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Direct observation of the electronic states of single crystalline rubrene under ambient condition by photoelectron yield spectroscopy

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The electronic states of single crystalline (SC) rubrene were experimentally observed by photoelectron yield spectroscopy without the sample charging problem. The ionization energy (I_s) in the SC phase was determined to be $4.85(\pm 0.05)$ eV, which is reduced by 0.45 eV compared to that of the amorphous film. The changes in the electronic states during photo-oxidation reaction and under ambient air were also observed directly to reveal the further reduction in I_s , which can be attributed to the generation of polar oxide molecules and reversible physisorption of H_2O , respectively. © 2008 American Institute of Physics. [DOI: 10.1063/1.2998650]

Rubrene (5,6,11,12-tetraphenyltetracene) is one of the most promising materials for organic field effect transistors due to its high hole mobility in the single-crystalline (SC) phase.^{1–3} Beside vigorous explorations to improve the field effect transistor performance of the rubrene SC, fundamental information about its electronic structures has been still insufficient. In addition to the *intrinsic* properties of rubrene itself, the effect of exposure to ambient air or oxidation on its transport characteristics is also controversial.^{4–10} While it is more or less common to other organic semiconductors that the transport nature is easily influenced by ambient conditions,¹¹ the rubrene case is of particular interest because it has long been well-known to change into rubrene-endoperoxide ($RubO_2$) quite sensitively in the presence of oxygen and visible light.¹² Despite the explicit nature of the reaction itself, the relevance of its product $RubO_2$ to the actual transport characteristics is still unclear.

The most serious reason for the above incomprehension is ascribed to the absence of direct observation of its electronic structure. Photoemission spectroscopy (PES) is a routinely utilized method to probe the electronic structures of materials. In the case of organic crystals or thick films, however, the sample charging problem due to their insufficient electrical conductivity generally hinders PES investigation. Although the avoidance of the charging problem has been realized even on thick organic films by simultaneous laser irradiation during PES measurement,¹³ other concerns caused by the irradiation itself (such as a photovoltaic effect and radiation damage) cannot be excluded in that case.

Recently, we discovered that reliable measurement of the electronic states unhampered by the charging problem is possible even on extreme insulators by means of photoelectron yield spectroscopy (PYS) by probing the total electron yield as photoelectron current using sweeping incident photon energy ($h\nu$).¹⁴ By utilizing this characteristic of PYS, direct observation of the electronic states of the rubrene SC will be

realized without any special artifices. Furthermore, for the sake of specifying the air effect on the electronic states, this method has another advantage in that it enables one to conduct measurements in an arbitrary atmosphere (in vacuum, in air, etc.) on an identical sample.¹⁵

In the present study, we have conducted PYS on the rubrene SC to determine its electronic states directly. For the purpose of elucidating the effect of ambient air exposure and/or oxidation, changes in the electronic states during and after air exposure were also studied.

Rubrene SCs were produced by a physical vapor transport technique in a separate system.¹⁶ Amorphous films of rubrene were made by vacuum deposition of as-purchased rubrene powder (Aldrich) onto indium-tin-oxide-coated glass plates. A $RubO_2$ film was produced through exposing the amorphous film to ambient light in air for a couple of weeks. A detailed description of the PYS measurement and analysis procedures was reported elsewhere.¹⁴ PES spectra were obtained by an electron spectrometer (VG; ARPUS-10) on BL8B2 at UVSOR in the Institute for Molecular Science (IMS). Surface morphologies of the samples were observed by a noncontact mode atomic force microscopy (AFM) apparatus (Seiko Seiki; SPA-400) in air.

