Transferred wrinkled Al$_2$O$_3$ for highly stretchable and transparent graphene–carbon nanotube transistors

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Despite recent progress in producing transparent and bendable thin-film transistors using graphene and carbon nanotubes$^{12}$, the development of stretchable devices remains limited either by fragile inorganic oxides or polymer dielectrics with high leakage current$^{13}$. Here we report the fabrication of highly stretchable and transparent field-effect transistors combining graphene/single-walled carbon nanotube (SWCNT) electrodes and a SWCNT-network channel with a geometrically wrinkled inorganic dielectric layer. The wrinkled Al$_2$O$_3$ layer contained effective built-in air gaps with a small gate leakage current of $10^{-13}$ A. The resulting devices exhibited an excellent on/off ratio of $\sim 10^5$, a high mobility of $\sim 40$ cm$^2$/V·s and a low operating voltage of less than 1 V. Importantly, because of the wrinkled dielectric layer, the transistors retained performance under strains as high as 20% without appreciable leakage current increases or physical degradation. No significant performance loss was observed after stretching and releasing the devices for over 1,000 times. The sustainability and performance advances demonstrated here are promising for the adoption of stretchable electronics in a wide variety of future applications.

In contrast to rigid electrical devices, the successful fabrication of stretchable thin-film transistors (TFT) requires that the active channel, electrodes and gate dielectric be engineered to withstand high levels of strain without degradation of the electrical properties. In such TFTs, carbon materials are a promising candidate for both the conducting electrodes and the semiconducting channel. Highly transparent, flexible semiconducting SWCNTs with a high mobility of $\sim 40$ cm$^2$/V·s and an on/off ratio of $\sim 10^5$ are ideal for use as an active-channel material for stretchable devices$^{3,9}$. Likewise, the low sheet resistance ($\sim 300 \ \Omega$), high transmittance ($\sim 97.7\%$) and high fracture strain resistance ($\sim 20\%$) of monolayer graphene make it an excellent complementary electrode material$^{10-12}$. However, the limited tensile strength of dielectric gate materials is the primary challenge for producing stretchable devices. Typical inorganic gate oxides are fragile and easily degrade in both bendable and stretchable devices, and polymer dielectrics have high leakage current despite their excellent bendability$^{13,14}$. Therefore, to maximize the performance of the oxide without compromising the ability to stretch and bend, we propose a new approach for preparing a wrinkled gate dielectric using a transfer method.

Figure 1 shows a schematic representation of the fabrication of stretchable graphene/SWCNT TFTs on a thin polydimethylsiloxane (PDMS) film. Initially, a 200-nm-thick sacrificial Al layer was deposited onto a SiO$_2$/Si substrate. A thin polyimide (PI) layer was formed on the Al film by spin-coating and annealing polyamic acid$^{14}$ (PAA) (see Supplementary Information S1). Monolayer graphene was then transferred onto the PI film and patterned as source, drain and gate electrodes using photolithography and O$_2$ plasma etching. The monolayer graphene was grown on copper foil using atmospheric pressure chemical vapour deposition (APCVD) and had a sheet resistance of 366 $\Omega$ per square and a transmittance of 98% at a wavelength of 550 nm (ref. 15). Our main challenge was to fabricate the stretchable gate dielectric using a thin layer of aluminium oxide (Al$_2$O$_3$). A 50-nm-thick Al$_2$O$_3$ layer was deposited onto rough Cu foil using atomic layer deposition (ALD) followed by edge coating with poly(methyl methacrylate) (PMMA). This selective PMMA edge-coating was necessary to prevent fracture of the Al$_2$O$_3$ layer. When the PMMA was coated on the whole oxide layer area, the Al$_2$O$_3$ layer was fractured easily during acetone cleaning owing to the strong adhesion between the PMMA and the Al$_2$O$_3$ layer (Supplementary Fig. S3). The Cu foil was chemically etched with a Cu etchant (CE-100), and the Al$_2$O$_3$ layer was then transferred onto the graphene electrodes. The transferred Al$_2$O$_3$ layer was patterned using photolithography and chemically etched with hydrofluoric acid (HF). The resulting Al$_2$O$_3$ layer was wrinkled with a wavy structure, as shown in the scanning electron microscopy (SEM) image in Fig. 1c. The wrinkled structure imparts stability to the gate dielectric under high tensile strain$^{16,17}$, which is remarkably different from a flat structure. It is also noted that our wrinkled oxide is naturally formed during the transfer process and randomly oriented, in good contrast with uniaxially grooved structures$^{16,17}$, allowing the realization of biaxial stretchability. Next, the SWCNT network was prepared using APCVD (ref. 20), transferred onto the device and then patterned using photolithography and O$_2$ plasma etching. After transferring the APCVD-grown SWCNT network, photoresist was patterned to cover both the active-channel region and graphene electrodes (S, D, G) to prevent graphene damage (Supplementary Fig. S5). Using this process, SWCNTs remained on the graphene electrode surfaces after photoresist removal. Finally, the resulting TFT-patterned PI film was detached from the Si wafer by etching the sacrificial Al layer and transferred onto a PDMS

