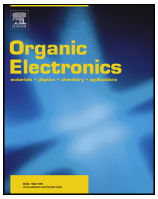
Organic Electronics 59 (2018) 213–219

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Understanding hydroscopic properties of silk fibroin and its use as a gate-dielectric in organic field-effect transistors

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ARTICLE INFO

Keywords:
Organic transistor
Organic semiconductor
Silk fibroin
Gate dielectric
Hydroscopic
Crystal structure

ABSTRACT

Silk fibroin (SF) has attracted great interest as gate dielectric in organic field-effect transistors (OFETs), owing to outstanding characteristics such as high dielectric constant, transparency, flexibility, and solution processability. In this report, we investigated the relationship between the structural properties of SF films and their performance as SF gate dielectrics in OFETs. Solvent vapor treatment with water or methanol altered the structural properties of the SF films, which adopted a β-sheet structure; accordingly, both the surface energy and areal capacitance of the SF films were reduced. Notably, atmospheric water contributed to the increased capacitance of the SF film, especially before the solvent vapor treatment. The growth characteristics of pentacene on the SF films were determined by the surface conditions of the films; in particular, Stranski-Krastanov (layer-plus-island) growth mode with mixed standing-up/lying-down orientation of pentacene on the SF film was observed before solvent vapor treatment, whereas Volmer-Weber mode with standing-up orientation dominated after solvent vapor treatment. Pentacene OFETs based on the untreated SF film exhibited a higher on-current compared with the devices based on the solvent vapor-treated SF film. The hydroscopic characteristics of the untreated SF film enhanced its capacitance, thereby inducing accumulation of hole carriers. The present results show that the structural characteristics of SF films have a marked impact on the electrical properties of OFETs based on SF gate dielectrics. In particular, the water uptake capability of SF is a key factor in the electrical properties of organic electronic devices using SF materials.

1. Introduction

Organic field-effect transistors (OFETs) have attracted considerable interest in recent years, owing to their unique applications such as electronic paper, radio-frequency identification (RFID) tags, organic light-emitting diodes, and bio/chemical sensors [1–6]. To further develop these applications, several properties of the OFETs such as field-effect mobility, on/off current ratio, and bias stability need to be significantly improved. To this end, some studies have been conducted to develop new materials for organic semiconductors, gate-dielectrics, and source/drain/gate electrodes. Newly developed polymeric semiconductors show field-effect mobilities exceeding 5 $cm^2/V\ s$ [7–10]. However, high field-effect mobilities have typically been observed in inorganic gate-dielectrics such as SiO_2 and Al_2O_3. For this reason, organic gate dielectrics, which are compatible with plastic substrates and easy-to-write printing processes, are required to develop plastic electronics based on OFETs [11–14]. Furthermore, the organic gate dielectrics must possess a high dielectric constant (k) to reduce the driving voltage of the fabricated OFETs [15–17].

Silk fibroin (SF) derived from *Bombyx mori* (*B. mori*) silkworm has been considered as a potential gate dielectric in OFETs due to its flexibility, optical transparency, and compatibility with a biological environment such as that of the human body [18–27]. Furthermore, the solubility of SF in water enables its use in water-based environmentally friendly processes [20]. Several studies confirmed that SF thin films have a higher dielectric constant than other organic dielectric materials such as poly (methyl methacrylate), which enabled the development of low-voltage driven OFETs based on SF gate dielectrics [18,22,25]. However, the hydroscopic properties of SF films are not yet fully understood, and only few reports investigated the effect of structural changes on the dielectric properties of SF films [26,27]. Spin-casting of an aqueous SF solution was found to lead to the formation of an

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https://doi.org/10.1016/j.orgel.2018.05.012
Received 12 April 2018; Received in revised form 9 May 2018; Accepted 9 May 2018
1566-1199/ © 2018 Published by Elsevier B.V.

amorphous SF film, whose internal chemical structure was changed by a subsequent solvent vapor treatment [28,29].

In this study, the structure of an as-spun SF film was controlled by vapor treatment with two solvents (i.e., water and methanol). This post-treatment process led to the formation of β-sheet structures within the SF film, which not only altered the surface energy of the film, but also modulated the dielectric properties of the corresponding SF gate dielectrics. We investigated the effect of the different internal structure on the dielectric properties of the SF films and the electrical characteristics of OFETs based on SF gate dielectrics. The hydroscopic properties of the SF films and their effect on the OFET performances were analyzed by varying the conditions (atmospheric or vacuum) used to measure the characteristics of SF-based gate dielectrics and OFETs.

2. Experimental

2.1. Materials

Cocoons of *B. mori* silkworms were obtained from Uljin Farm, Republic of Korea. To remove sericin and other impurities in silk, the cocoons were boiled for 30 min in a water-based solution containing 0.02 M Na_2CO_3. After rinsing several times with purified water, the resulting silk fibroin (SF) was dried at atmospheric temperature for 3 days. Aqueous solutions of regenerated SF were prepared via the following procedure: first, degummed SF was dissolved in an aqueous solution of 9.3 M LiBr (99% purity; Sigma-Aldrich) at 60 °C, and the dissolution was carried out for 6 h; then, the solution was dialyzed in purified water for 48 h using a Slide-a-Lyzer dialysis cassette (MWCO 3500, Pierce); finally, the solution was centrifuged at 9500 rpm for 30 min. The final concentration was 6–7 wt%.

