

An Exothermal Energy Release Layer for Microchip Transience

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Abstract— A single layer nanothermite spin coated gel has been utilized as a solid-state exothermic energy release layer for triggered microchip transience. A proportional combination of self-assembled CuO/Al nanothermite and Napalm-B as gelling agent has been used to develop for the first time a spinable nanothermite film onto the surface of a micro-chip. This layer when ignited instantaneously releases enough heat energy to melt the surface of the underlying substrate and any surface-bound microdevices, electronic feature or any surface deposited component. We observe the effect of thermite enabled destruction prior and post ignition through microscopic imaging and electrical measurements on surface bound components.

Keywords—chip transience; Nanoenergetics; Nanothermite; Self-Assembly; MEMS

I. INTRODUCTION

Many sophisticated electronics are in use in critical defense, financial and technological fields. Protection of these technologies and data are hence of outmost importance. Many protocols based on chemical attack, encryption algorithms, self-destructing electronics are in place to for data and technology protection [1-3]. In most of such devices an explosive material, a flammable element or an acid reservoir is stationed near the electronic circuit that needs to be destroyed and when needed, these destructive devices were triggered to release the destructive agent. The main drawback in these kinds of devices was that these methods would only partially destroy a chip, which could still lead to data and technology being lost to the wrong hands. For complete destruction a layer of transient material needs to be integrated with the microchip.

In this paper we present the use of nanothermite films as instruments for devising self-destructing microchips. Nanothermites have been studied before for their ignition properties [5], combustion wave speeds [6] and reaction temperatures [7]. Since thermite combustion is a solid state diffusion controlled reaction, the best way to achieve this is to ensure maximum interfacial contact between the oxidizer and the fuel. Various mixing techniques viz. physical mixing [8], sol-gel synthesis [9], self-assembly [10] and ultrasonic mixing [11] have been reported earlier. Comparatively self-assembled CuO/Al nanocomposite have been shown to have better energy release characteristics, due to better interfacial contact between the fuel and oxidizer and no particle sintering as might be the case with ultrasonic mixing. Hence we choose CuO/Al nanocomposite as the material of our choice.

Self-assembly of CuO/Al nanocomposites via electrostatic interaction [12], charge transfer [13], polymer assisted binding [14] have been reported. In this paper we concentrate on polymer assisted binding, since it allows for multiple particle binding at the same oxidizer particle, with the polymer of choice being Poly (4-vinylpyridine) P4VP. The pyridyl group of P4VP allows binding for both metal and metal oxides [15]; hence P4VP can be used to bind both oxidizer and fuel together forming a self-assembled homogeneous composite held together by chemical bonds between fuel-polymer-oxidizer.

Nanothermites as coatable thin films have never been studied before; hence this study is first of its kind. The coated energy release layer is ignitable using a microfabricated heater or an electric spark and does not require external oxygen; hence can be incorporated within a sealed chip package. We report the first results of chip transience experiments when this layer is deposited on top of a MEMS chip. We observed that upon ignition the chip Al metallization is burned and fused within seconds, destroying metal semiconductor junctions and other features on the chip. We also report the electrical measurements on a surface resistor during the transience.

II. MATERIALS AND METHODS

A. Materials

Copper Oxide (CuO) Nanopowder / Nanoparticles (CuO, 99%, <80nm) and Aluminum (Al) Nanopowder / Nanoparticles (Al, 99.9%, <40nm, metal basis) were purchased from US Research Nanomaterials, Inc. Houston, TX. Poly 4-vinylpyridine (P4VP) average Mw ~160,000, 2-Propanol anhydrous and analytical standard Benzene ($\geq 99.9\%$) were purchased from Sigma Aldrich, St. Louis, Missouri. Gasoline was purchased from local gas stations. Polystyrene beads were also purchased from local stationary stores.

B. Exothermal Energy Release

The exothermic spontaneous reaction follows reaction as shown in equation 1, where CuO is the oxidizer (A) and Al is the fuel (F). The equation also gives the value for ΔH_f which is the heat of formation. The energy release during the reaction depends on number of parameters such as equivalence ratio, size of Al nanoparticles and time of sonication.



Al nanoparticles are chosen such that their size are at least half of the size of CuO nanoparticles so as to allow for more

binding of fuel particles per oxidizer particle. Sonication time is optimized as described in [3] and equivalence ratio is defined as in Eq. (2).

$$\varphi = \frac{F}{A} \cdot \left(\frac{A}{F}\right)_{stoichiom} \quad (2)$$

It has been noted before that the best burning characteristics are observed for an equivalence ratio of 1.6 for CuO/Al. The oxidizer/fuel ratio $\left(\frac{A}{F}\right)_{stoichiom}$ is obtained from Eq. (1), and since we already know φ we can find the amount of fuel needed for any amount of oxidizer.

