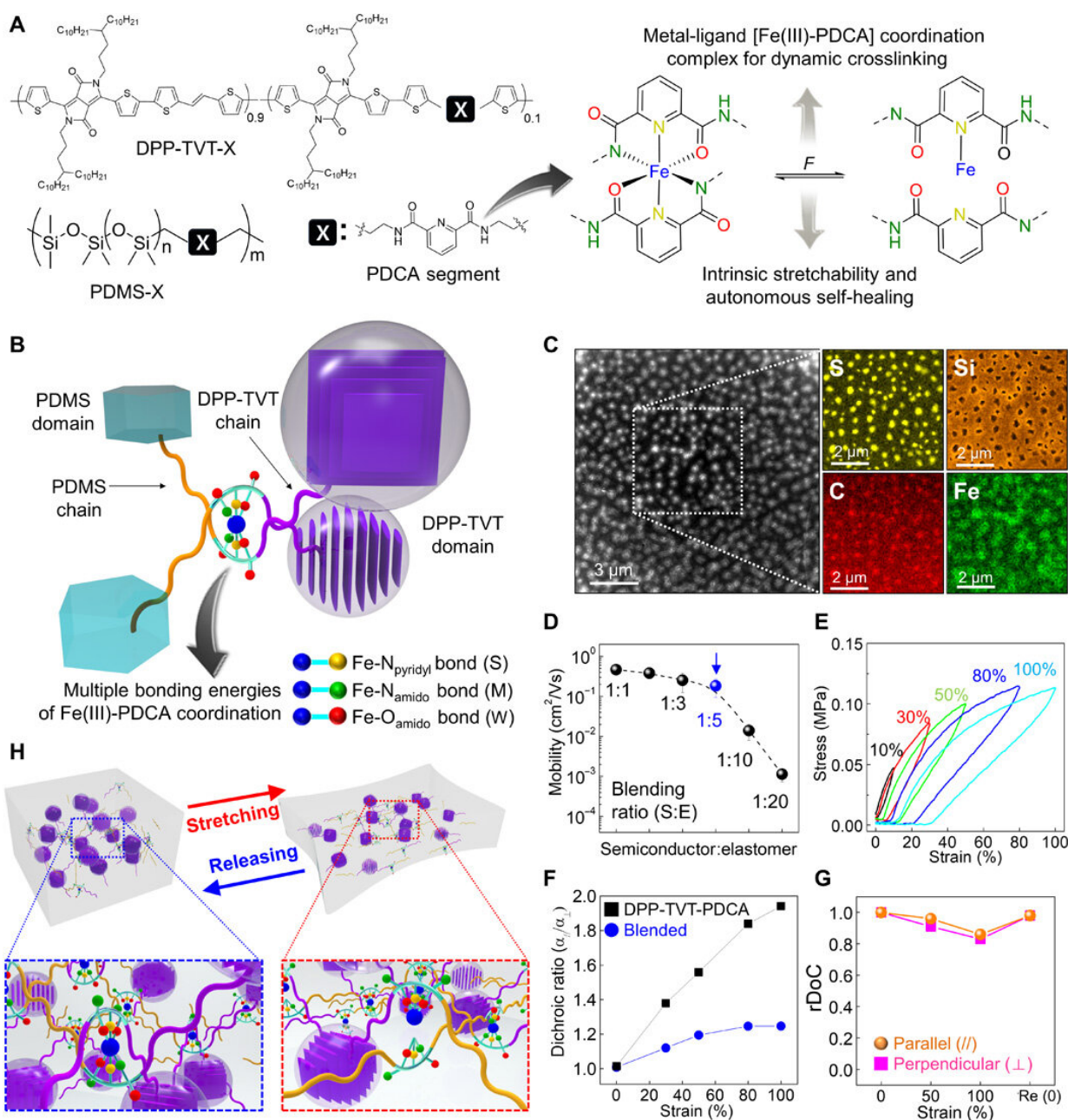


Stretchable, self-healing and semiconducting polymer films for electronic skin (e-skin)

