Eco-Friendly Solution Combustion Processed Thin-Film Transistors for Synaptic Emulation and Neuromorphic Computing

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ABSTRACT: The eco-friendly combustion synthesis (ECS) and self-combustion synthesis (ESCS) have been successfully utilized to deposit high-kaluminum oxide (AlOx) dielectrics at low temperatures and applied for aqueous In2O3 thin film transistor (TFTs) accordingly. The ECS and ESCS processes facilitate the formation of high-quality dielectrics at lower temperatures compared to conventional methods based on ethanol precursor, as confirmed by thermal analysis and chemical composition characterization. The aqueous In2O3 TFTs based on ECS and ESCS AlOx show enhanced electrical characteristics and counterclockwise transfer curve hysteresis. Due to the memory-like behavior in the transfer curve modulated by the gate bias voltage is comparable to the signal modulation by the neurotransmitters. ECS andF ESCS transistors are employed to perform synaptic emulation; various short-term and long-term memory functions are emulated with low operating voltages and high excitatory postsynaptic current levels. High stability and reproducibility are achieved within 240 pulses of long-term synaptic potentiation and depression. The synaptic emulation functions achieved in this work match the demand for artificial neural networks (ANN), and a multi-layer perceptron (MLP) is developed using ECS AlOx synaptic transistor for image recognition. A superior recognition rate of over 90% is achieved based on ECS-AlOx synaptic transistors, which facilitates the implementation of the metal oxide synaptic transistor for future neuromorphic computing via an eco-friendly route.

**1. Introduction**

Over the past few years, the traditional computers based on the von Neumann architecture encountered the bottleneck due to the inefficient data processing and high-power consumption1-5. Inspired by the human brain nervous system, the neuromorphic computing system exhibiting parallel-processing and power efficiency is considered as an alternative approach for advanced computing system4-8. Synaptic devices, as one of the basic components in hardware artificial neural networks (ANN) where neuromorphic computing can be performed, have attracted extensive attention for promoting the development of the artificial neuromorphic computing system. In recent few years, various two-terminal and three-terminal devices, such as memory transistor 9-10, memristor11-13, and synaptic transistors4, 6, 14, have been investigated to emulate synaptic functions. Among various synaptic devices, three-terminal metal-oxide thin-film transistors (MOTFT) employ high-*k* dielectrics have emerged with advantages including synapse behavior emulation, low-cost, long-term stability, and integrated-circuit compatibility.2, 15 R. Martins et al. reported high-performance memory transistors and non-volatile paper memory transistor based on Indium gallium zinc oxide (IGZO) channel in 2008 and 2009, respectively.9, 16 Liang et al. reported an artificial synaptic In2O3 thin film transistor and demonstrated various synaptic plasticity including paired-pulse facilitation (PPF) and spike-timing-dependent plasticity (STDP).17 Zhou et al. proposed an In2O3 synaptic transistor based on high-*k* Gd2O3 and studied STP behavior.2

MOTFTs have been studied intensively for the next-generation electronics owing to their excellent environmental stability, optical transparency, and high field-effect mobility, which are applicable in large-area flat-panel displays, transparent electronics, and artificial synapses.17-23 By incorporating a high dielectric constant (high-*k*) oxide instead of the conventional SiO2, high-performance thin-film transistors (TFTs) with low-operating voltages have been demonstrated accordingly.21, 24-25 However, the typical deposition methods for metal-oxide high-*k* dielectric and semiconductor thin films are high vacuum-based techniques, such as magnetic sputtering and atomic layer deposition.26-27 With the exponentially growing demands for low-cost electronic applications, solution-based deposition techniques have emerged and been considered as one of the most promising candidates considering their low cost and simplicity for atmosphere manufacturing. Up to date, solution-process methods have been well established for crystalline metal oxide semiconductors such as In2O3, ZnO, and SnO2 and amorphous ternary and quaternary materials such as Zn-Sn-O (ZTO), In-Zn-O (IZO), In-Ga-Zn-O (IGZO) and so on.21, 28-33. Among various metal oxide semiconductors, Indium-based metal-oxide materials have been intensively studied because their high electron mobility originating from the ns orbital of indium, which can be deposited by solution process based on various organic solvents and water.29, 34-40 In addition to metal oxide semiconductors, solution-processed high-*k* metal oxide gate dielectrics, such as HfO2, Al2O3, ZrO2,21, 29, 41 have been well studied to achieve low-voltage operation fully solution-processed TFTs. Although the solution-processed metal oxide thin films exhibit significant potential in next-generation electronics, high annealing temperatures (above 400 ºC) are generally required due to the necessary sol-gel condensation, densification, and removing impurity.42-43 To ensure the desirable electrical performance of solution-processed MOTFTs while reducing annealing temperature, several novel processing techniques like laser annealing, UV/Ozone treatment, deep-UV photochemical activation, and combustion synthesis have been devised elaborately.24, 44-45 Among these methods, combustion synthesis (CS) has been regarded as a time-saving and low-cost technique for producing desired metal-oxide semiconductor and dielectric thin films at relatively low temperature without additional post-treatment.18, 24, 46 No extra special equipment is mandatory to provide additional energy to reduce the processing temperature, since the combustion synthesis reaction of precursor compounds itself induce extensive heat within the thin film to form the metal oxide framework.47 By exquisitely adjusting the chemical composition and proportion of the oxidizer (e.g., nitrates and chlorides) and the fuel (e.g., urea and acetylacetone) in the precursor solution, a localized exothermic reaction occurs within the as-deposited precursor during the annealing process.48 The induced internal heat within the gel leads to the decomposition of the precursor and the complete formation of metal–oxide framework at low temperature, avoiding high external energy from the supplier. However, organic solvent 2-Me (toxic for humans and harmful to the environment) is widely used for preparing the combustion precursor solution.24, 43-44, 49-50 Therefore, the design and implementation of proper eco-friendly solvents, metal solvents (metal source), and compatibility for solution process MOTFT is crucial to achieve high-performance metal-oxide TFTs at low temperatures.

