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 $\operatorname{Rossi}$ 

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## Fast circuit breaker based on integration of Al/CuO

## nanothermites

Andréa Nicollet, Ludovic Salvagnac, Vincent Baijot, Alain Estève, Carole Rossi\*

University of Toulouse, LAAS-CNRS, 7 avenue du Colonel Roche, F-31400 Toulouse, France

#### Highlights

- A novel miniaturized circuit breaker integrating nanothermites is developed.
- The actuation is based on the pressure generated by the reaction of a confined and safe Al/CuO nanothemites placed below the circuitry to be destroyed.
- Easy tunability of the pressure burst by modifying the Al/CuO mixing characteristics: equivalence ratio, solids loading...
- Fast response and excellent repeatability is demonstrated.
- The concept and technology hold potential for commercial scale production.

#### Abstract

Pyroswitches and circuit breakers play an important safety role in electrical systems. A miniature oneshot circuit breaker based on the violent reaction of a nanothermite is presented for safety application as protection against overcurrent, external perturbation and short circuit of a broad range of equipment and systems. This device consists of two circuits assembled together to define a cavity. An ignition chip is placed into this cavity and ignites, within less than 100  $\mu$ s, a few milligrams of nanothermites powder. The resulting violent reaction interrupts a thick copper connection within 1 ms. After the presentation of the device design, fabrication and assembly, we demonstrate the good operation and reproducibility of the device (100 % of success rate) with a response time much lower than that of classical mechanical circuit breakers, which are slow. The response time can be tuned from 1.02 ms to 0.57 ms just by adjusting the mass of nanothermites from 5.59 to 13.24 mg, i.e., adjusting the volumetric solid loadings from 5.6 to 19 %. The nanothermite-based circuit breaker presented in this paper offers unprecedented advantages: it is built using only safe substances and is based on a lowcost mass fabrication process that is compatible with electronics. The proposed concept is generic and can be applied to a large number of applications (electrical storage, aerospace manufacturing, human safety, demolition parachute opening, road vehicles, battery powered machines...).

#### Abbreviations

CB, Circuit Breaker. PCB, Printed Circuit Board. TGA, ThermoGravimetric Analysis. NPs, Nanoparticles. Al-NPs, Al nanoparticles. CuO-NPs, CuO nanoparticles.

#### **Keywords**

pyroMEMS; Circuit Breaker; Al/CuO nanothermites;

#### 1. Introduction

Energetic materials are the only attractive sources of "dormant" energy, exhibiting long shelf life (decades) that can very quickly deliver gas, heat, and chemical species. For context, the decomposition of thermites can produce ~4 MJ/kg, which approaches the combustion of hydrocarbon materials (~50 MJ/kg), whereas a modern chemical lithium-ion battery stores only 0.5 MJ/kg [1]. Therefore, energetic materials remain very attractive, even with a conversion efficiency of 10 %, because they can provide fast reactions and high energy densities concomitantly with long shelf life, thus enabling autonomous actions under infrequent and extreme conditions better than any other systems. The technology for making traditional energetic materials still relies on either the physical mixing of solid oxidizers and fuels or the incorporation of oxidizing and fuel moieties into one single molecule, referred to as monomolecular energetic materials. Although much progress has been made in traditional energetic formulations and their integration into miniaturized devices, they still emanate *from old and unsafe technologies* based on the processing of granular solids. Manufacturing these granular substances into complex precise shapes is often difficult because of limitations in processing highly solid filled materials and the danger in processing energetic materials. In addition, there are as many different energetic materials as there are desired effects (rapid or slow energy release, high or

