ACS APPLIED MATERIALS & INTERFACES

www.acsami.org

Research Article

Mechanochemical and Thermal Treatment for Surface Functionalization to Reduce the Activation Temperature of In-Ga-Zn-O Thin-film Transistors

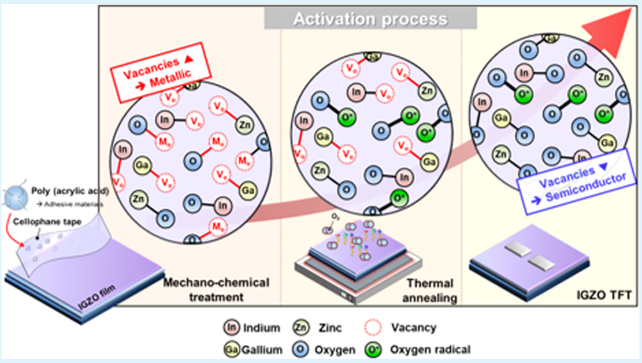
I. Sak Lee,[†] Young Jun Tak,[†] Byung Ha Kang, Hyukjoon Yoo, Sujin Jung, and Hyun Jae Kim*

Cite This: *ACS Appl. Mater. Interfaces* 2020, 12, 19123−19129

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Amorphous indium-gallium-zinc oxide (a-IGZO) films, which are widely regarded as a promising material for the channel layer in thin-film transistors (TFTs), require a relatively high thermal annealing temperature to achieve switching characteristics through the formation of metal−oxygen (M−O) bonding (i.e., the activation process). The activation process is usually carried out at a temperature above 300 °C; however, achieving activation at lower temperatures is essential for realizing flexible display technologies. Here, a facile, low-cost, and novel technique using cellophane tape for the activation of a-IGZO films at a low annealing temperature is reported. In terms of mechanochemistry, mechanical pulling of the cellophane tape induces reactive radicals on the a-IGZO film surface, which can give rise to improvements in the properties of the a-IGZO films, leading to an increase in the number of M−O bonds and the carrier concentration via radical reactions, even at 200 °C. As a result, the a-IGZO TFTs, compared to conventionally annealed a-IGZO TFTs, exhibited improved electrical performances, such as mobility, on/off current ratio, and threshold voltage shift (under positive bias temperature and negative bias temperature stress for 10,000 s at 50 °C) from 8.25 to 12.81 $cm^2/(V{\cdot}s)$, 2.85×10^7 to 1.21×10^8, 6.81 to 3.24 V, and −6.68 to −4.93 V, respectively.



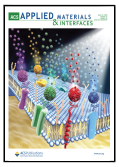
KEYWORDS: *indium-gallium-zinc oxide, mechanochemical, organic radical, surface charge, surface functionalization*

1. INTRODUCTION

In recent years, evolving technologies based on flexible, low-cost, and easily fabricated electronics have been extensively studied because of their promising prospect in display and sensors.[1−5] Accordingly, the interest in these technologies has mainly focused on thin-film transistors (TFTs), which are considered one of the most fundamental devices used within display backplanes. In particular, amorphous indium-gallium-zinc oxide (a-IGZO) TFTs have attracted much attention for next-generation display devices because of their superior performance compared to conventional amorphous silicon TFTs across a number of parameters: high field-effect mobility, high uniformity over large areas, low leakage current, and high transparency in the visible light.[6−8] Despite these advantages, there are still some challenges to the use of a-IGZO TFTs in wearable, flexible display devices. One of the main issues is a high-temperature annealing process (>300 °C)[9] because the a-IGZO film deposited by sputtering requires a thermal annealing process (i.e., the activation process) to obtain proper electrical characteristics. However, the high-temperature activation process damages flexible substrates such as poly(ethersulfone) (PES), poly(etheretherketone) (PEEK), and poly(ethylene naphthalate) (PEN), which have a relatively low glass-transition temperature.[10] To overcome this problem, several studies have been proposed for low-temperature activation processes using additional external energy such as chemical combustion processes, the use of microwave radiation, and high-pressure annealing, to achieve switching characteristics at temperatures below 300 °C.[11−13] However, these methods require a relatively complicated fabrication process or expensive equipment. Additionally, these complex fabrication processes cannot be applied to selective area treatment, which may limit the diversity of a-IGZO TFT-based applications.

In this study, we propose a facile method to reduce temperature for the activation process of a-IGZO film just using a cellophane tape, which is commonly used in everyday life. With simple taping and detaching on a-IGZO film, it is

Received: December 17, 2019
Accepted: March 31, 2020
Published: March 31, 2020



https://dx.doi.org/10.1021/acsami.9b22831

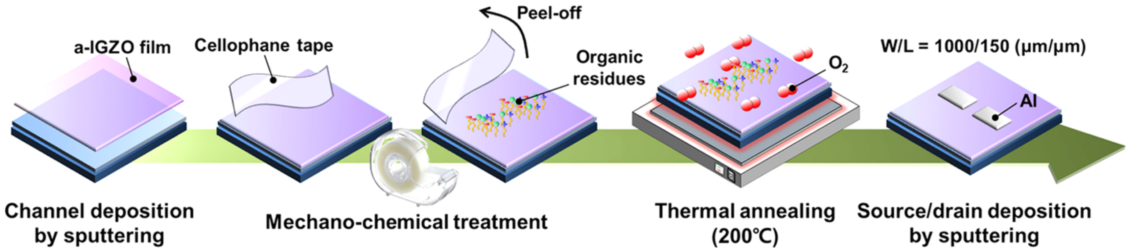


Figure 1. Fabrication process of a-IGZO TFTs with mechanochemical treatment using cellophane tape to reduce activation temperature.

possible to perform the activation process at low temperature without external energy. From this technique, we were able to discuss two effects of unstable radical species formed by functionalization: (1) through the reaction of a-IGZO films with radical species, the annealing temperature of the a-IGZO film could be lowered compared to the conventional process temperature of the a-IGZO film used in commercialized display backplanes (>300 °C) and (2) the improvement of electrical characteristics especially reliability due to the generation of negatively charged species. In addition, we are the first team to demonstrate the connection between oxide thin films and the mechanochemical phenomenon. Furthermore, we are able to say that our method has the potential to be used in various applications by selectively taping only desired areas of a-IGZO films.

