Thermally Triggered Degradation of Transient Electronic Devices

*Chan Woo Park, Seung-Kyun Kang, Hector Lopez Hernandez, Joshua A. Kaitz, Dae Seung Wie, Jiho Shin, Olivia P. Lee, Nancy R. Sottos, Jeffrey S. Moore, John A. Rogers, and Scott R. White**

Electronics that disintegrate after stable operation for a desired amount of time are of great interest for biomedical implants, secure memory devices, and environmental sensors.[1–6] Transient electronics have been demonstrated with hydrolyzable thin inorganic components such as silicon nanomembrane semiconductors,[1–3] various metals (e.g., Mg, Mo, etc.) electrodes,[4] and MgO, SiO_2 or SiN_x dielectrics.[1,5] Exposure of the device to aqueous conditions leads to the subsequent dissolution of the packaging that protects circuits. The timescale of transience is controlled by the dissolution rate of water-soluble polymer substrates such as silk and poly(vinyl alcohol) which vary based on thickness, crystallinity, and use of fillers.[1,7] Despite this success, the lifetime of the device is largely predetermined based on the selection of materials and transience occurs rather than on-demand.

Stimuli-responsive packaging materials enable the fabrication of transient electronics that are triggered to degrade in response to a specific environmental stimulus. Low-ceiling temperature (T_c) polymers that rapidly depolymerize by a variety of stimuli are suitable candidate materials.[8–10] Recently, UV-triggered transience of electronic devices were demonstrated with an acid-sensitive low-T_c polymer substrate, cyclic poly(phthalaldehyde) (cPPA) (T_c = 43 °C).[6] Films of cPPA were prepared containing photoacid generators and UV-triggering promoted acid-catalyzed depolymerization of cPPA, ultimately resulting in substrate disintegration and device destruction within 20 min. Here, we seek to provide easier device fabrication, faster device destruction, and expand the types of triggering modes for transience. Among various stimuli-responsive systems, heat triggers have been widely studied with thermo-sensitive materials including phase-change and volume-change materials for drug delivery, membranes, and battery shutdown.[1,11,12] Notably, the thermal activation can be coupled with other triggering modes such as light, magnetic, or radio frequency (RF) for noncontact heating based on photothermal nanomaterials or induction heating.[1,11,13]

In this paper, we report thermal-triggered transient electronics based on protective wax coatings that contain encapsulated acid microdroplets. Upon exposure to sufficient heat, the melting of the wax releases the encapsulated acid which then enables rapid device destruction via acidic degradation of electronic components with or without cPPA substrate disintegration (**Figure 1**). Inert and hard silicone waxes with rapid phase

Dr. C. W. Park[+]
Beckman Institute for Advanced Science and Technology
University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA

Dr. S.-K. Kang, D. S. Wie
Department of Materials Science and Engineering
Frederick Seitz Materials Research Laboratory
University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA

H. Lopez Hernandez
Department of Mechanical Science and Engineering
Beckman Institute for Advanced Science and Technology
University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA

J. A. Kaitz, Dr. O. P. Lee, Prof. J. S. Moore
Department of Chemistry
Beckman Institute for Advanced Science and Technology
University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA

J. Shin
Department of Chemical and Biomolecular Engineering
University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA

Prof. N. R. Sottos
Department of Materials Science and Engineering
Beckman Institute for Advanced Science and Technology
University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA

Prof. J. A. Rogers
Department of Materials Science and Engineering,
Chemistry, Mechanical Science and Engineering
Electrical and Computer Engineering
Beckman Institute for Advanced Science and Technology,
and Frederick Seitz Materials
Research Laboratory
University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA

Prof. S. R. White
Department of Aerospace Engineering
Beckman Institute for Advanced Science and Technology
University of Illinois at Urbana-Champaign
Urbana, IL 61801, USA
E-mail: swhite@illinois.edu

[+]Present address: Decontamination and Decommissioning Research Division, Korea Atomic Energy Research Institute, Daedeok-daero 898-111, Yuseong-gu, Daejeon, South Korea