low amount of gas generated), limiting their integration into generalized processes and hindering their incorporation into modern technologies and products. For two decades, nanotechnologies appear as the key to the development of future energetic materials. Nanothermites, obtained by mixing Al with oxide nanopowders (CuO, Fe<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, I<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, ...) [2-7] have attracted much interest because they can release twice as much energy than the best molecular explosives in a much more controlled and safe manner. Nanothermites can also have better combustion efficiencies and better ignitability compared to typical explosives [8]. In addition, the high interfacial contact between the nanoparticles (NPs) and small diffusion length scales, among other possible mechanisms, enhance the chemical kinetics between Al and oxidizer, resulting in rapid pressurization and high energy release [5,9]. In this paper, we exploit the high-pressurization capability of Al/CuO nanothermites to design and fabricate a miniature nanothermite-based circuit breaker (CB) ideally suited to protect against overcurrent, external perturbation and short circuit of a broad range of equipment and systems. A circuit breaker is a switching device capable of making, carrying and breaking currents under normal circuit conditions. Further, a CB should be capable of interrupting the current at a succeeding current zero. All of these features make the CB an important component. Mechanical circuit breakers [10] take a relatively long time (over 1 ms) to open the circuit and have excessive volumes. A miniature (2.3 cm<sup>3</sup>) nanothermite-based circuit breaker contains a switching unit, including a pyroMEMS, i.e. a pyrotechnical micro-chip capable of generating heat and pressure burst [9]. The use of pyroMEMS as a switching unit greatly miniaturizes the CB and ensures rapid interruption within less than 1 ms. After the presentation of the CB concept and design, the fabrication of each part of the device is presented in detail. The electrical testing achieved on several fabricated devices demonstrates 100 % success of current interruption. Results also show that the current interruption time can be easily tuned from 1.02 ms to 0.57 ms just by adapting the nanothermites solids loading, i.e. the mass of nanothermites deposited on the pyroMEMS. The nanothermite-based CB presented in this paper offers unprecedented advantages, such as the following: (1) harmless manipulation of the substances for humans; (2) integrated fabrication framework enabling low cost as well as mass fabrication, reliability and nanoscale precision; (3) increased environmental protection, only safe and environmental friendly substances and components are chosen to produce the energetic layers; and (4)

versatile design that can be applied to a large number of applications (electrical storage, aerospace manufacturing, human safety, demolition parachute opening, road vehicles, battery powered machines, ...).

#### 2. Materials and experimental methods

All PCBs (Printed Board Circuits) used in this paper are fabricated by CIRLY Company (France) using standard PCB technology. Al/CuO nanothermites prepared by mixing Al and CuO nanopowders are chosen because it possesses the following characteristics: a high energy release per unit of volume (3.9 kJ/g) and a high-pressure peak with the highest pressurization rate while being safe and relatively insensitive to ESD (ElectroStatic Discharge) [11] in comparison with other gas generator nanothermites, such as Al/Bi<sub>2</sub>O<sub>3</sub>. Moreover, Al/CuO displays higher combustion speed, in open combustion, than the standard nanothermites couple (Al/MoO<sub>3</sub>, Al/Bi<sub>2</sub>O<sub>3</sub> and Al/WO<sub>3</sub>) [12].

The CuO nanoparticles are supplied by Sigma Aldrich with a mean length of 50 nm and random shapes. The Al nanoparticles (Al-NPs) are supplied by US Research Nanomaterials, with a nominal diameter of 100 nm; they display spherical shapes with an alumina shell thickness of 4 nm, corresponding to a purity of 71 %, calculated from TGA (Thermo Gravimetric Analysis) curves of the Al-NPs under air in the temperature range of 30 - 1000 °C at a heating rate of 10 °C / min using a Mettler Toledo instrument (see Supplementary SI-1). Based on mass gain measurements ( $\Delta m$ ), the mass of aluminum  $m_{Al}$  can be determined ( $m_{Al} = \frac{2.M_{Al}}{3.M_0} \Delta m$ ) with  $M_{Al}$  and  $M_0$  the molar mass of aluminum (27 g.mol<sup>-1</sup>) and oxygen (16 g.mol<sup>-1</sup>). Then the thickness of the oxide layer ( $t_{oxide}$ ) is calculated according to Eq. 1.