2. EXPERIMENTAL SECTION

2.1. Device Fabrication. Figure 1 shows the fabrication process flow of a-IGZO TFTs. To fabricate a-IGZO TFTs with an inverted staggered structure, heavily doped p^+-type Si wafers with 120 nm thick thermally oxidized SiO_2 were prepared. After cleaning the substrate, we deposited the a-IGZO channel layer on SiO_2 with a shadow mask on top by radio frequency (RF) magnetron sputtering at room temperature using an $In_2O_3-Ga_2O_3-ZnO$ (molar ratio 1:1:1) sputtering target. The sputtering power, chamber working pressure, and time of the channel deposition were set at 150 W, 5.0×10^{-3} torr, and 5 min, respectively. After the tape was attached on the channel surface and peeled off in three cycles at 1 cm/s speed (Figure S1, Supporting Information), activation of a-IGZO film was performed in air for 1 h using a hot plate. The activation temperature range was set from 100 to 300 °C (Figure S1, Supporting Information). Finally, aluminum (200 nm thick) source/drain electrodes were deposited by RF magnetron sputtering with a shadow mask. The width and length of the channel (W/L) were 1,000 and 150 μm, respectively.

2.2. Analysis Method for Thin-Film Characteristics. The transfer characteristics of the a-IGZO TFTs were measured with a parameter analyzer (4156C; Hewlett-Packard). The a-IGZO TFTs were measured with V_g sweep from −30 to 30 V, with a V_D of 10 V. To analyze the stability of the a-IGZO TFTs, a positive bias temperature stress (PBTS) test was conducted under $V_G = 20$ V, $V_D =$ 10 V, and temperature = 50 °C for 10,000 s. In addition, a negative bias temperature stress (NBTS) test was performed under $V_G = -20$ V, V_D = 10 V, and temperature = 50 °C for 10,000 s. Fourier transform infrared (FT-IR) (Jasco 6800) spectroscopy was used to measure the organic residues on the surface within the range of 1,000−4,000 cm^{-1}. The X-ray photoelectron spectroscopy (XPS) spectra were obtained in a constant analyzer energy mode at 50 eV with an Al Kα source. The surface morphology and distribution were studied with atomic force microscopy (AFM) (Park NX10; Park Systems).

3. RESULTS AND DISCUSSION

The process flow for the realization of a-IGZO TFTs using mechanochemical and thermal annealing (MCT) treatment is shown in Figure 1. Before thermal annealing, we performed a mechanochemical treatment using cellophane tape by simple sticking and pulling, which can leave organic residues on the surface of the a-IGZO film. Subsequently, the mechanochemical-treated a-IGZO film was annealed at 200 °C for activation. In this process, we analyzed the physical surface properties of the a-IGZO film before and after the mechanochemical treatment.

Figure 2 shows the surface analyses of the a-IGZO film according to the mechanochemical treatment. Surface images before and after mechanochemical treatment on the as-deposited a-IGZO film were first investigated by scanning electron microscopy (SEM), as shown in Figure 2a, b, respectively. As a result, it is clearly confirmed that the surface of the a-IGZO film with mechanochemical treatment had organic residues within the size ranges from a few nanometers, which appeared to have been transferred from the cellophane tape to the a-IGZO surface, as shown in Figure 2b. In parallel, to investigate transferred organic residues in more detail, the phase was analyzed using an atomic force microscope (AFM), as shown in Figure 2c, d; the phase image can vividly exhibit the image of a heterogeneous surface with different mechanical and adhesion properties.[14,15] As shown in Figure 2c, the surface of the untreated a-IGZO film was rather smooth with a relatively uniform phase distribution; however, according to Figure 2d, in the treated a-IGZO film, there were sharp peaks in the surface phase distribution due to the formation of organic residues. Therefore, we verified that the organic residues transferred from the cellophane tape to the

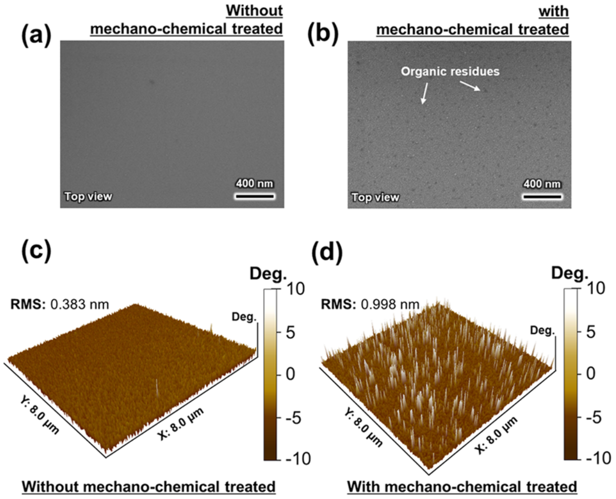


Figure 2. Surface analysis of the a-IGZO film: SEM images (a) without mechanochemical treatment and (b) mechanochemical treatment; AFM phase images (c) without mechanochemical treatment and (d) with mechanochemical treatment.

surface of the a-IGZO film. We also compared the surface properties of the untreated and treated a-IGZO films after thermal annealing through SEM and AFM phase images. Interestingly, organic residues could not be observed after thermal annealing, indicating that the organic residues disappeared (Figures S2 and S3, Supporting Information). From these results, we investigated two possibilities: that the organic residues either reacted with the a-IGZO film or evaporated. Meanwhile, we analyzed the effects of the organic residues on the properties of the a-IGZO film annealed at various temperatures. In this case, if the organic residues reacted with the a-IGZO film, the properties of the film would be changed; however, if the organic residues simply evaporated, there would be no observable effects on the film. Therefore, the electrical characteristics were evaluated to verify whether the organic residues affected the a-IGZO film after annealing.

