



Crystallization of solution processable amorphous tetrabenzoporphyrin films

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ARTICLE INFO

Article history:

Received 12 February 2015

Received in revised form 15 July 2015

Accepted 19 July 2015

Available online 21 July 2015

Keywords:

Organic semiconductor

Small molecules

Crystallization from precursor

Nucleation and growth

Solution process

ABSTRACT

The dynamic process of crystallization of nickel-tetrabenzoporphyrin (NTBP) from its amorphous precursor film was investigated. NTBP crystalline films with a preferential orientation were obtained through the recrystallization from its precursor film deposited on polyimide (PI) substrate. This preferential orientation, with (001) plane lies in the film plane, increases the in-plane electrical conductivity of the film dramatically in comparison with that deposited on a glass substrate where no preferential orientation was observed. Such a preferential orientation of NTBP is caused by the local order of the PI surface molecules which act as favorable nucleation sites to grow NTBP in preferential crystallographic direction. This view is supported by the observed lower activation energy (0.96 eV) required for continuing crystallization on PI than that on glass (1.27 eV). The time dependence of the nucleus density of NTBP follows $N \sim t^n$, where $n = 1$ and 1.5 for PI and glass substrates, respectively. This can be interpreted as a result of lacking of nucleation centers on the glass substrate hence newly activated sites are required to continue the crystallization, while on the PI substrate such process is not required.

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1. Introduction

Understanding and optimizing the growth process of organic molecular crystals in thin film geometry are of particular interest as thin films are required by most experiments and applications, e.g. organic light emitting diodes [1–3], photovoltaic cells [4–6], and field effect transistors/circuits [7–9]. Organic small molecule semiconductors show much higher charge carrier mobility than that of polymer semiconductors because a high degree molecular packing/ordering is favorable for charge transportation [10,11]. The vacuum sublimation process has been widely used to deposit thin film materials [12,13], however, to realize low-cost of organic electronic product the vacuum-processes have to be replaced by solution-processes, like spin-coating and ink-jet printing, which are lower in both capital and operation costs [14,15]. This has in turn driven by the development of solution-processable small molecule semiconductors that allows to form crystalline film of small molecules through depositing their precursors by solution-process and subsequent chemical or thermal conversion [16]. A number of solution-processable molecule materials with high charge mobility, like pentacene [16,17], oligothiophene [18], rubrene [19], and porphyrin [20] have been developed successfully. Thus an investigation of the crystallization process of small molecule semiconductors from their amorphous precursors is interesting for optimizing the film quality, molecule packing, and device performance.

The crystal nucleation and growth process from amorphous phases have always been interesting topics for a range of materials from nanocrystalline metallic materials [21–23] to polycrystalline silicon films [24–26]. There are some fundamental differences between the inorganic and organic semiconductor materials during the re-crystallization process as the former involves breaking and forming strong valence bonds, like in the case of silicon [27], while the latter involves mostly weak Van der Waals force. Furthermore, in the case of organic materials, the molecule conversion from its precursor and transforming into crystals at interface between the two phases are different from its inorganic counterpart. Here, we report an experimental study on the recrystallization of nickel-tetrabenzoporphyrin (NTBP) [28,29] from its amorphous precursor films deposited by spin-coating. The tetrabenzoporphyrin is a promising material with high charge mobility for application of printed electronics [28]. The dynamic process of crystallization of NTBP was investigated at the crystal nucleation and growth stages for fabrication of the crystalline thin films with a desired molecule orientation.

2. Experimental results and discussion

The synthesis process of NTBP precursor can be found in reference [30]. Precursor films were formed by spin-coating from chloroform solution (10 mg ml^{-1}) onto substrates and subsequently baked at 60°C for 30 min. Thermal treatment of such films (above $\sim 165^\circ\text{C}$) converts the amorphous precursor into crystalline NTBP (Fig. 1). Both bare glass and polyimide (PI) coated glass were used as substrates in our

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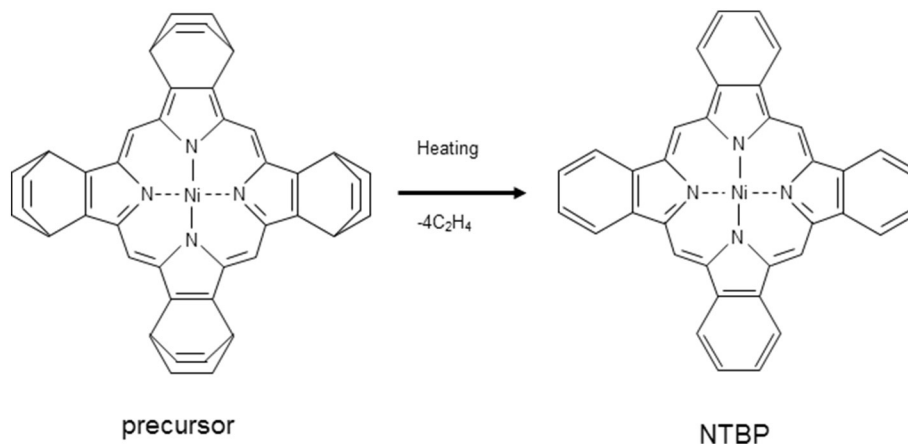


Fig. 1. Schematic illustration of the conversion of TBP from its precursor.

