

Preparation of polydiacetylene single crystals based on physical vapor growth technique

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Abstract

We have succeeded in obtaining 10-mm-size polydiacetylene (PDA) single crystals using the physical vapor growth technique followed by the irradiation of ultraviolet (UV) rays, for the first time. The variety of growth conditions, such as growth temperature, growth time, carrier gases, and flow rate of gases are examined. Especially, the growth temperature and growth time have clear effects on the quality of crystals. Morphologies and sizes with relation to the various growth conditions are also observed. They show only one type of plateletlike shape with a pair of large parallel planes, regardless of variety of growth conditions. The crystal thickness was estimated as about 500 nm by the observation of atomic force microscopy. The solubility of diacetylene (DA) and PDA to some organic solvents, and the X-ray diffraction data indicate that the obtained crystals are single crystals.

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1. Introduction

Many studies focusing on polydiacetylene (PDA) have been steadily carried out in recent years. For example, Okawa and Aono selected one type of PDA for nano metal wires to construct a nanoscaled transistor in 2001 [1,2]. Ikoma et al. discovered the existence of spin soliton in a ladder-type PDA in 2002 [3]. Masuda and coworkers succeeded in fabricating PDA nanofibers [4,5]. These remarkable achievements promise the development of new type devices using PDA, and the estimated large mobility certainly makes us hopeful to variety of device applications. To achieve such aims, a high quality single crystal must be needed as an important device unit. Vigorous research studies of the structures and defects of PDA crystals have been carried out for long years, such as that in references [6–8]. From the view point of the growth technique, the physical vapor growth has been re-appreciated for obtaining high quality crystals in these

days. The achievement that Karl obtained 10-mm-ordered anthracene single crystals by the physical vapor growth for the first time can be recognized as an important historic aspect [9]. From his work, the physical vapor growth of a variety of organic materials has been successfully performed mainly by Laudise et al. [10] and Kloc et al. [11]. It is noteworthy that the physical vapor growth technique has various excellent properties, such as the ability to remove impurities due to the difference in vapor pressure among mixed materials, and the ability to grow 10-mm-sized single crystals within only 1–5 h. Detailed theory regarding the growth process has constructed by Laudise et al. [10] and Kloc et al. [11] by applying the conventional Handley cell model [12], which successfully explain the growth mechanism. The application of the physical vapor growth technique to organic materials has a certain possibility to aid the growth of high quality single crystals. Under such backgrounds, the physical vapor growth of the single crystals of 2,4-hexadiyne-1,6-diol, which is a typical PDA [13], was performed. The examination of the growth conditions, the change of sizes and shapes of crystals depending on the growth temperature, growth

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time, carrier gases, flow rate of gases will be reported in this paper.

2. Experimental

The source material, 2,4-hexadiyne-1,6-diol, was purchased from Tokyo Kasei Co., Ltd. Diacetylene (DA) crystals were grown by the physical vapor growth furnace, as shown in Fig. 1. Glass tubes of different diameters, a reaction tube and a crystal growth tube were placed coaxially. The lengths and diameters of both reaction and growth tubes were 500 and 30 mm, and 250 and 25 mm, respectively. The reaction tube was surrounded by a resistance wire at an equal distance. A band heater was set near the source boat to establish some desired temperature, which was provided by inputting a current to both the resistance wire and the band heater. The source material was set on the source boat. The temperature of the source boat was varied between 150 and 300 °C for evaporation, and the other regions were kept at 80–100 °C.