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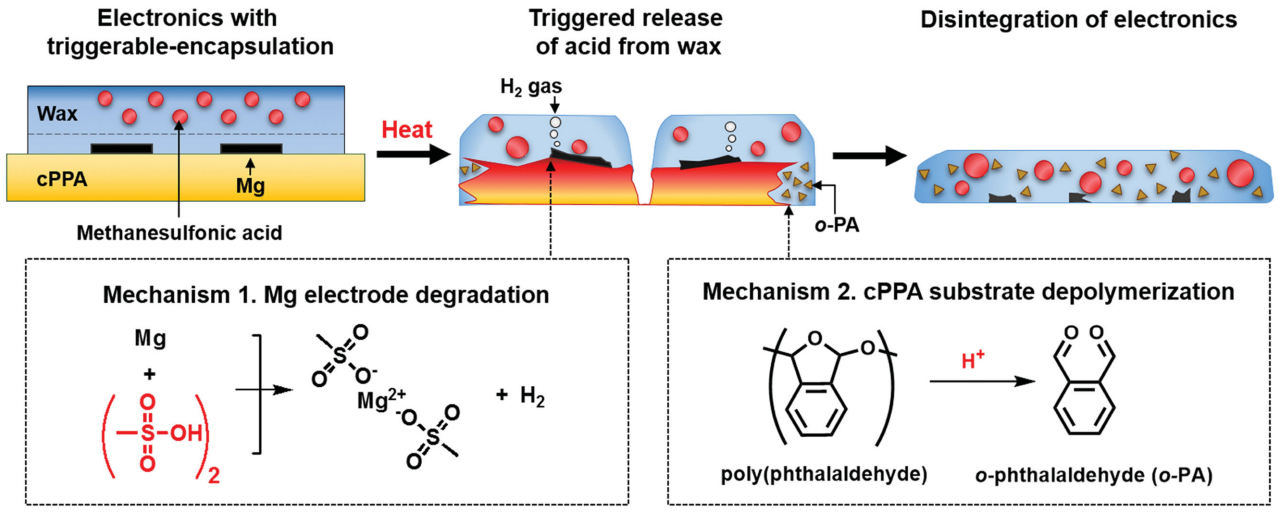

Figure 1. Heat-triggerable transient electronics coated with wax containing acid dispersions. Release of MSA by melting a wax coating leads to rapid electronic destruction by acidic degradation of Mg electrodes on glass. In addition, using a cyclic poly(phthalaldehyde) (cPPA) substrate affords a more rapid destruction of the device due to acidic depolymerization of cPPA.

changes above their melting point were selected for coating materials. Sequestration and encapsulation of methanesulfonic acid (MSA) were achieved by melt casting of an acid/wax emulsion. Melting of the wax releases the acid and device destruction follows rapidly. Along with the degradation of Mg traces by MSA,[14,15] Si-based devices are also destroyed by acid-triggered depolymerization of the cPPA substrate.

The wax coatings with encapsulated MSA were prepared by hot-melt casting of MSA-in-wax emulsion.[15,16] First, a protection layer of pure silicone wax (T_m = 43 °C) was spin cast onto the electronics from the molten state at 2000 rpm to prevent degradation of the circuit from direct contact with the MSA/wax coating. The protection layer had a uniform surface profile with an average thickness of 14.4 ± 0.9 µm based on profilometer analysis (**Figure 2**a). Next, MSA was emulsified into molten silicone wax (T_m = 43 °C) at 70 °C, and then deposited on top of the wax-protected circuits by doctor blading with an average thickness of 44.5 ± 3.8 µm. Optical microscopy of MSA/wax coatings (Figure 2b) revealed spherical droplets of MSA with an average diameter of 15.1 ± 5.9 µm that were well dispersed in the solidified wax up to 40 wt% in concentration. Unless otherwise indicated, 40 wt% MSA-in-wax coating (T_m = 43 °C, ca. 45 µm thickness) with a protection layer of neat wax (T_m = 43 °C, ca. 14 µm thickness) was used in this study.

Heat-triggered degradation of metal electronic components was demonstrated with a serpentine Mg resistor (≈300 nm thick) on a glass substrate with MSA/wax coating. The resistors were placed on a hot stage for accurate temperature control and continuously heated at the trigger temperature while resistance of the circuit was monitored with a Wheatstone quarter-bridge. Device failure (i.e., transience time) was defined as 500% increase in resistance in order to standardize our analysis.

