

Silver Dendrite-based Nanocomposites for Current Cutting-off Fuse

Rui Yang, Cheng Yang*, Xiaoya Cui, Zhexu Zhang

Division of Energy and Environment, Graduate School at Shenzhen, Tsinghua University,
Xili University Town, Shenzhen, China, 518055
yang.cheng@sz.tsinghua.edu.cn

Abstract—Microelectronics and micromechanical systems (MEMS) are gaining popularity by virtue of small size, high integration, diverse functionalities, mass production and low cost. However, the existing current cutting-off fuse components can hardly be used in a microelectronics or micromechanical system to realize circuit protection due to their large size and high fusing current. Herein we report a novel current cutting-off fuse component based on printed electrically conductive nanocomposites (ECCs), which are composed of silver micro-dendrites with fractal morphology as the fusible conductive fillers and the thermosetting resin matrix. The silver paste was pasted between two copper electrodes with controlled space. The current cutting-off performance of the fuses was investigated within different silver fillers, various paste sizes, and diverse electrode spaces. The results show that, the silver dendrite-based paste can be fused at a relative low current due to its abundant nano-sized rims at the edge of the dendrite branches. Furthermore, the minimum fusing current (530 mA) was achieved when the silver flake-based paste was dispensed between two electrodes with distance of 100 μm and width of 30 μm . It is obvious that the fusing current attenuates gradually with the increase of space between two copper electrodes, and the silver paste in large spot size possesses higher fusing current than in small one. The scanning electron microscopy (SEM) analyses suggest that the silver fillers go through the melting and shrinking stages during the fusing process, thus the adjacent silver fillers separate to break the circuit. Considering the low material cost and negligible environmental risk, this novel current cutting-off fuse can provide cost-effective and environmental-friendly protection for MEMS devices.

Keywords—current cutting-off fuse; silver dendrite; low fusing current; MEMS devices

I. INTRODUCTION

Current cutting-off fuse is a protective device widely used in electrical and electronic devices, such as program control exchanges, power rectifier, micromotor and integrated circuits, on account of its reliability, simplicity and low cost. When a given current exceeds the rated value, the fuse element melts and thus breaks the circuit effectively to prevent circuits from overheating or becoming overloaded [1-2]. Conventional current cutting-off fuse consists of a piece of metal wire connected between two terminals on a suitable support [3]. They are featured with high fusing current, and take up a large space. As the integration level of microelectronics and micromechanical systems (MEMS) gets higher, traditional

current cutting-off fuse components cannot meet the increasing needs. In recent years, a vast variety of novel current cutting-off fuses are expected to be utilized at wafer or package level, such as polycrystalline silicon fuses [4-5], silver nanobeam fuses [6], and carbon-based fuses [7-8]. However, on way or another, there are still some limitations in practical application.

Our previous research [9] showed that the micro-/nano-silver dendrite can be easily sintered at a relative low temperature due to its abundant nano-sized rims at the very outmost structure. It may become a promising alternative in achieving low-current fusing ability when being used as the fuse element in current cutting-off fuse. Here we demonstrate such possibility. The electrically conductive nanocomposites (ECCs), which consist of silver fillers and resin matrix, were pasted between two copper electrodes on FR-4 epoxy/glass circuit board with controlled space. Through controlling the experimental parameters, including silver fillers, paste sizes and electrode spaces, a variety of current cutting-off fuse samples are obtained and the fusing current is investigated by increasing the output current at a constant speed. Compared to the commercial silver flake-based paste, silver dendrite-based paste can be fused at lower current, especially when the distance between copper electrodes is less than 50 μm . Whereas the morphology of the silver fillers, the fusing current attenuated gradually with the increase of the space between each electrode, and the silver paste in large spot size possesses higher fusing current than in small one. The scanning electron microscopy (SEM) analyses suggest that the reliability of the silver dendrite-based paste is higher than the silver flake-based paste, when serves as current cutting-off fuse.

