Effects of microwave-assisted annealing on the morphology and electrical performance of semiconducting polymer thin films

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A R T I C L E   I N F O  
Article history:  
Received 2 October 2015  
Received in revised form  
22 December 2015  
Accepted 26 December 2015  
Available online xxx

Keywords:  
Microwave annealing  
Organic field-effect transistors  
Poly(3-hexyl)thiophene  
Diketopyrrolopyrrole-selenophene vinylene selenophene

A B S T R A C T  
Organic field-effect transistors (OFETs) based on p-channel polymer semiconductors such as poly(3-hexyl)thiophene (P3HT) and 30-diketopyrrolopyrrole-selenophene vinylene selenophene (30-DPP-SVS) were fabricated using a microwave (MW) irradiation process for thermal annealing. The influence of MW annealing was investigated based on microstructural characterizations such as X-ray diffraction (XRD) and atomic force microscopy (AFM). MW annealing not only shortened the annealing time, but also produced enhanced device performance including higher on/off ratio, lower threshold voltage, and higher field-effect mobility in comparison with the traditional annealing method. These microstructural analyses revealed that annealing by MW irradiation enhances the crystallinity and molecular orientation in the polymer thin films in a short time, thereby improving the electrical performance effectively. Our results suggest that MW-assisted annealing is a simple and viable method for enhancing OFET performance.

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1. Introduction  
Traditional heating methods, such as the hot plate (HP) annealing, are rather slow and transfer energy inefficiently. Because HPs depend on the convection currents and the thermal conductivity of the materials which must be penetrated, the temperature of the reaction vessel is higher than that of the materials [1]. In contrast, microwave (MW) irradiation produces efficient internal heating by direct coupling of MW energy with the molecules, and thus heats the reactants much more quickly than conventional methods in organic synthesis [2]. Reactions that usually take hours can be done in just a few minutes. Other reactions have higher selectivity, producing more of the desired molecule instead of by-products [3]. Because some reactions can even be performed in just water or without a solvent under MW irradiation, some researchers have used MW irradiation in the pursuit of ‘green’ chemistry [4]. MWs also have the useful property of heating some materials while leaving others cold. MWs cause free ions or electrons to move in the same direction due to the high-frequency electric field, while polar molecules, like water, which have an uneven distribution of electrical charge, are forced to wobble by the applied field forces. Both of these effects can generate heat; however, other materials do not respond strongly to the field and remain cool [5]. The heat generated by MWs arises by two main mechanisms: dipolar polarization and ionic conduction. Charged particles in the sample (usually ions) are affected by ionic conduction, while the dipoles in the materials are involved in the dipolar polarization effect [6]. Under MW irradiation, the dipoles or ions of the sample align in the applied field. They will realign with the alternating electric field when the applied field oscillates and energy is lost in the process, in the form of heat, through molecular friction and dielectric loss. Some studies on MW-assisted annealing have assessed improving the crystallization of amorphous silicon [7]. The behavior of conjugated polymers under MW irradiation [8,9] and the application of MW annealing to enhance the efficiency of polymer organic photovoltaic (OPV) devices have been reported [10]. Moreover, MWs have also been used widely in solid-state inorganic materials [11] and environmental engineering [12]. In addition, MW irradiation was even used for chiral discrimination [13,14].

Recently, the electrical performance of organic field-effect
transistors (OFETs) has greatly improved and a number of organic semiconductors exhibit high charge carrier mobility comparable to that of amorphous silicon FETs [15–23]. Annealing the semiconductor layers is of great importance for the fabrication of high performance OFETs because the molecular packing order in films and the contact between the organic semiconductor and the gate insulator are generally both improved after annealing [24]. One paper on a low-temperature solution-processable ZnO thin-film transistor using MW-assisted annealing has been published [25]. However, reports on the application of MW annealing to OFETs are still very rare.

In this work, we report the effects of MW annealing on the electrical performance of OFETs based on polymer semiconductors. Two kinds of p-channel polymer semiconductors, i.e., poly(3-hexyl) thiophene (P3HT) and 30-diketo-pyrrolopyrrole–selenophene vinylene selenophene (30-DPP-SVS), were chosen as a representative polymer semiconductor and a high-performance polymer semiconductor, respectively. The influence of MW annealing was investigated using microstructural characterizations and electrical performance measurements of the annealed films. The results obtained herein reveal that annealing by MW irradiation enhances the crystallinity and molecular orientation in the polymer thin films and thereby effectively improving the electrical performance of polymer-based OFETs. Our findings demonstrate that MW annealing is a promising tool for enhancing the crystallinity of conjugated polymer-based thin films and has great potential to be widely used in the organic electronics field.

