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Effect of solid-state polymerization on crystal morphology of a type of polydiacetylene single crystal obtained by physical vapor transport technique

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ABSTRACT

The effect of solid-state polymerization on the crystal morphology of a type of polydiacetylene single crystal grown by the physical vapor transport technique was experimentally investigated by optical microscopy and atomic force microscopy. The formation of backbone chains along the [001] direction was unequivocally confirmed by our experimental results. The specific cleavage characteristics of the polydiacetylene single crystal were confirmed to be strongly affected by a morphological change due to solid-state polymerization.

1. Introduction

Many research studies of nanoscale electronic devices using numerous types of functional organic material have been performed over the past decade, for example, in Refs. [1–5]. Polydiacetylenes (PDAs) with π-conjugated chains are expected to exhibit a variety of interesting physical properties [6–9]. To achieve PDAs with excellent physical properties that can be applied in electronic devices, organic single crystals have become important candidates. Since Karl's pioneering work [10], the physical vapor transport (PVT) technique has been developed to obtain high-quality organic single crystals, mainly by Laudise et al. [11] and Kloc et al. [12]. Recently, a type of PDA single crystal has been grown by the PVT technique [13]. This PDA single crystal is expected to contain a smaller amount of impurity, because its composites are separated during crystal growth owing to the vapor pressure difference between the source material and impurities. The crystal configuration of many polymer materials is affected by the formation of polymeric chains, which is different from the case of low-molecular-weight materials. In many cases, the formation of polymeric chains induces anisotropic changes in their configurations. This type of PDA is expected to polymerize along both the [001] and [101] directions [14]. Both of these predicted backbone chain directions effectively satisfy the suitable polymerization conditions for PDAs [15]. PDAs have backbone chains with a unique character of maintaining their rigid and linear shapes; as a result, their backbone chain directions coincide with some crystallographic orientations. The crystal morphology should be evaluated considering the effect of the formation of backbone chains on the crystal configuration. Atomic force microscopy (AFM) is suitable for investigating aspects of the crystal surface, such as the crystallographic orientation of backbone chains, and the specific configuration of backbone chains. Moreover, in many cases, PDAs exhibit unique cleavage characteristics owing to the formation of polymeric chains. The discussion on such a unique cleavage character is also effective for understanding the morphology of PDA single crystals.

In this study, the morphology of PDA single crystals grown by the PVT technique is discussed on the basis of the results of optical microscopy and AFM. The unique mechanical cleavage characteristics are also considered in order to understand such a morphology.

2. Experimental details

The source material, 2,4-hexadiyne-1,6-diol, was purchased from Tokyo Kasei Co., Ltd. Many diacetylene (DA) monomer single crystals were obtained by the PVT technique [13]. A schematic drawing of the horizontally arranged furnace used for the PVT technique is shown in Fig. 1. 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 were 500 and 30 mm, and 250 and 25 mm, respectively. Small tubes of 5 mm diameter were set at both edges of the reaction tube for the inflow and outflow of carrier gasses. The reaction tube was surrounded by resistance wire at a fixed distance from the tube, which maintained the desired temperature in the furnace. The band heater was set around the boat to establish a temperature gradient for the DA source. The temperature gradients required for physical vapor growth were provided by supplying a sufficient current to the resistance wire and band heater. The evaporation

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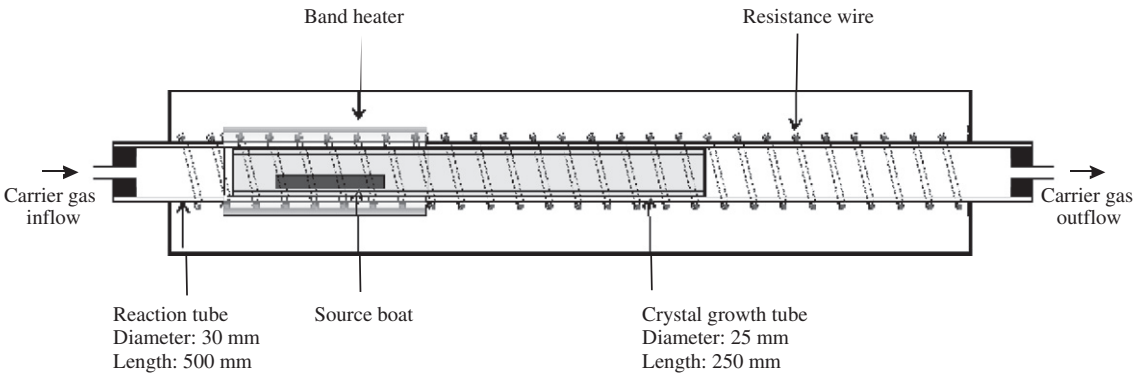

Fig. 1. Schematic drawing of the crystal growth furnace used for the PVT technique.

temperature was set at 150 °C and the growth time was set at 6 h, which provided a quasi-static growth condition. After the physical vapor growth, some appropriate DA single crystals were selected and extracted from the growth tube, and the samples were polymerized by irradiation with ultraviolet (UV) rays of 241 nm wavelength. The surface configuration was investigated by tapping-mode AFM (Nanoscope III, Digital Instruments, Inc.) and optical microscopy. The mechanical cleavage characteristics were then evaluated on the basis of the morphological change due to the application of localized stress to the crystals. It is easier to cleave PDAs along the corresponding backbone chain directions because of the rigidity of the backbone chains. Hence, it is important to discuss the polymerization directions of PDAs with regard to the cleaved planes.

