Examination of anodized aluminum for surface defects after thermal cycles.

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Abstract
A major cost in the fabrication of test sockets is the interposer, an interface layer that reroutes one connection to another. The interposer must have high resistivity with low loss, a smooth surface finish, high strength, resistance to chemicals involved in the process, and be extremely thin. Currently, the most common materials used for interposer are plastics, such as Torlon, Semitron, and PEEK. While these satisfy the requirements for test sockets, they do not perform well under higher ambient temperatures. Finding a less expensive, alternative material would be preferable.

In this study, anodized aluminum samples were subjected to repeat thermal cycling between 22°C -150°C for over 10,000 cycles. At certain intervals, 2000, 5000, 7500 and 10,000 cycles, the surface of the anodized aluminum samples were examined for tears or cracks that may result due to the differences in the thermal expansion rates between the aluminum matrix and the oxide layers. Results showed no critical defects that would compromise the oxide layer, and therefore reduce resistivity and its viability as an alternative interposer material.

Introduction
Interposers
Test sockets are used to ensure proper connections in circuit boards and reduce early component failure. As test sockets (see figure 1) must be long-lasting [1] and of the highest quality, they tend to be quite expensive. A major cost in the fabrication of these devices is the interposer, an interface layer that reroutes one connection to another (figure 2). The interposer must have high resistivity with low loss, a smooth surface finish, high strength, resistance to chemicals involved in the process [2], and be extremely thin. Currently, the most common materials used for interposer are plastics, such as Torlon, Semitron, and PEEK. However, these plastics do not do perform well under higher ambient temperatures. Presently new materials such as silicon and glass have been used in place of these plastic materials [2, 3, 4, and 5]. But these materials are more costly [3] as they are more difficult to fabricate. Finding a less expensive, alternative material would be preferable.

Figure 1. Example of a typical test socket [6].
Anodizing is the process of thickening the natural oxide coat on aluminum. This is an electrochemical process achieved by passing a current through an acid (usually sulfuric) electrolyte, where the workpiece is the anode [7]. When a current is applied through the anodizing cell (Figure 3), sulfuric acid starts to decompose and hydrogen ions move to the cathode where they are reduced to hydrogen gas according to Eq.1.

$$2H^+ + 2e^- \rightarrow H_2(g)$$  \hspace{1cm} \text{Eq.1}

Negatively charged anions, i.e. hydroxide ($OH^-$), sulfate ($SO_4^{2-}$), and oxide ions move to the anode. The electrical charge in the circuit causes positively charged aluminum ions ($Al^{3+}$) to be generated in the anode and in turn move toward the cathode (Eq.2).
\[
Al \rightarrow Al^{3+} + 3e^- \quad \text{Eq.2}
\]

At the anode’s surface aluminum ions (\(Al^{3+}\)) react with the oxide/hydroxide ions to form aluminum oxide (\(Al_2O_3\)), according to equations (3) and (4).

\[
2Al^{3+} + 3O^2- \rightarrow Al_2O_3 \quad \text{Eq.3}
\]
\[
2Al^{3+} + 3OH^- \rightarrow Al_2O_3 + 3H^+ \quad \text{Eq.4}
\]

The overall process can be described by Eq.5.

\[
2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^- \quad \text{Eq.5}
\]

**Coefficient of Thermal Expansion**

Most solids expand when they are heated and contract when they are cooled. The material property that describes the extent of expansion and contraction with changing temperatures is the linear coefficient of thermal expansion, \(\alpha\) [8]. The defining equation is:

\[
\alpha = \frac{\varepsilon_{th}}{\Delta T}
\]

where \(\varepsilon_{th}\) is the thermal strain (\(\Delta L/L_o\)) resulting from a temperature change \(\Delta T\).

The typical coefficient of linear thermal expansion \(\alpha\) of aluminum is \(25 \times 10^{-6} \, ^\circ C^{-1}\) while that of the aluminum oxide is \(6.5 \times 10^{-6} \, ^\circ C^{-1}\) [8].

In this project, the resistivity of the anodized aluminum were measured, the oxide layer were examined under the scanning electron microscope, SEM, and the thickness of the oxide layer determined. The time taken to anodize the aluminum samples were also noted. After the initial examination, samples of the anodized aluminum were subjected to thermal cycles to simulate actual working conditions (room temperature to 150\(^\circ\)C) of these test sockets in operation. Since the oxide layers and the aluminum matrix have different rates of thermal expansion, such differences might cause shearing of the oxide layer as the aluminum matrix expand, resulting in micro tears or cracks. This would compromise a continuous oxide coating. Should the oxide layer develop cracks or other critical defects, the anodized aluminum would lose its high resistivity, causing the test socket to fail.

