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A Robust Ionic Liquid-Polymer Gate Insulator for High-Performance Flexible Thin Film Transistors

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Herein, we propose an ionic liquid-polymer dielectric layer for the flexible electronics reinforced by a chemical interaction between the polymer matrix (PVP) and the ionic liquid. Due to the robust structures from cross-linked PVP matrix and hydrogen bonding between ionic liquid and PVP, the ionic liquid-PVP (IL-PVP) exhibited a good mechanical strength up to 1,000 times bending and a stable thermal behaviour up to 300 °C. Furthermore, the IL-PVP dielectric layer showed a high-capacitance value (~2 μF/cm^2) and was operated well as a gate insulator for flexible ZnO thin film transistors with a linear field-effect mobility of ~ 3.3 cm^2 V^{-1} s^{-1} at 3 V gate bias.

Flexible thin film transistors (TFTs) have received much attention as a basic component of next generation displays such as smart windows, flexible mobile displays, and e-paper due to its roll-able and foldable characteristics.[1, 2] In the development of flexible TFTs, solution processes are attractive methods for large-area and low cost fabrication. However, conventional solution-processed flexible TFTs have some obstacles, such as a high operating voltage, a high temperature annealing process and a decrease in charge carrier mobility compared to intrinsic values, which reduce the potential of solution-processed flexible TFTs.[3, 4] Therefore, many researchers have tried to improve these limitations by developing high capacitance dielectric layers[5-7] or low-temperature processed active layers[8, 9] for solution-processed flexible TFTs with a low operating voltage and high field-effect mobility. Recently, there have been several studies reporting that the field-effect mobility of TFTs is dramatically enhanced by improvement of the capacitance value of the gate insulator from experimental[5, 10, 11] and theoretical analyses.[12] In addition, it was reported that the high-performance gate insulator layer achieves successful operation of TFTs at a low voltage range. Therefore, developing gate insulators with a high capacitance value is the most efficient approach for high-performance TFTs with a low operating voltage.

As a solution-processed flexible gate insulator with high capacitance, ion-gels, which consist of ionic liquids in a flexible polymer matrix, have exhibited a large capacitance.[13-16] An ion-gel is a swollen polymer-gel with an ionic liquid[17] which is a molten salt with cations and anions of various combinations.[18, 19] Due to the sufficient amount of ionic liquids in the gel, the ion-gel has a high capacitance value. The gel matrix with the polymer and ionic liquids has flexible properties that can be adapted to flexible TFTs. The polymer matrix of ion-gels, usually ABA type tri-block copolymers, consists of ionic liquid phobic A blocks and ionic liquid philic B blocks.[13, 19] Under a sufficient amount of ionic liquid, the ionic liquid phobic A blocks are self-assembled and produce the polymer matrix by physical interactions. Otherwise, the ionic liquid philic B blocks interact with the ionic liquids in the matrix.[20, 21] Because the matrixes are based on these physical interactions, they are easily pulled apart when encountering high temperature or strain and have an intrinsically weak thermal stability and low mechanical strength.[22-24] Despite the good performance of ion-gel based flexible gate insulators, the fragile mechanical and thermal properties hinder the practical applications of flexible TFTs in various devices.

Herein, we introduce a solution-processed flexible ionic liquid - polymer dielectric layer consisting of an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)im-ide (EMIM-TFSI), and a thermally cross-linkable polymer, poly(4-vinylphenol) (PVP). In the matrix of the cross-linked polymer, the ionic liquid was physically well-dispersed and chemically interacted with functional groups in the polymer matrix, which enhanced the mechanical strength and thermal stability of the ionic liquid - polymer (IL-PVP) dielectric layer. This dielectric layer exhibited high capacitance value above ~2 μF/cm^2 at 20 Hz. In addition, it had a mechanically robust characteristic up to 1,000 times bending tests and a thermally stable characteristic up to 300 °C. Using the IL-PVP dielectric as a gate insulator layer, we fabricated successfully high-performance solution-processed zinc oxide (ZnO) flexible TFTs at a low operating voltage of 3 V. Even under a bending state with a 5