Although solution-processed metal oxide synaptic transistors have been achieved in few previous reports, the devices show poor electrical performance with associated low mobility (<10 cm2V-1s-1), being possibly attributed to residuals within the high-*k* dielectrics annealed at low temperatures.48, 51 In this paper, we demonstrate an eco-friendly route for water-induced In2O3 TFT with solution-processed AlOx thin films deposited by both eco-friendly combustion synthesis (ECS) and eco-friendly self-combustion synthesis (ESCS) employing ethanol as a solvent. The formation of AlOx thin films was intensively studied by investigating the chemical composition and electrical characteristics of metal-oxide thin films annealed at various low temperatures. ECS and ESCS AlOx thin films were then employed as the dielectric layer for MOTFTs, and water-induced In2O3 thin films were deposited accordingly. The effects of combustion synthesis along with annealing temperatures in water-induced In2O3 TFTs were investigated systematically via the TFT electrical characterization and chemical composition analysis. Transfer characteristics for both ECS-TFTs and ESCS-TFTs exhibit superior mobility and counterclockwise hysteresis, which could be a result of intrinsic donor-like electron traps in the dielectrics. Although hysteresis in transfer curve is not preferable for the conventional application like the logic circuit and the flat panel display, high-performance ECS and ESCS TFTs with appropriate counterclockwise hysteresis could be applied to emulate synaptic behavior to achieve low-temperature solution-processed synaptic transistor with low operating voltage and high excitatory postsynaptic current (EPSC). In this work, for the first time, a solution combustion process was employed to achieve a low-temperature and eco-friendly synaptic transistor with superior electrical performance. Synaptic transistors formed by both methods (ECS and ESCS) exhibit synaptic behavior and ECS-TFT was further used to perform various short-term and long-term synaptic emulations. Moreover, the synaptic emulation functions achieved by transistors in this work match the demand of ANN to simulate digit image pattern recognition. Simulation for artificial synaptic pattern recognition was demonstrated and a high recognition rate was achieved based on ECS-AlOx synaptic transistors.

**2. Experimental Details**

**Eco-friendly Solution Combustion Synthesis**

The schematic experimental process for the eco-friendly combustion process could be found in Figure 1. Compared with non-combustive conventional solution-processed aluminum oxides (AlOx), combustion synthesis between a fuel and an oxidizer reduces the thermal annealing temperature needed for forming the metal oxide framework from solution precursors (Figure 2a.). When a fuel-oxidizer pair receives heat at a certain temperature, a violent exothermic reaction occurs along with the release of massive heat within the thin film. This evolved heat results in the increase of local energy within the film, which accelerates the decomposition of residual impurities and forming a high-quality metal oxide framework at a lower temperature compared with a non-combustive method, as presented in Figure 2b. The eco-friendly combustion synthesis process of AlOx from aluminum nitrate (oxidizer and metal source) and urea (additive fuel) can be described as a combination of aluminum nitrate decomposition and exothermic redox reaction. The overall reaction for ECS-AlOx is shown in equation 1. During this process, the oxidizer (metal source) reacted with the additive fuel the nitrate. As a result, impurities were decomposed and internal heat was released.

(1)

(Note: theoretical reaction equations that neglect possible secondary reactions.)

For the eco-friendly self-combustion synthesis method of AlOx, two aluminum metal sources were dissolved into the precursor and no additive fuel or oxidizer was involved. The reaction between aluminum nitrate (as both the oxidizer and metal source) and aluminum acetylacetone (as both the fuel metal source) releases heat and no additive organic fuel is required, as shown in equation 2.

(2)

(Note: theoretical reaction equations that neglect possible secondary reactions.)

