Cathode Metal Patterning in Top Emission OLED through Insertion of Low Surface Energy Organic Molecules

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ABSTRACT

In this paper, we report a cathode metal patterning method by the surface energy control of organic material in thermal evaporation process. In order to make the self-metal patterning, a metal patterning layer (MPL) was introduced before the metal deposition. Among several MPLs, the lowest surface energy materials result in excellent patterning properties in both Mg as well as Ag.

1 Introduction

Nowadays, under display camera technology has been reported by utilizing the transparent area as one of the sensors embedded displays [1]. Also the transparent active matrix organic light emitting diode (OLED) is also required a see-through area with no metal layer to achieve the high transparency [2]. For ensuring the transparent area a fine patterning of the cathode metal technology is essentially needed. Usually, silver (Ag) and magnesium (Mg) alloy is used as cathode metals in top emission OLED and those metals required high temperature for the deposition. Unlikely organic material deposition, fine metal mask (FMM) cannot be used in metal deposition because FMM cannot withstand such high deposition temperatures and is distorted [3]. To date several pattern metallization techniques have been reported but all technologies have several issues and unable to adopt for the large area display production. Indeed, a new metal patterning method with simple process is required for mass production.

In this study, we applied a metal patterning layer (MPL) before the deposition of metal electrode. In order to confirm the deposition property of metal on organic materials, we measured the surface energy related to the interaction energy force between deposition metal and organic under layer. Among MPL materials, the lowest surface energy material showed excellent deposition inhibition properties in the Ag:Mg(10:1) cathode. It was confirmed through the measurement of transmittance. The Ag deposited film showed a high transmittance of over 95% compared with the non-deposited film area. We have checked that there is almost no deposition of metal on the MPL. Our simple metal patterning method could be applicable to transparent display, sensor embedded display, and under display camera applications.

2 Experiment

We measured the optical transmittance of fabricated films by using UV-vis. spectrophotometer (Jasco, V-700). To check the electrical property, sheet resistance of fabricated cathode unit films was measured by 4-point probe station (DASOL Eng., FPP-2000). To estimate the surface energy, contact angle of fabricated organic films was measured by equipment, Phoenix 600 with water droplet. We performed molecular simulation for calculation of dipole moment of organic molecules. For this calculation, we optimized the molecular structure and calculated by DFT calculations with B3LYP/6-31G(d) using Schrödinger 2021-3 program.

Table 1. Summarized measured and calculated characteristics of MPL materials

Material	Dipole moment (D)	Contact angle (°)	Surface energy (mJ/m^2)
TAZ	5.61	8.8	72.4
DPEPO	6.20	47.7	60.9
BPhen	3.72	65.5	51.5
BPPB	0.84	67.8	50.2
DDBFT	0.92	78.9	43.4
CBP	0.98	79.3	43.2
PFTC	0.24	120.3	18.0

3 Results and Discussion

In general, the surface energy includes a London dispersion component and a hydrogen bond component in addition to the polar component. Among several interaction energies to determine the surface energy, London dispersion and hydrogen bond values are relatively weak compared with dipole values. Thus, we calculated the dipole moment that affects the intermolecular interaction due to the formation of its separated partial charge in the molecule. Calculated dipole moment values are summarized in Table 1. The highest calculated dipole moment value of 6.20 D was obtained in DPEPO material. Whereas perfluoro-tetracosane (PFTC) showed the lowest dipole moment value of 0.24 D amongst the selected materials which means that it shows a weak interaction with the metal gases. From the perspective of intermolecular attraction, higher dipole moment material induces the enhanced values of surface energy.

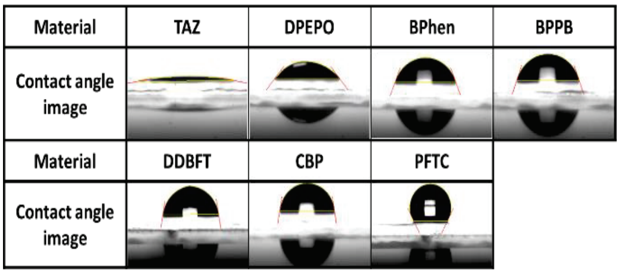

Figure 1. Measured contact angles of organic materials.