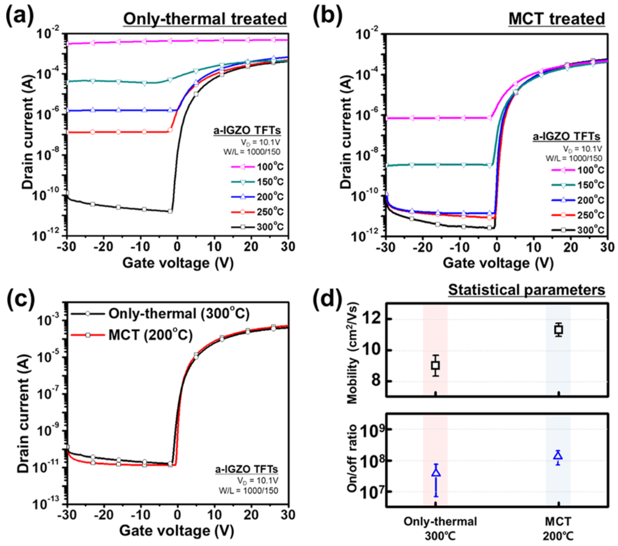


Figure 3. Transfer characteristics of the a-IGZO TFTs with (a) only-thermal-treated and (b) MCT-treated samples, (c) comparisons of only-thermal (300 °C)- with MCT (200 °C)-treated samples, and (d) statistical parameters including mobility and on/off current ratio of only-thermal (300 °C)- and MCT (200 °C)-treated a-IGZO TFTs.

Figure 3a, b indicates the transfer characteristics of the a-IGZO TFTs with the only-thermal and the MCT treatment as a function of temperature, respectively. As shown in Figure 3a, the only-thermal-treated a-IGZO TFTs annealed at below 250 °C did not exhibit sufficient on/off current ratios for applications as switching devices (i.e., > 10^6).[16,17] Thus, we confirmed that a-IGZO films eventually achieve a proper switching characteristic above 300 °C with thermal treatment, indicating that sufficient formation of metal−oxygen (M−O) bonding requires at least 300 °C of external energy to activate the a-IGZO film. In contrast, the MCT-treated a-IGZO TFTs exhibited effective reduction of the off current at 200 °C, as shown in Figure 3b. Furthermore, the switching characteristics of the a-IGZO TFT with MCT treatment at 200 °C were comparable to those of the a-IGZO TFT with thermal treatment at 300 °C, as shown in Figure 3b. From these results, Figure 3c represents the transfer characteristics of a-IGZO TFTs with only-thermal and MCT treatment, respectively. In this case, both "only-thermal (300 °C)"- and "MCT (200 °C)"-treated a-IGZO TFTs exhibit semiconducting characteristics. Notably, the MCT (200 °C)-treated a-IGZO TFT showed proper electrical characteristics for application as a switching device, even below 300 °C. Furthermore, the on/off current ratio and subthreshold swing (SS) values of MCT (200 °C)-treated a-IGZO TFTs were comparable to those of only-thermal (300 °C)-treated a-IGZO TFTs, as shown in Table S1 (Supporting Information). Figure 3d shows the statistical parameters including the field-effect mobility (μ_{FET}) and on/off current ratio of only-thermal and MCT-treated a-IGZO TFTs, respectively. These results indicate that MCT treatment can be possible with low-temperature processing by activating the a-IGZO films at a lower temperature and providing better electrical characteristics. In addition, from the results of applying various kinds of tape in this technique, we could confirm that the amount of adhesive material was an important factor in the experiment (Figure S4, Supporting Information).

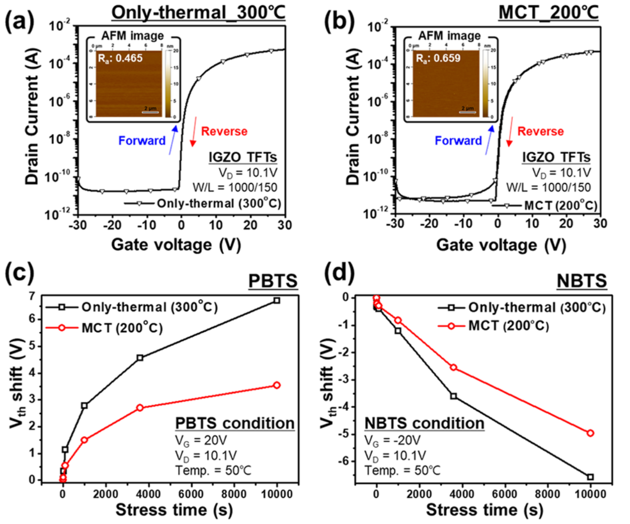


Figure 4. Hysteresis characteristics of a-IGZO TFTs for (a) only-thermal samples at 300 °C and (b) MCT samples at 200 °C. The inset shows the AFM image of the thermal-treated IGZO film. Time-dependent plots showing the positive and negative V_{th} shifts of the only-thermal (at 300 °C)- and MCT (at 200 °C)-treated a-IGZO TFTs: (c) positive bias temperature stress test and (d) negative bias temperature stress test.

