Nitrocellulose-based collodion gate insulator for amorphous indium zinc gallium oxide thin-film transistors

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ABSTRACT
A novel organic material named ‘collodion’ was suggested as a gate insulator for amorphous indium gallium zinc oxide thin-film transistors (a-IGZO TFTs). To find the optimized condition of the collodion gate insulator (CGI), the following three parameters of collodion solution were controlled: (1) the concentration of collodion solution; (2) the number of stacked layers; and (3) the spin-coating speed. The single-layered diluted CGI (collodion:ethanol = 1:1) that was fabricated with a 3 krpm spin-coating speed exhibited an acceptable dielectric strength ($J < 10^{-10} \text{A/cm}^2$ in the range of 1.1 MV/cm) and a high-dielectric constant ($\sim 6.57$) for the gate insulator layer. As a result, a-IGZO TFTs with CGI showed high-field effect mobility ($\sim 17.11 \text{cm}^2/\text{V}s$).

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1. Introduction
Researches have been conducted of late on several solution-processed dielectric materials, including organic, inorganic, and hybrid organic-inorganic materials, to serve as a gate insulator layer for field effect transistors [1–5]. In particular, solution-processed organic materials have been extensively investigated due to their low-temperature process and high flexibility, which can enable their wide use for applications such as flexible, stretchable, and bendable electronic devices [6–10]. Furthermore, they have a lower manufacturing cost than vacuum-processed gate insulators [11,12]. They have a critical limitation which is more vulnerable to ambient gas molecules such as oxygen, hydrogen, and water compared to inorganic gate insulators.

In our previous research, a novel organic material called ‘collodion’ was investigated for its possible use as the passivation layer of amorphous indium gallium zinc oxide thin-film transistors (a-IGZO TFTs) [13]. Collodion is composed of nitrocellulose (C$_6$H$_7$(NO$_2$)$_3$O$_5$), which is generally used for different purposes, such as for artificial billiard balls, manicure, flash paper, and the membrane substrate of protein chips. It has not been applied to electronic devices, however, except for the passivation layer of a-IGZO TFTs.

In this research, nitrocellulose-based collodion was applied to a gate insulator of a-IGZO TFTs, and the optimized condition of the collodion gate insulator (CGI) was found by controlling the following three parameters of collodion solution: (1) the concentration of collodion solution; (2) the number of stacked layers; and (3) the spin-coating speed. CGI-based a-IGZO TFTs, which have high field effect mobility, were also fabricated.

2. Experiments
Fabrication process of a-IGZO TFTs with CGI
Top-gate coplanar a-IGZO TFTs were fabricated in the following order. First, an a-IGZO channel layer (40 nm) was deposited on a cleaned heavily-boron-doped silicon ($p^+$-Si) substrate using radio frequency (RF) magnetron sputtering at room temperature. The composition ratio of the a-IGZO target was In$_2$O$_3$:Ga$_2$O$_3$:ZnO = 1:1:1.

The RF power, operation pressure, and deposition time were fixed to 150 W, $5.0 \times 10^{-3}$ Torr, and 5 min, respectively. Second, aluminum (Al) source/drain electrodes (200 nm) were deposited using thermal evaporation via shadow mask (1000/1000 μm). The collodion solution was dissolved in two solvents (ethanol and diethyl ether), and its viscosity was controlled to fabricate diluted collodion solutions by adjusting the ratio of ethanol. The volumetric ratios of the diluted collodion solution were 1:1, 1:2, 1:3, 1:4, and 1:5 (collodion:ethanol). The CGI was deposited on the a-IGZO layer by spin-coating it with...
various revolutions per minute (rpm) for 30 s (3, 4, and 5 krpm). Then post-annealing in air was conducted at 125°C for 1 h. Finally, the Al gate electrode (200 nm) was deposited using thermal evaporation via shadow mask.

**Measurements and analysis method**

Under an ambient atmosphere in a dark condition, the leakage current density–electric field (J–E), current–voltage (I–V), and capacitance–voltage (C–V) curves of the CGI were measured with a semiconductor parameter analyzer (Hewlett Packard 4284A). The cross-section of the CGI was measured via field emission scanning electron microscopy (FESEM) (JEOL Ltd., JEOL-7800F). The root-mean-square (RMS) surface roughness was measured by atomic force microscopy (AFM) (JPK instrument).

