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Aqueous Solution-Deposited Gallium Oxide Dielectric for Low-Temperature, Low-Operating-Voltage Indium Oxide Thin-Film Transistors: A Facile Route to Green Oxide Electronics

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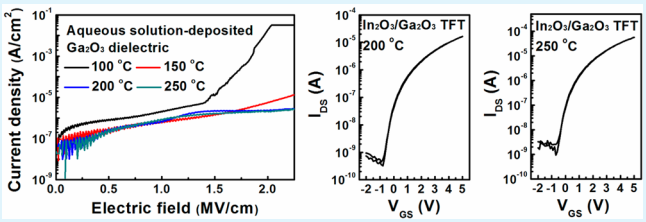
Supporting Information

ABSTRACT: We reported a novel aqueous route to fabricate Ga_2O_3 dielectric at low temperature. The formation and properties of Ga_2O_3 were investigated by a wide range of characterization techniques, revealing that Ga_2O_3 films could effectively block leakage current even after annealing in air at 200 °C. Furthermore, all aqueous solution-processed In_2O_3/Ga_2O_3 TFTs fabricated at 200 and 250 °C showed mobilities of 1.0 and 4.1 cm^2 V^{-1} s^{-1}, on/off current ratio of ~10^5, low operating voltages of 4 V, and negligible hysteresis. Our study represents a significant step toward the development of low-cost, low-temperature, and large-area green oxide electronics.



KEYWORDS: *aqueous route, gallium oxide dielectric, indium oxide, oxide thin-film transistors, low-temperature, green oxide electronics*

1. INTRODUCTION

Metal oxide semiconductors have attracted considerable attention as the channel materials for thin-film transistors (TFTs) due to their high carrier mobility and excellent uniformity.[1−4] Besides, the solution processability has opened new venues for low-cost and large-area oxide electronics.[5−10] Unfortunately, the sol−gel condensation, densification, and impurity removal typically require a high-temperature annealing step, which is one major obstacle in the fabrication of devices using flexible substrates.

Many attempts have been made to reduce the annealing temperature, and recent significant advances include sol−gel on a chip,[8] combustion process,[9] and deep-ultraviolet photochemical activation.[10] However, the use of toxic organic solvents such as 2-methoxyethanol (2-ME) in the majority of the reported studies would cause health risks and environmental impact. The environmentally friendly trend must also be seriously considered in future research. Most recently, some groups have demonstrated the aqueous precursor solution-processed indium oxide (In_2O_3) TFTs with good performance.[11−13] In this method, commercially available nitrate precursors are dissolved in water, which are then converted to the fully coordinated oxide during low annealing temperature. Because water is used as a solvent, the novel "aqueous route" is considered to be healthier, safer, and more environmentally friendly.

On the other hand, solution-processed oxide TFTs usually exhibited high operating voltages due to the use of thermally grown or vacuum-deposited SiO_2 as dielectrics. For this reason, much effort has been devoted to develop novel gate dielectrics for low-power applications.[14−26] Among them, gallium oxide (Ga_2O_3) is one of the most promising dielectric materials due to its wide bandgap and good chemical/thermal stability.[27−35] However, most of the Ga_2O_3 thin films were prepared by vacuum-based techniques such as sputter deposition,[30,31,33] electron beam evaporation,[28] chemical vapor deposition (CVD),[27] and atomic layer deposition (ALD),[32] which are not good for low-cost and large-scale fabrications. With the consideration that the group 13 ions of In(III) and Ga(III) exhibit similar chemical behavior in aqueous solution,[36−39] this raises the intriguing question of whether the aqueous route could be applied to fabricate Ga_2O_3 dielectric and realize green oxide TFTs.

In this work, we developed a simple and low-temperature aqueous route to fabricate Ga_2O_3 dielectric. The formation and properties of Ga_2O_3 were investigated by a wide range of complementary characterization techniques. This method enables deposition of high-quality Ga_2O_3 insulator at temperature as low as 200 °C. To evaluate Ga_2O_3 as gate dielectrics, aqueous solution-processed In_2O_3/Ga_2O_3 TFTs were fabricated with maximum annealing temperature of 200 and 250 °C, with resulting mobilities of 1.0 and 4.1 cm^2 V^{-1} s^{-1}, respectively. Besides, the devices showed low operating voltages of 4 V and negligible hysteresis.