To investigate changes in electrical stability due to MCT treatment, we performed various stability tests such as stability of the hysteresis loop, the voltage bias, and the temperature. From the hysteresis results, shown in Figure 4a, b, both the only-thermal and the MCT treatment of devices show clockwise hysteresis, which is as small as 0.1 V of window even under a higher gate sweep voltage of ±30 V. This negligible hysteresis of both only-thermal- and MCT-treated a-IGZO TFTs demonstrates that MCT treatment does not lead to electron trapping or charge migration within the back-channel region through hysteresis curves on a linear scale (Figure S5, Supporting Information).[18] From these results, the MCT-treated a-IGZO films were comparable to the only-thermal-treated films at 300 °C. To further evaluate the stability, we investigated the effect of the MCT treatment of a-IGZO film under long-term stress and positive and negative bias temperature stress (PBTS and NBTS, respectively). As shown in Figure 4c,d, the threshold voltage (V_{th}) shift of MCT-treated a-IGZO TFT was less than that of thermal-treated a-IGZO TFT under both PBTS and NBTS. In detail,

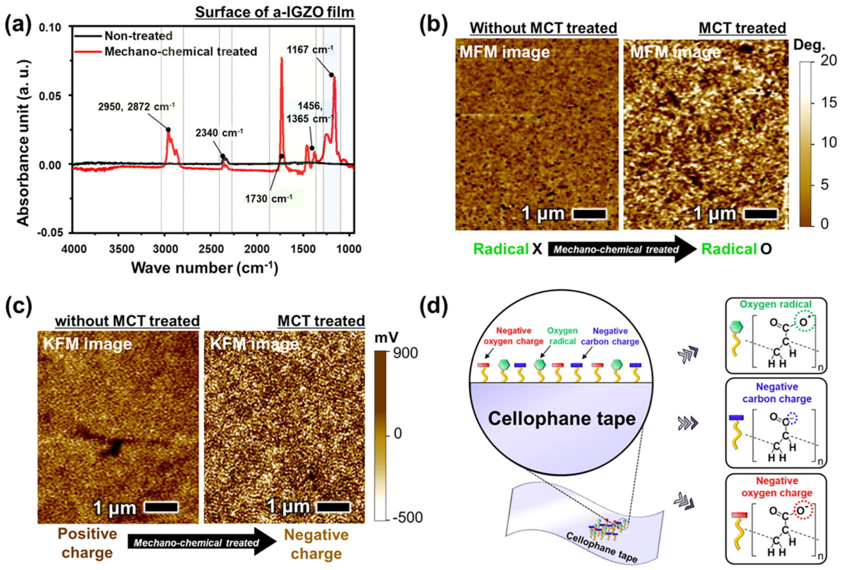


Figure 5. (a) ATR FT-IR spectroscopy on the surface of nontreated (black line) and mechanochemical-treated (red line) IGZO films, (b) MFM map imaging the presence of mechanoradicals (white spots). (c) KFM map evidencing the negative charge comprising both oxygen and carbon atoms (white spots). (d) Schematic illustration of mechanochemical residues composed of polyacrylate on cellophane tape.

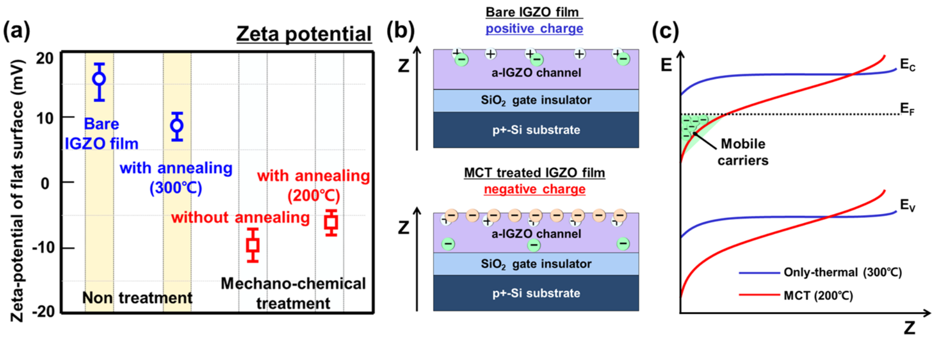


Figure 6. (a) ζ-potential profiles of various a-IGZO samples. (b) Schematic illustration of interfacial charge states. The red spots represent the mobile charge at the interface. (c) Energy band diagram by the mechanochemical-treated a-IGZO film.

the V_{th} shifts of the thermal- and MCT-treated a-IGZO TFTs decreased from +6.81 to +3.24 V under the PBTS test and from −6.68 to −4.93 V under the NBTS test. Furthermore, as shown in Figure S6, it was confirmed that the electrical properties of the devices fabricated at a temperature higher than 200 °C were not degraded. Since the process temperature of the oxide TFT used in the industrial display is commonly below 300 °C, we set the highest annealing temperature to 300 °C. Two possible mechanisms of instability could explain these results: (1) the defect creation model and (2) the charge trapping model. In the defect creation model, the turn-on voltage (V_{on}) shift and change in the SS value are caused by bias and temperature stress generating trap sites.[19,20] However, the SS value did not change with stress time (Figure S6, Supporting Information). Therefore, the defect creation model could be excluded, and charge trapping should be considered instead.[21] Because the MCT treatment was performed only at the back-channel region, a negative charge trap could be considered for the adsorption of molecules from the environment in the back-channel surface. Note that the MCT treatment can result in the formation of organic residues on the surface of the a-IGZO film, which can react with the a-IGZO film rather than evaporating during thermal annealing. As a result, MCT treatment reduces the adsorption of environment gas molecules such as H_2O and O_2 through the formation of hydrophobic carbon groups such as −CO and −COO on the surface.[22] In addition, the organic residues can change the potential of the back-channel surface from positive to negative and prevent the adsorption of $-OH^-$ species.[23] For the verification of two effects, the additional surface analysis was performed as shown.