mm radius, the flexible ZnO/IL-PVP TFTs exhibited stable operation without degradation in the TFT performance.
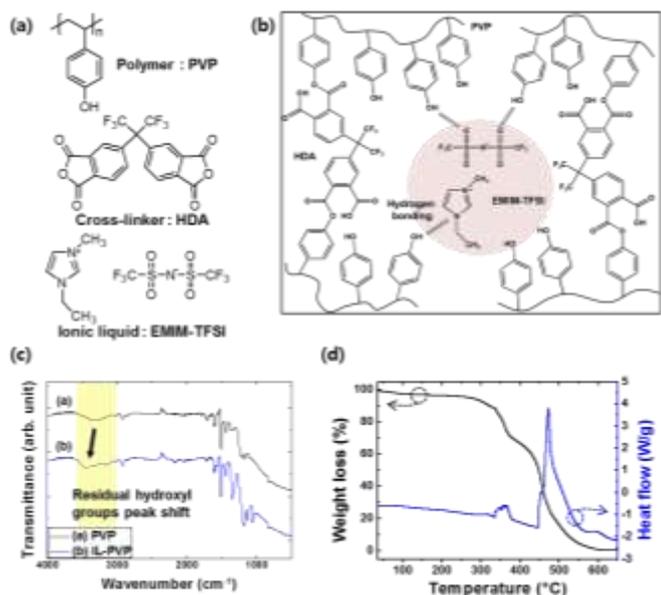

Fig. 1 Chemical structures of materials (a), chemical structure of IL-PVP (b), ATR-FT IR results of PVP and IL-PVP dielectric layer (c) and TG-DSC analysis results of IL-PVP dielectric layer (scan rate : 5 °C min⁻¹, air : 100 mL min⁻¹) (d)

As a robust flexible matrix, we introduced the cross-linkable polymer which consisted of PVP as the polymer matrix and 4,4'-(Hexafluoroisopropylidene diphthalic anhydride) (HDA)[25] as cross-linker. The PVP solution was prepared by dissolving the PVP and HDA in propylene glycol monomethyl ether acetate (PGMEA) at 15 wt%. To prepare the ionic liquid mixed PVP (IL-PVP) solution, EMIM-TFSI was mixed with the PVP solution (1:1 weight ratio with PVP:EMIM-TFSI). As a gate insulator, the IL-PVP solution was spin-coated on substrates and then kept in a vacuum oven at 70 °C for 12 hr to evaporate the residual solvents. After that, the cross-linking of PVP and HDA, and the chemical interaction between the PVP and ionic liquid were achieved with an annealing process at 110 °C for 1 hr.

Figure 1a and b shows the chemical structure of the polymer, cross-linker, ionic liquid and the chemical structure of the IL-PVP dielectric layer. After the chemical cross-linking between the PVP and HDA, the EMIM-TFSI chemically bound with the PVP through the hydrogen bonding interaction with the residual hydroxyl groups in the cross-linked PVP matrix. To characterize the interaction between the polymer and ionic liquids, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT IR) analysis was performed. In Figure 1c, the ATR-FT IR spectra for the cross-linked PVP and IL-PVP layers are shown in the range of 4000 – 500 cm⁻¹. The absorption peak appearing at 720 cm⁻¹ in the PVP is assigned to the CH_2 long chain of the polymer. The band at 3400 cm⁻¹ is attributed to the hydrogen bonded –OH groups of the residual hydroxyl groups of the PVP after cross-linking.[26] According to the mixing of EMIM-TFSI with PVP, IL-PVP layer had the characteristic absorption vibrations of the EMIM-TFSI (see table S1). After the chemical interaction of the cross-linked PVP and EMIM-TFSI, it can be seen that the hydrogen bonded residual hydroxyl band near 3400 cm⁻¹ shifted to higher wave numbers.[27, 28] This result indicates that the residual hydroxyl groups interacted with the cations and anions of the ionic liquids through hydrogen bonding. The residual hydroxyl groups in the cross-linked PVP act