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Table 1. Microstructural and Dielectric Properties of Ga_2O_3 under Various Annealing Temperatures

annealing temp (°C)	thickness (nm)	roughness (nm)	refractive index at 550 nm	leakage current at 2 MV/cm (A/cm^2)	capacitance (nF/cm^2) at 100 Hz	dielectric constant at 100 Hz
100	82	1.73	1.607	1.8×10^{-2}	151	14.0
150	65	0.84	1.653	5.6×10^{-6}	216	15.9
200	55	0.22	1.695	2.4×10^{-6}	193	12.2
250	52	0.19	1.719	2.0×10^{-6}	172	10.1

2. EXPERIMENTAL SECTION

2.1. Precursor Preparation. All chemicals were purchased from Sigma-Aldrich and used as received without further purification. The Ga_2O_3 precursor solution was prepared by dissolving gallium nitrate hydrate ($Ga(NO_3)_3{\cdot}xH_2O$) in water with a concentration of 1.0 M. The In_2O_3 precursor solution was prepared by dissolving indium nitrate hydrate ($In(NO_3)_3{\cdot}xH_2O$) in water with a concentration of 0.15 M. Prior to spin coating, all the precursor solutions were ultrasonicated vigorously and then filtered through a 0.45 μm poly(ether sulfone) (PES) syringe.

2.2. Film and Device Fabrication. The heavily doped Si substrates were sonicated with acetone, isopropanol, and deionized water, respectively. The synthesized Ga_2O_3 precursor solution was spin-coated at 3000 rmp for 20 s on substrates that were treated by oxygen plasma, and the coated layer was annealed at various temperatures (100, 150, 200, and 250 °C) for 0.5 h under ambient atmosphere. The spin coating and heat treatment processes were repeated again. For the metal−insulator−metal (MIM) devices, an Al electrode (100 nm) was deposited on the insulator layer by thermal evaporation. The area of the circular Al electrode was 0.03 mm^2. Bottom-gate top-contact TFTs were fabricated by spin coating the In_2O_3 solution on the annealed Ga_2O_3 dielectric at 3000 rmp for 20 s and then annealed at desired temperatures for 1 h to achieve thicknesses of about 10 nm. Subsequently, the Al source and drain electrodes were deposited by thermal evaporation through a shadow mask. The channel width (W) and length (L) were 1500 and 100 μm, respectively. It has been shown that a small W/L ratio of 5 could induce mobility overestimation up to ~200% and the overestimation dropped to 10% as the W/L ratio increased to 10.[15,21] Therefore, the large W/L ratio over 15 in this study could efficiently limit mobility overestimation.

2.3. Film and Device Characterization. The thermal behavior of the Ga_2O_3 precursor powder (dried at 110 °C for 12 h) was obtained by thermogravimetric analyzer (PerkinElmer, TGA 6) and differential scanning calorimeter (PerkinElmer, DSC 7) at a heating rate of 10 °C/min from 50 to 550 °C. The chemical characteristics of the Ga_2O_3 films were examined by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Bruker). The thicknesses and optical properties were measured via variable angle spectroscopic ellipsometry (J. A. Woollam Co., Inc.). The surface morphologies were characterized by atomic force microscopy (AFM, Veeco Dimention V). The structures were determined using X-ray diffraction (XRD, Siemens) with Cu Kα radiation. The frequency-dependent capacitance characteristics of the Ga_2O_3 dielectrics were performed using a HP 4284A in a frequency range from 100 Hz to 1 MHz. The leakage of the Ga_2O_3 films and the electrical characteristics of the TFTs were measured with a precision semiconductor analyzer (Keithley 4200) under ambient conditions. Threshold voltage (V_{th}) was extracted from measurements in the saturation region by plotting $(I_{DS})^{1/2}$ versus V_{GS} and extrapolating to $I_{DS} = 0$ plots. The mobility (μ) and subthreshold swing (S) were calculated by the following formulas

$$I_{DS} = \left(\frac{\mu C_i W}{2L}\right)(V_{GS} - V_{th})^2$$

$$S = \left(\frac{d(\log_{10} I_{DS})}{dV_{GS}}\right)^{-1}$$

where C_i, W, and L are the capacitance of the gate dielectrics per unit area, channel width, and channel length.