November 15 2019, by Thamarasee Jeewandara



Design and characterizations of strain-sensitive, stretchable, and self-healable semiconducting film. (A) Chemical structure of DPP semiconducting polymer, PDMS, and PDCA moiety introduced in both polymer backbones as dynamic bonding sites through metal-ligand interaction. Structure of the $[\text{Fe}(\text{HPDCA})_2]^+$ moiety that is reversible dynamic bonds by force. (B) Schematic illustration of DPP and PDMS dynamically cross-linked through Fe(III)-PDCA complexation. (C) STEM dark-field and STEM-EDS elemental mapping of the DPP-TVT-PDCA (1): PDMS-PDCA-Fe (5) blend film. (D) Field-effect mobilities of the blend film organic thin-film transistors (OTFTs) (source and drain electrode: Au, 40 nm; dielectric layer: SiO_2 , 300 nm; gate electrode: highly doped silicon substrate) as a function of blending-weight ratio (semiconductor: elastomer). (E) Strain cyclic testing of the blend film (1:5). (F) Plot of dichroic ratio ($\alpha_{\parallel}/\alpha_{\perp}$) of 1:5 blend film as a function of strain. (G) Relative degree of crystallinity (rDoC) calculated from (200) peak for both “parallel” and “perpendicular” directions to x-ray beam line. (H) Proposed mechanism for reinforcement of stretchability in blend film via metal-ligand dynamic bonding based on analyzed information. Credit: Science Advances, doi: 10.1126/sciadv.aav3097

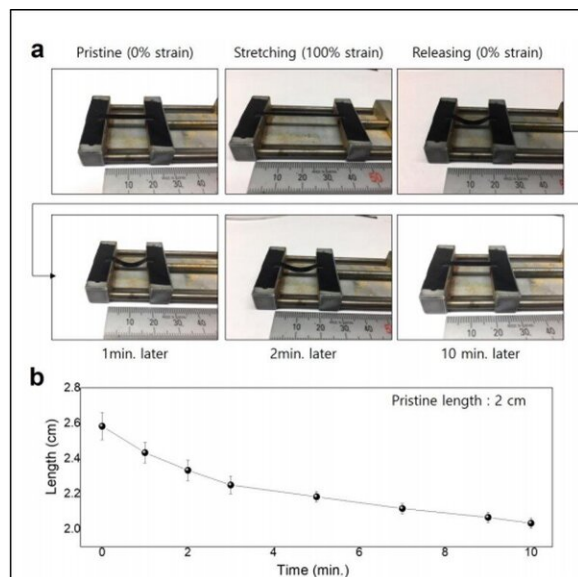
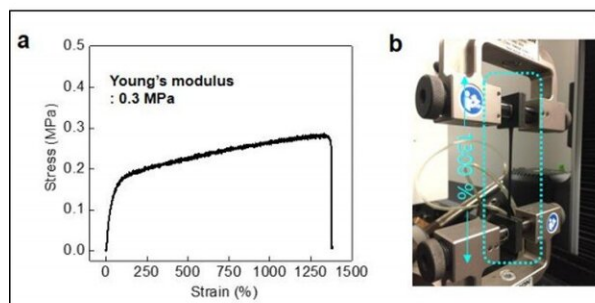
Next-generation polymers developed in the lab must become stretchable and self-healing to form novel skin-like sensory devices to meet the demands of futuristic electronic skin applications. Although researchers have made notable advances in skin-inspired electronic materials, it is challenging to include desired functions into an active semiconductor for improved sensing. In a new report on *Science Advances*, Jin Young Oh and an interdisciplinary research team in the departments of Chemical Engineering, Biomedical Research, Electrical Engineering, Materials Science and Mechanical Engineering in the U.S. and South Korea, developed a strain-sensitive, stretchable and autonomous self-healing semiconductor film.