Figure 5a represents the attenuated total reflectance Fourier transform infrared (ATR FT-IR) absorption spectrum in the range of 1,000−4,000 cm^{-1} for the MCT-treated a-IGZO films to investigate the composition of the organic residues. From a mechanochemistry perspective, peeling off the cellophane tape could result in the breakage of organic bonds (i.e., weak van der Waals bonds) and the generation of surface charges. As a result, we observed the four sharp peaks identified, which resulted from polyacrylates within the adhesive surface of the cellophane tape.[24,25] This indicated that the organic residues were composed of the above-mentioned carbon groups (i.e., −CO and −COO groups). At a microscale, magnetic force microscopy (MFM) provides evidence for the distribution of magnetism by measuring the magnetostatics coupling between a magnetized probe-tip and the surface of the sample. In this case, the separation of the adhesive materials and the tape can result in bond cleavage that can generate surface radicals that

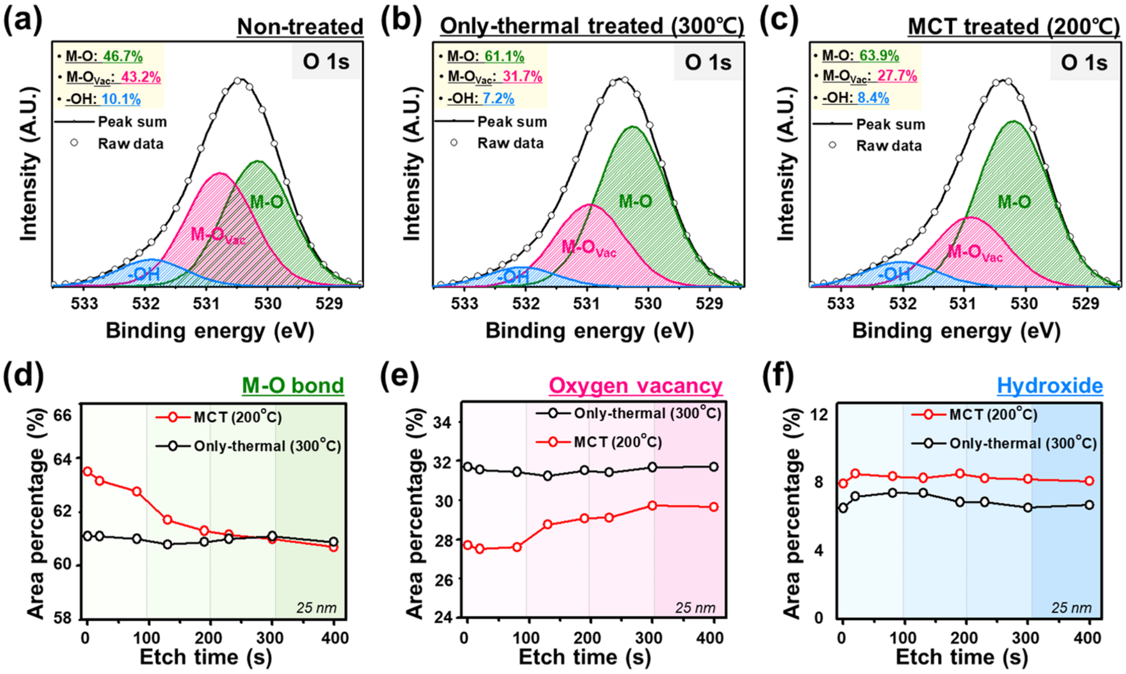


Figure 7. XPS-surface O 1s spectrum analysis for the a-IGZO films: (a) nontreated, (b) only-thermal (300 °C)-treated, and (c) MCT (200 °C)-treated films. XPS-depth spectrum analysis for the a-IGZO films: (d) metal−oxygen bonding, (e) oxygen vacancy, and (f) hydroxide bonding.

can be visualized by MFM.[26,27] As a result, the surface of the a-IGZO film without MCT treatment and little surface magnetism was reversed after MCT treatment, as shown in Figure 5b. Similarly, the charge distribution of the surface was confirmed by Kelvin force microscopy (KFM) analysis. Figure 5c shows that organic residues can change the charge distribution on the surface of the a-IGZO film. In the case of the a-IGZO film without MCT treatment, the thin film has a uniform positive potential. On the other hand, the surface of the MCT-treated a-IGZO film changes appreciably, which has a negative potential due to the organic residues formed by the MCT treatment. Consequently, Figure 5d is a schematic representation of the results from FT-IR, MFM, and KFM analyses, which can be verified to characterize the organic residues formed on the surface of the films.

To further unveil the mechanism of the charge effect of MCT treatment, the surfaces were characterized by a ζ-potential analysis, which can measure the quantitative data on the magnitude of surface charge. As shown in Figure 6a, the surface of the untreated a-IGZO film had a positive ζ-potential (18.56 mV). After thermal annealing at 300 °C, the value was reduced (8.72 mV) but maintained a positive ζ-potential. In contrast, after the MCT treatment, the surface of the a-IGZO film had a negative ζ-potential (−10.68 mV), and after 200 °C thermal annealing, the magnitude was reduced although the ζ-potential remained negative (−8.45 mV). Consistent with the previous report, the surface potential of nontreated a-IGZO films has a positive value, but we have noticed that the surface potential of the mechanochemical-treated a-IGZO film changed to a negative potential.[28] As could be seen from KFM imaging, the organic residues formed by mechanochemical treatment have immobile negative charges (Figure 5c). Therefore, the immobile negative charges on the surface of the a-IGZO film imposed an electrical field from the back channel, which could lead to the repulsion of the trapped electrons to the front channel, as shown in Figure 6b. As shown in the energy band diagram of Figure 6c, the band bending is induced by the surface potential because of the negatively charged organic residues at the surface of the a-IGZO layer and the energy bands bending upward for an n-type semiconductor.[29] Electrons accumulated at the interface between the channel and the insulator layer due to the field-effect-induced band bending from the surface of the MCT-treated a-IGZO film. Electrons are enough to fill trap sites and thus Fermi energy (E_F) pinning is eliminated in TFTs.[30] In this case, the trapping in the a-IGZO layer significantly decreased, known as field-effect passivation.[31] Hence, more electrons will accumulate at the same gate voltage, which can be expected to have higher carrier mobility.

