One-Step Fabrication of Copper Nanopillar Array-Filled AAO Films by Pulse Electrodeposition for Anisotropic Thermal Conductive Interconnectors

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ABSTRACT: By using pulse electrodeposition, a copper nanopillar array (CuNPA) was filled into porous anodized aluminum oxide (AAO) films to achieve a highly thermal conductive interconnector with anisotropic property. After 120 min pulse deposition, CuNPA uniformly filled the pores of AAO with a pore-filling percentage of 99.4%, as the ion concentration in AAO pores can re-equilibrate to electrolyte concentration during the current-off period. The CuNPA-filled AAO film showed a high thermal conductivity of 153.12 W/(m·K) in the vertical direction and a low thermal conductivity of 3.43 W/(m·K) in the horizontal direction. Hence, the anisotropic ratio of the thermal conductivity reached 44.64. Moreover, the fabrication process was facile and cost-effective, showing a potential application prospect in the field of high-density packages and power electronic devices.

INTRODUCTION

With rapid development of electronic packaging technologies and increasing pitch densities in next-generation electronics, heat transmission has become a critical factor that affects the performance and reliability of electronic devices. 1,2 In addition, coefficient of thermal expansion (CTE) mismatches among the packaging materials lead to cracking and delamination of chips during temperature cycling in fabrication or working. 3-4 To address these issues, anisotropic conductive adhesive (ACA) is applied in fine-pitch and high-power electronics, which have been considered as potential replacements for solder interconnections, as they exhibit thermal and electrical conductivities only in vertical or horizontal direction for anisotropic interconnections. 5-8

However, thermal conductivity of the adhesive [varying from 3 to 12 W/(m·K)] was far lower than that of metal materials. 9-11 To enhance their thermal and electrical performances, fillers such as Ag, Au, and graphene were added into ACA at the expense of high cost and complex fabrication processes. 12 More essentially, the base materials of ACA were mostly organics and, thus, they were unstable under high temperature, causing mechanical performance degradation over time. Hence, more efficient and stable heat dissipation materials are required when electronic devices, especially for power devices, are assembled on substrates. 11,12 Copper (Cu) is an outstanding thermal and electrical conductor and is vastly used in electronic packaging, but it is hard to achieve the anisotropic interconnection due to its isotropic conductivities. Anodized aluminum oxide (AAO) films are aluminum-based materials composing with an individual cylindrical channel array with high hardness, 13 and they are a kind of excellent dielectric materials with dielectric constant ~4.5 varying from 10 to 20 GHz. 14 Moreover, the CTE of AAO is 5.4 ppm/K, and it is compatible with Si (2.5 ppm/K). Nevertheless, the AAO films were usually used as a template for synthesis of various nanowires and nanotubes, and will be etched out after electrodeposition. 15,16 Considering the complementary advantages of copper and AAO films, it is believed that the Cu-filled AAO possesses the merits of both components and will be used in the electronic package field as an excellent anisotropic interconnector.

In this work, a copper nanopillar array (CuNPA)-filled AAO film was achieved for electronic interconnection. The different growth mechanism of CuNPA between constant current (CC) and pulse deposition was explained. By tuning parameters of electrodeposition processes, the Cu nanopillars uniformly filled the AAO film. Compared with conductive adhesive, the film showed superior anisotropic thermal conductivity. Besides, the CuNPA-filled AAO film can also provide electrical and thermal tunnels with a fine pitch in the nanoscale for high-density electronic devices. Moreover, a reflow soldering process was employed to connect the film with the Cu substrate using Sn63Pb37, demonstrating its compatibility with the traditional electronic packaging process.

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Figure 1. (a) Illustration of the electroplating process and structures for the CuNPA-filled AAO film. The top-view SEM images of AAO (b) before and (c) after filling with CuNPA. (d) Cross-section image of the CuNPA-filled AAO film and (e) high-resolution image of CuNPA in AAO. The inset image of (d) shows CuNPA without AAO, and its scale bar is 5 μm.

Cu layer was employed as a template and a cathode. During the depositing process, CuNPA forms a CuNPA-filled AAO structure. In this structure, the AAO film provided dielectric performance and a supporting frame in the horizontal direction, and the CuNPA worked as electrical and thermal tunnels for vertical interconnection. Figure 1b,c shows the top morphology of AAO before and after electrodoposition, respectively. After deposition for 120 min, CuNPA uniformly filled the pores of AAO in the pulse mode with an on/off time of 20 ms/20 ms. The cross-section scanning electron microscopy (SEM) images (Figure 1d,e) confirmed that CuNPA grew through the pores of the AAO without breaks, and the vertical nanopillar array was produced by removing AAO as shown in the inset image of Figure 1d. Apparently, the uniformity was essential to the CuNPA-filled AAO film for high-density devices and power devices, in which field the electrical and thermal performances were critical.