3. RESULTS AND DISCUSSION

To understand the conversion process from liquid precursor to solid Ga_2O_3 film, systematical investigations with TG-DSC, ATR-FTIR, spectroscopic ellipsometry, XRD, and AFM characterization were carried out, and relevant results are summarized in Table 1. TGA-DSC measurement was initially performed as shown in Figure 1a. In general, the hydrolysis

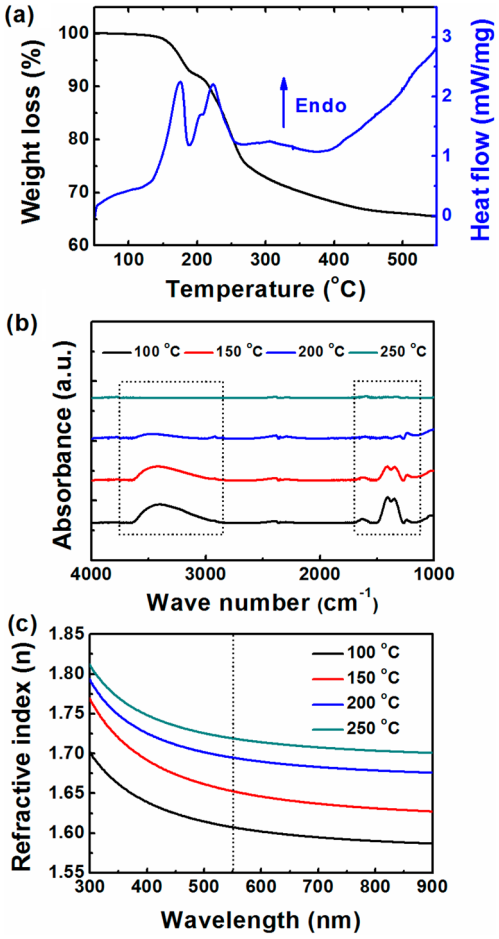

Figure 1. (a) TGA and DSC curves of Ga_2O_3 powder from 50 to 550 °C. (b) ATR-FTIR spectra and (c) refractive index-wavelength curves of Ga_2O_3 films annealed at indicated temperatures.

reaction took place in the range 100−150 °C.[11−13,36−39] However, no hydrolysis-related peaks were observed since the Ga_2O_3 powder prepared at 110 °C was already hydrolyzed. The first endothermic peak at 174 °C indicates the dehydroxylation behavior of the hydrolyzed gallium hydroxide and forms metal oxide lattice.[11−13] Another peak at 224 °C could be related to the decomposition of residual nitrate.[11−13]

To further clarify the formation process of the Ga_2O_3 thin film, ATR-FTIR measurements were performed, as shown in Figure 1b. The broad peak in the range 3000−3700 cm^{-1}

