

## Dependence of O<sub>2</sub> Plasma Treatment of Cross-Linked PVP Insulator on the Electrical Properties of Organic-Inorganic Thin Film Transistors with ZnO Channel Layer

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**Abstract:** The organic-inorganic thin film transistors (OITFTs) with ZnO channel layer and the cross-linked PVP (Poly-4-vinylphenol) gate insulator were fabricated on the patterned ITO gate/glass substrate. ZnO channel layer was deposited by using atomic layer deposition (ALD). In order to improve the electrical properties, O<sub>2</sub> plasma treatment onto PVP film was introduced and investigated the effect of the plasma treatments on the electrical properties of the OITFTs. The field effect mobility and sub-threshold slope (SS) values of the OITFT decreased slightly from 0.24 to 0.16 cm<sup>2</sup>/V·s and from 9.7 to 9.2 V/dec, respectively with increasing RF power from 30 to 50 Watt. The I<sub>on/off</sub> ratio was about 10<sup>3</sup> for all samples with O<sub>2</sub> plasma treatment.

**Keywords:** *Organic-inorganic thin film transistor, Cross-linked Poly-4-vinylphenol, ZnO, Atomic layer deposition, O<sub>2</sub> plasma treatment, Field effect mobility*

### 1. Introduction

The organic thin film transistors (OTFTs) have been investigated for many years due to their good features such as simple soluble process on the large area flexible substrate with low cost.<sup>1)</sup> Also, OTFTs have considerable attention because of its potential applications in the flat panel displays such as active matrix (AM) liquid crystal display and AM organic light emitting diodes, radio frequency identification tags and electronic bio-sensing devices, etc.<sup>2)</sup>

Generally, it is established that the structure of the organic-inorganic hybrid TFTs (OITFTs) is very similar with the OTFTs except the channel layer materials. Furthermore, OITFTs using inorganic semiconductor in the channel layer can be improved the electrical properties such as field effect mobility and switching speed compared with the OTFTs in which the organic semiconductor is used in the channel.<sup>3)</sup> To improve the mobility and I<sub>on/off</sub> ratio, it is important to control the interface trap density by mean of the surface characterization between organic insulator and active channel layer.

The electrical properties of the OITFT are strongly dependent on the film surface properties such as adhesion,

micro-sticky, wettability and chemical reactivity caused by mainly a molecular aggregation state of surface.<sup>4,5)</sup> One of the effective investigation methods on the surface properties is the contact angle measurement and surface energy calculation through the liquid drop profile to the surface at the intersection of the liquid and the solid. A low contact angle between solid surface and liquid drop indicates that the surface is hydrophilic and has high surface energy.

In this study, the OITFTs with ZnO channel layer on cross-linked PVP (Poly-4-vinylphenol) gate insulator<sup>6,7)</sup> treated by O<sub>2</sub> plasma were fabricated by atomic layer deposition (ALD) method and spin coating method on the patterned ITO gate/glass substrate. The mobility and I<sub>on/off</sub> ratio were investigated for the prepared OITFTs through the film surface characteristics using contact angle measurement and surface morphologies.

### 2. Experimental

#### 2.1. Device Fabrication

The ITO coated glass with the size of 1×1 inch square was used as substrate. To make gate electrode, ITO transparent gate electrode was patterned with the size of

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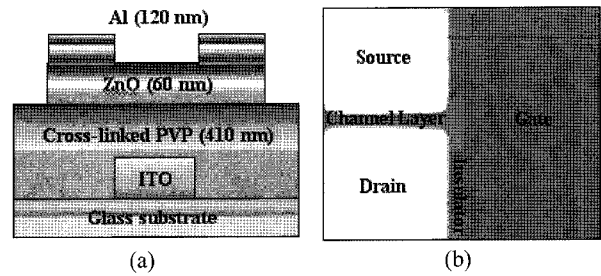
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2.0 mm×3.3 mm by using conventional lithography etching method. In order to remove the organic particles, the patterned gate ITO/glass substrate was cleaned using the SC-1 process<sup>8</sup>), which is generally used for semiconductor wafer process, followed by an ultrasonic precision cleaning process with acetone, isopropyl alcohol and de-ionized water. The cross-linked PVP organic material was used as the gate insulator.

