the transmission spectrum 11. For that reason, we use the transmission spectrum to look at the ratios of S1a to S1b, as it is evident that the $\Delta R/R$ spectrum is convoluted with other processes.



Figure 11: Transmission spectrum of ADT-TES-F at many incident light polarization angles. From 0° to 180° polarization angle by 10° steps. A value of 1 is total transmission. The peaks S1b and S1a are located at 517nm and 548 nm respectively. The S2a peak is seen at 420 nm.

Both the $\Delta R/R$ and Transmission spectrum of ADT-TES-F both show the immense anisotropy with respect to polarization angle. The magnitude of the transmission or reflection through the sample fluctuates immensely between 0 and 180 degrees of polarization in both cases. The reflection peaks at 400 nm and 425 nm (designated S2b and S2a respectively) are the next highest set of transitions (after S1). Of the S2 transitions, only S2a was resolved clearly in the transmission spectra, at 420 nm. The transmission spectra shows that the peaks S1b and S1a are located at 518nm and 548 nm respectively. The reflection spectrum tells us that the peaks S1b and S1a are at 525 nm and 553 nm. Thus the peak locations are approximately the same. One may notice that the centering of the peaks (in nm) shifts slightly with respect to polarization angle, this was not investigated in this work.



Figure 12: Transmission spectrum of ADT-TSBS-F as a function of the polarization angle of the incident light. A value of 1 is total transmission.

The polarization dependence of ADT-TSBS-F, seen in Fig. 12, is minimal. Thus this ADT-TSBS-F sample is isotropic with respect to polarization. Only one polarization angle, 20°, shows a significant deviation from the spectrum at other angles. And beyond 550 nm, the 20° trace appears to be statically offset by a constant, thus it is possible the deviation mentioned is erroneous.



Figure 13: Transmission spectrum of ADT-TDMS-F.

Fig. 13 does not show the expected absorption peaks from the TDMS-F sample. The sample was extremely thick (50 micron), so many domains of different angles were stacked vertically through the sample which would obscure fine absorption features.



Figure 14: Ratio of the S1a transmission peak to the S1b transmission peak in ADT-TES-F. Peaks are designated in Fig. 11. The data from 190 to 360 degrees is simply a copy of the data from 0 to 180 degrees, indicated by the dotted trace.

Figures 14 and 15 show the ratios of the S1a and S1b transmission peaks in Fig. 11. At 30° polarization, S1a is 0.55 times as prominent as S1b, and at 120° S1b is dominant over S1a by a factor of roughly 1.05, thus a single crystal domain of ADT-TES-F is highly anisotropic with respect to polarization. In particular, we see that 30° polarization is highly resonant with the dipole transition responsible for the S1a transition.



Figure 15: Ratio of the S1a transmission peak to the S1b transmission peak in ADT-TES-F. Peaks are designated in Fig. 11. The data from 190° to 360° is simply a copy of the data from 0 to 180 degrees. The 3 dotted lines of constant radius indicate peak ratios of 0.5, 1 and 1.5, in order of increasing distance from the origin. The minimum and maximum S1a/S1b responses are at $30 \pm 5^{\circ}$ and $120 \pm 5^{\circ}$ respectively.

2.5 Discussion

The anisotropy of absorption for ADT-TES-F shown here should be present in TSBS-F and TDMS-F as well [5]. The fact that we do not see similar anisotropy of absorption in the latter two molecules is probably due to a few issues. First, the TDMS-F sample was very thick (nearly 50 micron thick, much larger than a single crystal domain), so many crystal domains of different axis orientations would respond simultaneously to the excitation light, giving an isotropic absorption curve. The unpolarized transmission spectrum in Fig. 13 showed no absorption peaks, indicating that there are many differently angled domains in the light path. Thus a polarization dependent measurement would not be useful, as we cannot resolve the absorption peaks necessary for peak ratio analysis.

