Synthetic Metals 227 (2017) 29–36

Contents lists available at ScienceDirect

Synthetic Metals

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

Layer-by-layer coating of oriented conjugated polymer films towards anisotropic electronics

Manish Pandey[a], Shifumi Sadakata[a], Shuichi Nagamatsu[b,c], Shyam S. Pandey[a], Shuzi Hayase[a,c], Wataru Takashima[a,*]

[a] Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu, Kitakyushu, Fukuoka 808-0196, Japan
[b] Department of Computer Science and Electronics, Kyushu Institute of Technology, 680-4 Kawazu, Iizuka, Fukuoka 820-8502, Japan
[c] Research Center for Advanced Eco-fitting Technology, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu, Kitakyushu, Fukuoka 808-0196, Japan

ARTICLE INFO

Article history:
Received 16 December 2016
Received in revised form 10 February 2017
Accepted 22 February 2017
Available online 21 March 2017

Keywords:
Casting
Orientation
Anisotropy
Conjugated polymers
Multilayer
Floating film

ABSTRACT

Dynamic casting of floating-film and transferring method for preparing oriented multilayer films of conjugated polymers is reported. This method is based on dynamic casting of a floating-film on liquid substrate to obtain oriented thin-film followed by its transfer on a desired solid substrate. The uniqueness in this method lies in the isolation of casting and coating procedures of oriented films, which enables us to fabricate the oriented multilayer with minimum interlayer interference. It provides a key-technology to build up the organic multi-layered architecture while preserving oriented morphologies. Several types of multilayer films have been prepared and investigated in detail in terms of their film characteristics. The layer-by-layer coating of oriented films demonstrated by this method is found to be a unique feature which overcomes cumbersome procedures in the conventional orientation methods. The coating procedure demonstrated in this study provides a facile methodology to construct anisotropic architectures.

1. Introduction

Solution processed semiconductor thin film is one of the important features for organic electronics which enables us for large scale and facile fabrication of thin film photonic and electronic devices. Device performance strongly changes with the film morphology of the semiconductor layer [1–3]. The casting procedure of semiconductor layer from solution is, therefore, the key-technology to fabricate organic electronic devices. Drastic change in the organic device performance is essentially caused by the anisotropic structure of conjugated molecules and polymers [4–7]. The molecular alignment is, therefore, very important to induce the potential performance for organic semiconductors. Conjugated polymers are structurally the most anisotropic organic semiconductors due to their one-dimensional expansion of conjugation on main-chain. In the recent past, amorphous film formation has been favored for reproducible electronic performance due to its uniform characteristics [8]. Currently, however, it has been realized that high transport performance is required in semiconductor even with the existence of anisotropy in carrier transport [5–7]. This offers a strong urge for suitable thin film fabrication processes capable of promoting the alignment of macromolecules in order to attain enhanced device functionality.

Molecular ordering is essentially required to improve the intermolecular transport for organic semiconductors, where drop-casting is thermodynamically favorable to attain this goal [9]. Many types of drop-casting procedures from various organic solvents combined with developed nozzles have been reported for obtaining highly crystalline films by many researchers [10]. Apart from this, drop-casting on various liquids is another unique approach to obtain thin-films. In the case of hydrophobic semiconductor solution, hydrophilic materials such as water, ethylene glycol and/or glycerol can be utilized as the “liquid-substrate” for drop-casting. On liquid-substrates, we obtain the organic semiconductor thin-film as a floating-film after the solvent evaporation, which can be easily transferred on a desired substrate by stamping. The procedure for casting a thin floating-film followed by its transfer on desired substrate can be expressed as floating-film transfer method (FTM) [11].

* Corresponding author.
E-mail addresses: wtakashima@gmail.com, wtakashima@life.kyutech.ac.jp (W. Takashima).

http://dx.doi.org/10.1016/j.synthmet.2017.02.018

Gradually vaporizing solvent after the expansion of dropped semiconductor solution on the liquid-substrate semi-statically provides a floating-film in FTM (represented as static-FTM). In contrast, simultaneous solidification of the floating-film along with the expansion of the semiconductor solution is dynamically occurred just after dropped on the liquid surface (represented as dynamic-FTM), leading to a concentric orientation of conjugated polymers. Poly(3,3‴-dialkyl-quaterthiophene) (PQT) as well as polyfluorene derivatives can be easily oriented by this procedure [12]. The solvent volatility of semiconductor solution, generally, identifies the types of FTM. Namely, under ambient condition static-FTM occurs after the complete expansion of semiconductor solution utilizing high boiling point solvents like chlorobenzene because of their slow evaporation. In contrast, for dynamic-FTM semiconductor solution prepared in the relatively low boiling point solvents (such as chloroform, tetrahydrofuran and dichloromethane) leads to simultaneous film expansion and solidification [13].

Casting of thin-films at the air-liquid interface proceeds under isothermal condition like Langmuir-type methods have been studied and developed by many researchers [14]. Introduction of liquid-crystal molecules with conjugated polymer successfully forms transversally oriented films where thin-film is formed by applying surface pressure in Langmuir isotherm [15]. In contrast, in the dynamic-FTM self-caused motion of liquid substrate and/or semiconductor solution spreading on the liquid-substrate, casts a thin floating-film automatically as shown in Fig. 1. These differences suggest that FTM process should be characterized little apart from the Langmuir process in spite of their methodological analogy.

