EFFECTS OF ELECTROLYTES ON NANOPOROUS ANODIC ALUMINUM OXIDE FORMATION ON AN AL SUBSTRATE FOR ELECTRONIC PACKAGING

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Abstract. Recently, nanoporous anodic aluminum oxide (AAO) structure is receiving great interest from various researchers owing to its potential impact on thermal management in electronic packages. Dimensions such as the pore diameter, pore height, and interpore distance of nanoporous AAO are factors influencing effective heat dissipation. For proper AAO dimensioning, this work fabricated the nanoporous structure on Al5052 using three different types of electrolytes. In a two-step anodization process, a nanoporous template was fabricated using phosphoric (0.3 M), sulfuric (0.3 M), and oxalic (0.3 M) acids. Porosity and morphology were investigated via field emission scanning electron microscopy. The morphology of AAO showed that oxalic acid forms a uniform honeycomb-like structure over other electrolytes. Furthermore, this electrolyte resulted in 22% porosity, 36–50-nm pore diameter, and ~2.6-μm pore height, thereby helping in effectively dissipating the heat of components in an electronic packaging.

Keywords: nanoporous, two-step anodization, AAO, porosity, FESEM

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Introduction

In strategic efforts to improve the quality of electronic devices in packaging, lightweight substrates such as Al and its alloys are being considered as possible replacements for other substrates. Al has a distinctive effect, i.e., when it is anodized under suitable process settings, a well-aligned porous structure can be formed on the surface [1]. The nanoporous AAO structure can be a starting point for several templates, photonic structures, membranes, drug delivery platforms or nanoparticles, and electronic packages [2,3]. To fabricate a self-organized porous structure on an Al substrate, two-step anodization has been preferred by most researchers. The first step of the anodization process results in a disordered arrangement of the nanoporous oxide layer. After removing the oxide layer, one receives highly ordered concaves on a substrate. During the second step of the anodization process, these ordered concaves are served as the pore nucleation sites. Mostly, the same experimental conditions are followed on both the first and second steps of the anodization process [4]. However, optimizing suitable process parameters is crucial because different combinations of anodizing processes influence the formation of nanoporous AAO structures. Each process parameter is artificially controlled to obtain proper AAO according to the purpose of the user. The porous dimensions of the AAO pattern are closely related to the application and formation of the nanopore structure, which is related to the factors such as the type of electrolyte, concentration, temperature, time, and applied voltage [4,5].

Anodizing can be performed in borate or tartrate baths in which aluminum oxide is insoluble. In these processes, growth stops when the surface is fully covered, and the thickness is linearly increased related to the applied voltage. These oxide layers are free of pores, whereas anodizing aluminum with a porous structure is usually performed in electrolytes containing sulfuric, oxalic, or phosphoric acid [6]. To develop regular nanopores ranging in size from ~10 to 240 nm, most researchers' choice is to use any one of electrolytes such as oxalic, phosphoric, or sulfuric acid [7]. The choice of electrolyte in the anodization process determines the voltage window, i.e., oxalic acid (15–100 V), phosphoric acid (30–195 V), and sulfuric acid (15–22 V) [8]. However, higher voltage or current density ranges are widely used for various industrial applications to form relatively higher thicknesses, such as the surface finishing of aluminum cookware, automobile engineering, and textile machinery [9]. Notably, a higher applied voltage increases the pore radius (r) and interpore distance (D_{int}), but it worsens the regularity of the nanopore arrangement, which is agreed by other researchers [10]. Moreover, the same authors [11] already experienced that AAO with >7-μm thickness formed using oxalic acid has no significant increase in thermal performance such as device junction temperature and total thermal resistance.

