SCIENTIFIC REPORTS

OPEN

Rare-metal-free high-performance Ga-Sn-O thin film transistor

Tokiyoishi Matsuda¹, Kenta Umeda², Yuta Kato², Daiki Nishimoto², Mamoru Furuta³ & Mutsumi Kimura^{2,4}

Received: 21 November 2016

Accepted: 07 February 2017

Published: 14 March 2017

Oxide semiconductors have been investigated as channel layers for thin film transistors (TFTs) which enable next-generation devices such as high-resolution liquid crystal displays (LCDs), organic light emitting diode (OLED) displays, flexible electronics, and innovative devices. Here, high-performance and stable Ga-Sn-O (GTO) TFTs were demonstrated for the first time without the use of rare metals such as In. The GTO thin films were deposited using radiofrequency (RF) magnetron sputtering. A high field effect mobility of 25.6 cm²/Vs was achieved, because the orbital structure of Sn was similar to that of In. The stability of the GTO TFTs was examined under bias, temperature, and light illumination conditions. The electrical behaviour of the GTO TFTs was more stable than that of In-Ga-Zn-O (IGZO) TFTs, which was attributed to the elimination of weak Zn-O bonds.

Oxide semiconductor materials such as In-Ga-Zn-O (IGZO)^{1–4}, In-Sn-Zn-O (ITZO)^{5,6}, In-Ga-O (IGO)⁷, and In-Sn-O (ITO)⁸ have several advantages as active layer of thin film transistors (TFTs) such as steep subthreshold swing (*S* factor), transparency, and extremely low leak current in off state when compared to conventional semiconductors such as hydrogenated amorphous silicon (a-Si:H)⁹ and polycrystalline silicon¹⁰. In addition, oxide TFTs have high field effect mobility (μ_{FE}) and can be easily fabricated on large-area substrates by deposition processes with low cost, low toxicity, and low risk of explosion, such as radiofrequency (RF) or direct current (DC) magnetron sputtering. These techniques are used in the TFT fabrication processes to deposit IGZO as semiconductor, ITO as the transparent electrodes for displays, and metallic materials (Cr, Mo, and Al) for electrodes. The fabrication processes for oxide semiconductors can be easily integrated into or replace conventional TFT processes, such as photolithography and etching. Hence, not only information displays but also novel devices have been proposed such as memories¹¹, processors, and other electronic elements¹². However, IGZO, ITZO, IGO, and ITO include In in the matrix which is associated with high fabrication costs as In is a rare metal with few mining sites¹³ and is hence expensive. On the other hand, the In-free oxide semiconductor materials such as ZnO^{14–18}, Al-Zn-Sn-O (AZTO)¹⁹, Zn-Sn-O (ZTO)²⁰, ZnON²¹ include Zn, which is thought to be the reason of the instability of devices with forming the weak Zn-O bond²². The electrical characteristics and those stability of In-free TFTs were not enough for application to the novel devices. In addition, multi-metallic materials (especially IGZO) are difficult to mass produce because the stoichiometry of the deposited films can be different to that of the sputtering target due to preferential sputtering of some elements². Sputtering targets can be of poor quality due to low crystallinity or incomplete oxidation of compounds²³, which may reduce device performance. Furthermore, there are many defects in the semiconductor films^{4,24–31}, and it is difficult to control the density of oxygen vacancies induced during the deposition^{32–34}. Therefore, new semiconductor materials that do not use rare metals and consist of fewer elements are being explored.

In this paper, we first report a stable TFT with a high μ_{FE} that incorporate Ga-Sn-O (GTO) as the amorphous and transparent oxide semiconductor. This material is a dual metallic oxide without rare metals such as In. The stability of the GTO TFT was evaluated under various stress conditions and compared to that of IGZO TFTs.

