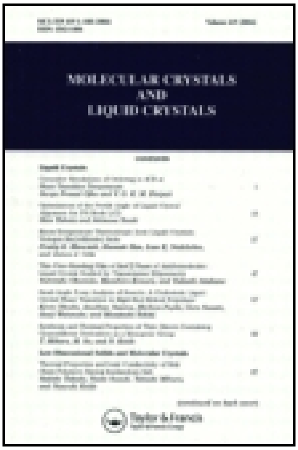

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Large Domain Growth of N,N′-bis(octyl)-1,4,5,8-naphthalenetetracarboxylicdiimide Film by Annealing Under Sealed Condition

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A novel method of "sealed annealing" was proposed to obtain large crystalline domains in organic deposited films. The deposited film of naphthalene tetracarboxylic derivative having long alkyl chains (NTCDI-C8H) was annealed with a cover substrate put on it near the melting point. The cover substrate prevented melting or sublimation of the deposited film, resulting in a growth of large domains having a size reaching several hundreds microns, which can be clearly observed by a polarizing microscope.

Keywords: anneling; crystalline domains; naphthalene tetracarboxylic derivative; organic field effect transistors

INTRODUCTION

A great deal of efforts has been reported to make the crystal domain of the deposited film larger in the field of organic field effect transistors (OFETs). The deposited films of acene materials, that are known to show high performance, basically have a polycrystalline structure, and its grain boundary decreases the carrier mobility of the gate-induced charges at the semiconductor/insulator interface. If we could grow large crystalline domains bridging a gap between the source and drain electrodes, higher performance of OFETs would be expected. There are many approaches to reduce the grain boundary, using alkyl substituted molecules [1] or single crystal of organic materials [2],

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elevating the substrate temperature [3], and treating the substrate surface [4].

In this study, we proposed a novel method of annealing under sealed condition to obtain a large crystal domain in the deposited films. A naphthalene tetracarboxylic derivative having long alkyl chains (Fig. 1, NTCDI-C8H) was used as an active layer, which is known as an excellent n-type organic semiconductor [5]. The deposited film on a SiO_2/Si substrate was annealed with a cover substrate put on it. The film structures were evaluated by a polarizing microscopy and an X-ray diffractometer. This sealed annealing method prevented melting or sublimation of the organic film, and finally achieved a growth of large crystalline domains having a size reaching several hundreds microns.

EXPERIMENT

Figure 1 shows the schematic diagram of the annealing method under sealed condition. The compound N,N′-bis(octyl)-1,4,5,8-naphthalenetetracarboxylicdiimide (NTCDI-C8H, supplied from Dainichiseika Color

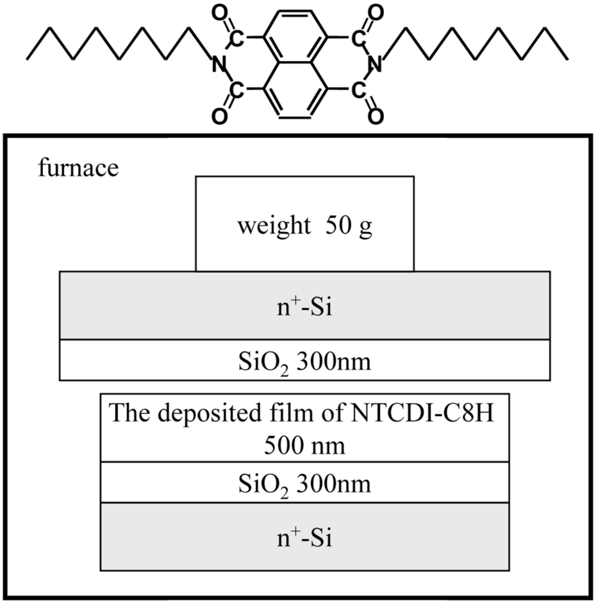

FIGURE 1 The schematic diagram of the annealing method under sealed condition. Chemical structure of *N,N′*-bis(octyl)-1,4,5,8-naphthalenetetracarboxylicdiimide (NTCDI-C8H) is also shown.

& Chemicals Mfg. Co. Ltd.) was purified twice by the train sublimation technique. First, the NTCDI-C8H was deposited on a SiO_2/Si substrate at deposition rate of 0.1–0.2 nm/s under a base pressure of 1.0×10^{-5} torr. The film thickness was 50 nm. Next, a covering substrate of SiO_2/Si was put on it with a weight of 50 g to produce the sealed condition. Then, they were annealed near the melting point under atmospheric condition in the furnace. In order to prevent the crack formation, the substrate was cooled gradually at a rate of 0.1°C/min.

The film structure was evaluated by a polarizing optical microscope (Nikon, Eclipse Me 600) and an X-ray diffractometer (XRD, Rigaku, RINT-2200). The thermal property of the film was measured by a differential scanning calorimetry (DSC, Seiko Instruments, DSC 22C).

