Effects of Process Induced Damages on Organic Gate Dielectrics of Organic Thin-Film Transistors

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Abstract

The effects of plasma damages to the organic thin film transistor (OTFT) during the fabrication process are investigated; metal deposition process on the organic gate insulator by plasma sputtering mainly generates the process induced damages of bottom contact structured OTFTs. For this study, various deposition methods (thermal evaporation, plasma sputtering, and neutral beam based sputtering) and metals (gold and Indium-Tin Oxide) have been tested for their damage effects onto the Poly 4-vinylphenol(PVP) layer surface as an organic gate insulator. The surface damages are estimated by measuring surface energies and grain shapes of organic semiconductor on the gate insulator. Unlike thermal evaporation and neutral beam based sputtering, conventional plasma sputtering process induces serious damages onto the organic surface as increasing surface energy, decreasing grain sizes, and degrading TFT performance.

1. Introduction

For a few years, there has been noticeable progress in study of organic thin-film transistors (OTFTs) with organic gate insulator as PVP *(Poly 4-vinylphenol)*, PI (Polyimide) and other high k/ low k organic materials. Still OTFTs cannot rival the performance of inorganic thin-film transistor due to their lower field-effect mobility (< $1cm^2/V{\cdot}s$). Although OTFTs cannot compete with inorganic silicon based TFT, they are suitable for the new applications such as large sized device and/or flexible device because of their low-temperature and low cost process adaptability.

Recently, Organic TFT array and its LCD module is to be combined with several technical breakthroughs include new organic gate dielectric materials, improvement of ohmic contacts between source-drain metal electrode and semiconductor, and well-optimized process-architectures. Base on the newly developed organic gate dielectric with pentacene as an organic semiconductor, the world-record field effect TFT mobility in excess of $7cm^2/Vsec$ and excellent on/off ratios as ~ 10^6 have been presented by Samsung Electronics.[1] For jumping up the OTFT research activities from laboratory scale to real production line, some key technologies must be breakthrough. One of them is a new ohmic contact technology with very common materials in the current LCD manufacturing such as ITO; requirement of the bottom contact structured OTFT with ITO source-drain electrode is much the same performances as that with gold source-drain electrode without thermal and plasma damages during the TFT fabrication processes.

Generally, plasma based deposition processes including sputtering, PECVD, and dry etching are basic tools in the fabrication of thin-film structures of microelectronics. Especially for the mass production, metal and ITO deposition processes by DC or RF sputter are more convenient than other deposition methods including evaporations. However, the plasma sputter cannot avoid the damage caused by ion bombardments during processes onto the organic layers such as organic semiconductors (OSCs) and organic gate insulators (OGIs). Therefore, sometimes,

thermal evaporation system should be used for metallization of bottom contact structured OTFTs with organic gate insulators. Even if, the evaporation process can easily keep away from the plasma damages, but this process is not so adaptable to mass productions and large area applications. The problems associated with both of the plasma sputter and the evaporator for the metal & ITO deposition could be overcome by newly suggested neutral beam based process, which might be free from charging effects without sacrificing the process efficiency of sputtering system, and works at room temperature because some neutral particles with a hyper thermal energy can drive similar effects as high temperature process conditions.

In this study, gold and ITO have been used as a source-drain material and their metallization on the OGI were carried out by various deposition technique including conventional plasma sputtering, thermal evaporation, and neutral beam based sputtering processes. The process induced damages on the OGI were characterized by measuring surface energy, grain size of organic semiconductor on the gate insulator, Capacitance-Voltage measurement and TFT electrical characteristics.

2. Experimental Procedure

In this experiment, the device configuration was fabricated with top-contact structure. The glass substrates were successively cleaned up with hot acetone, hot methanol, hot isopropanol and D.I. water cleaning for each 10 min in ultra sonic bath, followed by baking in high vacuum anneal chamber (<10^{-5} torr, 130℃) for 30mins. The aluminum gate electrodes were prepared by a thermal evaporation with shadow mask. Cross-linking Poly 4-vinylphenol (PVP) was coated by a 2-step spin coating and cured in high vacuum anneal chamber at 190℃ for 2hr. The total thickness of cross-linking PVP layer was about 4000Å. All of thicknesses are measured by alpha-step surface profiler.

