Development of a nano-Al/CuO based energetic material on silicon substrate
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Nanenergetic materials (nEMs) have shown improved performances in terms of energy release, ignition, and mechanical properties compared to their bulk or microcounterparts. As a class of nEMs, nanothermite composites, also termed as metastable intermolecular composites (MICs), have been an extensive research subject. In MIC, oxidizer and fuel are mixed at nanoscale, thus leading to the enhanced reactivity caused by the reduced mass transport limitations between the reactants. Different approaches have been employed to synthesize MIC such as physical mixing of nanopowders of fuel and oxidizer, sol-gel, aerogel, atomic layer deposition, deposition of multilayer foils of oxidizer and fuel, integration of porous silicon with oxidizers, embedding $\text{Fe}_2\text{O}_3$ nanowires inside an Al film, and employment of molecular self-assembly.

In this study, Al/CuO based MICs are realized by integrating nano-Al with CuO nanowires grown from Cu thin film deposited onto silicon substrate. The fabricated MICs are characterized by scanning electron microscopy (SEM), high resolution transmission electron microscopy, x-ray diffraction, differential thermal analysis, and differential scanning calorimetry. © 2007 American Institute of Physics.

FIG. 1. 30° tilted view SEM images of the annealed Cu film before Al deposition and CuO nanowires grow from the Cu film after annealing. Figure 1(b) is a SEM image of the nanowires after Al deposition. Nano-Al is uniformly integrated around the CuO nanowires, thus enhancing the interfacial contact and the reactivity. The average diameter of the nanowires is about 40–80 nm. After Al deposition, the average diameter becomes around 150–250 nm. Figures 2(a) and 2(b) are cross-section view SEM images of the CuO nanowires before and after Al deposition. Al is both integrated with the CuO nanowires to form a core-shell nanostructure and also deposited onto the film under the nanowires to form a layered structure. The compositions of the MIC are identified by XRD, as shown in Fig. 3. Al, CuO, and $\text{Cu}_2\text{O}$ diffraction lines can be seen from the XRD pattern. When Cu film is annealed in static air, Cu is first converted into $\text{Cu}_2\text{O}$. Then, CuO is formed slowly through a second step oxidation of $\text{Cu}_2\text{O}$. The inset picture in Fig. 3 is a HRTEM image of an individual nanowire. Each side of the nanowire is a single crystal with a distinct fringe space pattern. The interplanar spacing for one side is 2.46 Å and 1.99 Å for the other side; these inter-

![FIG. 1. 30° tilted view SEM images of the annealed Cu film (a) before Al deposition and (b) after Al deposition.](image-url)
planar spacings are similar to those for \( \{111\} \) and \( \{11\} \) planes in monoclinic CuO. There are no peaks for Al\(_2\)O\(_3\) and Cu, indicating that no significant reaction between Al and CuO/Cu\(_2\)O occurs during the Al deposition due to the high vacuum level and low substrate temperature.

The exothermic reaction of the MIC is characterized with DTA, as shown in Fig. 4. There are two major exotherms. The first exotherm is observed with an onset temperature of about 500 °C, which means that the nanocomposite seems to react prior to the melting of Al. This suggests that the first exotherm is caused by the thermite reaction between the CuO nanowires and nano-Al. The second exotherm is found with an onset temperature of around 720 °C. After melting, the remaining Al reacts with the Cu\(_2\)O (and also perhaps some CuO) film under the CuO nanowires.

To quantitatively determine the heat of reaction, the MICs are characterized with DSC, as shown in Fig. 5. The first exothermic peak with an onset temperature of about 500 °C, which corresponds to the first peak in DTA curve in Fig. 4, is caused by the reaction between the CuO nanowires and nano-Al. The second endothermic peak (660 °C) is caused by the melting of the remaining Al. Integration of the first exothermic peak in DSC gives a heat of reaction equal to 1085±160 J/g. Assuming that the DTA signal is proportional to the heat of reactions, we use the area of the first peak, calculated from DSC analysis, to scale the DTA curve. Though it is not accurate because the relationship between temperature and heat is not exactly linear, it allows us to roughly estimate the total heat of reaction of the MIC to be about 2950 J/g. This value is between the theoretical heat of reaction of CuO with Al (4067 J/g) and Cu\(_2\)O with Al (2434 J/g). The performance of the MIC can be improved by adjusting the dimensions of the CuO nanowires and by tuning the Al deposition to reach a stoichiometric reaction.

Figure 6 shows the XRD pattern of the MIC after DTA testing. The final reaction products are identified to be Al\(_2\)O\(_3\), CuAlO\(_2\), and CuO. The Al peaks seen in Fig. 3 before reaction is no longer present. CuAlO\(_2\) is formed from the reactions of Al\(_2\)O\(_3\) with CuO/Cu\(_2\)O. However, XRD pattern does not show the Cu lines that should be there after CuO/Cu\(_2\)O reduction by Al. The Cu produced from Al/CuO/Cu\(_2\)O thermite reactions is most likely oxidized by O\(_2\) contained in Ar flow and/or generated from the reaction of Al\(_2\)O\(_3\) with CuO.

This approach has some advantages compared to previous investigations. First, the MICs are realized by integrating nano-Al with CuO nanowires, thus enhancing the interfacial contact and reactivity. Second, the presence of impurities and Al oxidation is smaller because the MICs are fabricated in a
high vacuum and with a low substrate temperature. Third, since the dimensions of CuO nanowires can be tailored, the oxidizer/fuel dimensions can be controlled at the nanoscale. Fourth, the process uses standard microfabrication technologies and therefore it is suitable for mass production. The MICs are deposited onto silicon, a basic material for microelectronics and microsystem. Consequently, it is straightforward to integrate the MIC into microsystem to result in nanostructures, for example, high performance nanoigniters.

In conclusion, nano-Al/CuO based MICs have been realized by integrating nano-Al with CuO nanowires grown from Cu film deposited onto silicon. The Cu film is converted into bicrystal CuO nanowires and Cu2O and also perhaps some CuO film after annealing. After Al deposition, nano-Al is integrated with CuO nanowires to form a core-shell nanostructure and also deposited onto the film under the nanowires to form a layered structure. DTA and DSC results suggest that nano-Al reacts with CuO nanowires with an onset temperature of about 500 °C prior to the melting of Al. After melting, the remaining Al reacts with the Cu2O (and also perhaps some CuO) film beneath the CuO nanowires. The total heat of reaction is estimated to be about 2950 J/g. The MICs are realized onto silicon. Therefore, this will probably open the door to the integration of the material into silicon based microsystem, thus leading to functional nanodevices.

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