RESULTS AND DISCUSSION

First, we measured the thermal property of NTCDI-C8H to decide heating condition. Figure 2 shows the DSC curves of NTCDI-C8H for two cycles of heating (from 40 to 240°C) and cooling (from 240 to 40°C) sequence at a scanning rate of 1°C/min. The heating curve showed only one endothermic peak at 180.4°C and the cooling curve also showed one exothermic peak at 184.1°C. The deposited film of NTCDI-C8H shows clear diffraction peaks at room temperature, which can be assigned to crystal phase, and the DSC peak around 180°C corresponds to the melting point. Therefore, it was concluded that NTCDI-C8H did not have liquid crystal phase between crystal and isotropic phase. Generally, many compounds having long alkyl chains (e.g. α,α'-didecyloligothiophenes) tend to have one or two liquid crystal phases [6], but the molecular packing of NTCDI-C8H seems to be so rigid that liquid crystal phase is not observed. This result is desirable for OFETs because the field effect mobility in liquid crystal phase is inferior to that of crystal phase for the same domain size [7].

The macroscopic film structures for various annealing conditions were evaluated by the polarizing optical micrographs. The annealing temperature was set to 180°C according to the DSC results. The As-deposited film grown at room temperature gave a uniform image with no structure at the magnification of 200, and any crystalline domains were not observed (Fig. 3(a)). When the film was annealed without a cover substrate (under open condition), it once melted and formed many isolated islands structures (Fig. 3(b)). On the other hand, in the film annealed at 180°C for 1 hour with a cover substrate (under sealed condition), a growth of large crystalline domains was observed and the size of domains reached several hundreds microns (Fig. 3(c)). Since the film annealed under open condition never showed large

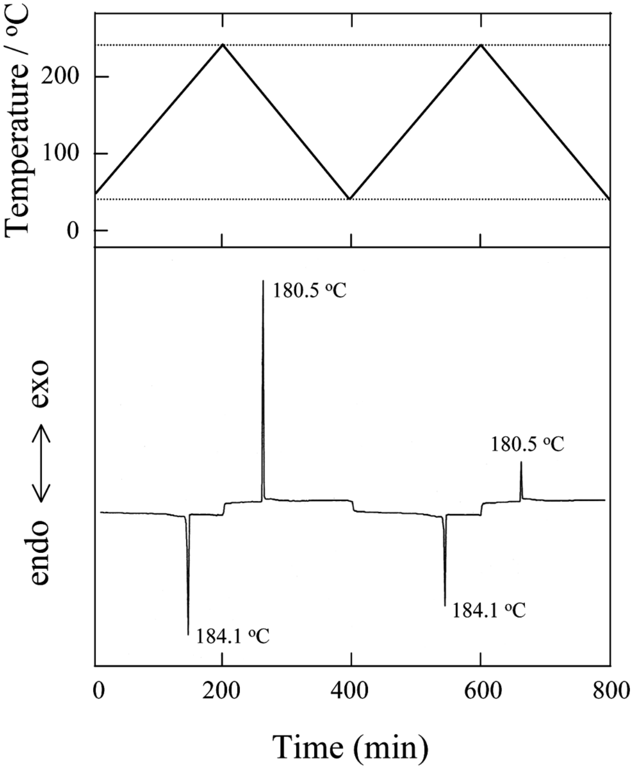

FIGURE 2 DSC thermogram of NTCDI-C8H for two cycles of heating and cooling processes. The measurement temperature was between 40°C and 240°C and the heating or cooling rate was 1°C/min.

domains in spite of tuning the annealing temperature, the large domain growth was attributed to the sealed annealing. The NTCDA-C8H film deposited at the substrate temperature of 70°C was investigated as a comparison, because it has been reported that the field effect mobility becomes the largest in that case. However, the micrograph (Fig. 3(d)) revealed that the deposited film composed of very small grains of 1–2 μm and that the domain size was not enough to cover the several microns gap generally used in OFETs.

To elucidate the microscopic structures of the annealed films, X-ray diffraction patterns were measured (Fig. 4). All the films, the As-deposited film, annealed under the sealed condition, and annealed under the open condition, showed a sharp diffraction peak at $2\theta = 3.95^\circ$ corresponding to an interplane distance of 22.3 Å. This peak was attributed to the length of the longest axis of NTCDI-C8H