They engineered the new material by blending a polymer semiconductor and self-healing elastomer, dynamically cross-linked using metal

coordination bonds. Young Oh et al. controlled the [percolation](#) threshold of the polymer semiconductor to form a strain-sensitive film with a [gauge factor](#) of 5.75×10^5 at 100 percent strain during [stretchable](#) transition. The composite film was highly stretchable with a fracture strain greater than 1300 percent with demonstrated autonomous self-healing at room temperature. The research team then developed an integrated five-by-five stretchable active-matrix transistor sensor array (electronic skin) to detect strain distribution during surface deformation.

Advances in [stretchable electronic materials](#) and [devices](#) have allowed scientists to mimic self-healing properties of human skin and accelerate the development of skin-inspired devices, [soft robots and biomedical devices](#). Materials scientists can integrate rigid sensing modules into an ultrathin platform with strain engineered designs to construct surfaces [via transfer printing](#). Bioinspired materials can also be created with improved sensitivity and compatibility for [implantation in the human body](#). Alongside [mechanical stimuli modulation](#) to represent [electronic skin](#) (e-skin) function for biomimetic human skin sensory functions.

[Active-matrix transistor array-based sensors](#) can provide high quality sensing signals with reduced crosstalk between individual pixels, where each pixel contains a sensor connected with a [transistor](#). Researchers had previously used [strain engineering](#) to embed rigid sensors and transistors into stretchable, biomimetic systems to assist patients with movement disorders. To eliminate mechanical mismatch between rigid and soft components; the sensors and transistors must be intrinsically stretchable. A strain-sensing transistor can simplify the fabrication process to improve mechanical robustness and conformability. An additional [capacity for self-healing](#) can increase the benefits of e-skin to warrant a longer lifetime.