As shown in Fig. 1(a), the PES spectrum of a rubrene SC exhibited no feature derived from the highest occupied molecular orbital (HOMO), despite the fact that an amorphous thin film exhibited a HOMO peak around 6.4 eV, but only a broad structure at the higher binding energy side. Such spectral distortion can be ascribed to the sample charging.¹³ In contrast to the PES results, both PYS spectra [Fig. 1(b)] look properly shaped without any sign of the charging problem.¹⁴ Differentiation of the photoelectron yield (Y) by roughly corresponds to the density of states of the specimen.¹⁷ In the case of the film, despite the fact that the HOMO shows an obvious peak on the PES spectra, one can barely find a broad feature around $h\nu=6.4$ eV after taking a close look. Taking into consideration that the probing depth of PYS is deeper than that of PES because PYS detects extremely slow photoelectrons (mainly slower than 1 eV), such breadth is probably due to the spatial inhomogeneity of molecular orienta-

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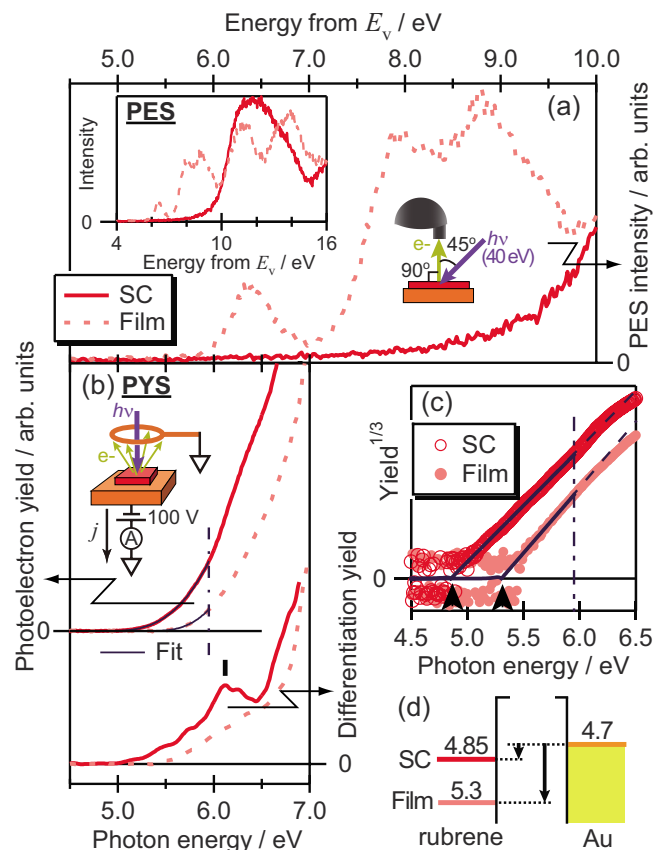


FIG. 1. (Color online) (a) PES spectra of a SC and an amorphous film of rubrene. The abscissa is the energy from the vacuum level (E_v). (Inset) Wide range spectra. (b) PYS (Y : upper panel and $dY/d(h\nu)$: lower panel) spectra of a SC and an amorphous film of rubrene. Fitting curves and the upper limit of the fitted region are displayed as thin solid and dot-dashed lines. The horizontal axes of (a) and (b) are aligned for comparison. (c) Cube-root spectra of Y shown in (b). Respective I_s are indicated as wedge marks. (d) Energy level positions of the HOMOs of the SC and the amorphous film with respect to the work function of a Au electrode [the adopted value of which is that of contaminated Au (Refs. 22 and 23)] under the assumption of vacuum level alignment at the interface.

tion in the amorphous film. On the contrary, the $dY/d(h\nu)$ spectrum of the rubrene SC reveals an apparent peak at $h\nu=6.2$ eV that can be attributed to the HOMO of the rubrene SC.

As shown in Fig. 1(b), the onset of the Y spectra of the SC is apparently lower than that of the film, which can be ascribed to a smaller ionization energy (I_s) of the rubrene SC compared to that of the amorphous film. Because Y is thought to be proportional to the cube of the excess of $h\nu$ over I_s [$Y \propto (h\nu - I_s)^3$] for organic solids when $(h\nu - I_s)$ is small,^{15,18} we evaluated I_s from the spectra around the onsets by the least-square fitting with the following equation: $Y = A(h\nu - I_s)^3 S(h\nu)$, where A is a spectral amplitude and $S(h\nu)$ is an adequate step function that turns from 0 to 1 across $h\nu = I_s$. The evaluated I_s are 4.85 ± 0.05 and 5.3 ± 0.1 eV for SCs and amorphous films of rubrene, respectively, as shown by the respective $Y^{1/3}$ spectra in Fig. 1(c). The value of the latter is in good agreement with the previous reports^{19,20} In comparison to the amorphous film, I_s of the rubrene SC is reduced by 0.45 eV. Although the reasons for this I_s reduction have not been completely specified, the upshift of the HOMO edge due to band formation probably plays an essential role in this behavior.²¹ The present results indicate that the actual barrier height for hole injection into the rubrene