2. Experimental section

2.1. Thin film preparation

Poly(3-hexyl) thiophene (P3HT, Mₙ = 85,000 g mol⁻¹, 4 mg mL⁻¹) and 30-diketo-pyrrolopyrrole–selenophene vinylene selenophene (30-DPP-SVS, Mₙ = 385,000 g mol⁻¹, 2 mg mL⁻¹) [26] were dissolved in chloroform and chlorobenzene, respectively. Polymer thin films were prepared by spin-coating onto an n-octadecyl-trimethoxysilane (OTS)-treated SiO₂/Si wafer at a speed of 3000 rpm for 60 s. For OTS self-assembled monolayer (SAM) treatment [27–30], 3 mM OTS solution in trichloroethane was spin-coated onto the piranha-cleaned SiO₂/Si wafer at the speed of 3000 rpm for 30 s. Then, the wafer was exposed to ammonia vapor for approximately 12 h to facilitate the formation of OTS SAM, followed by sonication cleaning, sequential washing, and drying. The contact angle on the hydrophobic OTS-modified wafer with a droplet of deionized (DI) water was greater than 106°.

The polymer films were subsequently annealed using MWs or the HP. In the case of MW annealing, the MW oven used had pursed output power of 800 W. The polymer film-coated substrate was placed in a glass Petri dish and the device was irradiated with MWs. The surface temperature was measured with commercial thermocouples immediately after taking the devices out of the MW oven. When only the glass Petri dish without a wafer was irradiated with MW for 1 min, the temperature increased to 80 °C. The surface temperature was verified with a thermocouple in contact with the samples. The measured temperatures were 120, 140, and 180 °C after MW irradiation for 1, 3, and 5 min, respectively.

2.2. AFM characterization

An Agilent 5000 (Agilent, USA) scanning probe microscope (SPM) equipped with a Nanoscope V controller was used to obtain AFM images of P3HT thin films. AFM images were recorded in high-resolution tapping mode under ambient conditions.

2.3. FET fabrication and testing

FET devices with bottom-gate top-contact configuration were prepared to characterize the electrical performance of the MW and HP annealed polymer thin films. A highly n-doped (100) Si wafer (ρ<0.004 Ω cm) with thermally grown SiO₂ (300 nm, Cₒ = 10 nF cm⁻²) was utilized as the substrate and dielectric. The surface of SiO₂ was modified with OTS SAM. The polymer solution was spin-coated on the substrate. Then the polymer films were annealed with either MW or HP. After preparing thin films, gold contacts (40 nm) were thermally evaporated onto the polymer film to form source and drain electrodes with a channel length (L) of ~50 μm and a channel width (W) of ~1000 μm using a shadow mask. The electrical performance of polymer thin film FETs was measured in a N₂-filled glove box using a Keithley 4200 semiconductor parametric analyzer. The field-effect mobility was calculated in the saturation regime using the following equation:

\[ \mu_{\text{sat}} = \frac{W}{2L} \frac{1}{C} \left( \frac{V_{\text{GS}} - V_{\text{T}}}{T^{2}} \right) \]

where \( I_{D} \) is the drain-to-source current, \( W \) and \( L \) are the semiconductor channel width and length, respectively, \( \mu \) is the mobility, and \( V_{\text{GS}} \) and \( V_{\text{T}} \) are the gate voltage and threshold voltage, respectively.

3. Results and discussion

3.1. Microstructural analysis of polymer films

To investigate the MW annealing effects on organic semiconductors, a well-known p-channel polymer semiconductor P3HT was selected for our experiment because it exhibits large variation in FET mobility before and after HP annealing [31]. Conventional HP annealing at 150 °C for at least 10 min (usually, 30 min) improves the charge transport properties. This effect has been attributed to increased crystallinity of the P3HT. To compare the MW and HP annealing-induced enhancement of electrical properties, we prepared P3HT thin films by spin-coating P3HT solution in chloroform (4 mg mL⁻¹) on OTS-modified SiO₂/Si substrates for film uniformity.

