

Near-Surface Structure Analysis of Organic Semiconductor Rubrene Single Crystal

A combination of surface X-ray scattering measurement and a new method of analysis makes it possible to observe the near-surface electron density distribution of an organic semiconductor, which has a far more complicated structure than common objects of surface X-ray scattering such as Si or Au. The observed electron density profile of a rubrene single crystal, which is known as a high-mobility organic transistor material, shows a large positional distribution of the molecules forming the first layer. Moreover, molecular deformation that affects the molecular orbital is also found only in the first layer of molecules.

The development of organic devices has progressed dramatically. Organic electroluminescence displays are now commercially available, and ink-jet printers for fabricating organic transistors are being built in labs. Because of their unique characteristics, organic semiconductors have a wide range of possible applications, and therefore have been studied extensively in recent years. In field-effect transistors, carriers move at the interface and so the properties of the interface are important. Structural information on the surface or the interface is especially important, because the transport properties of organic material are closely related to the structure.

The best organic semiconductor known is single crystal rubrene ($C_{28}H_{20}$). This material has larger mobility than amorphous silicon [1] and has sufficient performance for various applications. The crystal structure of this material [2] is shown in Fig. 1(a). The surface of as-grown crystal made by the physical vapor transport method is parallel to the c-plane. The structure of this surface was studied by using the four-circle diffractometer at BL-4C [3].

A sudden termination of the crystal, or a flat surface, gives rise to rod-shaped scattering, which is called

crystal truncation rod (CTR) scattering. The scattering amplitude of CTR is the Fourier transformation of the electron density around the surface. Thus, the surface structure can be obtained by measuring the CTR profile. CTR measurement at BL-4C was performed in air at room temperature. Single crystal rubrene was placed on a silicon substrate covered with a several hundred nm thick layer of SiO_2 . The result of the CTR measurement along (00z) is shown in Fig. 1(b). Bragg reflections were observed at $z = 2n$ (n : integer) positions, and clear CTR intensity was observed up to $z = 14.4$, except for a limited region around $z = 9$.

The experimental data fall on the red curve, which shows the calculated profile for the structural model having larger values of the atomic displacement parameters for the molecules only at the surface than those for other molecules inside the crystal. The excellent agreement with the experimental values shows that the surface structure is well reproduced by this single structural model. However, there is some ambiguity such as the decay depth for the surface effect on molecular deformation.

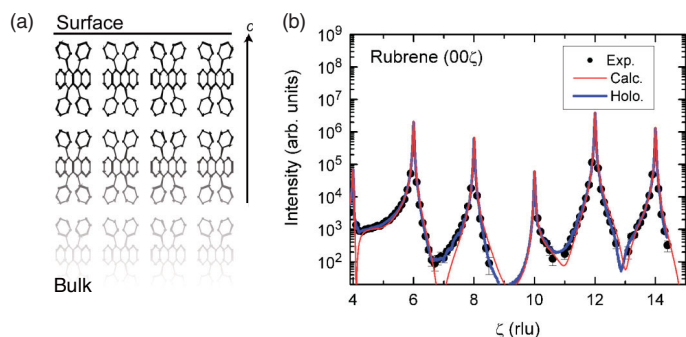


Figure 1 (a) Crystal structure of a rubrene single crystal [2]. (b) CTR intensity profile along (00z) rod. The black plots show the experimental results, the red and the blue curves show the profile calculated from the structural model and the result of coherent Bragg rod analysis, respectively (see text).

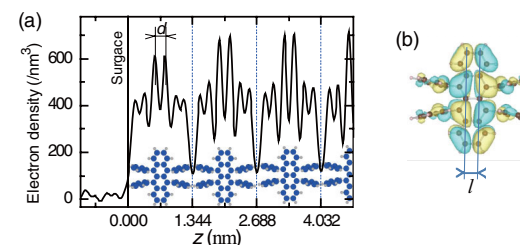


Figure 2 (a) Electron density of a rubrene crystal as a function of depth from the surface of the crystal. (b) Schematic view of the highest occupied molecular orbital of rubrene molecule.

In ordinary methods of surface structure analysis, the structural model is refined by a least-squares fitting. However, the large number of atoms prevents us from making such a traditional analysis; we would need to refine 420 parameters for three molecular layers. Instead of making a least-squares fitting, we used coherent Bragg rod analysis [4], which is a holographic method. This method was proposed in 2002 and has been applied to several inorganic semiconductors [4] and metal oxides [5]. This method gives the phase of the scattering amplitude from the surface relaxed structure by using the CTR scattering amplitude from the unrelaxed part as the reference light of the holography.

Figure 2 (a) shows the electron density profile of a rubrene single crystal obtained by Fourier transformation of the scattering amplitude; the blue curve in Fig. 1(b) shows the intensity distribution calculated from the electron density. This is the first observation of the electron density of an organic material as a function of depth from the crystal surface. Based on this profile, the structural relaxation of the surface was examined. All of the surface effect on the structure is limited to one molecular layer, and the first layer has a molecular deformation that affects the energy of the highest occupied molecular orbital (HOMO) as well as translational molecular displacement of ± 0.025 nm. The HOMO of a ru-

brene molecule is mainly on the tetracene backbone, as shown in panel (b). The intra-tetracene peak distance d in panel (a) increases in the surface molecule by 0.01 nm from that in the bulk. If we assume that this change in distance reflects the change in bond length l in panel (b), the HOMO energy level decreases by 0.1 eV, which may make the surface insulating.

REFERENCES

- [1] V. Podzorov, E. Menard, A. Borissov, V. Kiryukhin, J.A. Rogers and M.E. Gershenson, *Phys. Rev. Lett.* **93** (2004) 086602.
- [2] RefCode QQQCIG01, Cambridge Crystallographic Data Centre.
- [3] Y. Wakabayashi, J. Takeya and T. Kimura, *Phys. Rev. Lett.* **104** (2010) 066103.
- [4] Y. Yacoby, M. Szwed, E. Stern, J.O. Cross, D. Brewe, R. Pindak, J. Pitney, E.M. Dufresne and R. Clarke, *Nature Materials* **1** (2002) 99.
- [5] P.R. Willmott, S.A. Pauli, R. Herger, C.M. Schlepütz, D. Martocchia, B.D. Patterson, B. Delley, R. Clarke, D. Kumah, C. Cionca and Y. Yacoby, *Phys. Rev. Lett.* **99** (2007) 155502.

BEAMLIN

4C

Y. Wakabayashi, J. Takeya and T. Kimura (Osaka Univ.)