**3. Results and discussion**

Figure 1 shows the fabrication process of top-gate coplanar a-IGZO TFTs with CGI using the spin-coating method. The collodion solution is mainly composed of nitrocellulose, which is made by exchanging the hydroxyl groups (–OH) in cellulose with nitro-ester groups (–ONO₂–) [14]. It is synthesized with nitrocellulose (solute), ethanol (solvent I), and diethyl ether (solvent II).

First, for the concentration adjustment of the collodion solution, a collodion solution was diluted by controlling the amount of ethanol solvent at the ratios of 1:1, 1:2, 1:3, 1:4, and 1:5 (collodion:ethanol). Figure 2 shows the current density–electric field (J–E) characteristics of single-layered non-diluted and diluted CGIs with various collodion concentrations fabricated with a

![Figure 1. Fabrication process of an a-IGZO TFT with a CGI.](image)

![Figure 2. J–E characteristics of a (a) non-diluted CGI and (b) single-layered diluted CGIs with various collodion concentrations (1:1, 1:2, 1:3, 1:4, and 1:5) and a 3 krpm spin-coating speed.](image)
spin-coating speed of 3 krpm. Although a single-layered non-diluted CGI fabricated with a 3 krpm spin-coating speed has a proper dielectric strength \((J < 10^{-11} \text{ A/cm}^2)\) in the range of 1.1 MV/cm), as shown in Figure 2(a), it is too thick \( (> 1 \text{ µm})\) to be used for the gate insulator layer. Figure 2(b) shows single-layered diluted CGIs (1:2, 1:3, 1:4, and 1:5) fabricated with a 3 krpm spin-coating speed and with low dielectric strength \((J < 10^{-2} \text{ A/cm}^2)\) in the range of 0.1 MV/cm), and a single-layered CGI (1:1) fabricated with a 3 krpm spin-coating speed and with high dielectric strength \((J < 10^{-10} \text{ A/cm}^2)\) in the range of 1.1 MV/cm) for use as the gate insulator layer.

Furthermore, the stacking number of single-layered diluted CGIs (1:2, 1:3, 1:4, and 1:5) was changed to quintuple-layered because they have low-dielectric strength in the single-layered condition. Then the J–E characteristics of a single-layered diluted CGI (1:1) were compared with those of five-stacked diluted CGIs (1:2, 1:3, 1:4, and 1:5), as shown in Figure 3. Although the five-stacked diluted CGIs (1:2, 1:3, 1:4, and 1:5) had relatively higher dielectric strength than the single-layered diluted CGIs, their dielectric strength \((J < 10^{-4} \text{ A/cm}^2)\) in the range of 0.4 MV/cm) was still too low for use as a gate insulator layer. From the results of the various concentrations and stacked-layer numbers, it was found that a single-layered diluted CGI (1:1) has an appropriate dielectric strength for the gate insulator of a-IGZO TFTs. Thus, the spin-coating rpm was finally varied to create the optimized condition. Figure 4 shows the J–E characteristics of single-layered diluted CGIs (1:1) fabricated with various spin-coating speeds (3, 4, and 5 krpm). The single-layered diluted CGIs fabricated with the spin-coating speeds of 4 and 5 krpm had low-dielectric strength \((J < 10^{-2} \text{ A/cm}^2)\) in the range of 0.7 MV/cm) whereas those that were fabricated with a spin-coating speed of 3 krpm had an appropriate dielectric strength \((J < 10^{-9} \text{ A/cm}^2)\) in the range of 1.1 MV/cm) for the gate insulator layer.

Until now, the three aforementioned parameters (the concentration of the collodion solution, the number of stacked layers, and the spin-coating speed) have been varied to optimize the CGIs. From these results, it was found that a single-layered diluted CGI (1:1) fabricated with a 3 krpm spin-coating speed is the optimized condition for the gate insulator. Compared to the conventional organic gate insulators, such as poly(methyl methacrylate), polyimide/polyvinyl alcohol, and poly(4vinylphenol), the single-layered diluted CGI (collodion:ethanol = 1:1) fabricated with a 3 krpm spin-coating speed exhibited high-dielectric strength \((J < 10^{-10} \text{ A/cm}^2)\) in the range of 1.1 MV/cm) [15–17]. Thus, additional analyses were done, such as FESEM and analyses of the C–V curve of CGI and of the I–V curve of an a-IGZO TFT with CGI, to determine if a single-layered diluted CGI (1:1) fabricated with a 3 krpm spin-coating speed could be used for the gate insulator of a-IGZO TFTs.

