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Thermally deposited silk fibroin as the gate dielectric layer in organic thin-film transistors based on conjugated polymer

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ABSTRACT

This study investigated the morphology, structural transformation, and electric properties of organic thin-film transistors (OTFTs) with silk fibroin as their dielectric layer at different annealing temperatures. Silk fibroin was employed because it can simplify the OTFT fabrication process and decrease fabrication cost. We successfully fabricated OTFTs based on poly(3-hexylthiophene) (P3HT) dissolved in chlorobenzene (CB) or 1,2,4-trichlorobeneze (TCB). The P3HT had fiber-like network structures when TCB was used and isolated spherical domains when CB was employed. The nanowire morphology obtained when TCB was used may have enabled efficient charge transport. The silk fibroin layer annealed at 40 °C had the smallest particles and least aggregate. The calculated field-effect mobility was 2.06×10^{-3} cm^2 (Vs)$^{-1}$ (when TCB was used), and the highest on/off ratio was 10^3, obtained for the silk fibroin annealed at 40 °C. The OTFT with the 40 °C-annealed-layer had the best performance because of the smooth surface of the α-helix structure of this silk fibroin layer, with such smoothness enabling favorable P3HT crystalline formation. Biological materials such as silk protein are low cost and environmentally friendly and require low temperature in manufacturing. This study indicates the suitability of silk fibroin for use in various electronic devices.

1. Introduction

Organic thin-film transistors (OTFTs) have gained considerable attention in recent years, especially in the field of flexible substrate design and for use in electrical consumer devices such as active matrix displays, e-paper, radiofrequency identification tags (RFID), and biosensors [1,2]. OTFTs are solution processable and have a low-temperature process, low cost, and flexibility [2–7]. Because the performance of solution-processed OTFTs is usually poorer than that of OTFTs produced using vapor-deposition techniques, numerous researchers have focused on enhancing OTFT performance by adjusting several factors including regioregularity [8], molecular weight [9], solvent [10], and the surface treatment of self-assembled monolayers [11]. In designing an environmentally friendly and sustainable manufacturing process, the major challenge is switching from nonrenewable energy manufacturing to “ecosustainable” processes. The use of biologically based materials and the technological integration of these materials into manufacturing processes is a promising path toward fulfilling this goal.

Several biobased dielectric polymers in OTFT components are receiving considerable research interest because of their highly ordered structure and unique properties [2,4,12–15]. The performance of OTFTs that employ a biomaterial—such as silk fibroin, chicken albumen, or deoxyribonucleic acid—as their gate dielectric layer has been greatly improved through the efforts of many research groups [2–5,14,16]. Silk fibroin is commonly used because it may be used in fabricating an OTFT with high charge carrier mobility (μ_{FE}), which is calculated from the slope of the square root of drain current versus gate voltage. Wang et al. reported μ_{FE} to be approximately 23 cm^2 (Vs)$^{-1}$ at a low operating voltage of −3 V [2], and this charge carrier mobility was higher than that of amorphous $InGaO_3(ZnO)_5$ TFTs [17]. Hence, the advantages of using silk fibroin as the dielectric layer in an OTFT

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are the material's low cost, low weight, which make such an OTFT suitable for a wide variety of applications.

In this study, we fabricated regioregular poly(3-hexylthiophene) (P3HT)-based OTFTs with silk fibroin as the dielectric layer. Biomaterials are biodegradable, bioresorbable, biocompatible, and typically environmentally friendly, and they do not require chemical synthesis [18]. Biomaterials are thus candidates for use when desiring to simplify the OTFT fabrication process and decrease OTFT fabrication cost [2,4,13–15]. Although numerous research groups have investigated the electric properties and morphology of biodevices based on various proteins [19–22], the annealing process used to deposit a silk protein dielectric layer and the process solvent have not been comprehensively investigated. In this paper, we report the effect of dielectric layer annealing temperature on the resulting OTFT's morphology and electrical properties, such as switching voltage, carrier mobility, and threshold voltage.

2. Experimental section

2.1. Materials

P3HT (Mw = ~50,000, regioregularity = 90%–95%) was purchased from Reike Metals Inc. (Lincoln, USA). *Bombyx mori* silk cocoons were purchased from mulberry farms. Lithium bromide (Alfa Aesar; anhydrous, 99%), chlorobenzene (anhydrous, 99.8%), 1,2,4-trichlorobenzene (anhydrous, 99%), sodium carbonate (ACS reagent, 99.5%) were purchased from Sigma Aldrich.

