Investigation on an optically-controlled phase-shifter based organic semiconductor poly-(3-hexylthiophene) (P3HT)

Hongyan Tang, Feifei Zhao, Fuyun Zhang

School of Electronic Engineering, University of Electronic Science and Technology of China, Chengdu, China, 610054
hongyan.tang@gmail.com

Abstract. In this paper, an investigation on optically-controlled phase-shifter based organic semiconductor P3HT is presented. The operation principle of optically-controllable phase-shifters and the applicability of organic semiconductor P3HT to such devices have been demonstrated. The reversible, optically-controlled phase-shifter employing P3HT as an active device layer, yielded differential phase shifts which varied with light intensity and signal frequency as well as device architecture. The results are non-optimized, and impedance matching needs to be improved in the future in order to obtain better signal transmission performance through the device.

1. Introduction
In the last couple of decades a significant amount of research has gone into optically controlling microwave and millimeter wave devices. Activity in the fields of lasers and photonics has led to such development. Research and development of photonic devices is driven by the need for dynamic control, fast response, immunity from electromagnetic interference and good isolation between the controlling and controlled devices [1]. Phase shifters, modulators, attenuators, slow wave structures etc, are some of the components of this important class of devices. The potential for the use of the optically-controlled phase-shifter in phased-array antenna systems lies in cost effectiveness, its low weight and low power consumption [2].

2. Organic semiconductor for optical techniques
Optical techniques offer the following advantages: 1) near perfect isolation, 2) low static and dynamic insertion losses, 3) fast response, 4) high power handling capability, 5) when nanosecond pulses are used, it is possible for very high density plasmas to be injected without damaging the material, 6) by a proper choice of semiconducting material and laser wavelength one can generate plasma with any desirable density distribution and at any desired time, 7) ultra fast switching and gating of microwave and millimeter-wave signals are possible, and 8) using nanosecond exciting-probing techniques, the dynamic evolution of the injected plasma can be studied in detail. Parameters related to transport properties of the carriers can be accurately determined.

The operating principle of these devices is photo-excitation. When a semiconductor substrate is being illuminated by the light source whose photon energy is greater than the bandgap energy of the semiconductor material, plasma (electron-hole pairs) is induced near the surface of the medium due to photo-absorption by the semiconductor [3]. The photo-excited carriers can change the propagation
characteristics of the electromagnetic signals being propagated through the photo-illuminated semiconductor.

Organic semiconductors bring together the virtues of plastics and semiconductors in materials. This opens up new directions for electronic and optoelectronic materials. They have many advantages, such as easy fabrication, mechanical flexibility, tunable optical properties and low cost; therefore have outstanding potential for emerging technologies. There are a large number of applications for organic semiconductors, for instance organic light-emitting diodes (OLED), organic solar cells, organic field effect transistors (OFET). In the future, a number of new exciting developments are foreseeable.

3. Phase shifter employing P3HT/ITO

Organic semiconductor polymers have been the focus of many studies because they have shown promise for many applications such as organic solar cells, flexible display technology and radio frequency identification tags. Among various types of polymeric semiconductors, regioregular P3HT is the most explored due to its wide commercial availability and high carrier mobility [4]. The optically-controlled phase-shifters that have been reported so far were composed of conventional inorganic semiconductors like Si. In this section an optically-controlled phase-shifter comprised of organic semiconductor P3HT on an indium tin oxide (ITO) covered substrate is investigated.

3.1 Characteristics of Regioregular P3HT

The physical form of P3HT is dark brown to black power. Different processes and conditions for polymerization of 3-hexylthiophene may give rise to either regioregular P3HT (RR-P3HT) or regiorandom P3HT (RRa-P3HT) [5]. The degree of order in polymer films can have a drastic effect on both absorption properties and charge transport. This has fundamental effect on the absorption. The absorption peak for RR-P3HT is shifted to lower energies and shows more vibronic structure, all indicative of a higher degree of polymer chain ordering. It is clear that good ordering is essential for achieving high transport performance. It has also been demonstrated that the RRa-P3HT excitations consist primarily of intra-chain excitons, whereas RR-P3HT has a larger inter-chain component. Based on these advantages, RR-P3HT has much wider applications than RRa-P3HT. In this section, P3HT refers to RR-P3HT thereafter.

