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Formamide Mediated, Air-Brush Printable, Indium-Free Soluble Zn–Sn–O Semiconductors for Thin-Film Transistor Applications

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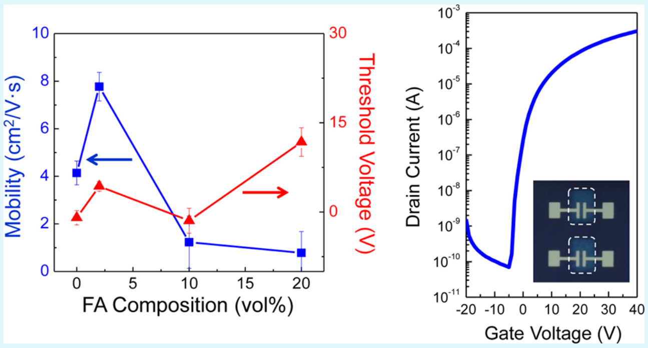
Supporting Information

ABSTRACT: In this study, for high-performance indium-free metal oxide channel layer, we synthesize Zn–Sn–O (ZTO) precursor solutions in which formamide is incorporated as an additive for catalyzing the subsequent sol–gel reactions and the evolution of chemical structure. It is revealed that the formamide plays a critical chemical role in evolving a chemical structure with more oxygen-deficient oxide lattice and with less hydroxide, allowing for high field-effect mobility over 7 cm^2/V·s. Furthermore, it is for the first time demonstrated that electrically active metal-oxide films can be patterned, using an air-brush printing technique, by directly depositing formamide-mediated ZTO-precursor solutions in patterned geometries.



KEYWORDS: *formamide, print, indium free, zinc tin oxide, semiconductor, transistor*

In the recent decade, amorphous oxide semiconductors have drawn tremendous attention as an alternative channel material for thin-film transistors (TFTs), to replace conventional Si and organic semiconductors in a variety of optoelectronic applications.[1,2] In general, high-performance oxide semiconductors have been formed by expensive, vacuum-based, physical vapor-deposition techniques. Recently, the generation of amorphous oxide TFTs using cost-effective wet chemical methodologies, has been intensively investigated with the expectation of great benefits including simplicity, low cost, and high throughput. A variety of multicomponent materials (e.g., In–Ga–Zn-O (IGZO),[3] In–Zn–O,[4,5] and Zn–In–Sn-O[6]) have been explored via their characteristic synthetic pathways, and implemented into TFT structures, with resulting mobilities exceeding 10 cm^2/(V s). However, in the quest to exploit the advantageous soluble oxide semiconductors in terms of both the cost-effectiveness and the device performance, there remains the significant challenge of avoiding the use of the expensive rare-earth element indium, which is currently indispensable for formulating electrically active, high-performance soluble oxide semiconductors.

To date, to improve device performance even in low-temperature annealed soluble-oxide TFTs, much effort has been devoted to developing alternative routes in supplying the energy needed to convert the precursor layers into the desired corresponding metal-oxide frameworks. Such alternatives have included ultraviolet/ozone annealing,[7,8] hydrolysis annealing,[9] high-pressure annealing,[10] and microwave annealing.[11] However, in some cases, those chemically activated annealing procedures are prevented from being applied to the multilayer stacked circuitries typical of practical applications, because of undesirable photochemical, and/or thermo-chemical impacts on underlying layers. Also, the issues for low-temperature annealing compatible to thermally vulnerable plastic substrates have not prevailed practically due to the current technological status in depositing other layers including gate insulators and passivation films.

Another approach is to formulate novel precursor solutions applicable to general thermal annealing techniques. Representative methodologies include a fuel-oxidizer pair combustion reaction[3,12] and a hydroxide-based synthetic way.[13,14] However, to date, in the case of Sn precursors for the combustion reactions and Sn-hydroxide precursors, the successful applicability to thin film transistors has not been demonstrated due to the difficulty in synthesizing air-stable chemical precursors. This has made it difficult to develop high-performance indium-free soluble-oxide semiconductors. Chemical additive methods, adaptable to conventional sol–gel chemistries, with versatile control of composition, could provide an alternative approach.[15−17] The chemical additives of ethylene glycol and formamide, which are incorporated simply together with metal

