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# Synthesis process of nanowired Al/CuO thermite

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## ABSTRACT

Al/CuO nanothermites were fabricated by thermal oxidation of copper layer at 450 °C for 5 h and by aluminum thermal evaporation: thermal evaporation allows producing thin layer less than 2 μm in size. The copper has been deposited by electroplating or thermal evaporation depending on the required thickness. The obtained diameter of Al/CuO nanowires is 150–250 nm. Al/CuO nanowires composite were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and differential thermal analysis (DTA). Two distinct exothermic reactions occurred at 515 and 667 °C and total energy release of this thermite is 10 kJ/cm$^3$.

## 1. Introduction

In recent years researchers have found that energetic materials which are produced on the nanoscale show significantly improved performances, especially in the area of sensitivity. Metastable intermolecular composites (MICs) or nanothermites represent one example of such materials. These systems consist of metals (e.g. aluminum) and oxidizers [1]. For MEMS applications, Al/CuO system is particularly interesting because aluminum and copper are commonly used in a microelectronic process and Al/CuO reaction can reach up to 4 kJ/g. However, produced at macroscale, composite reaction is relatively slow [2,3]. Produced at nanoscale, as the specific surface area increases, the intimacy between the reactants (Al and CuO) also increases and therefore the reaction rate increases, making Al/CuO nanothermite very interesting. Our team members, Zhang et al., have developed a simple process to produce array of nanowires of CuO covered by a thin layer of Al [4,5]. This paper describes an optimized thermal oxidation process to produce an auto organized array of CuO nanowires of 40–90 nm diameter from a Cu thin layer. Here, we also compare the effects of two kinds of copper deposition methods on the nanowires growth. Finally, the energetic performances of the optimized Al/CuO nanowired thermite are characterized using DSC and DTA to determine experimentally the heat of reaction.

## 2. Experiment

### 2.1. Al/CuO sample preparation

#### 2.1.1. Cu deposition

A 30-nm-thick layer of titanium is thermal evaporated under secondary vacuum ($3.75 \times 10^{-7}$ Torr) on the clean 4″ silicon substrate to serve as an adhesion layer between copper and silicon. After this stage two kinds of copper deposition methods are used electroplating and thermal evaporation.

For the electroplated copper, a 50-nm-thick layer of copper is evaporated to serve as a conducting layer for the second step, which is the electroplating of Cu film at 25 °C in a microfabCU200 bath (25 g(Cu)/L($H_2SO_4$)—Enthone Omi). The current density is 2 A/dm$^2$. Copper thickness is 1 μm.

For the thermal evaporated copper, the step following the titanium evaporation is the thin film copper evaporation. Copper thicknesses tested for the nanowires growth are 50, 300 and 1000 nm to determine the critical thickness below which there is no nanowire growth.

#### 2.1.2. Cu thermal oxidation

Next step is the removal of the native copper oxide using a diluted solution of hydrochloric acid (HCl). Then, the as-prepared wafers are cleaned, dried by nitrogen and oxidized in static air. The optimized oxidation process to get only CuO is as follows:

- a thermal ramp from room temperature to 450 °C with a heating rate of 2 °C/min
- a plateau at 450 °C during 5 h under static air (see Fig. 1)
- a cooling ramp from 450 °C to room temperature with a rate of 2 °C/min

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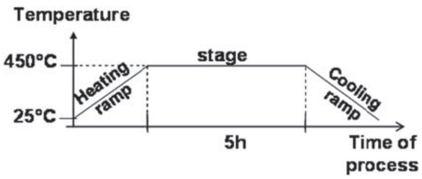

**Fig. 1.** Thermal oxidation cycle parameters.

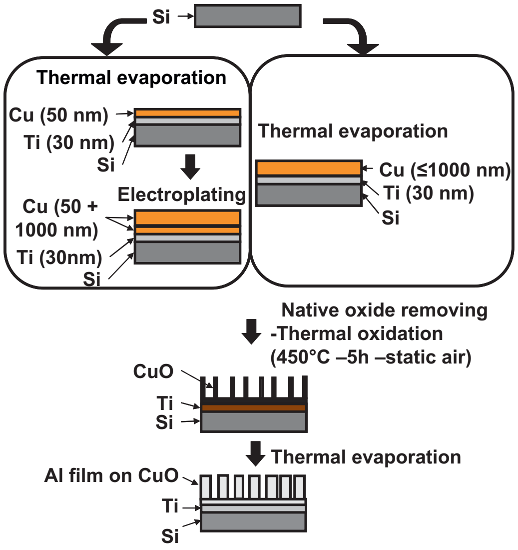

**Fig. 2.** Schematic view of the nanowired Al/CuO process.

For nanoenergetic application, it is important to have only CuO because Al/CuO exhibits the highest heat of reaction [6].