In recent years the potential application of P3HT in polymer electronics and optoelectronic applications, such as light emitting diodes, optical devices, solar cells etc, has gained significant attention [6]. The reason is its good spectral overlap with optical-wavelength irradiation, high charge-carrier mobility as well as having a low bandgap [7]. These features are relatively stable in ambient condition and it has excellent solubility in common organic solvents.

P3HT has a high absorption coefficient close to the maximum photon flux in the optical spectrum, peaking between the blue green (450nm) and green yellow (600nm). The UV-VIS absorption spectra for a thin film of pure P3HT indicates two peaks at 493 nm and 517 nm and one shoulder at 572 nm. These three bands can be attributed to the transition from valence band to conduction band. Therefore a general white-light source is sufficient for optical applications without particular equipment requirement.

In terms of literature, P3HT has the highest charge-carrier mobility among the conjugated polymers [7]. Mobility here can be referred to the agile movement of holes. Hole-mobility is typically $10^{-4} \sim 10^{-1}$ cm$^2$ $(V\cdot s)$. The high mobility is mainly attributed to the formation of extended polaron states as a result of local self-organization, in contrast to the variable-range hopping of self-localized polarons found in more disordered polymers.

Another important characteristic of P3HT is its lower bandgap energy i.e. the energy difference between the bottom of the conduction band and the top of the valence band of the semiconductor material. The band gap of P3HT to be approximately 1.9 eV has been reported, with a conducting band of negative -5.4eV ($1eV=1.6 \times 10^{-19}$ J). These properties render P3HT a good candidate for the polymer in polymer-photovoltaic applications.
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P3HT also has excellent solubility in common organic solvents, for instance Toluene, Chloroform, Chlorobenzene, Cyclohexylbenzene (CHB) or TriChloroBenzene (TCB). It has been reported that when different types of solutions were used with P3HT during the fabrication process, every solution revealed different mobility characteristics. It was discovered that using high boiling-point solvents such as Trichlorobenzene could lead to a high degree of crystallinity and enhanced mobility. So TCB is chosen to be the solvent for P3HT in our experiments.

3.2 Operating principle

Phase-shifting is a fundamental control operation. A general approach to this operation is to alter the phase-velocity along a fixed interval of a guided medium. In this case, the phase-shift per-unit-length is equal to the change in the propagation constant of the traveling wave. One well-know method of altering the dispersion of the signal is to introduce plasma into the medium.

According to the optical properties of organic semiconductor P3HT (as well as many other advantages), optically-controlled phase-shifters employing P3HT as an active device layer, has been investigated. The schematic cross-section of the proposed structure is shown in figure 1. Al microstrip is vapor-deposited onto a P3HT coated ITO substrate supported by glass. When illuminated with a white-light source, having component energy greater than the bandgap energy of P3HT, an electron-hole plasma region will be induced (in the active region, near the surface). This leads to a complex permittivity different from that of the complex permittivity of the non-illuminated region. As a result, electromagnetic waves will have different propagation factors through these activated regions. These yielded differential phase-shifts which varied with light intensity and signal frequency as well as device architecture.

**Figure 1:** Schematic cross-section of the optically controlled phase shifter.

The plasma region is close to the region under the Al microstrip line as the microwave electromagnetic field is concentrated underneath the microstrip line and falls off sharply away from that region. The initial depth of plasma-injection is controlled by selecting an appropriate combination of irradiation wavelength and semiconductor absorption properties. At sufficiently small injection depths, the final thickness of the P3HT plasma is determined primarily by the processes of carrier diffusion and recombination. The effect of the plasma-occupied volume is to introduce a layer whose refractive index at the microwave frequency is larger than the remaining volume of P3HT. From simple physical arguments, one would expect the effect to become strong as one approaches and then exceeds the plasma density at which the value of the plasma frequency equals the frequency of the transmitted signal. However, the form and magnitude of the phase-shift versus the intensity of illumination (and hence the plasma density), depends in detail on the material and geometrical factors that characterize the optically-perturbed active structure. Their determination requires a detailed solution of the corresponding boundary value problem.