For identifying process induced damages, Au metal film was deposited by a rf magnetron sputter and evaporated by a thermal evaporation. A thickness of the Au films was 300 Å, which was the same thickness of Au source/drain electrode. These Au films were etched. Using flesh D.I. water, the substrate was wash out and dried in high vacuum anneal chamber (140℃/1hour). After that, octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) treatment was followed. Wet-cleaned samples were dipped in the 15mM OTS solution for 5min and washed out with anhydrous IPA solution. Pentacene as a most common p-type organic semiconductor was deposited by thermal evaporation, keeping the rate of deposition as 0.2±0.1 Å/s and the substrate temperature as 90±1℃. Total thickness of the pentacene was 700 Å. The base pressure was 1×10^{-7} torr. To estimate the effect of HNB sputtering, an ITO source/drain was deposited directly on pentacene using shadow mask except ITO patterning processes. To analyze process induced damages on cross-linked PVP as organic gate insulators, surface energies, Capacitance-Voltage characteristics and surface morphologies were measured by contact angle measurement system (KRUSS DSA-100), LCR meter (HP4284A) and atomic force microscope(AFM), respectively. The OTFT performances were measured by semiconductor parameter analyzer (HP4156C) in dark spaced probe station.

3. Results and discussion

To analyze effects of surface damages, as a preliminary test, we checked out the process dependency to the surface damage between thermal evaporation and plasma sputtering with gold metal; Au layers were deposited on cross-linked PVP by the thermal evaporator and the plasma sputter, and then completely etched out by wet chemical etchant. Just after vacuum drying, contact angle and surface energy of etch prepared PVP samples were measured as shown in Figure 1. The surface energies were calculated by two contact angles with water and Diiodomethane using Owens and Wendt model[2].

As shown in Figure 1, the surface energy on the PVP suffered from Au deposition process by thermal evaporation was decreased as compared with that on clean PVP without any process history; it might be strong acid effect due to Au etchant. But, even if, under same chemical history, the surface energy on the PVP with plasma sputtering process increased more than 10% as compared with that on the PVP with thermal evaporations, which means PVP surface changes from hydrophobic to hydrophilic state by plasma damage during the sputtering deposition process. It is important that interface between pentacene and PVP as a gate insulator have to be hydrophobic state for pentacene growth with adequate grain size.

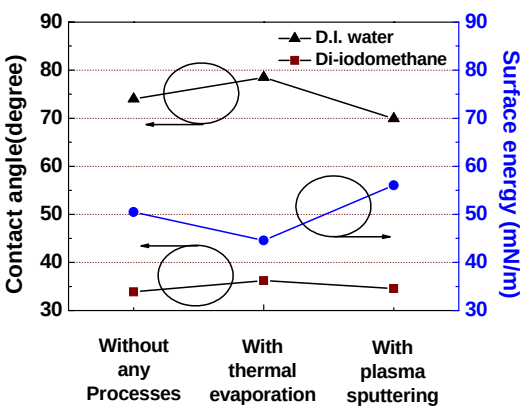


Figure 1. Contact angles and surface energies on PVP with different Au deposition process histories.

Figure 2 shows the PVP surface morphologies and pentacene grain shapes by AFM image which fully depends on process history on the PVP surface. Figure 2(a),(e),(i)