**Precursor Solution Preparation**

All experiments including precursor preparation, transistor fabrication, and electrical measurements were performed in the clean room (Room temperature, 35% Humidity). To prepare the ECS-AlOx precursor solution, 0.125 M aluminum nitrate nonahydrate (Al(NO3)3∙9H2O) was dissolved into 5 ml ethanol as the aluminum source and oxidizer. The fuel was prepared by dissolving urea into 5 ml ethanol. In order to guarantee the redox stoichiometry of the reaction, the urea to aluminum nitrate molar proportion was 2.5:1. The oxidizer and fuel precursor solutions were ultrasonicated for 10 minutes, and then mixed and stirred vigorously for 5 minutes to obtain the ECS-AlOx precursor solution. The self-combustion AlO­x precursor was prepared by equivalent concentrations of 0.125M aluminum nitrate nonahydrate (Al(NO3)3∙9H2O) and 0.125M aluminum triacetylacetone in ethanol. To fabricate conventional solution-processed AlOx as a control group (AlOx), 0.125 M aluminum nitrate nonahydrate (Al(NO3)3∙9H2O) was dissolved in ethanol. Then, ESCS-AlOx and AlOx precursors were stirred vigorously for 10 minutes. A 0.22 mm polytetrafluoroethylene (PTFE) syringe filter was used for filtering all the precursors before spin-coating. To prepare the In2O3 precursor solution, 0.4512g (0.15 M) indium nitrate hydrate (In(NO3)∙H2O) in 10 ml deionized (DI) water was stirred vigorously for 10 minutes, and a 0.45 µm polyethersulfone (PES) syringe filter was used to filter the precursor solution.

**Dielectric Deposition and Characterization**

Prior to the spin-coating of the dielectric precursor, a 30-minute air plasma treatment was performed on the substrates all substrates (heavily doped silicon and quartz substrates) for hydrophilicity. The conventional AlOx, ECS-AlOx, and ESCS-AlOx dielectrics were formed by spin-coating on the substrates in the air for 20 s at 2500 rpm. Then, annealing processes at 250 °C, 300 °C, and 350 °C temperatures were performed at ambient conditions for 1 h. A differential scanning calorimeter (TGA, Jupiter STA449F3) was used to characterize the thermal behavior of the ECS, ESCS, and conventional precursor solutions. Specifically, all the precursors were heated in an alumina crucible and air atmosphere to 500 °C with air gas flow of 60 sccm and a heating rate of 10 °C/min. X-ray diffraction (XRD, BRUKER D8 ADVANCE) with Cu Kα radiation was employed to collect the crystallization and structural information. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to evaluate the AlO­x thin film surface.

The chemical composition of the AlOx thin films was evaluated by X-ray photoelectron spectroscopy (XPS, Kratos) using Al Kα radiation (1486.6 eV) and a carbon 1s peak at 284.8 eV was used as a reference for calibration. To characterize the optical characteristics of thin films on quartz substrates, the 200 - 800 nm transmittance (T) measurement was performed by a UV/Vis system.

**Electronic Device Fabrication and Characterization**

Metal-insulator-semiconductor (MIS) capacitors were fabricated by depositing a single layer AlOx for each precursor solution on n-type heavily doped silicon substrates (<0.002 Ω·cm) as presented above. 0.07-mm2 Aluminum top electrodes (150 nm thick) were defined by thermal evaporation through the shadow mask on the top of the AlOx layer. The electrical characterization of the MIS and TFT devices including capacitance-frequency (C-F), leakage current versus gate voltage (I-V) measurements, and synaptic emulation tests were performed in the dark at a faraday cage by using an Agilent B1500A Semiconductor Device Analyzer at the clean room (Room temperature, 35% Humidity). The thickness data for AlOx thin films was measured by ellipsometry and shown in Table S1. A 30-minute air plasma treatment was implemented on the heavily doped n-type Si substrates firstly, and the as-prepared AlOx, ECS-AlOx, ESCS-AlOx precursor solution were spin-coated on heavily doped silicon substrates as presented above. To form the active layer on the dielectric, the In2O3 precursor solution was spin-coated on the dielectric layer directly at 3000 rpm for 20 s, followed by a 250 °C annealing process under ambient atmosphere for 30 minutes.

Finally, thermal evaporation was used to deposit 150 nm Al drain and source electrodes through the shadow mask, which defines the channel region with 100 µm length (L) and 1500 µm width (W). The mobility overestimation could be reduced efficiently by using a large W/L ratio over 10 according to previous reports.52 A semiconductor device analyzer (Agilent B1500A Semiconductor Device Analyzer) was used to measure the electrical characteristics of MIS and MOTFT devices. The field-effect mobility of the TFTs was extracted from the transfer curve as shown in equation 4.

(3)

where is field-effect mobility, is the areal capacitance of the gate dielectric, W is the channel width, L is the channel length, and Vth is the threshold voltage. The subthreshold voltage swing (SS) defined as the gate voltage required to gain the subthreshold drain-source current by one decade, is derived by equation 5.

(4)

Statistical data for the electrical performance shown in the supporting material is collected from 10 devices on two samples for each condition. Furthermore, the synaptic emulations were performed by Agilent B1500A Semiconductor Device Analyzer and the presynaptic input signal was sent to the gate of the synaptic transistor by semiconductor pulse generator unit (SPGU). Then the postsynaptic EPSC was received by monitoring the drain current.