3. Results and discussion

Fig. 2(a) shows the typical configuration of a PDA single crystal grown by the PVT technique. The crystal possesses a unique plateletlike morphology with a pair of large parallelogram (010) planes. The crystallographic indices of the narrow lateral planes are the (100), ($\bar{1}$00), (001), and (00$\bar{1}$) planes. The conventional crystallographic constants are those of the P21/c monoclinic system: a = 4.0891 Å, b = 15.991 Å, c = 4.7691 Å, and β = 106.6°. On the basis of the theoretical prediction by Hädicke et al., the backbone chains are expected to be formed along both the [001] and [101] directions [14]. Moreover, both the [001] and [101] directions satisfy the suitable polymerization conditions [15].

The photographs in Fig. 2(b) and (c) were taken with the aim of confirming the unique cleavage characteristics of this type of PDA single crystal. After taking the photograph of the PDA single crystal in Fig. 2(b), some mechanical stress was applied to the crystal. As a result, the aspect changed to that shown in Fig. 2(c). Fig. 2(c) shows that many long and narrow crystal fragments split from the original crystal. Most of the fragments were cleaved parallel to the [001] direction. The morphological change from Fig. 2(b) to Fig. 2(c) indicates that most of the polymeric backbone chains were constructed along the [001] direction owing to UV irradiation. Generally, the polymeric backbone chains of PDAs have a unique character of maintaining their rigid and linear shapes. This unique character is considered to affect the formation of the long and narrow configuration of the crystal fragments. For this type of PDA, both the [001] and [101] directions satisfy Baughman's suitable conditions for polymerization [15]. On the basis of the cleavage characteristic shown in Fig. 2(c), most backbone chains were thought to be formed along the [001] direction, and never along the [101] direction. The crystallographic [101] direction seems to be hardly used for polymerization for this type of PDA, even if this direction is theoretically suitable for polymerization.

Fig. 3(a) shows a tapping-mode AFM image of the DA single crystal surface. An atomically flat (010) surface with monomolecular and bunched steps was observed. The sectional profile along the white

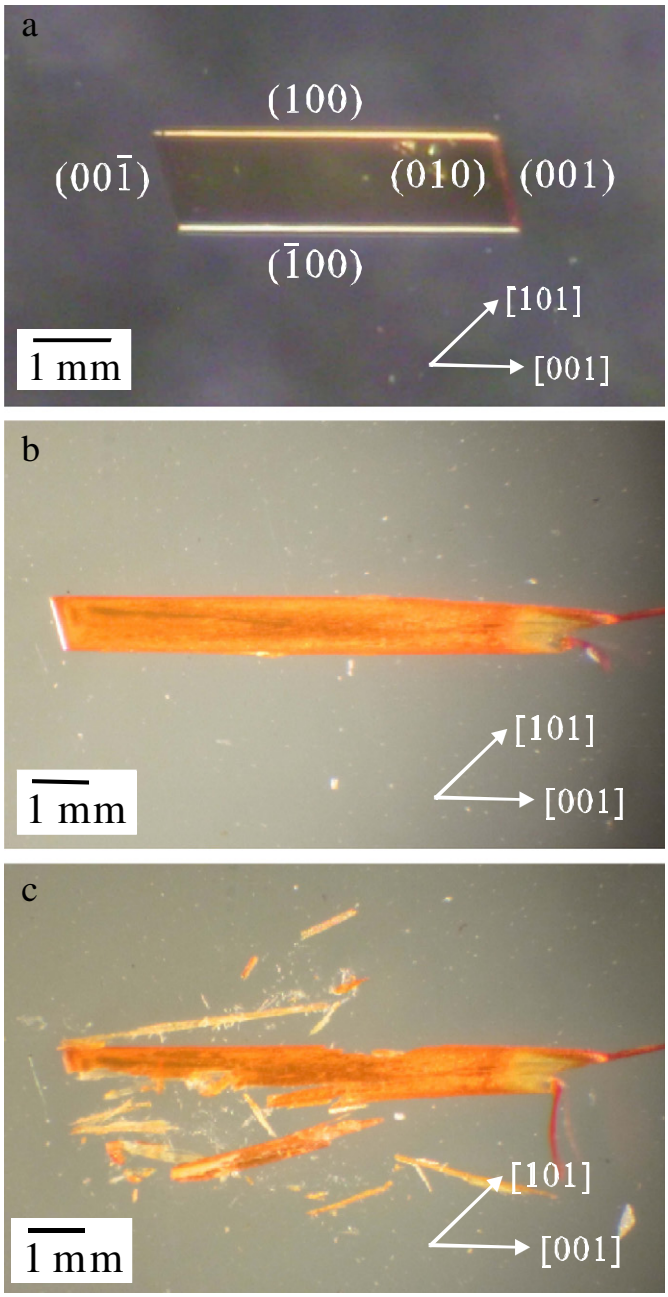

Fig. 2. (a) Typical configuration of a PDA single crystal grown by the PVT technique and images of the PDA single crystal before (b) and after (c) the application of mechanical stress.