II. EXPERIMENTAL

A. Materials

Hydroxyl amine (NH_2OH) solutions (50% aq.) and Silver nitrate (AgNO_3) powder (99%) were purchased from Alfa Aesar and Sinopharm Chemical Reagent Co., Ltd., respectively. The Bisphenol-A type epoxy (Epon 828) and methyltetrahydrophthalic anhydride (MTHPA) were provided by Shell and Lindau Chemicals, and hexamethylenetetramine (99%) was obtained from Guangzhou Chemical Reagent Factory, China. The silver paste BY-2000C, which serves as the control sample, was supplied by Shanghai BaoYin Electronic Materials Ltd.

B. Preparation and iodination of Ag dendrites

Equal volumes of silver nitrate aqueous solution (0.06 M) and hydroxyl amine solution (0.24 M) were simultaneously pumped into an erlenmeyer flask at a velocity of 15rpm by multichannel peristaltic pump at room temperature. The droplets are mixed homogeneously by shaking the erlenmeyer flask vigorously during the reaction [9]. The precipitate was washed by DI water for three times, and then dispersed in ethanol (99%, Sinopharm Chemical Reagent Co., Ltd.) with a magnetic stirrer. Simultaneously a small amount of iodine was dissolved in ethanol. After turning clear, the solution was added drop-wise to the stirring silver-ethanol solution to modify the surface of the silver dendrites [10-11]. And then the surface modified dendrites were collected using a simple filtration method and dried in a fume hood. All these processes were operated at ambient temperature.

C. Preparation of ECCs

The epoxy binder was obtained by mixing the Epon 828 epoxy and MTHPA according to the mole ratio of 1:1 based on the epoxide equivalent weight (EEW) of the epoxy resin and the hydroxyl equivalent weight (HEW) of the hardener. A small amount of hexamethylenetetramine, which acts as catalyst, was added to the resin dispersant to accelerate cross-linking. Subsequently, the treated silver dendrites were dispersed in the epoxy binder and they were mixed in a planetary rotary mixer (Hasai Co., Shenzhen, China) at 1000 rpm for 10 min. The silver contents of the ECCs was 25 wt%.

D. Fabrication and testing of current cutting-off fuse

FR-4 epoxy/glass circuit board, which possesses excellent flame-retardant properties, is one of the most widely used dielectric substrates in the fabrication of printed circuits board. The copper electrodes with different distances and the same width of 30 μm were prepared using the lithography process on the FR-4 epoxy resin glass fiber board. The distances between two electrodes were 30 μm , 50 μm , 80 μm and 100 μm , respectively. The prepared ECCs samples and commercial silver paste, which serve as current cutting-off fuse, were pasted between two copper electrodes using a signature pen. Hence, silver paste with different distances and same width could be obtained. By altering the silver paste volumes, different sizes of silver paste could be accessed when the electrode spaces are equal. All the samples were cured at 150 $^{\circ}\text{C}$ for 30 min. After thermal curing, copper electrodes at both ends of the silver paste were connected to the current output and the grounding end of the electrodeposition equipment, respectively. And then, the output current was increased at a constant speed (such as 10 mA/s) until the silver paste fused, which was considered as the fusing current.

E. Characterizations

The morphology of the silver dendrites and silver paste was investigated by the field emission scanning electron microscope (HITACH S4800, Japan). The crystal property of silver dendrites was recorded by powder X-ray diffraction using a Rigaku diffractometer (D/MAX-2500, Japan), which was equipped with Cu-K α radiation. The light absorption property of silver dendrites before and after iodine treatment

was characterized by UV-Vis spectroscopy (SCINCO, S-4100, Korea) with the wavelength from 190 nm to 1100 nm. The resistance of silver paste before and after fused was measured using a Victor 9801A+ multimeter. The fusing current was directly recorded according to the values on the electrodeposition equipment when the silver paste fused.

III. RESULTS AND DISCUSSIONS

A. Characterization of silver dendrites

The morphology of the silver dendrites is shown in Fig. 1. As shown in Fig. 1a and b, it is obvious that the silver dendrites are composed of trunk, branch and leave, containing huge amounts of dendrite-like fractal structures on the micron and nanometer scale. The size distribution of the silver dendrites is 3-5 μm . With the purpose of obtaining lower fusing current, the silver dendrites were treated by iodine to further increase the nanostructures on the surface according to procedures as we reported previously [10]. As demonstrated in Fig. 1c and d, many islands with the size measured in dozens of nanometers present on the surface of silver dendrites after the iodine modification, which were considered to contribute to lower fusing current.