**3. Results and Discussion**

To investigate the thermal behavior of the aluminum oxide precursors and corroborate the proposed theoretical exothermic reaction, thermal analysis, and chemical composition characterization were performed accordingly. Figures 2c-e show corresponding thermogravimetric and differential scanning calorimetry (TG-DSC) characteristics and Figures 3a-b show the corresponding XPS N 1s results for AlOx, ESCS-AlOx, and ECS-AlOx annealed at 250°C, 300°C, and 350°C. It should be noted that large weight loss and corresponding DSC peak were attributed to endothermic solvent evaporation at low temperature because precursor solution was heated directly in this study for better observation of the thermal behavior from precursor solution to metal oxide framework, which is inconsistent with previous work demonstrated by E. Fortunato et al..53 The DSC data for the ESCS-AlOx precursor shows a single and wide exothermic peak at 180 °C that corresponds exactly to the abrupt mass reduction shown in TG curve (Figure 2d). Negligible peaks in N 1s XPS spectra can be seen at around 400 eV for ESCS-AlOx annealed at 250 °C and 300 °C in Figure 3b, likely to be due to the organic byproducts. No peak was observed for 350 °C-AlOx indicating the full decomposition of the precursor solution. The DTA data for the ECS-AlOx precursor (Figure 2e) shows an intense exothermic peak at 170 °C and a wide peak at 200 °C corresponding to two abrupt mass losses finalized below 300 °C. N 1s peak was not observed for ECS-AlOx thin films annealed at 250 °C to 350 °C as can be seen from Figure 2h, which means nitrate-related groups were fully released before reaching 250 °C. On the other hand, in the case of the non-combustive AlOx precursor, a gradual mass loss is nearly completed at around 400 °C without any exothermic peaks (Figure 2c) and the existence of nitrate-related groups was confirmed by the N1s XPS spectra for all thin films (Figure 3). The structural characterization of the dielectric thin films was studied by XRD as shown in Figure 4a. Although both ECS and ESCS combustion methods provide additional energy during the annealing process, the amorphous structure was observed for all dielectric thin films, which is in agreement with a previously reported low-temperature solution-processed AlOx.35 Amorphous structure is preferred for TFT application because of leakage current and impurity diffusion attributed to grain boundaries acting as preferential paths, which results in poor dielectric electrical characteristic.24, 54 In addition, a smoother surface could be formed with an amorphous film compared with crystalline one, which enhances semiconductor/dielectric interface properties. SEM and AFM results shown in Figure S1 indicate compact and dense AlOx thin films annealed at 250 ℃ by ECS and ESCS methods. Both ECS-AlOx and ESCS-AlOx thin films exhibit smooth surface without evidence of pinhole and pore confirmed by the SEM results while AFM results indicate good surface morphology, which exhibits roughness standard deviation values of 0.18 nm for 250 °C-annealed ECS-AlOx thin film and 0.23 nm for ESCS-AlOx, which indicates uniform, dense and compact thin films.55 Additionally, XRD spectra of the active layer was presented in Figure S2, the In2O3 layers on AlOx showed nanocrystalline structures with a dominant peak at 31°corresponding to the (222) plane, which is inconsistent with previous reports of solution-processed In2O3 on high-k dielectrics.25 Further to the XRD structural characterization, the optical transmittance vs. wavelength spectra of the dielectric thin films were shown in Figure 4b and high average optical transmittance values over 90% in the visible range for both ECS and ESCS AlOx thin films were observed.

**MIS and TFT Electrical Performances**

Figure S3a-c show capacitance-frequency (*C-F*) characteristics for conventional AlOx, ESCS-AlOx, and ECS-AlOx MIS devices annealed at 250°C, 300°C, and 350°C with a measurement range from 1 kHz to 1 MHz. For conventional AlOx MIS devices, a higher capacitance value was observed for conventional devices at lower annealing temperatures compared with those conventional devices at higher annealing temperatures. Observed frequency dispersion of devices could be attributed to the existence of nitrate residuals and oxygen vacancy.56 Contrary to the conventional AlOx MIS devices, ECS-AlOx devices show negligible frequency dispersion and less difference in capacitance values between devices annealed at different temperatures (Fig. S1c) as a consequence of the low temperature required for the decomposition of combustion precursor. This result further substantiates the lower decomposition temperature of ECS-AlOx films seen by the TG-DSC (Fig. 1e) and XPS N 1s CL results (Fig. 1h). However, unexpected large frequency dispersion was observed in ESCS-AlOx device annealed at 250 °C, which might be attributed to the defect states as the result of organic by-products in low temperature annealed thin film.25, 56-57 Due to the existence of the frequency dispersion in C-F characteristics, the mobility calculated based on areal capacitance at 1 kHz might be overestimated.58 Several studies have demonstrated MOTFTs based on solution-processed high-*k* dielectrics with high mobilities over 100 cm2V-1s-1 using capacitance values measured at a high frequency. Daunis et al.59 reported a solution-processed TFT with mobility of 160 cm2V-1s-1 with a Ci at 10 kHz.59 Xu et al.60-61 reported a ZnInSnO TFT with mobility of 117 cm2V-1s-1 and Nayak et al.60-61 demonstrated an In2O3 TFT with mobility of 127 cm2V-1s-1, which both employed capacitance measured at 1 MHz for mobility derivation. For accurate estimation of the mobility derivation, X. Zhuang and T. J. Marks proposed measurement of capacitance values at low frequency by quasi-static capacitance measurement for solution-processed high-*k* dielectrics because the TFT transfer curve was usually measured at the quasi-static condition.62 Hence, in order to minimize the mobility overestimation due to the underestimated capacitance value, the quasi-static capacitance-voltage measurement (QSCV) with an integration time of 1 s and zero bias voltage was performed and used in mobility derivation, as shown in Table S2.