To investigate the filling and growth mechanism of the CuNPA-filled AAO film, a serial of experiments with different deposition parameters were introduced. In the pulse mode, the current on time (t_on) was actual Cu deposition time, and Figure 2 exhibits the height of Cu nanopillars as a function of t_on. According to Faraday’s laws, the height of the Cu pillar (H, μm) was proportional to the product of current density (j, A/dm²) and t_on (h), as follows

\[ H = \frac{k \cdot j \cdot t_{on}}{\rho_{Cu} \cdot P} \times 100 \]  

(1)

where \( k \) is the electrochemical equivalent of Cu²⁺ for 1.186 g/(A h), \( \rho_{Cu} \) is the density of Cu (8.9 g/cm³), and \( P \) is the porosity of AAO for 41%. The real height of the Cu nanopillar was coincident with theoretical calculation in the initial 50 min electroplating time. After that, the actual height was far shorter than the calculating value, especially for samples in the CC mode.

Figure 3 shows the overpotential of AAO as a function of total electroplating time. Considering the growth process of Cu pillars and changes of its overpotential, the deposition process could be divided into four stages. In the beginning, an electric double layer was formed, and a diffusion layer was created in the pores of AAO (I). After an initial Cu layer formed, Cu pillars began to grow in AAO. During this step, the overpotential remains constant (II). Because of overgrowth of Cu, the overpotential was decreasing when some pillars grew out of the AAO surface (III). Finally, the AAO surface covered by Cu, and the overpotential kept almost stable indicating that the growth process of Cu pillars was finished (IV). According to Figure 3a,b, the short constant time of stage II and a relatively long time in stage III of CC mode might be the reason for the significant difference with the theoretical value.

In the CC mode, Cu ions maintain at a state of depletion in the AAO pores, and their growth rate is limited by ion diffusion along the height of the pores. Hence, the pillars closer to the bulk electrolyte grow faster. Then, the unbalance growth between the pillars at the initial stage would intensify during deposition, leading to the short constant time of stage II. In an extreme situation, early formed Cu can quickly cover the AAO surface without concentration limitation and block the growth of Cu pillars in AAO pores. Figure 4a–c shows side-view SEM images of the CuNPA-filled AAO film depositing at 1 A/dm² for 25, 75, and 120 min, respectively. As shown in the inset image of Figure 4c, there is a noticeable shortage of Cu pillars upon where the Cu bulk presented. Though it has been reported in our previous research that low current density can alleviate the unbalanced growth of the pillars as the Cu diffusion rate can keep up with the electrodeposition rate at this status, meanwhile, the plating time is remarkably extended. Besides, considering that the overpotential is proportional with the current density, to reach the needed overpotential threshold, there is a minimum current density to trigger the deposition process. Thus, the pulse mode is applied to realize the Cu balance deposition in AAO pores.

In the pulse mode, the ion concentration in AAO pores re-equilibrated to the electrolyte concentration during t_off period, and the unbalanced growth was restrained between pulses. Moreover, the current density can maintain relatively higher reaching a shorter fabrication time. In 30 s/10 s pulse mode, t_on was relatively long, and the filling process was similar with the CC mode, as shown in Figure 2. To fill the pores completely, it is necessary to achieve a consistent growth rate
in the pores. When the $t_{on}/t_{off}$ ratio tuned to 30 ms/10 ms pulse mode, the height of the Cu pillar was closer to theoretical data, indicating the uniform growth of CuNPAs, but it needs longer time to fill the whole pores of the AAO film. In 20 ms/20 ms fast pulse mode, Cu pillars grew uniformly after depositing for 36 min (Figure 4d) and 110 min (Figure 4e). After 125 min deposition, the entire AAO was filled with Cu nanopillars forming a high-quality CuNPA-filled AAO film as shown in Figure 4f.

After deposition, thermal conductivities of the CuNPA-filled AAO film in vertical and horizontal directions were measured and calculated by the following equations\textsuperscript{22,23}

$$\lambda_v = \rho_{film} \times a_v \times C_p$$

$$\lambda_h = \rho_{film} \times a_h \times C_p$$

where $\lambda_v$ and $\lambda_h$ are thermal conductivities of the CuNPA-filled AAO film in vertical and horizontal directions, respectively. $\rho_{film}$ is the density of the CuNPA-filled AAO film, and $C_p$ is the specific heat capacity of the film at room temperature. $a_v$ and $a_h$ are measured thermal diffusivity of the CuNPA-filled AAO film in vertical and horizontal directions, respectively. $\rho_{film}$ of the film was measured to be 4.9 g/cm$^3$ by the Archimedes principle, which was usually employed for the density measurement of composite materials\textsuperscript{24,25}. The $C_p$ was 673 J/(kg·K) evaluated from the differential scanning calorimeter (DSC). The $a_v$ (46.43 $\pm$ 3.99 $\times$ 10$^{-6}$ m$^2$/s) and $a_h$ (1.04 $\pm$ 0.41 $\times$ 10$^{-6}$ m$^2$/s) were measured by a laser flash apparatus, and the measurement was repeated five times. According to eqs 2 and 3, the thermal conductivities of the CuNPA-filled AAO film at room temperature were 153.12 $\pm$ 13.16 W/(m·K) and 3.43 $\pm$ 1.35 W/(m·K) in vertical and horizontal directions, respectively, exhibited its superior thermal performance with an anisotropic character. Figure 5 shows thermal conductivities of various materials for electronic packaging. The thermal conductivities of AAO were only 2 W/(m·K). After filling with CuNPA, the thermal performance was improved vastly in the vertical direction, and the thermal resistance performance remained in the horizontal direction. Hence, the anisotropic

![Figure 3](image1.png)

**Figure 3.** Overpotential of the CuNPA-filled AAO film as a function of total electroplating time for (a) CC and (b) 20 ms/20 ms pulse electroplating, respectively.

