Thin-film transistors (TFTs) have broad applications for flexible electronics and information display. In the past, although the silicon-based TFTs have been primarily used for these applications,1,2 they all have been suffering from a number of limitations, including poor mechanical flexibility and/or indispensable high-temperature deposition processes, and particularly, much poorer performance as compared to the devices fabricated on a single crystalline wafer. Typically, α-Si TFT devices demonstrate a mobility of ∼1 cm²/V·s for display application,3,4 which limits their performance. The emerging organic TFTs can be processed essentially at room temperature but are also limited by poor mobility (∼1 cm²/V·s) and poor stability in the long run.5 So there is more and more research exploring new materials for higher performance devices.6,7 With excellent transparency, high stability, and low-temperature processes, amorphous metal oxide materials have drawn considerable attention for potential applications in transparent and flexible electronics, such as touch display panels. To date, most metal oxide TFTs have been fabricated with amorphous indium zinc oxide (α-IZO), zinc indium tin oxide,8 ZnO,9 In2O3,7 indium gallium zinc oxide,10–12 or some other oxide semiconductors as channel materials by the sol–gel route, with the performance approaching that of crystalline silicon based materials.13 Particularly for α-IZO TFTs prepared via the solution route, they have advantages over the vacuum deposition processes in terms of simplicity, cost, and scalability. High k self-assembled nanodielectrics has been explored as the gate insulator to fabricate amorphous metal oxide TFTs with the demonstrated mobility as high as 120 cm²/V·s.6 However, thermal stability is a key challenge to self-assembled nanodielectric development.

To implement high-performance electronics, materials with a high carrier mobility are required. With regard to the original α-IZO TFTs, the carrier mobility is too poor to promise potential applications (usually 1–10 cm²/V·s on SiO2 back gate).11,14–16 So it is important to further improve it in terms of mobility. On the other hand, although the mechanical flexibility of α-IZO thin film is better than that of crystalline phase, there were still reports on the drastic performance degradation after repetitive bending; thus, it is not satisfactory for practical flexible electronics, when compared with organic TFTs.17 In the past, single-walled carbon nanotubes (SWNT) have attracted substantial research interest for flexible electronics applications owing to their unique mechanical and electrical properties. They are among...
the strongest fibers in the world, with a Young’s modulus in the range of 1–2 TPa, fracture stress of 50 GPa, and a high mobility $\sim 10$ 000 cm$^2$/V·s.$^{18}$ Depending on their chirality and diameter, a SWNT can behave as either a metallic material ($m$-SWNTs) or a semiconductor material ($s$-SWNTs).$^{19}$ Nevertheless, there still lacks an effective method to control the chirality and assembling a large number of SWNTs deterministically to realize scalable device/circuit fabrication.

Herein, we propose a novel approach that addresses both the unsatisfactory mobility and mechanical behaviors of the $\alpha$-IZO thin film, through using a hybrid material structure consisting of SWNTs embedded directly into the $\alpha$-IZO thin film via a simple spin-coating process, which significantly improves electrical properties and mechanical behaviors of the thin films. In addition, this process is demonstrated to be compatible with different types of substrates.