To improve the thermal performance, a few researchers already worked on heat pipes and electronic packages with nanoporous AAO solutions and reported that nanoporous AAO significantly improves the heat transfer performance. According to Wang et al. [12], the AAO-np structure actively dissipates the heat produced by an electronic device and it escapes through a well-organized pore structure. The AAO-np structure prepared using the two-step anodization process was applied in the inner wall surface of the evaporator section of a gravity heat pipe, and it was observed that the heat transfer performance was improved significantly. Overall, the thermal resistance and temperature difference of the processed heat pipe is 59% and 46% lower than for the unprocessed heat pipe, respectively, and these developed nanopores had a diameter of ~35 nm and a height of ~6 μm. Cui et al. [13] worked on the heat transfer performance of AAO and inferred that the effect of the porous media thermal conductivity is negligible if the total thickness exceeds 5×10^{-3} m via model simulation and calculation. The appropriate pore diameter range of high thermal conductive nanoporous structure is approximately 30–70 nm with ~3.9% porosity on the Al surface [14]. However, no relative evidence is available on the impact of electrolytes and porosity on AAO preparation for thermal management applications. Thus, to support electronic packaging, this work is intended to fabricate a nanoporous AAO on an Al substrate under appropriate anodization conditions and recommend the nanoporous dimensions.

Materials and Methods

Commercially available Al5052 alloy with 0.6-mm-thick sheets and 1-mm-thick copper sheets were used as anode and cathode materials, respectively. The electrolytes such as sulfuric acid (95% AR grade, Merck & Co), oxalic acid (99% AR Grade, Merck & Co), and phosphoric acid (85% AR grade, Merck & Co) were used in the anodization process. The raw material was annealed using a muffle furnace at 350°C for 3 h to remove internal stress. Further, an alkaline soak cleaner was generally used, and the surface was cleaned with acetone for 15 min each. The first and second steps of the anodization process were conducted similar to those in the previous work of the same authors [3]. Three sets of experiments were conducted using three different types of electrolytes at 0.3 M concentration. The remaining parameters such as bath temperature (25°C), applied voltage (30 V), and anodization time (2 h) were kept constant. In the first experiment, 0.3 M phosphoric acid was used as an electrolyte for the anodization process. In the second experiment, 0.3 M sulfuric acid was used. The third experiment was conducted using 0.3 M oxalic acid in the anodization process. Figure 1 represents a schematic of the two-step anodization process.

The top view of the surface morphology of the nanoporous AAO was characterized using field emission scanning electron microscopy (FESEM) (Zeiss) at the magnification of 30 kX at an acceleration voltage of 5 kV. Similarly, the cross-section view was characterized using an extreme high-resolution FESEM (FEI Version 460L). The pore height was measured using cross-section focus by placing the sample in a vertical direction followed by 50 kX at the same accelerating voltage. The average pore diameter and interpore distance were reported on the basis of random spot of 400 nm × 400 nm area measurements. The below formula was used to calculate the porosity of developed nanoporous AAO structure, which relates the mean pore radius (r) and interpore distance (D_{int}), derived by [15]:

$$P = \frac{2\pi}{\sqrt{3}} \left(\frac{r}{D_{int}}\right)^2 \tag{1}$$

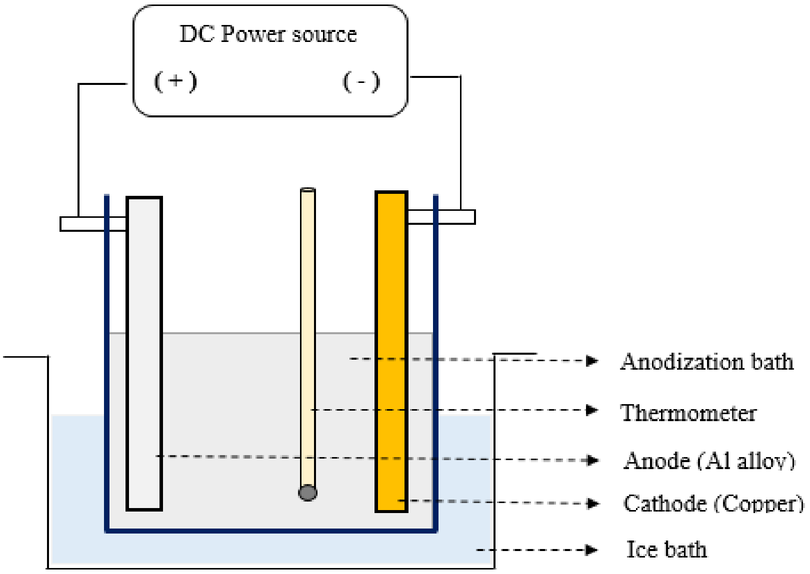

Figure 1. Schematic diagram of the two-step anodization process

Results and Discussion

In this study, the investigated morphology of nanoporous AAO prepared under various types of electrolytes produced a uniform porous formation. The regularly arranged pores under different electrolytes resulted in a difference in pore diameter size and maintained regularity in the porous texture. The observed top and cross-sectional views of the porous formation are shown in Figure 2(a)–(d). First, under different acidic electrolytes, the growth of nanoporous AAO after a two-step anodization process formed with hexagonally arranged nanopores. The template could be distinguished like hexagonal honeycomb-like structures that are arranged at the top surface, and parallel porous channels formed at the cross-sectional view.

As shown in Figure 2(a)–(c), pores diameter and interpore distance varied in phosphoric and sulfuric acids, whereas it was more regular in oxalic acid. Figure 2(a) shows that the arrangement of pores was uniform. However, several concave oxide layers were observed, and a lack of uniformity in the oxide layer was observed in the phosphoric acid. Moreover, the pores were formed as very tiny diameters (20–25 nm) with large spacing between two adjacent pores. The interpore distance between two pores was larger than the pore diameter (30–50 nm). Figure 2(b) shows that the dense pores were formed using sulfuric acid. The entire surface was covered with 52–78-nm pores, and there was no huge spacing between adjacent pores. The wall thickness was very minimum, and it resulted in 5–10 nm of interpore distance.

During the anodization process, the applied input voltage is a key factor for the self-ordered nanoporous formation. The variations in applied voltage with respect to the type of electrolyte change the growth of AAO, and the anodization time influences the pore dimensions. The rate of dissolution of aluminum oxide occurring at the base of pores is equal to the rate of oxide formation at the metal–oxide interface. Starting from that moment, a well-aligned growth of the nanoporous layer on anodized aluminum starts. In our study, phosphoric acid has a lack of impact on uniform porous structure growth because of its slower barrier layer etching rate [16]. The rapid growth of porous structure under sulfuric acid is due to the fast reaction oxide formation at applied potential, and this is agreed by a previous work [17]. The best arrangement of the nanopores is formed under 0.3 M oxalic acid. Figure 2(c) shows that the pores are arranged uniformly and that the interpore distances are almost similar to the size of pore diameter. When compared with other acids, the oxalic acid-based AAO were found to have more uniform nanopores and channels, fewer embodied anions, and better hexagonal ordering than the AAO formed in sulfuric and phosphoric acids, which is agreed by a previous study [18]. A cross-sectional view of the porous channel (as shown in Figure 2(d)) formed under oxalic acid shows the growth of porous height concerning the deposition time. The observed porous channel height under oxalic acid results in ~2.6 μm. These parallel channels will support dissipating the generated heat to the ambient from the hotspot of the package. The hotspot heat escapes through the porous channel that decreases the device temperature in electronic packages, and the relative thermal performance (total thermal resistance and rise in junction temperature) is discussed by the same authors [11]. The reason behind this effective heat dissipation is due to the regularity of the nanopore arrangement and also proper pore dimensioning such as pore diameter, pore height, interpore distance, and porosity.