![Figure 4](image2.png)

**Figure 4.** (a–c) are side-view images of the CuNPA-filled AAO film after 25, 75, and 120 min using CC electroplating at 1 A/dm$^2$, respectively. (d–f) are side-view images of the CuNPA-filled AAO film after 36, 110, and 125 min using 20 ms/20 ms pulse electroplating at 2 A/dm$^2$, respectively. The inset images in figures are zoomed-in side views of the top zone.

![Figure 5](image3.png)

**Figure 5.** Thermal conductivities of various materials.
ratio of the thermal conductivity reached 44.64. Meanwhile, the CuNPA-filled AAO film exhibited a superior thermal performance in the vertical direction compared with conductive adhesive [\(\sim 12 \text{ W/(m-K)}\)] and even higher than Si [149 W/(m-K)].

Figure 6a indicates the top-view SEM image of the mechanically polished CuNPA-filled AAO film. Pore-filling percentage of CuNPA is measured using Photoshop software, and it reaches 99.4%. The polished film is reflow soldered with a Cu substrate using Sn63Pb37 at 220 °C for 5 min. Figure 6b illustrates the cross-sectional images of the soldering interface, and there are not any obvious holes or cracks indicating a tight connection between the film and the paste. Moreover, element distributions from the corresponding energy-dispersive X-ray spectroscopy (EDX) mapping (Figure 6c) of Figure 6b also indicate the status of connection. Figure 6d shows that Cu elements are diffused into Sn63Pb37, and Sn and Pb are also detected in the Sn63Pb37/CuNPA-filled AAO film forming an interdiffused layer with a thickness of 3 μm. The presence of the interdiffused layer confirms the effective connection that is similar to the interface of the Sn63Pb37/Cu-substrate.

### CONCLUSIONS

In this work, we fabricated the CuNPA-filled AAO film for electronic interconnection successfully using the pulse electro-deposition method. For fast pulse mode deposition, Cu ions could uniformly diffuse into AAO pores during the \(t_{del}\) period, and CuNPA could fill the pores of AAO in the \(t_{del}\) period. In the film, AAO provided dielectric and adiabatic performances and CuNPA provided the high-density electronic interconnection through the nanosize tunnels. The film showed superior thermal conductivity than the traditional conductive adhesives. In addition, the film was successfully soldered with the Cu substrate, indicating its compatibility with the packaging process of high-density electronic devices and power devices.

### METHODS

Fabrication of CuNPA-Filled AAO Films by Electro-deposition. A commercial AAO film with an average thickness of 50 μm, and pores in 75 nm diameter (Shenzhen Tuopu Jingmi Ltd., China) was used as the template and substrate. To provide a conductive contact, a layer of dense copper was coated on one side of the AAO film using a magnetron sputtering equipment (Shenyang Bluesky Technology Ltd., China). Then, the AAO film was fixed onto indium tin oxide conductive glass sealed by waterproof glue as a cathode. A copper plate was washed by 1 mol/L \(\text{H}_2\text{SO}_4\) and employed as an anode. The electrochemical experiments were performed by the chronopotentiometry method (CHI-660E, CH Instruments, Inc., USA), and the \(\text{Hg}(s)/\text{Hg}_2\text{SO}_4(aq)/\text{SO}_4^{2-}(aq)\) was set as a reference electrode. During electro-plating, the temperature of the electrolyte (mixed by 1.5 mol/L \(\text{CuSO}_4\cdot\text{H}_2\text{O}\) and 1.5 mol/L \(\text{H}_2\text{SO}_4\)) was maintained at 30 °C in a thermostatically controlled water bath.

Reflow Soldering Process of CuNPA-Filled AAO Films. The as-prepared CuNPA-filled AAO film was polished using a mechanical polishing machine (UNIPOL-820, MTI Ltd., China). Then, the commercial solder paste, Sn63Pb37 (Senju Solnet Metal Co., Ltd., China), was coated on the polished side of the film, and a prepolished Cu substrate was placed on the paste forming a CuNPA-filled AAO film/ Sn63Pb37/Cu-substrate sandwich structure. Finally, the sample was heated in a reflow oven (Falcon SC, Sikama, USA) at 220 °C for 5 min.

Characterization. The morphologies of the CuNPA-filled AAO film were characterized using SEM (MERLIN Compact, ZEISS, Germany) with an EDX module (X-Max Extreme, Oxford, UK). The thermal conductivity was measured by DSC (STA449F, Netzsch, Germany) and a laser flash apparatus (LFA447, Netzsch, Germany).

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Notes

The authors declare no competing financial interest.

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