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# AL/CUO SPUTTERED NANOTHERMITES AS NEW ENERGETIC THIN FILMS FOR TUNABLE IGNITION AND ACTUATIONS

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**Topic : Integration and micro nanotechnology applications**

**Abstract — Sputter-deposited Al/CuO multilayers are used to manufacture tunable igniters and actuators with applications in various fields of application such as defense, space and infrastructure safety. This paper describes the technology of deposition and characteristics of Al/CuO multilayers followed by some examples of applications of these energetic layers.**

## I. INTRODUCTION

Energetic materials are widely used to generate suddenly high amount of thermal or mechanical energy under an electrical, mechanical or thermal stimulus. As typical energetic materials, nanothermites which contain Al and oxide, have attracted much attention as they exhibit not only better combustion efficiencies and better ignitability compared to traditional explosives but also the reaction outputs can be tuned thanks to the selections of fuels, oxidizers, architectures and reactant size allowing multiple actions. Among nanothermites, sputter-deposited Al/CuO multilayers represent an interesting energetic thin film nanomaterials for tunable ignition to replace old hot-wire ignitor.

In that context, our research group at LAAS-CNRS demonstrated several miniature pyrotechnical ignitions devices integrating Al/CuO multilayers within MEMS based microheaters, called pyroMEMS, for application in civilian and military applications such as triggering the inflation of airbags, micro-propulsion systems, and arm and fire devices.

This paper reviews the technological process focusing on sputter-deposition technique, presents the properties of Al/CuO multilayered films and details the fabrication process flow of a micro-igniter. As conclusion, some examples of applications of pyroMEMS are overviewed.

## II. AL/CUO MULTILAYERED NANOTHERMITES

Two decades ago, the introduction of nanotechnologies enabled the emergence of a new class of energetic materials called nanothermites that could play a great role in the future society. Nanothermites use raw materials that can be found in abundance, are low cost and non-polluting (green materials). They also exhibit better combustion efficiencies and better ignitability compared to typical CHNO energetic mixtures while being safer. Importantly, the reactions and ability to trigger specific actions can be

tailored by varying the size and composition of the oxide, allowing multiple applications. Focusing on thermite multilayers, the overwhelming majority of works concern Al/CuO systems, as they feature an exceptionally high-energy release with gaseous production.

### A. Sputter-deposition of Al/CuO multilayers

Al/CuO thermite multilayers are mainly produced by sputter-deposition technique [1]–[5] as it provides excellent control over the layering and stoichiometry. Cupric oxide thin film is synthesized using direct current (DC) reactive magnetron sputtering technique in an oxygen enriched environment. To produce Al/CuO multilayered films, layers of Al and CuO are deposited on top of each other in an alternating fashion (see Fig. 1) without venting the chamber. However, after each layer deposition, the sample stage is cooled at ambient temperature for 600 s. CuO is polycrystalline and characterized by XRD before deposition. At each interface between cupric oxide and Al layers an intermixing layer of 4-8 nm is present and formed during the deposition itself.

Depositions parameters have been published several times and can be found in [6], [7].

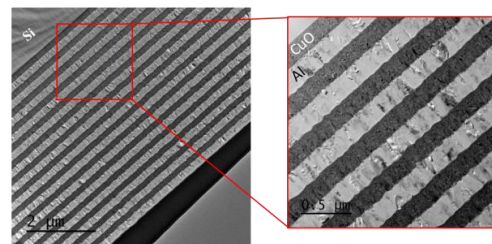
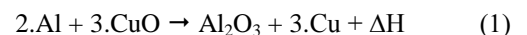


Figure 1. Cross sectional transmission electron micrographs of the Al/CuO multilayer obtained by magnetron sputtering.

### B. Ignition and reaction properties

Applying an external source of energy locally on the multilayer results in an increase of the temperature in the multilayer section directly in contact with the heated surface. This can be done by electrostatic discharge [8], mechanical impact [9], laser irradiation [10], electrical heating (spark) [11] and thermal hot points [12] which is the widest used. After being ignited, the multilayers react by a self-sustained propagating reaction following the chemistry of eq. 1.



In other words, after the temperature is raised locally and rapidly to a characteristic onset reaction temperature, the reaction enthalpy ( $\Delta\text{H}$ ) spreads into neighboring

unreacted portions of the film, leading to a self-sustained reaction wave, which is highly luminous.