$$t_{oxide} = R_0 \left( 1 - \sqrt[3]{\frac{m_{Al_2O_3}}{\sqrt{m_{Al_2O_3} + \frac{\rho_{Al_2O_3}}{\rho_{Al}}m_{Al}}}} \right)$$
 Eq. 1

where  $R_0$  is the total particle radius;  $m_{Al}$  and  $m_{Al_2O_3}$  are the masses of aluminum and alumina, respectively; and  $\rho_{Al_2O_3}$  (3.97 g.cm<sup>-3</sup>) and  $\rho_{Al}$  (2.7 g.cm<sup>-3</sup>) are the densities of amorphous aluminum oxide and aluminum at room temperature, respectively. Al-NPs and CuO-NPs are then mixed in different ratios, including the fractional alumina content [5]. Nanopowders are weighed and mixed in hexane with ultrasound agitation to achieve good mixing. Figure 1b displays a scanning electron microscopy image from Al/CuO mixing after ultrasonic mixing. These mixtures are then deposited by drop casting and, after evaporation step, pressed into Nylon washers (2.7 or 3.2 mm in diameter and 1 mm in thickness, giving a volume of  $5.7 \pm 0.9$  mm<sup>3</sup> or  $8.04 \pm 0.4$  mm<sup>3</sup>) using standard manual press leading to an applied force of ~ 2 daN. The pressure released by the nanothermites pellet is measured in a stainless steel cylindrical reactor, as described in a previous paper [5]. The free volume of the chamber is  $53 \pm 6$  mm<sup>3</sup> and the Al/CuO mass inside is  $8.3 \pm 0.3$  mg which corresponds to 3 % volumetric solids loading.



Figure 1: (a) Picture of one Al/CuO nanothermites pellet (Al/CuO nanopowders compacted into a Nylon washer) and, (b) SEM picture (x 150 000) of Al/CuO mixture before compaction and prepared at an equivalence ratio of 1.2.

The influence of the stoichiometric ratio of Al/CuO mixing, on the pressure released measurement, is investigated in this paper. Moreover, volumetric solids loading of Al/CuO is also varied to study its effect on the operating time of the CB.

#### 3. Operation principle and CB design

The proposed CB is schematically illustrated in Figure 2. The CB consists of two PCBs assembled to define a cavity of 39 mm<sup>3</sup> in volume (7 mm in diameter). The bottom PCB supports the pyroMEMS, i.e. the nanothermites ignitor on which an additional nanothermites pellet is glued. These two elements, constitutes the pyrotechnic actuator and are detailed in Figure 3. The top PCB has a separate copper track as part of the circuitry that must be disconnected as presented in Figure 2(b).



Figure 2: (a) 3D schematic of the device and (b) exploded views. (c)-(f) Principle of operation of the circuit breaker. The red dashed line represents the current flowing through the copper tracks before the switching occurs, and the blue line represents the current that triggers the nanothermites ignitor and subsequent Al/CuO nanothermites reaction.

For the demonstration, we make use of a 100-µm thick Cu track. The principle of operation is very simple and can be applied to a large number of applications just by adapting the nanothermites ignitor (see Figure 2): under external command, in the form of a current ( $I_{ignition}$ ) applied to the nanothermites

ignitor, the fast and violent reaction of the Al/CuO nanothermites pellet safely integrated into a hermetic cavity made by the assembly of two circuits, cut and propel a thick Cu track, thereby interrupting the current flowing through it ( $I_{cc}$ ).

The originality of our design relies on the simple soldering of the Cu track to be disconnected on the PCB's copper tracks. Therefore, the applied force necessary to eject it is independent of its thickness. For the demonstration, the overall size is set at  $30 \times 30 \times 2.6$  mm, and the copper track surface area is fixed at  $8 \times 10$  mm. The copper track is brazed on the PCB's Cu layer (brazing surface is of 8 mm<sup>2</sup>) using Sn<sub>42</sub>Bi<sub>57'6</sub>Ag<sub>0.4</sub> paste. The force required to disconnect the copper track has been experimentally measured at  $41 \pm 7$  N. Considering the copper track surface area of 80 mm<sup>2</sup>, a pressure greater than 1.1 MPa must be produced in the cavity.



Figure 3: (a) Schematic representation of the pyrotechnic actuator made of nanothermites ignitor on which a nanothermites pellet is glued using a thin layer of epoxy glue, (b) top view of one nanothermites ignition chip and (c) top view the nanothermites pellet.