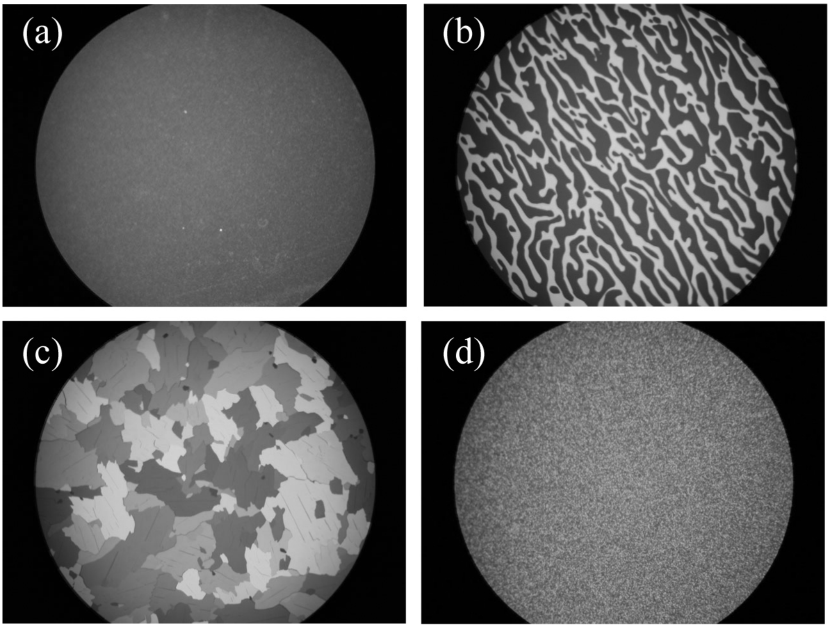

FIGURE 3 Polarizing optical micrograph of NTCDI-C8H films, (a) As-deposited film, (b) after annealing at 180°C for 1 hour under sealed condition, (c) under open condition, (d) deposited on a substrate heated at 70°C.

molecule, which indicated that the molecules were standing almost perpendicular to the SiO_2 surface. Hence, it was revealed that all the films had enough high crystallinity and there seemed to be no difference in microscopic structures or molecular stacking. Since uniform color in the each domain was observed in the polarizing micrographs and a molecular step having a height of this interplane distance was observed by atomic force microscopy (the data was not shown) on the surface, we concluded that the each domain had a single crystal structure.

Thus, the annealing under sealed condition was effective to obtain a large domain structure in the NTCDA-C8H deposited film. The effect of the covered substrate was essentially to prevent melting of the organic film for high temperature around the melting point. The high temperature annealing without aggregation by melting promotes rearrangement of the organic molecules efficiently. As a result, each molecule finds a more stable site and finally forms a large crystalline domain. The microscopic mechanism to prevent melting or sublimation is not clear, but it is plausible that the vapor pressure of the organic material in the confined space between the both substrates.

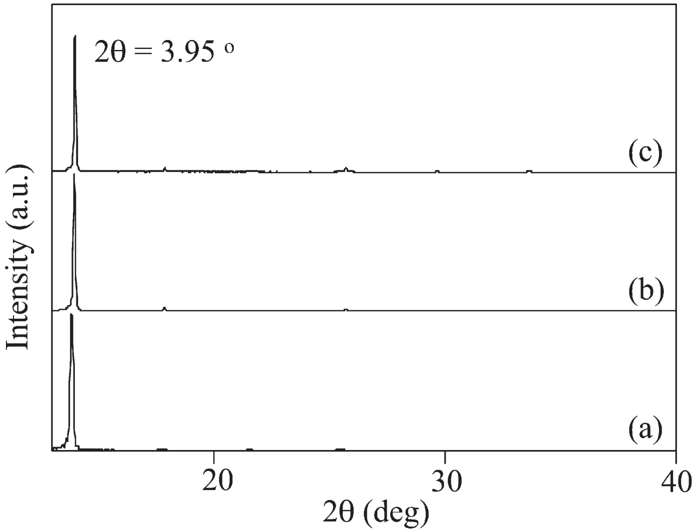

FIGURE 4 X-ray diffraction patterns of NTCDI-C8H films deposited on a SiO_2 substrate, (a) As-deposited film, (b) after annealing at 180°C for 1 hour under open condition, (c) under sealed condition.

That situation can increase the melting point compared to the case without the covered substrate.

The characteristics of the organic material are also important for the sealed annealing method. We found that this method is more effective for the molecules having long alkyl chains like NTCDI-C8H. The crystalline films composed of rigid molecules, such as pentacene or α-sexithienyl, sublimed easily and resulted in void formation [8]. While the subliming materials cannot rearrange on the film surface without desorption, the materials having clear melting point like NTCDI-C8H can rearrange on the surface without desorption as long as aggregation by melting is prevented. These materials having long alkyl chains are very interesting because they have both strong arranging force based on their alkyl chains and a clear melting point implying low sublimation tendency. We are investigating the melting behavior around the melting point and trying to control the rearrangement process dependent on the atmosphere.

CONCLUSION

In conclusion, we proposed the sealed annealing method to obtain large domains in organic deposited films. Since the sealed condition prevented melting or sublimation of the organic film, high temperature near the melting point can promote rearrangement of the surface molecule without aggregation or desorption, resulting in a growth of large domains having a size reaching several hundreds microns. Such large domains are expected to liberate channel charges of OFETs from grain boundaries reducing the field effect mobility.

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