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Author(s)	Ohtomo, Manabu; Itaka, Kenji; Hasegawa, Tetsuya; Shimada, Toshihiro
Citation	Applied Physics Express, 4(2), 021601-1-021601-3 https://doi.org/10.1143/APEX.4.021601
Issue Date	2011
Doc URL	http://hdl.handle.net/2115/44910
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Type	article
File Information	tetrasublim20101215revised.pdf



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Strong pressure effect in the sublimation from tetracene single crystals and development of surface cleaning technique for organic semiconductors

Manabu Ohtomo^{1,3}, Kenji Itaka², Tetsuya Hasegawa¹ and Toshihiro Shimada³,

¹Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

²North Japan Research Institute for Sustainable Energy, Hirosaki University, Aomori 030-0813, Japan

³Department of Materials Chemistry, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

Abstract

We studied the sublimation of tetracene single crystals under vacuum and 1 atm inert gas to develop the surface cleaning technique for organic semiconductors. It was found that the microscopic sublimation behavior is strongly dependent on the gas pressure. Nanometer-scale roughening is observed after heating in vacuum, while layer-by-layer sublimation was observed under 1 atm Ar gas. Reflection high energy electron diffraction of the topmost surface showed streak patterns, which shows surface contaminants were successfully removed.

Electronic properties of organic semiconductor single crystals are now studied by many researchers because of the fundamental interest in carrier transport mechanisms and of their potential utility to flexible electronics. It is established that some organic single crystals exhibit high mobility^{1,2} and various devices can be fabricated including double gated FETs^{3,4} and light emitting transistors⁵. Their surfaces, however, are treated "as grown" in inert environment or after exposure to ambient atmosphere. It is reported that the surface cleanliness greatly affect the device performance⁶ and the crystallinity at the gate insulator interface is very important.⁷ For the application to the flexible electronics and organic heterojunction formation, and also for the fundamental studies by electron spectroscopy etc., it will be of great merit if the organic single crystals can be stored in shelf and transported from place to place without strict conditions such as ultrahigh vacuum. We have to develop the cleaning technique of the crystal surfaces for that purpose. Although various surface cleaning techniques have been developed for almost all of single crystalline materials, organic materials are rare exceptions of them. Cleavage is indeed a general technique for the surface cleaning and can be applied to thick largely grown organic crystals with simple layered structures. However, for thin plate shape crystals which is often preferred in organic electronics due to its high crystallinity and conductivity, we found that it is very difficult to cleave them because of their small and thin plate shape e.g. 2mm × 0.2mm × 300nm.

In the present work, we examined the molecular-scale surface sublimation of tetracene (C₁₈H₁₀) single crystals by reflection high energy electron diffraction (RHEED) and atomic force microscopy (AFM) to develop the cleaning technique by sublimation. Tetracene has a layered structure with herringbone lattice, and it can be a typical example of the organic semiconductors used as single crystals, because almost all of them have similar layered structures. We found that the inert gas pressure during the sublimation greatly affects the sublimation. Layer-by-layer sublimation was achieved by blowing heated gas from the surface under 1 atm. We will briefly discuss the origin of these findings.

We used conventional physical vapor transport technique under 1 atm N₂ gas flow for the single crystal growth of tetracene. Reflection high energy electron diffraction (RHEED) and atomic force microscope (AFM) were used for the characterization of surface crystallinity and morphology. RHEED was equipped with microchannel plate⁸ (Hamamatsu F2226) which multiplies the signal intensity by $\sim 10^4$. Tapping mode AFM was measured with SII SPI-4000 using a silicon nitride cantilever. The surface of tetracene crystals stored in air was examined by XPS (JEOL JPS-9200) with flood guns to investigate the nature of the degradation.

The crystals grown in the furnace were carefully separated under ambient condition and one of them was laminated onto an Au-coated, thermally oxidized Si wafer (Fig. 1(a)). They were separately examined by AFM and XRD (Fig. 1(b)) in ambient atmosphere and RHEED in vacuum. From the AFM observation shown in Fig. 1(c), molecularly flat surfaces were observed from the crystals with $2\text{mm} \times 0.2\text{mm} \times (0.2 \sim 1)\ \mu\text{m}$. The terrace width was typically more than $10\ \mu\text{m}$, so that we seldom find steps even when the scanning area is more than $20\ \mu\text{m} \times 20\ \mu\text{m}$. But some of the largely grown crystals larger than several millimeters have screw dislocations, resulting in narrow terrace width around $1\ \mu\text{m}$ as shown in Fig. 1(d).