As the exothermic chemical reactions are controlled by the outward migration of oxygen atoms from the CuO matrix towards the aluminum layers, the reaction rate strongly depends on the reactant spacing (bilayer thickness). The sustained combustion rate is commonly characterized with a standard high-speed camera under ambient pressure [5], [7].

The combustion velocity increases for thinner bilayers with a maximum at  $\sim 90$  m/s for free-standing foils (see Fig. 2(a)). However, the reaction stops suddenly for extremely small bilayer thicknesses, which is due to the presence of interfacial layers, as described earlier which reduces the amount of stored energy i.e., reaction enthalpy,  $\Delta H$ .

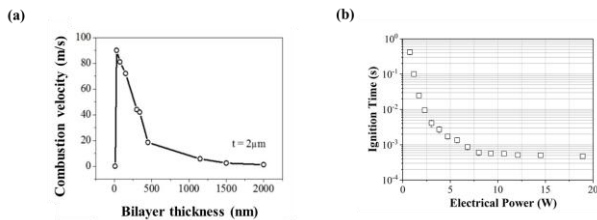


Figure 2. (a) Sustained combustion velocity in air of free-standing multilayers as a function of bilayer thickness (total thickness  $t=2 \mu\text{m}$ ); (b) ignition time as a function of the electrical power send through the micro-heater for 5 bilayers of Al/CuO (Taken from [12]).

### III. PYROMEMS INTEGRATION AND CHARACTERIZATION

When integrated on a device/substrate, the widest and simplest ignition method for igniting an Al/CuO multilayered thin film is hot-wire by a local metallic thin film resistance. A pyroMEMS is mainly composed of a substrate, a thin metallic resistance and the Al/CuO nanothermites (see Fig. 3(a)).

To minimize the ignition energy, the substrate must be a good thermal insulator. We chose  $500 \mu\text{m}$  thick 4-in. glass substrates (AF32 from Schott). After being cleaned in oxygen plasma to remove surface contaminants, 300 nm thick titanium followed by 300 nm thick gold layers are evaporated onto the glass substrate and the filament is patterned using lift-off technique. Then the gold is chemically etched and patterned to define the Ti resistance and Au electrical pads. Finally, Al/CuO multilayers are sputter deposited through a silicon shadow mask. A photo of a pyroMEMS thus manufactured is presented in Fig. 3(b).

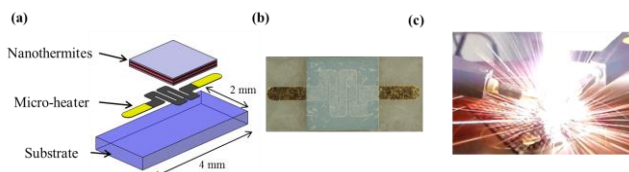


Figure 3. (a) 3D schematic representation of a pyroMEMS; (b) photo of the pyroMEMS; (c) photo during the nanothermite reaction.

We characterized that, for any heating surface areas (micro-heater sizes), the ignition time (delay between the

time of application of the electrical power and the emission of the light) rapidly decreases when the ignition power density increases until an asymptotic value, defining the minimum response ignition time, which is a characteristic of the multilayered film itself.

As an illustration, Fig. 2(b) provides the ignition time vs the ignition power for a thermite made of fifteen 300 nm thick 1:1 Al/CuO bilayers. Below a certain electrical power, no ignition occurs, regardless the duration of application of the power. This is simply explained by the fact that, below this ignition power threshold, the electrical energy supplied to the micro-heater is not sufficient to compensate for the energy lost by conduction through the substrate, by radiation from the exposed surface, and by convection in the air. The multilayer cannot reach its ignition temperature, also known as onset reaction temperature.

This threshold highly depends on the heating surface area and detailed results can be found in [12].

### IV. EXAMPLES OF APPLICATIONS

To date, igniters are the widest investigated applications and widely used to trigger the inflation of airbags, micro-propulsion systems, and arm and fire devices used in missiles, rockets and any other ordnance systems. Traditionally, igniter technology consists of a metallic hot wire (Ni/Cr, ...) or bridge wire in contact with a secondary or primary explosive. The fabrication and integration of explosives in igniters require extreme precautions due to high sensitivity to the electrostatic discharge, friction or shock.

