



Highly ordered alignment of conducting nano-crystallites on organic semiconductor single crystal surfaces



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ARTICLE INFO

Article history:

Received 8 August 2014

Received in revised form 10 February 2015

Accepted 12 February 2015

Available online 20 February 2015

Keywords:

Organic solids

Crystal surfaces

TTF–TCNQ

Nano-crystallites

ABSTRACT

A conducting thin layer of aligned fibrous nano-crystallites of tetrathiafulvalene–7,7,8,8,-tetracyanoquinodimethane (TTF–TCNQ) is fabricated directly on semiconducting organic crystals under ambient conditions. The widths of the crystallites are 50–100 nm. Their growth direction is governed by the direction of the intermolecular charge transfer interactions in the substrate crystal. The carrier transport in the film is metallic between 150 K and 300 K, reflecting the uniform alignment of the TTF–TCNQ nano-crystallites on the substrate crystal.

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1. Introduction

Organic solids with electrical conductivity, ferroelectricity or ferromagnetism, called functional molecular solids, have been widely investigated since the organic semiconductor perylene–bromine complex and the organic conductor TTF–TCNQ (tetrathiafulvalene–7,7,8,8,-tetracyanoquinodimethane) were initially synthesized [1–6]. Two of the most advantageous properties of the component compounds are their solubility in organic solvents and their ability to vaporize at low temperatures. These properties are expected to be employed in next-generation devices such as flexible, low-cost and large area devices. In addition, because their functions are originated by unique electronic or band structures, functional molecular solids have become a target of basic research interest [7].

Recently, various organic electronic devices based on organic films have been developed by world-wide researchers [8–12]. High performance devices were fabricated by using TIPS pentacene (6,13-Bis(triisopropylsilylethynyl)pentacene) or C8-BTBT (2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene) [13,14]. In these devices, the carrier transport axes are aligned along one direction. Such crystal growth is a key process in fabricating high performance semiconducting layers. However, fabrication of such films of functional organic materials is difficult.

Generally, the functions and physical properties of organic solids are anisotropic. Therefore, to use the “function” efficiently in thin film organic electronics it is necessary to align the crystallites. For example, TTF–TCNQ is a typical molecular conductor that has metallic transport properties along the *b*-axis, while the *a*- and *c*-axes are insulating [2]. TTF–TCNQ thin films fabricated with simple deposition techniques have random orientations of the crystallites and do not exhibit metallic behavior [15]. Alternative approaches to the control of the morphology of functional organics on inorganic substrates have been performed using Langmuir–Blodgett and chemical vapor deposition methods [16–18]. In the case of the TTF–TCNQ thin film growth, there were some reports of molecular orientation control with special equipments, for example vacuum deposition by applying electric fields or epitaxial growth on alkali-halide crystals [19,20]. The crystallites grown by such methods laid down on the inorganic substrates, forming two dimensional thin films that were suitable for use as electrodes for organic devices. In this paper, an efficient fabrication method to form conducting organic thin films with a highly ordered alignment of the crystallites is demonstrated. The films were formed directly on the semiconducting organic crystals of anthracene-TCNQ (Ant-TCNQ).

2. Experimental section

2.1. Materials and methods

Anthracene, TCNQ and TTF were purchased from Tokyo Kasei Co., Ltd. All materials were purified by vacuum sublimation before use.

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The Ant-TCNQ single crystals were prepared by co-sublimation of the respective components under 2.7×10^{-1} Pa in a sealed glass tube. The average crystal size was about $0.5 \times 0.5 \times 2.0$ mm.

Crystal structure and surface plane of Ant-TCNQ were determined by the X-ray diffraction method using an automated RIGAKU R-Axis Rapid X-ray diffractometer with graphite monochromated Mo K α radiation, at room temperature.

Scanning electron microscope (SEM) observations of the nanocrystals were carried out using a JEOL JSM-6700FT field-emission scanning electron microscope (FESEM). The sample crystals that were examined using the SEM were mounted on a sample holder with adhesive carbon tape. An acceleration voltage of 5.0 kV was applied during the observations. Raman scattering spectra were obtained with a RMP-510, JASCO Co., Ltd. A source-measurements unit R6243, Advantest Co., Ltd. was used to measure the current–voltage characteristics with a DC two probe method. The temperature dependence of the sheet resistance was measured by a DC four probe method with using R6243 as the current source and a nanovoltmeter 2182, Keithley Co., Ltd. The electron spin resonance (ESR) spectra of a bulk TTF–TCNQ crystal and the aligned crystallites on Ant-TCNQ were obtained using an EMX electron paramagnetic resonance spectrometer, Bruker Biospin Co., Ltd. Magnetic fields were applied perpendicular to the molecular stack axis of each crystal. Atomic force microscope (AFM) images were obtained by using Nanocute, SII Nanotechnology Inc., with a tapping mode.

2.2. Fabrication of TTF–TCNQ films on Ant-TCNQ

Charge transfer (CT) complex semiconductors have been used in high mobility transistors [21–23]. In this study, single crystals of the CT complex Ant-TCNQ were used as organic semiconducting substrates (Fig. 1a). Ant-TCNQ is classified as a weak CT complex because it contains the weak electron donor Ant. The resistivity of this complex is $1 \times 10^7 \Omega \text{ cm}$ at room temperature and the optical gap is 1.5 eV [24]. The crystal elongated axis corresponded to the *c*-axis. Fig. 1b shows the crystal structure of the Ant-TCNQ single crystals projected along the *c*-axis. The space group is *monoclinic C2/m*. The molecular long axes of both the Ant and TCNQ molecules coincided with the mirror plane. The donor and acceptor molecules were packed with a *mixed-stacked* motif along the *c*-axis, forming a one-dimensional column with π – π CT intermolecular interactions. The crystals had an irregular hexagonal cylinder shape, as shown in Fig. 1a. The largest surface plane corresponded to the (110) plane. The other two narrow planes corresponded to the (100) and (010) planes.

