Electrical Conduction of Organic Thin Film with Copper/Thiol-based Self-Assembled Monolayer Anode

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We have improved lifetime and low driving voltage of the device using an electrode modified by a silane-based fluorinated self-assembled monolayer (FSAM) on ITO (transparent electrode). In the process of fabricating organic light-emitting diodes (OLEDs) devices using Ag or Cu electrode modified by a fluorinated thiol-based SAM, anomalous current saturation phenomena was observed on current-voltage characteristics only when using a thiol-SAM-modified Cu anode. When the performance of the OLED with thiol-SAM-modified Cu or Ag anode were compared with that of the OLED with FSAM-modified ITO, the thiol-SAM-modified Ag anode showed more excellent performance than the FSAM-modified ITO. The OLED with thiol-SAM-modified Cu anode also showed the strange EL efficiency behavior in the saturation current region.

Keyword: electrical conduction, copper anode, thiol, self-assembled monolayer

1. Introduction
The electrical conduction of organic materials strongly depends on carrier injection as well as carrier mobility because organic materials are inherently insulators due to a covalent bonding. However, if carriers are appropriately injected into the organic materials developing \( \pi \)-conjugate system, carriers can be transported in the organic materials. When currents are adequately flowed in the typical organic semiconductors by smooth carrier injection, organic semiconductors can be widely used as active devices; display (organic light-emitting diode (OLED)), RFID tag (organic field-effect transistor), solar cell and photodetector (organic photoelectric conversion device) and etc. Carrier injection from an electrode is determined by the interface energy conditions. Especially the barrier height between the electrode and the organic material is important. Of course, the carrier injection also depends on the energy correlation between the two, i.e. the difference of both Fermi levels.

We used a fluorinated self-assembled monolayer (FSAM, (heptadecafluoro-1,1,2,2-tetrahydrodecyl) triethoxy silane) as a hole injection layer of OLEDs. The introduction of FSAM suppressed the polycrystallization of a hole transport material, lowered the driving voltage and improved the lifetime of device[1-3]. In addition, we introduced the new process of organic nano-dot by growing FSAM[4]. The work function of FSAM-modified indium tin oxide (ITO) becomes higher than that of bare ITO because of large interface dipole moment due to fluorine atoms with high electronegativity[5]. In addition, we applied the improvement of open voltage for organic photovoltaic cell (OPV)[6]. Although it is very effective to use FSAM as a hole injection layer of ITO anode, some metal anodes are used in the top-emission OLED. Therefore, we try to apply
FSAM to the metal anodes. We used fluorinated silole in order to combine FSAM with –OH or =O groups on ITO substrate. However, since silole groups are not suitable to metal, we select a thiol derivative and Ag and Cu anodes. In this paper, we introduce the electrical behavior of the OLEDs fluorinated thiol-SAM–modified anodes.

2. Experimental

2.1. Materials

We used N,N’-di(1-naphthyl)-N,N’-diphenyl -1,1’-diphenyl-1,4’-diamine) (α-NPD) as a hole-transport material and 8-hydroxyquinoline aluminum (Alq3) as an emission material from Nippon Steel Chemical Co. We used 1H,1H,2H,2H-perfluorodecanethiol as a SAM material from sigma-aldrich.

Figure 1. Chemical structure of fluorinated thiol-SAM.

2.2. Fabrication and Measurements

We used Corning glass substrates (EAGLE XG™). The substrates were cleaned by acetone, pure water and 2-propanol with ultrasonic cleaning method. Finally they were cleaned by UV-ozone cleaning. Anode metal (Ag, Cu) electrodes were evaporated on the substrates through a patterning mask. Thiol-SAM was modified on the metal anode by immersion of ethanol solution for 1 hour. Organic thin films were prepared on substrates. The organic thin films were prepared using the vacuum deposition at a pressure of 0.8 ~1x10⁻³ Pa at room temperature. We carried out a vacuum-deposition with EO-55 (EIKO Co.). The contact angle was measured with CA-VP (Kyowa Interface Science Co.).

The work functions of bare and FSAM-modified anodes are measured with the photoemission yield spectroscopy in air (AC-2, Riken Keiki Co.). Luminance-current-voltage characteristics were measured using a source measure unit (Keithley 2400 Source Measure Unit) and a luminance meter (TOPCON BM-8). The measurements of luminance-current-voltage characteristics were carried out under vacuum of ~0.1 Pa.

3. Results and Discussion

3.1. Surface energy states of bare- and SAM-modified anodes

Figure 2 shows the contact angle vs. immersion time of fluorinated thiol-SAM on Ag. The formation of fluorinated SAM can be observed by measuring a contact angle to water. The contact angle of fluorinated thiol-SAM-modified Ag is almost 115° and same as FSAM-modified SiO₂[6]. Since the modification of SAM is carried out by being immersed in liquid, the contact angle does not depend on the immersion time.