Results and Discussion

Abundance in the Earth's upper continental crust. The abundance of Ga and Sn in the Earth's upper continental crust is 18 ppm and 2.2 ppm, respectively, much higher than that of In (0.25 ppm)¹³, as shown in Fig. 1a. Therefore, substituting Sn for In is a reasonable countermeasure for avoiding the use of rare earth metals. Moreover, In and Sn have similar electronic structures and electrical properties. The high μ_{FE} observed for

¹Innovative Materials and Processing Research Center, Ryukoku University, Japan HRC205, 1-5, Seta Oe-cho, Otsu, Shiga, 520-2194, Japan. ²Department of Electronics and Informatics, Faculty of Science and Technology, Ryukoku University, Japan. ³School of Environmental Science and Engineering, Kochi University of Technology, Japan. ⁴Joint Research Centre for Science and Technology, Ryukoku University, Japan. Correspondence and requests for materials should be addressed to T.M. (email: toki@rins.ryukoku.ac.jp)

Figure 1. Subset of the periodic table of elements showing metallic elements of interest to oxide semiconductors, electron orbital of In and Sn in ground state³⁵, and current path formed by metallic ions. (a) The relative abundance of the elements in the Earth's upper continental crust is indicated by the green circles and the absolute values (ppm) are shown¹³. Ga and Sn as metallic elements of GTO are surrounded by red line, and In, Ga, Zn, elements of IGZO are surrounded by dashed blue line. (b) 5s orbitals are indicated by red circles, 5p orbitals are indicated by orange ovals, electrons are indicated by yellow particles. In³⁺ ions and Sn⁴⁺ ions have the same electronic structure, and the path of electrons in IGZO and GTO can be formed by 5s orbital without electrons described with red circles.

Figure 2. Electrical characteristics of the GTO thin film transistor. (a), transfer characteristics (drain current vs. gate voltage for various drain voltages) with left axis in log scale and right axis in linear scale, respectively, and (b) output characteristics (drain current vs. drain voltage for various gate voltages) in linear scale. The electrical characteristics of GTO TFT was excellent with low off current in negative gate voltage region in transfer characteristics, and high on current in positive gate voltage. The saturation characteristics in high drain voltage were clearly observed in output characteristics.

amorphous IGZO TFTs has been attributed to the electron path formed by the broad In 5s orbital. In with atomic number 49 has an electronic structure in ground state; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$. On the other hand, Sn with atomic number 50, the next element after In in the periodic table, has a similar electronic structure in ground state; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$ as shown in Fig. 1b³⁵. As a result, In³⁺ ions in IGZO and Sn⁴⁺ ions in GTO have the same electronic structure of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$. Therefore, a high μ_{FE} is expected for GTO TFTs because the 5s orbital of Sn serves as a path for current flow, similar to the 5s orbital of In as shown in Fig. 1b¹.

Electrical characteristic of the GTO TFT. Figure 2 shows the drain current (I_{ds}) as a function of the gate voltage (V_{gs}) from -30 to 30 V with a 0.1 V step, and fixed drain voltage (V_{ds}) of 0.1 V, from 5 to 30 V with a 5 V

Figure 3. Optical absorbance and XRD pattern of the GTO film. (a) optical absorbance as a function of wavelength. The inset is a photograph of a GTO thin film deposited on a quartz glass substrate put on the top of a printed paper, showing the transparency of the thin film. (b) XRD pattern showing amorphous structure of GTO thin film deposited on a quartz substrate.

step. The ratio between the on current of the TFT (I_{on}) at $V_{gs} = 30$ V and the off current (I_{off}) at $V_{gs} = -10$ V, (I_{on}/I_{off}) was over 10^8 . The threshold voltage, $V_{th} = -1.49$ V, subthreshold swing, $S = 0.33$ V/dec where $S = dV_{gs}/d\log I_{ds}$, and the highest μ_{FE} of $25.6 \text{ cm}^2/\text{V}\cdot\text{s}$, were achieved for the GTO TFT in linear region at $V_{gs} = 29.5$ V and $V_{ds} = 0.1$ V, which values were comparable to those observed for IGZO TFTs³⁶ and ITZO TFTs^{5,6}. In the saturation region, the value of μ_{FE} was slightly lower than that of linear region. High μ_{FE} of linear region would be due to the path of electron formed in the conduction band at high V_{gs} and low V_{ds} , whereas lower μ_{FE} of saturation region would be because the route of electron was partially formed by percolation path in pinch off region at high V_{ds} . In addition, the saturation characteristics of GTO TFTs were excellent, and the TFT characteristics did not deteriorate, even after measurement at high voltages of $V_{gs} = 30$ V and $V_{ds} = 30$ V, as shown in Fig. 2b. The abovementioned excellent performances show that the GTO TFTs are suitable for use in next-generation displays such as 8 K ultra-high-definition televisions (UHDTV), LCD, and OLED³⁷. The other GTO TFTs with different composition ratio from Ga: Sn = 1: 3 were fabricated, however, the best TFT performance was achieved with the current composition ratio.