Because the annealing process changes the thin film crystallinity, we performed out-of-plane X-ray diffraction (XRD) analysis of P3HT films to investigate the molecular packing and crystallinity and to determine the optimal MW treatment time. P3HT thin films were treated with MW annealing (1, 3, and 5 min) and HP annealing (150 °C for 30 min). The surface temperatures of SiO₂/Si substrates were measured after MW irradiation, and maximum temperatures of approximately 120, 140, and 180 °C were measured after 1, 3, and 5 min of MW treatment, respectively. Fig. 1 shows the out-of-plane XRD patterns of the MW-annealed and HP-annealed P3HT thin films. A well-defined (100) reflection peak was observed at 2θ = 5.4° (16.35 Å) in the 5-min MW-annealed film, while the as-cast and other MW annealed P3HT films exhibited relatively weak and broad diffraction peaks at the same position. This result may be attributable to the different degrees of crystallization in the films induced by the temperature increase of the substrates under various MW irradiation time. These results substantiated the effects of MW short-time annealing (5 min) on P3HT film, which showed enhanced film crystallinity versus that fabricated by HP with longer annealing time (150 °C for 30 min).

To further investigate the effect of MW annealing on the thin-film morphology, the surfaces of the MW- and HP-annealed films (150 °C for 30 min) were analyzed using tapping-mode AFM. Fig. 2 shows the AFM height and phase images (2 μm × 2 μm scan) of 3-
min MW-annealed, 5-min MW-annealed, and HP-annealed P3HT films. The 3-min MW-annealed film exhibited a similar morphology to the surface of HP-annealed P3HT film with nanoscale granules distributed over the surfaces. The 5-min MW-annealed film showed a nanofibrillar morphology in an ordered crystalline lamellar structure, which differed from the morphologies observed in 3-min MW-annealed and HP-annealed samples. This result corresponds to the sharp crystalline peak of 5-min MW-annealed film, which was observed in the XRD analysis (Fig. 1).

3.2. Fabrication of solution-processed FETs and I–V characterizations

To investigate the charge transport properties of the MW- and HP-annealed P3HT films, a series of field-effect transistor (FET) devices based on P3HT thin films were fabricated in bottom-gate top-contact geometry. Experimental details are included in the Experimental Section. The P3HT-FETs exhibited typical p-channel characteristics and average I–V characteristics were obtained from more than 10 devices. For comparison, we fabricated devices simultaneously under 1, 3, and 5 min of MW or HP annealing. The FET performances of devices fabricated using the conventional HP annealing method (150 °C for 30 min) were also investigated. The electrical performances of FETs based on MW- and HP-annealed films are summarized in Table 1. Fig. 3 shows transfer curves, the average field-effect mobilities, and on/off ratio variations with standard deviation values obtained from MW- and HP-annealed P3HT films. Without annealing, the P3HT FET exhibited a hole mobility of 0.018 ±0.0063 cm² V⁻¹ s⁻¹, which is consistent with previously reported hole mobilities of pristine P3HT film [31]. After MW annealing treatment, gradually increased hole mobilities of 0.027 ±0.0052, 0.063 ±0.001, and 0.11 ±0.015 cm² V⁻¹ s⁻¹ for P3HT FETs under 1, 3, and 5 min of MW annealing, respectively, were observed. After MW annealing for 7 min, the electrical performance was degraded, possibly due to the thin-film over-heating issue (the device temperature increases up to 230 °C). Furthermore, the MW system showed much better electrical performance with higher on/off ratios and lower Vth values.

Three minutes of MW radiation was sufficient to yield high device performance comparable to the HP annealed devices. This enabled to reduce the thin-film annealing time by 60–90% (from 10 to 30 min for HP annealing to 3 min for MW annealing). After 3 min of MW annealing, the surface temperature of the thin film reached approximately 140 °C; thus, hole mobility similar to that of HP-annealed (150 °C for 30 min) P3HT-OFETs could be observed. This demonstrated that MW annealing of p-channel polymers is an effective method to develop thin film crystallinity to enhance electronic properties within short time.

Among the films obtained by MW treatment, the 5-min MW-treated P3HT films exhibited the highest mobility with values up to 0.13 cm² V⁻¹ s⁻¹ due to the well-developed film morphology with a higher surface temperature (180 °C) after 5 min of MW annealing. Typically, a fibrillar morphology is more favorable than a grain-like morphology for charge transport [31]. The longer MW treatment was also highly effective in making the films more crystalline, consistent with the results from XRD and AFM analyses.

