Electronic Structures and Electric Properties of Rubrene Single Crystal Studied By Photoemission, Time-of-Flight, and Displacement Current Measurements

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1. Introduction

The field of organic electronics using organic semiconductors has been growing up, and commercial products are now in the market. In spite of such extension, the fundamental aspects of device physics are not well understood. For example, carrier transport mechanism in organic semiconductors is not well established, and the guidline for molecular design to realize high mobility is not clear.

The single crystal (SC) of rubrene (5,6,11,12- tetraphenyltetracene) (Fig. 1) has attracted much attention because it revealed the highest hole mobility of all organic semiconductors reported so far (μ_h = 40 cm^{2}V^{-1}s^{-1} [1]). This system is suited to investigate intrinsic transport nature in molecular solids, and to discuss the guideline for better transporting materials. The hole transporting mechanism of rubrene SC should be described in the band transport framework at least along the most conductive axis based on the temperature-dependence of the conductivity and Hall effect [2,3]. Within the band transport framework, however, whether a hole behaves as a small polaron with relatively heavy effective mass ($> 2m_0$, where m_0 is the free electron mass)[2,4] or as a "light quasi-particle" ($< m_0$) [5] is still controversial.

To clarify these points, the electronic structures of rubrene SC, especially, the band dispersion relation of the top part of the valence band is definitely necessary. Usually, angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) is the most direct method to determine the band structures. But, for organic single crystals, it is not easy to perform ARUPS measurements without spectral shift and deformation due to charging problem: The holes left after photoemission process tend to stay at the surface region because of the low intrinsic carrier concentration and the large thickness of organic single crystals (typically in the order of μm). Very recently, we have succeeded to measure ARUPS of rubrene single crystal and determine the band dispersion and the effective mass of hole state [6] by reducing the charging effect with laser irradiation to the crystal.

In the present study, we report on our recent efforts to investigate the transport mechanism of rebrene single crystal. Main part of the presentation is on the ARUPS measurements of rubrene SCs. The direct observation of band dispersion indicated the extremely light effective mass of hole for rubrene, strongly suggesting band transport nature. In addition, the difference in electronic structure between single crystal and amorphous film is also discussed. In order to completely understand the transporting mechanism, the relation between the electronic structures and the electric properties should be clarified. Especially, the orientation dependence of carrier mobility should be measured. So far, it has been reported by measuring transistor performance. But, to discuss the intrinsic nature, the time-of-flight measurement is desired by using lateral time-of-flight measurement. So, we have also examined the validity of lateral TOF method.
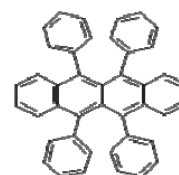

Fig.1 Chemical structure of rubrene.

2.Experimental

Rubrene single crystals were produced by a horizontal physical vapor transport technique in purified nitrogen stream. Oblong plates (typically 1 mm × 5 mm × 20 μm) were picked up and bounded by Ag paste onto Au-coated Si substrates for ARUPS. UPS measurements were carried out by a high-resolution angle-resolved electron spectrometer (VG-Scienta; R3000) in an ultra-high vacuum system (base pressure of 5×10^{-8} Pa) with He I (21.22 eV) light source. The whole area of the sample was illuminated by a defocused laser light (405 nm; spot size of ca. 30 mm^2) during the UPS measurements. The measurement setup is illustrated in Fig. 2(c) .

For time-of-flight measurement, the rubrene SC was mounted in a surface cell as shown in Fig.4(a). A bias of 600V was applied between the two electrodes and the transient current induced by a pulse N$_2$ laser was recorded.

3. Photoemission Measurements of Rubrene SC

Fig.2 shows the ARUPS spectra of rubrene single crystal and film. As in the Fig.2(a), the laser illumination removed the spectral deformation due to sample charging. By the comparison with the crystal and amouphous film, the highest occupied molecular orbital (HOMO) band indicated the 0.66eV energy shift while the other peaks did 0.25eV. The latter is due to the polarization effect: The ionized hole state cation is screened by the surrounding molecules. The former is not only due to the polarization effect but also additional 0.4eV shift by the extension of the π band.