Figure 1a presents an analogy of the design concept: with a high mechanical strength and toughness, reinforced concrete, which is made of concrete and cement, is widely used in the construction industry. Concrete is a brittle material and is strong in compression; however, it is weak in terms of tension. On the other hand, steel has a high tensile strength. When completely surrounded by the hardened concrete mass it forms an integral part to interlock both materials, forming “Reinforced Concrete” (Figure S1, Supporting Information). Similarly, we propose the model of hybrid thin film composed of SWNTs and $\alpha$-IZO. On one hand, SWNTs could give rise to dramatic enhancement of mechanical behaviors; on the other hand, by utilizing the sol–gel route SWNTs are embedded into $\alpha$-IZO to form a three-dimensional (3-D) evenly distributed hybrid thin film which serves as electron-conducting channels. The hybrid thin film is composed of a large number of nanotubes in the form of a random network embedded in the $\alpha$-IZO block; hence the 2/3 inherent s-SWNTs were passivated, leading to an even metallic SWNTs network in the hybrid nanosystem.$^{20}$ So the superior transporting channels result in a significant improvement on mobility. Figure 1b shows the fabrication process of a hybrid TFT array. Briefly, SWNTs (>$90$ wt %, 0.5–2 $\mu$m in length, AlphaNano Technology Co., Ltd.) were added into 2-methoxyethanol (2-ME) and then ultrasonized to achieve uniform dispersion in the solution, labeled as solution A. Then a 0.03 M mixture of zinc acetate dihydrate $[\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}]]$ and indium nitrate hydrate $[\text{In(NO}_3)_3 \cdot 4\text{H}_2\text{O}]]$ was used as the sol–gel precursor; the mole ratio of In/Zn was fixed at 1:1, which were dissolved in 2-ME. Monoethanolamine (EA) was added with the mole ratio of In/E A = 1:10 and then stirred for $1$ h at room temperature to form stable IZO precursor solutions. Thereafter, solution A with the SWNT/IZO weight concentration ranging systemically from 0 to 1% was added into IZO precursor solutions. Finally, ultrasonication was performed for 2 h to form homogeneous hybrid thin film precursor solutions, and the total volumes of the solutions were all fixed at 50 mL. The precursor solution was then spin-coated onto $\text{SiO}_2$ (300 nm) coated $p$-Si substrate (TFT back-gate contact) at 2400 rpm for 60 s and prebaked on a hot plate at 150 $^\circ$C for $10$ min to remove the organic solvent. After prebake, the films were cooled to room temperature, and the aforementioned processes were repeated subsequently. The as-prepared thin films were annealed on the hot plate at 350 $^\circ$C for 40 min in the atmosphere. Finally, the 60 nm thick $\alpha$-IZO/SWNTs thin films were obtained. A first photolithography and wet etch process was carried out to define the as-prepared thin film into isolated pads. Note that our back-gate device structure not only suppressed the gate leakage current but also reduced parasitic capacitance, both of which were essential for back-gate TFTs.$^{4,21,22}$ Subsequently, the second photolithography was conducted to pattern the source and drain, and the TFT structure was completed by the Cr/Au (15 nm/30 nm) evaporation and lift-off process.

The morphologies of the thin films are examined by atomic force microscopy. Figure 1c shows a 0.5 wt % $\alpha$-IZO/SWNTs hybrid thin film, indicating that the film is compact, uniform, and reasonably smooth with a few overweight SWNTs randomly on surface. The Raman spectrum of the hybrid thin film also indicates the matched peaks of SWNT (Figure S2, Supporting). The ultraviolet–visible transmission spectrum demonstrates that the hybrid thin films have good transparency in the visible region (Figure 1d). The inset image in Figure 1d shows an optical image and the transparent nature of the $\alpha$-IZO/SWNT film on glass. Therefore, the amorphous hybrid thin film prepared in this study is a good candidate for fabricating transparent devices.

After TFTs fabrication, the back-gated devices were evaluated in ambient conditions. The $I_{ds}–V_{gs}$ curves of $\alpha$-IZO based TFTs with SWNT weight concentrations from 0 to 1% were measured (Figure 2a–c). The channel length and width we used here are 20 $\mu$m and 75 $\mu$m, respectively, with a 300 nm thick $\text{SiO}_2$ gate insulator; the resulting field effect carrier mobility in the $\alpha$-IZO based TFTs increases from 1.9 $\text{cm}^2/\text{V·s}$
for pristine film to a high mobility of 140 cm²/V·s for the hybrid film with 1 wt % SWNTs. In addition, the \( I_{ds} - V_{ds} \) curves display a clear linear regime at low voltages (Figure 2d–f), indicating ohmic contacts formed between the Cr/Au electrodes and hybrid thin film. The clear pinch-off and \( I_{ds} \) saturation indicate that the carrier transport in active channels is completely controlled by the gate potential. As mentioned in the former, SWNTs replaced \( \alpha \)-IZO in the block and provided fast tracks for carrier transport with less scatter in the hybrid thin film.\(^{23}\) Due to the number of SWNTs imbedded into the hybrid thin film increased with the SWNTs weight concentration, the increasing SWNT weight concentration leads to the enhancement of both transfer and output characteristics, with the on/off ratio enhanced from \( \sim 5 \times 10^4 \) to \( \sim 1.3 \times 10^7 \).

