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Probing Electronic Structures of Organic Semiconductors at Buried Interfaces by Electronic Sum Frequency Generation Spectroscopy

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ABSTRACT We use Electronic Sum Frequency Generation Spectroscopy (ESFG) to study the electronic structures at a buried solid/solid interface for the first time. The system is an organic thin film, poly(3-hexylthiophene-2,5-diyl) (P3HT), supported on a silicon surface. The ESFG measurement is only in resonance with electronic (or vibronic) excitations, thus capable of yielding rich information of the band gap and electronic structures of the P3HT film at interface. We find the bandgap of P3HT in contact with silicon is 2.2 eV, with a narrowed bandwidth and Lorentzian lineshape. This is significantly distinct from the UV-Vis spectra of bulk P3HT, which contains multiple broad Gaussian peaks. Our measurement demonstrates at interfaces regioregular P3HT has a uniform electronic structure, which could improve the short circuit currents. The unique capability of ESFG to probe electronic structures at buried interface under atmosphere will be useful for investigating many buried interfaces.

TOC GRAPHICS

Introduction

Buried interfaces are ubiquitous in devices such as field effect transistors^{1,2}, light emitting diodes³ and photovoltaics.^{4,5} The band gap and electronic structures at buried interfaces are crucial in understanding and predicting the charge carrier behaviors at interfaces, such as exciton and polaron formations, charge separations and recombinations.^{4,6-9} However, the bandgap and electronics structures at the interfacial region, where two materials are in contact with each other, can differ from the bulk, because of interfacial interactions.¹⁰⁻¹⁴ Therefore, robust and direct methods are needed to probe the band gaps as well as electronic structures at buried interfaces.

Significant successes on determining interfacial electronic properties of materials in vacuum have been achieved by surface techniques. For example, UV photoelectron spectroscopy^{7,11,14} or Ballistic-Electron-Emission Microscopy¹⁵ can determine the band alignment at interfaces of films with precisely-controlled thickness. It is found that in the films that are a few molecules thick, electron tunneling between two domains significantly changes the electronic structures of the molecules at interfaces^{16,17}.

Aside from measurements in vacuum condition, determining electronic structure at interfaces under atmospheric conditions is also necessary. Atmosphere resembles the working environments of devices, and the electronic and molecular structures of interfacial molecules under atmosphere can be significantly different from the ideal vacuum condition¹². It is difficult to directly extend the vacuum techniques into measurements under atmosphere. Only some recent advances in differential pumping allow photoelectron spectroscopic techniques to study surfaces under ambient condition (a few Torr)¹⁸.

More often, optical spectroscopies are used and developed for probing electronic structure of interfaces under atmosphere. For instance, bulk sensitive optical techniques, such as linear

absorption spectroscopy, are widely used to probe nanometer-thick films, whose properties are used to approximate the interface properties.^{19–22} It is questionable whether such an approximation is valid. For instance, can we use the optical spectra of thin films to extract electronic structure information of the molecules at interfaces?

In this report, we demonstrate for the first time, that electronic sum frequency generation (ESFG) spectroscopy^{23–27} can determine electronic structures of interfacial molecules at solid/solid interfaces. Like other sum frequency generation techniques and electronic second harmonic generations^{28,29}, ESFG is intrinsically interface sensitive, since it is a second order coherent optical signal that can only be generated from non-centrosymmetric media.

We investigated the organic/inorganic semiconductor interfaces composed by poly(3-hexylthiophene-2,5-diyl) (P3HT) and n-doped Si (111). We found although the P3HT polymers have a complicated electronic structure distribution in the bulk, which results in multiple broad visible transitions, only one narrow Lorentzian peak dominates the ESFG spectrum, indicating that the conformation of P3HT at interfaces are more uniform than the bulk.