In TSBS-F, the sample was two years old at the time of measurement, thus the crystal structure could have deteriorated leading to crystal disorder and thus isotropic behavior. Additional absorption spectra of 'clean' areas of the substrate revealed the presence of a film (potentially decayed TSBS-F). We selected the most clean regions of substrate to account for that film. But we have no evidence that the TSBS-F is not decayed nor that the substrate regions we used were totally clean. Decay of the TSBS-F sample is the primary explanation for the isotropy observed. However, if the TSBS-F response really is isotropic (i.e. not due to disorder from decay), then this work shows that optical anisotropy in ADT can be turned on and off entirely via altering the side groups.

The ADT-TES-F samples were very high quality, and the regions around each crystal were meticulously cleaned, thus the substrate transmission signal was free of contamination. Thus we resolved the ADT-TES-F anisotropy very well in this study. The $\Delta R/R$ and transmission signals for TES-F both confirm anisotropic optical behavior. We believe the polarization dependence of absorption (see Fig. 15) in TES-F is due to exciting the H or J absorption modes, each of which correspond to different axis in real space. Armed with the crystal structure, in Fig. 16, we can make some qualitative conclusions based on the HJ model. The crystal axis a and b lie in the plane of polarization (plane of the substrate), while the c axis is out of the plane and thus parallel to the direction of incoming light, rendering it invisible to the incoming E field which is polarized in the a-b crystal plane. So we only probe the a-b crystal plane, seen in Fig. 16.b.



Figure 16: a) The 3D Crystal Structure of ADT-TES-F. b) The a-b plane of the ADT-TES-F crystal. Observe that along the axis a^* the crystal is packed so that the S1 dipole moments are aligned head to head (J like). And along b^* the dipoles are arranged side to side, or H-like. a and b lie in the plane of polarization (plane of the substrate), while the c axis is out of the plane and thus parallel to the direction of incoming light.

When the incident light is polarized along that a^* axis, the incident E-field (light) is aligned parallel to the transition dipole moment, thus the moments appear to be aligned head to head (J aggregate). However, when the light is polarized along that b^* axis, the incident E-field (light) sees the moments aligned side to side (H aggregate). As simulations show in Fig. 2.f, J aggregates tend to have a large (> 1) S1a (0-0) absorption response compared to the S1b (0-1) response. Thus we guess that the maximal S1a/S1b ratio seen in Fig. 15 of 1.05, at $120 \pm 5^{\circ}$ polarization, is due to the alignment between the E-field polarization and the a^* axis, where the crystal behaves like a J aggregate. In Fig. 2.e, H aggregates tend to have a S1a/S1b ratio (0-0/0-1 ratio) less than one. Thus we attribute the S1a/S1b ratio at $30 \pm 5^{\circ}$ polarization, of roughly 0.55, to the E field aligning with the b^* axis and thus 'seeing' the H aggregate side of the crystal. ADT-TES-F is not purely a J or H system along any axis, as the stacking structure is more like a brickwork pattern. Thus we expect peak ratios only qualitatively like that in Fig. 2. Furthermore, this analysis suggests that the angular separation between the b^* and a^* axis should be $120^{\circ}-30^{\circ} = 90\pm10^{\circ}$. The actual crystal packing structure in Fig. 16.b shows that the a^* and b^* axis are separated by roughly 90°, which is in excellent agreement with the previous discussion. Thus we attribute the anisotropy in absorption we have seen in this work, to the crystal behaving 'J-like' along one axis (a^*), and 'H-like' along another axis (b^*). It is important to note that if the packing structure was such that the S1 transition dipoles were not preferentially aligned along some axis, then the system would be isotropic with respect to polarization.

The *a* and a^* axis differ by only 20°, therefore by the previous analysis we know the *a* axis lies around $120 \pm 20^\circ$. We also know that typically the long axis of ADT-TES-F bulk crystals (110° line in Fig. 9) is the *a* axis of the structure [5], which further confirms that we are probing the desired crystal axes. Thus the a^* and b^* axis are indeed behaving J-like and H-like respectively.

