Al-CuO$_x$ multilayer nanostructures: formation features and thermal properties of new type of local heat source

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Abstract. In this work, multilayer nanostructured thermite materials are considered - a new type of local heat sources. Aluminium and copper oxide were chosen as components of the thermite mixture. The formation of multilayer structures was carried out on the surface of the substrate by the method of magnetron sputtering. The features of the deposition process as well as the energy properties of the formed materials have been investigated. The results obtained confirm the prospects of using this class of materials as local heat sources.

1. Introduction

Technological progress in micro- and nanoelectronics requires the solution of new problems associated with the technology of surface joining. Reaction bonding or soldering using thin layers of energetic materials, acting as local heat sources, already now make it possible to effectively solve a number of technological problems. Energy materials manufactured in the form of multilayer structures consist of two or more components and are able to maintain in their volume a self-propagating exothermic reaction in the wave combustion mode after initial initiation. The reaction front temperature can significantly exceed 1000 °C and reaches this value in milliseconds. For soldering, a layer of energetic material is placed between the solder layers, and initiation occurs with an electric spark or low-power laser. The heat released during the reaction melts the solder, which wets the surfaces to be joined and, after solidification, forms a reliable joint. Depending on the physical state of the surfaces to be joined, all joining processes can be divided into three groups - solid bonding [1], solder bonding [2] and fusion bonding [3]. In the latter case, melting of the surfaces to be joined is necessary, which, as a rule, is associated with significant heating of the object, which can lead to the loss of its unique properties. And this is precisely the main problem of micro- and nano-assemblies - how to limit and accurately dose the heating, and how to limit the heated volume or how to localize it? Energetic nanoscale multilayer foils for bonding surfaces have been developed and partially commercialized in the last decade. Due to their high reactivity and intense heat release, these functional foils can act as heat sources for joining thermosensitive materials and micro- and nano-sized components [4].
2. Experimental details
Multilayer structures with different thicknesses of individual layers were formed by alternate sputtering of Al and CuO targets by magnetron sputtering. Studies of the formed materials using energy-dispersive X-ray spectroscopy and stylus profilometry made it possible to reveal the dependences of the deposition rate and composition of copper oxide layers on the partial pressure of oxygen in the process of target sputtering. Thermal effects were measured by differential scanning calorimetry, and the propagation velocity of the wave combustion front was carried out using high-speed video camera.

3. Results
Multilayer Al-CuO structures were formed by magnetron sputtering. The rates of deposition of aluminum and copper oxide were preliminarily determined. The sputtering rate of aluminum was 0.125 nm / s at a sputtering power of 500 W. The copper oxide target was sputtered in a mixture of argon and oxygen at a power of 350 W. Deposition rate of copper oxide as well as the ratio of copper to oxygen in the formed layer varied depending on the partial pressure of oxygen during the sputtering process. The obtained experimental dependences are shown in Figure 1. The decrease in velocity is associated with a decrease in the sputtering efficiency due to the lower mass of oxygen ions in comparison with argon.

![Dependences of the copper oxide deposition rate and the composition of the formed layers on the partial pressure of oxygen during sputtering.](image)

Figure 1. Dependences of the copper oxide deposition rate and the composition of the formed layers on the partial pressure of oxygen during sputtering.

The presence of a minimum for a pressure of 1 mTorr was also revealed on the dependence of the atomic ratio of copper to oxygen. On the one hand, the increased oxygen content in the copper oxide layers will increase the energy properties of the multilayer structure, and on the other hand, additional technological difficulties appear - the deposition rate decreases and it becomes necessary to change the composition of the atmosphere, which in combination significantly increases the total duration of the process. Therefore, for further studies, the copper oxide target was sputtered in an argon atmosphere.

In this work, 3 multilayer structures with different bilayer thicknesses (the total thickness of one aluminum layer and one copper oxide layer) - 75, 150, and 300 nm were formed. The total thickness of the structure was the same in all cases and was equal to 3 μm. The deposition was carried out on various substrates - sitall and Kapton tape. The control of the geometric characteristics of the formed structures was carried out using an SEM and the resulting images are shown in Figure 2. The ratio of the thicknesses of the components was determined based on the chemical reaction $2\text{Al} + 3\text{CuO} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Cu} + \text{Q}$.

