High Performance IGTO Transistors with Stretchable Gate Dielectric Layer

Jae Kyeong Jeong , Jae Seok Hur and Jeong Oh Kim

Hanyang University, Seoul 04763, South Korea
Keywords: Metal Oxide, TFT, High mobility, Crystallization

ABSTRACT

Flexible/stretchable active-matrix electronics strongly demand the design of new concept material, which should have the good electrical properties and mechanical durability. In this paper, we will address the design of hybrid dielectric film, which consists of the polymer-based backbone and high permittivity additive. By virtue of smart cross linker selection, we are able to achieve the high performance oxide transistor with the hybrid polymer gate dielectric film. The fabricated transistors can withstand the 100 times mechanical bending stress under an extremely small curvature radius of 1mm. Simultaneously, they exhibit the high mobility of > 20 cm^2/Vs and $I_{ON/OFF}$ ratio of > 10^7, indicating that this approach can be one of the ways for the highly mechanically stable electronics.

1. INTRODUCTION

Stretchable electronics are a topic of intense research owing to the emerging application including wearable computer, biomedical patch and wall-scale displays.[1-2] In terms of the passive conductor component, the extensive research has been conducted where the geometry and nano-materials based approaches are available.[3] However, the gate dielectric and semiconductor ingredient with the good stretchability has been relatively overlooked despite their technical importance.

Inorganic dielectrics films such as high-κ ZrO_2, HfO_2, and Al_2O_3 as well as conventional SiO_2 have good insulating and dielectric properties. However, they usually require a high-temperature deposition and/or annealing process (≥ 300 °C), which makes them unsuitable for low-cost plastic substrates. In addition, their brittle nature causes uncontrolled cracking and peeling during mechanical stress (such as bending or stretching), leading to adverse defects or device failure. For these reasons, polymer-based organic dielectrics have been researched as gate insulators, particularly for flexible, organic thin-film transistors (TFTs). Most polymer-based organic dielectrics can be prepared at a lower temperature compared to inorganic dielectrics. Despite their superior intrinsic flexibility and low-temperature capability, the rather high leakage current and unstable electrical properties limit their use compared to inorganic counterparts. Recently, organic-inorganic hybrid dielectrics have been studied as feasible gate insulators for high-performance, flexible electronics. The flexibility of organic dielectrics and the high permittivity of inorganic dielectrics allow the resulting nanocomposite to have both a reasonable κ value and mechanical bendability.

In this study, the bottom gate, high performance metal oxide TFTs with a hybrid gate dielectrics were developed at an extremely low temperature (≤ 150 °C). First, solution-processed hybrid gate insulator film consisting of polymer poly(4-vinylphenol-co-methylmethacrylate) (PVP-co-PMMA) matrix and HfO_x was deposited by simply blending organic and inorganic materials, where PVP-co-PMMA and poly(melamine-co-formaldehyde) (PMF) was chosen as polymer backbone and cross-linking agent, respectively and high-κ HfO_x was blended to boost the permittivity of dielectric film.

2. EXPERIMENTAL PROCEDURE

The organic solution was prepared by dissolving PVP-co-PMMA (10 wt.%) and PMF (3.5 wt.%) in 5mL of PGMEA using PMF as the cross-linking agent. An inorganic precursor solution for HfO_x was synthesized using a sol-gel process with $HfCl_4$, HNO_3, and H_2O dissolved in PGMEA. The concentration of inorganic precursor was 0.2 M, where the molar ratio of $HfCl_4$: HNO_3: H_2O was 2: 7: 10. The two solutions were stirred for 6 h at 75 °C until each solute dissolved completely. Then, the organic and inorganic precursor solutions were blended at different volumetric ratios (organic solution/inorganic precursor solution, vol.%) of 100/0 (*H0*), 75/25 (*H25*), 50/50 (*H50*), and 25/75 (*H75*). The bare Si substrates were cleaned with acetone, isopropyl alcohol, and deionized water for 10 min each prior to deposition of the dielectrics. The prepared solutions were spin-cast onto the Si substrates at 1500 rpm for 30 s, followed by pre-baking on a hotplate for 10 min at 100 °C to remove residual solvent. For ultraviolet treatment, deep ultraviolet (DUV, 254 nm 90%, 194 nm 10%) photons were irradiated onto the prebaked films for 10 min. Then, the cast films were annealed at 150 °C for 3 h in an air ambient furnace. The bottom gate TFTs were fabricated by depositing an IGTO film as a channel layer onto the dielectric film/Si substrates using a dc sputtering system at room temperature. The fabrication detail can be found elsewhere.[4] The fabricated TFTs were subjected to thermal annealing at 150 °C for 2 h in an air ambient furnace.