Prior to thermal triggering, the 40% MSA/wax-coated resistor showed highly stable response (negligible resistance change) for a month at room temperature (Figure S1, Supporting Information). However, once heated to the trigger temperature of 55 °C, the resistance quickly increased and caused resistor failure within 2 min. The observed transience time was similar to that obtained by direct application of pure MSA onto the Mg resistor (Figure 2c). In situ microscopic observation of Mg degradation (Figure 2b and Figure S2, Supporting Information) revealed melting of the MSA/wax coating releases MSA, and the MSA etches the Mg traces to subsequently generate bubbles of H_2 gas, the byproduct of acidic degradation of Mg (Figure 1).[14,17] Most of the Mg trace eroded within 10 min at which point the generation of bubbles subsided (Figure 2b).

Transience time was tunable by adjusting acid concentration, trigger temperature, and thickness of the wax protection layer. As the amount of MSA in the coating decreased from 40% to 30%, the transience time was retarded from 2 to 11 min at 55 °C (Figure 2c). However, 20% MSA/wax did not exhibit transience and instead displayed a slow increase in resistance (≈60% in 60 min). Trigger temperature was also an effective modulator of transience behavior. For example, as the trigger temperature was reduced from 55 to 45 °C the failure of 40% MSA/wax-coated resistors was delayed by ≈8 min (Figure 4d). Similarly, for 30% MSA/wax-coated resistors, transience was delayed by ≈6 min as the trigger temperature was reduced from 65 to 55 °C (Figure S4, Supporting Information). And finally, the protection layer thickness can also be used to control transience. By reducing spin speed from 1500 to 500 rpm, the protection layer thickness was nearly doubled from 25 to 45 µm. As the thickness of the protection layer increases, the time to transient failure is increased as expected (Figure 2d).

The trigger temperature can be tailored by selecting a wax with a different melting temperature. The trigger temperature can be increased by using MSA/wax coatings prepared from a higher melting point silicone wax (T_m = 65 °C) than the one discussed earlier (T_m = 43 °C). When placed on an Mg resistor, rapid Mg degradation occurred above 70 °C within 2 min (Figure S5, Supporting Information). No change in resistance was observed at temperatures below the melting temperature, though a thicker protection layer of neat high melting point wax (25 µm) is required.

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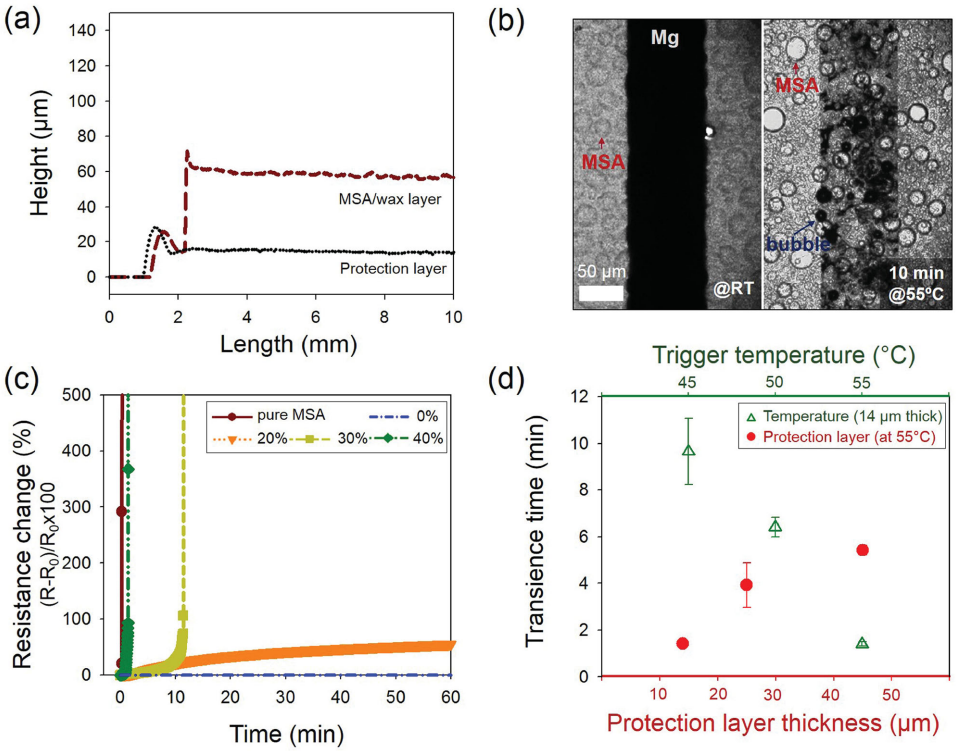