Furthermore, we found increased on/off ratio values in OFET performance that were approximately two orders of magnitude higher for MW annealing than for HP annealing. FETs based on MW-annealed thin films showed high on/off ratios, which might be attributable to the much faster heating process, which offers more uniform heat distribution with uniform internal heating (in core volumetric heating) by direct coupling of MW energy with the molecules in solvents [Fig. 3c] [6]. Such fast heating process might be comparatively more helpful for preventing the diffusion of oxygen to the semiconductor channel [32,33]. A lower off-current is important for efficient FET operations, in order to reduce unwanted power dissipation [34].

We further investigated the effect of MW annealing with OFETs based on 30-DPP-SVS [26], another p-channel polymer which shows high mobility and on/off ratios under conventional HP annealing. To establish that MW annealing can be a powerful tool and can be used widely for organic semiconductor film annealing, we conducted an additional experiment. Before analyzing FET characteristics, changes in film crystallinity were also monitored using XRD. The 30-DPP-SVS thin film was used to investigate the degree of molecular packing. Fig. 4a shows a sharp XRD peak at 2θ = 3.3° (26.74 Å) and increased thin film crystallinity of MW-annealed 30-DPP-SVS thin film in order of increasing MW treatment time from 1 to 5 min, similar to the P3HT thin films. This confirmed that the MW annealing method is feasible as another annealing tool in polymer semiconductor thin-film processing.

In addition, we evaluated OFET characteristics to investigate the effect of MW annealing on 30-DPP-SVS thin films. Transfer curves of OFETs based on MW-annealed and HP-annealed 30-DPP-SVS films are shown in Fig. 4b. After MW annealing, we observed gradually increased FET mobility and on/off ratios of 30-DPP-SVS FETs (Fig. 4c, d, and Table 2). The hole mobilities for devices based on MW-annealed 30-DPP-SVS films were found to be 2.69 ±0.31, 3.21 ±0.40, and 3.68 ±0.42 cm² V⁻¹ s⁻¹ after 1, 3, and 5 min of irradiation, respectively. Under MW annealing for 7 min, the electrical performance deteriorated as similar to the P3HT FETs. In contrast, a FET based on HP-annealed 30-DPP-SVS films showed hole mobilities of 1.44 ±0.32, 1.54 ±0.49, and 1.88 ±0.40 cm² V⁻¹ s⁻¹ for 1, 3, and 5 min, respectively. With an annealing time of 10 min, a value of 3.15 ±0.81 cm² V⁻¹ s⁻¹ was reached. Notably, the hole mobility for a 1-min HP-annealed 30-DPP-SVS FET was 1.44 ±0.32 cm² V⁻¹ s⁻¹, while the value measured for a device treated with 1 min of MW annealing was approximately 1.5 times higher with a value of 2.69 ±0.31 cm² V⁻¹ s⁻¹. These results demonstrate clearly that polymer film can be annealed effectively in a shorter time by MW annealing without loss of critical structural or electronic properties. Furthermore, the on/off ratio can be enhanced by MW annealing. The electrical performance of FETs
annealed with 5 min of MW irradiation was comparable to that of the FETs fabricated using HP annealing (180 °C for 10 min). The FET mobility and on/off ratio variation of 30-DPP-SVS FETs as functions of MW and HP annealing time indicated that MW irradiation can be used effectively as an annealing tool and can shorten the processing time compared with conventional heating (Fig. 4c). This MW annealing method is promising because it does not require long processing time (conventionally at least 10 min), while it enhances film crystallinity and improves electrical properties. Furthermore, MW annealing method can be applicable to FET fabrication on plastic substrates possessing high enough glass transition temperatures. Another supporting substrate with high thermal conductivity can be introduced for effective annealing, when considering the less MW absorption and low thermal conductivity of conventional plastic substrates [35]. Our experimental results demonstrated that MW annealing can be a useful way to anneal conjugated polymer thin films with advantages of reduced overall thin film preparation time and improved device performance compared with conventional heating methods.

Fig. 2. AFM height and phase images of (a,b) 3 min MW annealed, (c,d) 5 min MW annealed, and (e,f) 150 °C for 30 min HP annealed P3HT films on OTS-treated SiO$_2$/Si substrates. The scale bars represent 500 nm.
4. Conclusion

In this work, we demonstrated that the MW annealing on $p$-channel polymer semiconductors can improve device performance and shorten the thin film annealing time, both of which are difficult to achieve using short-time HP annealing. With 5 min of MW irradiation, the surface temperature can rise to approximately 180 °C providing an excellent annealing effect for both P3HT and 30-DPP-SVS thin films. For P3HT, 3 min of MW irradiation was sufficient to achieve high electrical performance, however, a more developed, fibril-like morphology was obtained by irradiation up to 5 min. More importantly, MW annealing allowed higher on/off ratio because of the much faster heating process, which offers uniform heat distribution with efficient internal heating via direct coupling of the MW energy with the molecules in solvents, enabling fabrication of high-performance OFET devices within short time. MW irradiation of polymer films is anticipated to replace conventional hot plate annealing for obtaining effectively annealed films of high quality. Our findings provide a promising tool for conjugated polymer-based thin film preparation and have great potential to be used widely in the organic electronics field.

