

Enhanced hole injection by oxygen plasma treatment on Au electrode for bottom-contact pentacene organic thin-film transistors

Woong-Kwon Kim, Kihyon Hong, Soo Young Kim, and Jong-Lam Lee
 Department of Materials Science and Engineering, Pohang University of Science and
 Technology (POSTECH), Pohang, Kyungbuk 790-784, Korea
 Phone: +82-54-279-2152 , E-mail: jllee@postech.ac.kr

Abstract

Thin AuO_x layer was formed by O_2 plasma treatment on Au electrode. The surface work function of plasma treatment showed higher by 0.5 eV than that of bare Au, reducing the hole injection barrier at the Au/pentacene interface. Using O_2 plasma-treated Au source-drain electrodes, the field-effect mobility of bottom-contact pentacene-OTFT was increased from 0.05 to 0.1 cm^2/Vs .

1. Introduction

Organic thin film transistors (OTFTs) are attracting much interest, due to its possibilities for simple, low cost fabrication process. The bottom-contact (BC) OTFT structure is suitable for the applications such as flexible displays, smart card, and identification tags.[1] But, in these OTFTs, low field-effect mobility was reported. This originates from high contact resistance (R_c), between source(S)-drain(D) (S/D) electrode and pentacene.[1,2] Due to its high work function, Au has been commonly used as S/D electrodes for OTFTs. But, it was reported that barrier height of ~ 1 eV exist between Au and pentacene due to the large shift of vacuum level at the interface.[3,4] To reduce R_c , self-assembled monolayer (SAM) treatments on the electrode were suggested, but the process condition is complex and the details of mechanism are not yet clear.[5,6] It was reported that O_2 plasma treatment on ITO surface increase the surface work function by introducing high electronegative oxygen at the ITO surface.[7] Because the electronegativity of oxygen atom is high, the surface electron density could be reduced when oxygen atoms were chemisorbed at the surface of Au electrode. Thus, it is expected that the injection barrier of holes from Au electrode to pentacene could be decreased by the oxygen plasma treatment.

In this work, we investigated the effect of O_2 plasma treatment on the reduction of contact resistance

between Au and pentacene in BC OTFTs. The changes of the surface work function and chemical composition of Au were measured using synchrotron radiation photoemission spectroscopy (SRPES). Electrical properties of devices were analyzed using an HP-4156A.

2. Experiment

The O_2 plasma treatment condition was optimized as follows. Because oxygen-covered surface exhibit hydrophilicity, high surface energy provides an evidence for the formation of dense AuO_x . So, the dependence of surface energy was estimated as a function of plasma treatment time. Cr/Au (3 nm/50 nm) thin films on glass were used as starting substrates. The RF plasma of 25 W was employed at a pressure of 100 mTorr. The Au films were treated with O_2 plasma for 0, 10, 30, 60, 120, 240, and 480 sec in a vacuum chamber, respectively. Surface energies were estimated from the contact angles of water and diiodomethane droplets using Young's relation.

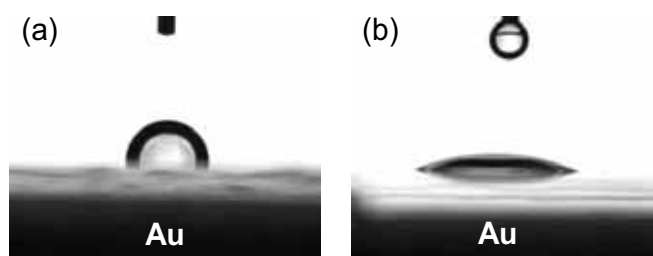


Fig. 1 Photographs of water contact angles on (a) bare Au and (b) O_2 plasma-treated Au.

Figure 1 shows the change of water contact angles on Au films before and after O_2 plasma treatment.

After O₂ plasma treatment for 120 sec, water contact angle was dramatically reduced from ~81° to ~14° and the surface energy was increased from 45.1 to 71.5 mJ/m². This represents the surface polarity was changed significantly by O₂ plasma treatment on Au electrodes. The changes of chemical compositions at the surface were analyzed using synchrotron radiation photoemission spectroscopy.

Figure 2 shows the bottom-contact OTFT structure used in this study. The devices were fabricated as follows. Highly conductive (~5Ω·cm) n-type Si (100) with thermal SiO₂ (300 nm) were used as starting substrates, which functioned as gate electrode and insulator, respectively. The substrates were cleaned sequentially with acetone, isopropyl alcohol for 2 min, followed by a rinse with de-ionized water, and dried with nitrogen gas. A channel blocking photo-resist (PR) patterns were produced on the insulator by photolithography. On the PR patterned substrates, Cr (3 nm) / Au (50 nm) films were sequentially deposited by e-beam evaporation method at a rate of ~1 Å/s. And then, O₂ plasma treatment was conducted to treat the surface of Au. So, the surfaces of Au electrodes were selectively exposed to O₂ plasma. Then, the S/D patterns were produced by removing the metals deposited on the PR patterns with a lift-off method. Finally, the pentacene films (50 nm) were deposited using organic molecular beam deposition through shadow mask to form the active channels of TFTs. The pentacene film were deposited at low rate below ~0.5 Å/s. During the film deposition, the chamber pressure was kept below 5×10⁻⁷ torr. All the films were deposited at room temperature. With this procedure, the OTFTs with channel length/width of 40 μm/2500 μm were fabricated.