To investigate this mechanism of radical reaction, we used X-ray photoelectron spectroscopy (XPS) to characterize the a-IGZO films. Figure 7a−c shows the O 1s peaks of the XPS images for the a-IGZO films under nontreated, only-thermal-treated, and MCT-treated conditions. The results of the XPS O 1s spectra can be used to index the change in oxide bonding composition. In particular, the relative M−O bonding, metal−oxygen vacancy (M−O$_{vac}$) bonding, and the oxygen−hydrogen (−OH) bonding peak value (%) can be extracted by deconvolution of the spectrum using a Gaussian distribution. In this case, the O 1s peaks were located at 530.2 ± 0.2, 530.8 ± 0.1, and 531.9 ± 0.2 eV.[32] In the nontreated a-IGZO films (M−O: 46.7%, M−O$_{vac}$: 43.2%), the peak of M−O bonding was lower and that corresponding to oxygen vacancy was higher than those for thermal-treated (M−O: 61.1%, M−O$_{vac}$: 31.7%) and MCT-treated (M−O: 63.9%, M−O$_{vac}$: 27.7%) a-IGZO films. Thus, the nontreated a-IGZO films had many oxygen vacancies, which means that the bond between the metal and the oxygen was not consolidated. However, the only-thermal- and MCT-treated a-IGZO films had a greater number of M−O bonds and a small M−O$_{vac}$ value compared to the nontreated a-IGZO films; both the only-thermal- and MCT-treated a-IGZO films were considered to have been oxidized sufficiently for activation. Furthermore, the MCT-treated a-IGZO films at 200 °C indicated a slight increase in the value of M−O bonding and a decreased value of $M-O_{vac}$, compared to the only-thermal-treated a-IGZO films (M−O increased from 61.1 to 63.9%, and $M-O_{vac}$ decreased from 31.7 to 27.7%). This demonstrates that a-IGZO films treated by an MCT treatment, even below 200 °C, were as effective as those activated at a high temperature of 300 °C. The increase in the value of M−O bonding, which generates carrier pathways for electron, was caused by the increase in organic residues in cellophane tape through the application of the MCT treatment. Then, the effect of MCT treatment was maintained with film depth, as shown in Figure 7d−f. Furthermore, the $M-O_{vac}$ value rapidly decreased in the area between the back- and front-channel regions by the radical oxidation, as shown in Figure 7e. Similar to the $M-O_{vac}$ value, it was found that the M−O value rapidly increases in the area between the back- and front-channel regions by the radical oxidation. Therefore, oxygen radicals can affect the back-channel area in a-IGZO films through reactions.

The chemical mechanism of MCT activation is illustrated in Figure 8. We previously reported these $O^{\bullet}$ radicals as a chemically reactive species with larger free energy than other species (i.e., O^- and C^-).[33] Hence, the mechanochemical treatment generates oxygen radicals, and the concurrent thermal annealing not only induces the generation of the M−O bonds but also promotes the reaction of O* radicals with vacancy sites, including oxygen vacancies and interstitial cations. Consequently, the MCT treatment improved film quality by increasing the number of M−O bonds and decreasing the number of defect sites.

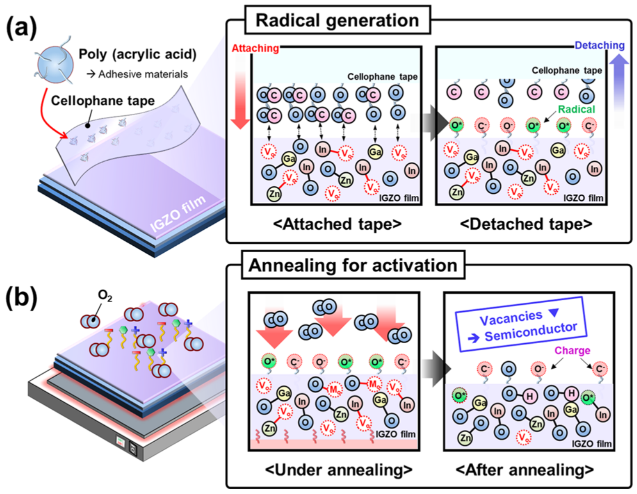


Figure 8. Illustration of the radical and annealing treatment mechanism for the activation of a-IGZO films using MCT treatment. MCT-treated a-IGZO films underwent (a) generation of radical species (due to mechanical peeling-off and decomposition of weak organic bonds) and (b) increase of metal−oxygen bonding (oxygen radical reaction with thermal annealing).

Additionally, the MCT treatment could be applied to large-scale electronics and specific areas for selective activation, respectively (Figures S8 and S9, and associated text, Supporting Information). Through this activation, the MCT treatment is simpler and requires less processing costs than conventional activation methods that require additional masks.

4. CONCLUSIONS

In this study, we successfully demonstrated a facile, novel MCT treatment for reducing the activation temperature of a-IGZO thin films. In addition, a comprehensive investigation based on surface analyses and electrical measurements was conducted to evaluate the underlying mechanisms based on radical and surface charge formation and moderate-temperature thermal annealing. Our findings showed mechanochemical-based activation to be efficient in generating M−O bonds and inducing surface potential. In addition, the approach enhanced the electrical characteristics and the stability of the MCT-treated a-IGZO TFTs at 200 °C compared to a-IGZO TFTs with thermal annealing at 300 °C. This indicates that the a-IGZO film can be activated using an easy low-temperature MCT method for application to various flexible substrates. Finally, selective area activation can minimize damage to the substrate, which is expected to be of use in various flexible and wearable device applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b22831.