Based on the successful demonstration of ECS and ESCS methods to deposit solution-processed high-*k* AlOx dielectrics at low temperatures without using any organic toxic components, aqueous In2O3 semiconductor layers were then deposited on AlO­x dielectrics by water-based In­2O3 precursor. Here, a low-temperature eco-friendly route for solution combustion processed TFTs was successfully demonstrated based on the water precursor for the metal-oxide semiconductor and ethanol precursor for the dielectric. Figure 5 shows the transfer characteristics for aqueous In2O3 TFTs based on ECS-AlO­x and ESCS-AlOx formed at 250 °C, 300 °C, and 350 °C respectively. The control group of In2O3 TFTs based on conventional AlOx thin films was shown in Figure S4. Compared with TFTs with conventional AlOx with clockwise hysteresis and low mobility values annealed at indicated temperature, TFTs formed on ECS-AlOx and ESCS-AlOx show significant improving electrical performance For TFTs based ESCS-AlOx, 250 °C-annealed device shows low average mobility of 3.67 cm2V-1s-1 derived from the areal capacitance at 1k Hz, an on/off current ratio of ~5104, and a subthreshold swing (SS) of 0.34 V/decade. Devices based on ESCS-AlOx annealed at 300 °C exhibit impressively enhanced electrical characteristics with an on/off current ratio of ~1105, a SS of 0.21 V/decade, and average mobility of 59.08 cm2V-1s-1, as a consequence of the full decomposition of organic and nitrate residuals. The electrical performance of the TFT based on 350 °C ESCS-AlOx was further improved, showing an on/off current ratio of ~1.6105,a SS of 0.17 V/decade, and average mobility of 61.67 cm2V-1s-1. Compared with TFTs based on ESCS-AlOxfabricated at low temperature, ECS-AlOx at 250 °C shows better average mobility of 49.18 cm2V-1s-1. The devices based on ECS-AlOx at 300 °C show superior characteristics with an on/off current ratio around 2.8106, a SS of 0.25 V/decade, and mobility of 49.19 cm2V-1s-1. The electrical performance of TFT on ECS-AlOx annealed at 350 °C is optimal with an on/off current ratio of ~3.2106, a SS of 0.16 V/decade, and mobility of 72.99 cm2V-1s-1. The detailed analytical electrical characteristics for TFTs based on ESCS-AlOx and ECS-AlOx are depicted in Figure S4. Although mobility values over 50 cm2V-1s-1 were derived based on the areal capacitance value at 1 kHz (the minimum C-F frequency), the mobility might be overestimated due to the intrinsic origin of the related frequency dispersion as discussed above. Therefore, the quasi-static capacitance measurement with an integration time of 1 s was used. The areal capacitance values measured at quasi-static (QS) conditions were used for mobility derivation, as shown in Table S2. Then, the mobility values were found to be 3.67 cm2V-1s-1, 59.08 cm2V-1s-1, and 61.67 cm2V-1s-1, for ESCS TFTsannealed at 250 °C, 300 °C and 350 °C respectively, as well as 50.1 cm2V-1s-1, 49.1 cm2V-1s-1, and 74.62 cm2V-1s-1 for ECS TFTs annealed at 250°C, 300 °C and 350 °C respectively. Detailed statistical data for TFT electrical performance can be found in Table S3. Using QS capacitance values for mobility derivation can still give relatively larger mobilities than most of the reported values; it is worth mentioning that the transistors on ECS and ESCS gate dielectrics exhibit counterclockwise hysteresis, being commonly observed in high-mobility devices based on high-*k* dielectrics annealed at low temperature. Similar counterclockwise hysteresis in high-mobility solution-processed MOTFTs have been observed and their relationship has been investigated in few previous reports.63-64 Daunis et al. have considered water absorption as the origin of hysteresis and high mobility.64 It has been argued that electrons from defect states in high-*k* dielectric from solution process could transfer to the gate electrode by applying a positive gate voltage, while positive charges remained in the dielectric along with an increased electric field within the dielectric. This results in a higher carrier concentration induced within the active layer (within the semiconductor layer near dielectric), leading to an increased channel current induced by the positive gate bias.