Figure 2. Thermally activated electronic transience via MSA/wax coatings monitored by resistance changes in Mg resistors. a) Thickness of wax coating with/without a MSA/wax layer measured by surface profiler. b) Optical microscopy images of Mg trace (≈300 nm thick) coated with 40% MSA/wax before (left) and after (right) triggering at 55 °C. c) Effect of acid concentration on transience observed by resistance changes. d) Transience time of Mg resistor as a function of triggering temperature (Δ, 14 μm thick protection layers) and protection layer thickness (●, at 55 °C). Unless otherwise indicated, the coating is 40% MSA/wax (45 μm) with a protection layer (14 μm).

To fabricate fully transient electronics composed of degradable substrate and electronic components, we selected metastable cPPA as a substrate material, which can be depolymerized with acid.[6,8,9] The cPPA was synthesized by cationic polymerization of *o*-phthalaldehyde (*o*-PA) initiated by boron trifluoride diethyl etherate at –78 °C.[8] The molecular weight of the cPPA was 134 kDa (M_n) with polydispersity index of 2.6. Free-standing cPPA substrates (≈30 μm thick) were prepared by solution casting from a polymer solution containing 2.5% diethylene glycol dibenzoate as plasticizer into a Teflon-coated Petri dish (Supporting Information).[6]

Depolymerization of the cPPA substrate by thermal activation of MSA/wax coating was characterized by visual observation and Raman spectroscopy. cPPA substrates containing methyl yellow, a yellow pH indicator which turns red in color below pH 2.9, showed a rapid color change and depolymerization by released MSA at 55 °C within 2 min, indicating an efficient delivery of MSA throughout the cPPA substrate (Figure S6, Supporting Information). For chemical analysis of the depolymerization, Raman spectrum of the residue was taken after heating the 40% MSA/wax-coated cPPA at 55 °C for 10 min (**Figure 3**a). The characteristic –COC– peak (1010 cm^{-1}) from the cPPA backbone significantly diminished while simultaneously the carbonyl peaks corresponding to the *o*-PA at 1680 and 813 cm^{-1} appeared in the spectrum of the residue.[18] The spectra of both the residue and that of pure *o*-PA were nearly identical, demonstrating that MSA released from wax coatings successfully led to depolymerization of the cPPA substrate.

Fully degradable electronics consisting of serpentine Mg resisters on cPPA substrate were prepared by electron-beam (e-beam) deposition of Mg followed by a wax protection layer and a 40% MSA/wax coating. Heat-triggered transience behavior of the free-standing device was observed (Figure 3b). After heating to 55 °C, the cPPA substrate began to degrade and generate brown byproducts, confirmed as *o*-PA by Raman analysis. As the cPPA substrate degrades, it undergoes large physical deformation and tearing that leads to the subsequent structural deformation and breaking of Mg traces within 1 min along with continued acidic degradation of Mg by MSA. To investigate the effect of substrate disintegration on transient behavior, we monitored the resistance of Mg resistors on cPPA and on glass after heating to 55 °C (Figure 3c). The resistor on cPPA substrate failed within 30 s while the resistor on glass failed in ca. 90 s, indicating that substrate depolymerization facilitates device destruction. Microscopic observation also showed that Mg degradation on cPPA, which is coupled by erosion and deformation of Mg trace by the substrate depolymerization, is faster than on glass which solely relies on acidic erosion (Figure S2, Supporting Information).