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salt precursors, could be used to tailor the chemical structures that determine the electrical performance of oxide semiconductors. In preliminary studies on IGZO semiconductors, the field-effect mobilities were boosted by a factor of 2−5, reaching the value of 10 $cm^2/(V\ s)$. To date, in the case of ZTO semiconductor (a representative indium-free oxide semiconductor), the field-effect mobilities have been limited to the level of 4 $cm^2/V{\cdot}s$, after conventional thermal annealing below 400 °C.[18] Furthermore, these ZTO semiconductors tend to be designed with an equivalent Zn/Sn stoichiometric ratio, in order to extract the best device performance;[19] but, this stoichiometric compound is hard to pattern using a wet-etching process, because of its limited solubility even in highly acidic etchant solutions. These limitations to fabricating patterned, device-quality ZTO channel layers have restricted the creation of cost-effective, high-performance oxide-based electronic circuit devices, for practical applications.

In this paper, we introduce new ZTO semiconductors with a field-effect mobility of 7.7 $cm^2/(V\ s)$, which were created from a new precursor solution of Zn nitrate hydrate, Sn chloride dihydrate, and formamide (FA). It is found that incorporation of FA into metal-salt derived, ZTO-precursor solutions effectively facilitates the formation of chemical structures that possess less hydroxide and more oxygen vacancy (than for those lacking FA), allowing for high-performance ZTO channel layers. In addition, we demonstrate the creation of TFTs employing wet-patterend ZTO semiconductors, using an air-brush-printing technique without further etching procedures.

First, we synthesized the precursor solutions for FA-free ZTO semiconductors, in which Zn nitrate and Sn(II) chloride were introduced as Zn and Sn sources, respectively, by adding both metal salts, together with the chelation agent, ethanolamine, in 2-methoxyethanol. After vigorous agitation for a prolonged time, the resulting solutions were spin-coated onto 100 nm thick SiO_2/n^+-Si substrate, followed by thermal annealing at 400 °C in air. Then, Al source/drain electrodes were formed by thermal evaporation through a shadow-mask with channel dimensions of 100 μm (length) and 1000 μm (width), to complete the device architecture. Figure 1a shows the transfer characteristics of TFTs employing ZTO channel layers with different molar ratios of Zn to Sn. It was clearly observed that the more conductive behavior in TFT performances evolves with increasing the Sn content. Above Sn composition of 60 mol %, the transistor would not transit to an off-state even under a negative gate bias of −20 V, showing a current level of 10^{-3} to 10^{-2} A. When the composition was Sn-deficient (below 20 mol %), the threshold voltage shifted to the positive, with reduced field-effect mobility, compared with TFT based on ZTO layers with Sn compositions ranging of 40−50 mol % (Figure 1b). This behavior is commonly observed in channel layers with less charge carriers, mainly related to the suppressed oxygen vacancy formation. The mobility enhancement observed at intermediate compositions is a representative characteristic of solution-derived ZTO semiconductors.[20] Note that the obtained field-effect mobility approached ∼4 $cm^2/V{\cdot}s$, unlike for conventional approaches incorporating an acetate compound as a Zn source for preparing ZTO precursor solutions. With previous approaches, the channel materials with mobilities below 2.5 $cm^2/V{\cdot}s$ have been derived after annealing at temperatures below 400 °C, which is compatible with the use of rigid glass substrates.[21] The influence of film-thickness on TFT performance parameters (field-effect mobility and threshold voltage) was also investigated by varying the molar concentration (from 0.05 to 0.3 M) of metal cations in the precursor solutions. The film thickness for ZTO layers derived from 0.05, 0.1, and 0.3 M precursor solutions were measured to be ∼4, 6, and 15 nm, respectively. As shown in Figure S1 in the Supporting Information, the device showed a high off-current and a hugely negative-shifted threshold voltage, when the ZTO channel layer was derived from a precursor solution at 0.3 M. The charge carrier-deficient characteristic, indicated by a decrease of field-effect mobility and a positive shift of threshold voltage, appeared when the precursor solution was 0.05 M. This is in accordance with the fact that charge carriers are depleted in a front-channel of bottom-gate device architectures, by film thickness-dependent chemical interactions with O_2 and H_2O molecules.[22] In this study, all devices were fabricated and measured in ambient atmosphere with relative humidity 20−40%, except for the preparation of precursor solutions, which occurred in an Ar-filled glovebox.