Since the channel current modulated by the charge transfer induced by the bias voltage is comparable to the signal modulation by the neurotransmitters, the artificial synaptic functions are therefore emulated by the In2O3 transistors based on ECS-AlOx and ESCS-AlOx accordingly. In our brain, learning, memory, and computing functions are based on the basic unit – neuron and the synapse is the structure to permit a neuron to pass impulses between two neurons.3, 15 When the nerve impulse was received by the receiver of the presynaptic neuron, the presynaptic membrane releases the neurotransmitters contained in synaptic vesicles by the action of Ca ions. This process is followed by the diffusion of the neurotransmitters across the synapse cleft to the receptor on the postsynaptic membrane, which results in an excitatory postsynaptic current in the postsynaptic neuron. In a biological synapse, the nerve impulse transferred between the post and the pre-synaptic neurons can also weaken or strengthen the synaptic weight, and thus different event-dependent synaptic plasticity related to neural functions such as learning and memory in the neural system can be achieved.65 For artificial synaptic emulation performed by the synaptic transistor in this study, the presynaptic neuron receiver was emulated by the gate electrode to receive presynaptic nerve impulse signal and the receptor of the postsynaptic neuron was emulated by the drain electrode of the synaptic transistor. Then, the programmed presynaptic pulse signal can be received by the gate, and then the excitatory post-synaptic current can be received at the drain electrode, while the synaptic weight was represented by the measured channel conductance.

**4. Artificial Synaptic Emulation**

In this work, ECS-AlOx and ESCS-AlOx annealed at 250 °C were employed to perform synaptic emulation. Figure 6a presents the schematic diagram of the synaptic emulation by MOTFT in this study. The presynaptic signal was applied on the gate and a constant voltage VDS was applied on the drain. As a result, the channel current was induced and received as the EPSC. Additionally, synaptic weight (W) was represented by the measured conductance value between the drain and source electrodes, while the modulation in synaptic weight is recognized as the synaptic plasticity. As the foundation of the learning and memory in the neural system, synaptic plasticity is activity-dependent at both or either sides of the synapse.66-67 Typically, synaptic plasticity can be categorized into long-term plasticity (STP) and short-term plasticity (LTP).68 Short-term plasticity represents a volatile alteration of synaptic strength after stimulation that can be preserved for a few minutes to tens of milliseconds, while on the contrary, long-term plasticity corresponds to non-volatile alteration of synaptic strength which can sustain from hours to years.69-70 Short-term plasticity is mandatory for the information filtering, encoding, and transmission of the neural signal. Meanwhile, more permanent modification in the neural microcircuitry is achieved by long-term plasticity and thus memory and learning are based on it.70

In this work, paired-pulse facilitation (PPF), a typical short-term synaptic plasticity, was demonstrated firstly to emulate neural facilitation. In Figure 6b, PPF is performed based on ECS-AlOx and ESCS-AlOx TFTs to perform the synaptic short-term plasticity emulation. In the neural system, PPF represents the receptivity of temporary information in synapses and therefore indicates the short-term plasticity.17 The bottom gate was applied with two pulses in succession as presynaptic signals (the internal time of two pulses is represented by Δt), and a reading voltage was applied on the drain to receive the EPSC signal. Then, the PPF index is derived by extracting the ratio of the second presynaptic pulse EPSC over the first presynaptic pulse EPSC. For the aqueous synaptic transistors based on ECS-AlOx and ESCS-AlOx, the PPF index values increase to 1.41 and 1.18, respectively (interval time reduced to 10 ms). A double-phase exponential function could be used to exquisitely fit the PPF index curve as equation 3:

. (5)