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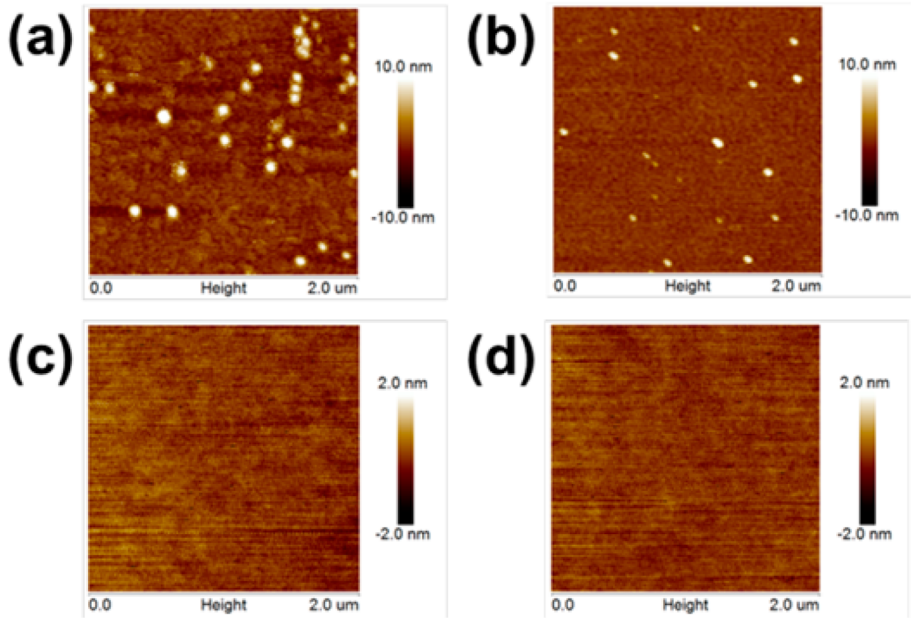

Figure 2. AFM images of Ga_2O_3 films with different annealing temperatures of (a) 100, (b) 150, (c) 200, and (d) 250 °C. Images are 2 μm × 2 μm.

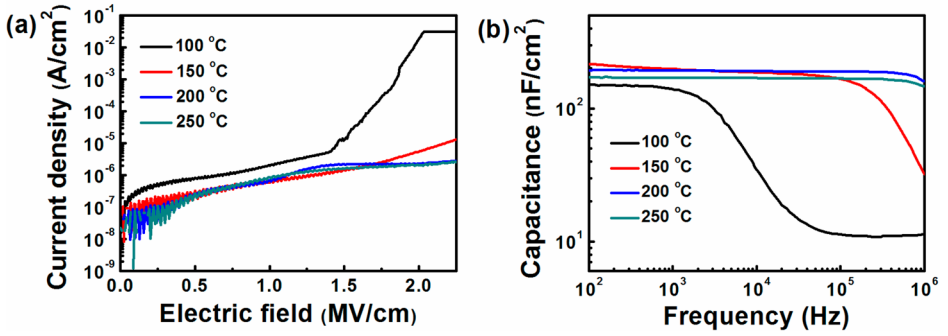

Figure 3. (a) Leakage current density vs electric field and (b) capacitance vs frequency of solution-processed Ga_2O_3 dielectrics annealed at indicated temperatures.

corresponds to hydroxyl (OH) group stretching vibrations.[12,13] The peak in the 1200−1700 cm^{-1} range could be assigned to hydroxyl group or nitrate (NO_3^-) deformation vibrations.[12,13,20,21] The 100 °C annealed film contained a large amount of hydroxyl and nitrate groups. As the annealing temperature increased, the hydroxyl and nitrate groups were gradually decomposed and completely removed at 250 °C.

To verify the condensation and densification behavior of the Ga_2O_3 film, spectroscopic ellipsometry measurements were performed. The thickness of the Ga_2O_3 decreased from 82 to 52 nm as the annealing temperature increased from 100 to 250 °C, which is due to the evaporation of solvent and the densification process of the thin film. Figure 1c shows the refractive index−wavelength curves of Ga_2O_3 films annealed under various temperatures. Note that the refractive index is the indicator of the packing density of the thin films.[22,31] The increase of the refractive index with the rise of annealing temperature could be attributed to the evaporation of solvent and decomposition of the nitrate and hydroxyl groups, in agreement with the reduction of thickness. The film annealed at 250 °C showed refractive index of 1.719 at 550 nm, which is comparable to the low-temperature vacuum-deposited counterpart.[24,31,32] Besides, the optical bandgaps of the Ga_2O_3 films determined from the spectroscopic ellipsometry were in the range 5.46−5.64 eV (Supporting Information Figure S1), similar to the reported values.[31,32] The wide bandgap of the dielectric material is good for restricting the leakage current.

