Pentacene-Based TTFTs with Polymer Gate Dielectric and NiO$_x$ Electrodes

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We report on the fabrication of pentacene-based transparent thin-film transistors (TTFTs) that employ pentacene, NiO$_x$, and poly-4-vinylphenol (PVP) for channel, source-drain (S/D) electrode, and gate dielectric, respectively. Spin-coated PVP showed decent dielectric strength (1.5 MV/cm) and constant ($k = 3.9$). Semitransparent NiO$_x$ for S/D electrodes of which the work function is well matched to that of pentacene were deposited on a 50 nm thick pentacene channel by thermal evaporation of NiO powder. NiO$_x$ electrodes showed effective transmittance of ~40% in the visible range along with good sheet resistance of ~60 Ω/□. Our pentacene-based TTFT exhibited a field effect mobility as large as 0.07 cm^2/V s in the dark, and an on/off current ratio of 10^5. Our work demonstrates that spin-coated PVP and thermal evaporated NiO$_x$ are promising gate dielectric and S/D electrode materials for organic TTFTs, respectively.
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Development of transparent thin-film transistors (TTFTs) for the driving circuits of a display pixel can have a dramatic impact on liquid crystal display (LCD) because the TTFTs are superior to conventional opaque amorphous Si TFTs in transporting light to the final LCD panel fabricated on glass substrates. The TTFTs that have been recently studied by several groups for display applications usually consist of inorganic channel oxides such as ZnO,[1-3] which contains a large number of light-sensitive deep-level defects.[4-6] Recently, a TTFT with an organic channel, thus constituting an organic-inorganic hybrid system, has also been reported by Ohta *et al.*[7] They employed an inorganic gate dielectric film for their TTFT using pulsed laser deposition (PLD) technique, which is an unusual way for large-area deposition. To make use of the full advantages of organic TFTs (OTFTs), namely, large area coverage, mechanical flexibility, and low-cost processing, it is necessary to employ polymer gate dielectric materials rather using solution processes. OTFTs with polymer gate dielectrics have been reported and some of them exhibited good electronic performance comparable to those with inorganic gate dielectric materials,[8-11] showing a field effect mobility over 0.1 cm^2/V s and an on/off ratio over 10^5 although researchers used opaque noble-metal source-drain (S/D) contacts for the polymer gate devices.[9-11]

In the present study, we report on the fabrication of transparent pentacene-based TFTs using poly-4-vinylphenol (PVP) gate dielectrics and thermally evaporated semitransparent NiO$_x$ S/D electrodes. Our TTFT have exhibited a field effect mobility of 0.07 cm^2/V s and an on/off current ratio of 10^5 which are quite decent values for TFTs with polymer gate dielectrics.

Experimental

Prior to the spin-coating of PVP film on indium-tin oxide (ITO) glass, the glass was cleaned with acetone, ethanol, and deionized water in that order. The thickness and sheet resistance of the ITO films were 79 nm and 30 Ω/□. PVP films were then prepared from solution of PVP and poly (melamine-*co*-formaldehyde), as a cross-linking agent, in propylene glycol monomethyl ether acetate (PGMEA), by spin coating and cross-linking at 175°C in a vacuum oven. Final thickness of the PVP films was ~650 nm as measured by a surface profiler (Alpha-Step IQ). Pentacene channels and source/drain NiO$_x$ films were then sequentially patterned on the PVP layer through shadow masks at a substrate temperature of 20°C (room temperature, RT) by thermal evaporation in a vacuum chamber that had been in a base pressure of 1×10^{-6} Torr. The thermal

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deposition rate was fixed to 1 Å/s for the pentacene (Aldrich Chem. Co., ~99% purity) and 30 Å/s for the evaporation of NiO (99.97% purity). The thicknesses of pentacene and NiO$_x$ films were 50 and 100 nm, respectively, as monitored by a quartz crystal oscillator and confirmed by ellipsometry. Figure 1a and b show the schematic cross-sectional and photographic plan views of our pentacene TTFTs, respectively. The nominal channel length and width were 90 and 500 μm, respectively. Figure 1b shows printed letters placed beneath the ITO glass on which our TTFTs have been constructed. Our NiO$_x$ S/D appears dark but is transparent enough to show the letters clear.

