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Integration of silk protein in organic and light-emitting transistors

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Abstract

We present the integration of a natural protein into electronic and optoelectronic devices by using silk fibroin as a thin film dielectric in an organic thin film field-effect transistor (OFET) and an organic light emitting transistor device (OLET) structures. Both n- (perylene) and p-type (thiophene) silk-based OFETs are demonstrated. The measured electrical characteristics are in agreement with high-efficiency standard organic transistors, namely charge mobility of the order of 10^{-2} cm²/Vs and on/off ratio of 10^4 . The silk-based optoelectronic element is an advanced unipolar n-type OLET that yields a light emission of 100nW.

The future of electronics has been envisioned as “soft and rubbery”(1). A step toward real – life applications of flexible electronics has been made by demonstrating silicon circuits bonded to elastomeric substrates (1,2) and innovative organic electronic and optoelectronics devices (3-5). Organic thin film field effect transistors (OFETs), organic light emitting diodes (OLEDs) and organic light emitting transistors (OLETs) (6-10) have been fabricated onto plastic substrates and integrated into plastic optics (11, 12). Nonetheless, in this era of heightened environmental awareness and of increasing demand for more eco-sustainable manufacturing processes, a major challenge is moving from non-renewable energy manufacturing to “eco-sustainable” processes. The use of biologically based materials and their technological integration provides a compelling path towards this goal (13). In this context, natural fibroin, the constituent protein of silk, may play a key role. Fibroin has been recently demonstrated to be an excellent material for fabrication of optical elements namely, refractive and diffractive lenses, gratings, photonic crystal structures, silk-holograms, silk-optical fibers, silk microfluidic silk-devices (14-22). Moreover, silk is an established biomaterial that has been used for centuries for medical sutures and successfully applied, among other things, for drug release, showing a controllable degradation lifetime range from weeks to years (23) and enabling targeted drug delivery in brain astroglial cells (24). Processing and manipulation are carried out in ambient conditions (21) and the unique properties of natural silk fibroin to host organic structures, enable the fabrication of bioactive optical devices (25). It is worth noting how very recently silicon electronics in form of nanomembranes has been integrated onto a water-soluble silk substrates demonstrating a largely, albeit not completely, bioresorbable, implantable silicon transistor (26). An alternative to silicon is the use of water-soluble, synthetic polymers like poly(vinyl alcohol) (PVA), and thermoplastic polyester poly(L-lactide-co-glycolide) (PLGA). Such polymers have been used as constituents of an organic (p-type) semiconductor film by using PVA as the dielectric layer and PLGA as the substrate of a biodegradable p-type thin-film transistor (27). These previous accomplishments point to the importance of combining

organic electronics and synthetic organic biodegradable materials to take a first step towards biodegradable and environmentally sustainable electronic devices.

We demonstrate here how a natural protein such as silk fibroin, can be integrated as a functional and efficient dielectric into organic optoelectronic devices, replacing traditional inorganic oxide layers such as SiO₂, plastic PMMA, or other synthetic organic materials.

Figure 1 shows the schematic of the fabricated n- and p-type silk organic thin film transistors. A 400nm thick film of silk fibroin is spin coated from aqueous solution onto an optically transparent glass/ITO substrate, patterned ITO acting as a gate contact. The silk film is rendered water insoluble by inducing beta sheet formation (i.e. crosslinking) as previously described (18). A 15 nm thick film of N,N'-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (P13) is vacuum deposited at a sublimation rate of 0.1 Å/s as a n-type organic semiconductor for electron conduction on top of the silk film. A 50 nm thick source and drain gold contacts are vacuum thermo-deposited through a metal mask thus completing a 70 μm and 15 mm channel length and width top-contact organic field-effect transistor (OFET) configuration. With the same protocol and parameters, a p-type semiconductor, namely the α,ω-dihexyl-quaterthiophene (DH4T) has been grown for hole conduction. It is worth noting that the semiconductor compounds were not modified or manipulated from their commercially available form namely, P13 by Sigma-Aldrich, and DH4T (ActivInk P0400) by Polyera Corporation. The molecular structure of the grown moieties and the output curves of the respective n- and p-type silk organic FET are shown as well in figure 1. Both P13 and DH4T are well known and extensively researched materials for electron (n-type) and hole (p-type) transport organic thin film transistors (6,28,29). As such, they provide an ideal system to benchmark the silk-based OFETs and OLETs. The electrical characterization of the fabricated silk-organic transistors has been performed with a probe station equipped with a parametric analyzer both in atmosphere controlled dry-box systems and in air at room temperature. It is worth noting how the I-V characteristics of OFETs can be adequately described by standard models (30, 31) and the mobility of the n- and p-type silk based transistors were derived from measured output curves in the saturation regime.

