

Growth of Rubrene Crystalline Wire via Solvent-vapor Annealing

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Abstract

We report on the growth of rubrene ($C_{42}H_{28}$) wire fabricated by thermal evaporation, followed by solvent-vapor annealing for the application of organic thin film transistor. Solvent-vapor annealing was carried out in precisely controlled vapor pressure at elevated temperature. Micro-sized, and elongated rubrene wire was obtained via solvent annealing process reproducibly. Optical image and XRD data shows highly crystalline quality of rubrene wire.

1. Introduction

Formation of high quality crystal as an active layer, probably single-crystal, is one of the goals for high performance organic thin film transistor. Of the organic semiconductor materials reported, rubrene ($C_{42}H_{28}$) crystal has been regarded as one of the potential active material due to its high mobility (up to $20 \text{ cm}^2/\text{V}\cdot\text{s}$).¹⁻² However geometry and orientation of its molecule structure hamper the crystallization during thermal evaporation process, which led to introduction of other process, such as “hot wall” deposition or physical vapor transport.²⁻⁴

Solvent vapor annealing is straightforward method to enhance ordering of organic / polymer thin film. Recently, Dickey et al. reported solvent-dependent crystallization of triethylsilylethynyl anthradithiophene (TES-ADT) thin film as an active layer of thin film transistor at room temperature.² Jo et al. reported self-organization of polymer blend via “solvent-vapor annealing” at room temperature.⁵

Solvent vapor annealing has desirable method to enhance crystallization in the following two aspects. (1) Solvent vapor permeates into metastable thin film fabricated by thermal evaporation to produce “plasticization effect”. Plasticization refers to the

reduction of glass transition / melting temperature (T_g / T_m) of glassy materials by adding low molecular additives. (2) Presence of solvent molecule in organic film involves change of interfacial tension between rubrene and substrate.⁶

In this report, we focus on the direct formation of high quality rubrene crystal on substrate fabricated by organic molecule beam deposition, followed by solvent-vapor annealing process. We introduce the concept of isothermal solvent annealing rather than room temperature-annealed process to enhance kinetics of solvent vapor.

2. Experimental

Silicon dioxide of 2000\AA thickness grown on p+ silicon was ultrasonically cleaned in conventional organic solvents. The oxide surface was modified with hexamethyldisilazane (HMDS) by spin coating. A rubrene powder was purchased from Aldrich, and used as received. The rubrene powder was thermally evaporated by organic molecule beam deposition (OMBD) without any patterning through shadow mask.

The rubrene films were exposed to benzene solvent vapor by placing them in a glass jar including a pool of benzene solvent. The glass jar was placed in conventional oven in order to control solvent vapor pressure by temperature. After solvent vapor annealing, the rubrene wire-laid substrate was dried on hot plate at 80°C in order to remove residual benzene solvent.

Optical microscope was utilized in order to identify the formation of organic crystal transformed from initially amorphous film. X-ray diffraction (XRD) characterization was performed with monochromatic

Cu Ka ($\lambda = 1.54 \text{ \AA}$) radiation and surface morphology was investigated by AFM (Nanoscope IV, Digital Instruments and PSIA, XE-100) in non-contact mode.

3. Results and discussion

Fig. 1 exhibits schematic solvent-vapor annealing setup of our work. Comparing to the solvent annealing process reported, benzene vapor pressure was adjusted by temperature in conventional oven, which enable us to obtain reproducible and well-defined rubrene crystal wire.

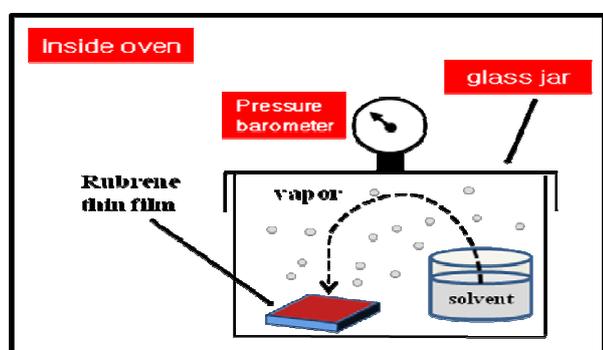


Fig. 1. Schematic of equipment setup for solvent vapor annealing experiment.