The PVP insulator solution was prepared by dissolving PVP powders with poly (melamine-co-formaldehyde) cross-linking agent, and propylene glycol mono methyl ether acetate (PGMEA) solvent. The cross-linked PVP have a strong chemical resistance to endure the subsequent chemical processes. The prepared PVP solution was spin coated on the ITO gate electrode with the thickness of about 410 nm and the heat-treatment was carried out at 200°C for 30°C min in vacuum oven for the hard curing.

In order to improve the electrical properties of the devices, O<sub>2</sub> plasma treatment was introduced onto the PVP insulator surface. The condition of plasma treatment was 30 sccm of O<sub>2</sub> gas flow for 30 sec under the RF power of 30, 40 and 50 Watt. The dependence of RF power intensities on the surface morphology and contact angle of the PVP film was also investigated.

The ZnO channel layer was deposited onto the PVP insulator film by using ALD process. The precursor source for ZnO was used with DEZ (Diethyl Zinc) [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> Zn] and de-ionized water with the oxygen reactants. The pulse time of the DEZ and H<sub>2</sub>O precursor sources was 0.5 sec and the total number of cycles during the deposition process was 300. A purge process using N<sub>2</sub> gas was carried out for 10 sec every cycle. The thickness of ZnO layers was about 60 nm. The ZnO channel layer was patterned by using photolithography process. Finally, the aluminum (Al) as the source and drain contact metal was deposited on the top of



**Fig. 1.** Schematic drawings of the (a) cross-sectional and (b) photographic top views of the OITFT device.

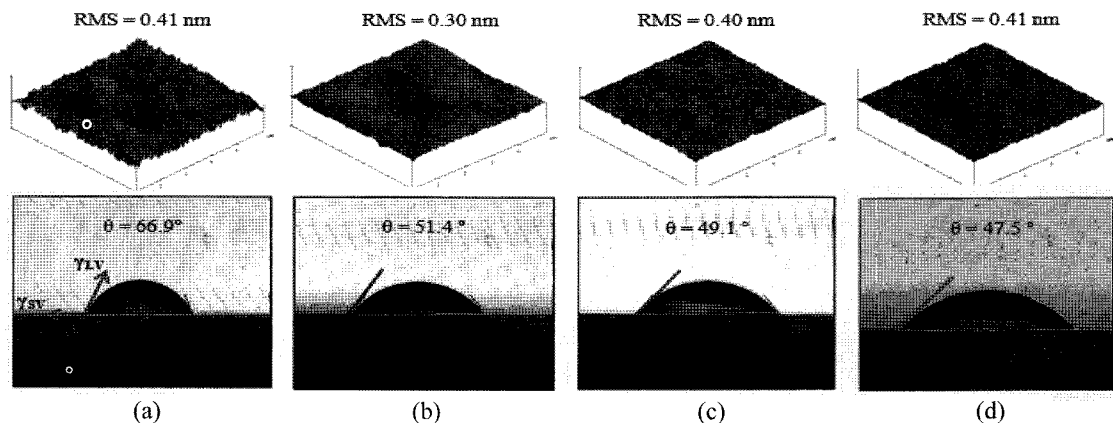
the ZnO channel layer using a shadow mask.

## 2.2. Measurements

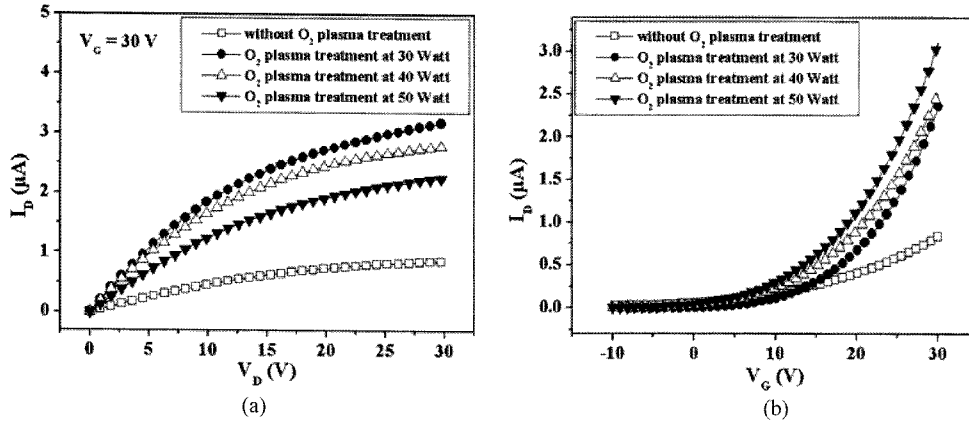
The electrical properties such as current-voltage of the OITFTs were investigated using an HP4145B semiconductor measurement system and the film capacitance was measured by RLC meter. The surface morphology and roughness of the PVP films were examined by Digital Instruments (Dimension 3100-IVa) atomic force microscope (AFM). The AFM quantitative surface analysis with resolution in the nanometer region in all three dimensions is possible. In this experiment, the silicon cantilevers integrated tip of 125 μm length, and resonant of 300 kHz were used for tapping mode image. The contact angle was measured by the Girifalco-Good-Fowkes-Young method with Tensiometer (Kruss Co) contact angle measurement system with D.I. water as the drop method.