Experimental Methods and Theoretical Background

A Ti:Sapphire regenerative amplifier is used to generate 6mJ, 35 fs, 800nm pulse at 1kHz (Astrella, Coherent). Majority of the beam is sent to an OPA system (TOPAS, Light Conversion) to generate the signal and idler beams. Based on the band gaps of the materials, either signal or idler is used as near IR beam in ESFG. A small amount 800nm (<0.5mJ) pass through a band narrowing filter (Idex Optics & Photonics) to create narrowband 800nm spectrum (fwhm = 1.5 nm). The relative delay between 800nm and near IR is controlled by a mechanical stage. Both the near IR and narrowband 800 nm beams are focused by a gold parabolic mirror (EFL= 10 cm, Edmund Optics) onto the sample, with both incident angle to be 60° relative to the surface

normal. The ESFG signal is reflected off the sample surface and is collimated by another gold parabolic mirror (EFL = 5 cm, Edmund optics). The signal is sent through short-wavelength pass filter (Newport) to remove residue 800nm beam, and finally sent into a spectrograph to be dispersed and recorded on a CCD camera (Andor). Both near-IR and 800 nm beams are attenuated to reduce sample damage due to multiphoton absorptions. We do not observe any ESFG signal decrease over the course of ESFG measurement (10 mins), which indicates that there is no sample degradation happening.³⁰ The polarization of ESFG pulse sequence is *SSP*, where the order of the letters corresponds to ESFG, 800 nm and near IR beam. We use this polarization scheme to remove nonresonant contributions from Si substrates. Since the near IR spectra range might not be broad enough to cover the entire electronic transition, we scan the near IR wavelength from 1840 to 2300 nm in a step of 20 nm and plot the overall ESFG counts versus the sum of near IR and 800 nm beams' frequency to find the resonant transitions. ESFG signals of bare Si, GaAs and gold surfaces are also recorded as control and reference samples.

The emitted SFG signal can be expressed as

$$I_{SFG}(\omega) \propto |x_{eff}^{(2)}|^2 I_{800nm}(\omega_{800nm}) I_{IR}(\omega_{IR}) = \left| x_{NR}^{(2)} + \sum_n x_{ijk,n}^{(2)}(\omega_{SFG}) \cdot e^{i \cdot \varphi_n} \right|^2 I_{800nm}(\omega_{800nm}) I_{IR}(\omega_{IR})$$

Eq. 1

where $x_{eff}^{(2)}$ is the second order susceptibility, which is often composed by the sum of various nonresonant ($x_{NR}^{(2)}$) and resonant ($x_{ijk}^{(2)}(\omega_{SFG})$) transitions. In the homodyne detection scenario, the signal I_{SFG} is proportional to the square of $x_{eff}^{(2)}$, and the products of near IR (I_{IR}) and 800nm (I_{800nm}) beam intensities. As we show below, by normalizing I_{SFG} of the sample to a SFG signal from the reference sample, the dependence on I_{IR} and I_{800nm} can be removed. As a result, we can directly determine $x_{eff}^{(2)}$, which contains $x_{ijk,n}^{(2)}(\omega_{SFG})$. The

term $\chi_{ijk,n}^{(2)}(\omega_{SFG})$ reflects physical properties such as bandgap energy and transition dipole strength of the systems. The resonance second order susceptibility $\chi_{ijk}^{(2)}(\omega_{SFG})$ ^{27,31-40} can be written as (Fig.1a),

$$\chi_{ijk}^{(2)}(\omega_{SFG}) \propto \sum_e \frac{\langle 0|\rho|0\rangle \langle 0|\mu_i|e\rangle \langle e|\alpha_{jk}|0\rangle}{\omega_{e0} - \omega_{SFG} - i\epsilon} \quad \text{Eq. 2}$$