### Table 1

**OFET performance of MW annealed and HP annealed P3HT thin films.**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Post annealing treatment</th>
<th>$V_{th}$ [V]</th>
<th>$I_{on}/I_{off}$</th>
<th>$\mu_{0,avg}$ [cm² V⁻¹ s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>n/a</td>
<td>12.54</td>
<td>$&gt;10^7$</td>
<td>0.018 (±0.0063)</td>
</tr>
<tr>
<td>MW annealed P3HT</td>
<td>1 min</td>
<td>9.81</td>
<td>$&gt;10^4$</td>
<td>0.027 (±0.0052)</td>
</tr>
<tr>
<td></td>
<td>3 min</td>
<td>-3.20</td>
<td>$&gt;10^4$</td>
<td>0.063 (±0.01)</td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td>-1.71</td>
<td>$&gt;10^4$</td>
<td>0.11 (±0.015)</td>
</tr>
<tr>
<td>HP annealed P3HT at 150 °C</td>
<td>1 min</td>
<td>5.84</td>
<td>$&gt;10^4$</td>
<td>0.011 (±0.0014)</td>
</tr>
<tr>
<td></td>
<td>3 min</td>
<td>10.29</td>
<td>$&gt;10^4$</td>
<td>0.020 (±0.0049)</td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td>14.77</td>
<td>$&gt;10^4$</td>
<td>0.024 (±0.0068)</td>
</tr>
<tr>
<td></td>
<td>30 min</td>
<td>16.66</td>
<td>$&gt;10^4$</td>
<td>0.075 (±0.026)</td>
</tr>
</tbody>
</table>

* The $p$-channel characteristics of P3HT-FETs measured with $V_{GS} = -100$ V.

* The average mobility over 10 FET devices with channel length ($L$) of ~50 µm and channel width ($W$) of ~1000 µm.

* The standard deviation.

**Fig. 3.** FET characteristics obtained from MW annealed and HP annealed P3HT films; (a) transfer curves of as cast, MW annealed, and HP annealed P3HT films (b) FET mobility and (c) on/off ratio variations as functions of MW and HP annealing time.

**Fig. 4.** (a) Out-of-plane X-ray diffraction (XRD) patterns of MW annealed 30-DPP-SVS thin films. (b) FET characteristics obtained from MW annealed and HP annealed 30-DPP-SVS films. (c) FET mobility and (d) on/off ratio variations of 30-DPP-SVS FETs as a function of MW and HP annealing time.
Table 2

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Post annealing treatment</th>
<th>p-channel (I_{D-	ext{sat}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW annealed 30-DPP-SVS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 min</td>
<td>-7.36</td>
<td>1.22 (±0.28)</td>
</tr>
<tr>
<td>3 min</td>
<td>-3.52</td>
<td>2.69 (±0.31)</td>
</tr>
<tr>
<td>5 min</td>
<td>-5.31</td>
<td>3.21 (±0.40)</td>
</tr>
<tr>
<td>HP annealed 30-DPP-SVS</td>
<td>-1.32</td>
<td>3.08 (±0.42)</td>
</tr>
<tr>
<td>at 180 °C</td>
<td>-5.94</td>
<td>1.88 (±0.40)</td>
</tr>
<tr>
<td>10 min</td>
<td>-6.91</td>
<td>3.15 (±0.81)</td>
</tr>
</tbody>
</table>

a The p-channel characteristics of P3HT-FETs measured with \(V_{GS} = -100\) V.

b The average mobility over 10 FET devices with channel length (L) of 50 μm and channel width (W) of 1000 μm.

c The standard deviation.

Acknowledgments

This work was supported by the Center for Advanced Soft Electronics under the Global Frontier Research Program (2013M3A6A5073175) of the Ministry of Science, ICT and Future Planning, and by the National Research Foundation of Korea (2014R1A2A2A01004767). H.Y. acknowledges financial support from the Global Ph.D. Fellowship. The authors acknowledge Prof. Yun-Hi Kim at Gyeongsang National University for providing 30-DPP-SVS.

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