The RHEED image of “fresh” as-grown tetracene crystal, which was exposed to air less than 3 hours, is indicated in Fig. 2. It was introduced in the ultrahigh vacuum chamber equipped with an image intensified RHEED using a microchannel plate. The acceleration voltage and the emission current of RHEED were 20 kV and 10 pA, respectively. We noticed that RHEED patterns are easily degraded without sufficient suppression of incident current. Streak patterns were clearly observed, which shows the good crystallinity and the flatness of the surface. However, the streak patterns were only observed when the incident angle of the electron beam was greater than 2° . Halo patterns were observed with smaller incident angles. Since the mean free path of 20keV electron in organic compounds is $L_0 \sim 40\ \text{nm}$ ⁹⁻¹¹, probing depth of RHEED is $L=L_0 \sin \theta$, $\theta=2^\circ$ correspond to 1.4 nm. This value coincides with the thickness of molecular

layer of tetracene. The result shown above indicates that the topmost surface does not have crystalline order if the crystals were exposed to air, even if it was for several hours. After the crystals were kept in air for 7 days, RHEED patterns were no longer observed with any incident angles ($<4^\circ$). It shows that the crystal surface was completely degraded in terms of crystallinity.

In order to distinguish the nature of the surface degradation, we measured XPS of tetracene surface exposed in air for 7 days under room light. C1s spectra showed strong extra peaks at 283.1 eV and 285~286 eV in addition to the peak 284.3 eV belonging to tetracene¹². O1s signal intensity was comparable to C1s. It was reported that the XPS spectrum of *p*-Benzoquinone adsorbed onto cold finger have peaks in 283.4 eV and 286.0 eV¹³, which is comparable to the extra peaks in tetracene spectrum. These results clearly show that oxidized tetracene, which is probably tetracenequinone or tetracenedione, covers the surface after the exposure to air.

Since many of organic semiconductors can be sublimed, sublimation from the surface might be simple technique to remove the surface contaminant. We first attempted vacuum sublimation by mildly heating the crystal. A tetracene crystal laminated on Au/Si substrate was heated at 60 °C for 15 min in ultrahigh vacuum chamber. Temperature lower than that did not change the RHEED pattern (or AFM images shown later) significantly within one hour. Figure 3(a) shows the RHEED pattern of the heated sample. The streak pattern in Fig. 2 turned into a spotty pattern, which indicates that the surface became rough and that the electrons penetrate through the crystalline bumps. Figure 3(b) shows the AFM images of the sample after heating in vacuum. The images show that many holes with 20 -100 nm width and 1~2 nm height were formed all over the surface. At least 4 molecular layers coexist in the observed area (3 $\mu\text{m} \times 3 \mu\text{m}$). This result agrees well with the RHEED observation since the depth of the holes might be underestimated by the curvature of the AFM tip. It can be concluded that the surface cleaning by vacuum sublimation is very difficult because of this thermal roughening.

The single crystals are grown under 1 atm Ar gas flow at elevated temperatures and the grown surface is molecularly flat. We therefore attempted heating by hot Ar gas flow in 1 atm Ar gas. We used the heated gas flow rather than the uniform heating in a furnace although expected result will be the same. That is because the smaller heat capacitance by limiting the heated volume leads to shorter timescale of the heating and, consequently, easier to control heating and cooling process. The purity of the Ar gas was 99.9999% and filled in a small vacuum chamber with conflat flange connected with the RHEED chamber. We made a Pyrex glass tube with a narrow end (inner diameter 3mm). Ar gas with 150 sccm was injected into the tube. Tungsten spiral heater was inserted in the tube and red heated by Joule heating. A thermocouple was attached to the narrow end of the tube and the temperature of the exiting gas was monitored. The narrow end of the tube was placed 5mm from a tetracene crystal laminated on Au/Si. The chamber was connected with a bubbler using diffusion pump oil and the pressure of the chamber was kept 1 atm even with the Ar gas flow. The temperature of the tetracene surface was monitored by gluing very thin thermocouple (0.05 mm in diameter) onto the surface.

Figure 4(a-d) shows the result of AFM measurements of tetracene surface after successive heating by blowing Ar gas heated at 300 °C. The surface temperature was stabilized at 140 °C within seconds after starting the blow. The result shows striking difference from heating in the vacuum (Fig. 4). The terraces with 1 molecular height (1.4nm) were gradually etched out by blowing for 1 min, 2 min and 5 min. After 5 min, one molecular layer was almost etched out and a molecularly flat surface with remaining monolayer islands was obtained. The existence of molecular height step edge apparently enhances the etching speed, but the resulted surface was equally flat even when the wider terraces were treated with the same procedure. RHEED image of this surface (Fig. 4(f)) showed streak pattern with a very small incident angle ($<0.5^\circ$), indicating that the topmost surface has crystalline order. We succeeded in the cleaning of tetracene crystal by hot Ar blowing in 1 atm. Since the crystal structure of tetracene

is layered one with a herringbone lattice, which is common to organic semiconductors used as a single crystal form, it is expected that the present technique can be readily used for various organic semiconductors.