Fig. 1c shows a picture and schematic image of the method for fabricating TTF–TCNQ films. In the picture, black crystal is Ant-TCNQ crystal, and was placed on a silicon substrate whose thickness was 0.5 mm. TTF powder was put near the crystal with avoiding direct contacts between them. All solids which were Ant-TCNQ crystal, silicon substrate, and TTF powder were kept for a week under the ambient conditions in a polystyrene container at room temperature. The TTF–TCNQ thin film was formed on the semiconducting crystals via contact with the TTF vapor. Eventually, the silicon substrate became an effective shadow mask, contributing to a reduction in the amount of TTF that could react with the Ant-TCNQ in the masked area.

3. Results and discussions

3.1. Alignment of the TTF–TCNQ nano-crystallites

Fig. 2a shows a SEM image of the (110) surface of an Ant-TCNQ crystal that was reacted with a TTF vapor. The yellow broken line in Fig. 2a separates the unmasked and masked regions. In the masked region, fibrous TTF–TCNQ crystallites were observed along the *c*-axis of the Ant-TCNQ substrate crystal. Because this region was masked, these crystallites did not cover the entire region. The widths of the crystallites were 100–300 nm. In contrast, the surface in the unmasked

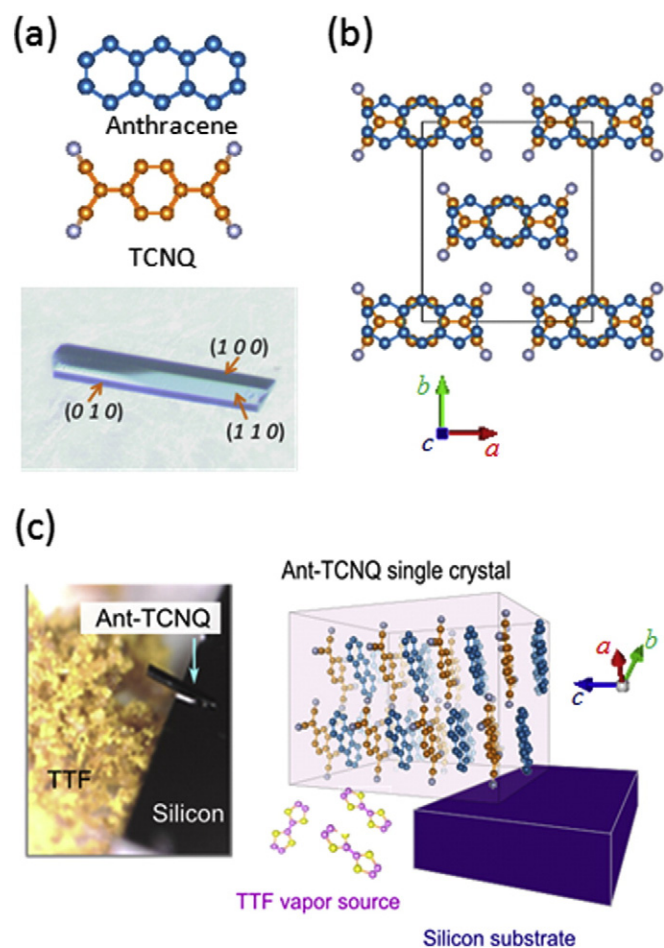


Fig. 1. (a) A photograph of an Ant-TCNQ crystal with the Anthracene and TCNQ molecular structures, (b) crystal structure of an Ant-TCNQ complex projected along the *c*-axis, and (c) schematic and real images of the fabrication process of a conductive thin film on a semiconducting organic crystal with unmasked and masked regions.

region was completely covered with thin TTF–TCNQ crystallites. The vertical intervals of the crystallites were too small to be observed on the scale used. A SEM image that focuses on the unmasked region is shown in Fig. 2b, where the aligned fibrous crystallites that grew along the *c*-axis of the crystal substrate covered the entire Ant-TCNQ surface. The widths of the crystallites were 50–100 nm. The growth difference between the masked and unmasked regions was caused by the difference in the amount of TTF vapor available to the Ant-TCNQ surface. Fig. 2c depicts the Raman scattering spectra of the surface that was reacted with a TTF vapor, an as-grown Ant-TCNQ crystal and TTF–TCNQ crystal. The spectral region corresponded to the C=C stretching mode of TCNQ (A_g), which was sensitive to the charge on TCNQ [25]. In the spectrum of the as-grown Ant-TCNQ, ν_4, A_g ; the C=C stretching mode of TCNQ at 1458 cm^{-1} and ν_6, A_g ; the C=C stretching mode of Ant at 1403 cm^{-1} were observed [26]. After the crystals had been exposed to the TTF vapor, a new peak at 1420 cm^{-1} appeared in the spectrum. The peak corresponded to that in the TTF–TCNQ spectrum, which is the ν_4, A_g mode of TCNQ $^{-0.59}$ [25]. As a result, it can be confirmed that the fibrous crystallites on the Ant-TCNQ single crystal were TTF–TCNQ. Thus, the TTF vapor efficiently reacted with the TCNQ at the Ant-TCNQ crystal surface.

The direction of the alignment corresponded to the *c*-axis of the semiconducting substrate crystal, which is the alternative molecular stack direction for Ant and TCNQ. Fig. 2d focuses on the fibrous crystallites grown at the crystal edge, formed between the (110) and (100) planes. The yellow broken line in Fig. 2d indicates the crystal edge, which corresponds to the *c*-axis of Ant-TCNQ. TTF–TCNQ strings grew

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