Where A1 and A2 are the initial magnitudes, while and are the characteristic relaxation times of the first and second phases, respectively. The fitting / values were 49 ms/758 ms and 11 ms/421 ms for ECS-AlOx and ESCS-AlOx transistors respectively, being analogous to values previously reported for solution-processed synapses.17 To further study the short-term and long-term synaptic memory characteristics, the transistor based on ECS-AlOx is then characterized since a relatively lower off-current of ECS-AlOx based synaptic transistor would lead to lower power consumption and the effects of organic residuals on synaptic behavior could be minimized accordingly. The long-term potentiation and short-term potentiation behaviors of the ECS synaptic transistor were further emulated. Consecutive pulses with various interval times, amplitudes, pulse numbers, and widths were then applied on the gate electrode. As shown in Figure 6c, the transistor modulated by 5 consecutive pulses (1 V) shows short term potentiation behavior with large EPSCs over 200 µA; note that the EPSC decays to the initial state soon after removing the stimulus with the amplitude of 1 V. The EPSCs can be further enhanced over 500 µA with a 1.5 V pulse amplitude, which is attributed to the high mobility of the transistor. While the pre-synaptic pulse is further increased to 2 V, the potentiation induced by each pulse can be preserved and activate the next potentiation, which indicated a long-term potentiation behavior. Besides, pulse width modulation to achieve short-term and long-term potentiation was also investigated by modifying the width of a single pulse from 20 ms to 1.5 s, as shown in Figure 7a. With the increase of single pulse width, the EPSC spike was further enhanced and long term potentiation was then achieved with duration over 400 ms and a comparatively low pulse amplitude of 0.8 V. Long term potentiation was also realized by increasing the continuous pulse number, as shown in Figure 7b. It can be seen that long-term potentiation behavior is observed clearly by applying a continuous pre-synaptic signal with pulse number over 10. In addition to potentiation memory behavior, depression behavior was also investigated in the synaptic transistor and synaptic depression could be achieved by applying negative pre-synaptic signal. As shown in Figure 7c, by applying negative five pairs of presynaptic spikes (-0.5 V), short-term depression was realized. Another important synaptic plasticity, such as spike-timing-dependent plasticity (STDP) is emulated as shown in Figure 7c inset. Five sequential combinations of one presynaptic spike and one postsynaptic spike with an interval time were received by the gate and drain, respectively. If the presynaptic spike was applied prior to the postsynaptic spike, the synaptic weight will gain. On the contrary, if the presynaptic spike was applied later than the postsynaptic spike, the synaptic weight will be reduced accordingly. The channel current is read before and after STDP modulation (I0 and I5) and the I5/I0 ratio reflects the synaptic plasticity. The potentiation is induced under the presynaptic signal before the postsynaptic signal and the ratio increases with interval time decreasing. On the contrary, depression is then induced under the presynaptic after the postsynaptic spike.

Based on the successful demonstration of potentiation and depression synaptic emulation based on ECS-AlOx devices, to further achieve neuromorphic computing, potentiation and depression behaviors of synapses were simulated. By applying 20 positive pulses and 20 negative pulses, synaptic weight reflected by the channel conductance was increased and then decreased, which achieve long-term potentiation and long-term depression, respectively, as presented in Figure 7d. Over 200 pulses of potentiation and depression have been made in the ECS-AlOx based synaptic transistor to evaluate the reproducibility of the synapses, as shown in Figure 8a. The synaptic weight modulation shows superior consistency within 250 pulses of potentiation and depression. Furthermore, a neural network structure with an artificial neural network (ANN) structure has been demonstrated in Figure 8b. ANN is usually called as neural networks or just multi-layer perceptron (MLP) – an artificial neural network mode mapping sets of input data into a set of appropriate output. A classical MLP is composed of an input layer receiving the signal, an output layer outputting the decision, and numbers of hidden layers between input and output layers. As a fully connected neural network, each neuron node in one layer is connected to every node in the next node. MLP trains on a set of input-output pairs, and learns to optimize the correlation between the inputs and outputs. For our case, the input set consists of a 28\*28-pixel image, which includes 784 inputs, while the output consists of 10 neurons corresponding to 0-9 digit. Modified National Institute of Standards and Technology (MNIST) digital images or pattern recognition was simulated based on potentiation and depression behavior to analog the training performance of ECS-AlOx synaptic transistors. As shown in Figure 8b, 28×28 input neurons (28×28 image pixels) in the synapse layer are included in the input pattern. A synapse was used to connect two neuron nodes from each layer and their connection or correlation strength can be represented by synaptic weight, which is dynamic modulated based on our synaptic device. More simulation details can be found in the supporting materials. The simulation read the input image of 28×28 pixels from MNIST data set and achieve image recognition utilizing 784 input neurons, 100 neurons within the hidden layer, and 10 output neurons corresponding to 0-9. The simulator could reach 85% recognition accuracy after 3000 learning cycles, and finally reached a recognition rate of over 90% (Figure 8c). The output digit ‘3’ was plotted in the mapping images (28×28 pixels) presented in Figure 8d. After a period of learning epochs (Figure 8e), the digit “3” was initially recognized in progress. After more learning epochs, the figure of ‘3’ was distinguished more clearly and the recognition rate finally reached 90 % as shown in Figure 8f. To evaluate the characteristics of pattern recognition, recognition accuracy is the significant criteria to evaluate the characteristics of pattern recognition, which reflects the identification of the environment by the artificial intelligence system instead of a human neural network. For an artificial neural network in a robot or a computing system, high recognition accuracy is crucial for efficient information processing. In this work, the remarkable synaptic emulation based on solution-processed synaptic transistor indicated by the high accuracy after training in pattern recognition indicates it has the potential to be a promising candidate for the artificial neural network in a low-cost and eco-friendly route.