Optical absorbance and XRD intensity of the GTO film. Figure 3a shows the optical absorbance of a GTO thin film deposited on a quartz substrate. The inset shows a photograph of the sample laid over printed text in red, green, and blue, showing the good transparency of the film in the visible wavelength range. The absorbance of the GTO thin film was lower than 20% at a wavelength of 300 nm and approximately zero above 380 nm. Figure 3b shows the XRD pattern of GTO thin film deposited on a quartz substrate. The structure of GTO thin film is amorphous, because the no diffraction peak was observed in the XRD pattern.

Characteristic stability of the GTO TFT. A major drawback of conventional amorphous oxide semiconductors is the poor stability of TFTs under the driving conditions of devices³⁸. In order to investigate the stability of the GTO TFTs, we performed accelerated operating tests such as the positive bias stress (PBS), positive bias temperature stress (PBTs), positive bias illumination stress (PBIS), negative bias stress (NBS), negative bias temperature stress (NBTS), and negative bias illumination stress (NBIS) tests.

Figure 4 shows the I_{ds} - V_{gs} characteristics of a GTO TFT under the NBIS test conditions. Generally, amorphous oxide semiconductor TFTs have poor I_{ds} - V_{gs} behaviour under NBIS testing³⁶. However, only a negative shift of 4.3 V in V_{gs} was observed after applying NBIS conditions of a gate voltage of -20 V under light illumination for 3600 s. Excellent TFT characteristics were maintained even after the NBIS tests, such as low I_{off} values in the negative V_{gs} region and high I_{on} values in the high V_{gs} region. In addition, no degradation in the S factor was observed in the subthreshold region of V_{gs} from around -10 V to 5 V after the NBIS test. Therefore, we can conclude that the no trap state was generated close to the conduction band and NBIS effects were due to the capturing of fixed charges in the insulator, similar to the reported effect for IGZO TFT³⁸. This effect is different from the hypothesis such as elimination of dangling bonds with O_2 annealing³⁹, and defect formation in semiconductor layer or interface between the semiconductor and gate insulator^{40–42}. The shift in the electrical characteristics is due to a similar mechanism to that known for IGZO TFTs; holes from electron-hole pairs excited by the light and heat are transported from the back channel of the semiconductor to the gate surface and are captured close to the interface between the gate insulator and the semiconductor³⁸.

Figure 5 shows the stability of GTO TFT under the PBS, PBTs, PBIS, NBS, NBTS, and NBIS tests without passivation. The stress conditions are shown in the table in Fig. 5. The shifts of the turn-on voltage, which is defined as V_{gs} for $I_{ds} = 1 \times 10^{-9}$ A, (ΔV) of all stress tests were less than that of NBIS tests. These results for NBTS and NBIS testing of GTO are better than those for IGZO TFTs, where the shift was over 10 V in the negative direction at 1000 s³⁶. Therefore, it can be generally concluded that the stability of TFTs fabricated using GTO is better than that observed for IGZO. It was reported in the literature that weak bonds were formed between the Zn and O in IGZO²². As GTO does not include Zn in the matrix, we expect that the improved stability of the GTO TFT may

Figure 4. Negative bias illumination stress characteristics of the GTO TFT. The drain current is shown as a function of the gate voltage for various times up to 3600 s. The shift of electrical characteristics under the NBIS was parallel, and, therefore, the degradation of subthreshold swing was not observed.