Figure 5(a) shows the cross-sectional SEM image of a single-layered diluted CGI (1:1)/p+−Si. The measured thickness of a single-layered diluted CGI was about 900 nm. The capacitance–voltage (C–V) characteristic of a single-layered diluted CGI was also measured. As shown in Figure 5(b), the capacitance of the single-layered diluted CGI (1:1) was determined to be 6 nF/cm². Based on such cross-sectional SEM image and C–V characteristics, the relative dielectric constant of a single-layered diluted CGI (1:1) was determined to be about 6.57. Finally, the single-layered diluted CGI was applied as the gate insulator of a top-gate coplanar a-IGZO TFT. Figure 6 shows the transfer characteristics of an a-IGZO TFT with a single-layered diluted CGI. The electrical parameters of the a-IGZO TFT with a single-layered diluted CGI are summarized in Table 1. The a-IGZO
Figure 5. (a) Cross-sectional SEM image of a single-layered diluted CGI (1:1)/p$^+\text{-Si}$. (b) C–V characteristics of a single-layered diluted CGI (1:1) fabricated with a spin-coating speed of 3 krpm.

Figure 6. Transfer characteristics of an a-IGZO TFT with a single-layered diluted CGI (1:1) and a 3 krpm spin-coating speed.

Table 1. Summarized electrical characteristics of a-IGZO TFTs with a single-layered diluted CGI (1:1) and a 3 krpm spin-coating speed.

| Sample               | Mobility (cm$^2$/Vs) | S.S (V/dec) | On/off ratio | $N_t$ (cm$^{-2}$) |
|----------------------|----------------------|-------------|--------------|-------------------|
| a-IGZO with diluted CGI | 17.11                | 1.25        | 1.05 $\times$ 10$^7$ | 8.09 $\times$ 10$^{11}$ |

TFT with a single-layered diluted CGI had high-field effect mobility ($\sim$ 17.11 cm$^2$/Vs). In addition, we measured the output curve and hysteresis of the a-IGZO TFT with a single-layered diluted CGI and show the electrical characteristics of field-effect mobility, and S.S shown with error bar in Figure S1. The output characteristics of all of the IGZO TFTs exhibited n-type transistor behavior at a drain-to-source voltage and are saturated in range of gate voltage. The clockwise hysteresis observed in Figure. S1(b) is compatible with the existence of electron trapping. Also, we measured positive bias stress (PBS), negative bias stress (NBS), and negative bias illumination stress (NBIS) of a-IGZO TFT with a single-layered diluted CGI, as shown in Figure S2. Under PBS, NBS, and NBIS conditions, threshold voltage ($V_{th}$) shifts of a-IGZO TFT with the single-layered diluted CGI (1:1) are 5.2 V, −3.86 V, and −5.6 V, respectively. Furthermore, we measured AFM images of a single-layered diluted CGI (1:1) at 3 krpm spin-coating speed and its RMS (root-mean-square) surface roughness in Figure S3. It was found that the RMS roughness value of that is 6.81 nm. From these results, it was confirmed that electrical polarization occurs in a single-layered diluted CGI, and as such, it can be used as a gate insulator for a-IGZO TFTs.

4. Conclusion

Nitrocellulose-based collodion was suggested for use as a gate insulator of amorphous indium gallium zinc oxide thin-film transistors (a-IGZO TFTs) for the first time. The single-layered diluted CGI (1:1) fabricated with a 3 krpm spin-coating speed was found to have high-dielectric strength ($J < 10^{-10}$ A/cm$^2$ in the range of 1.1 MV/cm) and a high-relative dielectric constant ($\sim$ 6.57) that make it appropriate to be used a gate insulator. The fabricated a-IGZO TFT with a single-layered diluted CGI was found to have high-field effect mobility ($\sim$ 17.11 cm$^2$/Vs). This research showed that the nitrocellulose-based collodion material could be used as a gate insulator layer and has a potential for use in the next-generation flexible, stretchable, and bendable electronic devices.
Disclosure statement
No potential conflict of interest was reported by the authors.

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