In the plasma region, the conductivity $\sigma$ is a function of the mobility and the density of charge carriers:

$$\sigma = e(\eta \mu_e + p \mu_p)$$

(1)
where \( n \) is electron concentration, \( p \) is hole concentration, \( \mu_e \) is electron-mobility and \( \mu_p \) is hole-mobility.

If the conductor loss factor of the P3HT is neglected, and optically induced plasma is assumed to be of infinite extent in the transverse direction, then an equivalent dielectric constant of the plasma occupied region is expressed as [1]:

\[
\varepsilon = \varepsilon_s - \sum_{i=e,h} \frac{\omega_p^2}{\omega^2 + \nu_i^2} \left( 1 + j \frac{\nu_i}{\omega} \right) = \varepsilon_r + j\varepsilon_i \tag{2}
\]

where \( \varepsilon_s \) is the dielectric constant of the host lattice, \( \nu_i \) is the collision frequency, \( \omega \) is the radian frequency, and \( \omega_{pi} \) is the plasma frequency given by

\[
\omega_{pi}^2 = \frac{N_p q^2}{\varepsilon_0 m_i^*} \tag{3}
\]

where \( m_i^* \) is the effective mass of electron and hole, and \( q \) is the electronic charge. \( \varepsilon_0 \) is the free-space permittivity, and \( N_p \) is the density of the plasma-excited by optical illumination.

Since a quasi-TEM mode is the dominate mode of the microstrip line, the differential phase shift is given by:

\[
\Delta\Phi = (\gamma_1 - \gamma_2)L \tag{4}
\]

where \( L \) is the length of illuminated transmission line, \( \gamma_1, \gamma_2 \) are the propagation constant of the propagating wave during and before illumination. Here propagation constant is a function of both conductivity and equivalent dielectric constant.

### 3.3 Experiments and Results

![Figure 2: The measured differential phase shift for sample with different power lever at frequencies of 2GHz and 3GHz: 34.7%, 50.1%, 77.3% and 100%](image-url)
Sample was fabricated for measurement. To measure the differential phase-shift with different power lever, three light filters were used to change the light intensity by 34.7%, 50.1% and 77.3%. Figure 2 gives the measured differential phase-shift for sample with different power lever at frequencies of 2GHz and 3GHz. Considering the 1V input signal at frequency of 2GHz, the amplitude of output is 109mV. The phase shift 3.2°/cm at 2GHz with energy of 90mW.

The reversible phase-shifts obtained by the two rudimentary devices presented here are comparable to phase shifts obtained using conventional silicon semiconductors and, given the lack of device optimization, very promising. They certainly demonstrate the principle of operation of optically controllable phase shifters and the applicability of organic semiconductors to such devices.

Qualitatively, one would expect a larger phase shift as one increases the signal dwell length/time over the illuminated dielectric and this is seen in the larger phase-shift obtained in sample A, which possessed the longer, meandering conductor, versus that obtained in sample B under otherwise identical conditions (figures 5.13b and 5.14b). Larger overall phase shifts can thus be obtained by increasing the length of the illuminated portion of the structure. As the charge carrier mobility of P3HT is currently less than 0.1 cm$^2$/Vs, which is much smaller than that of inorganic semiconductors (>100 cm$^2$/Vs), a relatively large power lever is needed to achieve the same phase-shift. Further development is needed to improve photo-coupling efficiency.

4. Conclusion
In this paper, an investigation on optically-controlled phase-shifter based organic semiconductor P3HT has been presented. The operation principle of optically-controllable phase-shifters and the applicability of organic semiconductor P3HT to such devices have been demonstrated. The reversible, optically-controlled phase-shifter employing P3HT as an active device layer, yielded differential phase shifts which varied with light intensity and signal frequency as well as device architecture. The results are non-optimized, and impedance matching needs to be improved in the future in order to obtain better signal transmission performance through the device.

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