Destruction of a silicon-based electronic device driven by both substrate disintegration and Mg degradation was also demonstrated with an array of silicon PIN diodes prepared by transfer printing of doped silicon nanomembranes (Si NMs)

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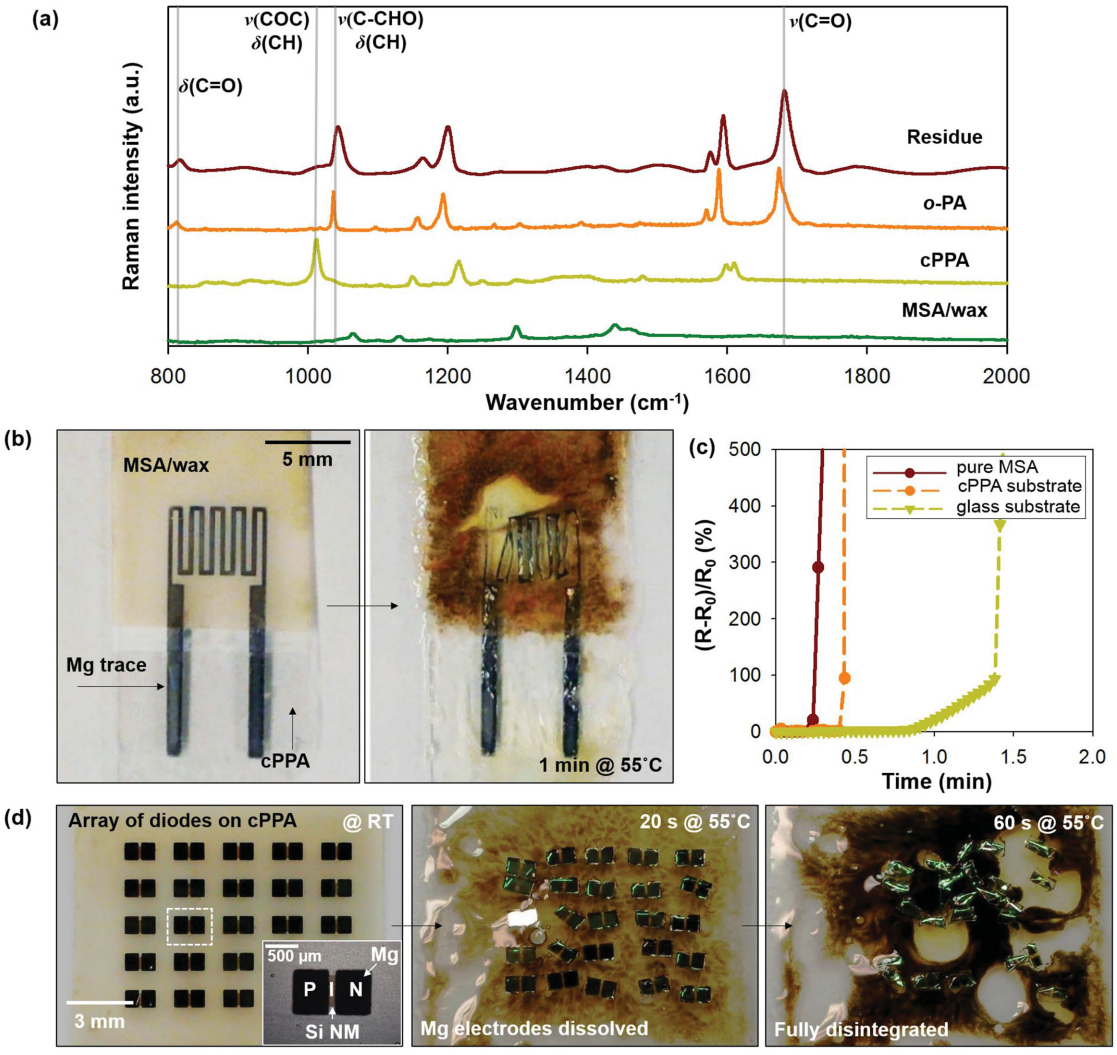