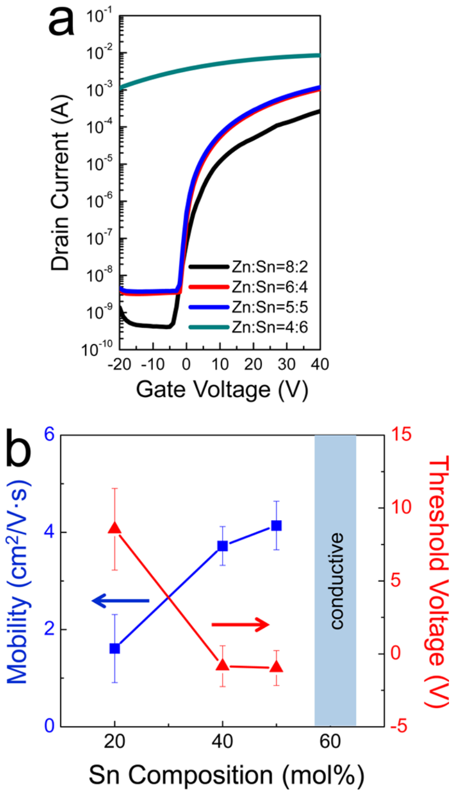

Figure 1. (a) Transfer characteristics and (b) variation in field-effect mobility and threshold voltage for TFTs employing FA-free ZTO channel layers with different Zn:Sn molar compositions. The molar concentration of metal cations in precursor solutions was 0.1 M.

To further improve the field-effect mobility, we next incorporated FA into the 0.1 M ZTO-precursor solutions with the equivalent composition of Zn and Sn. As shown in Figure 2, when 2 vol % FA was added without further treatments, the field-effect mobility increased by a factor of 1.9 (from 4.1 to 7.7 $cm^2/V{\cdot}s$). Considering only field-effect mobility, this mobility approaching 8 $cm^2/V{\cdot}s$ is near that of vacuum-deposited metal-oxide semiconductors that are industrially commercialized.[23] It should be noted that most high-mobility soluble-oxide semiconductors reported to date, have contained predominantly In_2O_3 as a mobility enhancer.[24] When more than 2 vol % FA was added, the device performance gradually degraded owing to the presence of impurities caused by excessive chemical additive, as seen in previous studies.[15,16]

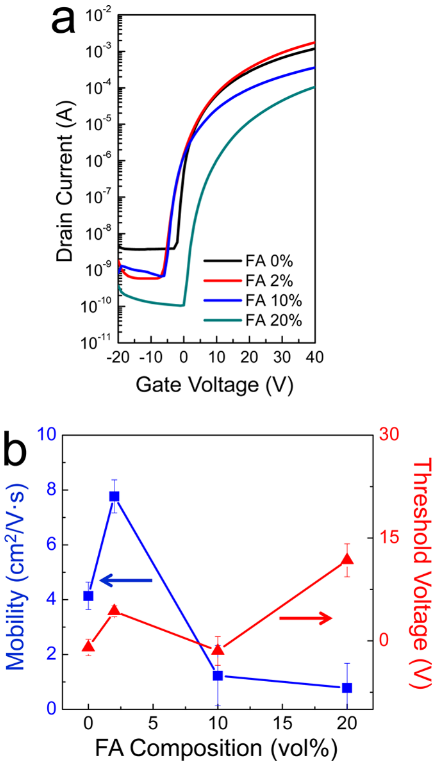

Figure 2. (a) Transfer characteristics and (b) variation in field-effect mobility and threshold voltage for TFTs employing ZTO channel layers with different FA composition in precursor solutions. The molar concentration of metal cations was 0.1 M, and the ratio of Sn to Zn was kept at 1.