Figure 5. Results of various stress tests on the GTO TFT. Shifts in the turn-on voltage, which is defined as V_{gs} for $I_{ds} = 1 \times 10^{-9}$ A at the subthreshold region, (ΔV) at the subthreshold region are shown as a function of stress time under conditions of positive bias stress (PBS), positive bias temperature stress (PBTS), positive bias illumination stress (PBIS), negative bias stress (NBS), negative bias temperature stress (NBTS), and negative bias illumination stress (NBIS). The original state refers to the conditions before the stress test. The shift of the GTO TFT characteristics was largest for NBIS test.

be due to the absence of such weak bonds, because the enthalpy (heat) of formation of ZnO is smaller than Ga_2O_3 and SnO_2 , which means that the bonds in GTO are more stable than ZnO in IGZO. Therefore, the GTO lattice is expected to be stable during plasma processes, such as sputtering and CVD, for deposition of passivation films and dry etching process. In addition, the optical band gap of a GTO film obtained from a Tauc plot was 3.12 eV, which is larger than silicon-based semiconductors, and comparable to other oxide semiconductors, such as IGZO, ZnO, SnO_2 and Ga_2O_3 . This means that the generation of holes is limited. Hence, highly stable TFT characteristics are expected for GTO TFTs, because the large band gap means that the number of holes generated by light illumination is limited; the holes are the main reason for the NBIS instability of oxide semiconductor TFTs³⁸. Moreover, the GTO is amorphous, and hence, large area uniformity is expected during the device fabrication process, because the amorphous oxide materials are thought to be more stable against grain boundaries formed in crystalline oxide semiconductors. The path of electrons in the GTO thin film is formed by the 5s orbital of Sn ions, which is largely spreading in the matrix as shown in Fig. 1b. The uniform shape of the 5s orbital maintains the current path in random direction of the bond between the elements in amorphous GTO matrix which was confirmed by XRD pattern. The role of Ga in GTO is similar to Ga and Zn in IGZO, which stabilize the amorphous structure with Coulomb potential. Zn stabilizes the amorphous structure in IGZO, however, Zn element is not needed in GTO for stabilizing the amorphous GTO TFT characteristics. In addition, improvement in the

μ_{FE} and stability of GTO TFTs can be expected by appropriate passivation or treatment of the back channel and optimization of the fabrication process applied for IGZO TFTs^{25,43,44}.

Conclusion

High field effect mobility TFT with a low S factor was prepared using GTO, where the rare earth In was replaced by Sn. The stability of the GTO TFT without a passivation film under various accelerated operating conditions was significantly higher than that of equivalent IGZO TFTs. Although we compared the IGZO and GTO TFTs fabricated in our laboratory just for evaluation of the materials themselves, because TFT characteristics are influenced by the treatment of backchannel such as passivation materials and methods^{25,44,45} and surface treatment^{36,43}, the effective treatments for IGZO TFT can also be effective for GTO TFT. We propose such GTO TFTs as key devices suitable for use in next-generation technologies such as displays, power devices, and artificial intelligence devices such as neural networks.

Methods

Samples. The fabricated GTO TFTs have a structure with a bottom gate and top contact. We used the same structure as that of previously reported IGZO TFTs³⁶ in order to evaluate the compatibility of GTO with the other oxide semiconductor materials and compare their performance under the same conditions. The GTO active layers were deposited by RF magnetron sputtering using a sintered GTO ceramic target (99.99%, Ga:Sn = 1:3 in atomic ratio). The vacuum chamber was evacuated to 1×10^{-4} Pa and the sputtering gas pressure was controlled using a vacuum valve to introduce Ar and O₂ gas into the chamber at a fixed flow rate of Ar:O₂ = 20:1 sccm determined by a mass flow controller. The GTO was deposited on Si wafers (p-type; 0.01 Ω -cm; 50 mm in diameter) for use as gate electrodes in the TFT which had a 150 nm thermal oxide (SiO₂) layer as the gate insulator. Source and drain (S/D) electrodes of Ti (20 nm in thickness) and Au (20 nm in thickness), respectively, were deposited using thermal evaporation on the GTO active layer. Both the semiconductor layer and S/D electrodes were patterned using stainless steel shadow masks set on top of the substrates. Post annealing was performed in air at 350 °C for 1 h using an annealing furnace. No passivation layer was deposited on the back channel of the TFTs³⁶ to avoid undesired effects from plasma processes such as CVD for the fabrication of passivation films and dry etching processes⁴³.