Figure 3. Transience behavior of electronics on the cPPA substrate with MSA/wax coating. a) Raman spectra of *o*-phthalaldehyde (*o*-PA), cPPA, MSA/wax, and the residue of 40% MSA/wax-coated cPPA after degradation for 10 min at 55 °C. b) Images of the Mg resistor on cPPA substrate coated with 40% MSA/wax and heat-triggered degradation of the device at 55 °C. c) A resistance change of the device by heat trigger at 55 °C. Degradation of the cPPA substrate facilitates device destruction. d) Degradation of a Si PIN diode array on cPPA substrate with 40% MSA/wax coating at 55 °C.

and e-beam deposition of Mg electrodes onto cPPA substrate (Figure S8, Supporting Information).[6] Figure 3d shows the array of Si diodes coated with 40% MSA/wax. After triggering at 55 °C, acidic degradation of Mg electrodes was observed with cPPA substrate degradation within 20 s, and complete disintegration of the device was achieved within 1 min. Holes and tears in the cPPA substrate by acidic depolymerization promoted disassembly of Si NMs, which are acid insensitive, and device failure. It is important to note that the MSA/wax-based transience is not limited to acid-degradable electric components and can be extended to the destruction of acid-insensitive electronics via substrate depolymerization and disassembly of electronic components.

Programmed degradation of selected electronic components can change the device geometry or direction of current flow in a circuit, altering or transforming the functionality of the electronics. Previously reported transient systems which rely on the dissolution of components are comparably much more difficult to design selective or programmed transience.[19] Selective heat-triggered destruction of an electronic device was achieved by selectively coating with different melt point waxes containing MSA. The device was composed of three light emitting diodes (LEDs) in parallel with an Mg electrode. The Mg traces connected to red and yellow LEDs were partially coated with 40% MSA/wax from a low-melting wax (T_m = 43 °C) and high-melting wax (T_m = 65 °C), respectively. The Mg trace to the green LED was left uncoated (**Figure 4**a). The 25 μm thick protection layer (8 mm × 10 mm) and 45 μm thick MSA/wax (5 mm × 7 mm) layers were cast by doctor blading with poly(ethylene terephthalate) (PET) masks. Next, a stepwise heating profile was applied to the circuit with a 1 min ramp to 55 °C and a 9 min hold at that temperature, followed by another 1 min ramp to 70 °C and another 9 min hold. After heating to 55 °C, the first trigger was activated and the red LED dimmed as the Mg interconnect was destroyed by acidic degradation at the coated area. After the second heating step