3. Result and Discussions

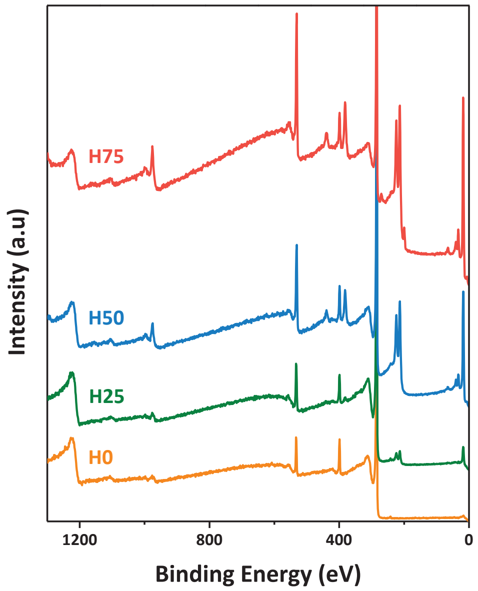

Fig. 1. XPS spectra of the polymer dielectric films.

Figure 1 shows the wide XPS survey scan of the PVP-co-PMMA-based dielectric films. The H0 sample contained carbon, oxygen and nitrogen peak coming from the PVP-co-PMMA and PMF substances. Hybrid film had additional Hf-ion-related peaks such as Hf 4d and Hf 4f, which increased with increasing fraction of hafnia solution. As the inorganic volumetric ration increased, the O-C or C-OH bond related peaks diminished whereas the O-M peak grew. It suggests that the loading of HfO_x reduces the residual hydroxyl groups (-OH) in the phenol group. The additional UV treatment caused the further reduction in C-O or C-OH bond whereas the portions of O=C and O-M were increased substantially compared to the H50 sample (without UV). The consistent trend was also observed in the FTIR spectra (Figure 2). It was anticipated that the UV treatment can reduce residual trap sites and improve the adhesion between organic and inorganic materials in the hybrid film.

Figure 3 shows the electric field (E)-dependent leakage current density (J_g) of the fabricated MIM capacitors. The J_g values for the MIM capacitors were plotted as a function of thickness-normalized E for a fair comparison. An excellent low J_g value of 1.1×10^{-8} A/cm^2 at the 1 MV/cm was observed for the MIM capacitor with the H0 dielectric film. However, it suffered from a rather low breakdown E-field (E_{br}) (~ 1.9 MV/cm) due to the softness of the chemical bonds and film density. Breakdown E-field values were improved to 2.9 – 3.2 MV/cm for the H25 and H50 hybrid dielectric films with intermediate loadings of HfO_x, while low leakage current densities were maintained ($1.4 – 5.4 \times 10^{-8}$ A/cm^2). Conversely, the H75 dielectric film with the largest loading of HfO_x suffered from an unacceptable high J_g value of 7.7×10^{-4} A/cm^2 at 1 MV/cm, which was attributed to its rough morphology and the presence of many pinholes, which can act as leakage paths. The inorganic HfO_x dielectric film had the similar high J_g value (~10^{-4} A/cm^2) because the low temperature annealing of 150 °C caused the considerable impurity residues such as H, N, Cl as well as the incomplete Hf-O lattice bonding in the hafnia film (data not shown). Notably, the UV-treated H50UV dielectric film exhibited the lowest J_g value (5.8×10^{-9} A/cm^2) and highest breakdown E-field (~ 3.8 MV/cm), suggesting its suitability as a flexible gate dielectric film.

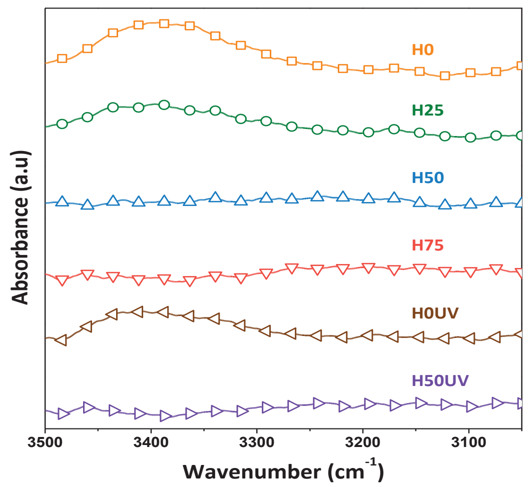

Fig. 2. FTIR spectra of the polymer dielectric films.

