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Letter

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

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ABSTRACT

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.

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

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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 semiconducting 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-diketopyrrolopyrrole-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 in short time, 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, M_n ~ 85,000 g mol^{-1}, 4 mg mL^{-1}) and 30-diketopyrrolopyrrole-selenophene vinylene selenophene (30-DPP-SVS, M_n ~ 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-octadecyltrimethoxysilane (OTS)-treated SiO_2/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 trichloroethylene was spin-coated onto the piranha-cleaned SiO_2/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 5500 (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 (<0.004 Ω cm) with thermally grown SiO_2 (300 nm, C_i = 10 nF cm^{-2}) was utilized as the substrate and dielectric. The surface of SiO_2 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 N_2-filled glove box using a Keithley 4200 semiconductor parametric analyzer. The field-effect mobility was calculated in the saturation regime using the following equation:

$$I_D = \frac{W}{2L}\mu C_i\ (V_{GS} - V_T)^2$$

where I_D is the drain-to-source current, W and L are the semiconductor channel width and length, respectively, μ is the mobility, and V_{GS} and V_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 SiO_2/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 film 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 SiO_2/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 $2\theta = 5.4°$ (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-