Figures 3a and 3b show the photoelectron yield vs. photon energy spectra of bare and thiol-SAM modified Ag (a) and Cu (b) anodes. The work functions of bare and thiol-SAM modified Ag anodes are estimated to be 4.7 and 5.7 eV, respectively. The work functions of bare and thiol-SAM modified Cu anodes are estimated to be 4.7 and 5.5 eV, respectively. The work functions of Ag and Cu are reported to be 4.0-4.2 and 4.65 eV, respectively[6]. Those of Ag(100) and Ag(111) are reported to be 4.64 and 4.74 eV, respectively[7]. The measurement of AC-2 is carried out in air atmosphere. Therefore, it is inevitable that the surface of metal anode is oxidized. Ag₂O is reported to show p-type semiconducting properties and its work function is 4.8-5.1 eV[8-11]. We think that the oxidation of Ag little influences the work function of our evaporated Ag thin film. On the other hand, the work functions of CuO and Cu₂O are reported to be 5.3 and 4.6 eV, respectively[12-14]. As you see, the photoemission...
curve of bare Cu anode shows a folding point. The value of the folding point is estimated to be 5.2 eV, which agrees the above value of CuO. This suggests the formation of Cu Oxide on the evaporated Cu thin film.

When the fluorinated thiol-SAM is formed on both Ag and Cu thin films, the work functions of the fluorinated thiol-SAM-modified metals are higher than those of bare metals. The increase in work function will lead to the increase in hole injection from the anode to hole transport layer.

3.2. Electrical conduction

Figure 4 shows the current density – voltage characteristics of the OLEDs with bare and thiol-SAM Ag or Cu anodes. The former moderately increase with voltage but the latters drastically increase around 2 V. Chen et al. reported that Ag2O as a hole transport material is more effective for low driving voltage[15]. In this report, the current of OLED with unoxidized Ag anode showed the same behavior as our device’s. We analyze the electrical conduction of OLEDs with bare Ag or Cu. The Schottky current is described as

\[ J = A T^2 \exp \left( \frac{\beta E^{1/2} - \phi}{kT} \right) \] (1)

\[ \beta = \frac{e}{4 \pi \varepsilon} \] (2)

where \( J \) is a current density, \( A \) is the Richardson -Dushman constant, \( T \) is temperature, \( E \) is electric field, \( \phi \) is the barrier potential at the interface, \( k \) is the Boltzmann constant, \( e \) is the elementary charge, \( \varepsilon \) is the permittivity of material.

Figure 5 shows the Schottky plot (log \( J \) vs \( E^{1/2} \)) of the current of the OLED with bare Cu. The high-field current can be approximated as a line. The relative permittivity of material is estimated to be 2.73 from the line’s slope. This value almost agrees with the dielectric constant of hole transport material. It is concluded that the electrical conduction of the OLED with bare Ag or Cu is controlled by the hole injection from the anode metal, that is, Schottky injection.

The OLED with thiol-SAM Ag have an more excellent conduction property than the other. The current of the OLED with thiol-SAM Cu shows the same behavior at an initial rise region, but it begins to be saturated and increases gradually. And it rises...
at the same gradient as the current of OLEDs with bare metal. The necessary voltage that the current increases slowly again is an additional 6 V and the threshold voltage is ~12 V.

Figure 5 The Schottky plot of the current density – voltage characteristics for the OLED with bare Cu.

Figure 6 Typical SCLC \( J - V \) curves: broken line, trap-free SCLC; solid line, shallow trap SCLC; \( V_{tr} \), the transition voltage from \( J \propto V \) to \( J \propto V^2 \); \( V_{TFL} \), the trap-filled voltage.

As the famous electrical conduction mechanism that shows folding points in current curve, the space charge limited current (SCLC) is well-known. SCLC is caused by the electric field distortion due to the space charge near injection electrode because of small carrier mobility. Typical current curve in SCLC is described in Figure 5. The carrier injection of SCLC must be an Ohmic injection because the electric field on injection electrode is zero. In th trap-free SCLC, the injected carrier from the electrode can move smoothly in the low voltage region. With increasing voltage, carrier are injected more and more. However, since carrier mobility is small, carriers cannot move from the front of the injection electrode. These carriers act as a homo space charge to the injection electrode. The homo space charge reduces the electric field of injection electrode. That is, the homo space charge can control the carrier injection. The expression for SCLC can be developed from the Poisson’s and drift current equations.