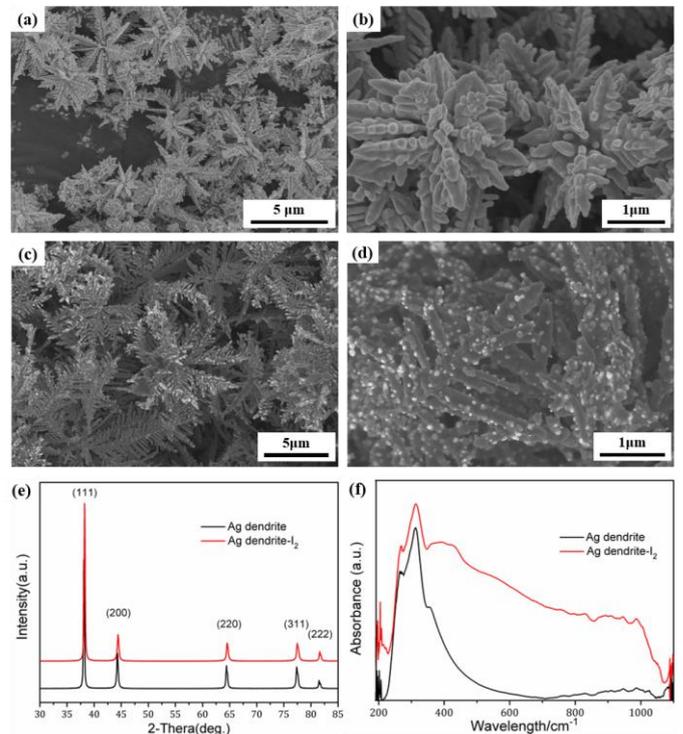


Fig. 1. (a) SEM image of silver dendrites. (b) A zoom-in area in (a) which shows the dendritic structures of silver dendrites. (c) SEM image of surface-modified silver dendrites. (d) A zoom-in area in (c) which shows the small islands on the silver dendrites. (e) XRD patterns of the as-prepared and surface-modified silver dendrites. (f) UV-Vis absorption spectra of the as-prepared and surface-modified silver dendrites.

The dendritic structure was further studied by the powder XRD analysis and UV-Vis spectroscopy. Fig. 1e shows the XRD patterns of the silver dendrites before and after surface modification, which indicates that the crystallographic structure of the silver dendrites is face centered cubic. The intensity ratio

of the (111) peak to (200) peak is 3.62, while the standard silver powder pattern is 2.1 (JCPDS). After surface modification, the value reaches 5.95, higher than before. It can be deduced that the silver dendrites are prone to orientate along the (111) lattice plane, and the small islands make the tendency more significant. As displayed in Fig. 1f, the evolution of the optical absorption characteristic is observed, which is related to the surface plasmon resonance property and can be analyzed by UV-Vis spectroscopy. It is found that silver dendrites exhibit three absorption bands located at 265 nm, 310 nm and 360 nm, corresponding to the surface plasmon resonance of the dendritic branches of different sizes. After iodine treatment, a wide absorption bands in the range of 350-460 nm occurs. This is due to the islands on the surface of silver dendrites after the iodine modification, with the size of several dozens of nanometers.

B. Properties of current cutting-off fuse

In this study, different kinds of silver pastes serve as current cutting-off fuse, which are composed of silver fillers and the thermosetting resin matrix. As depicted in Fig. 2, silver fillers both in commercial silver paste and silver dendrite-based ECCs are uniformly distributed in the matrix resin. Nevertheless, the morphology of the silver fillers in commercial silver paste has significant difference compared with the silver dendrite-based ECCs. As shown in these SEM images, silver flakes are the main fillers in commercial silver paste, with sizes ranging from 1 μm to 5 μm . It is clear that there are more micro-/nano- structures in silver dendrites compared to silver flakes, which make it possible to be fused rapidly at a relative low current density.

