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Orientational Re-ordering of Polar Organic Monolayers by Cooperative Molecular Field Effect

Dai Taguchi, Norifumi Kajimoto, Takaaki Manaka, and Mitsumasa Iwamoto*

Department of Physical Electronics, Tokyo Institute of Technology,
2-12-1, O-okayama, Meguro-ku, Tokyo, Japan 152-8552
Phone : +81-3-5734-2191 E-mail: iwamoto@pe.titech.ac.jp

1. Introduction

For organic electronic devices such as organic field effect transistors (OFET), and organic electroluminescence (OEL) devices, it is well known that carriers injected from metal electrodes dominate the device performance [1]. Therefore, understanding of charge transfer between metal and organic film is important. Up to now, extensive studies such as ultraviolet photoelectron spectroscopy (UPS) unveiled interfacial energy structures of organic films step by step [2]. However, understanding of charge transfer mechanism at metal-organic interface is far from satisfaction. The author's group studied, firstly, charge transfer between metal and non-polar organic films such as polyimide and phthalocyanine using Kelvin probe method [3,4]. We concluded that the surface Fermi level alignment accounts for the charge transfer phenomena of non-polar organic films. Then, we studied the dipolar film such as Alq₃ [5], where decay of surface potential built across the Alq₃ film was analyzed with taking into account the cooperative molecular field effect (CMFE) [6]. Note that the re-ordering problem was minor for the Alq₃ film.

In the present study, we studied the surface potential of liquid crystal (LC) films taking into account the CMFE, where re-ordering of the polar orientation is probable and it is induced by the injected charge. Experimentally, surface potential measurements were conducted during liquid crystal film evaporation onto metal electrodes. The metal work function dependence of the surface potential was discussed, keeping in mind that the re-ordering of the orientation is induced by injected charge.

2. Analysis

Figure 1 shows a model of a polar mono-molecular layer with electron donor state localized at a distance z_0 from the interface. The sum of electrostatic energy and potential energy, U , stored in the dipolar film is calculated as,

$$U = \frac{1}{2} \frac{n^2 \mu^2 S_1^{02} + 2\sigma^0 n \mu S_1^0 + \sigma^{02} z_0 / \delta}{\epsilon_s / \delta} - A \sigma^0, \quad (1)$$

where σ^0 is the surface charge density, n is the molecular density, μ is the permanent dipole moment, and ϵ_s is the permittivity of monolayer. $S_1^0 = \langle \cos \theta \rangle$ is the first orientational order parameter where θ is the tilt angle of molecule from surface normal and $\langle \rangle$ is

thermodynamic average. Taking into account the CMFE, differentiating U by σ^0 yields the following relationship between induced surface charge σ^0 and S_1^0 minimizing U .

$$\sigma^0 = \frac{\epsilon_s A}{z_0} - n \mu \frac{\delta}{z_0} S_1^0. \quad (2)$$

We shall focus on the re-ordering of polar orientational order by the injected charge σ^0 due to the interaction between the permanent dipole and electric field. We here simply describe interaction energy W_i as $W_i = \mu \sigma^0 \cos \theta / \epsilon_s$. With the assumption that W_i induces re-ordering of the orientational order, we obtain S_1 as,

$$S_1 = \frac{1}{Z_0} \int_0^\pi \cos \theta \exp\left(\frac{W \cos \theta - W_i}{kT}\right) \sin \theta d\theta, \quad (3)$$

where Z_0 is the partition function, k is Boltzmann's constant, T is absolute temperature. W is a potential giving $S_1 = S_1^0$ for the film without charge injection, that is,

$$S_1^0 = \frac{1}{Z_0} \int_0^\pi \cos \theta \exp(W \cos \theta / kT) \sin \theta d\theta, \quad (4)$$

As a first order Onsager's approximation, $W_i \ll kT$, we obtain,

$$S_1 = S_1^0 - 2g \frac{U_d}{kT} \left(\frac{2S_1^0 + 1}{3} - S_1^{02} \right) \left(\frac{A}{V_0} - S_1^0 \right), \quad (5)$$

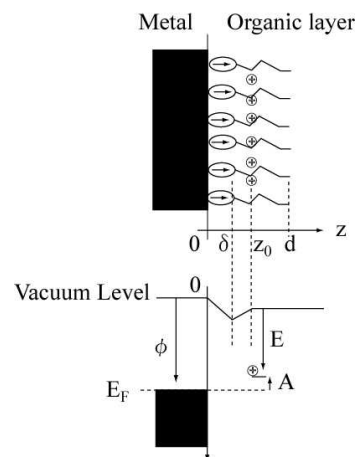


Figure 1, A model of metal-organic layer interface with electron donor state. ϕ is metal work function, E_F is Fermi level, E is the energy depth of electron donor, and A is barrier height.