By detailed angle-resolved measurements, the HOMO peak showed energy shift due to band dispersion effect as
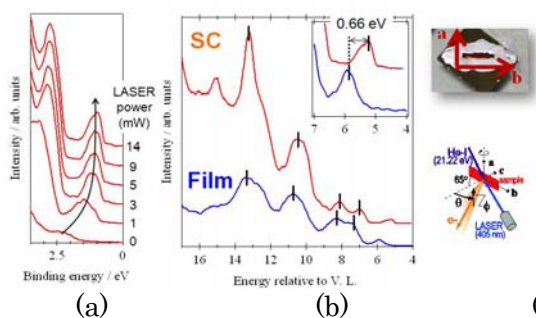
Fig.2 UV photoemission spectra of rubrene single crystal. (a) Laser radiation effect to reduce the sample charging. (b) The wide spectra of rubrene single crystal (SC) and evaporated thin film. (c) The orientation of the crystal and the measurement setup.

shown in Fig.3. Dispersion of the main peak position was well fitted by a cosine curve which is expected in tight-binding-approximation. From the fitting, the transfer integral was determined as 0.11eV, and the effective mass as $(0.65 \pm 0.05)m_0$. The obtained effective mass was the lightest one among the organic semiconductors reported so far. This is directly connected to the highest hole mobility of rebrene.
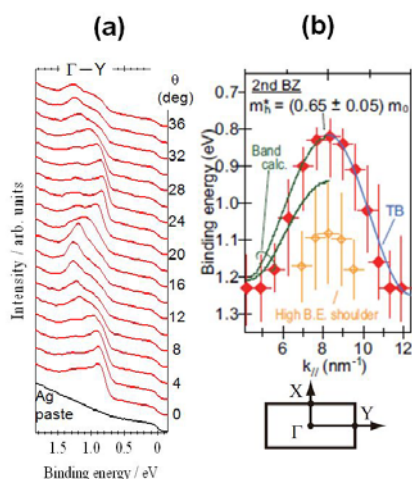

Fig.3 (a) The angle-resolved spectra of rubrenen single crystal. (b) The obtained band dispersion from the analysis of the ARUPS.

4. Time-of-Flight Measurement of Rubrene SC

As shown in Fig.5(a), the two electrodes with a separation of 3mm were indirectly attached to the surface of rubrenene SC through a myler sheet which suppressed the carrier injection to the crystal. N_2 pulse laser light was introduced to the beneath of one of the electrodes through a slit of 200μm. The transient current was monitored as displacement current. In order to avoid possible gate-induced-field effect, the crystal was mounted on a thick teflon block. In the direction of Γ-Y, where the highest mobility was reported for rubrene, the transient current showed non-dispersive curve and a clear kink corresponding to the transient time. The obtained mobility was ca. 5 cm^2/Vs. In the different direction,

45 degree from Γ-Y, the mobility was ca. 3.5 cm^2/Vs. For electron, dispersive curve was observed, suggesting the existence of trap site. This type of measurement enables us to discuss the nature of transport mechanism in detail on the basis of the electronic structure.
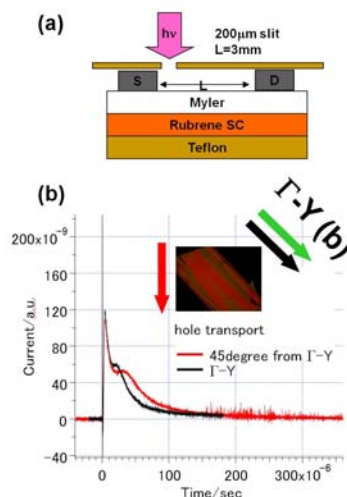

Fig.5 Time-of-flight measurement of rubrene SC. (a) the setup of the surface cell. (b) Transient current for the two orientation.

5. Conclusions

In order to understand the carrier transporting nature of rubrene single crystal, we performed two comprehensive experiments: Photoemission study and electrical property measurements. Photoemission experiments revealed the band dispersion relation and very light effective mass. These findings strongly support the validity of band transport. We also demonstrated that lateral time-of-flight measuement can be applied to rubrene SC and the orientation dependence of mobility can be determined. On the basis of these results, the factors such as the enlargement of Brillouin zone and the π−π overlap to get higher carrier mobility will be discussed.

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