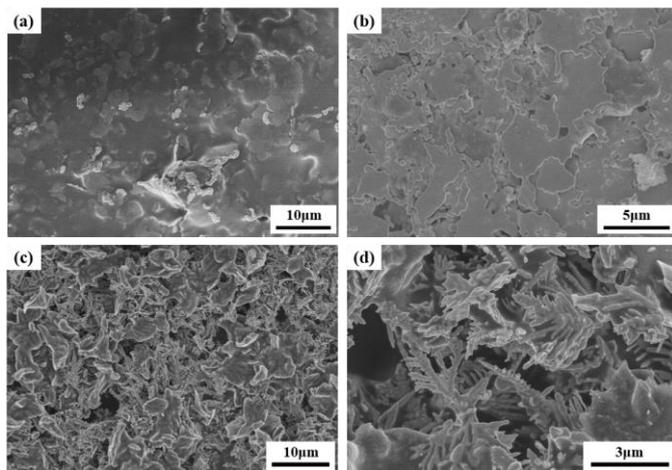


Fig. 2. (a) SEM image of commercial silver paste. (b) A zoom-in area in (a) which shows the structures of silver fillers. (c) SEM image of silver dendrite-based ECCs. (d) A zoom-in area in (c).

In the experiment, silver dendrite-based paste and silver flake-based commercial paste were pasted between two copper electrodes, thus the current cutting-off fuses were obtained. Before curing, the resistances between two copper electrodes were infinite, indicating failure in forming conductive network. After curing at 150 $^{\circ}\text{C}$ for 30 min, all the samples resistances range from 0.1 Ω to 0.3 Ω , which depends on the volume of the silver paste and the morphology of the silver fillers. The reduction of the resistances is due principally to the shrinkage

of resin matrix, which can promote the contact among silver fillers to form conductive network. On the other hand, there is no doubt that the sintering of the contact areas among the adjacent silver fillers contributes to the reduction of the contact resistance.

The current cutting-off performance of the silver paste fuses with dendrite-like silver and flaky-like silver fillers is presented in Fig. 3. As demonstrated in Fig. 3a, no matter what the morphology of the silver fillers is, the fusing current decreases with the increase of distance between two copper electrodes. The tendency is the most obvious when the fuses are composed of silver flake-based paste in small size. When the distances between copper electrodes are controlled to be 30 μm , 50 μm , 80 μm and 100 μm , the fusing currents are 2.86 A, 2.54 A, 1.29 A and 660 mA, respectively. As compared, the tendency was not significant when the silver paste increases by volume. The fusing current keeps stable when the distance between the two copper electrodes is less than 80 μm . They are 2.94 A, 2.93 A and 2.92 A, corresponding to the distances of 30 μm , 50 μm and 80 μm . When the distance increases to 100 μm , the fusing current begins to decrease slightly, with the value of 2.82 A. The fusing current of silver paste in large size is higher than in small size at each electrode distance. This phenomenon might be related to the fact that redundant silver paste is conducive to the buildup of parallel circuits. When redundant silver paste was pasted between two copper electrodes with confined space, it can spread in larger area on account of the low viscosity of the silver paste, which enables the formation of better conductive network. During this experiment, the silver fillers in the controlled space may fuse first. However, the redundant silver paste outside the controlled space can still connect to the adjacent copper electrodes, which needs higher current to fuse. When the silver paste outside the confined space is far more than that within the confined space, increasing the confined space does little to help reducing the fusing current. As a consequence, both increasing the distance between copper electrodes and decreasing the silver paste size are beneficial to obtain lower fusing current.

Compared to the control commercial silver flake-based paste (BY-2000C), silver dendrite-based paste can be fused at lower current, especially when the distance between copper electrodes is less than 50 μm . As demonstrated in Fig. 3a, the fusing currents of silver flake-based fuses in large and small sizes are 2.94 A and 2.86 A, when the distance is 30 μm . While it is only 1.59 A in silver dendrite-based fuses. Likewise, the fusing currents are 2.93 A, 2.54 A and 1.17 A, corresponding respectively to large silver flake-based fuses, small silver flake-based fuses and silver dendrite-based fuses when the distance is 50 μm . In our experiment, the minimum fusing current (530 mA) was achieved, when the silver flake-based paste was dispensed between two electrodes with electrode distance of 100 μm and width of 30 μm . The possible explanation can be as follows: when an electric current flows through the silver paste fuses, a lot of Joule heat was generated because of internal resistance. Consequently, the surface structures of silver dendrites or silver flakes melt and shrink, until the silver fillers separate among the adjacent dendrites or flakes. Since the higher surface energy of silver dendrites in comparison to silver flakes due to abundant micro-/nano- sized structures on

the surface, dendrites separated in the case of lower heat, which means lower fusing current.