$$3CuO+2Al \rightarrow 3Cu+Al_2O_3,\ \Delta H = 21\,\mathrm{kJ/cm^3}\ \text{or}\ 4.1\,\mathrm{kJ/g} \tag{5}$$

$$3Cu_2O+2Al \rightarrow Al_2O_3+6Cu,\ \Delta H = 13\,\mathrm{kJ/cm^3}\ \text{or}\ 2.5\,\mathrm{kJ/g}$$

#### 2.1.3. *Al/CuO nanothermite finalization*

A 1 μm aluminum is thermally evaporated on and inside the CuO nanowires array obtained from the evaporated or electroplated Cu (see Fig. 2).

The Al/CuO samples preparation are illustrated in Fig. 2.

### 2.2. *Characterization*

The Al/CuO nanowires are observed using scanning electron microscopy (SEM); S-4800.

Oxide nanowires are also characterized by X-ray diffraction (XRD). Thermal analyses are performed by differential scanning calorimetry (DSC) and differential thermal analysis (DTA). For DSC measurements, each sample undergoes a temperature increase from 300 to 1000 K with a heating rate of 5 K/min under a nitrogen flow (99.999% purity). DTA measurements allow us to work on a widest temperature range (up to 1200 °C (1473K) with a speed of 5 °C/min under a 4.5 argon flow (99.995% purity)).

## 3. Results

### 3.1. *Copper oxide nature*

After copper oxidation, a large area of copper oxide nanowires is observed by SEM on the surface of the silicon wafer. The observed diameter of the nanowires is between 40 and 90 nm. The XRD pattern shows only CuO peaks (see Fig. 3).

After aluminum deposition, the nanowire diameters are in the range 150–250 nm. As shown in Fig. 4, the aluminum coats all the copper oxide nanowires surface and even penetrates between each nanowire. The specific Al growth on the nanowires could be observed in Fig. 4b.

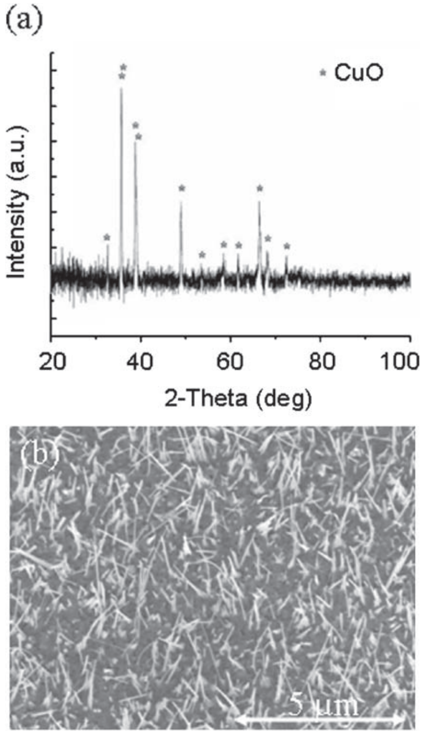

**Fig. 3.** (a) X-ray diffraction analysis of a CuO sample and (b) SEM image of CuO nanowires.

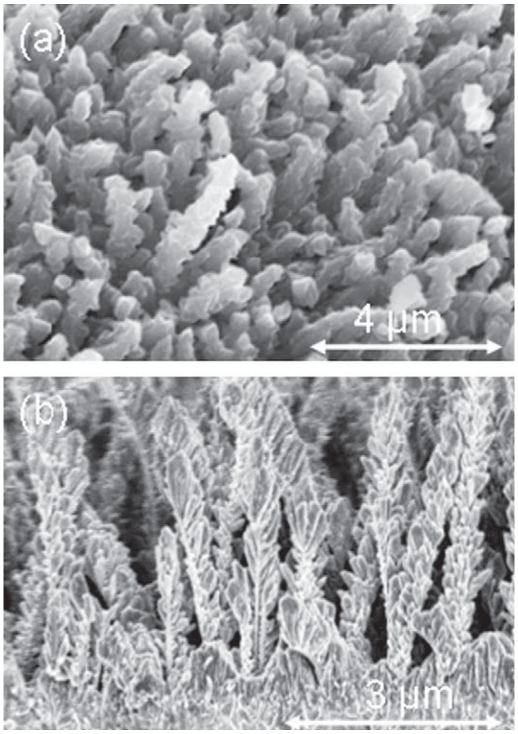

**Fig. 4.** SEM images of Al/CuO nanowires: (a) top view and (b) cut view.

### *3.2. Thermal evaporation vs. electroplating*

SEM observations and XRD analyses of CuO grown from 1 µm copper evaporated or 1 µm electroplated showed that (see Fig. 5):