Where $|0\rangle$ and $|e\rangle$ are the ground and excited electronic states of the system, $\langle 0|\rho|0\rangle$ is the initial population at ground electronic state, $\langle e|\alpha_{jk}|0\rangle$ is the hyperpolarizability of two-photon absorption, which promotes systems from $|0\rangle$ to $|e\rangle$ through virtual states $|v\rangle$, and $\langle 0|\mu_i|e\rangle$ corresponds to the electronic dipole transition that brings the system from $|e\rangle$ to $|0\rangle$ by emitting visible lights. In the denominator, ω_{e0} is the frequency difference between $|e\rangle$ and $|0\rangle$, ω_{SFG} is the frequency of emitted SFG signal, which satisfies $\omega_{SFG} = \omega_{NIR} + \omega_{nm}$, and the $i\epsilon$ is the dephasing contribution. At resonance condition ($\omega_{e0} = \omega_{SFG}$), the denominator in Eq.2 approaches to zero, and the ESFG signal is enhanced. Therefore, at resonant, the photon energy of the emitted electric fields equals to the band gap.

We emphasize this equation differs from the formula for vibrational sum frequency generation (VSFG)^{4,41-50}, in which one of the two incoming pulses are tuned in resonant with molecular transitions. First, all states are electronic states and the contribution from vibrational states are treated implicitly. Second, in a typical VSFG case the hyperpolarizability term corresponds to Raman transition³⁹, where for ESFG, the hyperpolarizability represents two photon absorption process, as firstly pointed out by Moad and Simpson.³⁸ Last, the light-matter interaction sequences differ in VSFG and ESFG. In ESFG, the two photon absorption-like light-matter interactions first populate the electronic coherences and then the SFG signal is emitted through a

dipole interaction and relaxes the systems from excited coherence state to ground electronic states; In VSFG, a vibrational coherence is excited first, followed by the Raman-like process. We note that in either ESFG or VSFG processes, only coherence states are excited.

To demonstrate our method, we investigate the prototype interfaces of hybrid organic/inorganic photovoltaics composed by poly(3-hexylthiophene-2,5-diyl) (P3HT) and n-doped Si (111).⁵¹ Although P3HT is a well-studied organic semiconductor, a fundamental understand of its bandgap and electronic structure at buried interfaces is still far from being complete. Here we show that ESFG can provide insights on both the band gap and the electronic structure at interfaces. We focus on the regioregular (RRE) form of P3HT, which has all sidechains organized to minimize structural twist from steric effects. The P3HT/Si interfaces are prepared by spin coating onto Si substrate at 2000 rpm speed and 6mg/ml concentration. The thickness of P3HT film is determined to be ~150nm by profilometry. The P3HT/sapphire thin film sample is prepared by the same way, which is used to measure UV-Vis spectra. The UV-Vis is used to remove the reabsorption effects, and also to determine the absorption spectrum of bulk P3HT.

Results and Discussions

The ESFG spectra of RRE P3HT/Si and bare Si substrates are collected and compared in this work (Fig.1b). The ESFG spectra of RRE P3HT/Si and bare Si substrates show different intensities. In Fig.1b, ESFG spectra of both samples at $\lambda_{\text{NIR}}=1954$ nm indicate that the RRE P3HT/Si has larger ESFG signal than pure Si substrates. This indicates that the ESFG signals of P3HT/Si are dominated by the P3HT at P3HT/Si interfaces, since the ESFG signal from Si substrates is much smaller comparing to the P3HT/Si samples. The signal from Si is suppressed because the SSP polarization is used to suppress any non-resonance ESFG signal from Si.

To ensure the measured signal is from the ESFG process described by Eq.1, we also measure how the signal depends on the power of near IR beam. We control the power of near IR by a pair of waveplate and polarizer, where the polarizer defines the near IR beam polarization and we use the waveplate to control the portion of near IR beam that transmits through the polarizer. We find the measured signal depends on the near IR power linearly (Fig.2a), as described in Eq.1.

Figure 1. ESFG Feynman Diagram (a) and ESFG spectra (b) of regioregular P3HT on Si and bare Si surfaces. The regioregular P3HT on Si has stronger signal than bare Si, indicating the ESFG signal is generated from P3HT layers at the interfaces. The features at 2.22 and 2.23 eV in both spectra are originated from the near IR spectrum.