Additional SEM images and AFM images of conventional and MCT-treated IGZO TFTs; electrical stability of all of the a-IGZO TFTs; and PBTS and NBTS characteristics (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Hyun Jae Kim − *School of Electrical and Electronic Engineering, Yonsei University, Seoul 03722, Korea;* orcid.org/0000-0002-6879-9256; Email: hjk3@yonsei.ac.kr

Authors

I. Sak Lee − *School of Electrical and Electronic Engineering, Yonsei University, Seoul 03722, Korea*
Young Jun Tak − *School of Electrical and Electronic Engineering, Yonsei University, Seoul 03722, Korea*
Byung Ha Kang − *School of Electrical and Electronic Engineering, Yonsei University, Seoul 03722, Korea*
Hyukjoon Yoo − *School of Electrical and Electronic Engineering, Yonsei University, Seoul 03722, Korea*
Sujin Jung − *School of Electrical and Electronic Engineering, Yonsei University, Seoul 03722, Korea*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.9b22831

Author Contributions

[†] I.S.L. and Y.J.T. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Industrial Strategic Technology Development Program (10063038, development of submicro in situ light patterning to minimize damage on flexible substrates) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

REFERENCES

(1) Na, J. W.; Kim, H. J.; Hong, S.; Kim, H. J. Plasma Polymerization Enabled Polymer/Metal−Oxide Hybrid Semiconductors for Wearable Electronics. *ACS Appl. Mater. Interfaces* **2018**, *10*, 37207.

(2) Zhu, H.; Shin, E.-S.; Liu, A.; Ji, D.; Xu, Y.; Noh, Y.-Y. Printable Semiconductors for Backplane TFTs of Flexible OLED Displays. *Adv. Funct. Mater.* **2019**, No. 1904588.

(3) Petti, L.; Munzenrieder, N.; Vogt, C.; Faber, H.; Buthe, L.; Cantarella, Gl.; Bottacchi, F.; Anthopoulos, T. D.; Troster, G. Metal Oxide Semiconductor Thin-Film Transistors for Flexible Electronics. *Appl. Phys. Rev.* **2016**, *3*, No. 021303.

(4) Heremans, P.; Tripathi, A. K.; Meux, A. dJ. d.; Smits, E. C. P.; Hou, B.; Pourtois, G.; Gelinck, G. H. Mechanical and Electronic Properties of Thin-Film Transistors on Plastic, and Their Integration in Flexible Electronic Applications. *Adv. Mater.* **2016**, *28*, 4266.

(5) Cantarella, G.; Costanza, V.; Ferrero, A.; Hopf, R.; Vogt, C.; Varga, M.; Petti, L.; Munzenrieder, N.; Buthe, L.; Salvatore, G.; Claville, A.; Bonanomi, L.; Daus, A.; Knobelspies, S.; Daraio, C.; Troster, G. Design of Engineered Elastomeric Substrate for Stretchable Active Devices and Sensors. *Adv. Funct. Mater.* **2018**, *28*, No. 1705132.

(6) Nomura, K.; Ohta, H.; Takagi, A.; Kamiya, T.; Hirano, M.; Hosono, H. Room-Temperature Fabrication of Transparent Flexible Thin-Film Transistors Using Amorphous Oxide Semiconductors. *Nature* **2004**, *432*, 488.

(7) Lee, H.; Chang, K. S.; Tak, Y. J.; Jung, T. S.; Park, J. W.; Kim, W.-G.; Chung, J.; Jeong, C. B.; Kim, H. J. Low-Temperature Activation Under 150 °C for Amorphous IGZO TFTs Using Voltage Bias. *J. Inf. Disp.* **2017**, *18*, 2158.

(8) Kim, K. M.; Jeong, W. H.; Kim, D. L.; Rim, Y. S.; Choi, Y.; Ryu, M.-K.; Park, K.-B.; Kim, H. J. Low-Temperature Solution Processing of AlInZnO/InZnO Dual-Channel Thin-Film Transistors. *IEEE Electron Device Lett.* **2011**, *32*, 1242.

(9) Liu, F. M.; Wu, Y. C.; Hsu, Y. J.; Yu, M. J.*P169: A 31-inch 4K2K Top-emission OLED Display Using Good Uniformity and Long-term Reliability Top-gate Self-aligned IGZO TFTs*, SID Symposium Digest of Technical Papers; 2018; p 1796.

(10) Choi, M.-C.; Kim, Y.; Ha, C.-K. Polymers for Flexible Displays: From Material Selection to Device Applications. *Prog. Polym. Sci.* **2008**, *33*, 581.

(11) Park, S.; Kim, K.-H.; Jo, J.-W.; Sung, S.; Kim, K.-T.; Lee, W.-J.; Kim, J.; Kim, H. J.; Yi, G.-R.; Kim, Y.-H.; Yoon, M.-H.; Park, S. K. In-Depth Studies on Rapid Photochemical Activation of Various Sol−Gel Metal Oxide Films for Flexible Transparent Electronics. *Adv. Funct. Mater.* **2015**, *25*, 2807.

(12) Song, K.; Koo, C. Y.; Jun, T.; Lee, D.; Jeong, Y.; Moon, J. Low-Temperature Soluble InZnO Thin Film Transistors by Microwave Annealing. *J. Cryst. Growth* **2011**, *326*, 23.

(13) Kim, W.-G.; Tak, Y. J.; Ahn, B. D.; Jung, T. S.; Chung, K.-B.; Kim, H. J. High-Pressure Gas Activation for Amorphous Indium-Gallium-Zinc-Oxide Thin-Film Transistors at 100 °C. *Sci. Rep.* **2016**, *6*, No. 23039.

(14) Ruozi, B.; Tosi, G.; Tonelli, M.; Bondioli, L.; Mucci, A.; Forni, F.; Vandelli, M. A. AFM Phase Imaging of Soft-Hydrated Samples: a Versatile Tool to Complete The Chemical-Physical Study of Liposomes. *J. Liposome Res.* **2009**, *19*, 59.

(15) Nenadović, M.; Potocnik, J.; Ristic, M.; Strbac, S.; Rakocevic, Z. Surface Modification of Polyethylene by Ag^+ and Au^+ Ion Implantation Observed by Phase Imaging Atomic Force Microscopy. *Surf. Coat. Technol.* **2012**, *206*, 4242.