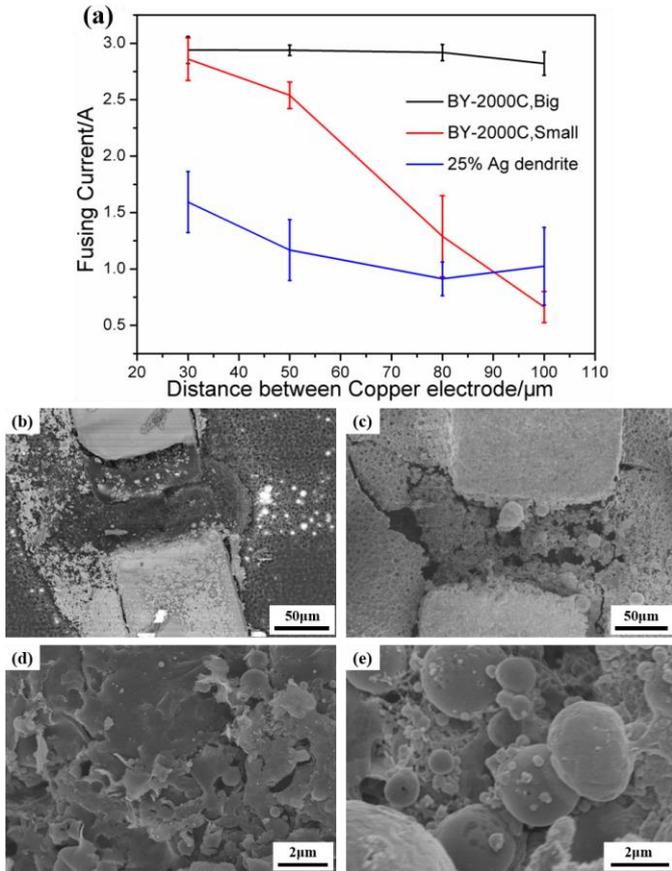


Fig. 3. (a) Fusing current of the silver dendrite-based paste and silver flake-based commercial paste (BY-2000C) with different electrode distances and sizes of silver paste. (b) and (d) SEM images of fused silver flake-based commercial paste at different magnifications. (c) and (e) SEM images of fused silver dendrite-based paste at different magnifications.

The SEM images of fused silver flake-based paste and silver dendrite-based paste are shown in Fig. 3. As indicated in Fig. 3b and c, it can be seen that much of silver flakes remains on the FR-4 epoxy/glass circuit board, but scarcely any of silver dendrites. The details can be seen at higher magnifications. As shown in Fig. 3d and e, there still are massive silver flakes contacting after fused. Contrarily, little fused silver dendrites remains on the spherical glass, which results from the melting of glass fiber in the FR-4 due to superabundant heat. From the SEM images, it can be deduced that the insulation resistance is higher in the fused silver dendrite-based paste than in the fused silver flake-based paste, which is consistent with the measured value. That is to say, the reliability of silver dendrite-based paste is higher compared with silver flake-based paste, when serve as current cutting-off fuses.