The critical effect of the SWNTs used in the precursor solutions is demonstrated in the field effect mobility versus SWNTs weight concentration, which is shown in Figure 3a. Also it demonstrates an approximately clear linear relationship between them. To explain the improvement on TFT performance with incorporating SWNTs, we present equivalent circuit diagrams in Figure 3b,c. The transconductance can be obtained in the form of \( g_m = (\partial I_d/\partial V_g) \), and considering the totally collective effect,
The photograph that measures the repeated bending performance. (d) The ultraviolet–visible transmission spectrum of the real device, and the inset is the optical image. (e and f) Electrical characteristics of the transparent 0.5 wt % α-IZO/SWNTs TFT fabricated on ITO coated glass; the inset in e is the schematic diagram of the transparent TFT, where the fabricated device shows a reasonable field effect mobility of 63.4 cm²/Vs.

\[
g_{m} = \frac{\Delta V_{ds}}{V_{g} - V_{T}} \approx \frac{V_{ds} - V_{th}}{V_{g} - V_{T}} \cdot \frac{1}{nR_{g}} \tag{1}
\]

The pristine α-IZO TFT can be regarded as \( n \) parts individual small FETs connected in series, shown in Figure 3b. In this case, each FET has a resistance \( R_{i} \) at the ON state. As the on/off ratio of the fabricated devices are all larger than 10⁴, overall \( R_{on} > 10^{4} R_{on} = 10^{4} nR_{g} \) hence

\[
g_{m1} = \frac{V_{ds} - V_{th}}{V_{g} - V_{T}} \approx \frac{V_{ds}}{V_{g} - V_{T}} \cdot \frac{1}{nR_{g}} \tag{2}
\]

On the other hand, the equivalent circuit for the hybrid thin film is depicted in Figure 3c, in which some SWNTs “short” α-IZO FETs in the hybrid thin film.⁴ Compared with \( R_{g} \), the resistance of an individual SWNT we used here can be ignored. Then, assuming that \( m \) \((m < n)\) parts of the α-IZO are shorted by SWNTs; therefore,

\[
g_{m2} = \frac{V_{ds}}{V_{g} - V_{T}} \approx \frac{V_{ds}}{V_{g} - V_{T}} (n-m)R_{g} \tag{3}
\]

Hence

\[
\mu_{2}/\mu_{1} = g_{m2}/g_{m1} = \frac{n}{n-m} \tag{4}
\]

\[
\mu_{2} = \frac{n}{n-m} \mu_{1} \tag{5}
\]

As the SWNT molar concentration is close to the precursor of α-IZO, this leads to the number of SWNTs incorporated in the hybrid system approaching to that of the α-IZO parts; hence the measured mobilities demonstrate a close to linear dependence on the SWNTs concentration shown in Figure 3a. This clearly explains that the field effect mobility increases with the concentration of SWNTs. In accordance with this rationale, we intended to exploit the limitations of the achievable mobility. Figure 3d shows the transfer characteristics as we doubled the SWNTs concentration to 2 wt % corresponding to the largest mobility we have obtained (140 cm²/Vs). Interestingly, the film presents high conductance but a weak p-type field effect, indicating the SWNTs are starting to make a fully percolation network to dominate the charge transport. The pristine-SWNT devices have been fabricated by electron beam lithography (JEOL SEM with an NPGS system), the electrical properties are similar with that of 2 wt % SWNT into α-IZO film (shown in Figure S3 of the Supporting Information). As coessential materials, we also demonstrated that the MWNTs were valid for improving the mobility of α-IZO thin film as well, shown in Figure 3e. However, as both the volume and mass of an individual MWNT are much larger than SWNT, so the numbers of MWNTs embedded into the hybrid system were much less than SWNTs with the same weight concentration. Thus the mobility of 0.5 wt % α-IZO/MWNTs TFT is lower than that of equal weight concentration α-IZO/SWNT TFTs that we have demonstrated.