2.6 Conclusion

This study of three different ADT derivatives: ADT-TES-F, ADT-TSBS-F and ADT-TDMS-F, resolved a high degree of anisotropy in the absorption response of ADT-TES-F with respect to the polarization angle of incident light. Furthermore, we found the HJ model of crystal aggregates predicted qualitatively the optical behavior of ADT-TES-F. ADT-TSBS-F was isotropic with respect to polarization. But it is possible that the TSBS-F sample was degraded or amorphous, which would give an isotropic signal due to a disordered crystal. The polarization dependence of absorption for ADT-TDMS-F was not attempted at all due to the huge thickness of the sample. Future work aims to resolve the polarization dependence in a single crystal of ADT-TDMS-F and either confirm or disprove the polarization isotropy seen in ADT-TSBS-F.

The absorption spectra of the three derivatives in solution are approximately identical [5]. We have shown in this work that the absorption spectra in crystalline form differ drastically between the TES-F and TSBS-F derivatives. The discrepancy in optical behavior between those molecules thus is due entirely to structure, and future work will pin down the structural parameters that differ between those molecules.

2.7 Future Directions

Ongoing work is investigating the excitation spectra of the three materials in this study. Excitation spectra are measures of the photo-luminescence (PL) response (how much light the material emits at a certain fixed wavelength) over a range of energies of incident (excitation) light. These three materials have a broad main PL response with minor responses convoluted in. Excitation spectra reveal the origin of PL peaks. Thus analyzing differences between the excitation spectra of the main PL peak and the side peaks could tell us differences in their origins. We could single out those PL peaks due to crystal structure, and those originating from the intrinsic molecular structure. Additionally, polarization dependent studies of PL and excitation hold huge potential in revealing more structural parameters under the HJ model.

3 Amorphous Semiconductors

In the search for the next generation of transistors and solar cells, researchers have turned to amorphous materials. Amorphous silicon is a popular amorphous channel device in transistors, but it has drawbacks. It has a low stability relative to other materials like IGZO [3], and needs to be annealed (baked) at high temperatures to improve performance. By contast, IGZO (In-Ga-Zn-O), a relatively new amorphous semiconductor holds huge promise. It can be annealed at less than 350° Celsius, thereby cheap and flexible plastic substrate can be used, instead of glass [3]. Amorphous semiconductor can also be grown in large films, opening up swaths of new applications. One potential disadvantage of amorphous semiconductor, like IGZO, is that there exist electronic states that are normally not present in pure crystalline semiconductors like silicon, called mid-gap states. Thus investigating the impact, and presence, of these mid-gap states is of crucial importance. The density of states determines conduction in the material (i.e. whether it behaves like a conductor or insulator) and where defects in device performance arise. Specifically, how do mid-gap states affect carrier dynamics and do these states originate from crystal or molecular structure? We address that question by measuring directly the density of states. This work uses a novel technique, photo-excited-chargecollection spectroscopy (PECCS), to measure the density of states of amorphous semiconductors. We build on the PECCS theory and develop a novel simulation code to extract the intrinsic Fermi energy and band gap of materials. However, the analysis and data collected on IGZO devices are protected by Apple Inc and are not presented herein. Thus we present the analysis technique and mock results on a simulated device.

To measure the density of states of an amorphous semiconductor, a MOSFET (metal oxide semiconductor field effect transistor) transistor is built with the semiconductor as the channel material. A MOSFET transistor is diagrammed in Fig. 18. A transistor is a device that allows current to flow between the source and drain leads, only when the voltage on the gate lead reaches a threshold voltage, V_{Th} . The turning on of the current through the device is measured in an I-V transfer curve, an example of multiple transfer curves are shown in Fig. 21.

Charge traps are important in transistor devices because they change current flow and the turn on voltage (threshold voltage) of the device. Charge traps are intrinsic defects in the transistor device which attract and trap charge carriers, preventing them from being extracted as current. Usually charge traps increase the magnitude of the threshold voltage, as more traps lead to less free carriers for current extraction. As will be discussed, the PECCS measurement is measuring the change in I-V transfer curves when electrons that are stuck in mid-gap states (charge traps) are liberated through the photoelectric effect. Theory then relates the changes in those transfer curves to the mid-gap states of the density of states.

3.1 Density of States

When individual atoms are arranged in a crystal lattice, the physics of the system is very different compared to one of the free atoms. New quantities emerge, one of which is the density of states, which indicates the allowed energy levels for charge carriers in the crystal. Normally, atoms have discrete allowed energy levels for electrons to occupy, but in a solid these electrons can occupy a range of energies. The number of electronic states that exist per unit energy at each energy is referred to as the density of states, g(E), and determines most of the electronic behavior of the solid. See Fig. 17 for an example of a density of states and the mid-gap states that we discuss shortly.