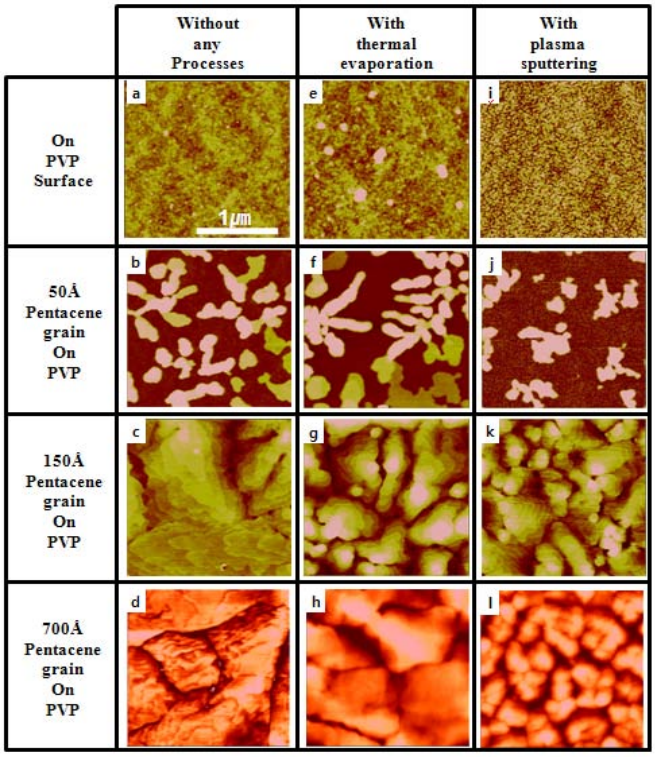


Figure 2. The Atomic Force Microscopy(AFM) images of PVP and pentacene grain on PVP with different Au deposition process histories. Without any processes, (a) just PVP treated with OTS SAMs, (b) 50Å pentacene, (c) 150 Å pentacene, (d) 700 Å pentacene. With thermal evaporation and etching processes, (e) PVP treated with OTS SAMs, (f) 50Å pentacene, (g) 150 Å pentacene, (h) 700 Å pentacene. With plasma sputtering processes and etching processes, (i) PVP treated with OTS SAMs, (j) 50Å pentacene, (k) 150 Å pentacene, (l) 700 Å pentacene.

show PVP surface morphologies with different Au deposition processes. After plasma sputtering process, PVP roughness was changed from 0.342nm to 0.835nm. It means that the PVP surface morphology is physically changed more roughly by the bombardment of energetic particles as neutral and ion particles. And these affect the growth of pentacene and the electrical performance of OTFTs. After pentacene of 50Å, 150Å and 700Å thicknesses was evaporated on the PVP surface with various Au deposition processes, additionally, the pentacene grain shapes were observed in Figure 2. The result is in good agreements with the PVP surface morphology. The pentacene grain on the PVP with plasma sputtering process has the smallest size and drives most poor TFT performance.

And then it was expected that the bulk damage was also induced by the plasma process. For estimating the bulk damage, capacitance-voltage measurement was used. We propose that the dielectric constant of OGI would be changed by induced-damage. During plasma enhanced deposition as sputtering, it was expected that a cross-linking of PVP would be severed by plasma damage as ion bombardments, UV and so on. To investigate the change of a dielectric constant, Capacitance-Voltage was measured. The capacitance-voltage is shown in Figure 3 with different area. And the dielectric constant of PVP was calculated from

$$C_i = \varepsilon_0 \varepsilon \left(\frac{A}{d} \right)$$

where C_i is the capacitance(F), ε_0 is the dielectric constant in vacuum, ε is the dielectric constant of PVP, A is the area(mm^2) and d is the thickness(Å) of PVP. The calculated dielectric constants of PVP were 4.09 without any processes, 4.01 with thermal evaporation and 3.83 with sputtering deposition. However, these small differences of dielectric constants with various processes would not explain clearly whether bulk property of PVP was changed by plasma enhanced deposition.

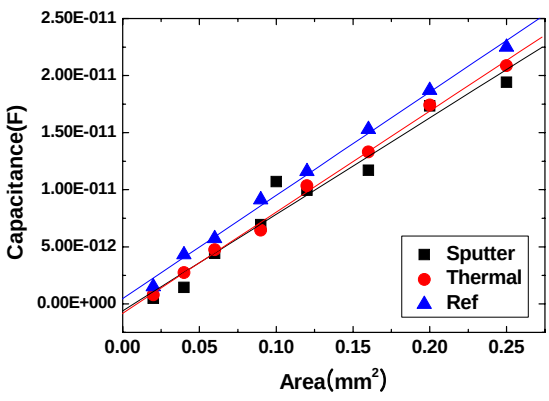
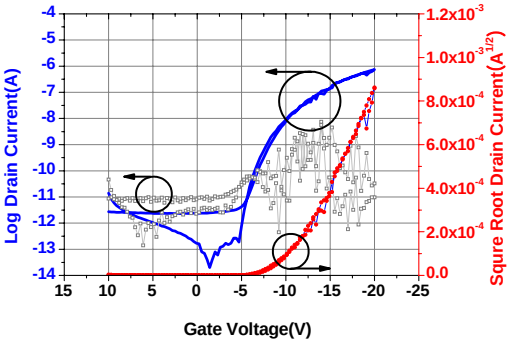


Figure 3. Capacitance-Voltage characteristics with various areas.