2.2. Extraction and purification of silk fibroin solution

The preparation of aqueous silk fibroin solution involved three steps: degumming, dissolution in aqueous LiBr solution, and dialysis [23,24]. The cocoons of the *B. mori* silkworm were boiled for 30 min three times in an aqueous solution of 0.02 M Na_2CO_3. During this process, sericin was removed and the silk cocoons lost their shape to form a cotton-like fluffy mass of fibers. The boiling process was repeated once more with a fresh Na_2CO_3 solution to ensure complete removal of sericin and other wax-like materials. The degummed silk fibroin was rinsed with deionized water and then oscillated for 30 min. After oscillation, the extracted silk fibroin was placed in an oven for 1 day to remove the deionized water. Subsequently, the silk fibroin was dissolved in 9.3 M LiBr solution at 60 °C for 4 h, after which it was dialyzed with distilled water for 72 h by using a dialysis membrane with a molecular weight cutoff of 3.5 kDa, which removed LiBr impurities. This was followed by centrifugation. The final concentration of aqueous silk solution was approximately 2.0–2.5 wt%. A 10 wt% fibroin solution was obtained by placing this solution in an oven at 45–50 °C for a few days. The 10 wt% silk fibroin was stored in a refrigerator to maintain its conformation.

2.3. Characterization

Atomic force microscopy (AFM) measurements were obtained using a NanoScope IIIa model at room temperature. Commercial silicon cantilevers with typical spring constants of 21–78 Nm^{-1} were used to operate the AFM instrument in tapping mode at room temperature. The thermal decomposition temperature was determined using a thermal gravimetric analysis (TGA; TGA Q50, TA Instruments) over a heating range of 100 to 800 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed under a nitrogen atmosphere at room temperature to 250 °C with a heating rate of 10 °C min^{-1} by using a Bruker AXS DSC 3100. Fourier transform infrared spectroscopy (FTIR) was performed using a Bio-Rad 155 FTIR spectrometer at ambient temperature in the range 650–4000 cm^{-1}. Grazing incidence wide-angle X-ray diffraction (GIXRD) was employed to determine the micro- and nanostructures of thin films in both the perpendicular and parallel directions. The internal molecular structure of pure P3HT thin films obtained with different solvents was investigated using GIXRD (Nano-Viewer, Rigaku) with an imaging plate (Fujifilm, BAS-IP SR 127). The instrument was equipped with a 31 kW mm^{-2} generator, which rotated an anode X-ray source with Cu Ka radiation of wavelength $\lambda = 0.154$ nm. The scattering vector q ($q = 4\pi/\lambda\sin\theta$) and the scattering angles in X-ray diffraction spectra were calibrated using silver behenate as a control. The swelling test was employed to investigate the water absorption property of silk fibroin. The swelling ratio of a fibroin film was calculated as follows [25]:

$$\text{Swelling ratio}\ (\%) = (W_1 - W_1)/W_2 \times 100 \quad (1)$$

where W_1 is the weight of the swollen sample and W_2 that of the completely dry sample. W_2 was measured directly, whereas the weight of the samples swollen in distilled water at room temperature for 24 h was measured after removing excess water from the sample's surface.

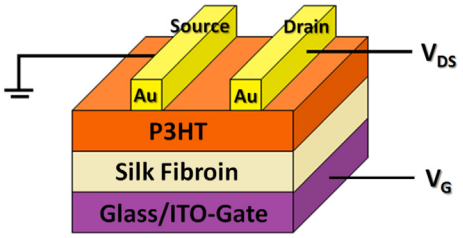

Fig. 1. Schematic of an OTFT using a silk fibroin thin film as the gate dielectric layer.

2.4. Device fabrication

The device design used was the “BG-TC” structure. As indicated in Fig. 1, OTFTs based on a silk fibroin thin film were fabricated on indium tin oxide (ITO) glass (Uni-onward Corp.). After cleaning the ITO glass with detergent, deionized water, acetone, and isopropyl alcohol in an ultrasonic bath, the surface of the patterned ITO glass was cleaned in a plasma cleaner. Subsequently, 10 wt% silk fibroin solution was spin-coated on the ITO glass at 1000 rpm for 120 s. The thin films were dried on a hot plate for 1 h to remove residual solvent. The thickness of the obtained silk fibroin films was approximately 300 nm. After annealing a silk fibroin layer, P3HT was dissolved in chlorobenzene and 1,2,4-trichlorobenzene and then spin-coated onto the layer's surface at 1000 rpm for 60 s in a N_2-filled glove box. The P3HT thin film was then dried under vacuum (10^{-6} Torr) at room temperature for 24 h to remove remaining chlorobenzene and 1,2,4-trichlorobenzene. Gold source and drain electrodes with thickness 70 nm were defined on the P3HT film by using a shadow mask. The channel length (L) and width (W) were 50 and 1000 μm, respectively. The characteristic properties of the OTFT devices were carefully measured using a Keithley 4200 semiconductor parametric analyzer in a nitrogen-filled glove box. The OTFTs exhibited typical p-type I−V characteristics with accumulation mode operation. The field-effect mobility was calculated from the saturated transfer characteristics of a plot of $I_d^{0.5}$ versus V_g, which are related as follows [26]:

$$I_d = \frac{WC_o\mu_h}{2L}(V_g - V_t)^2 \quad (2)$$

where I_d is the drain current, V_g is the gate voltage, V_t is the threshold voltage, μ_h is the hold mobility, W is the channel width, L is the channel length, and C_o is the capacitance of the gate dielectric per unit area (for a silk fibroin layer of width 300 nm, C_o = 30 nF cm^{-2}).