Characterisation. Electrical properties such as I_{ds} - V_{gs} and I_{ds} - V_{ds} of GTO TFTs were measured in air at around 25 °C using a semiconductor parameter analyser (Agilent 4156 C). TFT parameters such as μ_{FE} , S factors, and V_{th} were calculated from TFT theory, such as $I_{ds} = \mu_{FE} c_i (W/L) (V_{gs} - V_{th}) V_{ds}$, where, c_i is the capacitance of the TFT of unit area (F/cm²), W/L is the ratio of the channel width to the channel length defined between the S/D electrodes. The stability of the GTO TFTs was evaluated under accelerated operating conditions of devices, including voltage, temperature, and light illumination stresses using conditions of $V_g = 20$ V / -20 V for positive or negative bias, respectively, 60 °C, and irradiation from an white LED lamp with wavelength from 450 nm to 780 nm. By combining these conditions, we evaluated the stability of the material under positive bias stress (PBS), positive bias temperature stress (PBTS), positive bias illumination stress (PBIS), negative bias stress (NBS), negative bias temperature stress (NBTS), and negative bias illumination stress (NBIS). The optical absorbance (A %) was obtained from the transmittance (T %) and reflectance (R %) using $A = (100 - (R + T))$, measured using a spectrometer from the ultraviolet to visible range (UV-VR) (300 nm to 800 nm). XRD pattern in $2\theta/\theta$ scan of GTO thin film deposited on a quartz substrate was measured with Rigaku SmartLab X-ray diffractometer (Cu K α radiation).

References

1. Nomura, K. *et al.* Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. *Nature* **432**, 488–492 (2004).
2. Yabuta, H. *et al.* High-mobility thin-film transistor with amorphous InGaZnO₄ channel fabricated by room temperature rf-magnetron sputtering. *Appl. Phys. Lett.* **89**, 112123 (2006).
3. Hosono, H. Ionic amorphous oxide semiconductors: Material design, carrier transport, and device application. *J. Non. Cryst. Solids* **352**, 851–858 (2006).
4. Kamiya, T., Nomura, K. & Hosono, H. Present status of amorphous In–Ga–Zn–O thin-film transistors. *Sci. Technol. Adv. Mater* **11**, 044305 (2010).
5. Fukumoto, E. *et al.* High-mobility oxide TFT for circuit integration of AMOLEDs. *J. Soc. Inf. Disp.* **19**, 867–872 (2011).
6. Tomai, S. *et al.* High-Performance Thin Film Transistor with Amorphous In₂O₃-SnO₂-ZnO channel layer. *Jpn. J. Appl. Phys.* **51**, 03CB01 (2012).
7. Ebata, K. *et al.* High-mobility thin-film transistors with polycrystalline In-Ga-O channel fabricated by DC magnetron sputtering. *Appl. Phys. Express* **5**, 011102 (2012).
8. Miyasako, T., Senoo, M. & Tokumitsu, E. Ferroelectric-gate thin-film transistors using indium-tin-oxide channel with large charge controllability. *Appl. Phys. Lett.* **86**, 1–3 (2005).
9. Street, R. A. *Hydrogenated amorphous silicon*. (Cambridge Univ. Press, 1991).
10. Kagan, C. R. & Andry, P. *Thin-film transistors*. (Marcel Dekker, 2003).
11. Suresh, A., Novak, S., Wellenius, P., Misra, V. & Muth, J. F. Transparent indium gallium zinc oxide transistor based floating gate memory with platinum nanoparticles in the gate dielectric. *Appl. Phys. Lett.* **94**, 123501 (2009).
12. Kamiya, T. & Hosono, H. Material characteristics and applications of transparent amorphous oxide semiconductors. *NPG Asia Mater.* **2**, 15–22 (2010).
13. Haxel, G. B., Hedrick, J. B. & Orris, G. J. Rare Earth Elements — Critical Resources for High Technology. *United States Geol. Surv. Fact Sheet* **87**, 4 (2002).
14. Ohya, Y., Niwa, T., Ban, T. & Takahashi, Y. Thin film transistor of ZnO fabricated by chemical solution deposition. *Jpn. J. Appl. Phys.* **40**, 297–298 (2001).
15. Masuda, S. *et al.* Transparent thin film transistors using ZnO as an active channel layer and their electrical properties. *J. Appl. Phys.* **93**, 1624–1630 (2003).