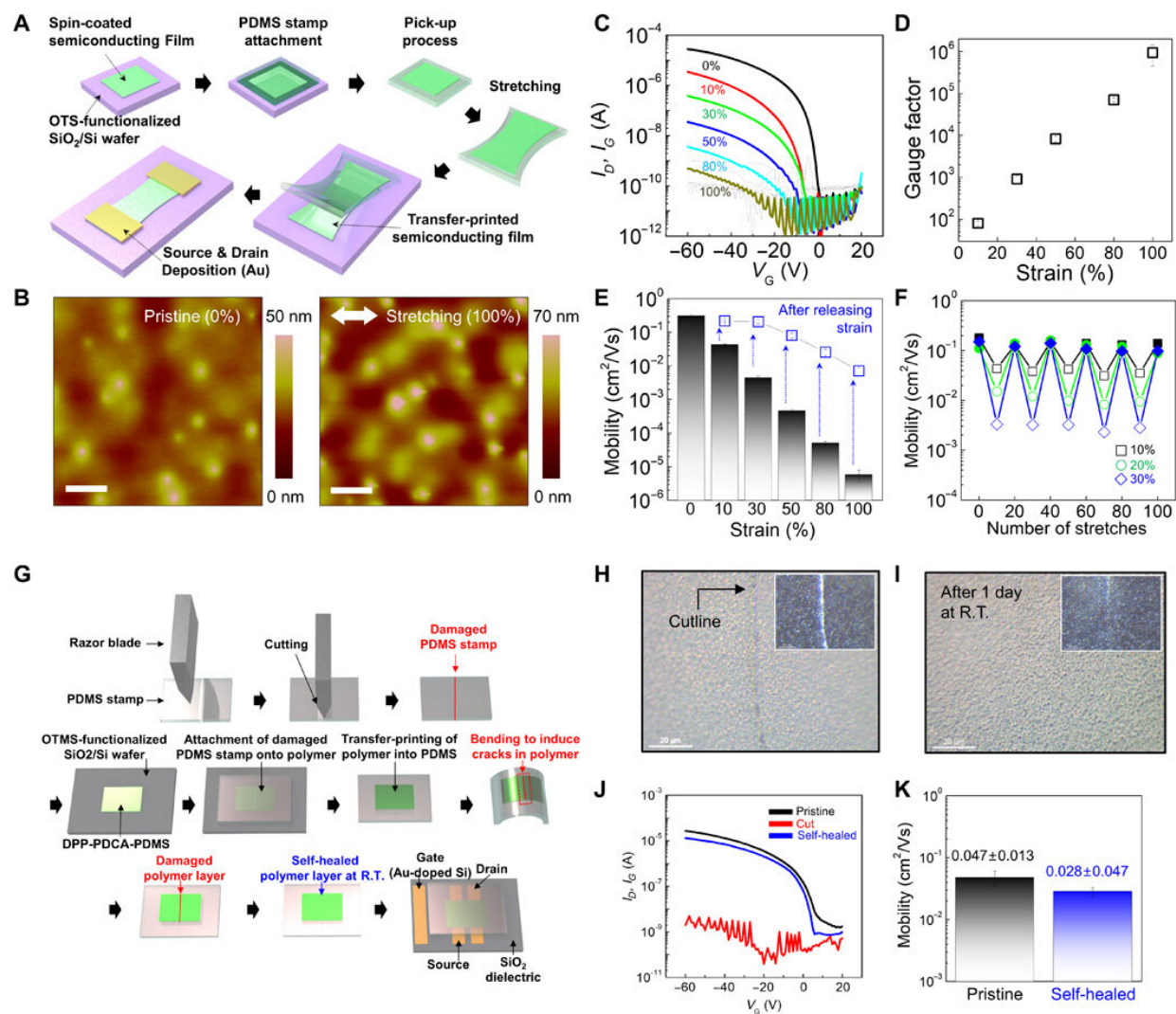
LEFT: Strain and stress curves of a blend film. a) The blend film (200 μm in thickness, semiconducting DPPTVT-PDCA to PDMS-PDCA-Fe elastomer with a weight ratio of 1:5) was elongated to over 1000% strain. The calculated Young's modulus is 0.3 MPa. b) A photograph of a blend film being stretched to 1300% strain. RIGHT: Recovery test of an elongated blend film. a) photographs of a stretching cycle to 100% strain of blended film (semiconducting DPP-TVT-PDCA to PDMS-PDCA-Fe elastomer of 1:5) and waiting time needed for the elongated blend film to return to its original size. b) Length of the blend film as a function of waiting time after initial strain at 100%. Photo credits: Jin Young Oh, Department of Chemical Engineering, Kyung Hee University. Credit: Science Advances, doi: 10.1126/sciadv.aav3097

In the present work, Young Oh et al. presented an intrinsically stretchable and self-healing semiconducting film with strain-sensitive electrical behavior included into a stretchable transistor. They fused two materials to form a semiconducting film by blending a polymer semiconductor and an insulating elastomer to demonstrate the new property. When they broke the metal coordination bonds of the fused material, the construct could spontaneously reconstruct to transfer

stretchable, tough, self-healing properties to the brittle semiconducting film.

The elastomer in the blended film maintained a [low modulus](#) to absorb the external mechanical strain to engineer a multifunctional electronic material. The scientists then fabricated a stretchable active-matrix sensory transistor array, where they integrated the semiconducting film, dielectric electrode and interconnect using a transfer-printing process. The semiconductor/dielectric interface of the sensor array was waterproof, even after contact with artificial sweat for 15 hours. Young Oh et al. envision that the strain-sensitive, stretchable and self-healing semiconductor will change the standard of e-skin for expanded applications.