To check the surface energy of the selected materials, we measured the contact angle as shown in Figure 1. These contact angle images were measured by the water drop on the deposited organic materials. In this measurement, the TAZ exhibited the lowest value of contact angle and PFTC showed the highest value among the measured organic materials. Surface energy can be calculated as follows equations $\gamma^{S}=\gamma^{SL}+\gamma^{L}\cos\theta$, $W_a=\gamma^{S}+\gamma^{L}-\gamma^{SL}=\gamma^{L}(1+\cos\theta)$ γ^{SL} is interfacial free energy between surface and liquid. γ^{S} and γ^{L} are surface free energy of substrate and liquid, respectively. θ is contact angle between substrate and liquid. The W_a is work of adhesion that means the required work to separates two phase materials. We calculated the surface energy of the organic materials by using this simple equation and it shown in Table 1. The TAZ having the lowest contact angle exhibited the highest surface energy value of 72.4 mJ/m^2. In contrast to TAZ, the PFTC showed the highest contact angle value of 120.3° and exhibited the lowest surface energy of 18.0 mJ/m^2. This surface energy is related with the intermolecular attraction, and higher intermolecular attraction results in the higher surface energy value. As a result, it can affect the inhibition property of the metal deposition by the influence of interaction energy between metal gas and substrate. The simulated dipole moment and measured contact angle show similar tendency.

We fabricated the cathode unit to evaluate the MPL characteristics of organic materials. The deposition metals were fixed as Mg and Ag. The cathode unit structure: glass substrate ((0.7 mm) / MPL (20 nm) / cathode (Mg or Ag, 20 nm). Firstly, we have measured the transmittance of cathode unit as shown in Figure 2. When Mg and Ag deposited on PFTC, the transmittance at 550nm shows 99.5% and 98.7%, respectively. While using other organic materials as MPL, the transmittance at 550nm shows under 80.0% and minimum 24.4%. Secondly, we have measured the sheet resistance, BPPB and CBP showed 2.1 Ω/□ and 399.0 Ω/□ after Ag deposition, respectively. Reported BPPB has a strong coordination interaction with Ag, which causes easy nucleation compared with the CBP [4]. However, the sheet resistance of PFTC film cannot be measured because there is almost no deposition of the Ag. These results are in good agreement with the transmittance results. These measured results confirmed the surface energy of organic materials directly affect the deposition property. More detailed of cathode unit property and device performances will be present at the conference.

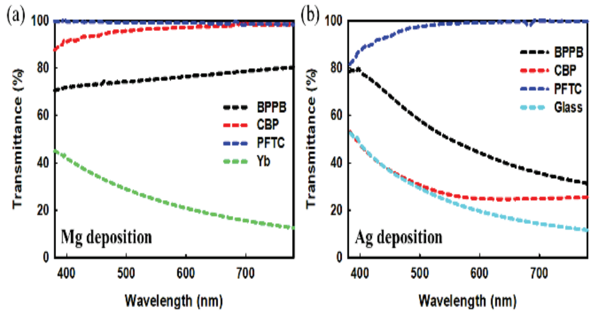

Figure 2. Measured transmittance of (a) Mg (b)Ag deposited cathode unit film on MPL materials.

4 Conclusions

We applied the MPL concept which inhibits the metal deposition. To search the good MPL material, we calculated the dipole moment values of MPL materials that are directly related to interaction force which affect the deposition property with the metal materials. We also measured the contact angle to determine the surface energy of MPLs for identifying the relationship between the dipole moment and the surface energy. Both surface energy and dipole moment values showed similar tendencies. The strong dipole moment can enhance the surface energy of molecule by increasing the intermolecular attraction. Further to gather precise knowledge of inhibition characteristics of MPL, we investigated the metal deposition properties on the low surface energy materials like CBP and PFTC. In the Ag deposition, only PFTC showed an inhibition property due to its lowest surface energy value. A low surface energy, low dipole moment, and excellent thermal stability of fluorinated organic layer are crucial characteristics for the selective deposition of metal vapor.

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References

[1] J. Lee, Y. Choi, H.-S. Lee, E. Heo, D. Lim, G. Lee, S. Song, "Under Display Camera Image Recovery

through Diffraction Compensation," Proc. IS&T Int'l. Symp. pp 68-1,5 (2021)
[2] Q. Li, K. Liu, J. Jia, W. Hu, H. Lu, W. Chen, S. Zhao, Q. Li, Z. Lai, H. Zhao, Y. Du, Z. Yu, S. Li, C. Liang, P. Qi, Y. Feng, H. Qiu, "A 12.3-in. Top-Emission AMOLED Transparent Display," Symposium. SID 'V 52, p. 1426-1428 (2021)
[3] S.-H. Lee, Y.-C. Jeong, K. Y. Shin, C.-R. Yoon, "Analysis of OLED Fine Metal Mask Cleaning Process Using a Microstructure," ECS Meeting, Vol. MA2019-01 No. 3, pp. 481-484 (2019).
[4] S. K. Kim, R. Lampande, J. H. Kwon, "Electro-optically Efficient and Thermally Stable Multilayer Semitransparent Pristine Ag Cathode Structure for Top-Emission Organic Light-Emitting Diodes," ACS Photon, 6, 11, 2957-2965 (2019)