Al/CuO multilayers can efficiently replace the hot wire and primary explosive. Another advantages of replacing traditional hot-wire with pyroMEMS are : (1) the overall integration is easier requiring only the electrical connections of the pyroMEMS whereas traditional pyrotechnical igniters required at least two steps (hot wire and primary pyrotechnic composition deposition). (2) the Al/CuO multilayers are safe and less sensitive to environment. (3) ignition threshold and reaction output (flame temperature and gaseous products) can be easily tuned by changing the Al/CuO bilayer thickness and stoichiometry (bilayer thickness ratio).

Taton *et al.* [13] first reported the design, realization and characterization of hot-wire ignition integrating Al/CuO multilayers (see Fig. 4) for application in pyrotechnical systems for space applications. The reactive Al/CuO multilayered thin film resides on a  $100\text{-}\mu\text{m}$ -thick epoxy/polyethyleneterephthalate (PET) membrane to insulate the reactive layer from the bulk substrate. When current is supplied, Al/CuO reacts and the products of reaction produce sparks that can ignite any secondary energetic composition, such as RDX. The authors demonstrate a 100% success of ignition over 0.25–4 A firing current range corresponding to 80–244  $\mu\text{J}$  and with response times ranging from 2 to 260  $\mu\text{s}$ . Then, Glavier *et al.* [14] used this igniter to cut and propel a thin metallic foil and ignite RDX in a detonation. Authors showed that a stainless steel flyer of 40 mg can be properly cut and propelled at velocities calculated from 665 to 1083 m/s as a function of the RDX extent of compaction and ignition charge. The impact of the flyer can directly initiate the detonation of an RDX explosive, which is very promising to remove primary

explosives in detonators. A schematic view and photo of one miniature detonator is given in Fig. 4.

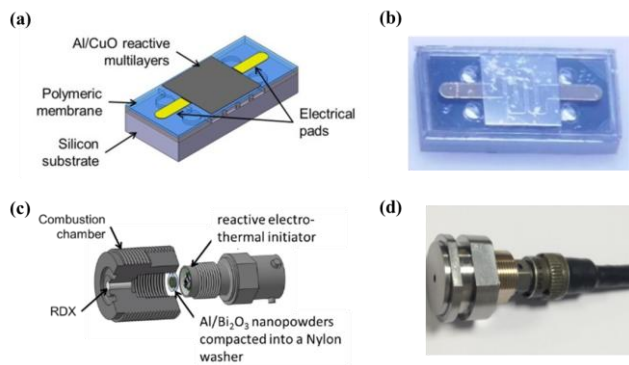


Figure 4. (a) Schematic and (b) photo of the reactive electro-thermal initiator on Epoxy/PET membrane. Chip dimension is 4 mm x 2 mm. (c) Schematic and (d) photo of one miniature detonator integrating Al/CuO multilayers as initiator. Taken from [14].

More recently, Nicollet et al [12] derived the Al/CuO multilayer igniter concept for several substrates and simplified the fabrication process to adapt it to airbag initiation. Additionally, our team has demonstrated miniature one-shot circuit breakers [15] based on the combustion of a nanothermite. Each device is simply made from two assembled Printed Board Circuits (PCBs) to define a hermetic cavity in which an Al/CuO multilayer initiator chip ignites –in less than 100  $\mu$ s– a few milligrams of nanothermite to cut a thick copper connection (see Fig. 5). The authors demonstrated 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 (> ms).

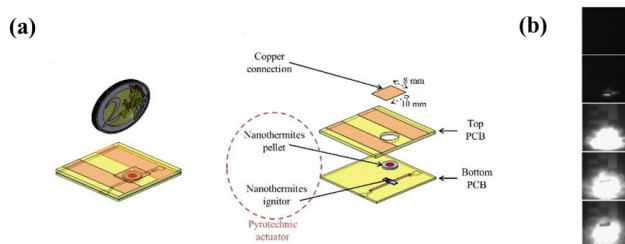


Figure 5. (a) 3D schematic of the nanothermite based circuit breaker; (b) exploded views and (c) snapshots of high speed images taken for the tested circuit breaker. The time between each picture is 100  $\mu$ s. Taken from [15].