Fig. 2 displays micro-sized rubrene wire fabricated after solvent-vapor annealing. In this case, solvent-vapor annealing process was conducted at $60 \text{ }^\circ\text{C}$, corresponding to 393 mmHg of benzene vapor. Initially amorphous rubrene thin film was transformed to micro-sized rubrene wire in the presence of benzene vapor during the annealing process. When amorphous rubrene film was exposed to benzene solvent, rubrene film aggregates (white circle inside Fig. 2 (a)) and experiences solvated phase on substrate. Reduced viscosity of rubrene aggregates under benzene condition allowed the rubrene aggregates to be transformed into thermodynamically stable phase, micro-sized wire in this condition.

In Fig. 3 out of plane X-ray diffraction (XRD) data reveals the concrete evidence of highly crystalline structure. An initial rubrene film fabricated by thermal evaporation exhibits amorphous structure, which is due to intrinsically strained geometric structure of rubrene. Pristine rubrene film (Fig. 3(a)) does not show any crystal peak, in other words, initially amorphous structure is formed after thermal

evaporation. However, thermally evaporated rubrene film was exposed to benzene solvent at $60 \text{ }^\circ\text{C}$ for extended time, it undergoes structural rearrangement. Penetration of benzene vapor into wetted rubrene film induces change of interfacial energy, which provide mobile convection medium for crystallization.

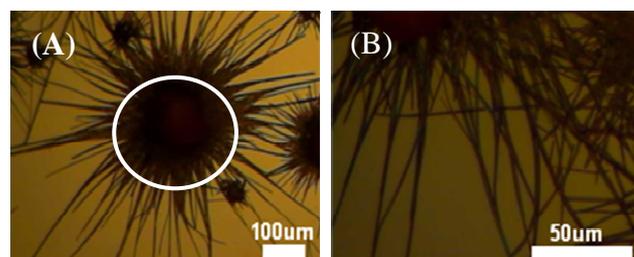


Fig. 2. Rubrene wire transformed from initially amorphous rubrene film.

To the best of our knowledge solvent-annealed organic film reported elsewhere shows increased grain size, however the solvent annealing was conducted only at room temperature for extended time. Provided that the amount of solvent vapor permeated has an influence to the degree of crystallization, our attempt to increase the vapor pressure by controlling the system temperature is not only simple but valuable enough to apply.

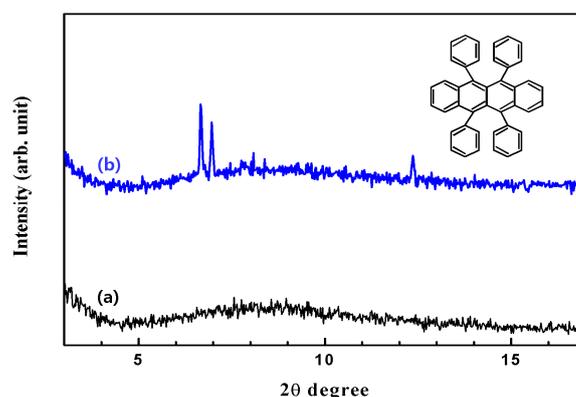


Fig. 3. XRD data of (a) pristine rubrene after thermal evaporation, (b) microwire grown on substrate during subsequent solvent annealing. Molecular structure of rubrene is shown in inset.

We also investigated surface morphology of rubrene wire and background substrate by AFM. Fig. 4. shows 2-D surface morphology of rubrene wire. Well faceted and flat rubrene wire was found.



Fig.4. 2-D AFM image of micro-sized rubrene wire grown on substrate. Scale of y-axis is 10um. Inset shows image of optical microscope.

4. Summary

We conducted solvent-vapor annealing on amorphous rubrene film initially fabricated by thermal evaporation. A solvent-vapor annealing process at elevated temperature within glass jar allowed amorphous film to be transformed elongated 2-D rubrene wire. AFM image shows well-elongated and faceted rubrene wire and XRD data exhibits well-ordered crystal structure. The formation of rubrene wire is attributed to the change of interfacial tension between substrate and rubrene film during solvent annealing, which lead to mobile convection medium during crystallization.

Our novel attempt, solvent annealing at elevated temperature, may be able to open the new way for organic thin film to be highly crystallized on substrate directly at suitable temperature.

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