The team engineered a composite semiconducting material as [developed previously](#) by the same research group. In this work, they abbreviated the new composite DPP-TVT-PDCA; where they mixed poly(3,6-di(thiophen-2-yl)diketopyrrolo[3,4-c]pyrrole-1,4-dione-alt-1,2-dithienylethene) with 10 mol percent 2,6-pyridinedicarboxamine (PDCA) moieties.



Strain-sensitive property of self-healable semiconducting film. (A) Schematic illustration for sequential fabrication procedures of the OTFT with stretchable self-healable semiconducting film (200 nm) using transfer-printing assembly. (B) AFM height images for pristine and stretched (100%) semiconducting films. Scale bars, 1 μ m. (C) Transfer curves of OTFTs as a function of strain applied to semiconducting film along the tensile stretching direction and (D) GFs extracted from on-current of OTFTs. (E) Field-effect mobilities on strain and after releasing strain measured for the same device. (F) Field-effect motility as a function of stretching cycle at different strains. (G) Schematics for fabrication methods of the self-healed semiconducting film that was cut by bending a partially cracked PDMS stamp and its OTFT. (H) Optical microscope (OM) images of damaged semiconducting film through self-healing process and (I) self-

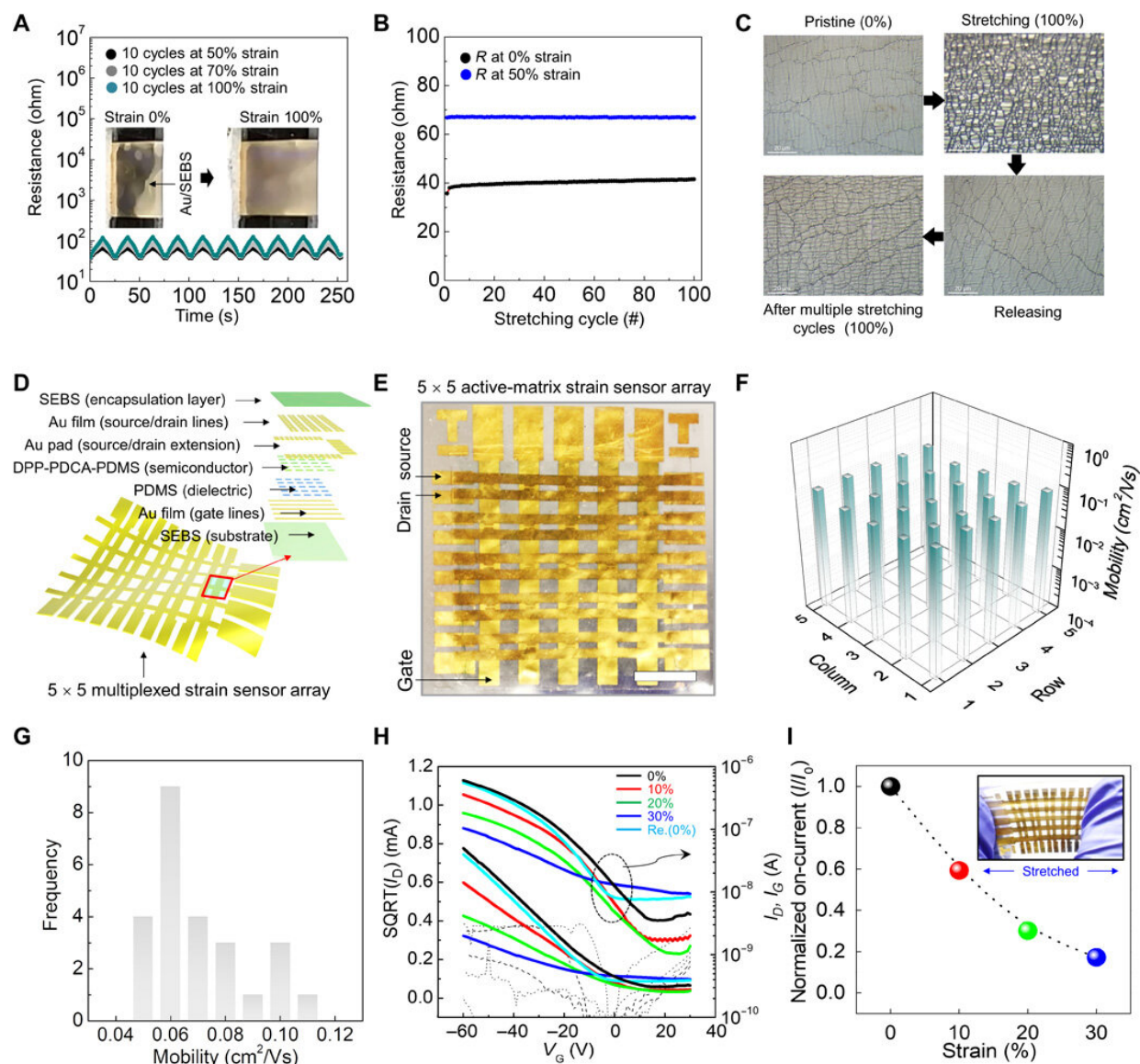
healed film. Inset: Corresponding dark-field OM images. (J) Transfer curves and (K) field-effect mobility of pristine and autonomously healed OTFTs. R.T., room temperature. Credit: Science Advances, doi: 10.1126/sciadv.aav3097