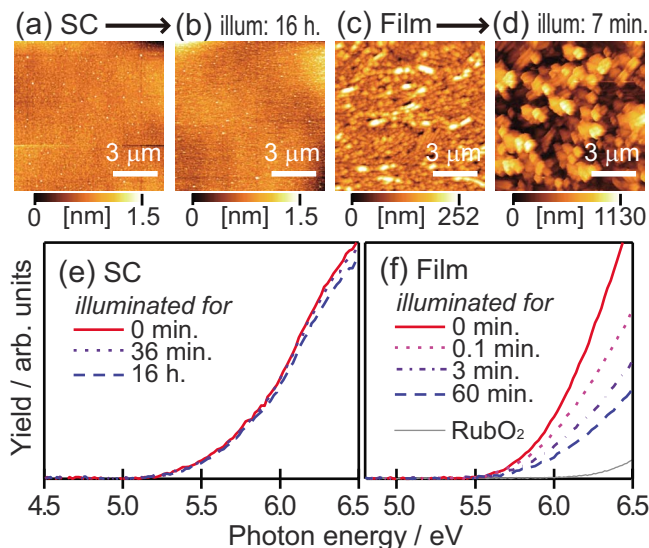


FIG. 2. (Color online) [(a)–(d)] AFM images of a SC and an amorphous film of rubrene before and after light illumination from a halogen lamp in air. [(e) and (f)] Y spectra of (e) the SC and (f) the film after light illumination from a D₂ lamp through an ozoneless quartz filter in air. The spectrum of a completely oxidized rubrene film (RubO₂) is also presented as a thin line in (f). All spectra were obtained in vacuum.

SC from an electrode [e.g., Au (Refs. 22 and 23)] will be much lower than the expected value using I_s of the amorphous film instead of the actual value of SC [Fig. 1(d)].

Visible light illumination in the ambient air did not cause any apparent change in the surface morphology for the SC [Figs. 2(a) and 2(b)], whereas significant surface roughening was brought about on the film by rather short time illumination [Figs. 2(c) and 2(d)]. Taking into consideration that the substantial thickness of the rubrene film increases with the proceeding of this photo-oxidation reaction,²⁴ the surface roughening observed on the film can be ascribed to the photo-oxidation of rubrene. On the other hand, the unchanged morphology of the SC surface after light illumination in air suggests that the RubO₂ production is hindered. This interpretation is also supported by the PYS results. The spectra of the SC were substantially unchanged by visible and near-ultraviolet light illumination in air [Fig. 2(e)], whereas those of the film show apparent degradation of the spectral amplitude [Fig. 2(f)]. This change corresponds to the decrease in *unreacted* rubrene underneath the RubO₂ layers whose contribution to Y occurs only when $h\nu$ is greater than 6 eV. These results prove the reported durability of the rubrene SC to the photo-oxidation compared to its amorphous phase.⁸

Insofar as the measurements were conducted in vacuum, I_s of the SC is properly unchanged after illumination in air [Fig. 3(a)], whereas a rather short time (0.1 min) photo-oxidation causes a slight but considerable (~ 0.1 eV) reduction in I_s for the amorphous film [Fig. 3(b)]. Further illumination of the film did not lead to an additional downshift of I_s . Such behavior of the I_s shift shows a close resemblance to the vacuum-level shift resulting from interface formation.²⁵ Taking into consideration that a RubO₂ molecule has a significant dipole moment (2.55 D) while rubrene itself is nonpolar,²⁶ a possible origin of this vacuum level shift can be ascribed to a slight alignment of the polar RubO₂ at the interface between unreacted rubrene beneath. On the other hand, the values of I_s under the ambient condition are appar-