\[
J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^3} \quad \text{trap-free case} \tag{3}
\]

\[
J = \frac{9}{8} \theta \varepsilon \mu \frac{V^2}{d^3} \quad \text{shallow trap case} \tag{4}
\]

where \( \mu \) is the carrier mobility of specimen (\( \mu \) is assumed to be constant), \( V \) is an applied voltage, \( d \) is the thickness of specimen, and \( \theta \) is the ratio of trap carrier density to free carrier density. The ideal curve line of the trap-free SCLC (Equation (3)) is as the broken line in Fig. 6. If shallow carrier traps exist in the specimen, initial carriers move and fill the traps simultaneously. When all traps are filled by carriers, the current curve recovers as the original trap-free curve. This current curve is described as the solid line in Fig. 6. The SCLC is understood as a bulk-controlled conduction mechanism but is not done as such an injection-controlled conduction mechanism as the Schottky current.

Rakhshani reported the electrical conduction of evaporated Cu2O film (\( d = \sim 3 \mu m \)) [16]. He analyzed the current by means of SCLC mechanism. Current was measured to 13 V for 3.2 \( \mu m \)-thick Cu2O film. In the low voltage region of \(< 1 \text{ V} \), the current was proportional to apllied voltage. After that, the current increased drastically over 2 orders to 2.5 V. In the range of 2.5 \( V \leq V \leq 7 \text{ V} \), the current was proportional to the squared voltage. And then, the current increased steeply.

The behavior of Rakhshani’s current is similar to our current in Fig. 4. However, the Cu2O layer that is naturally oxidized in Cu is predicted to be at most 1-2 nm-thick. As explained above, since the SCLC is the bulk-controlled conduction, it is difficult to apply SCLC to the electrical conduction in this ultra thin film. If the electrical conduction is limited by carrier mobility, it should be limited by the carrier mobility of organic materials. It is clear that the thiol-SAM-modified Cu anode shows the same carrier injection potential as the thiol-SAM-modified Ag anode. In addition, both initial curves in the low voltage region of \(< 4 \text{ V} \) almost conform. But only the current of the OLED.
with thiol-SAM-modified Cu is suppressed. The almost same curve is obtained at the rise and fall processes of applied voltage.

After considering the above, strangely, the interface between thiol-SAM and Cu or between thiol-SAM-modified Cu and \( \alpha \)-NPD will control the carrier injection from Cu anode into \( \alpha \)-NPD. The width of these interfaces is thought to be less than 1 nm. Since the necessary voltage is \(~6\) V, the electric field of the interface is estimated to be \(6\times10^9\) V/m. This value is higher than the breakdown strength of silicon dioxide and aluminum oxide. Unfortunately, we cannot explain the origin of specific behavior of the OLED with thiol-SAM-modified Cu.

Instead of fabricating top emission device, we fabricate the bottom emission device with a thin metal electrode.

The transmittances of ITO, Ag(20nm) and Cu(20nm) are 94, 40 and 31 % at 555 nm, respectively. Especially, the \(~20\)% of visible light cannot pass through Cu (20nm) electrode, as shown in Fig. 7.

Figures 8 (a) and (b) shows the current density – voltage and the EL efficiency – current density characteristics for the OLEDs with FSAM-modified ITO or thiol-SAM-modified Ag or Cu, respectively. The OLED with thiol-SAM-modified Ag shows the most performance of driving and EL efficiency. In spite of low transmittance, its EL efficiency is twice as high as compared with that of the OLED with FSAM-modified ITO. This can be explained by the microcavity effect[17,18].

However, the EL efficiency of the OLED with thiol-SAM-modified Cu shows the strange behavior. In the saturation (slow-increasing) region of current density, the EL efficiency increases gradually. When the current begins to increase again, the EL efficiency is the maximum at the rising threshold and decreases. The increase in EL efficiency is not thought to relate to the microcavity effect because the microcavity depends on the optical device structure. The hole injection is controlled by the thiol-SAM-modified Cu but the electron injection of LiF/Al has the same potential as the other OLEDs. If the aplied voltage is shared to the interface between the thiol-SAM-modified Cu and \( \alpha \)-NPD, the
electric field of the emitting region may be moderated and the quenching due to electric field may be suppressed. This speculation must be checked physically.

4. Conclusion
We introduced the potential of bottom anode for top emission on the thiol-SAM-modified Ag and Cu. The thiol-SAM-modified Ag showed more excellent hole injection than the FSAM-modified ITO. It is possible to substitute ITO anode with thiol-SAM-modified Ag anode. On the other hand, the thiol-SAM-modified Cu also showed a good hole injection to \( \alpha \)-NPD. However, the OLED with thiol-SAM-modified Cu showed the anomalous saturation of current and the strange change of EL efficiency. These phenomena were found to relate to the interface between the thiol-SAM-modified Cu and \( \alpha \)-NPD.

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