Excessive amounts of chemical additives in precursor solutions leads to the presence of undecomposable impurities that adversely affect device performance, both by impeding charge-transport and by suppressing oxide formation.[25]

To study the chemical structural adjustment that might be achieved simply by adding the chemical additive, FA, we carried out X-ray photoelectron spectroscopy (XPS) analysis for two ZTO films prepared from precursor solution: one with 2 vol % FA, and one without FA. Prior to the in-depth investigation on O 1s spectra, we identified the valence of Sn in ZTO layers from Sn 3d spectra; as seen in Figure S2 in the Supporting Information, the valence was measured to be 4 for both FA-free and 2 vol % FA-added ZTO layers. Figure 3a shows the O 1s spectra for both films. The peaks, centered at ∼530.3 and ∼531.7 eV, were attributed to the oxygen in the oxide lattice without oxygen vacancies and with oxygen vacancies, respectively. The feature at ∼532.4 eV was associated with oxygen in the hydroxide. As seen in semiquantitative calculations for each structural component (oxide lattice (O_o^x), oxygen deficient lattice ($V_o^{\cdot\cdot}$), and hydroxide; see Figure 3b), upon the addition of 2 vol % FA, the oxide lattice with oxygen vacancy, which can act as the major source of charge-carrier generation, increased to a fraction of 0.11 from 0.02 while the fraction of hydroxide decreased from 0.29 to 0.20. Because the hydroxyl group is known as a trap-site for electrons, a major carrier in n-type semiconductors, such a chemical structural transition would be beneficial to create high-mobility channel materials. The absence of critical impurities that could be derived from FA molecules, was confirmed from the signal extinction in the N 1s XPS spectra (see Figure S3 in the Supporting Information). As shown in Figures S4−S6 in the Supporting Information, for both the FA-free and the 2 vol % FA-added ZTO layers, amorphous structures were observed in the X-ray diffraction (XRD) spectra and in the atomic force microscopy (AFM) images. The presence of uniformly dense, nanoscopic pore-free microstructures was confirmed, without noticeable differences in high-resolution transmission electron microscopy (HRTEM) images. This implies that the FA-mediated adjustment of chemical structure plays a dominant role in determining the device performance of the ZTO TFTs investigated in this study.