with $g = d/z_0$, $U_d = 1/(nd) \cdot (n\mu)^2 / (2\epsilon_s/\delta)$, and $V_0 = n\mu\delta/\epsilon_s$. Here, $S_2^0 = \langle (3\cos^2\theta - 1)/2 \rangle$ is the second orientational order parameter. As discussed in our previous paper [5], the surface Fermi level alignment holds when Eq. (2) is satisfied. That is, surface potential, V_s , of polar film without re-ordering of the orientational order is determined simply by the barrier height, A ,

$$V_s = A \quad (6)$$

However, as is described in Eq. (5), S_1 changes due to the injected charge for polar liquid crystal monolayers. In this case, using S_1 and σ^0 , the surface potential built across the film is written as,

$$V_s = (1 - \alpha)A + \beta \quad (7)$$

with

$$\alpha = 2g \frac{U_d}{kT} \left(\frac{2S_2^0 + 1}{3} - S_1^{02} \right) \quad (8)$$

$$\beta = 2gV_0S_1^0 \frac{U_d}{kT} \left(\frac{2S_2^0 + 1}{3} - S_1^{02} \right) \quad (9)$$

Eqs. (7), (8), and (9) show that the re-ordering of the orientational order directly gives effects on the surface potential V_s . It is noteworthy that Eq. (7) returns to Eq. (6) when $\mu = 0$. This clearly shows that the permanent dipole moment accounts for the change of the surface potential due to the re-ordering of the orientation. In addition, parameters α and β are functions of S_1^0 and S_2^0 . In other words, the surface potential of a dipolar monolayer at interface is depending on the polar and axial orientational orders of the monolayer. Furthermore, it is clear that the ratio of the two energies, i.e. the electrostatic energy stored in the dipolar film per molecule, U_d , and thermal energy, kT , is an important factor for α and β as is shown in Eqs. (8) and (9).

3. Experimental

Liquid crystal, 4-n-pentyl-4'-cyanobiphenyl, was used because orientation direction of LC is easily re-ordered by the external field. During LC evaporation onto aluminum (Al), chromium (Cr), gold (Au), and silver (Ag) electrodes, in-situ surface potential measurements were conducted in the air using Kelvin probe method. The metal work functions of Al, Cr, and Ag were determined by contact potential difference relative to the Au reference. For Au, the work function was determined by photoelectron spectroscopy in air.

4. Results and Discussion.

Figure 2(a) shows a typical result of in-situ surface potential measurements. Surface potential of LC film gradually increases at the beginning of evaporation, then approaches a constant value V_{const} after LC mono-molecular layer is deposited. Figure 2(b) shows metal work function dependence of V_{const} . V_{const} is the same for Al and Cr while it increases as metal work

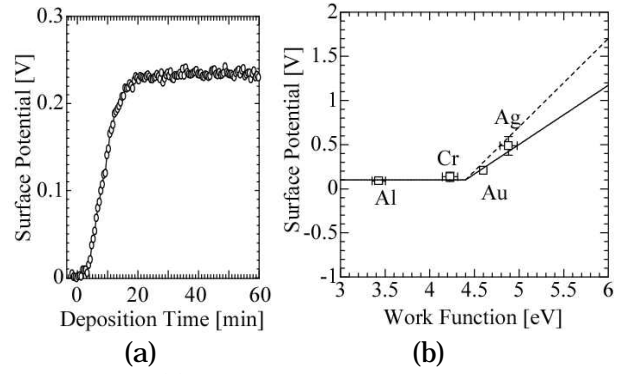


Figure 2. (a) Typical result of in-situ observation of the surface potential during LC evaporation. (b) Work function dependence of V_{const} . Solid and dashed lines are analytical fitting based on CMFE with and without the re-ordering of the orientational order, respectively.

function increases for Au and Ag. Taking into account the CMFE and orientational re-ordering, work function dependence of V_{const} in the region $4.4 \text{ eV} < \phi$ was fitted while the surface potential in the region $\phi < 4.4 \text{ eV}$ was ascribed to the ordered permanent dipole without charge injection. Parameters were chosen to reproduce the experimental data as $n = 2.32 \times 10^{27} \text{ m}^{-3}$, $\mu = 4.87$ Debye, $\delta = 0.047 \times 10^{-9} \text{ nm}$, $\epsilon_s = 8.85 \times 10^{-12} \text{ Fm}^{-1}$, $d = 2.2 \text{ nm}$, $z_0 = 0.61 \text{ nm}$, $T = 300 \text{ K}$, $S_1^0 = 0.5$, and $S_2^0 = 0.07$. Here, S_1^0 and S_2^0 were calculated with the same potential, $-W \cos \theta$, as is described in Eq. (4) where $W = 3.0 \times 10^{-21} \text{ J}$. Figure 2(b) shows the CMFE accompanying the re-ordering accounts for the work function dependence, and the re-ordering of the orientation suppresses the surface potential. Further experimental investigation is required to clarify whether the re-ordering effectively occurs or not.

3. Conclusion

Injected-charge-induced orientational re-ordering of the dipolar monolayer at interface was studied focusing on the cooperative molecular field effect (CMFE). Deviation from the initial orientational order due to the injected charge and the surface potential of the film accompanying the re-ordering were analyzed. It was found that the polar and axial orientational orders directly give effects on the orientational re-ordering phenomena. Surface potential V_{const} of LC films was determined experimentally by the in-situ observation during evaporation. The work function dependence of V_{const} was successfully explained, taking account of the CMFE accompanying the re-ordering.

References

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