Figure S2 in the Supporting Information shows the XRD spectra of Ga_2O_3 films as a function of annealing temperature. The Ga_2O_3 films showed an amorphous phase up to 250 °C. Previous studies have demonstrated that the Ga_2O_3 could maintain amorphous state up to 500 °C.[31,33] The amorphous structure is desirable because grain boundaries usually act as preferential paths for impurity diffusion and leak current.[16] Figure 2 shows the AFM images of Ga_2O_3 thin films treated at different temperatures. The root-mean-square (rms) roughness of Ga_2O_3 films annealed at 100, 150, 200, and 250 °C were 1.73, 0.84, 0.22, and 0.19 nm, respectively. Note that there were considerable quantities of gaseous byproducts such as H_2O and N_2 evolved in the conversion process. These gaseous byproducts could not be easily removed at low temperature, making the film discontinuous and rough.[9] The Ga_2O_3 film showed ultrasmooth surface as the annealing temperature rose up to 200 °C, consistent with the amorphous structure, which is ideal for suppressing the surface roughness induced leakage current and achieving high charge carrier mobility in the TFT channel.[14,16] From the above TGA-DSC, ATR-FTIR, spectroscopic ellipsometry, XRD, and AFM results, we could conclude

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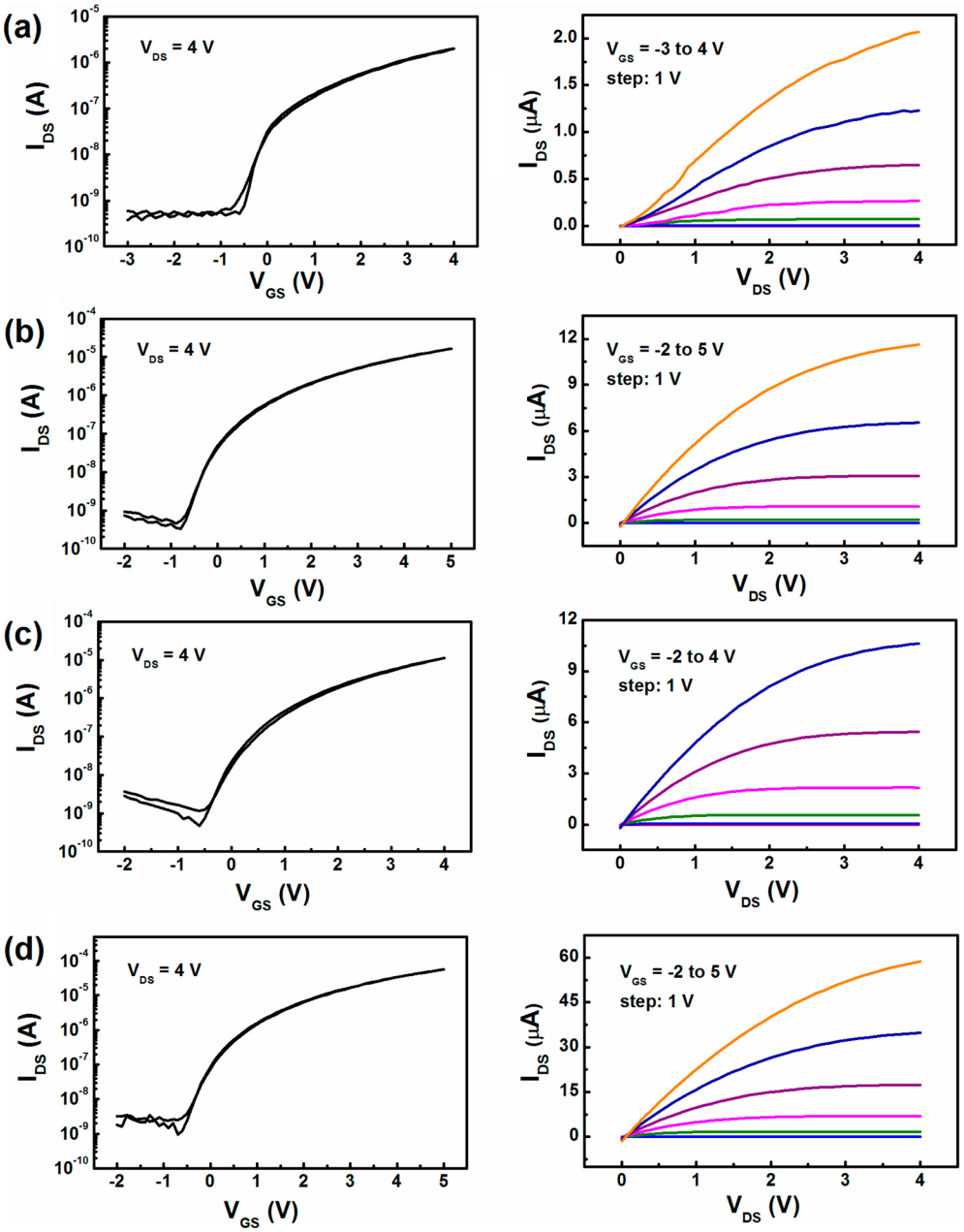

