The Impact of Thermal Annealing Temperature On The Low-Frequency Noise Characteristics of P3HT:PCBM Bulk Heterojunction Organic Solar Cells

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Abstract

We investigate the dark low-frequency noise characteristics of P3HT:PCBM bulk heterojunction organic solar cells in both forward and reverse bias conditions. The current noise power spectral density (S_I) is “1/f”-like and is compared among cells annealed at different temperatures (60 °C to 140 °C). The asymmetric relationship of S_I versus DC dark current (I_{DC}) can be explained by the competition between the recombination current noise and tunneling current noise. Among the different annealing temperatures, we find that higher annealing temperature yields smaller ratio of the Hooge parameter to the carrier recombination lifetime, which is reflected in the forward bias S_I versus I_{DC} relationship. We demonstrate that the low-frequency noise can serve as a non-destructive diagnostic indicator of the performance of organic solar cells.

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1. Introduction

Organic solar cells are promising renewable energy sources that can achieve low production cost and extremely high production rates [1,2]. Recent efforts have resulted in the highest power conversion efficiency of 10.7 % reported by Mitsubishi Chemical [3], and the performance continues to improve. However, many challenges to understanding the underlying physics remain, such as the exciton loss mechanism [4], carrier recombination, and charge transport mechanisms [5,6].

The poly (3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) bulk heterojunction (BHJ) organic solar cell is a polymer-based organic photovoltaic device that has been extensively studied. It is well known that the thermal annealing conditions during the fabrication of P3HT:PCBM cells have a significant impact on the device characteristics, such as absorption spectra, series resistance [7,8] and carrier mobilities [9]. Devices show better performance as the annealing temperature increases up to a certain level, usually between 110 °C and 160 °C depending on the fabrication conditions [8]. Studying the origin of such phenomenon will benefit the optimization of the fabrication organic solar cells. However, the traditional studies on the thermal annealing effect using current-voltage (IV) characteristics and atomic force microscopy (AFM) only reveal limited information related to carrier dynamics [8]. Additional methods can provide additional physical insights.

Understanding the low-frequency noise (LFN) in electronic devices, such as diodes [10,11] and transistors [12], has been an active topic since the 1950s [13,14]. The correlation of LFN to

material quality and device reliability has also made it a useful non-intrusive characterization tool [15–18]. Recently, LFN studies have also been extended to non-traditional materials and devices, such as nanowire transistors [19,20], graphene devices [21], organic light-emitting diodes [22], and organic thin-film transistors [23,24]. However, there are few reports on the noise measurements of polymer solar cells. Bag et al. correlated the LFN of P3HT:PCBM BHJ solar cells with light-induced degradation [25]. Landi et al. investigated the dark LFN noise of P3HT:PCBM BHJ organic solar cells and correlated the noise spectrum with trapping states of the materials [26]. Nevertheless, the understanding of the relationship between LFN and carrier transport is still largely incomplete.

In this paper, we study the dark LFN of P3HT:PCBM BHJ solar cells that are thermally treated at different annealing temperatures. The noise spectra of both the forward and reverse biased devices are measured and analyzed. In the forward bias, we show that the LFN level is proportional to the ratio of Hooge’s parameter to carrier recombination lifetime, and LFN is higher for devices annealed at lower temperatures. Under reverse bias, the noise mechanisms are more complex since another noise generating process (i.e., tunneling current noise) becomes prevalent. We also demonstrate that the low-frequency noise is a material quality indicator related to the device performance.

2. Material and Methods

The P3HT:PCBM organic solar cells were fabricated according to the following procedure: P3HT (from Rieke Metals) and PCBM (from American Dye Source) were dissolved and stirred

separately in chlorobenzene for 12 hours before being mixed and stirred for another 12 hours at room temperature. The density was 2 wt.% in total, composed of a ratio of 11:9 of P3HT to PCBM. Indium tin oxide (ITO)-coated glass substrates were ultrasonically cleaned with acetone, isopropyl alcohol, and de-ionized water and subsequently blow dried by compressed air. Highly conducting aqueous PEDOT:PSS (Clevious PH 500) solution was spin-coated onto the ITO substrates with a spin rate of 4000 rpm. The substrates were baked for 15 minutes at 120 °C in vacuum before another spin-coating of P3HT:PCBM blend with a spin rate of 900 rpm. After that, the 100-nm Al top electrode layer was thermally evaporated onto the blend. Finally, the samples were annealed at different temperatures for 30 minutes in vacuum before further tests. The active area of the devices was approximately 1 mm². The active layer thickness was 85 ± 5 nm as measured by a Veeco Dektak profilometer. The photovoltaic performance was characterized by a calibrated Oriel solar simulator, and the results are tabulated in Table 1. The dark current-voltage (IV) characteristics were measured with a Keithley 2400 source meter.