C. Self Assembled Nano-Thermite Synthesis

The process involves three major steps (a) Coating P4VP on CuO nanoparticles, (b) Assembling with Al nanoparticles and (c) Separation of free particles from the thermite. The entire process is summarized in Fig. 1. We start with 0.5g of CuO nanoparticles and sonicated with 500 ml of 2-Propanol with 0.1% (w/v) P4VP for 4 hours. The polymers coats on the surface of the nanoparticles and the coated nanoparticles are separated from the solution by centrifuging at 4000 rpm for ~ 10 minutes. The separated particles are re-suspended, sonicated for 2 hours in 200 ml 2-Propanol and centrifuged for at least 4-5 times to remove excess polymer sticking to the nanoparticle surface. Post sonication we are left with uniformly coated CuO nanoparticles ready to be assembled with Al nanoparticles. Prior to mixing with Al nanoparticles the polymer coated CuO nanoparticles are baked at 120°C for 1.5 hours to dry out any residual solvent trace and catalyze bonding between the polymer and the CuO particle surface. The particles are not ready to be mixed with Al nanoparticles.

In order to achieve proper assembling we begin with 0.4g of the polymer coated CuO nanoparticles and mix them with equivalent amount of Al nanoparticles (0.17g) in 1.5 ml of 2-Propanol in a sealed vial and sonicate for at least 4 hours to ensure proper dispersion. The mixture was diluted with 2 ml of 2-Propanol and sonicated further for 30 minutes. The assembled particles were retrieved from the mixture by repetitively centrifugation and washing with 2-Propanol for 4-5 times and finally dried at 95°C for 10 minutes. At the end of the drying step we are left behind with fine self-assembled nanothermite powder.

D. Napalm-B gelling agent

We prepare the gelling agent with gasoline, benzene and polystyrene. To improve the flammability and fluidity of the substance the compositional ratio for polystyrene is reduced from 46% to 30% and the percentage for gasoline is 40% and Benzene 30%. In a beaker of 300 ml capacity we add 40 ml gasoline and 30 ml of Benzene and to this is added grounded polystyrene small amounts at a time and allowed to foam and settle by gentle stirring.

After preparing Napalm gel, nanothermite and the gel were mixed together to create a uniformly suspended sol-gel of nanothermite. 0.5 ml of the gelling material is taken in a glass vial and to that is added 2g of thermite and sonicated for several hours to achieve homogeneous consistency of the

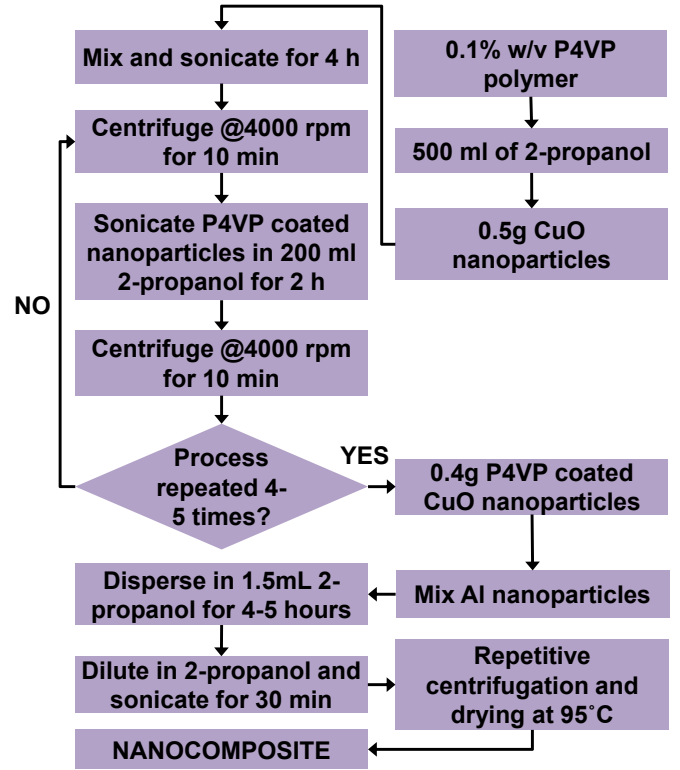


Figure 1. Flowchart describing steps for synthesizing nanocomposite powder starting with CuO and Al nanoparticles and Poly(4-vinylpyridine) as assembling matrix.

nanothermite suspension in Napalm gel.