To confirm the critical role of SWNTs for achieving excellent device mechanical behaviors, we fabricated two pairs of α-IZO and α-IZO/SWNT (with 0.5 wt % SWNTs) devices both on polyimide substrate via the same processes. Generally, the lack of SWNTs in the pristine α-IZO thin film led to more fragility. Dynamic loading tests were carried out (see the inset of Figure 4a). The actual bending radius of the loaded substrates was measured by fitting circles to images taken by an optical camera mounted facing the edge of the film. All devices under test were characterized at a specific bending radius by measuring the channel resistance and then normalized to the strainless state. It is evident that, as the radius decreased to less than 2 mm, the conductance of pristine α-IZO thin film deteriorated dramatically, until it reached the scrapped state of more than 3200% variation, when the substrate was pushed at the smallest radius of 700 μm (the bending radius is limited by the rigid areas within the substrate, and the thickness of the substrate is about 200 μm). In contrast, the hybrid thin film exhibits much better mechanical stability with the largest variation of only 17%, as shown in Figure 4a. To our knowledge, the smallest
bending radius of α-IZO/NT film in this work is also the smallest among most of oxide film transistors (~10 mm). Notably, it is even of comparability with the organic TFTs that were demonstrated to possess extreme bending stability. The repeated bending test of the devices was evaluated by bending the substrate into an ultrasmall radius along the axis running exactly through the channel, with the direction of the bending-induced strain aligned perpendicularly to the direction of the current flow from drain to source (as shown in Figure 4c). Figure 4b shows the normalized channel resistance as a function of bending cycles. As it can be seen, the variation is less than 8% for the α-IZO/SWNT hybrid thick film, which indicates the hybrid thin film devices are stable for a series of rigorous bending tests even after 300 cycles of repeated bending. However, the pristine α-IZO thin film showed quick performance degradation. To our knowledge, the overall mechanical performances reported here are among the best performance degradation. To our knowledge, the overall mechanical performances reported here are among the best performance degradation.

To fabricate transparent TFTs, 200 nm SiN<sub>x</sub> was deposited on ITO glass by plasma enhanced chemical vapor deposition (the C–V curve of SiN<sub>x</sub> is shown in Figure S4 of the Supporting Information, indicating a capacitance per unit area of 29.5 nF/cm<sup>2</sup>), and then α-IZO/SWNT hybrid thin films with 0.5 wt % SWNTs were fabricated with the aforementioned processes, followed by photolithography process to define the source/drain patterns on the thin film. Eventually, the transparent TFTs array was fabricating after sputtering 50 nm ITO film. Figure 4d is the ultraviolet–visible transmittance spectrum of the real device, with the inset optical image indicating the transparency. The I–V characteristics of a hybrid α-IZO/SWNT n-channel TFT are shown in Figure 4e.f. Accordingly, we have obtained the field effect mobility from \( I_D - V_D \) curve in Figure 4e, leading to a reasonable result of 63.4 cm<sup>2</sup>/Vs comparable to the TFTs fabricated on silicon oxide. This result indicates that the α-IZO/SWNT hybrid thin films used in this experiment are stable and could be generalized to other nanosystems to obtain transparent and flexible devices defined on some types of substrates.

In conclusion, we have demonstrated that the sol–gel processed α-IZO/SWNTs composite thin film shows promises as a transparent, flexible, and high mobility material. In the composite, SWNTs provide fast tracks for carrier transport to significantly improve the apparent field effect mobility. Furthermore, SWNTs render excellent mechanical flexibility for flexible electronics. Finally, we have successfully demonstrated the transparent TFTs by processing the composite thin film on commercial ITO glass substrate, which indicated our methods and materials were environmentally stable, compatible, and suitable for being generalized on other substrate for flexible and transparent electronics.

**ASSOCIATED CONTENT**

Supporting Information

Schematic diagram of the analogic design conception of reinforced concrete (Figure S1); Raman spectrum of SWCNTs and the hybrid thin film (Figure S2); electrical transfer characteristics of the pristine SWCNTs network (Figure S3); C–V curve of the SiN<sub>x</sub> insulator deposited by plasma enhanced chemical vapor deposition (Figure S4); electrical characteristics of the 1.5 wt% α-IZO/SWNT TFT (Figure S5); and the curve of mobility versus SWNT concentration and the matched function (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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**REFERENCES**