Figure 4. Transfer and output characteristics of (a) In_2O_3 (185 °C)/Ga_2O_3 (200 °C) TFT, (b) In_2O_3 (200 °C)/Ga_2O_3 (200 °C) TFT, (c) In_2O_3 (200 °C)/Ga_2O_3 (250 °C) TFT, and (d) In_2O_3 (250 °C)/Ga_2O_3 (250 °C) TFT.

that the aqueous-derived Ga_2O_3 film undergoes the decomposition of the nitrate and hydroxyl groups, as well as the formation of metal oxide framework after low-temperature post-annealing treatment.

The dielectric properties of Ga_2O_3 were measured by MIM structures and summarized in Table 1. As shown in Figure 3a, the 100 °C annealed device showed large leakage current due to the existence of large amounts of nitrate and hydroxyl groups. The 200 °C and 250 °C annealed films showed low leakage currents of 2.4×10^{-6} A/cm^2 and 2.0×10^{-6} A/cm^2 at 2 MV/cm, which were attributed to the decomposition of hydroxyl and nitrate groups as well as the formation of metal oxide framework.[19−21] The capacitance−frequency curves in the range 100 Hz to 1 MHz are shown in Figure 3b. The films annealed at 200 and 250 °C had capacitances of 193 and 172 nF/cm^2, corresponding to dielectric constants of 12.2 and 10.1, similar to the reported vacuum-fabricated counterparts.[27,32] The weak frequency dependence of capacitance at high annealing temperature is consistent with the low leakage current of insulator, suggesting low defect concentrations.[3,16] The dielectric properties of Ga_2O_3 are in good agreement with the above thin-film characterization.

To demonstrate the feasibility of using Ga_2O_3 as gate dielectrics, we fabricated bottom-gate top-contact TFTs employing previous reported aqueous-derived In_2O_3 as channel layer.[11−13] Figure 4 demonstrates the transfer and output characteristics of In_2O_3/Ga_2O_3 TFTs under various annealing temperatures, with electrical performance summarized in Table 2. The In_2O_3 (185 °C)/Ga_2O_3 (200 °C) TFT showed a low mobility of 0.2 cm^2 V^{-1} s^{-1} (Figure 4a), whereas the In_2O_3 (200 °C)/Ga_2O_3 (200 °C) TFT exhibited an acceptable mobility of 1.0 cm^2 V^{-1} s^{-1}, subthreshold swing 0.28 V/decade,

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Table 2. Electrical Performance of In_2O_3/Ga_2O_3 TFTs under Various Annealing Temperatures

TFTs	mobility ($cm^2 V^{-1} s^{-1}$)	subthreshold swing (V/decade)	threshold voltage (V)	on/off current ratio
In_2O_3(185 °C)/Ga_2O_3 (200 °C)	0.2 ± 0.1	0.26 ± 0.04	0.4 ± 0.4	~10^4
In_2O_3(200 °C)/Ga_2O_3 (200 °C)	1.0 ± 0.3	0.28 ± 0.03	0.6 ± 0.2	~10^5
In_2O_3(200 °C)/Ga_2O_3 (250 °C)	1.0 ± 0.2	0.29 ± 0.04	0.7 ± 0.3	~10^5
In_2O_3(250 °C)/Ga_2O_3 (250 °C)	4.1 ± 0.6	0.26 ± 0.04	0.6 ± 0.3	~10^5