Next, to determine the interfacial band gap and its distribution, we investigate the ESFG intensity dependence on near IR frequency. We found both the ESFG emission photon energy and the intensity change as the near IR frequency is scanned (Fig.2b). The center frequency of ESFG emission directly matches with the sum of the frequencies of the near IR and the 800 nm beams, which indicates there are no competing processes such as relaxation from high energy manifolds^{7,51-54} or coherence transfer⁵⁵⁻⁵⁷ happening during the ESFG signal emission.

The ESFG intensity dependence on near IR frequency is a result of resonance enhancement, which serves as a measure of band gap transitions at the interface, as discussed in the Theory section. To quantify the resonant enhancement, we plot the ratio of ESFG intensities between P3HT/Si and gold surfaces (PPP polarized) as a function of the sum frequency of near IR and 800 nm beams²⁵. This analysis effectively removes intensity fluctuation of the near IR beam as it being tuned to different center frequency (see SI). The SFG intensity ratio is directly correlated to $|x_{eff}^{(2)}|^2$ of the P3HT/Si interfaces. As we discussed below, although there is no resonant absorptions for the incoming pulses, the emitted SFG signal can be reabsorbed by the bulk materials. Therefore, we normalized the ESFG signal by the transmission spectrum of the P3HT to remove effects from reabsorptions.

Figure 2. ESFG signal as a function of near IR wavelength and power. (a) The ESFG signal depends on the IR power linearly, which agrees with Eq. 1. (b) 2D plot of ESFG signal as a function of sum of incoming beam frequencies.

For RRE P3HT/Si sample, ESFG signals peak at 2.2 eV (Fig. 3b) and the signal is enhanced by 80%. Similar enhancement is seen in a previous SHG study on organic field-enhanced-transistor (OFET) composed by P3HT.⁵⁸ This enhancement is well above the instrumental uncertainty of

our measurement ($\pm 20\%$ fluctuation of the ratio between two nonresonance SFG signals from GaAs and gold surfaces, see Fig. 3a). We note that there is another small 20% enhancement at $\sim 2.12\text{eV}$, since it is on the margin of the instrumental uncertainty, we decide not to focus on this peak in details.

As shown in the section of theoretical background, the spectrum in Fig. 3b measures $|x_{eff}^{(2)}|^2$, which possesses many terms, including the electronic resonance and nonresonance terms of P3HT. Moreover, since the sum frequency of the two input pulses are well above the band gap of Si, which has continuous density of states, there should be a contribution $x_{Si}^{(2)}$ from the Si surface as well. Therefore, the measured spectrum should be fitted by⁵⁹,

Figure 3. ESFG intensity as a function of the sum frequency of incoming photons. (a) normalized intensity ratio between two nonresonant ESFG signals from GaAs and Au surfaces, which represents the noise level of the measurement. (b) normalized ESFG intensity ratio between P3HT/Si and Au. More than 80% of signal enhancement is seen at 2.2 eV. The RMSE of Lorentzian fit is 0.23, and is 0.33 for the Gaussian fit. (c) curve fitting breakdown of (b)

$$|x_{eff}^{(2)}|^2 = \left| x_{NR}^{(2)} + \sum_n x_{ijk,n}^{(2)}(\omega_{SFG}) \cdot e^{i \cdot \varphi_n} + x_{Si}^{(2)}(\omega_{SFG}) \right|^2 \quad \text{Eq. 3}$$

With at least three unknown $\chi^{(2)}$, it is difficult to get unique fittings. However, we can independently determine $\chi_{Si}^{(2)}(\omega_{SFG})$ by measuring and fitting the ESFG spectrum of Si surface (Fig. 3b). We fit the spectrum by a linear function, since the corresponding UV-Vis absorption of Si is approximately linear. Then $\chi_{Si}^{(2)}(\omega_{SFG})$ becomes a known parameter in Eq. 3. Since $\chi_{NR}^{(2)}$ is a constant, the fitting procedure is significantly simplified and more reliable. We can use one Lorentzian function as the $\chi_{ijk}^{(2)}(\omega_{SFG})$ term to fit our data well. The center of the Lorentzian is 2.199 ± 0.004 eV, with fwhm to be 0.014 ± 0.006 eV and phase to be $83 \pm 16^\circ$. Therefore it indicates only one electronic transition of P3HT is observed at the interfaces.