All current-voltage (I-V) measurements for our TTFTs were performed with a semiconductor parameter analyzer (Agilent 4155C) and the electrical properties of the PVP films were also evaluated from capacitance-frequency (C-f) and current density-electric field (J-E) measurements with Au/spin-coated PVP/p$^+$-Si structure. The C-f measurements were made with an impedance analyzer (HP 4192A) in the dark at RT. The sheet resistance of NiO$_x$ films was determined by Hall measurements. Transmittance or transparency of our TTFT was measured with a Varian Cary 5G spectrophotometer.

Results and Discussion

Figure 2 exhibits three transmittance spectra obtained from PVP/ITO/glass, pentacene (50 nm)/PVP/ITO/glass, and NiO$_x$ (100 nm)/pentacene (50 nm)/PVP/ITO/glass stacks. As expected from the photograph of Fig. 1b, NiO$_x$ source-drain (S/D) electrode regions showed a low transmittance of about 40% in visible region but pentacene channel (dotted squares) and PVP background regions did quite a high transmittance over 70% in the visible region. An absorption dip (indicated by arrows) observed near 670 nm in the spectra corresponds to the optical absorption peak at 1.82 eV due to the formation of Frenkel excitons and other spectral features are related to unoccupied energy level of pentacene.[12,13] The optical bandgap of our NiO$_x$ was ~4.1 eV (according to the square of absorption coefficient times angular frequency ($\alpha^2\omega^2$) *vs.* photon energy (eV) plot obtained from direct absorption NiO$_x$ films on clean corning glass substrates) although here we do not show the transmittance spectra of NiO$_x$ alone. According to Hall effect measurements, our NiO$_x$ electrode presented n-type conduction with a sheet resistance of ~60 Ω/□ while usual transparent stoichiometric NiO is p-type with a bandgap of 3.8 eV[14-16] showing a high transmittance of about 70%.[17] (We checked the conduction type many times with Hall measurement using a standard n- and p-Si samples.) It is highly probable that our semitransparent NiO$_x$ is off-stoichiometric and is in an oxygen-deficient Ni-rich state as well.

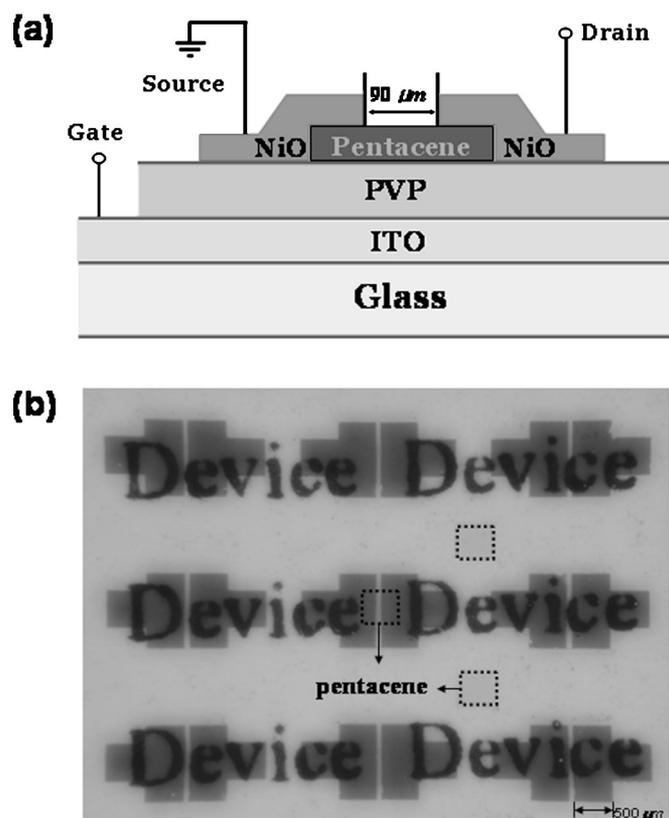Figure 3 displays C-f and J-E characteristics (inset) measured

Figure 1. The structure of our pentacene TTFT (a) the schematic cross-sectional view and (b) the photograph plan view (channel length, L = 90 μm, width, W = 500 μm). Also, see the letters placed beneath the devices. Dotted squares are the markers for the region of 50 nm thick pentacene/PVP/ITO glass.