The saturation curves measured at $V_{d-s} = \pm 90$ V, where V_{d-s} is the voltage between drain-source contacts depending on the n- or p-type semiconducting material, are reported in figure 1. The two nearly overlapping lines are for forward and backward scanning of the Gate-Source voltage while V_{d-s} is kept constant. This indicates the near absence of hysteresis and consequently low charge trapping in the silk dielectric layer in particular for electron transport, i.e. the silk-P13 device.

The charge mobility values associated to the measurement are $\mu_n = 4 \cdot 10^{-2} \text{ cm}^2/\text{Vs}$ for the silk-P13 and $\mu_p = 1.3 \cdot 10^{-2} \text{ cm}^2/\text{Vs}$ for the silk- DH4T. A comparison of the parameters of the silk-based devices and PMMA and SiO₂-based devices are reported in Table 1. We note that the measurements are comparable to efficient charge mobility values (n- and p-type) of thin film OFET reported in the literature (28-30) and with our previously obtained results from standard SiO₂ – PMMA gated OFETs (28). Moreover, we should underline how the measured voltage threshold for the silk-P13 transistor is one order of magnitude lower, namely 1.8 V at 20 V, than the respective standard OFET. The other defining parameter to assess the performance of an OFET is the on/off switch ratio which is also included in table 1. In this case, the switching rate of 10^4 matches the highest values reported for thin film organic transistor based on P13 and DHFT organic semiconductors

To explore optical utility in these devices, organic light emitting transistors have been also studied. These recently designed structures (6-11) have the ability to combine in a single

device the advantages and functions of a transistor and of electroemission. Moreover, electroemission efficiency and nanoscale localization of the light emission make OLETs a breakthrough multifunctional device concept. The first evidence of OLETs emission has been demonstrated for a unipolar emitting device (6,7). To study these results in silk, we have leveraged the best-performing silk-transistor, (the silk-P13), and operated the device in the locus mode. The emission was collected by using a calibrated photodiode. The obtained results are shown in figure 2.

When $V_{gs}=V_{ds}$ of 75 V, a nonlinear intensity of the emitted light is observed. The measured relevant operation parameters assessing the performance of the unipolar silk-OLET device are: $V_{th}=1.4V$; $n\text{-Mobility}=0.013\text{ cm}^2/Vs$; light emission intensity= 100nW at $V_{gs}=V_{ds}=90V$.

The present results demonstrate how natural silk fibroin can be successfully used as a dielectric material for fabrication of advanced n- and p- type silk-based organic transistors and light emitting transistors. The combined use of silk in electronics as presented here in combination with previous work on silk-based photonics, thin-film and conformal electronics sets the stage for a powerful approach towards the fabrication of eco-sustainable and multifunctional bioactive devices. The favorable substrate properties of this all natural biopolymeric substrate (ref. Tao, H., J. J. Amsden, A. C. Strikwerda, K. Fan, D. L. Kaplan, X. Zhang, R. D. Averitt, F. G. Omenetto. 2010. Metamaterial silk composites at terahertz frequencies. *Advanced Materials* July 21 Epub ahead of print [PMID 20665563], Kim, D. H., J. Viventi, J. J. Amsden, L. Vigeland, Y. S. Kim, J. A. Blanco, B. Panilaitis, E. S. Frechette, D. Contreras, D. L. Kaplan, F. G. Omenetto, Y. Huang, K. C. Hwang, M. R. Zakin, B. Litt, J. A. Rogers. 2010. Dissolvable films of silk fibroin for ultrathin conformal biointegrated electronics. *Nature Materials* 9(6):511-517 [PMID: 20400953]) can be also exploited in the future as an alternative to the rigid substrates used here enabling fully degradable devices and opening a path for sustainable high-tech manufacturing.

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Figure 1. Molecular structures and device architecture **a)** Electrical characterization of n- and p-type silk-OFET **b)** transfer curves and **c)** saturation curves. The double experimental points are for forward and backward cycle.

Figure 2. Electroluminescence collected from a glass/ITO/Silk/P13/Au top contact unipolar silk-OLET device. The device is biased in the locus mode. The double experimental points are for forward and backward cycle.

Table 1

Comparison of the mobility, threshold values and On/Off ratio for silk p and n –type OFETs and respective standard PMMA and SiO₂ devices. The measured silk dielectric constant in the device configuration $\epsilon_s \approx 6$. The channel length and width are 70 μm and 15 mm respectively for both Silk and PMMA devices. For SiO₂ the channel length is 300 μm and width 10 mm.

	DH4T p-type		P13 n-type	
	Mobility (μ)	Threshold (V_T)	On/Off ratio	Threshold (V_T)
SiO ₂	$4 \cdot 10^{-2} \text{ cm}^2/\text{V s}$	-3V	10^3	21 V
PMMA	$9 \cdot 10^{-2} \text{ cm}^2/\text{V s}$	-20 V	10^2	18 V
SILK	$1.3 \cdot 10^{-2} \text{ cm}^2/\text{V s}$	-17 V	10^4	2 V