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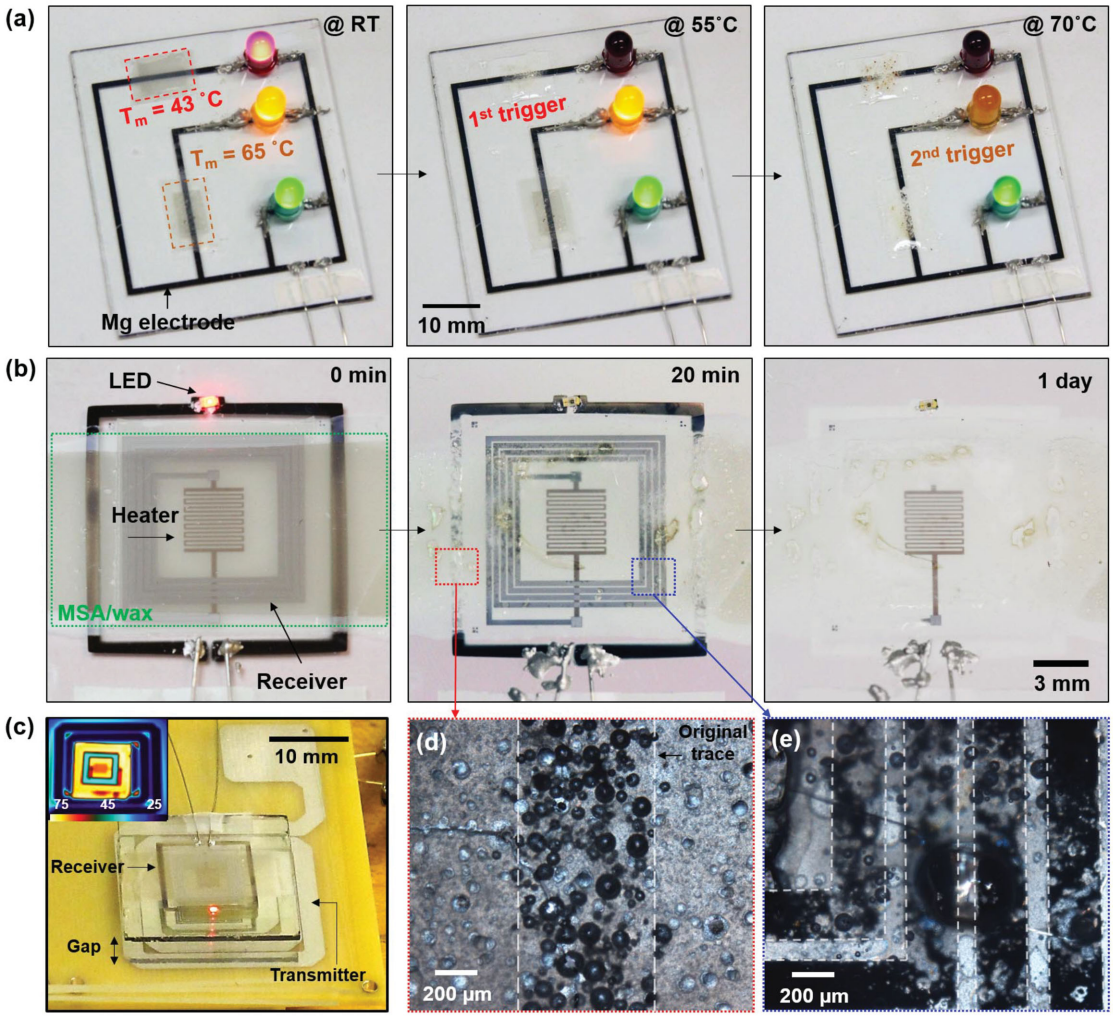

Figure 4. Applications of the MSA/wax coating for multistage transition and remote-triggered self-destruction of electronic. a) Multistage transition of LEDs achieved by stepwise heating of different melt point waxes (T_m = 43 or 65 °C) containing MSA (40%). The melting of MSA/wax degrades the coated area at desired temperature. b) Self-destructive device integrated with inductive heater (Mg/SiO_2/Mg) and LED with Mg interconnects on glass with MSA/wax coating. The LED dimmed in 4 min after inductive heating, and the degradation of Mg trace is observed in 20 min. After 1 day, Mg traces are fully disintegrated by diffused acid while the part of heating resistor underneath SiO_2 (≈900 nm thick) remains intact since it is protected by SiO_2. c) Image of the inductive heating system and the infrared image of the heater (inset). Optical microscopy images of eroded d) Mg interconnect (initial thickness: ≈300 nm) and e) receiver coil (initial thickness: ≈2 μm) after 20 min of induction heating (white dashed line: original Mg trace).

to 70 °C, the second trigger was activated and the yellow LED dimmed. Afterwards, only the green LED continued to operate and was unaffected by the thermal treatment.

We finally sought to demonstrate an autonomic and self-destructive device where heat triggering can be remotely controlled by inductive coupling. Our design (Figure 4b) consists of a 40% MSA/wax (T_m = 43 °C) coated self-destructive device with a resistive heater (Mg/SiO_2/Mg) connected to an Mg receiver coil and a separate LED circuit connected to Mg electrodes on glass. Our self-destructive device was placed on a transmitting coil with glass slides separating the device and coil (Figure 4c). The resistive heater was wirelessly powered through inductive coupling of transmitter and receiver coils at 15 MHz resonance frequency,[1] and the device immediately heated up to 75 °C as measured by an infrared camera (Figure 4c, inset). Melting of the MSA/wax coating began at the heater region and propagated to the Mg electrode connecting the LED, causing the LED to turn off within 4 min (Video, Supporting Information). Degradation of the heater system composed of Mg receiver coil and resistive heater was also observed. The reflective molten wax eventually hardened to a non-reflective solid upon cooling due to failure of induction heater (ca. 10 min). After 20 min of RF transmitting, optical and microscopic images of the device (Figure 4b,d,e) show that the 300 nm thick Mg electrode for LED is fully disintegrated while the thicker Mg receiver coil (≈2 μm) is only partially eroded by acid. The residue of Mg traces continued to erode as released acid diffused across the device, and the entire Mg traces disappeared within a day except for the part of Mg resistive heater underneath the SiO_2 dielectric layer. In addition to the self-destructive device described above, the wireless RF heating can also be used for triggered transience of electronics on a