## 3. Results and discussion

The OITFT devices were fabricated with inverted staggered structure as shown Figure 1. The performance dimension of the channel layer was 1600 μm in the width (W) and 200 μm in the length (L) with 8 of W/L ratio.



**Fig. 2.** AFM images (top) and contact angles (bottom) of the PVP insulator films (a) without and with O<sub>2</sub> plasma treatment at (b) 30 (c) 40 and (d) 50 Watt in RF power.



**Fig. 3.** Plots of the (a) drain current *versus* drain voltage ( $I_D$ - $V_D$ ) output curves at gate voltage ( $V_G$ ) = 30 V and (b) transfer curves of drain current *versus* gate voltage ( $I_D$ - $V_G$ ) at drain voltage ( $V_D$ ) = 30 V for the OITFT without and with O<sub>2</sub> plasma treatment of PVP at various RF powers.

Figure 2 shows the AFM images and contact angle of the PVP insulator films after O<sub>2</sub> plasma treatment at the RF power of 30, 40 and 50 Watt. Root-mean-square (RMS) values increased slightly from 0.30 to 0.41 nm as the RF power increased from 30 to 50 Watt, showing the rough PVP film surface at higher RF power. We expect that the surface roughness may affect the carrier mobility and switching speed at the channel layer of the device. Therefore, the electrical properties of OITFTs were investigated according to the surface state of the PVP films at various RF power.

The contact angle of PVP film without plasma treatment was found to be about 66.9° (degree). After O<sub>2</sub> plasma treatment of the PVP film surface at 30 Watt RF power, the contact angle was decreased below 51.4°. The contact angle decreased down to 47.5° at the highest RF power of 50 Watt. In addition, the surface energy,  $\gamma_{SV}$  of the PVP film was calculated with contact angle ( $\theta$ ) by following equation (1).

$$\gamma_{SV} = \frac{\gamma_{LV}(1 + \cos\theta)^2}{4\pi^2} \quad (1)$$

where,  $\gamma_{SV}$  is the surface free energy of the solid and the vapor, and  $\gamma_{LV}$  is the surface tension of the liquid and the vapor, respectively.<sup>9,10</sup> The calculated surface energy of the PVP film was 28.46 mN/m for the OITFT without O<sub>2</sub> plasma treatment. Whereas, the surface energy of OITFT with plasma treatment increased from 45.35 to 49.16 mN/m as the RF power increased from 30 to 50 Watt (refer to table 1).

As a result, we found that the PVP film surface can be changed to be more hydrophilic condition with increasing the RF power.<sup>11,12</sup> These results are important to control the surface characteristics of micro-sticky and interface defects between the PVP insulator and ZnO channel layers because

ZnO inorganic material shows hydrophilic state. In general, the mismatch of the surface state such as hydrophilic and hydrophobic between interfaces may bring about the interface defects, which result in the carrier trap problem at the interface.

For the investigation of the co-relationship between the surface states (contact angle and surface energy) and the electrical properties of the OITFT at various RF powers, the current values of the prepared OITFT samples as a function of the input voltages were measured and compared.

The electrical properties such as the leakage current and capacitance of the cross-linked PVP gate insulator were investigated from the Al/PVP/ITO/glass (metal-insulator-metal) structure. The cross-linked PVP film thicknesses was measured to be 410 nm, in which the leakage current and capacitance values were  $2.8 \times 10^{-10}$  A and  $9.1 \times 10^{-10}$  F, respectively. The capacitance per unit area was calculated to be  $7.28 \times 10^{-9}$  F/cm<sup>2</sup> by dividing the electrode area ( $A = 0.126$  cm<sup>2</sup>).