Table 1

Figure 1

Figure 1 shows the experimental setup of the low-frequency noise measurement. The dark current from the organic solar cell was first amplified by an SR570 low-noise transimpedance amplifier, which also provided the bias to the device under test. The device is placed in a metal case for measurement. The maximum bias voltage from the SR570 was ±5V, which was sufficient for our application (-1V to 1V depending on the dark current level). The output signal from the SR570 was passed through a high-pass filter, and then further amplified by a voltage

amplifier built from a low-noise operational amplifier. The SR570 amplifier was bandwidth limited below 10kHz or 2kHz depending on the gain. The 3dB cut-off frequency of the high-pass filter was 0.3Hz. The output voltage of the SR570 was kept below ± 1 V to ensure that the amplifier operated in the linear region. For the second amplifier, $C2 = 1$ nF, $R2 = 10$ k Ω and $R3 = 1$ k Ω . The amplifier showed stable behavior during a frequency sweep test up to 20kHz. Both amplifiers were powered by the ± 12 V batteries for better noise immunity. The final output signal was digitized by a National Instruments USB-6211 data acquisition unit. The current noise power spectra were calculated by Fast Fourier Transform (FFT). To smooth the noise power spectra, 100 FFT traces were averaged based on Welch's method [27,28] for each measurement. All of the measurements were done under room temperature. Although no systematic test on how the room temperature influenced the LFN was done, two identical measurements carried out with 10-hour interval showed very similar results.

3. Results and Discussion

Figure 2 shows the dark IV characteristics of four P3HT:PCBM organic solar cells annealed at different temperatures. Under low forward bias (below 0.5 V), the IV characteristics of the 110 °C and 140 °C samples follow the diode equation

$$I = I_0(e^{\frac{qV}{nkT}} - 1) \quad (1)$$

where I_0 is the reverse saturation current and n is the ideality factor. I_0 and n can be obtained by fitting the curves in Figure 2 to Equation (1) between $3kT/q$ and 0.5 V. We find I_0 and n to be $6.0 \times 10^{-8} \text{ A/cm}^2$ and 1.5, respectively, at 110 °C, and $2.7 \times 10^{-8} \text{ A/cm}^2$ and 1.8 at 140 °C. The IV characteristics of the devices annealed at 60 °C and 95 °C are symmetric in the low forward and reverse voltage range. This is an indicator of significant shunt leakage current, which is common in organic solar cells [29]. Since the IV characteristics deviate from Equation (1), I_0 and n were not calculated for the two lower temperatures.

Figure 2

Figure 3 shows four measured LFN spectrum examples for the four different annealing temperatures. All measured LFN curves are higher than the reference noise tested with a 1 MΩ resistor, which shows negligible LFN in the frequency range of interest. A general expression for the current noise power spectral density (PSD) S_I has the form

$$S_I \propto \frac{I_{DC}^\gamma}{f^\beta} \quad (2)$$

where I_{DC} is the DC current level, β is usually between 1 and 2 for “1/f”-like spectra on different devices and operating conditions [16,30], and γ determines the relationship between S_I and I_{DC} .

Figure 3

To compare the LFN of different devices, the current noise PSD at 10 Hz (S_{10}) is plotted against I_{DC} in Figure 4. The fitted γ values are listed in Table 2. Two distinctive features are observed: for 60 °C and 95 °C, the $S_{10} \sim I_{DC}$ relationship is almost linear (γ close to 1) and S_{10} is relatively symmetric for the forward and reverse bias; for 110 °C and 140 °C, however, γ is close to 1 in forward bias and close to 2 in reverse bias, and S_{10} is asymmetric for forward and reverse bias. The origin of this phenomenon can be explained in terms of the competition between generation-recombination (G-R) current noise and tunneling current noise which will be elaborated later.