as hydrogen donors to the ionic liquids, and the nitrogen atoms and oxygen atoms in the ionic liquids act as hydrogen acceptors. Therefore, the hydrogen bonded interactions between PVP and EMIM-TFSI contributed by maintaining the polymer film state with robust mechanical and thermal stability. Figure 1d shows the thermal behaviors of the cross-linked IL-PVP after the annealing process which were determined by thermo-gravimetric and differential scanning calorimetry (TG-DSC). As shown in Figure 1d, the IL-PVP layer maintained stable thermal behaviors until 300 °C, and a large amount of weight loss occurred at ~350 °C due to the thermal decomposition of the organic materials. According to the heat flow, exothermic peaks appeared at 350 °C and 450 °C which correspond to the thermal decomposition of the ionic liquids and PVP.
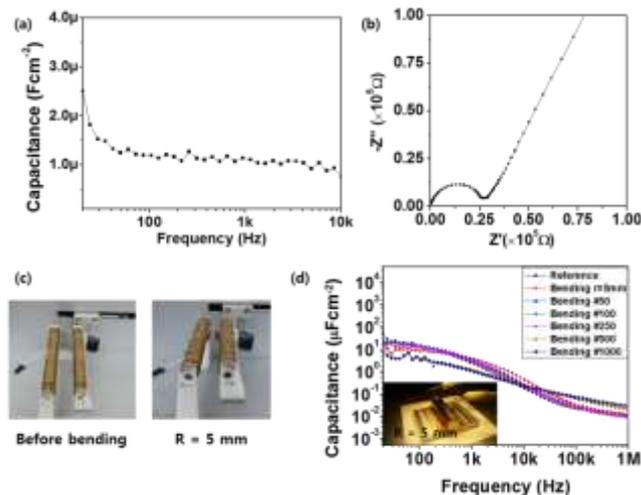
Fig. 2 Capacitance vs. frequency result with log-log plot (P⁺⁺-Si/IL-PVP 1.7 μm /Al, frequency range : 20 Hz~10 kHz) (a), Nyquist plot (SUS/IL-PVP 300 μm /SUS, frequency range : 1 Hz~1 MHz) (b) of the IL-PVP dielectric layer with metal-insulator-metal structures, optical images of bending test (bending radius with 5 mm) (c) and capacitance values of bending tested samples with MIM structures on PAR films (Ag 200 nm / IL-PVP 700 nm / Ag 200 nm) (d).

The electrical characteristics of the IL-PVP dielectric layer were investigated by capacitance and impedance analysis. Figure 2a shows the capacitance versus frequency of the IL-PVP dielectric layer in metal-insulator-metal (MIM) (P⁺⁺-Si/IL-PVP/Al) capacitors which included an ~1.8 μm thick IL-PVP layer. Due to the high ion mobility of the ionic liquids in the IL-PVP layer, it showed a high capacitance above ~2 μF/cm² at 20 Hz. Despite the frequency dependence of the ions in the IL-PVP dielectric layer which is induced by the limitation of the polarization response time, it maintains high values, ~1 μF/cm², above 1 kHz. To determine the ion conductivity, the AC impedance characteristics were analyzed with a coin cell that was composed of two SUS electrodes and the IL-PVP dielectric layer (300 μm thick). The amplitude of the AC voltage was 5 mV, and the applied AC voltage was from 1 Hz to 1 MHz. From the Nyquist plot in Figure 2b, the calculated value of the ion conductivity, which is affected by the charge transfer, was 0.636 μS/cm at room temperature (see Figure S1). For the flexibility test of the IL-PVP dielectric layer, the MIM structure (200 nm Ag / 700 nm IL-PVP / 200 nm Ag), which is fabricated on a polyarylate film, was tested with a bending machine (Figure 2c). In Figure 2d, the capacitance values of the IL-PVP dielectric layer were the same for the un-bended and bended states with a 5 mm bending radius. The capacitance values were maintained during the bending test carried out 500 times with a 5 mm bending radius. Even after conducting the bending test 1,000 times, it had similar capacitance values within the