IV. CONCLUSIONS

We have demonstrated a novel current cutting-off fuse component based on electrically conductive micro-/nanocomposites (ECCs) and expatiated the principle of its fusing. The current cutting-off performance of the fuses was

investigated within different silver fillers, various paste sizes, and diverse electrode spaces. The results show that the fusing current attenuates gradually with the increase of space between two copper electrodes, and the silver paste in large spot size possesses higher fusing current than in small one. While, the variation tendency is not significant when the fuses are in large size. Compared to silver flake-based fuses, silver dendrite-based paste can be fused at lower current due to its abundant nano-sized rims at the very outmost structure, especially when the distance between copper electrodes is less than 50 μm. In the experiment, the minimum fusing current (530 mA) was achieved, when the silver flake-based paste was dispensed between two electrodes with distance of 100 μm and width of 30 μm. SEM analysis suggests that the silver fillers go through the melting and shrinking stages during the fusing process, thus the adjacent silver fillers separate to break the circuit. From the SEM images and insulation resistance of fused silver paste, it can be deduced that the reliability of the silver dendrite-based paste is higher than the silver flake-based paste, when serves as current cutting-off fuse. Considering the low material cost and negligible environment risk, this novel current cutting-off fuse can provide cost-effective and environmental-friendly protection for MEMS devices.

ACKNOWLEDGMENT

The authors thank National Nature Science Foundation of China Project No. 51202120, Shenzhen Government Technical Project No. JCYJ20130402145002411, Shenzhen Peacock Plan Project No. QQCX20120814155245647, and Nanshan District "Rising Stars" Project No. KC2014JSQN0010A for financial supports.

REFERENCES

- [1] A. Pleșca, "Numerical Thermal Analysis of Fuses for Power Semiconductors," *Electr. Pow. Syst. Res.*, vol. 83, pp. 144-150, 2012.
- [2] E. Torres, A.J. Mazón, E. Fernández, I. Zamora, and J.C. Pérez, "Thermal Performance of Back-up Current-Limiting Fuses," *Electr. Pow. Syst. Res.*, vol. 80, pp. 1469-1476, 2010.
- [3] A. Pleșca, "High Breaking Capacity Fuses with Improved Cooling," *Int. J. Therm. Sci.*, vol. 70, pp. 144-153, 2013.
- [4] T. S. Doorn, "A Detailed Qualitative Model for the Programming Physics of Silicided Polysilicon Fuses," *12th IEEE Trans. Electron Devices*, vol. 54, pp. 3285-3291, 2007.
- [5] W. T. Lee, A. C. Fowler, O. Power, S. Healy, and J. Browne, "Blowing of Polycrystalline Silicon Fuses," *Appl. Phys. Lett.*, vol. 97, pp. 0203502-3, 2010.
- [6] B. J. Wiley, Z. H. Wang, J. Wei, Y. D. Yin, D. H. Cobden, and Y. N. Xia, "Synthesis and Electrical Characterization of Silver Nanobeams," *Nano Lett.*, vol. 6, pp. 2273-2278, 2006.
- [7] B. Ren, L. Wang, L. J. Wang, J. Huang, K. Tang, Y. Y. Lou, D. C. Yuan, Z. M. Pan, and Yiben Xia, "Investigation of Resistive Switching in Graphite-like Carbon Thin Film for Non-volatile Memory Applications," *Vacuum*, vol. 107, pp. 1-5, 2014.
- [8] J. L. Xu, D. Xie, T. T. Feng, C. H. Zhang, X. W. Zhang, P. G. Peng, D. Fu, H. Qian, T. Ren, and Litian Liu, "Scaling-down Characteristics of Nanoscale Diamond-like Carbon Based Resistive Switching Memories," *Carbon*, vol. 75, pp. 255-261, 2014.
- [9] X. Y. Cui, C. Yang, Z. X. Zhang, H. Y. Wu, S. W. Chiang, Z. J. Su, J. P. Liu, and F. Y. Kang, "Scalable Synthesis of the Mono-dispersed Silver Micro-dendrites and Their Applications in the Ultralow Cost Printed Electrically Conductive Adhesives," *IEEE-ICEPT, Dalian*, pp. 273-279, 2013.

- [10] C. Yang, Y. T. Xie, M.M.F. Yuen, B. Xu, B. Gao, X. M. Xiong, and C. P. Wong, "Silver Surface Iodination for Enhancing the Conductivity of Conductive Composites," *Adv. Func. Mater.*, vol. 20, pp. 2580–2587, 2010.
- [11] C. Yang, C. P. Wong, and M.M.F. Yuen, "Printed Electrically Conductive Composites: Conductive Filler Designs and Surface Engineering," *J. Mater. Chem. C*, vol. 1, pp. 4052–4069, 2013.