**5. Conclusions**

In summary, the eco-friendly combustion and self-combustion methods have been successfully developed to form high-kAlOx dielectrics at low temperatures and applied for aqueous In2O3 thin-film transistors respectively. Confirmed by thermal analysis and chemical composition characterization, the ECS and ESCS processes facilitate the formation of high-quality dielectrics at lower temperatures than conventional dielectrics. The electrical characteristics of TFTs based on ECS and ESCS AlOx show enhanced electrical characteristics, while counterclockwise hysteresis was also observed in the transfer curve attributed to donor-like electron traps within the AlOx even at low annealing temperatures. Considering the electrical behavior, synaptic emulation was performed to analog the specified synapse application. Various short-term memory and long-term memory functions, including PPF, STP, LTP, LTD, and STDP, were emulated with low operating voltages and high excitatory postsynaptic currents levels. Based on the demonstration of synaptic potentiation and depression, a MLP was finally developed to recognize the handwritten image, which achieved excellent recognition accuracy and reproducibility. Successful image recognition and high recognition accuracy have been achieved based on the ECS synaptic transistor synaptic emulation. Compared with recent advances on solution-processed metal-oxide synaptic transistor shown in Table S4, an eco-friendly synaptic transistor with various synaptic emulation functions was achieved while high electrical performance was preserved, and its application for ANN was tested through a MLP simulation. As summarized in Table S4, this study enables a diversified eco-friendly route for synaptic transistors with high electrical performance and all-round synaptic functions. The results show promising applications of high-performance eco-friendly solution-processed metal oxide synaptic transistors for future artificial neural networks and neuromorphic computing.

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**Figure 1.** Eco-friendly process flow for solution-processed metal-oxide transistors with solution combustion processed high-*k* AlOx dielectrics.



**Figure 2.** (a) Schematic illustration of the combustion process for the fabrication of the dielectric thin films; (b) Energetics of the combustion process vs. conventional solution process; TG-DSC analysis of (c) conventional AlOx, (d) ESCS-AlOx, and (e) ECS-AlO­x.



**Figure 3.** XPS N 1s CL spectra for (a) conventional AlOx, (b) ESCS-AlOx, and (c) ECS-AlOx annealed at indicated temperatures.

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**Figure 4.** (a) XRD spectra of the AlOx, ECS-AlOx, ESCS-AlOx, and In2O3/dielectric thin films deposited on quartz substrates. (b) UV-vis optical transparency spectra for various dielectric and semiconductor/dielectric thin films on quartz substrates.

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**Figure 5.** Transfer characteristics for In2O3 TFTs based on ESCS-AlOx annealed at (a) 250 ℃, (b) 300 ℃, and (c) 350 ℃; Transfer characteristics for In2O3 TFTs based on ECS-AlOx annealed at (d) 250 ℃, (e) 300 ℃, and (f) 350 ℃.

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**Figure 6. (a)** Setup of the pre-synapse and post-synapse for the synaptic simulation and the functional connections between biological neurons. (b) PPF index as a function of the interval time for synaptic transistors based on ECS-AlOx and ESCS-AlOx annealed at 300 ℃. (c) EPSCs stimulated by positive pulses with various amplitudes to realize STP and LTP.

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**Figure 7.** (a) EPSCs stimulated by negative pulses to achieve STD. The inset shows STDP simulation results. (b) EPSCs modulated by positive pulses with various pulse widths to realize STP and LTP. (c) EPSCs stimulated by positive pulses with various pulse numbers to realize STP and LTP.; (d) Synaptic plasticity modulated by consecutive positive pulses to achieve remember behavior (potentiation) and consecutive negative pulses to achieve forgetting behavior (depression).



**Figure 8.** (a) Synaptic weights modulation for 240 pulses; (b) Hierarchical neural network for pattern recognition of 28 × 28 images with the input and output neurons; (c) Learning accuracy for numbers of weight bits; (d) Mapping images with different synaptic weight updates as an increase of learning epochs. (e) – (f) Mapping images with updating synaptic weights.

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**Supporting Information.** SEM and AFM images of dielectric thin films; XRD spectra of In2O3 thin films; C-F characteristics of dielectric thin films; transfer characteristics of TFTs based on conventional AlOx; analytical data for TFT electrical performance; thickness data and quasi-static areal capacitance values for dielectrics; summary of recent advances on solution-processed metal-oxide synaptic transistors; synaptic emulation experimental details; ANN simulation experimental details.

ABBREVIATIONS

ECS, eco-friendly combustion synthesis; ESCS eco-friendly self-combustion synthesis; MOTFTs, Metal oxide thin-film transistors; high-k, high dielectric constant; TFTs, thin-film transistors; IZO, In-Zn-O; ZTO, Zn-Sn-O; IGZO, In-Ga-Zn-O; CS, combustion synthesis; PPF, paired-pulse facilitation; STP, short term potentiation; LTP, long term potentiation; STDP, spike-timing-dependent plasticity; STM, short-term memory; LTM, long-term memory; AlOx, aluminum oxides; TG-DTA, thermogravimetric and differential scanning calorimetry; XRD, x-ray diffraction; C-F, capacitance-frequency; QS, quasi-static; ANN, artificial neural network; MLP, multi-layer perceptron; MNIST, Modified National Institute of Standards and Technology; AFM, atomic force microscopy; FTIR, Fourier Transform Infra-Red; XPS, X-ray photoelectron spectroscopy.

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