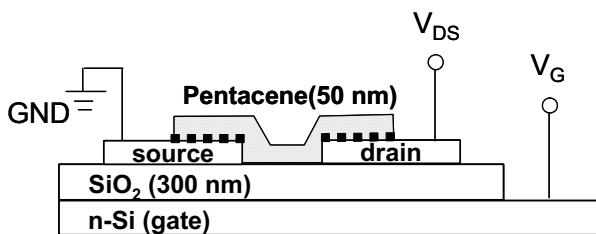


Fig. 2 Bottom-contact OTFT structure fabricated in this study.

(Dashed lines on the source-drain electrodes represent the Au surface treated with oxygen plasma.)

Electrical properties of devices both bare Au and O₂ plasma-treated Au were measured in an air ambient at room temperature. The relative work function changes of Au surface were investigated using SRPES at the 2B1 beam line in the Pohang Acceleration Laboratory. For the measurement of SRPES spectra, both treated and untreated Au films were prepared ex-situ and introduced into an analysis chamber. SRPES measurement was performed with a base pressure below 5×10⁻¹⁰ Torr. The onset of photoemission was measured with substrate bias of -20 V to avoid the work function of the detector. SRPES spectra were measured using an incident photon energy of 650 eV and the photon energy was calibrated with the Au 4f core level spectrum.

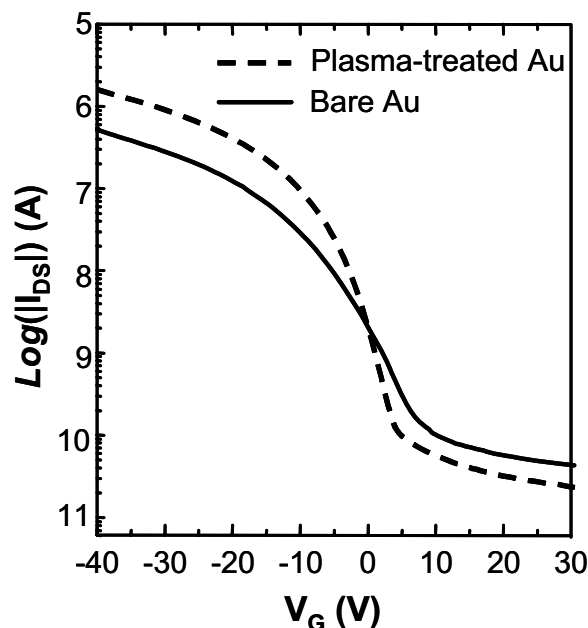


Fig. 3 Transfer characteristics of OTFTs. (at a drain bias of -1 V)

3. Results

Figure 3 shows the transfer characteristics of (-IDS) vs. VG for devices with bare Au and O₂ plasma-treated Au S/D electrodes, respectively. Drain currents were obtained by scanning VG from -40 V to +30 V at a constant VDS of -1 V.

The device with O₂ plasma treated Au S/D electrodes exhibited improved device performance. The charge injection characteristics for devices both treated and untreated electrodes were compared in the linear region. The field-effect mobility (μ_{FE}) can be calculated in the linear region from the transconductance, $g_m = \partial I_{DS} / \partial V_G$ at low V_{DS} using the equation.[8]

$$-I_{DS} = \frac{WC_i}{L} \mu_{FE} \left(V_G - V_T - \frac{V_{DS}}{2} \right) V_{DS}$$

where W is channel width (2500 μm), L channel length (40 μm), C_i insulator capacitance ($\sim 10 \text{ nF/cm}^2$), and V_T threshold voltage. For both devices with untreated and treated Au electrodes, the linear field-effect mobilities were extracted at V_G of -30 V with low drain voltage of -1 V . Compared with the linear field-effect of mobility of $\sim 0.03 \text{ cm}^2/\text{Vs}$ in bare Au device, higher field-effect mobility of $\sim 0.07 \text{ cm}^2/\text{Vs}$ was obtained in O₂ plasma-treated Au device. This means that the holes are injected more efficiently from the source electrode to the channel region.