Figure 17: General example of a density of states for an amorphous metal. The mid-gap states in the center are the charge trap states, which populate the band gap region. The valence and conduction bands are regions where a high density of states exist, allowing charge carriers to flow easily. The valence band maximum (VBM) and conduction band minimum (CBM) are the energy values at which the conduction and valence band contact the energy axis (approximately 1.2 eV and 3 eV in this example). Figure from J. Wager [13].



Figure 18: General MOSFET configuration transistor. IGZO or another suitable semiconductor could be used as the channel material (labelled semiconductor).

The band gap of a semiconductor is the size of the region (in energy) of the density of states where barely any electronic states exist. In Fig. 17, this would be the energy difference between the tails of the valence and conduction band. Photons equal or greater in energy to the band gap are often absorbed most intensely by the material. Thus the band gap is a parameter of great interest. Of crucial importance is the Fermi energy of a material. The Fermi energy, along with the Fermi-Dirac distribution function, dictate which electronic states are filled at what temperatures, and which band (valence or conduction) the primary charge carriers reside.

However, amorphous semiconductors like IGZO typically have electronic states in the middle of the bandgap, so called mid-gap states. These mid-gap states can alter drastically electronic properties, thus mapping the mid-gap states in various materials is a major interest. Typically, mid gap states effects the voltage required to start current flow through the transistor (that effect is the basis of PECCS) [12]. However measuring the density of states of a material is difficult, and was especially so on actual transistors (due to surface passivization layers). However, a novel technique of measuring the density of states of devices, called PECCS, was developed in 2010 [12], which we use in this investigation. We extended the PECCS theory to simulate the Fermi energy of devices. The analysis on specific Apple devices is I.P protected, so we discuss primarily computer generated data. ¹.

¹The data presented is in no way, qualitatively or quantitatively, related to any measurements on Apple Inc. devices, or any real devices or physical measurements. The data is only characteristic of transistors and how they are affected by incident light

3.2 Photo Excited Charge Collection Spectroscopy (PECCS)

Photo excited charge collection spectroscopy is a method of probing the electronic trap states of a channel material in a transistor, near the dielectric - channel interface. The transistor geometry is diagramed in Fig. 18. PECCS works as a consequence of the photo-electric effect, along with a few approximations we make in the following derivation. Photons incident on the channel liberate trapped electrons which are then extracted through the source-drain by a constant voltage. As discussed earlier, a transistor has a 'turn-on voltage' where a high enough gate voltage, negative or positive depending on n or p type semiconductor used in the channel, starts current flowing between the source and drain on the transistor. Because incident light, or photons, liberates trapped electrons, a shift in the turn on voltage towards 0 volts is observed as the photon energy is increased. If the channel semiconductor has more trap states, more electrons are liberated by the incident light and thus the current through the device is increased, leading to a lower turn on voltage. PECCS theory also assumes there are many more incident photons than electronic trap states, i.e. the light intensity is in the electronic state saturation regime. Usually this is true, for instance our light source outputs a peak flux of 10^{15} (cm⁻²s⁻¹) photons (from 15 mW on a 0.01 cm by 0.01 cm sized illumination area), while the typical number of trap states is estimated to be around 10^{13} (cm⁻²eV⁻¹) [12]. The relation between turn on voltage and incident photon energy allows us to quantitatively extract the trap density of states.