Transverse orientation methods of conjugated polymers also have been developed and investigated by many researchers [16]. In these reports, fine orientation of conjugated polymers at micrometer-scale along with the demonstration of high optical and electronic dichroism. Most of these methods prepare oriented films directly on the device substrate, for example, mechanical rubbing, friction transfer and flow-coating with post-annealing [17–19]. These methods essentially require various chemical, mechanical or thermal stimuli for the promotion of macromolecular orientation. At the same time, these stimuli provide mechanical and/or chemical damages on the coated-surface, in particular, the surface consisted of soluble or soft organic materials. This makes it impossible to build up organic multi-layered structure consisted of oriented films, which is a bottleneck for the application of in particular oriented functional layers into organic electronic devices.

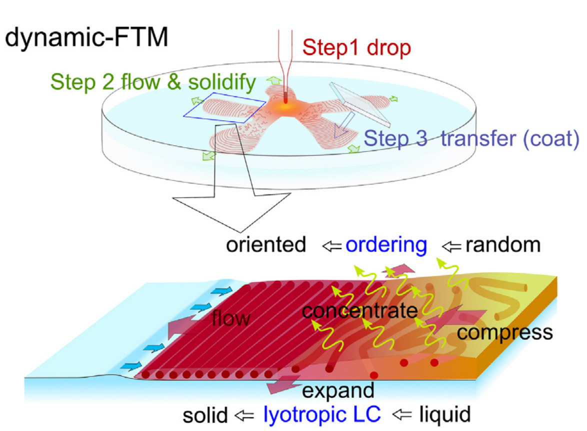

Fig. 1. Schematic illustration of the overview of dynamic-FTM (upper) and a possible mechanism to cause the orientation (lower) during casting.

FTM is essentially consisted of the two-step processes, namely to pre-cast an oriented thin-film on liquid substrate as solution process followed by the post-transfer of the film on the solid substrate like a dry process. The isolation of the orientation process from the coating process enables us to overcoat the oriented film on any surface without chemical or mechanical damages. In particular, conjugated polymer acts as active layer for photonic and electronic devices. As already mentioned above the device performance is sensitive to the film morphology as well as the film purity. Thus, a mild coating procedure of organic semiconductor-layer with conserving the oriented film-morphology and without the mixture of organic semiconductor with under-lying other materials is strongly required for constructing multi-layered structure. In this context, FTM as the solution-based casting procedure provides a mild coating while maintaining the purity as well as the morphology both of the under as well as over-coated layers.

Recent past has witnessed the design and development a variety of conjugated polymers in order to provide the tailored functionality [20–22]. For analyzing newly synthesized materials, spectroscopic characterizations are very powerful way to clarify the chemical structure at molecular level. The polarized analyses of the oriented film provide further details about the structural information together with non-polarized spectra. A quick casting method to prepare the oriented thin-film with minimal materials wastage is, therefore, very useful for the material characterization utilizing polarized spectroscopy.

In this article, we propose dynamic-FTM as the casting procedures to prepare the multi-layered films consisted of oriented conjugated polymers. The oriented multi-layer formation renders the realization of anisotropic electronics into the practical devices [23,24]. The proposed dynamic-FTM is not only simple and quick oriented film casting procedure but also leads to the utilization of small amount of the materials with minimum wastage. In this study, we investigated the orientation characteristics of dynamic-FTM films with conjugated polymers. Efforts have also been directed towards the preparation and characterization of variety of multi-layered structures consisted of conjugated polymers fabricated using dynamic-FTM.

2. Experimental

All of the chemicals and the reagents employed in this work are used without further purification. Three types of conjugated polymers, viz. non-regiocontrolled poly(3-hexylthiophene) (NR-P3HT) [25,26], poly(3,3-didodecylquaterthiophene) (PQT) [27] and poly(9,9-dioctylfluorene-*co*-bithiophene) (F8T2) [28], were synthesized as per the reported procedures. Chemical structures were identified by ^{1}H NMR. In particular, the regioregularity of NR-P3HT was estimated at α-methylene region in ^{1}H NMR spectra [29]. Major emphasis in this study has been directed with NR-P3HT as the main polymer due to the fact that it is easy to prepare well-oriented floating-film and to check the orientation intensity simply by the naked eyes through a polarizer-film easily [5]. Typically, 10 mg of polymer powder was dissolved in 1 ml of dehydrated chloroform to obtain a uniform 1% (wt/wt) semiconductor solution.

Hydrophilic liquids such as water, ethylene-glycol and glycerol were chosen for the materials of liquid-substrate to cast floating-films. Solvents were well-mixed at an appropriate mixing ratio in order to tune the viscosity of the liquid substrate and temperature was also optimized for obtaining the high orientation [30]. The mixture was poured in a 15 cm-diameter petri-dish, stirred and controlled at a suitable temperature. The dynamic-FTM was carried out by putting single droplet (about 10–20 μl) of semiconductor solution at the center of liquid-substrate without