2.2. Fabrication of SF thin films

Thin SF films were fabricated via spin-casting on a silicon wafer containing a 300 nm-thick SiO_2 layer, which was cleaned by immersion in boiling acetone for 30 min, followed by exposure to UV ozone for 30 min. The aqueous SF solution was deposited on top of a silicon wafer by spin-coating at 7000 rpm, and the thickness of the SF films was approximately 200 nm. After the spin-coating process, the SF films were treated with either water or methanol vapor for 4 h, to induce a crystalline structure of SF film. The resulting SF films were denoted as SF_No treatment (untreated film), SF_Water (film treated with water vapor), and SF_MeOH (methanol vapor-treated film).

2.3. Device fabrication

The SF films were then used to fabricate metal-insulator-metal (MIM) devices and top-contact/bottom-gate OFETs. The MIM devices were fabricated by thermally depositing gold electrodes on SF films using a metal shadow mask. To fabricate the OFET devices, a pentacene layer of ~50 nm thickness was deposited by thermal evaporation on each processed SF film at a rate of 0.1 Å/s. Then, to obtain top-contact OFETs, Au source-drain electrodes were thermally evaporated onto a pentacene film using metal shadow masks (channel length 150 μm, width 1500 μm).

2.4. Characterization

The surface morphologies of pentacene and SF films were characterized by atomic force microscopy (AFM, Park Scientific Instrument Autoprobe-PC). The internal structure of the pentacene film formed on each SF layer was characterized by two-dimensional grazing incidence X-ray diffraction (2D-GIXD) measurements, recorded at the Pohang Accelerator Laboratory of Korea (3C and 9 A beamlines). The surface characteristics of thin SF films were determined from contact angle measurements with DI water and diiodomethane (SEO, Phoenix 300). The capacitances of silk films and SiO_2 were measured using a precision inductance-capacitance-resistance (LCR) meter (HP, 4284 A). The current-voltage characteristics of all FET devices were measured by a Keithley 4200-SCS system and a probe station operating under air and vacuum conditions. After deposition of the source and drain electrodes, each device was isolated by mechanical scratching. In order to measure the transfer characteristics, the gate voltage (V_G) was swept from 80 to −80 V, while the source-drain voltage (V_D) was maintained constant at −80 V.

Table 1
Contact angles and surface energies for the three types of SF films.

	SF film		
	SF_No treatment	SF_Water	SF_MeOH
Contact angle with water (°)	39	44.2	58.7
Contact angle with CH_2I_2 (°)	27	39	44
Surface energy (mJ/m^2) [a]	61	56	47

[a] Calculated using geometric mean equation.

3. Results and discussion

The contact angles of the SF films were used to evaluate surface energy changes following treatment with different solvents (Table 1). The contact angles of water and diiodomethane increased after treatment with water or methanol vapor. The surface energies of the SF_No treatment, SF_Water, and SF_MeOH samples, calculated by using a geometric mean equation [30], were 61, 56, and 47 mJ/m^2, respectively. These results reflect changes in the internal structure of the SF films associated with crystallization [26]. Vapor treatment with a more hydrophobic solvent reduced the surface energy of the SF film due to the formation of β-sheet crystal structures [28,29]. These structures confine the hydrophilic NH and CO groups inside the SF film, resulting in a decrease in its surface energy. Fig. 1 and Table 2 show the total capacitance of each sample as a function of frequency, under air and vacuum environments. The total capacitance was calculated according to Equation (1):

$$1/C_{tot} = 1/C_{SF film} + 1/C_{SiO2} \quad (1)$$

Here, C_{tot} denotes the total capacitance of the dielectric layers, C_{SF_film} represents capacitance of silk film treated with different solvent vapor annealing, and C_{SiO2} is capacitance of SiO_2 (11.5 nF/cm^2) [31]. The capacitances of the SF films used in the above equation were derived from the structure of the corresponding MIM devices and are shown in Figure S1 and Table S1 in the Supporting Information. Because the capacitance of SiO2 did not change with the frequency (Figure S2 and Table S2 in the Supporting Information), the observed decrease in capacitance upon increase in frequency reflects the hydroscopic characteristics of silk, as discussed below. The capacitance of the SF_No treatment sample was higher than that of the solvent vapor-annealed SF films. Because the internal structure of the untreated SF film is amorphous (Fig. S3a, Supporting Information), the polar side groups of the amino acids are randomly oriented, which allows moisture to penetrate the film, resulting in the increased capacitance (Fig. 2) [26]. Increasing the frequency resulted in an abrupt decrease of capacitance, mainly due to the slow polarization of water molecules within the SF films. When the measurement conditions were changed to vacuum, a large amount of water was removed from the SF film, resulting in a decreased capacitance. In contrast, annealing with a more hydrophobic solvent yielded a more stable β-sheet crystal structure (see Supporting Information, Fig. S3b). The hydrogen bonds in this structure keep the polar side chains in the bulk dielectric, thereby preventing water molecules from penetrating the bulk SF films. This resulted in a substantial decrease in capacitance following treatment of the SF films with methanol vapor. In addition, no capacitance decrease was observed when

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