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Figure 1 | The fabrication scheme of the device array. a, Stretchable device fabrication procedure. PI was coated onto an Al-deposited SiO$_2$/Si wafer. Once a monolayer of graphene was patterned for the electrodes, and the active-channel SWCNT film was deposited, the aluminium layer was removed by etching, and the PI/devices were then transferred onto a stretchable PDMS substrate. The photograph illustrates the stretchable device array. b, Graphene/SWCNT TFT fabrication procedure. The transferred monolayer of graphene was patterned by O$_2$ plasma to form source, drain and gate electrodes. The wrinkled oxide was transferred directly onto the prepared substrate. The patterned gate oxide was formed on the channel region by HF etching. The APCVD-grown SWCNT random network was transferred and patterned to form an active-channel area. c, The wrinkled Al$_2$O$_3$ layer transfer process. A 50 nm-thick Al$_2$O$_3$ layer was deposited onto copper using ALD, followed by PMMA edge-coating. The copper layer was removed with Cu etchant (CE-100) and then the PMMA-attached wrinkled Al$_2$O$_3$ layer was transferred onto the prepared substrate, and the PMMA was removed. The wrinkled aluminium oxide layer is clearly visible in the SEM image.
presence of air gaps resulted in an order of magnitude decrease in the gate leakage current compared with the flat oxide layers (Supplementary Fig. S13). The device characteristics strongly relied on the density of the SWCNTs, which was controlled by the concentration of the catalyst. By decreasing the SWCNT density, the on/off ratio increased, whereas the mobility was degraded (Fig. 2f). This trade-off results from the presence of metallic SWCNTs in the channel. The parallel-plate model is widely used for calculating the mobility of common TFTs such as silicon, organic and other semiconductor TFTs. In the case of the CNTs, the CNTs are sparsely distributed in the channel (Fig. 2f, insets) particularly at a low CNT density, and the parallel-plate capacitor model overestimates the gate capacitance and underestimates the mobility. A realistic cylindrical model that considers the electrostatic coupling between the CNTs (refs 23,24) was also used to calculate the mobility (see Supplementary Table S1 and Fig. S14). The cylindrical model yielded a high mobility of 624.8 cm²·V⁻¹·s⁻¹ at a low SWCNT density of 0.7 SWCNTs µm⁻². However, at the high CNT density limit, both models approached a similar value of ~800 cm²·V⁻¹·s⁻¹. The subthreshold swing was 98 mV dec⁻¹, which is similar to that of an individual CNT TFT (ref. 25). Our graphene/SWCNT TFT array with PI showed a high transmittance of 78% (device itself shows 84%) at the wavelength of 550 nm, because of the highly transparent graphene electrodes, the SWCNT channel and the Al₂O₃ dielectric as shown in Fig. 2h. The inset presents an optical image that illustrates the transparency of a graphene/SWCNT TFT array on the PI/PDMS substrate.

To provide a proof of concept for the feasibility of the wrinkled oxide for stretchable electronics, the device was stretched along both the channel length and width axes. Optical images of the devices stretched along the length direction (16% strain) and along the width direction (20% strain) are shown in Fig. 3a,b (see also Supplementary Fig. S17). The graphene/SWCNT electrodes, the SWCNTs channel and the dielectric layer were simultaneously stretched. The transfer characteristics were obtained in terms of strain (Fig. 3c,d). The on-current value was linearly reduced by 4% per strain in the length direction and 2% per strain in the width direction with respect to the unstrained current value because of the increase in the contact resistance between the CNTs (refs 26,27; see Supplementary Information, S14). This result contrasts with previous studies in which the resistance increased exponentially with strain in high-density CNT films. The device failed at strains above 20% for both directions when the leakage current of the oxide layer surged (see Supplementary Information, S15). Furthermore, the large built-in air gap in our wrinkled oxide can act as a secondary dielectric layer to prevent leakage current in spite of the presence of local Al₂O₃ cracks. Nevertheless, the on/off ratio fluctuated but did not degrade as the strain increased (Fig. 3g,h). The graphene/SWCNT
Figure 3 | The device performance changes with tensile strain, and fatigue testing when stretching and releasing 1,000 times. 