Figure 4

Table 2

Although there is still some disagreement on the origin of the low- frequency noise (LFN) in electronic devices, mobility fluctuation [31–33] and number fluctuation [13,14] are two of the leading theories that can explain significant subsets of the observations thus far. It is instructive to fit the LFN results of P3HT:PCBM BHJ solar cells to the theory of number fluctuation, which has as its origin from carrier trapping or surface recombination. The superposition of Lorentzian distributions in the frequency space as the result of carrier trapping can yield “1/f”-like noise spectra [18]. However, this will result in $\gamma \approx 2$ regardless of bias conditions [34], which contradicts our observations in the forward bias. The origin of 1/f noise has also been attributed to surface recombination [35]. However, the planar structure of BHJ solar cells does not have an

exposed open surface area that can greatly influence the charge transport. It follows that number fluctuation does not apply to the BHJ devices structure studied in this work. Kleinpenning modeled the LFN generation in p-n junction diodes by extending Hooge's empirical law [32] to inhomogeneous media and derived formulas showing linear relationship between S_I and I_{DC} in the low voltage range [10,11]. Here we use Kleinpenning's model to explain some aspects of the LFN results in Figure 4.

We choose Kleinpenning's formula for G-R limited current because the calculated ideality factors are closer to 2 than 1. In this scenario, the current noise PSD of P3HT:PCBM cells can be expressed as follows [10]:

$$S_I = \frac{\alpha_H c q I_{DC}}{f \tau_r} \quad (3)$$

where α_H is the Hooge parameter, I_{DC} is the DC dark current in Equation (1), τ_r is the carrier recombination lifetime, and $c=2/3$ when the current is dominated by G-R [11]. Equation (3) can explain the 60 °C and 95 °C data in Figure 4 very well: $\gamma \approx 1$ and S_{I0} is symmetric in forward and reverse bias. However, for the 110 °C and 145 °C data S_{I0} is unambiguously larger in reverse bias, and scales quadratically with I_{DC} . This suggests that there is another noise source that dominates in reverse bias but not for forward bias. The asymmetry in the noise characteristics was also observed in other material systems such as quantum well photodetectors [36].

Although the reverse current of P3HT:PCBM organic solar cells could increase rapidly beyond a specific electric field value (larger than 5×10^7 V/m according to Ref. [38]), there is still no report on associating such current breakdown to the carrier avalanche. Instead, in Ref. [38], it was reported that the tunneling current can be the major effect in the reverse bias. Therefore, we

believe impact ionization may not play a major role in the reverse bias for P3HT:PCBM organic solar cells.

We attribute the excess LFN in the reverse bias from devices annealed at 110 °C and 140 °C to the tunneling current noise. While the total dark current in diodes may consist of diffusion, generation-recombination, shunt leakage, and tunneling, only the tunneling current, which increases with the electric field [37,38], is significantly larger in the reverse bias than forward bias. The thin active layers of the P3HT:PCBM devices favor a tunneling mechanism. In fact, trap-assisted tunneling [39,40] is probable since organic solar cells are known to have high densities of localized states. Previous work has shown that the tunneling current noise PSD generally has $\gamma \approx 2$ for planar devices [41–43]. When the device is under forward bias, the current noise arises primarily from the recombination current so that $\gamma \approx 1$. However, the tunneling current noise dominates the recombination current noise in the reverse bias for the 110 °C and 145 °C devices, which drives γ close to 2. At the same time, $\gamma \approx 1$ in the reverse bias for the 60 °C and 95 °C data indicates that the magnitude of the tunneling current noise may still be less than the recombination current noise owing to the higher degree of material disorder which facilitates recombination in the active layer.

However, the difference in the tunneling current noise is less obvious among the four different temperatures. From Figure 4, the magnitude of LFN in the reverse bias for the 60 °C and 95 °C devices where the tunneling current noise is not prevalent is no larger than the 110 °C and 145 °C devices where the tunneling current noise dominates. It follows that there is at least no significant reduction in the tunneling current noise when the annealing temperature increases. While the improved morphology as a result of higher annealing temperature should yield less

pronounced trap-assisted tunneling, in fact, the tunneling current is also related to other factors such as the material band structure and the carrier effective mass [37,38]. While there have been few studies on how the carrier effective mass changes with the annealing temperature, it is observed that thermal annealing modifies the band structure of P3HT:PCBM films manifested by the red-shift in the absorption spectrum [7]. Therefore, higher annealing temperature does not necessarily result in lower tunneling current noise. Future work is required to understand the physical details of the relationship between the tunneling current noise and thermal annealing.