They then combined PDCA with poly(dimethylsiloxane-alt-2,6-pyridinedicarbozamine) to form the [PDMS-PDCA polymer](#). The PDCA polymer formed metal-ligand coordination complexes (Fe(III)-PDCA) with multiple dynamic bonds and three different bonding strengths to facilitate dynamic cross-linking, intrinsic stretchability and self-healing potential. The scientists demonstrated Fe(III)PDCA ligand bonding with PDMS-PDCA and DPP-TVT-PDCA in the blend film.

They optimized the field-effect mobility on the semiconductor film (DPP-TVT-PDCA) by introducing varying ratios of an elastomer (PDMS-PDCA-Fe) to form a blend film with an optimized weight ratio. The resulting semiconducting polymer maintained reasonable charge carrier mobilities and formed sufficient electrical percolation paths. The blend film retained a high stretchability, [Poisson's ratio](#) and [Young's modulus](#) similar to human skin and better than [typical semiconducting polymers](#). Rheological analysis of the blend film at room temperature showed the material to behave similarly to a solid with metal-ion coordination cross-linking. The glass transition temperature of the material was similar to typical [PDMS rubber](#).

They tested the film's stretchability using repeated strain cyclic tests, and credited the observed energy dissipation to Fe(III)-PDCA coordination bond breakage during stress relaxation. Even after elongating the blend film beyond 100 percent strain, it recovered to its initial length after an hour of resting due to reorganization of polymer chains. The team characterized the morphology and electrical percolation of the blend

film using [transmission electron microscopy](#). Followed by mapping the elements of the material using [energy-dispersive X-ray spectroscopy](#) to identify sulfur (S), silicon (Si) and iron (Fe) peaks. The results indicated high sensitivity of the material to strain, where the elastomer absorbed the applied strain while retaining the crystalline region of the semiconducting film, to enable the proposed stretching mechanism of the blend film.