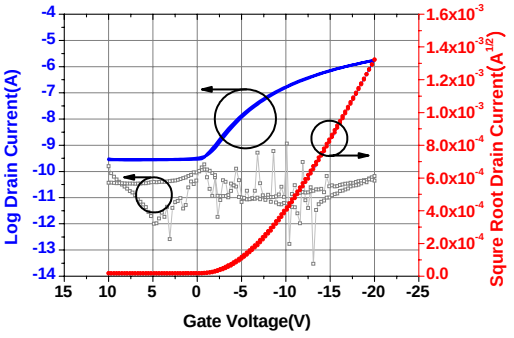
Figure 4 shows the electrical characteristics of the OTFT with three different processes. First of all, the field-effect mobility of OTFT with plasma sputtering processes was about 100 times lower than these of the others from 0.2 to $0.01 cm^2/Vs$. The field-effect mobility at $V_D=V_G$ was calculated by

$$I_{d,sat} = \left(\frac{W}{L} \right) \mu C_i (V_g - V_T)^2$$

Where μ is the field-effect carrier mobility, V_T is the threshold voltage, W is the channel width, L is the channel length, C_i is the capacitance per unit area. The observed decrease in field-effect mobility of the OTFT with plasma sputtering processes corresponds to the surface energy and



(a)



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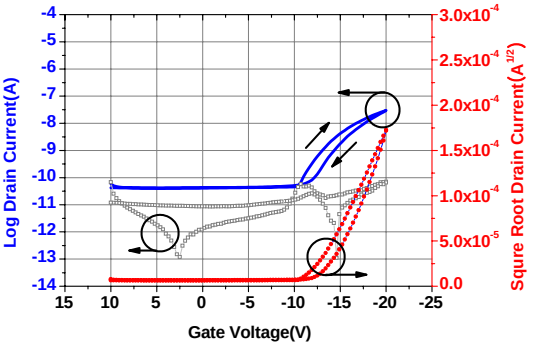


(c)

Figure 4. Electrical characteristics of OTFT with various processes. (a) without any processes (b) with thermal evaporation processes (c) with plasma sputtering processes.

grain shape of pentacene thin film. On the other hand, the field-effect mobility of the OTFT with thermal evaporation was not changed nearly. In this case, however, off current level was increased because it would be caused that moisture or oxygen were absorbed onto PVP during the washing process. Thus, sub-threshold slope was increased from 1.3 to 2.9 and on/off ratio was decreased.

We have repeated similar analysis with ITO layers as a one of good candidate for an alternative source-drain electrode material as presented by M.P. Hong, et al.[1]. Because ITO is hardly deposited by conventional thermal evaporation process, the PVP samples for estimation of process dependency to the surface damage were prepared by the plasma sputtering and the HNB sputtering as a plasma damage free system. Process conditions and properties of the HNB ITOs are presented by J.N. Jang.[3]. ITO layers were deposited on cross-linked PVP by the plasma sputter and the HNB sputter, and then completely etched out by wet chemical etchants. Just after vacuum drying, contact angle, and surface energy of prepared PVP samples were estimated and AFM images of pentacene on each prepared PVP surface were shown in Figure 5 and Figure 6. Figure 5 shows that the surface energy on the PVP suffered from ITO deposition process by the HNB sputter was lower than that on the PVP with plasma sputtering, which means the HNB sputtering gives less plasma damage rather than conventional plasma sputter. Although using same plasma sputter system, the plasma damage by ITO deposition looks more severe than that by Au deposition, because oxygen plasma brings to additional damages on the organic layer surface; just oxygen plasma treatment pushes to be most hydrophilic surface.

Figure 6 shows the changes of pentacene grain shapes are fully depending upon process histories on the PVP surface; unlike the ITO plasma sputtering process, the HNB sputtering process for the ITO deposition never cause too much changes or damages on the organic films. Sometimes OTS SAMs treatment can be helpful to recover the surface energy changes; after OTS SAMs treatment, surface energies can be reduced near the OTS own energy as about 40 mJ/cm^2, if the plasma damage may not be excess beyond a critical value. Because PVP contains hydroxyl (OH) groups, which might allow an OTS monolayer to self-assemble on surface, similar to a SiO_2 surface. Surface homogeneity and low surface energy are one of key parameter to grow a large grain of pentacene which is very important to OTFT performance[4][5][6].

Figure 7 shows the output characteristics of the OTFT with ITO source/drain deposited by HNB sputtering and normal rf magnetron sputtering. These results would indicate the effect of HNB sputtering as plasma damage free process. The output current level with HNB sputtering was 4 times better than with rf magnetron sputtering.