It is widely acknowledged that the thermal annealing of BHJ organic solar cells improves the crystallinity of the active layer, which further influences the absorption spectrum, series resistance [7,8] and charge transport properties such as the charge carrier mobilities [9] and lifetimes [44]. While the traditional methods such as current-voltage (IV) characteristics and atomic force microscopy (AFM) only provide qualitative and mingled insights [8], the LFN characteristics provide a clear indicator of carrier transport properties. The current noise PSD in the forward bias can be related to the ratio of the Hooge parameter α_H to the carrier recombination lifetime τ_r as shown in Equation (3). It is known that the value of α_H varies with type of material, and a low-value α_H usually indicates better material quality and higher device reliability [16,45]. Thermal treatment of BHJ devices usually results in increased τ_r [44]. Figure 5 plots the α_H / τ_r ratio versus annealing temperature. Note that α_H / τ_r is three orders of magnitude less for the 140 °C-annealed device compared to the device annealed at 60 °C. This is consistent with the observation that P3HT:PCBM devices thermally treated beyond the glass transition point have better photovoltaic performance compared to those annealed at low temperatures as shown both in Table 1 and literature [7]. There is still no report on whether α_H is also a function of the annealing temperature for P3HT:PCBM BHJ solar cells. To extract the carrier lifetimes

from the LFN results, the quantitative relationship between the Hooge's parameter and annealing temperatures could be the subject of future work.

Figure 5

The LFN measurement has the potential of being applied in organic solar cell manufacturing and device optimization. Although the power conversion efficiency is the ultimate benchmark of solar cells, it lacks the details that are beneficial for optimization of device performance. The underlying physical parameters such as carrier lifetimes provide the guidelines for device optimization. Compared with other methods used to measure carrier lifetimes such as transient photoconductivity method [6,46,47], the transient photovoltage method [48,49], impedance spectroscopy [50] and time-resolved vibrational spectroscopy [51], the LFN measurement has the advantage of being compact and not requiring sophisticated test equipment in the experimental setup. It can potentially be integrated as part of a more comprehensive testing system.

4. Conclusion

In conclusion, we have studied the low-frequency noise characteristics of P3HT:PCBM bulk heterojunction organic solar cells in the dark condition. We find that the relationship between the current noise power spectral density and DC current level can be well explained by the competition between the recombination current noise and tunneling current noise. The interpretation of the noise characteristics is consistent with previous knowledge on the

performance of the devices annealed at different temperatures. This work demonstrates a useful approach to understanding the underlying physics of organic solar cells.

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Temperature (°C)	Voc (V)	Jsc (mA/cm ²)	FF	PCE
60	0.56	6	0.39	1.3%
95	0.58	6	0.39	1.3%
110	0.60	8	0.45	2.2%
140	0.62	8	0.49	2.4%

Table 1: Open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF), and power conversion efficiency (PCE) of P3HT:PCBM BHJ solar cells annealed at 60 °C, 95 °C, 110 °C and 140 °C.

Temperature (°C)	γ , forward bias	γ , reverse bias
60	1.0	1.2
95	1.2	1.2
110	0.8	1.7
140	0.8	1.7

Table 2: The fitted γ in Equation (2) for devices annealed at different temperatures.

Figure 1: The circuit diagram for the low-frequency noise measurement. The bias on the devices under test is applied from the SR570 amplifier. C1 and R1 make a high-pass filter with 3dB cut-off frequency of 0.3 Hz. C2=1 nF, R2=10 k Ω , and R3=1 k Ω .

Figure 2: The dark current-voltage characteristics of four P3HT:PCBM devices annealed at 60 °C, 95 °C, 110 °C and 140 °C.

Figure 3: Four LFN spectrum examples under forward bias. The system noise is tested with an 1M ohm resistor. The measured “1/f” slope is around 1.5.

Figure 4: Current noise power spectral density at 10 Hz (S_{10}) versus forward and reverse DC dark currents of devices annealed at different temperatures.

Figure 5: The ratio of the Hoge parameter to the carrier recombination lifetime as a function of the annealing temperatures. All values are calculated at $I_{DC} = 1 \times 10^{-7}$ A in the forward bias.