E. Transience Chip

A Si-based microchip with metal-Si junction components is used to demonstrate qualitatively the functioning of the thermite gel. Another Si microchip with Al resistors is fabricated to establish quantitatively the effect of thermite gel through real time resistance measurement. First a layer of

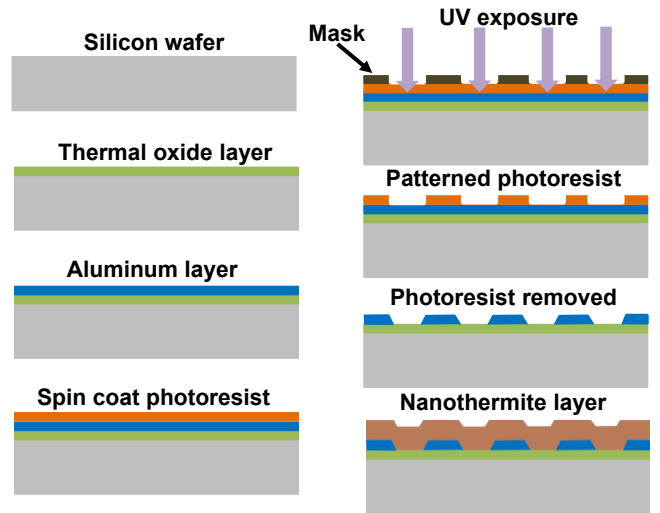


Figure 2. Simplified process flow for transience test chip.

0.5 μ m thickness aluminum was deposited by e-beam evaporation. After that the layer was patterned using standard photolithographic technique, in this case positive photoresist AZ9260 was used along with 1:1 400 MIF developer. The Fabrication steps for the chip are summarized in Fig. 2.

Both chips are spin coated with the Thermite-gel at 4000 rpm to create a thermite film of 0.5 mm thick. The ignition can be initiated by either an electric trigger through a micro heater or an electric spark.

III. EXPERIMENTAL RESULTS

A. Ignition

An electric spark was used to ignite the nanothermite gel. Once ignited the gel burns for a while because of the presence of Napalm. The adiabatic flame temperature of the thermite flame has been reported before to be $\sim 3794\text{K}$ and that for Napalm $\sim 2774\text{K}$. It is Napalm which ignites first and keeps the thermite burning. Due to the high temperatures of the reaction and the presence of polymer P4VP a lot of gaseous intermediates are generated during the reaction which causes a

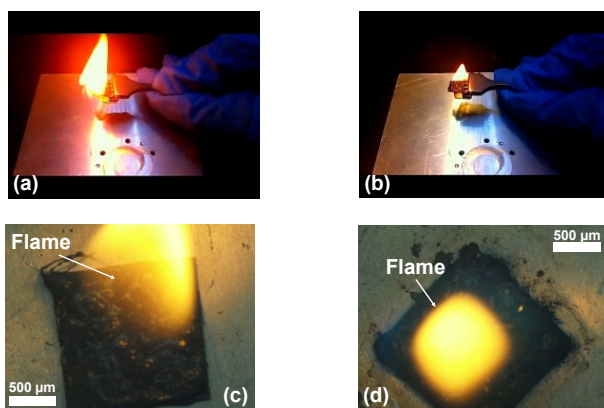


Figure 3. Ignition of CuO/Al nanothermite film deposited on top of MEMS chip as viewed simultaneously using a CCD camera and a stereoscopic microscope. (a) & (b) Side views through a CCD camera taken 5 seconds apart give an idea of combustion rate as flame is seen dying reduced in (b). (c) and (d) Top view as viewed from a stereoscopic microscope with a mounted camera taken at the same instances as the images in (a) & (b)

regional high pressure zone to develop propelling the flame front (combustion front) as if in an explosion. The high temperature prolonged burning of Napalm ensures that all the self-assembled nanothermite is used up and that the chip experiences a prolonged exposure to very high temperatures. Fig. 3 shows optical images of a burning microchip. The

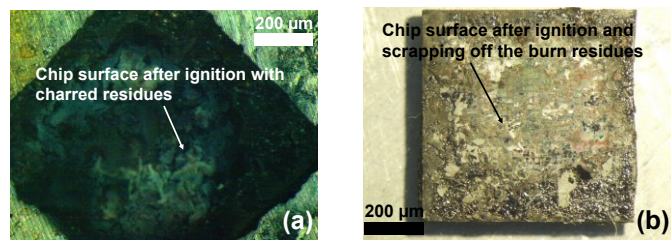


Figure 4. After burn image of the chip showing nanothermite fusion with the chip. (a) Before brushing off of charred after burn residue (b) After brushing off the charred residues off the surface showing fused nanothermite and chip surface and destruction of surface components

burning action appears to be concentrated in the middle region of the chip.

B. Chip Transience

Post combustion the charred nanothermite reaction residue is scrapped off the microchip surface with faint brushing and the chip was imaged under an optical microscope Fig 4. Shows images of the entire chip after the nanothermite combustion with charred reaction residue and after the residue is brushed off the surface of the microchip. which shows evidence of destruction of the components on the chip through burning and fusion of metals at the surface.