## V. CONCLUSION

Sputter-deposited Al/CuO multilayers, composed of alternating Al and CuO nanolayers with total thickness ranging from 1 to tens of  $\mu$ m, present an opportunity for tunable ignition and actuation. The interest and the integration in igniter applications have been demonstrated for different applications, such as inflators, aerospace or actuators.

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## REFERENCES

- [1] M. Petrantoni, C. Rossi, L. Salvagnac, V. Conédéra, a. Estève, C. Tenaillon, P. Alphonse, and Y. J. Chabal, "Multilayered Al/CuO thermite formation by reactive magnetron sputtering: Nano versus micro," *J. Appl. Phys.*, vol. 108, no. 8, p. 84323, 2010.
- [2] D. P. Adams, "Reactive multilayers fabricated by vapor deposition: A critical review," *Thin Solid Films*, vol. 576, pp. 98–128, Feb. 2015.
- [3] S. Fu, R. Shen, P. Zhu, and Y. Ye, "Metal–interlayer–metal structured initiator containing Al/CuO reactive multilayer films that exhibits improved ignition properties," *Sensors Actuators, A Phys.*, vol. 292, pp. 198–204, Jun. 2019.
- [4] N. A. Manesh, S. Basu, and R. Kumar, "Experimental flame speed in multi-layered nano-energetic materials," *Combust. Flame*, vol. 157, no. 3, pp. 476–480, Mar. 2010.
- [5] C. Rossi, "Engineering of Al/CuO Reactive Multilayer Thin Films for Tunable Initiation and Actuation," *Propellants, Explos. Pyrotech.*, Jul. 2018.
- [6] G. Lahiner, J. Zappata, J. Cure, N. Richard, M. Djafari-Rouhani, A. Estève, and C. Rossi, "A redox reaction model for self-heating and aging prediction of Al/CuO multilayers," *Combust. Theory Model.*, 2019.
- [7] J. Zapata, A. Nicollet, B. Julien, G. Lahiner, A. Esteve, and C. Rossi, "Self-propagating combustion of sputter-deposited Al / CuO nanolaminates," *Combust. Flame*, vol. 205, pp. 389–396, 2019.
- [8] C. Weir, M. L. Pantoya, G. Ramachandran, T. Dallas, D. Prentice, and M. Daniels, "Electrostatic discharge sensitivity and electrical conductivity of composite energetic materials," *J. Electrostat.*, vol. 71, no. 1, pp. 77–83, 2013.
- [9] J. L. Cheng, H. H. Hng, Y. W. Lee, S. W. Du, and N. N. Thadhani, "Kinetic study of thermal- and impact-initiated reactions in Al-Fe<sub>2</sub>O<sub>3</sub> nanothermite," *Combust. Flame*, vol. 157, no. 12, pp. 2241–2249, 2010.
- [10] D. Damm and M. Maiorov, "Thermal and radiative transport analysis of laser ignition of energetic materials," in *Optical Technologies for Arming, Safing, Fuzing, and Firing VI*, 2010, vol. 7795, p. 779502.
- [11] A. Hadjiafxenti, I. E. Gunduz, C. C. Doumanidis, and C. Rebholz, "Spark ignitable ball milled powders of Al and Ni at NiAl composition," *Vacuum*, vol. 101, pp. 275–278, 2014.
- [12] A. Nicollet, G. Lahiner, A. Belisario, S. Souleille, M. Djafari-Rouhani, A. Estève, and C. Rossi, "Investigation of Al/CuO multilayered thermite ignition," *J. Appl. Phys.*, vol. 121, no. 3, 2017.
- [13] G. Taton, D. Lagrange, V. Conedera, L. Renaud, and C. Rossi, "Micro-chip initiator realized by integrating Al/CuO multilayer nanothermite on polymeric membrane," *J. Micromechanics Microengineering*, vol. 23, no. 10, p. 105009, 2013.
- [14] L. Glavier, A. Nicollet, F. Jouot, B. Martin, J. Barberon, L. Renaud, and C. Rossi, "Nanothermite/RDX-Based Miniature Device for Impact Ignition of High Explosives," *Propellants, Explos. Pyrotech.*, vol. 42, no. 3, pp. 308–317, 2017.
- [15] A. Nicollet, L. Salvagnac, V. Baijot, A. Estève, and C. Rossi, "Fast circuit breaker based on integration of Al/CuO nanothermites," *Sensors Actuators A Phys.*, vol. 273, pp. 249–255, 2018.