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cPPA substrate. An array of Si PIN didoes on cPPA coated with 40% MSA/wax was placed on the resistive wireless heater, and destruction of the PIN diodes was successfully achieved within 2 min after transmitting wireless power (Figure S9, Supporting Information).

The heat-triggerable wax encapsulation system presented here, which sequesters and releases degradation agents on demand, provides a simple and versatile approach for thermally triggered device destruction. Transience response is fast and tunable, and a temperature-programmed multistage transition was demonstrated with waxes of different melting points. This system can be combined with either non-degradable or degradable substrates, and selection of degradation or dissolution agents with the appropriate substrate will further expand transition modes. Significantly, the wireless triggerable self-destruction system shows great promise for remote triggered device destruction, and various heating modes based on near-infrared, magnetic field, and microwave radiation may provide more varied triggering modalities.[11,13]

Experimental Section

Fabrication of Transient Electronics (Mg Resistors, Si PIN Diodes, and Self-Destructive Device): Serpentine-shaped Mg resistors (≈300 nm thick) were deposited on glass or cPPA substrates by electron-beam (e-beam) evaporation from 99.95% pure Mg source (Kulr J Lesker Co., USA) with the lift-off process or with a high resolution stencil mask (12.5 μm thick, Kapton, Dupont, USA). For Si PIN diodes, Si NMs (≈300 nm thick) were doped on silicon-on-insulator (SOI) wafer and transfer-printed on cPPA substrate after undercut of the buried oxide layer with hydrofluoric acid. P-channel and N-channel were defined by solid state diffusion of boron and phosphorus at 1000 °C. Mg electrodes (≈300 nm thick) were deposited by e-beam evaporation with a high resolution stencil mask. The RF-remote heater was designed as a serpentine-shaped resistor and spiral inductor coils. Mg resistor (≈300 nm thick) and Mg inductor coil (≈2 μm thick) were deposited through e-beam evaporation with the lift-off process. The SiO_2 (≈900 nm) was formed by plasma-enhanced chemical vapor deposition as an interdielectric layer. Mg electrodes (≈300 nm thick) for LED were deposited with e-beam evaporation with a high resolution stencil mask. LEDs and conductive wires were attached with silver conductive epoxy.

Wax Coating Containing MSA Dispersions: A thin protection layer (14 μm) of silicone wax was spin cast from molten wax at 70 °C on top of electronics for 30 s at 2000 rpm, and the wax was heated by hot air (60 °C) during the spin casting. Thicker protection layers (25 and 45 μm) were spin coated at reduced spin speeds from the molten wax at 70 °C. The emulsion of MSA-in-wax was prepared by slow addition of MSA into the molten wax containing 3% of Span 85 with vigorous stirring (1000 rpm) for 15 min at 70 °C, and amounts of MSA in the emulsion were varied from 20 to 40 wt%. The MSA/wax emulsion was subsequently deposited on top of the wax-protected electronics by doctor blading and solidified by cooling at room temperature (45 μm thick). For partial coatings, a PET film (23 μm thick) was used for masking.

Characterization of Heat-Triggered Transience: The samples were placed on a hot stage (Linkam) for accurate temperature control and heated up to the desired trigger temperatures at a rate of 30 °C min^{-1}. Resistance changes of serpentine Mg traces were measured by a Wheatstone quarter-bridge setup. For wireless-inductive heating, a MSA/wax-coated heater was placed on transmitting coils with a glass slide spacer (≈3 mm thick). A 15 MHz sine wave was generated with a function generator (8648A, HP, USA) and transmitted through an amplifier (210L, Electronics & Innovation, USA) for 20 min for remote triggering experiments.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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