For in situ observation of the growth process, both edges of the reaction tube were kept outside of the furnace; each window had 30 mm length. Helium was selected as a carrier gas, supplied at 50 ml/min; however argon and nitrogen were also effective. But argon or nitrogen carrier gases lead the growth of only 1 mm length crystals even the growth temperature and growth time were varied. It can be understood that the differences of crystal sizes corresponding to that of carrier gases were caused by the velocity distribution within the tube. Refs. [10–12] are quite useful for understanding the physical effects of gas flowing. After the vapor growth, a number of crystals were observed at the internal surface of the growth tube. The growth tube with a number of DA crystals was removed from the furnace smoothly. DA crystals were irradiated by the UV rays for about 10–30 min to obtain PDA single crystals. The crystal morphologies and molecular structures were examined by optical microscopy and C-13 nuclear magnetic resonance (C-13 NMR). X-ray diffraction was performed to decide the crystal structure. The solubility of DA and PDA crystals to several organic solvents are also examined.

For the purpose of the superpurification, the recrystallization was performed 2 or 3 times, which was clearly

effective to remove impurities in any cases. In this case, the difference of vapor pressure between DA and impurities effected for the superpurification.

3. Results and discussion

Fig. 2(a) and (b) show photographs of DA and PDA crystals with 10-mm-length of the identical sample, respectively. For crystals of paralleloiped shape, the longer size is used for discussion in this context. The crystal color was gradually changed under the UV irradiation for 10–30 min from transparent to gold. This result indicates that the solid-state polymerization occurred by the UV irradiation for 10–30 min. Additionally, the UV irradiation over 30 min lead only keeping the gold color.

The morphology shows plateletlike with a pair of large paralleloiped planes constructed by the angles of 108.5° and 71.5° [14]. The shape with anisotropic paralleloipe is one of the special characters of this type of PDA crystals. The crystal thickness was estimated as about 500 nm based on our observation by atomic force microscopy. Preliminary measurements of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been made for several kinds of DA compounds. By considering the results of the melting point and the corresponding data of the vapor pressure, we selected a 2,4-hexadiyne-1,6-diol. In order to optimize the growth condition, the evaporation temperature and the growth time were varied systematically. First, the evaporation temperature of the source boat was varied from 150–300 °C, for the growth area kept at 80–100 °C. The experimental results indicate that many crystals with a sharp facet in shape and ca. 10 mm in size were observed at the evaporation temperatures of 150–220 °C. Next, the respective growth times of 6 and 1 h were set for the fixed evaporation temperatures of 150 and 220 °C, i.e., two sorts of the growth condition of 6 h, 150 °C and 1 h, 220 °C. When crystals grown at the conditions were compared, the morphology was identical as shown in Fig. 2, but the size was different from each other. The crystal size in the 1 h, 220 °C was about a half, compared to that in the condition of 6 h, 150 °C. It seems that the 6 h, 150 °C provides a quasi-static condition suitable for the physical vapor growth.

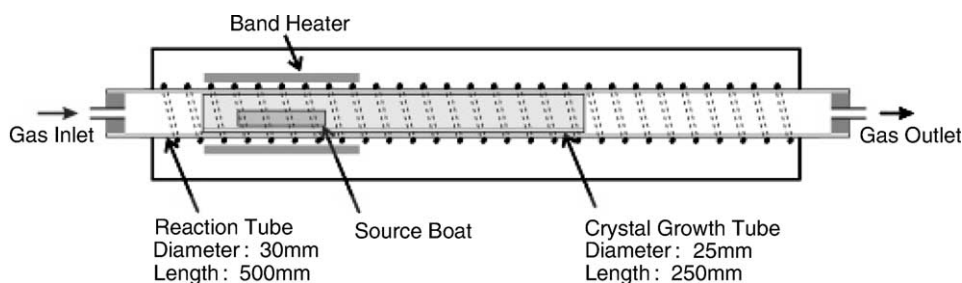


Fig. 1. Schematic drawing of the physical vapor growth furnace. A reaction tube, a crystal growth tube, a source boat, a resistance wire and a band heater were set in the furnace. The lengths and diameters of the reaction tube and crystal growth tube are 500 and 30 mm and 250 and 25 mm, respectively. The reaction tube was surrounded by the resistance wire at an equal distance. The band heater was placed at the boat to evaporate source materials.

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