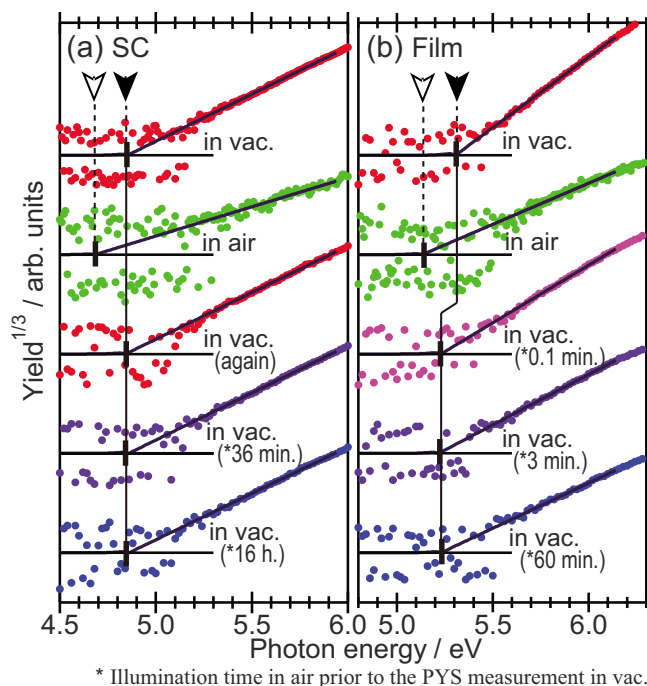


FIG. 3. (Color online) $Y^{1/3}$ spectra of (a) the SC and (b) the film of rubrene indicating I_s under various sample conditions (filled and open wedge marks indicate I_s in vacuum and in air, respectively). (Inset) A schematic of the expected molecular orientation of physisorbed H_2O on the rubrene surface.

ently (~ 0.15 eV) reduced compared to those in vacuum. These changes in I_s are reversible, especially for the SC [Fig. 3(a)], and should be ascribed to physisorption of some constituent gases of air, probably H_2O .¹⁵ We have also proved that this reduction in I_s did not take place in neither pure oxygen nor nitrogen atmosphere, which also supports our assignment that this I_s reduction is induced by H_2O . In the present case, taking into consideration that physisorbed H_2O is likely to undergo hydrogen bonding with slightly polarized H–C bonds at the outermost rubrene molecules, the observed reversible reduction in I_s in air can be convincingly attributed to the formation of a dipole layer induced by somewhat oriented H_2O molecules. It should be emphasized that such knowledge of the difference in the electronic states between that in vacuum and that in air can be extracted only from the direct comparison of the results obtained in the respective atmospheres for an identical sample.

So far, variation in the transport properties of rubrene SCs depending on the atmosphere or its crystal quality has been related to so-called “oxygen-related” gap states that act as acceptors or carrier traps.^{6–10} The product of oxidation $RubO_2$ itself is, however, unlikely to be the substance of any gap states because it has a deeper HOMO level and a wider energy gap resulting in broken conjugation with respect to rubrene, which was evinced by previous results¹² as well as ours [see Fig. 2(f)]. The present results suggested that the presence of polar $RubO_2$ molecules and/or physisorption of H_2O onto the rubrene surface can lift the HOMO level of neighboring unreacted rubrene above the original position. We therefore propose that the substance of the gap states is the slightly lifted HOMO of rubrene by the electrical field of the polar molecules in the vicinity. Charge traps caused by the electrical field originating from polar molecules were

also suggested for an organic light emitting diode structure.²⁷

In summary, we carried out direct observation of the electronic states of the rubrene SC to reveal that its I_s is considerably reduced compared to that of the amorphous film, probably due to HOMO-band formation. AFM observation and PYS measurement after light illumination in ambient air proved the durability against photo-oxidation of the crystalline phase compared to its amorphous phase. The effects of exposure to the ambient air on the electronic states of rubrene were directly explored and related to the reported transport characteristics of the SC devices.

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