As illustrated in Figure 3, the pyrotechnic actuator contains one nanothermites ignitor as presented in [13], which includes a Pyrex chip with a thin film resistance on which fifteen Al/CuO bilayers are sputtered, with each layer being 200 nm in thickness. A pellet of Al/CuO nanothermites is prepared as described in the methods section. When the current is supplied to the ignition chip, the chemical reaction occurs within less than 1 ms ( $I_{ignition}$ ), and sparks are spread to the nanothermites pellet, which reacts violently, producing the pressure burst plotted in Figure 5. The ignition time, i.e. the delay between the application of  $I_{ignition}$  and the appearance of sparks, as a function of the current applied to the nanothermites ignitor is presented in Figure 4. The minimum ignition time, 0.36 ± 0.07 ms, is

obtained for a current of 2 A. The fire/no fire threshold is 0.5 A, which means that there is no ignition before this value.



Figure 4: Plot of the ignition time as a function of the current applied to the nantohermites ignitor.

The nanothermites ignitor contains only  $282 \mu g$  of Al/CuO, leading to a pressure generation of 0.14 MPa [5] which is not enough to break the copper track (1.1 MPa of pressure needed). To generate the necessary pressure, nanothermites pellet made of nanoparticles mixing is used.

When preparing the nanothermites pellet, two parameters are important to control the pressure burst: (i) the solid loadings (in %) and, (ii) the equivalence ratios, i.e. the proportion of Al and CuO inside the nanothermites mixture. Sanders *et al.* [12] find that Al/CuO has the maximum peak pressure and the maximum burn rate near stoichiometric composition in a slightly fuel-rich configuration ( $\emptyset =$ 1.1). The same team shows that Al/Bi<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub> have optimum performances at an equivalence ratio between 1.2 and 1.4. They also demonstrate that increasing the density of the mixing (for Al/MoO<sub>3</sub>) inside the burn tube increases the pressure but decreases the combustion speed. Glavier et al. [5] experimentally investigate the pressure generated by Al/CuO nanothermites in a 9 mm<sup>3</sup> closed vessel and find that increasing the volumetric solid loadings from 10 to 50 % increases the pressure burst by a factor of 8. In the following sections, we consider very low solid loadings (~ below 5 %) to determine the optimum couple equivalence ratio, i.e. to produce the maximum pressure and pressurization rate. Three equivalence ratios near the stoichiometry are analyzed both experimentally and theoretically. Figure 5 shows the experimental temporal pressure evolution curves from ignition to 2 ms for 8.3 ± 0.3 mg of nanothermites prepared at three equivalence ratios ( $\emptyset = 1, 1.2, \text{ and } 1.4$ ). The pressurization rate is calculated as the slope of the initial pressure rise,  $\Delta P/\Delta t$ , and the delay time (t<sub>delay</sub>) as the time delay between ignition and pressure rise. The maximum pressure of 1.6 MPa is obtained for the stoichiometric mixing. For higher equivalence ratios of 1.2 and 1.4, the maximum pressure (P<sub>max</sub>) decreases to 1.3 and 0.9 MPa, respectively. However, the highest pressurization rate (33 MPa/ms) is obtained in the fuel-rich condition ( $\phi = 1.2$ ). A micro-kinetic model developed by LAAS-CNRS is used to predict the pressure burst generated by the reaction of *Al/CuO* nanothermites loaded in the hermetic cavity (53 mm<sup>3</sup> in volume) initially filled with ambient air. The model is not presented in detail in this article, as it is the topic of previous articles [14,15].



Figure 5: Experimental temporal pressure evolution curves for  $8.3 \pm 0.3$  mg of nanothermites in 53 mm<sup>3</sup> prepared at three equivalence ratios.

Table 1 summarizes the experimental and theoretical results obtained for Al/CuO nanothermites prepared at different equivalence ratios.

Table 1: Summary of experimental and theoretical maximal pressure, experimental pressurization rate and delaytime obtained for  $8.3 \pm 0.3$  mg of nanothermites in 53 mm<sup>3</sup> and prepared at three equivalence ratios.

Stoichiometry Ø	Theoretical P <sub>max</sub> (MPa)	Experimental P <sub>max</sub> (MPa)	ΔP/Δt ( <b>MPa/ms</b> )	t <sub>delay</sub> (μs)
1.0	1.23	$1.6 \pm 0.1$	31 ± 4	433 ± 12
1.2	1.10	1.3 ± 0.2	33 ± 4	215 ± 5
1.4	0.96	0.9 ± 0.1	12 ± 2	$261 \pm 9$

At very low volumetric solids loadings, Al/CuO nanothermites can generate a pressure burst with a maximum pressure ranging from 0.9 to 1.6 MPa, tunable by the Al/CuO equivalence ratio. The highest pressurization rate and lowest delay time is obtained for  $\emptyset = 1.2$ . Therefore, all Al/CuO nanothermites samples prepared for the CB tests will be prepared with an Al/CuO ratio of 1.2.