16. Hoffman, R. L., Norris, B. J. & Wager, J. F. ZnO-based transparent thin-film transistors. *Appl. Phys. Lett.* **82**, 733–735 (2003).
17. Hirao, T. *et al.* High Mobility Top-Gate Zinc Oxide Thin-Film Transistors (ZnO-TFTs) for Active-Matrix Liquid Crystal Displays Digest of SID'06, 18–20 (2006).
18. Hirao, T. *et al.* Novel top-gate zinc oxide thin-film transistors (ZnO TFTs) for AMLCDs. *J. Soc. Inf. Disp.* **15**, 17–22 (2007).
19. Jeong, J. K. *et al.* Impact of device configuration on the temperature instability of Al-Zn-Sn-O thin film transistors. *Appl. Phys. Lett.* **95**, 1–4 (2009).
20. Heo, J., Kim, S. B. & Gordon, R. G. Atomic layer deposited zinc tin oxide channel for amorphous oxide thin film transistors. *Appl. Phys. Lett.* **101**, 113507 (2012).
21. Ok, K. C., Jeong, H. J., Kim, H. S. & Park, J. S. Highly stable ZnON thin-film transistors with high field-effect mobility exceeding $50 \text{ cm}^2/\text{Vs}$. *IEEE Electron Device Lett.* **36**, 38–40 (2015).
22. Kamiya, T., Nomura, K. & Hosono, H. Subgap states, doping and defect formation energies in amorphous oxide semiconductor a-InGaZnO₄ studied by density functional theory. *Phys. Status Solidi Appl. Mater. Sci.* **207**, 1698–1703 (2010).
23. Huh, J. Y. *et al.* Effects of the composition of sputtering target on the stability of InGaZnO thin film transistor. *Thin Solid Films* **519**, 6868–6871 (2011).
24. Hoffmann, R. C. *et al.* Molecular precursor derived and solution processed indium-zinc oxide as a semiconductor in a field-effect transistor device. Towards an improved understanding of semiconductor film composition. *J. Mater. Chem. C* **1**, 2577–2584 (2013).
25. Nomura, K., Kamiya, T. & Hosono, H. Highly stable amorphous In-Ga-Zn-O thin-film transistors produced by eliminating deep subgap defects. *Appl. Phys. Lett.* **99**, 53505 (2011).
26. Chen, C., Cheng, K.-C., Chagarov, E. & Kanicki, J. Crystalline In-Ga-Zn-O Density of States and Energy Band Structure Calculation Using Density Function Theory. *Jpn. J. Appl. Phys.* **50**, 91102 (2011).
27. Matsuda, T., Furuta, M., Hiramatsu, T., Furuta, H. & Hirao, T. Crystallinity and resistivity of ZnO thin films with indium implantation and postannealing. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **28**, 135–138 (2010).
28. Kimura, M., Nakanishi, T., Nomura, K., Kamiya, T. & Hosono, H. Trap densities in amorphous-InGaZnO₄ thin-film transistors. *Appl. Phys. Lett.* **92**, 2006–2009 (2008).
29. Kimura, M., Kamiya, T., Nakanishi, T., Nomura, K. & Hosono, H. Intrinsic carrier mobility in amorphous In-Ga-Zn-O thin-film transistors determined by combined field-effect technique. *Appl. Phys. Lett.* **96**, 98–101 (2010).
30. Kimura, M. *et al.* Extraction of trap densities in ZnO thin-film transistors and dependence on oxygen partial pressure during sputtering of ZnO films. *IEEE Trans. Electron Devices* **58**, 3018–3024 (2011).
31. Matsuda, T. & Kimura, M. Comparison of defects in crystalline oxide semiconductor materials by electron spin resonance. *J. Vac. Sci. Technol. A* **33**, 20601 (2015).
32. Ryu, B., Noh, H. K., Choi, E. A. & Chang, K. J. O-vacancy as the origin of negative bias illumination stress instability in amorphous In-Ga-Zn-O thin film transistors. *Appl. Phys. Lett.* **97**, 22108 (2010).
33. Matsuda, T., Nishimoto, D., Takahashi, K., Ueno, T. & Kimura, M. ESR Evaluation of Damages Induced in InGaZnO₄ with Plasma. In *Proceedings of International Display Workshops/Asia Display 2012* 557–558 (2012).
34. Matsuda, T., Nishimoto, D., Takahashi, K. & Kimura, M. Evaluation of damage in InGaZnO₄ induced by plasma using electron spin resonance measurement Matching. *Jpn. J. Appl. Phys.* **3**, 03CB03 (2014).