To understand the fitting result, we breakdown the fitting curves and plot them in Fig.3c. Overall, terms that give rise to the peak around 2.2 eV are cross terms $\chi_{NR}^{(2)} \cdot \chi_{ijk}^{(2)}(\omega_{SFG})$ and $\chi_{Si}^{(2)}(\omega_{SFG}) \cdot \chi_{ijk}^{(2)}(\omega_{SFG})$ and the intensity term $\left| \chi_{ijk}^{(2)}(\omega_{SFG}) \right|^2$. All three terms peak at the same position. The leading term that contributes to the lineshape is $\chi_{NR}^{(2)} \cdot \chi_{ijk}^{(2)}(\omega_{SFG})$. This term has an absorptive lineshape, not a dispersive lineshape, because the phase difference between the P3HT resonant and nonresonant signals is close to 90° . The term $\chi_{Si}^{(2)}(\omega_{SFG}) \cdot \chi_{ijk}^{(2)}(\omega_{SFG})$ has similar lineshapes, because $\chi_{Si}^{(2)}(\omega_{SFG})$ is close to constant. The intensity term $\left| \chi_{ijk}^{(2)}(\omega_{SFG}) \right|^2$ contains a small dip at 2.18 eV. Nevertheless, it is only $< 10\%$ than $\chi_{NR}^{(2)} \cdot \chi_{ijk}^{(2)}(\omega_{SFG})$ and therefore, does not cause large lineshape changes. The rest of terms are almost all constant, which contribute to the large offset in the ESFG spectrum. Overall, from the fitting we can conclude that there are no significant interferences among the P3HT nonresonant, resonant signals and Si signals that cause lineshape distortions in the spectrum.⁵⁹

Another possibility is to fit the peak into a Gaussian, which indicates that the electronic transition is inhomogeneously broadened. We replaced the Lorentzian function with a Gaussian and used it to fit the data. The fitting result well match the bandwidth, but failed to reproduce the sharp peak at 2.2 eV. Therefore, we conclude that Lorentzian can reproduce the lineshape better than Gaussian, which agrees with the root-mean-square-error (RMSE) of the two fitting functions (Fig.3).

It is possible there are two interfaces in the P3HT/Si samples that could contribute to the ESFG signals: the P3HT/Si and P3HT/air interfaces. We conclude the measured spectra are mainly contributed from the P3HT/Si, or even if the P3HT/air interface contributes a weak signal, its peak position is coincident with the P3HT/Si signal, for the following reasons. From a Fresnel factor calculation (see SI for details), we show that the ESFG electric field from P3HT/Si interface is 7 times of the one from the P3HT/air interface. Since the signal is homodyne detected, the ESFG signal from P3HT/Si is more than 50 times larger than the P3HT/air signal. In principle, there should be cross-term between the signals from P3HT/Si and P3HT/air, which would lead to interference on the measured spectrum. Since only one peak is observed in the ESFG spectrum, it is either that the signal from P3HT/air is even smaller than we estimate here and therefore do not contribute to the measured signal or it has similar spectral peak and shape, which does not complicate ESFG spectrum. This conclusion also agrees with many previous vibrational SFG works on similar P3HT/solid samples, which concluded that the signal are dominated by the P3HT/solid interfaces.^{1,2,4,60,61}

Figure 4. UV-Vis spectrum of the RRE P3HT film on sapphire. UV-Vis probes the bulk electronic structures of the P3HT, which is fitted into four Gaussians, indicating structural inhomogeneity. The position and fwhm (in parenthesis) of the four peaks are 2.041 ± 0.002 eV (0.14 ± 0.08), 2.202 ± 0.007 eV (0.30 ± 0.03), 2.45 ± 0.03 eV (0.55 ± 0.05) and 3.02 ± 0.04 eV (1.08 ± 0.07), respectively.