Figure 3 shows (a) the drain current *versus* drain voltage ( $I_D$ - $V_D$ ) curves at 30 V in gate voltage ( $V_G$ ) and (b) transfer curves of the drain current *versus* gate voltage ( $I_D$ - $V_G$ ) at 30 V in drain voltage ( $V_D$ ) of the OITFTs without and with plasma treatment of PVP films at 30, 40 and 50 Watt in RF power.

From the  $I_D$ - $V_D$  output curves at gate voltage ( $V_G$ ) = 30 V in Figure 3 (a), the OITFT without plasma treatment of PVP showed that the saturation current and field effect mobility ( $\mu$ ) were found to be only about 0.75  $\mu$ A and 0.03 cm<sup>2</sup>/V·s. These low values of saturation current and  $\mu$  may be attributed mainly to the interface carrier trap between PVP film and ZnO channel layer due to the mismatch of the surface state. The maximum saturation current and  $\mu$  were found to be about 3.3  $\mu$ A and 0.24 cm<sup>2</sup>/V·s, respectively,

**Table 1.** Electrical and surface characteristics of the OITFTs without and with O<sub>2</sub> plasma treatment of PVP films at various RF powers.

PVP Surface Treatment	RMS (nm)	Contact Angle (°)	Surface Energy (mN/m)	Mobility (cm <sup>2</sup> /V · s)	I <sub>on/off</sub> Ratio	V <sub>th</sub> (V)	SS (V/dec) (Sub-threshold Slope)
without O <sub>2</sub> plasma	0.41	66.9	28.46	0.03	~10	3.0	16
O <sub>2</sub> plasma at 30 Watt	0.30	51.4	45.35	0.24	~10 <sup>3</sup>	9.2	9.7
O <sub>2</sub> plasma at 40 Watt	0.40	49.1	47.58	0.19	~10 <sup>3</sup>	6.8	9.6
O <sub>2</sub> plasma at 50 Watt	0.41	47.5	49.16	0.16	~10 <sup>3</sup>	4.1	9.2

when the PVP film was plasma-treated at 30 Watt RF power. As studied in advance, O<sub>2</sub> plasma treatment caused PVP surface to be more hydrophilic, and may improve the electrical properties by reducing the interface defect with ZnO film layer. In particular, the saturation current and  $\mu$  decreased from about 3.3 to 2.2  $\mu$ A and from 0.24 to 0.16 cm<sup>2</sup>/V·s, respectively, as the RF power increased from 30 to 50 Watt. The saturation current and  $\mu$  were decreased in spite of more hydrophilic state at higher RF power of 50 Watt. We suggests that this result may be originated from the etching effect by O<sub>2</sub> plasma treatment.<sup>13,14</sup> O<sub>2</sub> plasma treatment causes the thickness of PVP film to reduce by etching process, which leads to lower  $\mu$  due to the high capacitance. The field effect mobility ( $\mu$ ) was calculated by equation (2) at V<sub>G</sub> = 30 V.

$$I_D = \frac{W\mu C_{PVP}}{2L}(V_G - V_T)^2 \quad (2)$$

Where, I<sub>D</sub> is the drain current,  $\mu$  is the field effect mobility, V<sub>G</sub> is the gate voltage, V<sub>T</sub> is the threshold voltage of the OITFT, and C<sub>PVP</sub> is the capacitance per unit area of the PVP gate insulator.

From the transfer curve in figure 3 (b), the slope of the I<sub>D</sub>-V<sub>G</sub> output curve showed more steep with increasing the RF power from 30 to 50 Watt. The I<sub>on/off</sub> ratio for OITFT without plasma treatment was found to be about 10, and increased to 10<sup>3</sup> for the OITFTs with O<sub>2</sub> plasma treatment of PVP film. In addition, the V<sub>T</sub> and sub-threshold slope (SS) values of the OITFT were decreased from 9.2 to 4.1 V and from 9.7 to 9.2 V/dec, respectively with increasing RF power. These results may be strongly related to the lower contact angle and higher surface energy, suggesting more hydrophilic surface state of the PVP insulator film as described in figure 2.<sup>15</sup> That is, after O<sub>2</sub> plasma treatment of PVP film, the surface states for both the ZnO and PVP films seems to be changed into hydrophilic surface state.