35. Steven Dutch. Scale Drawings of Atoms and Orbitals: Cesium Through Radon. Available at: <https://www.uwgb.edu/dutchs/Petrology/ScaleAtomsCsRn.HTM>.
36. Kojiri, T., Matsuda, T. & Kimura, M. Thermally enhanced threshold voltage shifts in amorphous In-Ga-Zn-O thin-film transistor. *Jpn. J. Appl. Phys.* **53**, 125802 (2014).
37. Matsueda, Y. Required Characteristics of TFTs for Next Generation Flat Panel Display Backplanes. In *The Proceedings of the 6th International Thin-Film Transistor Conference* 314–317 (2010).
38. Nomura, K., Kamiya, T. & Hosono, H. Stability and high-frequency operation of amorphous In-Ga-Zn-O thin-film transistors with various passivation layers. *Thin Solid Films* **520**, 3778–3782 (2012).
39. Ji, K. H. *et al.* Effect of high-pressure oxygen annealing on negative bias illumination stress-induced instability of InGaZnO thin film transistors. *Appl. Phys. Lett.* **98**, 103509 (2011).
40. Ueoka, Y. *et al.* Density of States in Amorphous In-Ga-Zn-O Thin-Film Transistor under Negative Bias Illumination Stress. *ECS J. Solid State Sci. Technol.* **3**, Q3001–Q3004 (2014).
41. Oh, H. *et al.* Photon-accelerated negative bias instability involving subgap states creation in amorphous In-Ga-Zn-O thin film transistor. *Appl. Phys. Lett.* **97**, 183502 (2010).
42. Lee, K. H. *et al.* The effect of moisture on the photon-enhanced negative bias thermal instability in Ga-In-Zn-O thin film transistors. *Appl. Phys. Lett.* **95**, 232106 (2009).
43. Koretomo, D., Toda, T., Matsuda, T., Kimura, M. & Furuta, M. Anomalous Increase in Field-Effect Mobility in In-Ga-Zn-O Thin-Film Transistors Caused by Dry-Etching Damage Through Etch-Stop Layer. *IEEE Trans. Electron Devices* **63**, 2785–2789 (2016).
44. Furuta, M., Jiang, J., Hung, P., Toda, T. & Wang, D. Suppression of Negative Gate Bias and Illumination Stress Degradation by Fluorine-Passivated In-Ga-Zn-O Thin-Film Glass substrate. *ECS J. Solid State Sci. Technol.* **5**, Q88–Q91 (2016).
45. Bermundo, J. P., Ishikawa, Y., Yamazaki, H., Nonaka, T. & Uraoka, Y. Highly Reliable Polysilsesquioxane Passivation Layer for a-InGaZnO Thin-Film Transistors. *ECS J. Solid State Sci. Technol.* **3**, Q16–Q19 (2013).

Acknowledgements

We would like to thank Dr. Shigekazu Tomai from Idemitsu Kosan Co. Ltd., for helpful discussions regarding target preparation and TFT measurements. This work was partially supported by the MEXT Supported Program for the Strategic Research Foundation at Private Universities (S1311040), a JSPS Grant-in-Aid for Young Scientists (B) (No. 26870717), and a Grant-in-Aid for Scientific Research (C) (No. 16K06733).

Author Contributions

Tokiyoshi Matsuda conducted the research, contributed to the choice of GTO material, development of the TFT fabrication process, evaluation of the GTO thin films and TFTs, and writing the paper. Kenta Umeda fabricated and characterised the TFTs. Yuta Kato developed the GTO TFT fabrication process. Daiki Nishimoto carried out the deposition and evaluation of the films. Mamoru Furuta conducted the film evaluation. Mutsumi Kimura managed the research and laboratory, contributed to discussions about the TFT characteristics, and revised the paper.

Additional Information

Competing Interests: The authors declare no competing financial interests.

How to cite this article: Matsuda, T. *et al.* Rare-metal-free high-performance Ga-Sn-O thin film transistor. *Sci. Rep.* **7**, 44326; doi: 10.1038/srep44326 (2017).

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>

© The Author(s) 2017