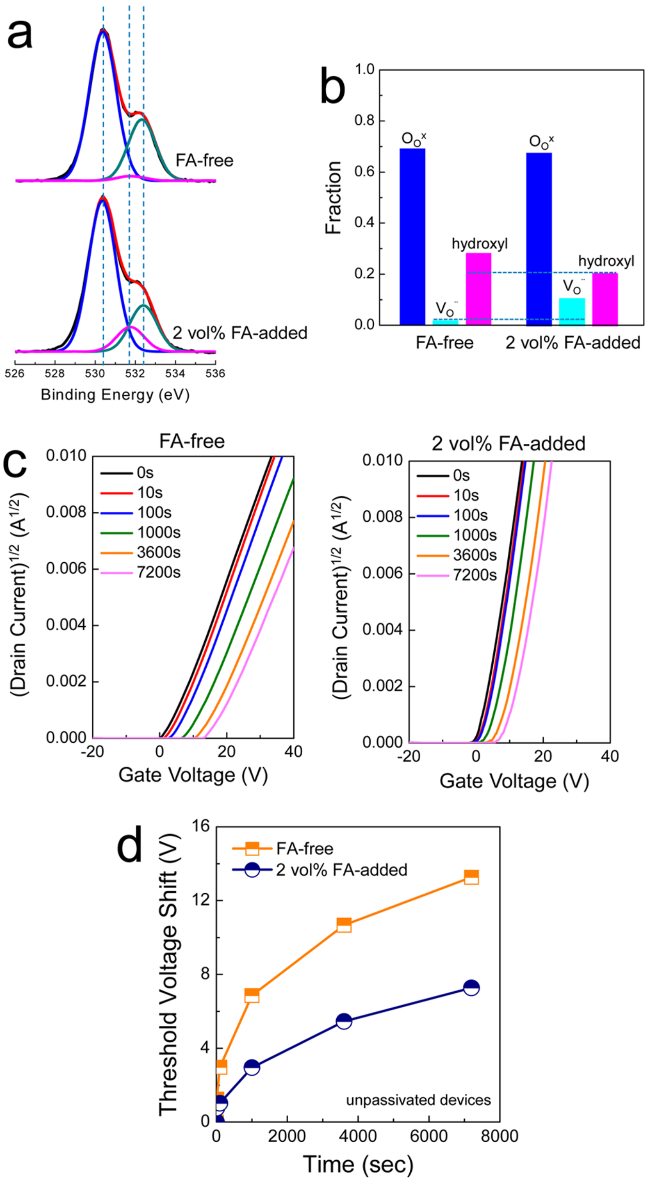

Figure 3. (a) O 1s XPS spectra and (b) semiquantitative analysis of ZTO layers prepared from FA-free and 2 vol % FA-added precursor solutions. The oxide lattice and oxygen deficient lattice are denoted by O_o^x and $V_o^{\cdot\cdot}$, respectively. (c) Plot of (drain current)$^{1/2}$ vs gate voltage and (d) the variation in threshold-voltage shift for unpassivated TFTs employing ZTO channel layers prepared from FA-free and 2 vol % FA-added precursor solutions, as a function of bias-stress time under a gate bias of 20 V. The molar concentration of metal cations was 0.1 M, and the ratio of Sn to Zn was 1:1.

This predominant contribution of the chemical structure was also confirmed with a positive bias stress (PBS) test for TFTs employing FA-free and 2 vol % FA-added ZTO channel layers. As shown in Figure 3c and 3d, as a positive gate bias of 20 V was applied (with a time frame up to 7200 s), a positive shift in the threshold voltage occurred. The threshold-voltage shift after applying a positive gate bias for 7200 s was significantly suppressed (from 13.3 to 7.3 V) by the addition of 2 vol % FA. In general, the metal oxide channel layers inherently suffer from bias instability due to a dynamic interaction with ambient, when the back channel is exposed in air, so that a passivation layer should be applied to enable the threshold voltage shift below 1 V.[26] However, to compare both devices, while excluding the secondary annealing effect by vacuum-deposited robust oxide films on top of the ZTO channel layer, the devices tested in this study were free of an additional passivation layer. In solution-derived oxide semiconductors, the degree of shift in a threshold voltage by PBS tests is influenced by the amount of hydroxide, as well as by the concentration of oxygen vacancies,[27,28] whereas the oxygen vacancy concentration is a predominantly determining factor for sputtered oxide semiconductors;[29] the amount of hydroxide overwhelmingly influences the threshold-voltage shift because of the presence of hydroxide as an inherent, intermediate chemical state in wet, chemically derived sol−gel materials.[27,28] This indicates that, for the case of TFTs with a 2 vol % FA-added ZTO layer, the reduction in the amount of hydroxide owing to the catalytic effect on the sol−gel condensation reaction, gives rise to the suppressed threshold-voltage shift in the PBS test. However, the positive shift, from −1 to 4.3 V of threshold voltage after adding of 2 vol % FA in unstressed, fresh devices is not clearly supportive of a change in the chemical structure, which indicates the involvement of another factor affecting device performance.