origin values and maintained good dielectric properties. This result shows that the IL-PVP dielectric layer has both high mechanical strength and flexibility due to the robust cross-linked polymer matrix and chemical interactions between the polymer matrix and ionic liquids. The elastic modulus of IL-PVP dielectric layer was 2.128 GPa at 100~200 nm displacement range of nano-indentation system (see Figure S2).
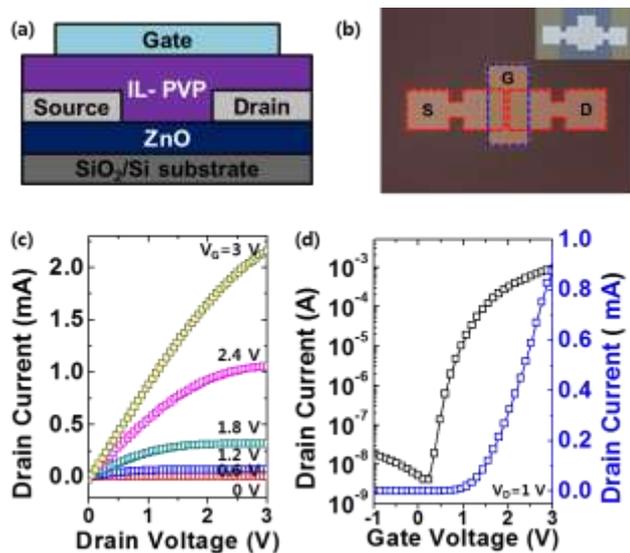

Fig. 3 Schematic diagram in cross-section (a), optical image (b), output (c) and transfer (d) characteristics of ZnO/IL-PVP TFTs. (V_{DS} = 1 V, V_{GS} = 3 V)

To characterize the IL-PVP dielectric layer as a gate insulator, a solution-processed ZnO TFT was fabricated. Figure 3a shows the device structure with a top-gate and bottom-contact ZnO TFT (SiO$_2$ substrate / 5 nm ZnO / 100 nm Al / 1.8 μm IL-PVP / 100 nm Ag). The ZnO layer was fabricated with a solution process and annealed at 300 °C for one hour as previously reported by our group.[29] Because IL-PVP was spin coated on the whole surface including the electrodes to obtain the contact area, the coated layer on the source and drain was cleaned off with acetone or PGMEA and cotton swab before the annealing process shown by the inserted image in Figure 3b. The RMS roughness of the ZnO layer on the SiO$_2$ substrate and IL-PVP layer on the ZnO layer was characterized by AFM. It was measured at 0.198 nm and 0.232 nm each which showed a very smooth surface roughness (see Figure S3). The output and transfer characteristics of the top-gate ZnO TFT that included the IL-PVP gate insulator layer are shown in Figure 3c and d. Because of the high capacitance value of the IL-PVP gate insulator layer, the TFT stably operated under a 3 V gate bias. The on/off current ratio of the ZnO TFT was ~10^5 at a 1 V drain voltage (V_{DS}) and 3 V gate voltage (V_{GS}). The calculated field-effect mobility (μ) of the linear region was obtained according to the following eqn. (1):

$$I_D = \mu C_i \frac{W}{L}((V_{GS} - V_{th})V_{DS} - \frac{V^2_{DS}}{2})$$

, where Ci is the capacitance of the dielectric layer, and W/L is the channel width and length. In the case they were 1000 μm and 50 μm. As a result, the charge carrier mobility was calculated as high as 8.45 cm^2 V^{-1} s^{-1} at V_{DS} = 1 V and V_{GS} = 3 V. In addition, it showed negligible hysteresis in the output and transfer characteristics under ambient conditions (see Figure S4). Therefore, we think that the high field-effect mobility of the TFT with high capacitance IL-PVP gate insulator can be achieved due to the stable IL-PVP dielectric layer without interface.[30]
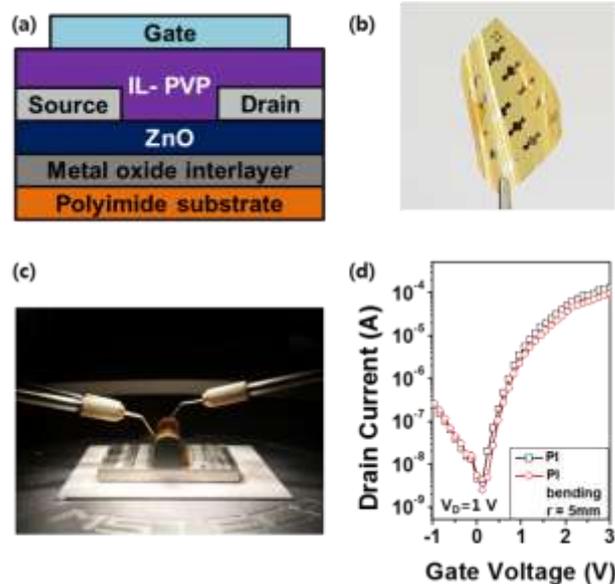