The obtained SEM images indicate the presence of a clear periodic structure with the required thicknesses of individual layers and the total thickness of the structure.
At the next stage of the study the wave combustion process for Al-CuO$_x$ structures deposited on sital wafers with different bilayer thickness was investigated using high-speed video at a speed of 15000 fps. The combustion rate of samples with a bilayer thickness of 75, 150, and 300 nm was 6.3, 4.0, and 1.9 m/s, respectively, which is close to a linear dependence.

![Figure 2](image2.png)

**Figure 2.** SEM images of cross-sections of Al-CuO$_x$ multilayer structures with different bilayer thicknesses - 75, 150, and 300 nm.

Combustion storyboards are shown in Figure 3. A decrease in the front velocity with an increase in the bilayer thickness is associated with an increase in diffusion lengths in the volume of the multilayer structure and a decrease in the contact area of the reagent layers. Combustion was initiated in all cases using an electric spark from a piezoelectric generator. Combustion took place in a wave mode.

![Figure 3](image3.png)

**Figure 3.** Storyboard of the combustion process of Al-CuO$_x$.

The combustion products of multilayer Al-CuO$_x$ structures were studied using scanning electron microscopy and elemental analysis. Despite active gas evolution during combustion, most of the reaction products remain on the substrate surface in the form of solidified melt droplets (see Figure 4).
Elemental analysis made it possible to determine the composition of the combustion products (see Figure 5) - these are solidified copper drops, the surface of which is partially covered with aluminum oxide. In addition, nanoscale fibers were found on the particle surface at higher magnification, the nature and properties of which will be studied in further studies.

The energy properties of multilayer materials were studied using DSC and TGA (obtained results presented at Figure 6). For these purposes, multilayer structures, formed on the surface of the Kapton tape, were separated from it with a scraper. The measurements were carried out on a TA Instruments SDT Q600 series instrument in air and in an argon atmosphere in ceramic crucibles with a heating rate of 10 degrees per minute in the range from 150 to 750 °C. Some general patterns were found - the change in the weight of the samples when measured in an argon atmosphere was less than 1%, which indicates the absence of the influence of the atmosphere. When measured in a stream of air, the weight gain in all cases was within 9%. One main exothermic effect was observed on the DSC curves in the temperature range from 475 to 625 °C.

Figure 5. Results of elemental analysis of combustion products of Al-CuOx multilayer thermite materials.

Figure 6. DSC and TGA curves obtained for multilayer Al-CuOx structures with different values of the bilayer thickness.
The position of the maximum of the peak in measurements in argon was found in the region of lower temperatures. However, a change in the value of the overall thermal effect was observed, which amounted to 730, 1050, and 550 J/g for the bilayer 75, 150, and 300 nm, respectively, for measurements in argon and 1120, 1690, and 870 J/g in argon. The variation in the value with a change in the bilayer thickness can be associated with both the completeness of the reaction in the multilayer material and the contribution of the mixed layer that forms at the interface between aluminum and copper oxide during magnetron sputtering. An increase in the general thermal effect in air indicates the occurrence of the oxidation reaction of aluminum with oxygen from the atmosphere, which is also evidenced by the weight gain.

4. Conclusion
In this work, we investigated the features of the process of the formation of multilayer structures by the method of magnetron sputtering. The effect of oxygen in the process of sputtering a copper oxide target on the deposition rate of layers and their composition has been studied. An experimental study of the size effect on the process of wave combustion of multilayer structures with different bilayer thicknesses has been carried out. A significant increase in the combustion front velocity from 1.9 to 6.3 m/s with a decrease in the bilayer thickness from 300 to 75 nm was found. The results of DSC and TGA measurements of samples of multilayer structures made it possible to evaluate the energy characteristics of the formed materials when they are heated in air and in argon atmosphere. The overall thermal effect during slow heating is influenced not only by the fraction of the material reacted during the deposition process at the boundary of the layers, but also, to a greater extent, by the completeness of the reaction. The contribution of the reaction of aluminum with oxygen from the atmosphere in all cases was approximately the same.

The studies carried out have confirmed the high potential of using Al-CuOₓ multilayer thermite materials in various fields as local heat sources.

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