The air brush-printing technique is one of the best deposition methods for processing the wet-phase oxide precursor solutions over a large area. Spraying the liquid droplets through a nozzle, driven by a high-pressure air, allows easy application to extremely large-area substrates when a moving stage is involved, and the solidification of droplets traveling through open windows onto preheated substrate enables the formation of patterned structures. The chemical reactions needed to derive the phase-pure oxide skeletons, are completed by following the annealing procedures at elevated temperatures, similar to the case of spin-coated films. Jet-printing methods, which have been widely employed with soluble-oxide semiconductors, suffer from difficulty in reproducible control of each jet since in practical applications, an individual nozzle may have as many as 100 or more. Polymeric mold-based roll-printing techniques have not demonstrated the ability to produce high-performance soluble oxide transistors due to the limitation in designing ink rheology adequate for sequential transfer processes.[30] As shown in the inset image of Figure 4a, well-patterned ZTO films were generated, the dimensions of which almost corresponded to that of open windows (1500 μm in width and 2000 μm in length) in a mask. This indicates that the lateral migration of droplets underneath a mask in contact with a substrate preheated at 150 °C was effectively suppressed by instant solvent evaporation. The boiling point of 2-methoxyethanol solvent, is 124 °C. The bulged patterns were obtained with substrate temperatures below 100 °C. Figure 4 shows the transfer and output characteristics for air-brush-printed, 2 vol % FA-ZTO TFT. The field-effect mobility of 2.0 cm^2/(V s) and threshold voltage of −2.8 V, were measured with a clear pinch-off behavior in output characteristics, indicative of the formation of device-quality oxide films, even with wet-phase printing techniques. Compared with spin-coated devices, the slight degradation in device performance is likely attributable to the poor morphological properties (see Figure S7 in the Supporting Information), as well as to the difference in chemical structural evolution caused by the characteristic solvent evaporation from droplets during a trajectory toward a substrate (see Figure S8 in the Supporting Information).[30] As shown in Table S1 in the Supporting Information, compared with a spin-coated 2 vol % FA-ZTO layer, the fraction of oxygen vacancy decreased from 0.11 to 0.06, with fractional increment of hydroxide from 0.20 to 0.24. However, this chemical structure was still more favorable in device performance than that of spin-coated FA-free ZTO layers. However, as confirmed by TEM images (Figures S6 and S7 in the Supporting Information), the air brush-printed ZTO layer was of a relatively porous morphology with nanovoids caused by uneven distribution of the film structural density. Note that the as-dried films, formed by the air brush-printing technique, could be compatible with a variety of postannealing methodologies that have been recently exploited to significantly improve device performance. This is in sharp contrast with conventional spray-pyrolysis methods, where all the reactions, including solvent evaporation and sol−gel chemical reactions, are completed on top of the substrate heated to elevated temperatures without further annealing steps. It is believed that further improvement in device performance could be accomplished by coordinating post-treatment methods other than conventional thermal annealing.

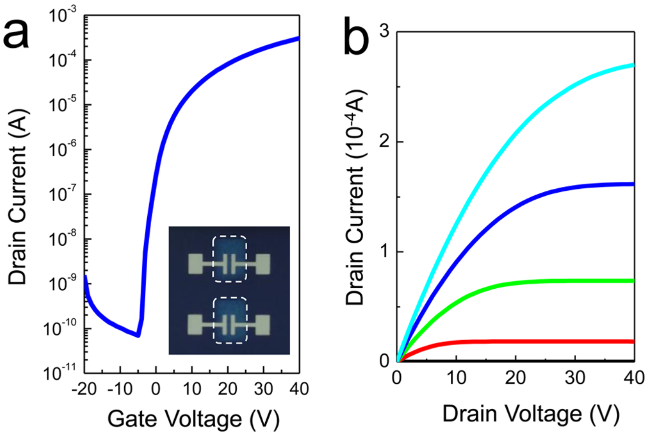

Figure 4. (a) Transfer and (b) output characteristics for TFTs employing air brush-printed, 2 vol % FA-ZTO channel layers. The molar concentration of metal cations in a precursor solution was 0.1 M, and the ratio of Sn to Zn was 1:1. The gate bias was varied from 0 to 40 V, with a bias interval of 10 V in measuring the output characteristics.

In summary, we demonstrated that FA-added ZTO precursor solutions enable the formation of chemical structures favorable for creation of high-performance metal oxide channel layers, resulting in ZTO TFTs having a mobility of 7.7 cm^2/(V s). It was revealed that the evolution of the chemical structure toward an oxide framework with a more oxygen-deficient lattice and with less hydroxide, was induced by the simple incorporation of a proper amount of FA into ZTO precursor systems. The FA-mediated ZTO channel layer was successfully implemented into the device architecture of TFTs as the first experimental demonstration that air brush-printed oxide semiconductors could be active channel layers for TFTs. It is believed that the development of chemical additive-driven, high-performance indium-free ZTO precursor, applicable to facile, easily accessible air brush-printing methods, would pave the way toward realizing low-cost, large-area, oxide-based electronic applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, the data for XPS semiquantitative analysis of spin-coated and air brush-printed ZTO layers, the device data for spin-coated FA-free ZTO TFTs as a function of a molar concentration in precursor solutions, XPS N 1s spectra, XRD results, AFM images, and HRTEM images for spin-coated ZTO layers, HRTEM image and XPS results for air brush-printed ZTO layer. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

§S.J.K. amd H.-J.J. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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