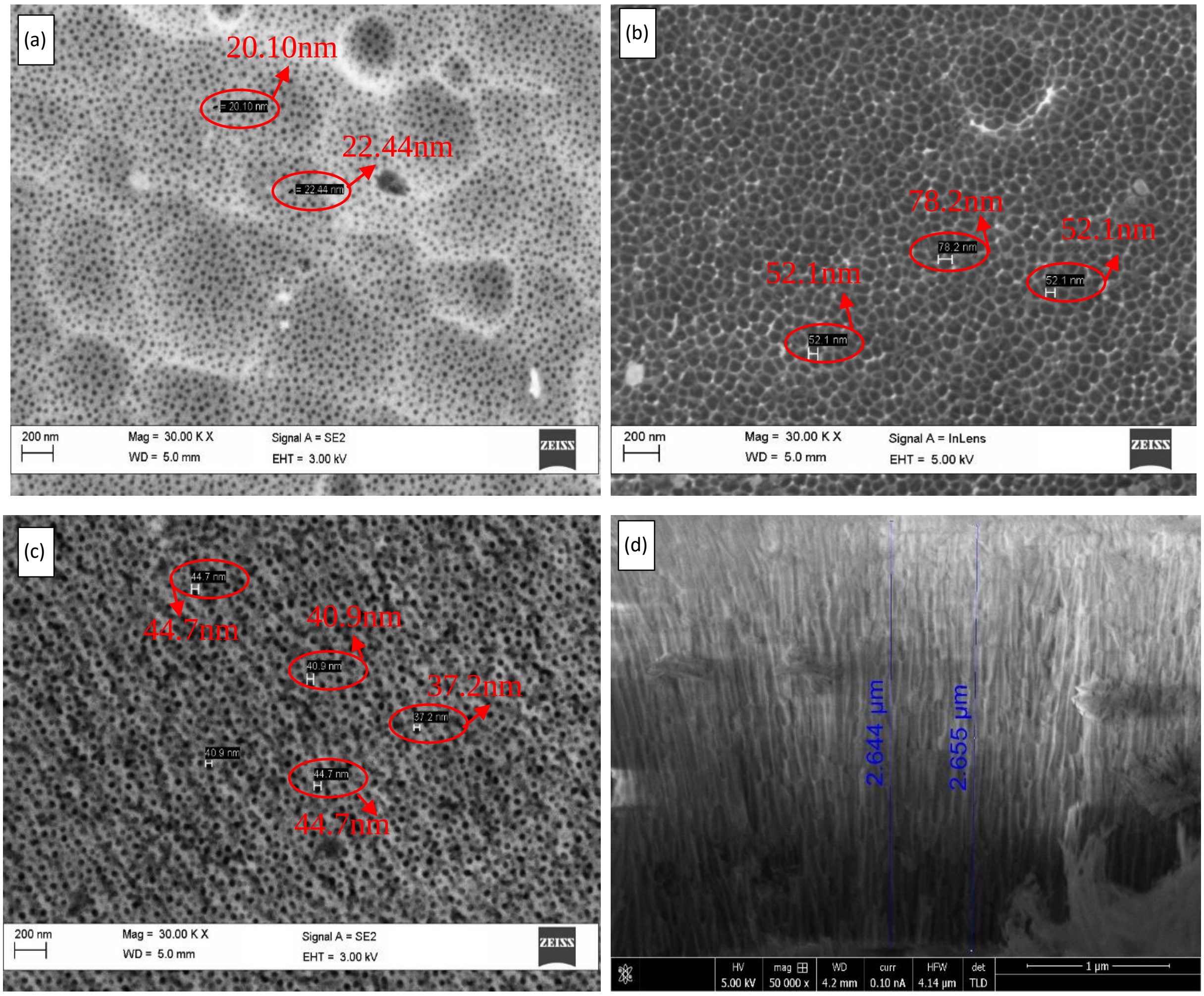

Figure 2. Top view morphology of nano porous AAO prepared using (a) phosphoric acid (b) sulfuric acid (c) oxalic acid (d) Cross-section of AAO prepared using oxalic acid