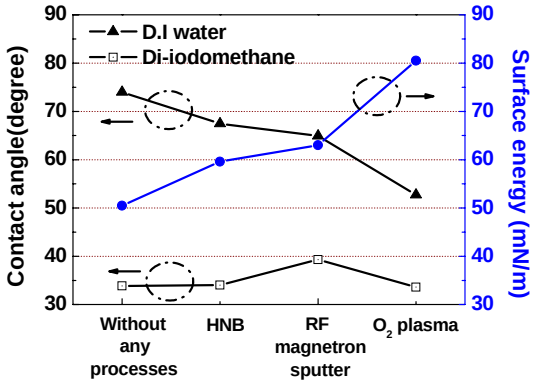


Figure 5. Contact angles and surface energies on PVP with different ITO deposition process histories.

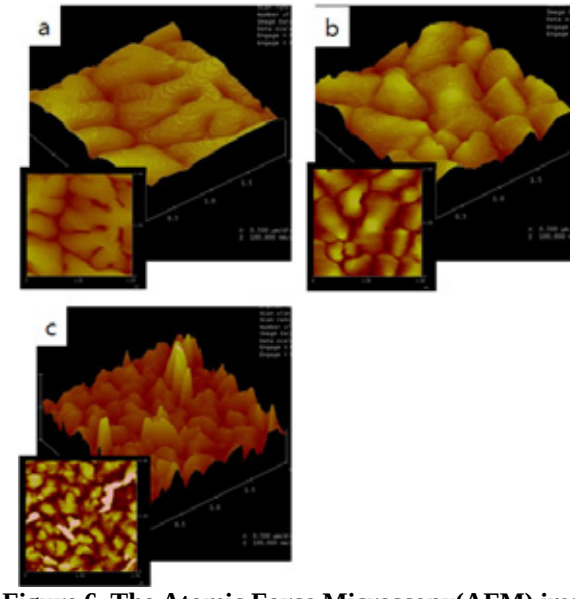
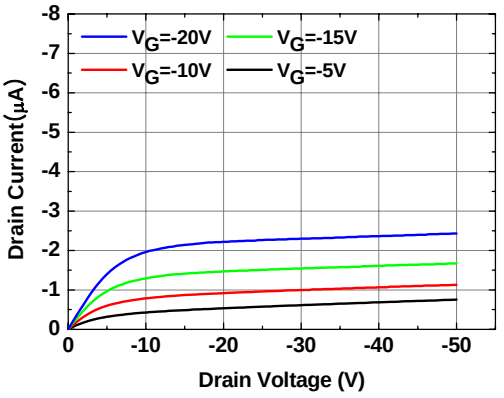


Figure 6. The Atomic Force Microscopy(AFM) images of pentacene grain on PVP with different ITO deposition process histories. (A)without any process, (b) with HNB sputtering, (c)with plasma sputtering.

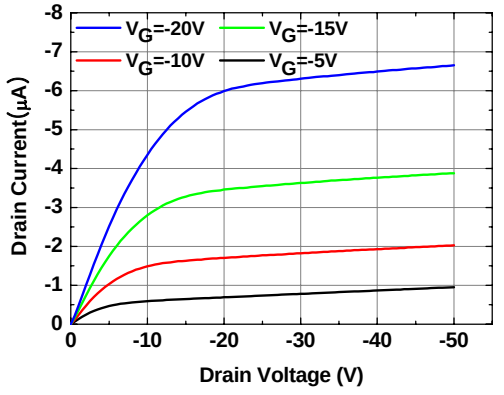
4. Summary

We have investigated process induced damages with various deposition methods. First of all, the surface energies each process were measured and obtained pentacene grain sizes by using AFM images.

Au and ITO deposition on the organic gate insulator by plasma sputter causes most serious process damages because of plasma ion irradiation and oxygen plasmas; the surface damage induced by plasma increases surface energy and affects the surface morphology. The hydrophilic surface of organic gate dielectric and rough surface morphology generate very small and unstable pentacene grain growth; it is directly related with electrical performances of OTFT device. For eliminating the process induced damages on



(a)



(b)

Figure 7. Electrical characteristics of OTFT with various processes (a) with plasma sputtering process (b) with HNB sputtering process.

OGI during the plasma processes, the HNB sputtering system is developed and proves their ability to be plasma-damage free process systems.

5. Acknowledgements

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5. References

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