Next, we follow closely the derivation for the PECCS theory given in *Photo-Excited Charge Collection Spectroscopy* [14]. The threshold voltage is the liberating potential that cancels out the attractive (trapping) potentials present in the device. The threshold voltage for a semiconductor is approximately given by the addition of four potential terms:

$$V_{th} = \Psi_{max} + \phi_{ms} + Vg + Q_{eff}/C_{ox} \tag{11}$$

Where V_{th} is the potential that a charge carrier must overcome to move from the semiconductor interface to the source drain and be extracted. Ψ_{max} is the potential term due to band bending at the oxide-semiconductor interface [14], ϕ_{ms} is the metal-semiconductor work function (i.e. the difference between the two work functions), and Q_{eff}/C_{ox} is the E field at the semiconductor-oxide interface due to the total trapped charges of Q_{eff} and oxide capacitance C_{ox} . The last term is arrived at using a Guassian pillbox argument and approximating the effective charge Q_{eff} trapped at the interface as a parallel plate capacitor. We then suppose that Q_{eff} is described as follows, specifically for an n-doped semiconductor, with quantities described in the simple band structure diagram of Fig. 19

$$Q_{eff} = -q \int_{VBM}^{CBM-\epsilon} DOS_{e^{-} traps}(E)F(E)dE + q \int_{Vol} N_{traps \ oxide}dV$$
(12)

 $N_{traps \ oxide}$ is the volume density of trap states for positive charge carriers in the oxide. The magnitude of the charge of the electron is q. $DOS_{e^- \ traps}(E)$ is the density of states of trap states in the semiconductor, and F(E) is the Fermi-Dirac distribution function. VBM (valence band maximum) is the energy of the highest lying valence band level, and CBM (conduction band minimum) is the energy of the lowest lying energy level in the conduction band. We now use three approximations to proceed with the derivation. First, we assume that we are at 0 Kelvin, thus F(E) becomes 0 at energies above the Fermi energy, and 1 below. We assume that the Fermi energy E_F is above the CBM, thus all mid-gap states in the bandgap are filled. And we assume that $\Psi_{max} + \phi_{ms} + V_g$ all depend on the material choice and are unaffected by incident photons. The only thing then that is affected by an incident photon flux is Q_{eff} (the trapped charge at the semiconductor-oxide interface).



Figure 19: Band structure of the TFT under illumination of photon energy ϵ The gate voltage fills the mid-gap trap states, the bumps between VBM and CBM, prior to photo-excitation. E_F is the Fermi-level of the semiconductor (SC). Fig. from Kimoon et al. [12]

Thus we differentiate the expression for V_{th} with respect to ϵ and obtain the following.

$$\frac{\partial V_{th}}{\partial \epsilon}(\epsilon) = \frac{\partial}{\partial \epsilon} \left(\Psi_{max} + \phi_{ms} + Vg + Q_{eff}/C_{ox} \right) \approx \frac{1}{C_{ox}} \frac{\partial Q_{eff}}{\partial \epsilon}$$
(13)

$$= \frac{1}{C_{ox}} \frac{\partial}{\partial \epsilon} \left(-q \int_{VBM}^{CBM-\epsilon} DOS_{e^{-} traps}(E) F(E) dE + q \int_{Vol} N_{traps \ oxide} dV \right)$$
(14)

$$\approx \frac{1}{C_{ox}} \frac{\partial}{\partial \epsilon} \left(-q \int_{VBM}^{CBM-\epsilon} DOS_{e^{-} traps}(E) dE + q \int_{Vol} N_{traps \ oxide} dV \right)$$
(15)

By the second fundamental theorem of calculus: (16)

$$= \frac{-q}{C_{ox}} DOS_{e^{-} traps} (CBM - \epsilon)$$
(17)

$$\Rightarrow DOS_{e^{-} traps}(CBM - \epsilon) \approx \frac{C_{ox}}{-q} \frac{\partial V_{th}}{\partial \epsilon}$$
(18)

3.3 Methods

In this section, we outline the procedure and set up for performing PECCS, as well as the data analysis procedure. To perform PECCS, we use a mosfet transistor with the desired material as the channel according to Fig. 20. The current through the transistor device is recorded by an Ithaco Pre-amplifier as the gate voltage is swept over a range, for example -3 Volts to 3 Volts, by a YokogawaTM GS200 voltage controller. That process records I as a function of gate voltage V, normally called a transfer curve. The transfer curve is always recorded from high voltage to low voltage, i.e. a down-sweep. Recording only the down-sweep ensures that all the electronic trap states are filled by charge carriers before photo-excitation begins. Monochromatic light is incident on the sample as the transfer curve is collected. The light source is a 500 W Horiba Flurolog. At a certain voltage the transistor "turns on", which is to say the current through the source and drain reaches a chosen high value, at a certain gate voltage - the turn on voltage. Thus from these transfer curves, The turn on voltage is recorded at each wavelength of light in the scan range. The wavelength of the photon is converted to an energy value via $E = hc/\lambda$. The scan range for IGZO transistors are typically 300 nm to 700 nm, which in energy is 4.1 eV to 1.7 eV. As the energy per photon incident on the sample is increased, the turn on voltage magnitude reduces. An example of the turn on voltage shift is shown Fig. 21. We calculate the change in the turn on voltage by subtracting the turn on voltage at a certain photon energy, from the turn on voltage at the first photon energy. We then differentiate the data set of the change in turn