## 4. Fabrication and assembly

This section presents the assembly protocol, as summarized in Figure 6. First, the pyroMEMS's ignitor is glued in the cavity using a thin layer of epoxy resin H70-E Epo-Tek, and then its electrical contacts are realized by ball-bonding (with 4 Au wires with 25 µm in diameter) to the electrical pads of the bottom PCB. The Au wires are encapsulated into a solid epoxy resin H70E-2 from Epo-Tek to ensure a good mechanical resistance. The free volume around the pyroMEMS is then filled with a resin from Polytec. The Al/CuO nanothermites pellet is then prepared as described in the Experimental section to obtain an equivalence ratio of 1.2. The pellet is glued onto the pyrotechnical ignitor before closing the cavity with the copper connection, which is brazed onto the top PCB. Finally, the cavity is hermetically sealed with the solid epoxy resin H70E-2 from Epo-Tek.



Figure 6: Pictures illustrating the main CB assembly steps.

#### 5. Testing and results

We characterize the switching characteristic and the CB performance for the fabricated devices using the following method: A constant current ( $I_{cc}$ ) from 1 to 80 A is supplied (Keithley 2430 generator) to the two contact pads on the top surface of the PCB. A pyrotechnic exploder (NIMTECH AKLV16) is used to supply the nanothermites ignitor with a current pulse ( $I_{ignition}$ ) of 2 A – 1 ms. Both current ( $I_{cc}$  and  $I_{ignition}$ ) and voltage ( $V_{ignition}$ ) across the nanothermites ignition chip are recorded using a Tektronix oscilloscope DPO4034.  $I_{ignition}$  is measured through the pyrotechnic exploder and  $I_{cc}$  with a Tektronix current probe TCP0030A. A high-speed Photron FASTCAM SA3 camera records the CB operation at a frame-rate of 30 000 images per second.

Once the  $I_{ignition}$  is supplied to the ignition chip, the copper connection, soldered onto the top PCB, is ejected, and  $I_{cc}$  becomes null.  $V_{ignition} / I_{ignition}$  ( $R_{ignition}$ ) represents the ignitor resistance measured between the two contact pads of the bottom PCB. Figure 7 shows a typical behavior and raw electrical curves recorded during one test.



Figure 7: Raw electrical curves (currents and resistance) recorded during one switching experiment (Test 2 with 10.6 mg of nanothermites)

 $I_{ignition} = 2$  A;  $R_{ignition}$  increases from 3.016  $\Omega$  to 4.032  $\Omega$  because of the heating of the Ti thin film. At 0.4 ms,  $I_{ignition}$  decreases at 1.927 A and  $R_{ignition}$  starts to drop rapidly because of the ignition of the nanothermites thin film reaction (see Supplementary file SI-2 for details). The switching time ( $t_{switching}$ ) of the CB, Figure 7, is defined as the time delay between the application of  $I_{ignition}$  and the time where  $I_{cc}$  becomes null; in this case, it is 0.57 ms. In summary, the nanothermites thin film, which is deposited on the ignition chip, ignites at  $t_{ignition}$ , producing a violent and intense spark that ignites the combustion of the Al/CuO nanothermites pellet. The combustion of the nanothermites pellet lasts for a period of time of  $t_{NP}$  before the switching occurs at  $t_{switching}$ .

Nine tests are operated using three masses of Al/CuO nanothermites, i.e. three CBs per solid loadings are tested. Each of the tests results in a successful switching. Table 2 summarizes the measured switching time for each test.

Table 2: Solids loadings and switching times of the different configuration tested. 3 CB are tested by

Configuration	Solids loading (%) (mass of nanothermite)	Switching time (ms)	
#1	5.6 ± 0.5 %	1.02 + 0.40	
	$(5.59\pm0.69~mg)$	$1.02 \pm 0.49$	
#2	$10.6 \pm 0.5$ %	$0.63 \pm 0.23$	
	$(10.58 \pm 0.69 \text{ mg})$	0.03 ± 0.23	
#3	$19.1 \pm 0.9 \%$	$0.57 \pm 0.11$	
	$(13.24 \pm 0.94 \text{ mg})$		

configuration.

