

Crystal Growth of Doped Organic Semiconductors

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1. Introduction

Single crystals of organic semiconductors are important for the basic study of transport mechanism of electrons, excitons and phonons in the soft material. It is also promising in the application of high efficiency solar cells because exciton mean free path might be elongated by orders of magnitudes compared with the ordinary amorphous semiconductors[1]. Thermoelectricity is another one of the promising applications of doped organic semiconductors [2]. In order to explore these possibilities, it is highly desirable to prepare doped organic semiconductor single crystals to enhance the electronic conductivity.

There are various methods to grow crystals of organic semiconductors: physical vapor transport, evaporation or cooling of solution and cooling of melt and so on. However, it is in principle difficult to make chemically doped crystals from the above methods. Physical vapor transport separates the dopant from the semiconductor very easily during the sublimation and the transport process. Solution method is difficult to control the size of the crystal and the dopant concentration. Growth from melt has only limited application because many organic semiconductors decompose before melting. We therefore focusing on flux methods[3].

Flux method is a variation of solution method in a sense, but the solvent is solid at room temperature. Only at elevated temperature the solvent melt and dissolves solute, which is organic semiconductor and dopant in the present case. We have studied this technique for the organic crystal growth and found that high solubility of the organic semiconductors is observed using aromatic compounds. We present our recent results with CuPc (copper phthalocyanine) as the organic semiconductor and anthraquinone (AQ) as the flux.

2. Cooling CuPc - AQ solution

We have found that AQ dissolves various organic semiconductors to high concentration. Concentrations up to 10 Molar % was obtained for CuPc solute. AQ is low toxic, very stable at high temperature (stable upto 390 °C), and relatively inexpensive (~ ¥20000 / kg), and melt at 286 °C. These characteristics makes AQ as an attractive choice for the flux technique.

We sealed CuPc with AQ at different molar concentrations (5-7%) in a glass tube (1cm diameter) and completely melted to make the solution. Then the entire

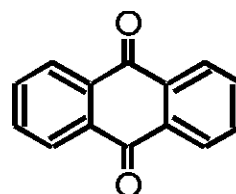


Fig. 1: anthraquinone (AQ)

sample was slowly cooled from one side. After cooling to room temperature, the tube was opened and the lump was washed in an Soxhlet extractor using ethanol and acetone in sequence. The lump was cut in various directions and characterized by various methods.

From X-ray diffraction, this sample is a mixture of CuPc and AQ. It shows that AQ was not completely removed. The SEM images are shown in Fig. 2. Thin needle crystals with the diameter of 1-5 μm are observed. In the perpendicularly cut sample, the needles are sticking out from the surface, while in the parallel cut sample, the needles are aligned. It indicates the orientation of the thin needle crystals are aligned to the cooling direction.

It was found that it is difficult to grow the crystals with macroscopic size by cooling. It might be due to possible peritectic nature of CuPc-AQ system.

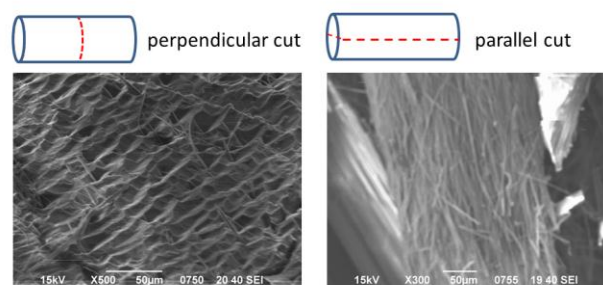


Fig. 2: SEM images of CuPc obtained by cooling of an AQ solution.

4. Removing AQ from an solution by two chambers method

Since we have noticed the difficulty of the crystal growth by simply cooling the CuPc-AQ solutions, we are attempting the "drying" of the flux solution. In the

drying method, it is difficult to control the speed of solvent removal, especially at high temperatures as in the present case. We have devised a new method using two chambers in order to solve this problem. Figure 3 shows the apparatus used in the experiment.

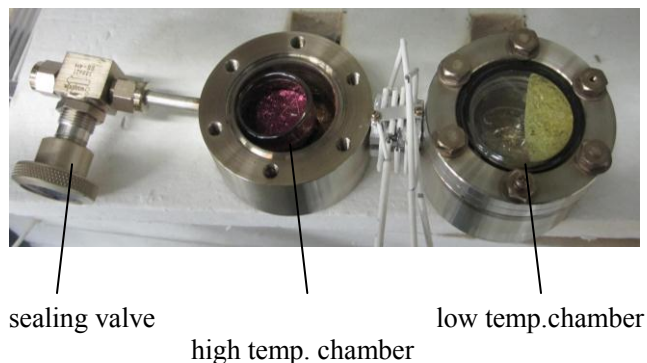


Fig.3 Two chambers apparatus for the gradual solvent removal.

The entire system is made from ultrahigh vacuum compatible parts. They are welded or connected with metal gaskets. In the high temperature chamber, the raw material (CuPc and AQ) was placed in a glass dish. In the low temperature chamber, AQ powder was placed in order to supply the vapor pressure during the initial heat-up. The chambers were closed and pumped out, then inert gas was filled in at 1 atm. The chambers were placed in three zone furnace. The temperatures of the three zones were raised to the melting point of CuPc-AQ solution and kept for a certain time. Then the low temperature side was gradually cooled. Since AQ has high vapor pressure at these temperatures ($\sim 280^\circ\text{C}$), AQ was gradually transported to the low temperature side, increasing the concentration of the solution as a result.

Figure 4 shows an optical microscope image of the crystals obtained by this technique. The size of the needle like crystals are $50\text{-}100\ \mu\text{m} \times 1\text{-}3\ \text{mm}$. It will be possible to increase the crystal size by precisely controlling the solvent removal process.

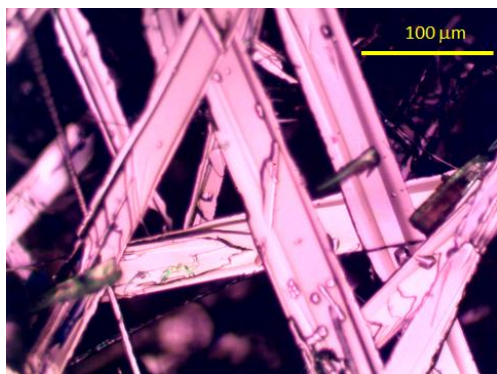


Figure 4: CuPc crystals obtained from two chambers method

5. Doping of CuPc with FeCl_3

FeCl_3 is frequently used as a dopant to organic semiconductors. We found that green-colored crystals are obtained by melting CuPc, FeCl_3 and AQ and using the solvent removal technique. It shows X-ray diffraction different from CuPc. We speculate that it is an indication of charge transfer complex. By lowering FeCl_3 concentration, it was found that the surface of the "crystal" becomes like a patchwork of Fe-rich portion and Fe-poor portion, which suggests the phase separation. It has not been reported what kind of materials exist (or not exist) between a charge transfer complex and pure materials. Since the electric conductivity of the material is substantially improved by mixing FeCl_3 , we expect an "doped" phase exist in CuPc- FeCl_3 system. Further analysis is underway.

5. Conclusions

In the attempt to make a single crystal of CuPc with a macroscopic size from flux solution, we found an indication that peritectic reaction might occur in CuPc-AQ system. We devised a new method of gradually removing the solvent using two chambers and succeeded in growing crystals with mm length. We found FeCl_3 forms a green-colored compound with CuPc and the conductivity was increased.

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