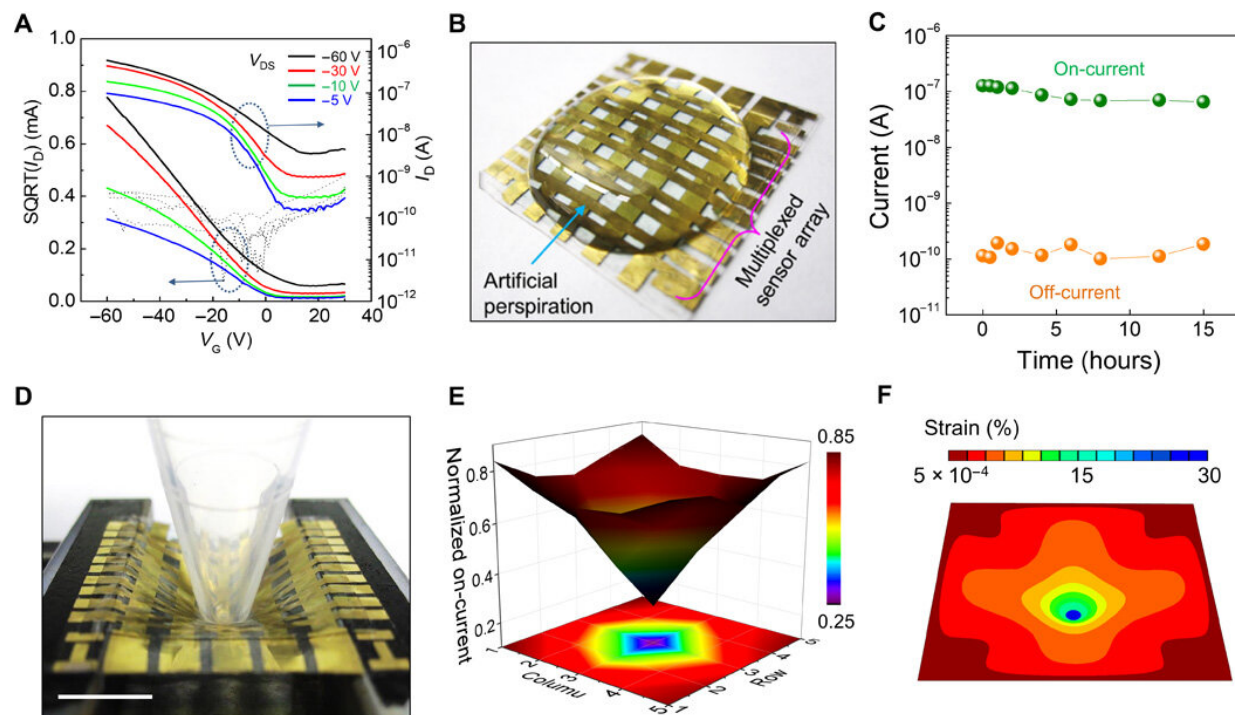


Characterizations of stretchable active-matrix transistor sensor array. (A) In situ measurement of resistance of Au/SEBS stretchable interconnect during 10 stretching cycles at different strains (50, 70, and 100%). Inset: Photographs of Au/SEBS interconnect at 0% (left) and 100% (right) strain. (B) Resistance change of Au/SEBS stretchable interconnect as a function of stretching cycle at 0 and 50% strain. (C) OM images of pristine (0% strain, upper left), stretched (100% strain, upper right), released (0% strain, lower right), and stretched (100% strain; 100 cycles, lower left) Au/SEBS stretchable interconnect. (D) Architecture and (E) photograph of a fully stretchable 5×5 active-matrix transistor strain sensor array fabricated via our developed strain-sensitive, stretchable, and self-healable semiconducting film. Scale bar, 5 mm. (F) Mapping and (G) statistical distribution of the field-effect mobility in our stretchable active-matrix transistor array. (H) Transfer curves and (I) normalized on-current of fully stretchable transistor in active-matrix array as a function of strain. Photo credits: Jin Young Oh, Department of Chemical Engineering, Kyung Hee University and Donghee Son, Biomedical Research Institute, Korea Institute of Science and Technology. SQRT, square root. SEBS, polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene. Credit: Science Advances, doi: 10.1126/sciadv.aav3097

The research team tested the strain sensitive charge transport of the semiconducting film using [organic thin-film transistors](#) (OTFTs) via transfer printing. They did not detect any nanocracks in the transferred film using [atomic force microscopy](#) (AFM) to eliminate the possibility of mechanical damage due to strain. The scientists then evaporated gold, an electrode material, on to the blend film and observed the on-current of the transistor to decrease as the percent strain increased. The gauge factor was highest at 5.7×10^5 at 100 percent strain, which was the highest value reported for semiconducting strain gauges, and comparable with state-of-art, conductor-based strain gauges. The devices showed fully reversible current-voltage character and repeatable cycling behavior, similar to the stretchability of human skin.