Increasing the nanothermites mass, and therefore the solids loading by ~3.5 permits the reduction of the switching time by a factor of 2.2. As expected, increasing the solids loadings reduces the free cavity volume, thus enabling a higher pressure and therefore a greater actuation power. The switching time, plotted in Figure 8, reaches an asymptotic value (0.4 ms) corresponding to the lowest value of  $t_{ignition}$ . This value can be reduced by tuning the nanothermites ignitor has published in our previous work [13], where the minimum ignition time that we are able to achieve is 59 µs.

Moreover, increasing the solids loadings increases the switching reproducibility.



Figure 8: Switching time as a function of the volumetric solids loading. The red dashed line corresponds to the ignition time of the nanothermites ignitor.

Finally, Figure 9 displays snapshots of the high-speed images for each tested CB configuration. The reactions are very bright, and we can easily see that the brightest reaction is obtained for the third test, in which the mass of nanothermites is the greater. The time t=0 corresponds to the image where a light is seen corresponding to the beginning of nanothermites combustion. Then, at t=33 $\mu$ s, the brightness of the reaction increases but the copper is still connected to the CB. And, finally, at t=462  $\mu$ s, the copper connection is ejected from the CB. But, for the tests Series #3 the copper connection (red line) is seen at the top of the images unlike the Series #1 and #2 where the copper is in the middle of the images. This remark is coherent with our expectation since the mass of Al/CuO nanothermites is greater for Series #3 than the others which leads to a fastest reaction.



Figure 9: (a) Screenshot of the image displays by the high speed camera before closing the diaphragm. (b)
Snapshots of high speed images taken for the three tested CB. The time between each picture is written on the left of the images. The copper connection is marked by red line on the images for more visibility.

#### 6. Conclusion

Miniature one-shot circuit breakers based on the combustion of a nanothermites are successfully manufactured and test. Each device is simply made from two assembled PCBs to define a hermetic cavity in which a pyroMEMS chip ignites within less than 100  $\mu$ s a few milligrams of nanothermites to cut a thick copper connection. We demonstrate the good operation (100 % of success rate) with a response time of 0.57 ms, which is much lower than the response time of classical mechanical circuit breakers (>1 ms).

We demonstrate that the response time can be easily tuned from 1 ms to 0.57 ms by adjusting the mass of nanothermites in the cavity from 5.59 to 13.24 mg. The proposed concept is generic and can be applied to a large number of applications (electrical storage, aerospace manufacturing, human safety, demolition parachute opening, road vehicles, battery powered machines, ...).

Note that one of the advantages of the proposed concept is that any size and Cu thickness can be designed and integrated, allowing the devices to be generic and adaptable to different applications

requirements. The pressure required to pull out the connection depends only on the surface brazed surface.

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#### **Supplementary files**

#### SI-1 : Electrical curves of the nanothermites ignitor

Figure SI-1 presents the TGA (thermo gravimetric analysis) curves of the Al-NPs under air in the temperature range of 30 - 1000 °C at a heating rate of 10 °C / min using a Mettler Toledo instrument. The mass gain  $\Delta m$  which is correlated to the Al content is measured as the difference between asymptotes at temperature 30 and 1000°C.



Figure SI-1: TGA curve of Al-NPs in air.

#### SI-2 : Electrical curves of the nanothermites ignitor

Figure SI-2 shows the electrical curves of one nanothermites ignitor alone inside the cavity of the CB. The nanothermites pellet and the copper connection are not assembled on top. Instead, a photodiode is placed facing the ignitor to detect the sparks emitted during ignition. The ignition time  $t_{ignition}$  of the ignitor chip is defined as the time between the application of the ignition current and the appearance of a signal from the photodiode. From the plot of Figure SI-2, we clearly see that the resistance value drop coincides with the appearance of the photodiode signal, i.e., nanothermites thin film ignition.



Figure SI-2. Raw electrical curves obtained for one single nanothermites ignitor (no nanothermites pellet on it).