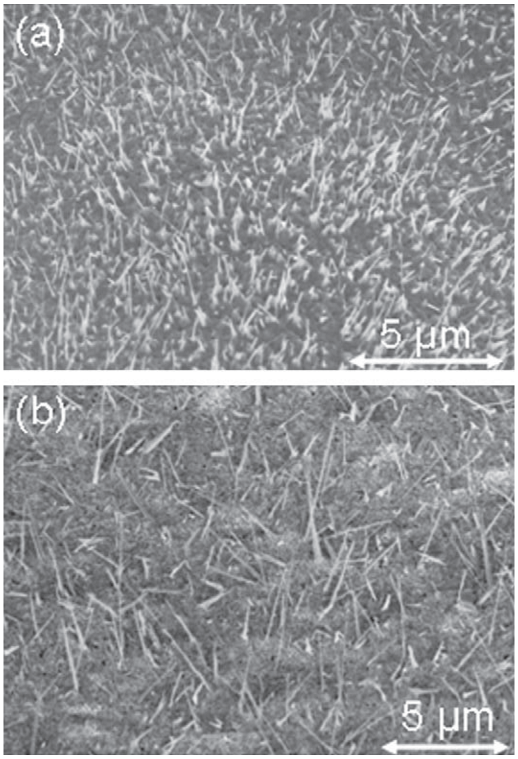

**Fig. 5.** SEM images of CuO nanowires: (a) from a 1-µm-thick thermal evaporated thin Cu film and (b) from a 1-µm-thick electroplated Cu thin film.

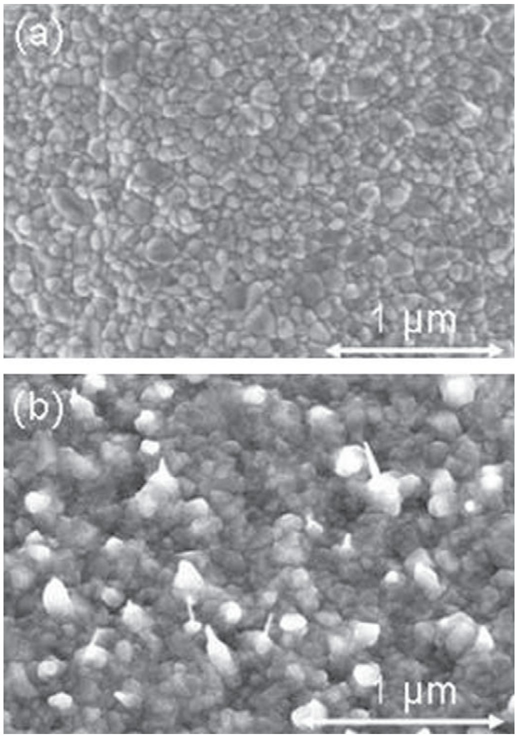

**Fig. 6.** SEM images of evaporated Cu film surface after thermal oxidation. Copper thickness is: (a) 50 nm and (b) 300 nm.

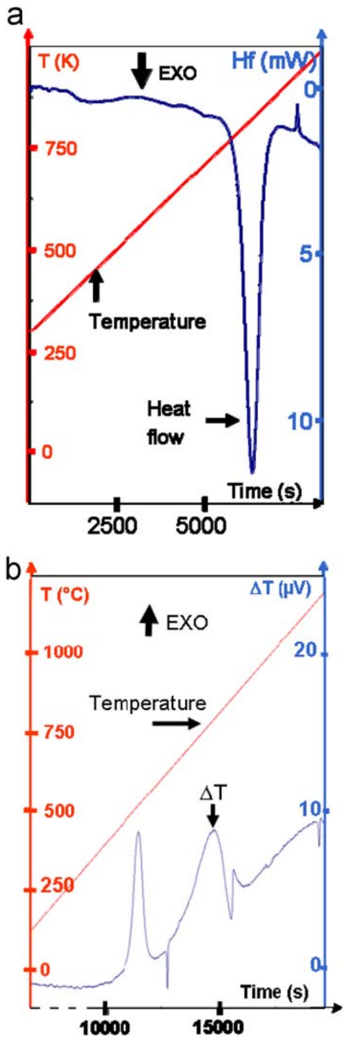

**Fig. 7.** Measurements of the heat of reaction in Al/CuO sample by: (a) DSC and (b) DTA.

1. The chemical composition between the two samples is the same with only CuO present.
2. Nanowires are present in both samples.

As a consequence, in order to have dense nanowires array with a less risk of impurity, it is preferable to start with a thermal evaporated copper thin film. But it is limited to copper thickness less than 1–2 µm.