Young Oh et al. obtained the unique self-healing characteristic of e-skin through dynamic metal-ligand coordination bonding. To test the self-healing capacity, they cut the material (200 nm in thickness) at room temperature, left it for 24 hours and observed the scar disappear autonomously. The healed film could be stretched to more than 200 percent strain before fracturing. When they tested the electrical property of the healed semiconducting film using a soft-contact method in OTFT, they recovered the field-effect mobility of the healed material. Comparatively, cutting a semiconducting material without self-healing properties did not retain transistor-like current-voltage behavior.

To enable newly developed semiconducting material for e-skin applications, Young Oh et al. fabricated a five-by-five fully stretchable, strain-sensitive active-matrix transistor array. For this, they built a highly stretchable and conducting interconnect using an electrode made of highly conductive stretchable gold (Au) and a polystyrene elastomer for high-speed multiple scans without signal delay or loss within the active-matrix architecture. To confirm mechanical reliability of the electrode they completed repeated cyclic testing of up to 100 cycles under 50 percent strain and obtained superior performance. The device showed reversible strain-sensing operations to fully recover to the original state after releasing the strain.



Strain-sensitive stretchable active-matrix transistor array as skin-like stretchable strain sensor. (A) Transfer curves of the stretchable active-matrix transistor array as a function of drain voltage with four different drain/source voltages. (B) Photograph of the stretchable active-matrix transistor array under artificial sweat and (C) on- and off-currents of the stretchable active-matrix transistor array as a function of time. (D) Photograph of stretched active-matrix transistor array by poking with a plastic bar and (E) normalized on-current of the poked active-matrix transitory array. (F) Simulation result of strain applied by poking to the stretchable active-matrix array. Photo credits: Jin Young Oh, Department of Chemical Engineering, Kyung Hee University. Credit: Science Advances, doi: 10.1126/sciadv.aav3097

For e-skin applications of the stretchable strain sensor array, the scientists lowered the device-operating voltage from -60 to -5 volts for long-term sustainability and medical safety. Despite the low-threshold voltage, the device was sensitive to applied strain. Waterproof

performance was a priority to prevent device malfunctions on contact with human skin-generated ionic sweat; which they achieved using an elastomer to passivate the five-by-five sensor transistor array against sweat, followed by submerging in artificial sweat for 15 hours. The monolithic sensing system could 3-D map e-skin deformation in a simplified fabrication process, combining a sensor and transistor architecture into a single device. The researchers "poked" the e-skin to quantify on-current changes of the active matrix sensor array and simulated the applied strain using [finite-element methods](#).

In this way, Jin Young Oh and colleagues presented an approach to engineer strain-sensitive, stretchable and self-healing semiconductor [films](#) to form skin-like active-matrix strain sensor arrays. The composite network of materials provided strain sensitivity to the blended film. The metal ligand coordination allowed the semiconductor to be highly stretchable and automatically self-heal at room temperature. Using the semiconducting film, the researchers developed an e-skin that detected pressure-induced deformation, alongside visualization of the applied strain. The synthetic e-skin was fully healable and able to operate within a medically safe voltage, with potential to incorporate [high-k dielectric materials](#) after further optimization.

More information: Jin Young Oh et al. Stretchable self-healable semiconducting polymer film for active-matrix strain-sensing array, *Science Advances* (2019). [DOI: 10.1126/sciadv.aav3097](https://doi.org/10.1126/sciadv.aav3097)

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