We found a strong pressure effect on the surface morphology after the sublimation, in which existence of the 1 atm gas prevents surface roughening. We briefly discuss its origin here. The AFM image of the vacuum-heated surface (Fig.3(b)) indicates that the evaporation of tetracene occurs on terraces, whereas it mainly proceeds from the step edges under 1 atm Ar. Usually the kinetics of evaporation is analyzed with Hertz-Knudsen-Langmuir equation¹⁴⁻¹⁸, in which the outgoing molecular flux at temperature T is expressed as follows:

$$J = \alpha (p_e - p) / (2\pi m k_B T)^{1/2},$$

where p_e and p are the equilibrium and actual partial pressure of the evaporating species, respectively, and m is the molecular mass. α is called “condensation factor” and is strongly influenced by the diffusion length of the molecules and spacing of the surface steps, because the evaporation usually occurs from the step edges as analyzed in the literature. Although the evaporation from the step edges indeed observed under 1 atm Ar, evaporation from terraces are dominant in vacuum, which is probably very specific to molecular crystals. Therefore ordinary treatment by the above equation is not valid in case of vacuum evaporation. We currently suspect that the layered structure of tetracene is very important. Since the van der Waals bonding within the layer is much stronger than those between layers, separation of the layers may be dominant deformation on the terraces. The deformation will lead to the peeling of one layer cluster at once, which will result in the uniform roughening of the surface. The separation of the layers should be suppressed by introducing environmental gas pressure from the surface, and the ordinary layer-by-layer evaporation from the step edges will dominate. This hypothesis can be examined by doing experiments on the materials with various crystal structures, but this kind of study is impossible at present because the crystal growth technique of molecules with non-layered structures has not

been established.

In summary, we found a strong pressure effect in the surface morphology of tetracene after sublimation in the search of the surface cleaning technique of single crystalline organic semiconductors. By using a hot inert gas blow in 1 atm, contaminants on the topmost surface can be removed and the surface can be etched layer by layer. Although future researches with organic single crystals with different structures are needed, this technique can readily be used in a load lock chamber to clean the surface of shelf stocked organic single crystals with layered structures.

The authors would like to thank Professors Jun Takeya of Osaka University for valuable discussions. This work has been supported by Global COE Program “Chemistry Innovation through Cooperation of Science and Engineering” from MEXT, Japan. M.O. is grateful for financial support of JSPS.

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Figure captions

Figure 1. (a) Optical microscope image of tetracene single crystal laminated on Au/Si. (b) The AFM image of tetracene single crystal with screw dislocations. (c) X-ray diffraction patterns of tetracene single crystal.

Figure 2. RHEED patterns of tetracene crystal exposed 3 hours in the air. The e-beam is parallel to (a) [100] direction and (b) [010] direction of tetracene single crystal. (c) Schematic diagram of RHEED setup. Probing depth is proportional to $\tan\theta$.

Figure 3. (a) RHEED pattern of a tetracene crystal annealed at 60 °C for 15 min in vacuum. The electron beam is parallel to [100] direction of single crystal. (b) Typical AFM image of a vacuum-annealed tetracene crystal.

Figure 4. AFM images of tetracene crystal surfaces annealed in 1 atm Ar gas by blowing hot Ar gas flow. (a) Before annealing. (b) After annealing for one minute. (c) After 2 min annealing. (d) After 5 min annealing. (e) Schematic diagram of Ar gas blower. (f) RHEED image of tetracene crystal annealed by hot Ar gas flow.

Figure 1.

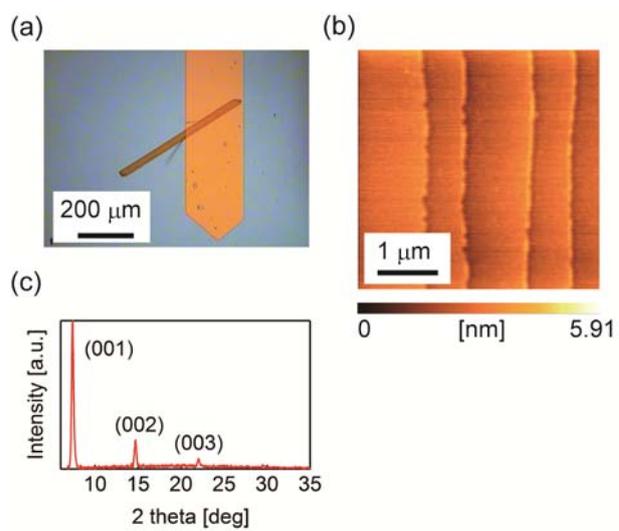


Figure 2.

(a) e-beam // [100]



(b) e-beam // [010]

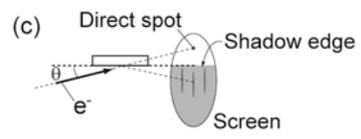
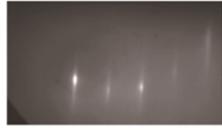
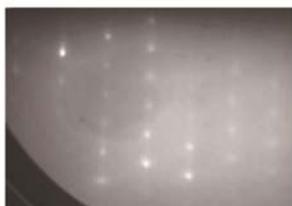


Figure 3.

(a)



(b)

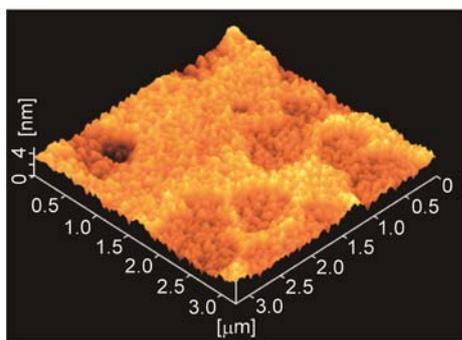


Figure 4.