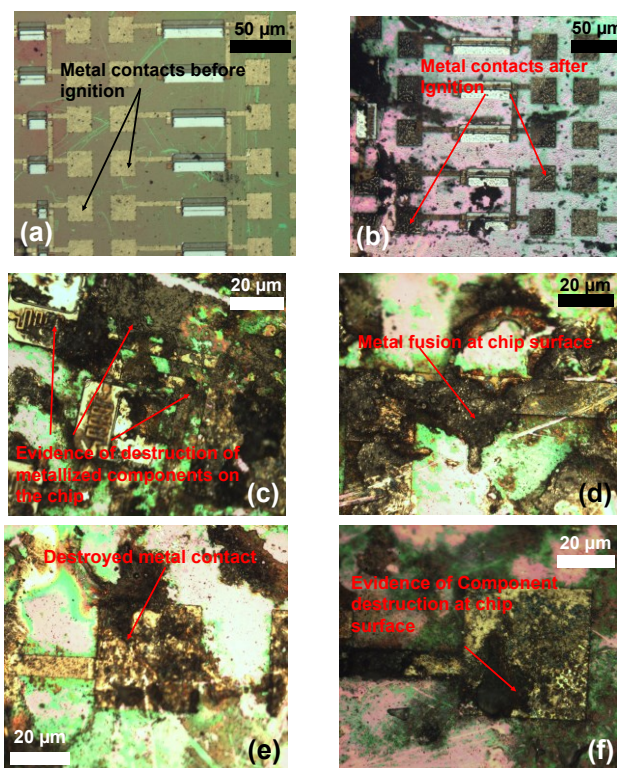


Figure 5. (a) 10x zoom before ignition, (b) 10x zoom after ignition showing metal fusion with chip surface and melting of deposited metal components. (c),(d),(e) and (f) show conclusive evidence of metallization damage component destruction at the chip surface at 20x zoom

A detailed view under 10x and 20x magnification under a microscope provides photographic evidence of complete and wide spread metallization damage on the chip surface. All the micro features and metal deposition on the chip surface has been completely destroyed as shown in Fig. 5.

C. Real-Time Electrical Resistance Measurements

Electrical measurements provide a quantitative measure of the damage caused under transience. In addition to the optical examination we measured the real-time resistance of an aluminum resistor on the substrate coated with the nanothermite before and during transience. Experimentally the resistivity of the nanothermite film prior to the ignition was very high and the value of the nominal resistance of the Al resistor was unchanged by the nanothermite coating. The sample was next placed under a probe station and ignited.

Fig. 6 shows the plot of the test resistance versus time during the ignition event. Note that the resistance increases from $\sim 100 \Omega$ to $\sim 2.3 \text{ k}\Omega$ in less than 5 seconds after ignition. The resistance change is irreversible. The measurements shown in Fig. 6 provide conclusive evidence that the thermite damage is extensive and sufficient to disable most silicon microchips.

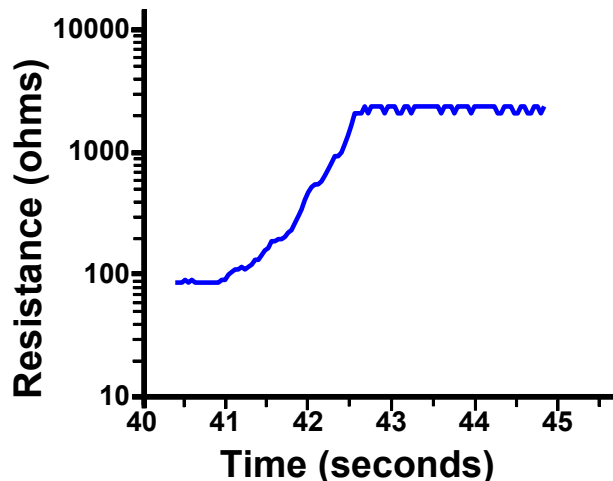


Figure 6. Resistance of aluminum test resistor at the surface of the chip during the transience event. Note that the resistance irreversibly increases several orders of magnitude in a few seconds after ignition.

IV. CONCLUSION

The paper discussed a method for deposition and use of a solid-state exothermal energy release layer for the triggered destruction of microchips (chip transience). We report for the first time the use of a spinable nanothermite film that when ignited releases intense heat sufficient to melt the surface of the underlying substrate and any surface-bound microdevices. The film contains a mixture of self-assembled CuO/Al nanothermite and Napalm B as a gelling agent. It is observed that the energy release layer is ignitable using a microfabricated heater with concerted electronics or even an electric spark and does not require external oxygen; hence can be incorporated within a sealed chip package. We report the first results of chip transience experiments when this layer is deposited on top of a MEMS chip. We observed that upon ignition the Al metallization is burned and fused within seconds, destroying metal semiconductor junctions and other features on the chip.

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