Figure 3. Plots of C-f and J-E characteristics (inset) measured from the Au/PVP/ heavily doped p$^+$-Si structure.

from Au/PVP/p$^+$-Si structures. The capacitance and dielectric strength of 650 nm thick PVP film were measured to be about 5.3 nF/cm^2 (which has not been varied with frequency) and over 1.5 MV/cm, respectively. To determine an optimum cross-linking condition of PVP film, we prepared three Au/PVP/p$^+$-Si structures using different curing temperatures (155, 175, 200°C) for the spin-
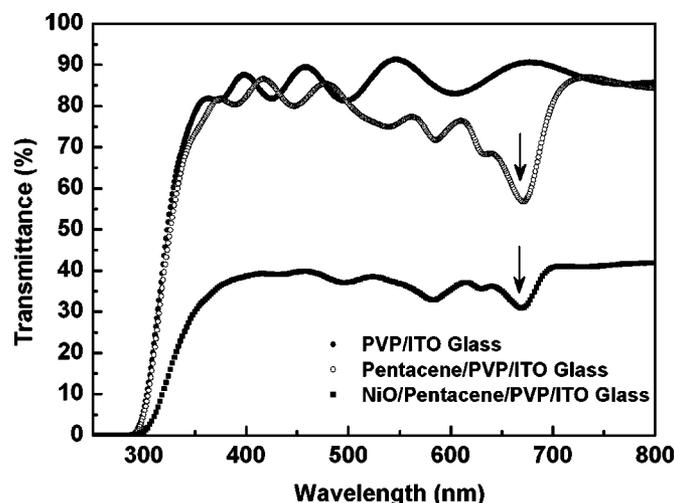

Figure 2. Transmittance spectra taken from PVP films on ITO glass, 50 nm thick pentacene films on the PVP/ITO glass, and 100 nm thick NiO$_x$ films on pentacene/PVP/ITO glass stacks.
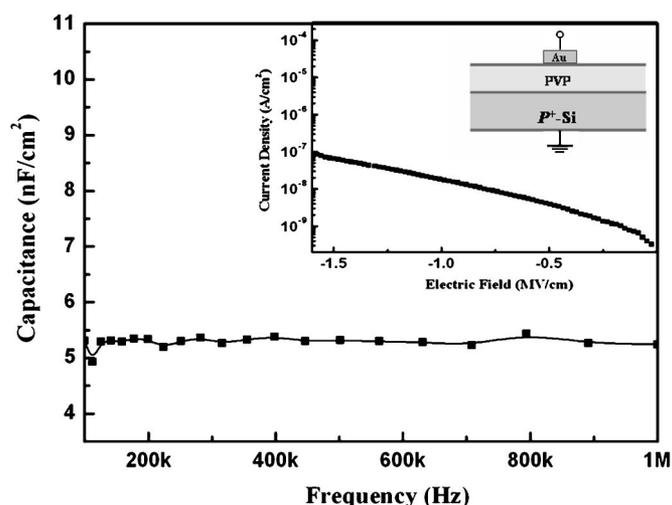
coated PVP layer. The capacitance and dielectric strength of the PVP film cured at 175°C appear the most optimum. According to the capacitance data, the dielectric constant k of the cross-linked PVP film was determined to be ~3.9, which is similar to value reported by Halik *et al.*[8-10] The gate dielectric leakage for the cross-linked PVP film was less than 100 nA/cm^2 at a bias of 100 V and is close to that for AlO$_x$ film deposited by radio-frequency magnetron sputtering at RT.[18] Based on the above results, our polymer gate dielectric films could be quite promising in charging holes at the pentacene/PVP interface without undergoing any electric breakdown.

Figure 4a shows the drain current–voltage (I$_D$-V$_D$) curves obtained from our pentacene-based TTFT. Maximum saturation current of ~1.2 μA was achieved under a gate bias (V$_G$) of −40 V while gate leakage current (I$_G$) was less than −10 pA. This saturation current value is comparable to that of a previously reported pentacene TFT for which we used a 450 nm thick AlO$_x$ gate dielectric and Au electrodes instead of cross-linked PVP gate and NiO$_x$ electrode.[18] Even though our NiO$_x$ is n-type, it is inferred that our semitransparent Ni-rich NiO$_x$ electrode has a larger work function than that of Au (~5 eV),[19] being better matched with the pentacene channel in terms of source-to-channel hole injection. It is because our metallic NiO$_x$ possesses excessive Ni of which the work function is known to be ~5.15 eV.[19] For comparison, we also show in Fig. 4a the I$_D$-V$_D$ results from a reference TFT that has an identical design but Au metal S/D electrodes (as we actually fabricated it for reference). The reference device demonstrated that Au/pentacene interface were relatively inferior to NiO$_x$/pentacene in respect of hole current injection. This comparison now evidences that the NiO$_x$ as a source has improved the hole injection efficiency at the source/channel interface. In addition to the enhancement of the hole injection efficiency, a smooth pentacene-channel/PVP-dielectric interface could be another advantage for the hole transport. The usual rms surface roughness of our spin-coated PVP film is less than 1 nm as measured with atomic force microscopy (AFM) while that of AlO$_x$ gate dielectric film has been reported to be more than 4 nm.[18] Although the charging capacitance of our 650 nm thick PVP films (5.3 nF/cm^2) appeared much lower than that of 450 nm thick AlO$_x$ films (10 nF/cm^2), the smooth pentacene/PVP interface seemed to overcome the drawback of our PVP dielectric.