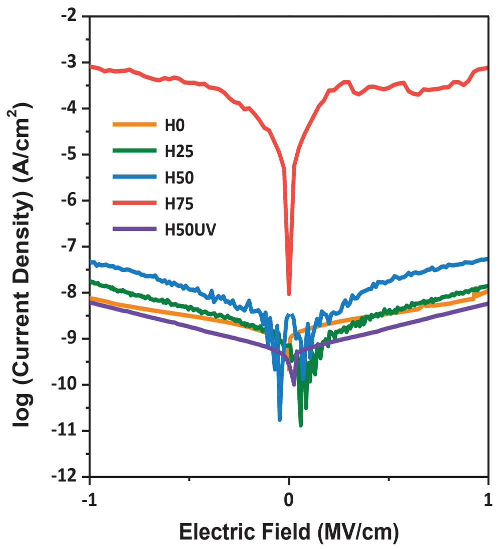

Fig. 3. Gate leakage current density (J_g) versus applied electric field (E) characteristics of the capacitors with polymer films with different inorganic volumetric ratios and UV treatment.

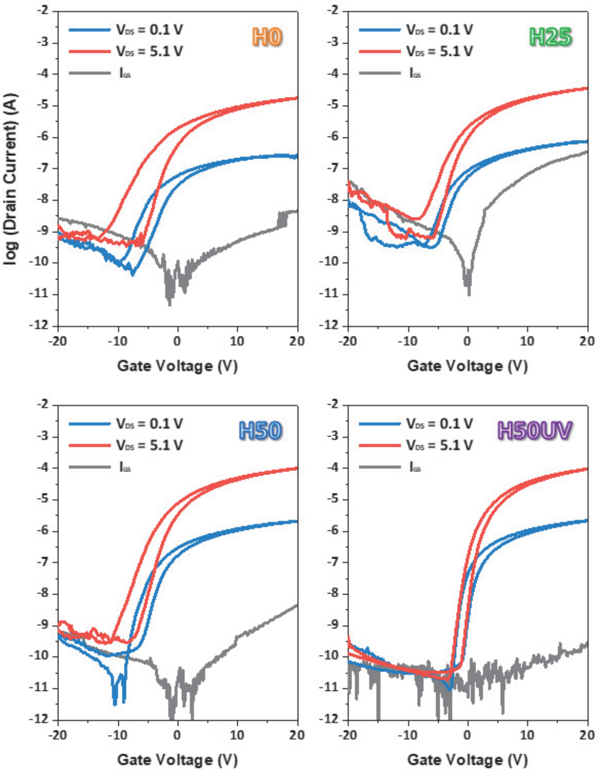

Fig. 4. Representative transfer characteristics of the IGTO TFTs with PVP-co-PMMA-based gate insulators.

Figure 4 shows the representative transfer characteristics of the IGTO TFTs with different gate insulators. The device with the control *H0* dielectric film had a reasonable μ_{FE} of 12.8 cm^2/(V s), presumably due to the efficient percolation pathway for electron carriers in the IGTO active layer. However, it suffered from a large *SS* of 2.8 V/decade, a negative V_{TH} of -6.5 V, and high I_{OFF} current of 1 × 10^{-9} A, which could be explained by the energetic ion bombardment effect. The in-diffusion of energetic In, Ga, and Sn cations into the polymer dielectric film during IGTO sputtering could induce image electron carriers in the channel layer, causing a negative V_{TH} and an unacceptably high I_{OFF} value. Simultaneously, the surface of the polymer dielectric film can be attacked by energetic particles, including high energy electron and charged ions, creating adverse defect states near the channel/polymer dielectric interface due to the low density of the polymer dielectric film. This is partially responsible for the large *SS* and high I_{OFF} values. The existence of residual hydroxyl groups as trap sites in the *H0* dielectric film was an additional origin for these deteriorated properties. The large clockwise hysteresis (~ 6 V) for the control device clearly indicates the existence of many temporal trapping sites due to the hydroxyl groups and bombardment-induced defects. Substantial improvements in μ_{FE}, *SS*, and V_{TH} were observed for the IGTO TFTs with *H50* and *H50UV* hybrid gate insulators. The device with a *H50* hybrid gate insulator exhibited a high μ_{FE} of 19.2 cm^2/(V s), an *SS* of 2.2 V/decade, and a V_{TH} of -5.9 V. It can be inferred that the hybrid dielectric film was less affected by the energetic ion bombardment or ion migration toward the dielectric film because the Hf-O (with strong ionicity) in the polymer matrix enhanced the mechanical hardness of the resulting hybrid dielectric film. The positive effect can be reflected in the high carrier mobility and low defect density of the device with a *H50* hybrid gate insulator. The switching capability, which is one of the critical parameters for the TFTs, can be further enhanced by using the UV-treated *H50UV* dielectric film: IGTO TFTs with *H50UV* hybrid gate insulators had a high $I_{ON/OFF}$ ratio of ~ 10^7 as a result of reduction in I_{OFF} value (Figure 4). In addition, the highest μ_{FE} of 25.9 cm^2/(V s), lowest *SS* of 0.4 V/decade, a V_{TH} of -0.2 V, and $I_{ON/OFF}$ ratio > 10^7 for this device correspond to the state-of-the-art characteristics for any sort of metal oxide transistor with a polymer and hybrid gate insulator (T_{max} ≤ 150 °C).