Fig. 4 Schematic diagram in cross-section (a), optical image (b), bending test (c) and transfer (d) characteristics of ZnO/IL-PVP flexible TFTs on PI films. (V_{DS} = 1 V, V_{GS} = 3 V)

To show the potential of the IL-PVP dielectric layer in flexible TFTs, a flexible ZnO TFT was fabricated on a polyimide film shown in Figure 4a. The ZnO has relatively good flexibility compared to other metal oxide semiconductors, and the thickness of the spin-coated ZnO layer was only 5 nm which is advantageous in fabricating flexible TFTs.[31, 32] Additionally, the solution-processed ZnO semiconductor has good electrical performance compared with solution-processed organic semiconductors. However, the metal oxide semiconductors on the organic gate insulator layer have suffered to gain stability and high-performance due to the interface traps between the inorganic and organic materials.[33, 34] Therefore, we used an aluminum oxide interlayer on polyimide films to improve the interface condition for a high-performance ZnO semiconductor layer. The ZnO semiconductor layer was spin-coated on a flexible substrate and annealed at 300 °C for 40 min. After the annealing process, a flexible ZnO TFT that included an IL-PVP gate insulator layer was fabricated with the above mentioned same procedure (see Figure 4b). The output and transfer characteristics of the flexible ZnO TFT with the IL-PVP gate insulator layer were characterized and shown in Figure 4c and d in the un-bending and tensile bending states with a 5 mm bending radius, respectively. The flexible ZnO TFT with the IL-PVP gate insulator layer, irrespective of the bending states, was successfully operated at 1 V_{DS} and 3 V_{GS} operation. The flexible ZnO TFT with the IL-PVP gate insulator layer showed a stable field-effect mobility around ~3.3 cm^2 V^{-1} s^{-1} at V_{DS} = 1 V and V_{GS} = 3 V. This result shows the potential of the IL-PVP dielectric layer as a flexible gate insulator for high-performance flexible TFTs because of the robust cross-linked polymer matrix and chemically interacted ionic liquid in a polymer matrix.

Conclusions

In conclusion, we have fabricated an ionic liquid - polymer gate insulator with PVP and EMIM-TFSI through chemical interactions. It shows good thermal and mechanical stability due to the stable cross-linked polymer matrix and the chemical interactions between the ionic liquid and polymer matrix through hydrogen bonding. The IL-PVP dielectric layer showed a high capacitance value and good

ion conductivity compared to conventional polyelectrolyte dielectric layers. Additionally, it maintained good mechanical strength under repeated bending tests up to 1,000 times with a 5 mm bending radius and showed a good thermal stability up to a temperature of 300 ºC which is expected to be useful in diverse electronic devices. The flexible ZnO TFTs with the IL-PVP dielectric layer exhibited stable performance with high field-effect mobility at a low operating voltage. This IL-PVP dielectric layer shows good potential as a flexible and high-performance dielectric layer, and we believe that this proposed IL-PVP dielectric layer will be useful in the next-generation flexible devices.

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Notes and references

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A Robust Ionic Liquid – Polymer Gate Insulator for High-Performance Flexible Thin Film Transistors

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The table of contents entry

A chemical structure of an ionic liquid-polymer dielectric layer for flexible thin film transistors. An ionic liquid–polymer (IL-PVP) dielectric layer with robust mechanical strength and flexibility was fabricated by a chemical interaction between the ionic liquid and polymer. Due to the cross-linked polymer matrix and hydrogen bonding interaction between the ionic liquid and polymer, the IL-PVP dielectric layer showed good mechanical characteristics up to 1,000 times bending tests and stable thermal behavior above 300 ^{o}C. In particular, the IL-PVP dielectric layer showed high capacitance value around 2 μF/cm^2 at 20 Hz and operated the flexible thin film transistors at 3 V with high performance under 5 mm bending radius.

TOC figure