experiment. The glass substrates were treated by oxygen plasma after sequential cleaning with acetone and isopropanol to remove any organic contamination. The PI films (1 μm in thickness) on glass substrates were deposited by spin-coating from N-methyl-2-pyrrolidone (NMP) solution (referred as PI substrate) and baked at 250 $^{\circ}\text{C}$ for 30 min. For all samples in this study the precursor film thickness was ~ 50 nm. Structure change was monitored under an optical microscope equipped with a digitally controlled heating system and optical images were taken from the top side of the transparent samples. For all samples the heating ramp was 30 $^{\circ}\text{C min}^{-1}$ and the time counting started immediately when the programmed annealing temperature was reached. Our experiments prove that the optical microscope is an effective way for this work because of the good optical contrast between the crystalline and amorphous phases. Other techniques we have used, like atomic force microscope (AFM), did not give clear information due to the poor contrast of morphologies in such thin films. Fig. 2 shows the recorded sequential images of the crystal nucleation and growth process under 205 $^{\circ}\text{C}$ annealing on the glass (left) and 200 $^{\circ}\text{C}$ on PI (right) substrates, respectively. In the case of the PI substrate, the crystallites appear to be in ellipsoidal form and gradually evolve to a leaf-like shape due to the developed fractal growth in the late stage of crystallization. In contrary, the crystallites grown on the glass substrate appear in irregular disk-like shape and hardly show any anisotropy. Fig. 3 shows the final “mosaic” and “leaf” crystalline structures on glass (Fig. 3a) and PI (Fig. 3b) substrates, respectively.

The time dependence of crystal size was measured by tracking individual crystals during the annealing. Fig. 4a and c shows the results taken from the crystals grown on the glass substrate under 205 $^{\circ}\text{C}$ and the PI substrate under 200 $^{\circ}\text{C}$, respectively. Average radius was measured for the disk-like crystals, while half the length of the axis (HLA) for both major and minor axes were measured for the ellipsoids. The growth speed (slope of the line) of the crystals on the glass substrate does not change, while on the PI substrate it changes in both axes of the ellipsoids after an initiation stage (as indicated by the arrows). For all the samples observed under a constant annealing temperature the measured speed of crystal growth is constant regardless of which crystal was chosen. The difference in the initiation time of nucleation only causes a line shift as shown in Fig. 4a and c. The growing speed of the crystal (V) for different annealing temperatures (T) from 190 $^{\circ}\text{C}$ to 220 $^{\circ}\text{C}$ was measured. By fitting the experimental data of $\ln V \sim 1/T$ with the relation:

$$V = V_0 \exp(-E/kT), \quad (1)$$

an activation energy E can be obtained by plotting $\ln V \sim 1/T$ (where V_0 is a constant and k is the Boltzmann constant). Fig. 4b and d shows the experimental $\ln V \sim 1/T$ plots from the two types of samples. The

obtained activation energy from the samples on the glass substrates is $E^G = 1.27$ eV, while for that on the PI substrates are $E_a^P = 0.99$ eV and $E_b^P = 0.94$ eV for the major and minor axes of ellipsoid, respectively with an average $E^P = 0.965$ eV. For evaluating E_a^P and E_b^P only the linear part as shown in Fig. 4c was used. The sudden change of the crystal growth speed in Fig. 4c can be explained by the facet-roughing Kosterlitz–Thouless (KT) transition as observed previously [31]. The reason of the observed KT transition here is not clear. It might be caused by a tensile stress induced by a volume reduction of the crystalline phase in comparison to its amorphous precursor. In order to better understand the observed crystalline structures, an X-ray diffraction (XRD) analysis of the crystallized films on both glass and PI substrates has been

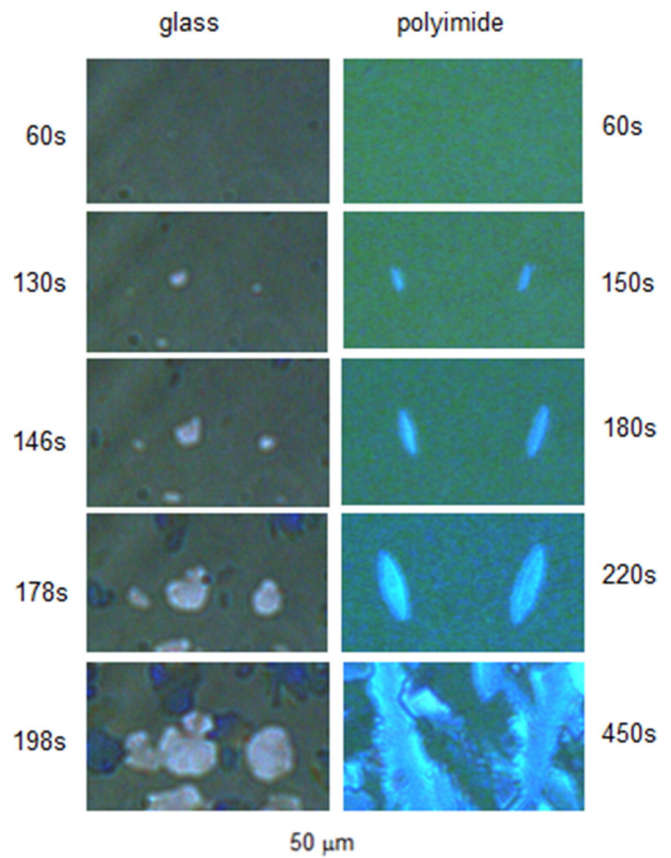


Fig. 2. Evolution of the crystal nucleation and growth of TBP on the glass substrate at 205 $^{\circ}\text{C}$ (left) and on the PI substrate at 200 $^{\circ}\text{C}$ (right).

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