### *3.3. Critical copper thickness*

We have also characterized the nanowires density for different thicknesses of evaporated oxidized Cu (50, 300 and 1000 nm) in order to determine the critical thickness to form CuO nanowires (see Fig. 6a).

In Fig. 6, it can be seen that the nanowires growth begins with a metal grain swelling (Fig. 6a), afterwards nanowires grow (Fig. 6b) with an inhomogeneous repartition on the sample surface. The critical copper thickness to get nanowires in our case is 300 nm.

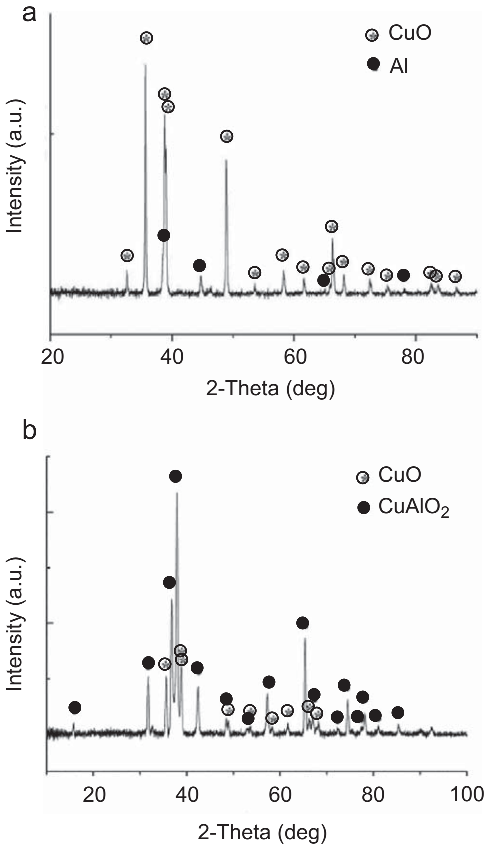

**Fig. 8.** XRD analyses: (a) after DSC measurement and (b) after DTA measurements.

### 3.4. Thermal decomposition

DSC and DTA results on CuO/Al samples (with 1 μm of electroplated Cu) are shown in Fig. 7a and b, respectively. An exothermic reaction occurs before the aluminum melting point (630 °C). This can be explained by the first solid Al–solid CuO reaction that occurs in the nanowires region and between Al/CuO interfaces. A second and more important exothermic reaction takes place around 667 °C, so after the melting point of aluminum. In that case, the aluminum should diffuse into the CuO thickness leading to a reaction in the volume.

The total heat of reaction is calculated to be 2.5 kJ/g or 10 kJ/cm$^3$, which is less than the theoretical one (3.9 kJ/g). This difference can be explained by the unoptimized stoichiometry of the reactants Al and CuO.

After the DSC analysis, XRD pattern indicates that the final products are Al and CuO (see Fig. 8a). This result could be interpreted by a none reaction of the thermite sample. But exothermic reaction has been observed and measured using the DSC method (see Fig. 7a). Therefore, we supposed that at 515 °C, which corresponds to a DSC maxima temperature is too low to permit a complete reaction in material bulk. At this temperature only interfaces reaction between Al and CuO may occur. In consequence, the products of the reaction are amorphous, or thickness is too low to be detected by the XRD method.

After DTA measurements, XRD analyses were realized and showed that the final products were CuO and CuAlO$_2$ (see Fig. 8b). In that case, the thermite has completely reacted but there are no copper and no Al$_2$O$_3$. The Cu formed by the Al/CuO reaction may have reacted with Al or Al$_2$O$_3$ to produce CuAlO$_2$ or may have formed CuO. Moreover, we should have excess of CuO in the Al/CuO stoichiometry.

## 4. Conclusion

Al/CuO nanowires were realised by thermal oxidation of copper thin film and the deposition of an aluminum thermal evaporated layer. The diameter of CuO nanowires is between 40 and 90 nm and the diameter of Al/CuO nanowires is between 250 and 350 nm. If the Cu layer thickness is less than 2 μm, thermal evaporation deposition method is preferable to get denser CuO nanowires. For thicknesses greater than 2 μm, electrodeposition is used and can also gives CuO nanowires. For Cu with thickness less than 300 nm, no nanowire has grown. Finally, DTA and DSC analyses estimated the heat of reaction to be 10 kJ/cm$^3$ and showed two distinct exothermic reactions: one at 515 °C and a second at 667 °C. The first exothermic peak corresponds Al/CuO reaction in the nanowires region, whereas the second exothermic peak (slower but more energetic) corresponds to the Al/CuO reaction in the bulk layer (underneath the nanowires).

This new nanosized energetic layer opens the door to many pyrotechnical applications such as micro-propulsion, pneumatic activation and pyrotechnic initiation [7–10].

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