Side View

Figure 20: Experimental setup for performing PECCS measurements. A Yokigawa voltage controller controls the voltage at the gate (V_G) and LabView controls the voltage across the source and drain (V_{SD}), LabView also records the current. In the bottom half of the figure, we see the side view of the transistor chip, with the appropriate gold contacts for the source, drain and gate.

on voltage, with respect to photon energy. The following algorithm is used to differentiate the turn on voltage shifts.

$$\frac{\Delta V}{\Delta \epsilon}(d) = \frac{1}{2} \left(\frac{V(d+1) - V(d)}{\epsilon(d+1) - \epsilon(d)} + \frac{V(d) - V(d-1)}{\epsilon(d) - \epsilon(d-1)} \right)$$
(19)

Assuming the discrete differentiation above is sufficiently accurate, Then PECCS theory tells us the resulting curve is proportional to the trap electronic density of states at the interface by C_{oxide}/q . Where q < 0 is the fundamental charge of the electron.

3.3.1 Data Analysis

The transfer curves (See Fig. 21) from any device, and the simulated device, are discrete. This poses an issue when calculating the threshold current based off an arbitrary threshold current which does not correspond to an actual current data point. To resolve that, a program I wrote in python fits a line of best fit (I = aV + b) to the two points with a current value (or any arbitrary number of points n) nearest the selected threshold current. See Fig. 22 for a visual of the line of best fit procedure. The program then finds the voltage value V such that $I_{th} = aV + b$, thus V is the threshold voltage V_{th} . The procedure is repeated for all transfer curves, thus a curve of threshold voltages as a function of photon energy is created. Using a different threshold current showed a negligible difference in the $\frac{\partial V_{th}}{\partial \epsilon}$ curves. The program then performs, discretely using center point differentiation, the rest of the PECCS analysis outlined in equations 14-19.



Figure 21: Sample of raw PECCS transfer curves. Increasing the photon energy causes the IV transfer curve to shift horizontally. This is simulated data and is not related to Apple devices. The threshold current used to calculate the threshold voltage is indicated.

3.3.2 Data Analysis - Fermi Energy

The Fermi energy determines the maximum energy of all electrons in the system at 0 kelvin. The Fermi energy also gives us information about the velocity of carriers in the conduction band, and is an important parameter for simulating any semiconductor or metallic system. From equation 15, we see the Fermi dirac distrubition and thus the Fermi energy, is intimately involved in the PECCS measurement. To first order, we can ignore it, as one does in basic PECCS analysis. However, it would be very valuable if one could use the PECCS theory to extract the Fermi energy for this material. What follows is a computational method we developed to extract the band gap energy and the Fermi energy using a modified PECCS theory. A Python program evaluates the computations. All integrals are evaluated using a finite Riemann method, and the *SciPy* least squares optimization is used to find the free parameters (BG energy and Fermi energy). The Fermi dirac distribution function is

$$F(E) = \left(e^{(E-E_F)/(kT)} + 1\right)^{-1}$$
(20)

From equation 18, we call $DOS_{e^-traps}(CBM - \epsilon)$ the 0 degree density of states (hereafter called DOS^0), because temperature was assumed to be 0 Kelvin and the Fermi energy was assumed to be above the conduction band minima energy (CBM). From equation 14 we have that:



Figure 22: The computer calculated best fit line (blue) at $I_{threshold} = 0.4$ mA (horizontal black line) for a simulated transfer curve (green) collected under illumination of photons energy 1.2 eV. This is repeated for every photon energy in the set of PECCS data

$$V_{th}(\epsilon) = \left(\Psi_{max} + \phi_{ms} + Vg + Q_{eff}/C_{ox}\right)$$
(21)

$$= U' + \frac{q}{C_{ox}} \left(-\int_{VBM}^{CBM-\epsilon} DOS(E)F(E)dE + \int_{Vol} N_{traps \ oxide}dV \right)$$
(22)

$$= U + \frac{q}{C_{ox}} \left(-\int_{VBM}^{CBM-\epsilon} DOS(E)F(E)dE \right)$$
(23)

$$\approx U + \frac{q}{C_{ox}} \left(-\int_{VBM}^{CBM-\epsilon} DOS^0(E)F(E)dE \right)$$
(24)

$$\approx U + \frac{q}{C_{ox}} \left(-\sum_{VBM}^{CBM-\epsilon} DOS^0(E)F(E)\Delta E \right)$$
(25)

Note we have grouped all the constant terms into one free parameter U. We now use the SciPy least squares optimization to fit equation 24 to the experimental $V_{th}(\epsilon)$ curve, see Fig. 23. The fitting parameters are U, CBM, E_F (E_F is incorporated into F(E)). VBM is fixed at 0 eV arbitrarily, and CBM is allowed to be between 1 and 6 (reasonable values for a semiconductor band gap). Note because VBM is set to 0, the band gap is simply BG = CBM - VBM = CBM. The temperature T can be fixed at any value, in Fig. 23 we chose T = 315 K (room temperature). Furthermore, values in the 0 degree density of states which occur outside the experimental data set, are set constant at the endpoint value, to allow integration. That is a major approximation, thus a large range of experimental data is recommended (e.g. from 1 eV to 4 eV).

Now we can go one step further and calculate the 'second order' density of states from

$$DOS_{e^- traps}(CBM - \epsilon) \approx \frac{C_{ox}}{-q} \frac{\partial V_{th}}{\partial \epsilon} \frac{1}{F(CBM - \epsilon, Ef, T)}$$
 (26)

We have to use a nonzero T, because 1/F(E,T) becomes infinite for energies above E_F if T = 0. The 'second order' density of states is shown in Fig. 24 along with the '0 degree' density of states.

3.4 Results

Using the model in the data analysis section, the bandgap of the fictitious semiconductor was found to be 2.901 eV (See Fig. 23). Furthermore, the Fermi energy for this fictitious material was found to be 3.870 eV, and -0.0985 V for the constant U. The bounds and values found for each parameter are summarized in Table 1 below.

Parameter	Lower Bound	Upper Bound	Value
Fermi Energy (eV)	0	$+\infty$	3.87
Band Gap (eV)	0	5	2.90
U (Volts)	-∞	$+\infty$	-0.0985

Table 1: Table of the parameters found by the program from the fictitious transfer curves. The oxide capacitance was set to 10^{-12} Farads and the oxide thickness set at 50 nm, realistic values for a mosfet transistor.



Figure 23: Threshold (turn-on) voltages of the simulated transfer curves in Fig. 21, as a function of the energy of incident photons. The best fit of V_{th} according to equation 25 (Theory fit) is plotted with the experiment V_{th} .

Fig. 23 shows that the fitting algorithm accurately reproduces the Vth measured. The oxide capacitance was set to 10^{-12} Farads and the oxide thickness set at 50 nm, realistic values for a mosfet transistor. In Fig. 24, the same parameters are used to create the 'second order' density of states.



Figure 24: Density of states calculated from the derivative of the threshold voltage curve in Fig. The two defect bands, DB1 and DB2, are labelled. The 'second order' density of states calculated from equation 26 is shown in green. The magnitude of the density of states is arbitrary because the data is simulated. Typical density of states magnitudes are on the order of 10^{13} cm⁻²eV⁻¹ [12]

The 0th degree density of states in Fig. 24 shows that the size (in energy) between peaks in the density of states, the band gap, is approximately 2 eV. Thus the software prediction is off. However the same analysis applied to IGZO devices agreed with the known band gap of the material to within 0.2 eV, for T = 315 K.