**Experimental Methods**

The electrolyte used in the anodizing experiment is a solution of 94% Reverse Osmosis (RO) water and 6% sulfuric acid by volume. The temperature of the solution is maintained at 23\(^\circ\)C before the start of the anodizing experiment. DC Power Pack Agilent E 3631A Triple Output DC Power Supply provides the power with the applied current maintained at around 10-20 mA/cm\(^2\) and the applied voltage is 25 volts. The electrical resistivity of the samples were measured using Keithley 2100/120 6.5 Digit USB Digital Multimeter. Electrical resistivity at the region close to the edge of the drilled holes were measured using an EP6 Probe Station (figure 4).
Samples of the aluminum sheet metal, with holes (diameter 0.5 mm) drilled through, were washed and degreased with isopropyl alcohol before dipping in sodium hydroxide for 2 minutes to obtain a clean surface for anodizing. These samples were subsequently anodized for 30 minutes and the electrical resistances of the anodized samples were measured. Samples were then prepared for evaluation in the Phenom desktop SEM to measure the thickness of the oxide layer.

In preparation for observation in the SEM, the samples were cut into smaller sections with some sections mounted on epoxy (figure 5) so that their edge can be easily viewed in the scanning electron microscope (SEM). Other sections were mounted directly onto the SEM mounting stub for observation of the oxide layer around the holes (figure 6).
To imitate the thermal cycling of test socket, a laboratory fixture involving a motor and linkages, a heater coil and a power supply unit was designed to allow the samples to be heated and subsequently cool to room temperature before repeating the process again (Figure 7). The motor runs at 0.5 rpm.

The surface of the anodized aluminum samples were initially examined in the SEM before the start of the thermal cycle treatment. The samples were re-examined after certain thermal cycles for possible micro cracks that might result due to the differences in the rate of thermal expansion between the aluminum matrix and the oxide layer.

Results and Discussion
Initial measurement of the resistance of the samples before anodizing were found to be around 1-10 ohms (depending on where the electrodes were placed to measure the resistance. The anodized samples had very high resistance causing the Digital Multimeter to read an OVERLOAD error.

The edge of the anodized aluminum sample was examined in the scanning electron microscope. The secondary electron (SE) image showed the oxide layer was fairly visible, sandwiched between the aluminum matrix and a backing material. Using the scale bar, the oxide layer was estimated to be around 10 micron thick. This layer of oxide was sufficient to create a very high resistance to the flow of electron and cause the multi-meter to read an “overload” error.
Figure 8. A portion of the aluminum showing the oxide layer after anodizing for 30 minutes. The oxide layer was approximately 10 microns using the scale bar inserted.

Figures 9-10 showed SE imaging of the topographical surface of the anodized aluminum samples, before and after thermal cycles. Figure 9a showed a portion of the anodized aluminum sample where the high magnification SE imaging was observed (see the small scan square). The SE image of the sample before thermal cycling is shown in figure 9b and figure 9c showed the same sample surface after 2000 thermal cycles. There were no noticeable differences between the pair. There was no micro-tears or cracks on the sample surface.

Figures 9. Anodized aluminum sample before (a) and after (b) 2000 thermal cycles.

Figure 10a showed a portion of another anodized aluminum sample where the high magnification SE imaging was observed (see the small scan square in the figure). Figure 10b is the SE image of the sample before the thermal cycle treatment and figure 10c showed the same sample after 5000 thermal cycles. Again there were no noticeable differences between the pair and no micro-tears or cracks on the sample surface too.

These thermal cyclic experiments showed that even though the aluminum matrix \((\alpha = \text{is } 25 \times 10^{-6} \degree \text{C}^{-1})\) will expand/contract almost 4 times longer/shorter than the oxide layer \((\alpha = \text{is } 6.6 \times 10^{-6} \degree \text{C}^{-1})\) the thin oxide layer (~10 microns) was able to yield sufficiently without causing any tears or cracks. These results suggested that the 10 micron thin aluminum oxide layer would withstand at least 10000 thermal cycles without resulting in critical defects that would compromise the oxide layer, and therefore reduce resistivity and its viability as an alternative interposer material.
Figures 10. Anodized aluminum sample before (a) and after (b) 5000 thermal cycles.

Figure 11 and 12 showed the SE imaging of the sample surfaces after 7500 and 10000 cycles. Again there were no visible sign of any micro cracks or tears of these samples after the thermal cycles.

Figures 11. SE image of the anodized aluminum sample surface after undergoing 7500 thermal cycles.

Figures 12. SE image of the anodized aluminum sample surface after undergoing 10000 thermal cycles.
While further thermal cycling beyond the 10000 cycles would be tested, the results suggested that the normal working temperatures of interposer at 150°C is not hot enough to cause a problem with the different rates of thermal expansion of the oxide and aluminum layers.

**Conclusions**

This study showed that aluminum alloy 6061 with holes approximated 0.5 mms can be anodized easily. The initial resistance of aluminum alloy was around 1-10 ohms. The resistance of the anodized aluminum alloy was too high to be read by the digital multimeter.

An anodizing process involving an electrolyte solution of 94% Reverse Osmosis (RO) water and 6% sulfuric acid by volume and supplying a voltage of 25 with the applied current maintained at around 10-20mA/cm² was be able to produce an aluminum oxide layer up to 10 microns within a 30 minutes process.

Aluminum oxide layer measuring 10 micron is sufficient to create a very high resistance to the flow of electron and cause the multi-meter to read an “overload” error.

Anodized aluminum with approximately 10 microns oxide layer would withstand at least 10000 thermal cycles without resulting in critical defects that would compromise the oxide layer.

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**References**