The ESFG spectrum appears to be significantly different from the corresponding UV-Vis spectrum (Fig.4) which probes the entire P3HT molecules in the bulk thin films. There are at least four peaks in the UV-Vis spectra. The first three are from various inter/intramolecular interactions or vibronic modes^{62,63}, where the long tail beyond 2.3 eV is attributed to oligomers that have short exciton delocalization⁶². Furthermore, all peaks are fitted into Gaussian lineshapes with fwhm between 0.14 to 0.30 eV (see SI), which indicates each peak is also inhomogeneous broadened. The fact that UV-Vis spectrum needs to be fitted into multiple broad Gaussian peaks indicates that there are a few different electronic structures of P3HT in bulk.

On the contrary, the single peak in ESFG is a clear indication that only one conformation dominates at the interface (there is also no peaks between 2.4 and 2.6 eV, see SI). Furthermore, the narrow Lorentzian lineshape indicates that this electronic structure at interfaces does not

subject significant inhomogeneous broadening, and the main lineshape broadening should be from electronic dephasing.

All of the ESFG spectral features indicate that the P3HT molecules have uniform electronic structures at the P3HT/Si interfaces, regardless the complexity of the P3HT electronic structures in the bulk. The uniform electronic structure distribution of P3HT on the Si interfaces indicates that order structures, such as crystallization, are formed at the interfaces. This ordered structure can allow the charges delocalized⁵¹ on the interfaces and also increase the carrier mobility in the two-dimensional plane.⁶⁴ Several previous results have pointed out extra delocalization can promote the charge separation at the interfaces.^{6,65} Furthermore, it has been shown that ordered structure at interfaces can prevent geminate recombination⁵¹ and mitigate bimolecular charge recombination.^{66,67} Therefore, all of these effects from ordered interfacial structures could lead to an increase in the short-circuit current, which improves the efficiency of the photovoltaics.

Our study demonstrates that the electronic structure measured from bulk thin film is not a good approximation to the electronic structures of interfaces. This finding agrees with previous works done on metal/metal oxide interfaces in vacuum^{16,17}, and suggests that the difference between bulk and interfaces is a ubiquitous phenomenon in many solid/solid interfaces. Therefore, interfacial specific methods need to be utilized to study buried interfaces under atmosphere.

Finally, we would like to emphasize that our approach of ESFG is robust for various sample conditions and the ESFG spectra interpretation is straightforward. First, by using two photon absorptions to reach the electronic states, we circumvented any distortions due to one photon absorption⁴⁰ of the input pulses from the bulk materials. For instance, for any SFG involved one photon absorption-like resonance, the incidence beams spectra can be distorted by absorption of the bulk materials. As a result, phantom peaks can be created.⁶⁸ In our two-photon-absorption

like resonance ESFG, neither of the incident pulse is absorbed by the bulk layer, and therefore largely mitigates the necessity to use ultrathin bulk materials in the experiments. The sample still needs to remain thin to avoid the reabsorptions of the emitted SFG signal, which could be on resonance with the bulk materials. Second, we simplify the spectroscopic interpretation by avoiding any vibrational resonances. By purposely using non-resonance near IR beam as one of the two excitation beams, spectral phase twists are avoided, which exist when both electronic and vibrational resonances are met in SFG^{40,69}.

In conclusion, we for the first time demonstrate that electronic sum frequency generation can determine the electronic structure of organic polymers at buried solid/solid interfaces. Since the optical beams have a long penetration depth, and do not require special conditions such as UHV, we anticipate broad applications of the electronic sum frequency generation spectroscopy to many complex buried interfaces, especially at the device working conditions in the near future.

Supporting Information. Data analysis method, additional ESFG data and data fitting details are available in the supporting information.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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