3.5 Discussion

The model and process presented show promising results, as seen in Fig. 23. The program was able to fit the DOS and threshold voltage curves well, and extract realistic values for the Fermi energy and band gap (on the order of eV). A drawback is that the 0 degree density of states is used as a starting point to estimate the Fermi energy. Thus we implicitly assume that the 0 degree density of states and the 'second order' density of states do not differ drastically. Fig. 24 seems to show this.

Measuring the size of the region between DB1 and DB2 in Fig. 24 shows that the bandgap is between 1.5 eV and 2.5 eV, thus the estimate of 2.9 eV is not very accurate. However, this simulated device has no valence or conduction band, just defect states. So the program found the bandgap had to be between the outer edges of the defect states DB1 and DB2 in order to reproduce the correct V_{th} curve. However the mock device shown shouldn't be taken too seriously as a test of the model. The model predicts closely the band gap of IGZO when a real IGZO transistor is studied, which is a much more rigorous test of the model.

The most exciting application of this model is in estimating the intrinsic Fermi energy of the material. The Fermi energy tells us what band (conduction or valence) that charge transport occurs, which is crucial for understanding device behavior. One issue however is that often the Fermi energy shifts due to an external electric field (called photostressing). If this shift is large, then the model is invalid. However, in prior application of PECCS, groups have assumed the Fermi energy to always lie above the conduction band [12].

3.6 Conclusion

The model and program presented is a fast track to PECCS analysis, which previously took hours per data set when done by hand. Additionally, the model extends the basic PECCS analysis to estimate the Fermi energy, optical band gap, and a second order density of states for the material. Results on IGZO gave realistic parameters: within 0.2 eV for the known optical bandgap, and a Fermi energy on the order of eV. Realistic parameters were also found for the simulated device.

3.7 Future Directions

Work is planned to investigate the effects of different post processing techniques on the DOS of devices, such as annealing and device coatings. We hope that the PECCS analysis and theory developed here will reveal changes to the Fermi energy of the material from those processes.

Future work is also focusing on improving the model and simulation code. A central assumption in PECCS is that the incident light is of such high intensity that it saturates all the trap states of the semiconductor. That is to say that there are many more incident photons than trap states. One knows they are in the saturation regime of a transistor if increasing the intensity of incident light does not increase the current response. Tests showed that for many wavelengths in the scan range the intensity is such that we are not saturation regime of the transistor. This means that the assumption that the incident photons are liberating *all* the trapped electrons at a given energy is wrong (for some wavelengths). Thus we need to include a factor in equation 23 of the form $P(DOS(E), I(\epsilon))$, such that:

$$V_{th}(\epsilon) = U + \frac{q}{C_{ox}} \left(-\int_{VBM}^{C_{BM}-\epsilon} DOS(E)F(E)P(DOS(E), I(\epsilon))dE \right)$$
(27)

Where presumingly, $P(DOS(E), I(\epsilon))$ is some function such that for a large light intensity relative to the density of states, $I(\epsilon) >> DOS(CBM - \epsilon) \quad \forall \epsilon$, we would have that $P(DOS(E), I(\epsilon)) \approx 1$, i.e. saturation.

The light source is not intense enough at some wavelengths to saturate all electronic states, thus basic PECCS analysis is inaccurate. We need to either figure out a function for $P(DOS(E), I(\epsilon))$ and use the same fitting program to fit to the free parameters involved, or increase the source intensity so that there are enough photons to excite all accessible electronic states. The latter fix is superior, but high energy (e.g. UV) and high intensity light damages most materials.

4 Concluding Statement

This work investigated changes in electron activity and optical characteristics due to crystal morphology, and is ongoing. We seek to answer the general question "In these new exotic materials, what role does structure play in electron dynamics, and can we control it?". We made considerable headway on that question for a class of organic photovoltaics, and amorphous semiconductors. In the former material, we investigated the role of different crystal structures on optical properties. In the latter, we developed novel a simulation code to determine parameters important to electron behavior: the Fermi energy and optical band gap. Pinpointing how structural changes affects those parameters in these systems is crucial for developing the next generation of OLED's, transistors and photocells.

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