The electrical and surface characteristics ( $\mu$ , I<sub>on/off</sub> ratio, V<sub>th</sub>, SS values, RMS values, contact angle, and surface energy) of the OITFTs with and without O<sub>2</sub> plasma treatment of PVP film are summarized in table 1.

## 4. Conclusions

The OITFTs with ZnO channel layer deposited on the cross-linked PVP gate insulator were fabricated on the patterned ITO gate/glass substrate. The dependence of O<sub>2</sub> plasma treatment of PVP insulator film on the electrical and surface properties of OITFTs was investigated.

The electrical properties of OITFTs depend strongly upon the O<sub>2</sub> plasma treatment of PVP film. The field effect mobility ( $\mu$ ) and I<sub>on/off</sub> ratio of the OITFT without plasma treatment was found to be about 0.03 cm<sup>2</sup>/V·s and ~10, respectively. In order to improve the electrical properties, O<sub>2</sub> plasma treatment was introduced onto the PVP insulator film. The saturation current and  $\mu$  were decreased from about 3.3 to 2.2  $\mu$ A and from 0.24 to 0.16 cm<sup>2</sup>/V·s as the RF power increased from 30 to 50 Watt. On the other hand, the slope of the I<sub>D</sub>-V<sub>G</sub> output curves showed more steeper with increasing the RF power. This may be ascribed to the matching of the hydrophilic surface state for both ZnO and PVP film layers after O<sub>2</sub> plasma treatment. For the OITFT deposited on PVP insulator film treated by O<sub>2</sub> plasma at 30 Watt, the  $\mu$  and I<sub>on/off</sub> ratio were about 0.24 cm<sup>2</sup>/V·s and ~10<sup>3</sup>, respectively. The interface matching between PVP film and ZnO channel leads to improve the electrical properties of OITFTs. Whereas, the etching effect of O<sub>2</sub> plasma treatment at higher RF power caused to lower  $\mu$ .

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## References

1. J. A. Rogers, Z. Bao, J. Polym. Sci. Part A: Polym. Chem., Vol. 40, p. 3327 (2002).
2. T. W. Kelly, P. F. Baude, C. Gerlach, D. E. Ender, D. Muyres, M. A. Haase, D. E. Vogel, S. D. Theiss, Chem. Mat., Vol. 16, p. 4413 (2004).

3. E. Fortunato, P. Barquinha, A. Pimentel, A. Goncalves, A. Marques, L. Pereira, R. Martins, *Thin Solid Films*, Vol. 487, p. 205-211 (2005).
4. R. H. Tredgold, *Order in Thin Organic Films*, Cambridge University Press (1994).
5. R. F. Gould (Ed.), *Contact Angle, Wettability and Adhesion*, Proceeding of the 144<sup>th</sup> Meeting of the American Chemical Society, Vol. 43, Washington, DC (1964).
6. J. G. Jang, M. H. Oh, H. J. Chang, Y. S. Kim, J. Y. Lee, M. S. Gong, Y. K. Lee, *J. Microelectron Packaging Soc.*, Vol. 13, No. 1, p. 37 (2006).
7. I. S. Shin, S. C. Gong, H. S. Lim, H. H. Park, H. J. Chang, *J. Microelectron Packaging Soc.*, Vol. 14, No. 1, p. 27 (2007)
8. H. T. Lu, M. Yokoyama, *J. Cryst. Growth*, Vol. 260, p. 186 (2004).
9. B. S. Lee, Y. S. Yu, J. C. Lee, D.J. Hur and H.J. Cho, *Hankook Kwanghak Hoeji*, Vol. 18, p. 452 (2007).
10. D. Ross, J. E. Rutledge, P. Taborek, *Science*, Vol. 278, p. 664 (1997).
11. M. Nakahara, K. Ozawa, Y. Sanada, *J. Mater. Sci.*, Vol. 29, p. 1646 (1994).
12. S. C. Lim, S. H. Kim, J. H. Lee, M. K. Kim, D. J. Kim, T. Zyung, *Synthetic Metals*, Vol. 148, p. 75 (2005).
13. G. N. Taylor, T. M. Wolf, *Polymer Engineering and Science*, Vol. 20, issue 16, p. 1087 (2009).
14. M. R. Sanchis, V. Blans, D. Garcia, R. Balart, *European Polymer Journal*, Vol. 42, p. 1558 (2006).
15. T. Khan, D. Vasileska and T. J. Thornton, *J. Vac. Sci. Technol. B*, Vol. 23, p. 1782 (2005).