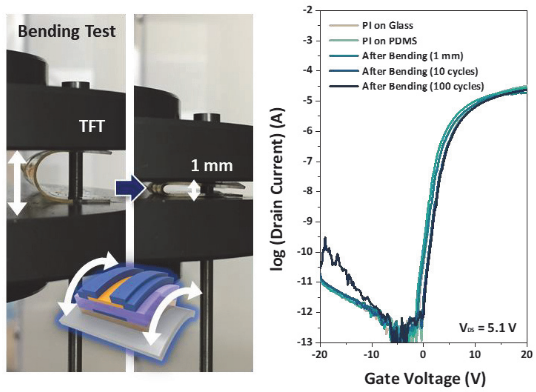

Fig. 5. Images of the transferred devices on PDMS film and their bending test procedure (left panel). Evaluation of transfer characteristics for the IGTO TFTs with *H50UV* gate insulator on PI/PDMS substrate under cyclic bending tests (right panel).

Finally, the electrical stability of the IGTO TFTs with *H50UV* hybrid gate insulator under a bending stress was evaluated by fabricating on plastic PI/PDMS substrate using a transfer method. Generally, it is known that metal oxide TFTs with a ceramic gate insulator such as Al_2O_3 film on plastic substrates lose their switching functionality under the bending stress less than the bending radius of 3 mm. The variations in the transfer characteristics of the IGTO TFTs with *H50UV* hybrid gate insulator on the PI/PDMS film were shown in Figure 5. The bending test of IGTO TFTs on PI/PDMS film was performed at the bending radius of 1 mm. The excellent switching capability of the IGTO TFTs was maintained even after 100 cycles of the bending tests at an extremely small bending radius of 1 mm, which was comparable to that of the as-fabricated IGTO TFTs on PI/glass substrate (Figure 5). This intriguing result can be explained by the inherent bendability and stretchability of the hybrid polymer dielectric film. The superior mechanical stability of flexible IGTO TFTs demonstrates the feasibility of the polymer-based hybrid gate dielectric layer and the IGTO system for high performance bendable electronics.

4. CONCULUSION

We examined the effects of hafnium oxide loading and UV treatment on the electrical performance of PVP-co-PMMA-based hybrid gate insulators for low-temperature-processed metal oxide TFTs. Insulating properties of the hybrid gate dielectric films were drastically improved due to the reduced residual hydroxyl groups resulting from incorporation of hafnium oxide (with its high ionicity) along with UV treatment. We found that the UV-treated hybrid dielectric film had a smoother surface roughness and better interface matching with an IGTO channel layer. Interestingly, the UV-assisted hybrid dielectric films were able to withstand energetic ionic bombardment during sputtering deposition of the IGTO channel layer, and this was attributed to its denser film nature. As a consequence, the bottom gate IGTO TFTs with a UV-treated hybrid gate insulator exhibited a high μ_{FE} of 25.9 $cm^2/(V\ s)$, a V_{TH} of -0.2 V, a low *SS* of 0.4 V/decade, and an $I_{ON/OFF}$ ratio > 10^7 even at a low annealing temperature of 150 °C. Furthermore, the IGTO TFTs with a UV-treated hybrid gate insulator on PI/PMDS film was shown to withstand the 100 times cyclic bending test under the curvature radius of 1 mm. Therefore, we concluded that UV-treated hybrid dielectrics are promising candidates as gate insulators for low-temperature-processed flexible and stretchable electronics. Their integration with a high mobility IGTO channel system enabled to successfully achieve state-of-the-art characteristics for a metal oxide TFT with a polymer-based dielectric film.

REFERENCES

[1] D.-H. Kim *et al*., “Materials for multifunctional balloon catheters with capabilities in cardiac electrophysiological mapping and ablation therapy”, *Nat. Mater.* **10**, 316 (2011).

[2] T. Sekitani *et al*., “Stretchable active-matrix organic light-emitting diode display using printable elastic conductors”, *Nat. Mater.* **8**, 494 (2009).

[3] W. Dang *et al*., “Printable stretchable interconnects”, *Flex. Print. Electron*. **2**, 013003 (2017).

[4] J. S. Hur *et al*., “Stretchable polymer gate dielectric by ultraviolet-assisted hafnium oxide doping at low temperature for high-performance indium gallium tin oxide transistors,” *ACS Appl. Mater. Interfaces*, **11**, 21675 (2019).