(16) Kim, W. G.; Tak, Y. J.; Kim, H. J. Nitrocellulose-Based Collodion Gate Insulator for Amorphous Indium Zinc Gallium Oxide Thin-Film Transistors. *J. Inf. Disp.* **2018**, *19*, 39.

(17) Kang, M.-S.; Cho, W.-J. Improvement of on/off Current Ratio of Amorphous In−Ga−Zn−O Thin-Film Transistor with Off-Planed Source/Drain Electrodes. *Nanosci. Nanotechnol.* **2019**, *19*, 1345.

(18) Jang, H.-W.; Kim, H.-R.; Yang, J.-H.; Byun, C.-W.; Kang, C.-S.; Kim, S.; Yoon, S.-M. Stability Improvements of InGaZnO Thin-Film Transistors on Polyimide Substrates with Al_2O_3 Buffer Layer. *Jpn. J. Appl. Phys.* **2018**, *57*, No. 090313.

(19) Lopes, M. E.; Gomes, H. L.; Medeiros, M. C. R.; Barquinha, P.; Pereira, L.; Fortunato, E.; Martins, R.; Ferreira, I. Gate-Bias Stress in Amorphous Oxide Semiconductors Thin-Film Transistors. *Appl. Phys. Lett.* **2009**, *95*, No. 063502.

(20) Chen, T.-C.; Chang, T.-C.; Hsieh, T.-Y.; Lu, W.-S.; Jian, F.-Y.; Tsai, C.-T.; Huang, S.-Y.; Lin, C.-S. Investigating the Degradation Behavior Caused by Charge Trapping Effect under DC and AC Gate-Bias Stress for InGaZnO Thin Film Transistor. *Appl. Phys. Lett.* **2011**, *99*, No. 022104.

(21) Nomura, K.; Kamiya, T.; Kikuchi, Y.; Hirano, M.; Hosono, H. Comprehensive Studies on the Stabilities of a-In-Ga-Zn-O Based Thin Film Transistor by Constant Current Stress. *Thin Solid Films* **2010**, *518*, 3012.

(22) Baytekin, H. T.; Baytekin, B.; Huda, S.; Yavuz, Z.; Grzybowski, B. A. Mechanochemical Activation and Patterning of an Adhesive Surface Toward Nanoparticle Deposition. *J. Am. Chem. Soc.* **2015**, *137*, 1726.

(23) Sung, S.; Park, S.; Cha, S.; Lee, W.-J.; Kim, C.-H.; Yoon, M.-H. Direct Patterning of Sol−Gel Metal Oxide Semiconductor and Dielectric Films via Selective Surface Wetting. *RSC Adv.* **2015**, *5*, 38125.

(24) Jiao, G.; Yu, G.; Wang, W.; Zhao, X.; Zhang, J.; Ewart, S. H. Properties of Polysaccharides in Several Seaweeds from Atlantic Canada and Their Potential Anti-Influenza Viral Activities. *J. Ocean Univ. China* **2012**, *11*, 205.

(25) Wang, Z.; Huang, H.; Zeng, L.; LV, L.; Dai, C.; Mao, W.; Chen, X.; Fang, D.; Eang Y. In-operando Deformation Studies on the Mechano-Electrochemical Mechanism in Free-Standing MWCNTs/V_2O_5 Lithium Ion Battery Electrode. *Electrochim. Acta* **2019**, *305*, 101.

(26) Akay, S. K.; Peksoz, A.; Kara, A. Magnetic Responses of Divinylbenzene-Fe_3O_4 Composite Film Deposited by Free Radical Polymerization Method. *J. Supercond. Nov. Magn.* **2018**, *31*, 849.

(27) Mazur, T.; Grzybowski, B. A. Theoretical Basis for the Stabilization of Charges by Radicals on Electrified Polymers. *Chem. Sci.* **2017**, *8*, 2025.

(28) Fukuda, N.; Watanabe, Y.; Uemura, S.; Yoshida, Y.; Nakamura, T.; Ushijima, H. In−Ga−Zn Oxide Nanoparticles Acting as an Oxide Semiconductor Material Synthesized via a Coprecipitation-Based Method. *J. Mater. Chem. C* **2014**, *2*, 2448.

(29) Zhang, Z.; Yates, J. T., Jr. Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces. *Chem. Rev.* **2012**, *112*, 5520.

(30) Ning, H.; Zeng, Y.; Zheng, Z.; Zhang, H.; Fang, Z.; Yao, R.; Hu, S.; Li, X.; Peng, J.; Xie, W.; Lu, X. Facile Room Temperature Routes to Improve Performance of IGZO Thin-Film Transistors by an Ultrathin Al_2O_3Passivation Layer. *IEEE Trans. Electron Devices* **2018**, *65*, 537.

(31) Gielis, J. J. H.; Hoex, B.; Sanden, M. C. M. V. D.; Kessels, W. M. M. Negative Charge and Charging Dynamics in Films on Si Characterized by Second-Harmonic Generation. *J. Appl. Phys.* **2008**, *104*, No. 073701.

(32) Jeong, S.; Ha, Y.-G.; Moon, J.; Facchetti, A.; Marks, T. J. Role of Gallium Doping in Dramatically Lowering Amorphous-Oxide Processing Temperatures for Solution-Derived Indium Zinc Oxide Thin-Film Transistors. *Adv. Mater.* **2010**, *22*, 1346.

(33) Lee, H.; Jung, T. S.; Park, J. W.; Kim, H. J. Boosting Modulation of Oxide Semiconductors via Voltage-Based Ambi-Ionic Migration. *ACS Appl. Mater. Interfaces* **2018**, *10*, 37216.

https://dx.doi.org/10.1021/acsami.9b22831
ACS Appl. Mater. Interfaces 2020, 12, 19123−19129