The field effect mobility and threshold voltage of our TTFT with NiO$_x$ electrodes were achieved from the $\sqrt{-I_D} - V_G$ curve of Fig. 4b to be 0.07 cm^2/V s and −5 V, respectively. The on/off current ratio was about 10^5 under a drain saturation condition [V$_D$ = −30 V, see
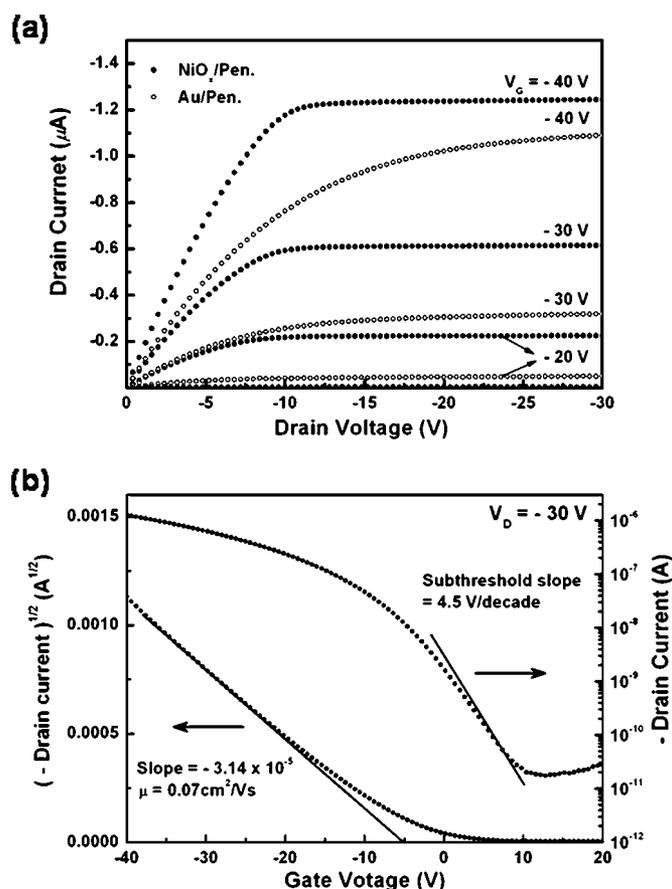
(a)

(b)

Figure 4. (a) Drain current-voltage (I_D-V_D) curves (b) $\sqrt{-I_D}$ − V_G plot and $Log_{10}(-I_D)$ − V_G plot obtained at $V_D = -30$ V. The I_D-V_D curves with open symbols show the characteristics obtained from a reference TFT with Au S/D electrodes.

the $Log_{10}(-I_D)$ − V_G]. Performance parameters of our TTFT, such as mobility, threshold voltage, and on/off ratio, were similar to those of our previous pentacene TFT with a 450 nm thick AlO_x gate dielectric and Au electrodes[18] and were also comparable to those of other pentacene-TFTs with polymer gate dielectric and noble metal contacts.[10,11]

Conclusion

We fabricated pentacene-based TTFTs that consist of NiO_x spin-coated PVP, and ITO for the source-drain (S/D) electrode, gate di-

electric, and gate electrode, respectively. The dielectric constant *k* and strength of 650 nm thick PVP film were measured to be about 3.9 and more than 1.5 MV/cm, respectively. The NiO_x S/D electrodes were deposited on a 50 nm thick pentacene channel by thermal evaporation of NiO powder and show effective transmittance of ~40% in the visible range along with good sheet resistance of ~60 Ω/□. Our pentacene-based TTFT exhibited a field effect mobility as large as 0.07 cm^2/V s in the dark, and an on/off current ratio of 10^5, and the values were comparable to those of previously reported pentacene transistors with polymer gate dielectric and opaque noble-metal contacts. It is concluded that spin-coated PVP and thermal evaporated NiO_x are promising gate dielectric and S/D electrode materials, respectively, to realize pentacene-based transparent TFTs.

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