a, b, Schematic illustrations and optical images of the stretchable graphene/SWCNT TFTs on PI/PDMS stretching along the channel length direction up to 16% (a) and stretching along the channel width direction up to 20% (b). c, d, Transfer characteristics ($V_{DS} = 1\, \text{V}$) with tensile strain applied along the length direction (c) and width direction (d). The insets show log-scale characteristics. The devices exhibit stable operation for stretching up to 16% in the length direction and 20% in the width direction. e, f, Normalized on/off ratio, transconductance, current levels (on-current (blue circle), off-current (red circle)) and mobility variation (black square) with respect to values at zero strain along the length direction (e) and the width direction (f). g, h, Normalized on/off ratio, transconductance, current levels (on-current (blue circle), off-current (red circle)), and mobility variation (black square) with 10% stretching and releasing cycles.
hybrid electrode helps to improve connectivity and hence the stretchability of electrodes. The mobility fluctuation precisely resembled the change in the transconductance, but the magnitude of the fluctuation was higher because of the incorporation of strain in the channel length and width (Fig. 3e,f). A fatigue test was also performed by repeating 10% stretching and releasing for both directions. Although the on/off ratio, transconductance and mobility of the devices fluctuated to some degree, the devices were stretched and released up to a maximum of 1,000 times without being deteriorated. We emphasize that the long-term stability was maintained with minimum leakage current because of the highly stretchable wrinkled gate dielectric.

To support the robustness of the wrinkled oxide for stretchable devices, a finite-element method was used to model the elongation-induced stress of a thin Al$_2$O$_3$ layer. Two models were considered: uniaxially wrinkled structures and randomly wrinkled structures. Figure 4a shows the stretchability of uniaxially wrinkled Al$_2$O$_3$ as a function of a ratio $R = P/H$, where $P$ is the period and $H$ is the height of the wrinkles). When $R = 2$, maximum stretchability of almost 30% was achieved at the given ultimate tensile strength of Al$_2$O$_3$ (1.9 GPa; ref. 30). This is in contrast to flat Al$_2$O$_3$, where the stretchability reaches only 0.475% at ultimate tensile strength. Also shown in Fig. 4a are the respective stress distributions for a given elongation (10% and 20%) with 50-nm-thick Al$_2$O$_3$ and $R = 2$. It is intriguing to note that the negative curvature area of the wrinkle is more severely stressed, as shown in the inset. A randomly wrinkled structure was generated from atomic force microscopy (AFM) topography scans of the transferred oxide. Figure 4b shows a three-dimensional mapping of the stress distribution on the randomly wrinkled oxide under elongations of 0 (pristine), 10 and 20%. At 20%, the maximum stresses (up to the ultimate tensile strength) are distributed randomly but are still localized in a wavy shape. It is again emphasized here that the highest stress is located in the negative curvature regions, similar to the uniaxial stress case (see also Supplementary Information S16).

Figure 5 demonstrates the compatibility of the devices on various stretchable media. These stretchable media include human skin, rubber, a toothpaste tube, aluminium foil, a plastic heart and a light-bulb surface (Supplementary Information S19). The technical relevance of our transparent devices is widespread, encompassing the areas of flexible, bendable, twistable and stretchable electronics.

Methods

Synthesis of the transferred wrinkled Al$_2$O$_3$. A 50-nm-thick alumina (Al$_2$O$_3$) layer was deposited on 3 cm x 3 cm Cu foil using ALD at 10$^{-4}$ torr and 200 °C. Scotch tape covered the centre part of the Cu foil during spin-coating of PMMA (1,000 r.p.m., 1 min). On removing the scotch tape, only the edge of the Cu foil is covered by PMMA. After edge-coating of PMMA, Al$_2$O$_3$ that deposited on the bottom side of the Cu foil was etched by HF, and then the Cu was etched by a wet etching process (CE-100). The PMMA-coated Al$_2$O$_3$ was rinsed four times using deionized water for ~10 min and transferred onto the target substrate. The sample was dried in a dry oven at 70 °C for 10 min. The PMMA was removed using acetone, and then the sample was baked at 150 °C for 3 h to give good adhesion between the Al$_2$O$_3$ and the substrate.