Table 1 presents the observed nanoporous AAO dimensions. Further, Figure 3 represents the calculated porosity (using Eq. 1) of nanoporous morphology prepared under different electrolyte baths. The porosity of AAO formation under phosphoric, oxalic, and sulfuric acids resulted in 0.63%, 22.7%, and 37.2%, respectively. For effective heat dissipation, a dense porous structure with better porosity is a much-needed template. From this study, sulfuric and oxalic acids produce considerably high porosity on the Al surface over phosphoric acid. However, sulfuric acid results in very thin porous wall thickness and >50-nm pore diameter. This structure may undergo deviation in thermal management during a high-pressure setting. Because of its thin wall channel, it is suspected to distort the AAO–nanopore structure [3]. This distortion may affect the heat escaping path or heat dissipation through the porous channel. In comparison with that in a previous work [14], 0.3 M oxalic acid has improved porosity, with a considerable range of pore diameter (36–50 nm) and wall thickness (~2.6 μm) that are suitable for effective heat dissipation in electronic packages.

Table 1. Average pore diameter and interpore distance of prepared samples under various electrolytes

Figure number	Electrolyte concentration	Average pore diameter (nm)	Interpore distance (nm)
2a	0.3M phosphoric	22.5 ± 2.5	40 ± 10
2b	0.3M sulfuric	65 ± 13	7.5 ± 2.5
2c	0.3M oxalic	43 ± 7	33 ± 5

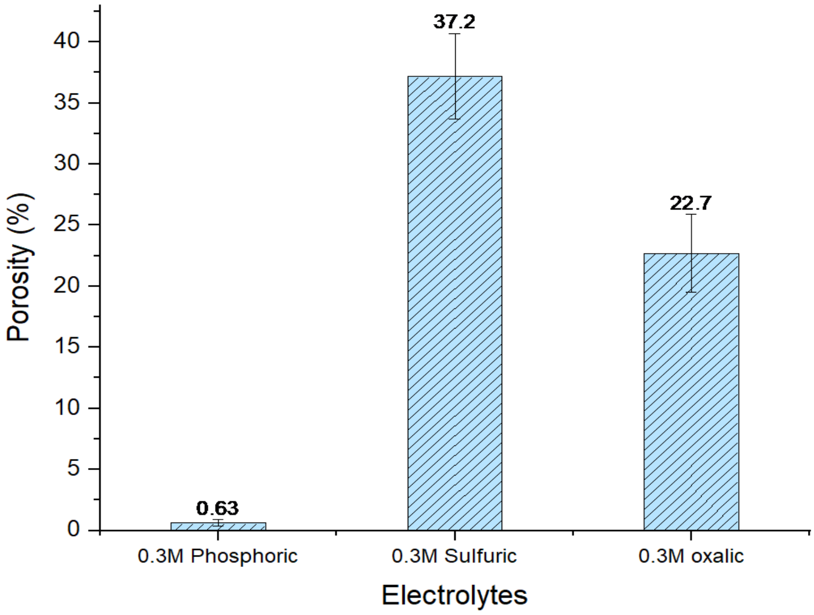

Figure 3. Porosity of nano porous AAO prepared using different electrolytes

Conclusion

The possible formation of nanoporous AAO with different electrolytes was investigated. The porosity effect of oxalic, sulfuric, and phosphoric acids was discussed in the AAO formation. In comparison with other electrolytes, 0.3 M oxalic acid with optimum porosity (22.7%), 36–50-nm pore diameter at the top view, and ~2.6-μm-high parallel channel at the cross-section helped in improving the heat dissipation property. Nevertheless, with respect to anodization time, an increase in porous height may further influence the heat dissipation in real-time conditions. The current findings in this work can assist in selecting appropriate conditions and electrolyte composition for fabricating nanoporous AAO on an Al substrate. The correlation of porosity and previous thermal performance results will add a significant impact to electronic packaging thermal management solutions.

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Author contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work

Disclosure of conflict of interest

The authors have no disclosures to declare

Compliance with ethical standards

The work is compliant with ethical standards

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