threshold voltage of 0.6 V, and on/off current ratio of ~10^5 (Figure 4b). The In_2O_3 (200 °C)/Ga_2O_3 (250 °C) TFT (Figure 4c) showed similar performance to the In_2O_3 (200 °C)/Ga_2O_3 (200 °C) one. A remarkable improvement was observed for the In_2O_3 (250 °C)/Ga_2O_3 (250 °C) TFT (Figure 4d), exhibiting a good mobility of 4.1 $cm^2 V^{-1} s^{-1}$, subthreshold swing 0.26 V/decade, threshold voltage of 0.6 V, and on/off current ratio of ~10^5. According to the above results, the device performance (mobility) is mainly dependent on the annealing temperature of the In_2O_3 semiconductor. The device showed improved performance as the annealing temperature of In_2O_3 increased from 185 to 250 °C. This is consistent with the previous studies on aqueous-derived In_2O_3 TFTs using thermally SiO_2 or solution-processed ZrO_2 dielectrics and could be attributed to the formation of indium oxide framework as well as the decomposition of nitrate and hydroxyl groups with the rise of annealing temperature.[11−13] Besides, the In_2O_3/Ga_2O_3 TFTs exhibited low operating voltages of 4 V and negligible hysteresis. These impressive results achieved by a simple and green process are comparable to the recently reported low-temperature solution-processed high-*k* dielectric/oxide semiconductor TFTs.[12,13,19,23−26] Besides, we have carried out the positive and negative bias stress study of In_2O_3/Ga_2O_3 TFTs at maximum processed temperature of 200 and 250 °C, as shown in Supporting Information Figure S3. The 250 °C annealed device showed better bias stress stability, owing to the improvement of In_2O_3 semiconductor quality and semiconductor/dielectric interface; detailed analysis can be found in the Supporting Information.

The use of water as solvent plays an important role in achieving respectably performing In_2O_3/Ga_2O_3 TFTs at low temperature. First, water is an excellent solvent because it has no organic residues to be removed for obtaining high-quality films.[11−13] Second, the large dielectric constant of water (>80) could effectively weaken the electrostatic force between the cation (In^{3+} or Ga^{3+}) and anion (NO_3^-). In aqueous solutions, In^{3+} or Ga^{3+} usually exists in the form of outer-sphere complex $[In(OH_2)_6^{3+}NO_3^-]/[Ga(OH_2)_6^{3+}NO_3^-]$ and/or $[In(OH_2)_6^{3+}]/[Ga(OH_2)_6^{3+}]$ with free nitrate.[11−13,36−39] As the coordination bond between the cation and neighboring aquo ion is relatively weak, it is easily broken with low thermal energy.[11−13] Thus, dense and smooth films could be achieved at low annealing temperatures. Further improvement of the device performance could be achieved by optimization of the channel layer, dielectric layer, channel/dielectric interface, as well as the introduction of passivation layer.

4. CONCLUSION

In summary, we have demonstrated the low-temperature fabrication of high-quality Ga_2O_3 dielectric via an aqueous solution process. The thin-film formation and properties of Ga_2O_3 were investigated by various characterization techniques including TGA-DSC, ATR-FTIR, spectroscopic ellipsometry, XRD, AFM, and electrical measurements. Besides, aqueous solution-deposited In_2O_3/Ga_2O_3 TFTs fabricated at 200 and 250 °C exhibited good mobilities of 1.0 and 4.1 $cm^2 V^{-1} s^{-1}$, as well as on/off current ratio of ~10^5. Our finding provides potential for realizing low-cost, low-temperature, and large-area green oxide electronics.

■ ASSOCIATED CONTENT

Supporting Information

Optical bandgap of the Ga_2O_3, XRD spectra of Ga_2O_3, and bias stress stability of In_2O_3/Ga_2O_3 TFTs. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02451.

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Notes

The authors declare no competing financial interest.

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