Transfer process of a graphene and SWCNT network. PMMA was spin-coated onto the graphene-grown Cu foil at 500 r.p.m. for 5 s and then 1,000 r.p.m. for 1 min. A Cu etchant (CE-100) was used to dissolve the copper. The SWCNT network grown on a Si wafer was PMMA-coated in a manner similar to the graphene transfer process. The SiO$_2$ layer was rapidly removed using HF. After rinsing (deionized water, ~10 min) four times, the PMMA-coated graphene/SWCNT was transferred onto the target substrate. This sample was dried in a dry oven at 70 °C. Finally, the PMMA was removed with acetone.

Fabrication of stretchable transistor array on PI/PDMS substrate. The 200 nm Al layer was deposited onto the SiO$_2$/Si layer using a thermal evaporator at 10$^{-7}$ torr. PAA was coated onto the Al/SiO$_2$/Si, which was followed by a heat treatment (300 °C) at 10$^{-2}$ torr. The PI layer converted from PAA has a thickness of 50 μm. Graphene was transferred onto the PI-coated Si wafer with an Al scarifying layer and patterned by photolithography and O$_2$ plasma etching (480 mtorr, 20 W, 10 s) to transparent source, drain and gate electrodes. The wrinkled Al$_2$O$_3$ was transferred and patterned by photolithography and HF wet etching on the patterned graphene as the dielectric layer. Finally, the APCVD-grown SWCNT-network channel was transferred and the photoreist was patterned on both the active-channel region and the graphene electrodes (S, D, G) to prevent graphene damage.
Before bending
After bending
Rubber tube

Before bending
After bending
Toothpaste

Before bending
After bending
Aluminum foil

Figure 5 | Photographs of stretchable graphene/SWCNT TFT arrays transferred onto various substrates and the related transfer characteristics.

a–c, Our devices were transferred onto a cylindrical rubber tube (outer diameter is 2 cm; a), a polypropylene toothpaste tube (b) and aluminium foil (c).

Transfer characteristics of stretchable graphene/SWCNT TFTs were measured before and after bending, where the estimated peak strains of each bending are 1.5% (a), 2% (b) and 1% (c), respectively. I–V results in linear scale show no appreciable difference even after bending.

unnecessary SWCNTs were selectively etched away by O$_2$ plasma. After finishing the device fabrication on the PI, the device on the PI was transferred to PDMS of with a 0.5 mm thickness using Al layer etching.

Device characterization and stretching tests. SEM images were recorded on a JEOL7600F, and a SPA400 (SEIKO; Renishaw) was used to characterize the SWCNTs and graphene with a wavelength of 514 nm (2.41 eV) and a Rayleigh line rejection filter. Ultraviolet–visible–near-infrared absorption spectroscopy (Varian, Cary 5,000) was used to analyse the transmittance of graphene. The device array was placed in a uniaxial stretch machine. One side of the PI/PDMS substrate was fixed, and the other side was pulled to stretch. Each fatigue test was performed for up to 1,000 cycles to 10% strain. Electrical measurements were performed using a probe station (Keithley 4200) while stretched.

References


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**Author contributions**

S.H.C. contributed to the experimental planning, experimental measurements, data analysis and manuscript preparation. W.J.Y. and X.D. performed the experimental planning. D.L.D. performed the AFM measurement, J.J.B. and Q.A.V. performed the finite-element method simulation, and H.Y.J. took the photographic images. D.P. and M.J.Y. contributed to the theoretical calculations. Q.H.T. and T.H.L. prepared the graphene samples for the experiments. Y.H.L. contributed to the experimental planning, data analysis and manuscript preparation.

**Additional information**

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to Y.H.L.

**Competing financial interests**

The authors declare no competing financial interests.
In the version of this Letter originally published online, in the left panel in Fig. 3a, the schematic of the device was missing. This error has been corrected in all versions of the Letter.