The saturation drain currents with constant drain voltage (V_{DS}) of -40 V were also measured from the transfer curves. The saturation drain current increased from $-12.3 \mu\text{A}$ to $-27.1 \mu\text{A}$ using O₂ plasma treated Au. And from the $(-I_{DS})^{1/2}$ vs. V_G curve, the field-effect mobility at the saturation region was extracted using $-I_{DS} = 1/2(WC_i\mu_{FE}/L)(V_G - V_T)^2$. [8] Using O₂ plasma-treated Au S/D electrodes, the field-effect mobility was increased from 0.05 to 0.1 cm^2/Vs . To determine the charge injection properties in the linear region ($|V_{DS}| \ll |V_G|$), the total TFT ON-resistance R_T in the linear region was calculated using the equation $R_T = V_{DS} / I_{DS} = 2R_S + R_{Ch}$ where R_S is series resistance from both the source and drain contact and R_{Ch} channel resistance. The R_T at $V_G = -40 \text{ V}$ was decreased from 1.42 to 0.74 $\text{M}\Omega$ as the bare Au S-D electrodes were replaced by O₂ plasma-treated Au electrodes. This implies that the contact resistance at the Au/pentacene interface by O₂ plasma treatment. Compared to the bare Au device, the device with O₂ plasma-treated Au S/D electrodes showed almost identical on/off current ratio of $\sim 10^6$, and subthreshold slope of 2.4~2.5 V/dec.

The change of relative surface work function of both treated and untreated Au films were measured using SRPES. The onset of photoemission was

determined by extrapolating two solid lines from background and straight onset in each spectrum. The SRPES spectra showed that the onset of photoemission shifted toward higher kinetic energy by $\sim 0.5 \text{ eV}$ after O₂ plasma treatment, meaning that the work function of O₂ plasma-treated Au is higher by 0.5 eV than that of bare Au. This result indicates that the injection barrier for holes between Au and pentacene was reduced by O₂ plasma treatment. So, the increase of field-effect mobility was due to the enhanced hole injection properties through the Au/pentacene interface.

The core level spectra of Au 4f for both treated and untreated Au films were examined by x-ray photoelectron spectroscopy. The atomic compositions at the film surface showed that the ratio of O/Au was changed from ~ 0.9 to ~ 1.5 and new bond state was appeared at the higher binding energy region after O₂ plasma treatment. This new bond state is attributed to the Au-O bond, indicating the formation of AuO_x at the Au surface by the treatment.

According to the previous reports on the oxygen chemisorption, the chemisorbed oxygen atoms on Au surface led to the increase of the surface work function *via* the charge transfer from Au to chemisorbed oxygen atoms, reducing the surface electron density.[9] Therefore, we concluded that the increase of surface work function of Au by O₂ plasma treatment is due to the formation of chemically bonded oxygen at the Au surface. These results agreed well with the previous reports.[9]

4. Conclusion

We have fabricated bottom-contact pentacene-OTFTs with O₂ plasma-treated Au S/D electrodes. The O₂ plasma treatment on Au electrode increased the surface work function of Au by 0.5 eV, *via* formation of AuO_x at the surface of Au, reducing the contact resistance at the Au/pentacene interface. Using O₂ plasma-treated Au S/D electrodes, the field-effect mobility at the saturation region was increased from 0.05 to 0.1 $\text{cm}^2/\text{V}\cdot\text{s}$. The increment of field-effect mobility by O₂ plasma treatment was comparable to that by self-assembled monolayer treatment on Au electrode.[10] Therefore, it was expected that O₂ plasma treatment could be used as S/D electrode for high performance OTFTs.

5. Acknowledgements

This work was supported in part by the Program for the Training of Graduate Students in Regional Innovation, which was conducted by the Ministry of Commerce, Industry and Energy of the Korean Government. It was also funded in part by the Korean Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-005-J13102).

6. References

- [1] C. D. Dimitrakopoulos and Patrick R. L. Malenfant, *Adv. Mat.* **14**, 99 (2002).
- [2] M. Kawasaki, S. Imazeki, T. Kamata, and M. Ando, *Ext. Abs. Int. Conf. Solid State Devices and Materials*. 690 (2003).
- [3] N. Koch, A. Elschner, J. Schwartz, and A. Kahn, *Appl. Phys. Lett.*, **82**, 2281 (2003).
- [4] N. J. Watkins, L. Yan, and Y. Gao, *Appl. Phys. Lett.*, **80**, 4384 (2002).
- [5] D. J. Gundlach, L. Jia, and T. N. Jackson, *IEEE Elec. Dev. Lett.*, **22**, 571 (2001).
- [6] D. Knipp and R. A. Street, *J. Non-Cryst. Solids*, **338**, 595 (2004).
- [7] K. H. Lee, H. W. Jang, K.-B. Kim, Y.-H. Tak, and J.-L. Lee, *J. Appl. Phys.*, **15**, 586 (2004).
- [8] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
- [9] J. M. Gottfried, N. Elghobashi, S. L. M. Schroeder, K. Christmann, *Surf. Sci.* **523**, 197 (2003).
- [10] S. H. Kim, J. H. Lee, S. C. Lim, Y. S. Yang, and T. H. Zyung, *Jpn. J. Appl. Phys.*, **43**, L60 (2004).