

Passivation Coatings for Micro-channel Coolers

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Abstract—Many high heat flux electronics applications have surpassed the limits of air cooling and are moving towards liquid cooling as a method to remove waste heat directly from electronics packages. In applications such as power electronics, high liquid velocities along with highly corrosive coolants (DI water in particular) limit the reliability and performance capability of many liquid cooling solutions. Engineering solutions include the use of stainless steel in place of better performing copper or aluminum materials and the use of costly nickel and gold plating where the performance of copper is required. The problem is particularly difficult with copper micro-channel coolers (MCCs), as conventional plating techniques are not capable of creating conformal coatings in the micro-channels. In this paper, preliminary results on the passivation capability of nano-scale alumina coatings deposited by atomic layer deposition (ALD) are presented. ALD coatings are deposited in the vapor phase, one atomic layer at a time, resulting in unmatched conformality and coating thickness uniformity on almost any geometry. Experimental results for thermal cycling, erosion and corrosion passivation performance with salt water are presented for a baseline (copper), gold plated copper, and ALD coated copper micro-channel cooler. In all cases the ALD coated samples demonstrated superior passivation properties.

I. INTRODUCTION

A. Reliability Issues in Micro-channel Coolers

Currently, the most effective method used to remove large amounts of heat is pumped single-phase coolant flowing through copper micro-channel coolers (MCCs). MCCs are fabricated using a combination of micro-machining, lithography, etching, and diffusion bonding [1]. Most commercially available MCCs are made with many thin sheets of photo-etched copper that are diffusion bonded together. Copper is used because of its excellent thermal and electrical conductivity (in applications where the MCC serves as both a cooler and as an electrical bus bar). The MCC design increases surface area and improves convection (due to the small channel diameters) which minimizes the overall thermal resistance of the cooling solution. To minimize conduction resistance, cooling fluids often pass very close to the heat source. De-ionized (DI-H₂O) water is often used as the cooling fluid because of its excellent thermo-physical properties. Although this design is thermally advantageous, the use of copper allows the electrical path to come into direct

contact with the water cooling fluid (this is true of cases where the copper is used as an electrical bus bar or is simply not completely electrically isolated from electrical live electronics devices). When an electric potential is applied to the copper, a very rapid reaction occurs between the copper and water that results in well-documented failure mechanisms including corrosion and erosion [2,3]. Even without the extreme case of applied electrical potential, electric potential differences stemming from having dissimilar materials (galvanic corrosion) or simply high purity DI water can also create highly corrosive conditions.

One solution to this problem is to electrically isolate the device from the cooling fluid by using ceramic materials. Ceramics are very inert and their high dielectric constant prevents electro-chemical corrosion with DI-H₂O. Ceramics are also hard, which improves erosion resistance. To maintain structural stability, the ceramic pieces must be rather thick. To maintain respectable heat transfer, only ceramics with high thermal conductivity may be used. Such ceramics include beryllium oxide, aluminum nitride, and thick films of chemically deposited diamond [4]. Although the thermal conductivity of these materials is decent, they are at best less than half that of copper. Another disadvantage of ceramic MCCs is cost. The use of exotic-thermally conductive materials is a driving factor, as well as the specialty fabrication processes required to manufacture precision structures from ceramics.

A typical, and more cost effective approach used to prevent corrosion in copper MCCs uses very thin barrier coatings consisting of nickel and gold. Corrosion prevention is primarily controlled using the gold thin film. To hinder copper diffusion into the gold and improve wear resistance, an intermediate layer of nickel is used. Although the nickel does impede copper diffusion, it does not completely prevent it [5,6]. Studies show that even at low temperatures, copper may diffuse across the nickel barrier [7,8]. Additionally, micro-channels with high aspect ratios tend to cause non-uniform electric fields during the metal plating process, and as a result, pinholes form in the gold/nickel film exposing bare copper.

Currently, failure of the MCC resulting from corrosion is a leading cause of power electronic systems failures. A passivation coating that significantly improves MCC

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reliability would in turn increase the reliability of high power electronic systems.

B. Corrosion and Erosion Mechanisms

When an electric potential is applied to a copper MCC, a very rapid electrochemical reaction may occur between the copper MCC and coolant fluid. For this reason, de-ionized water (DI-H₂O) is used as a cooling fluid. Not only does DI-H₂O have excellent thermo-physical properties, it also has a high electrical resistivity. DI-H₂O with a resistivity ranging from 0.1-0.5 MΩ/cm provides optimum corrosion prevention. A lower resistivity allows current flow resulting in increased electrochemical corrosion. As the resistivity increases, the pH decreases, and corrosion caused by hydrogen ions becomes dominant. DI-H₂O with the optimum resistivity reduces the flow of electrons, and consequently the electrochemical reaction is only driven by leakage current [2]. This corrosion process is further hindered by the use of nickel/gold (Ni/Au) thin films. However, pinholes in the plating significantly reduce MCC reliability by providing corrosion initiation sites.

Erosion on copper MCCs is also a significant problem [4]. High velocity water flow may disrupt adherence between the Ni/Au thin films and the copper MCC. In addition, the removal of surface films by erosion may accelerate corrosion. This phenomenon is known as erosion-corrosion. Defects in the coating surface allow turbulent eddies to form (Fig. 1a) which results in undercutting of the protective films (Fig. 1b-d). Debris that is spalled off and carried away in the high velocity fluid may impinge the coating, exacerbating the erosion process. Coatings that provide the best erosion protection are hard, dense, adherent, and continuous [9].

A conformal coating that is electrically insulating, hard, and easily deposited will economically reduce/eliminate the failure mechanisms facing Ni/Au plated copper MCCs. A thin electrically insulating barrier placed between the copper MCC and the DI-H₂O water cooling fluid will prevent charge migration and corrosion. A hard barrier coating will prevent erosion. The coating must also be easily deposited, highly uniform, and pinhole free.

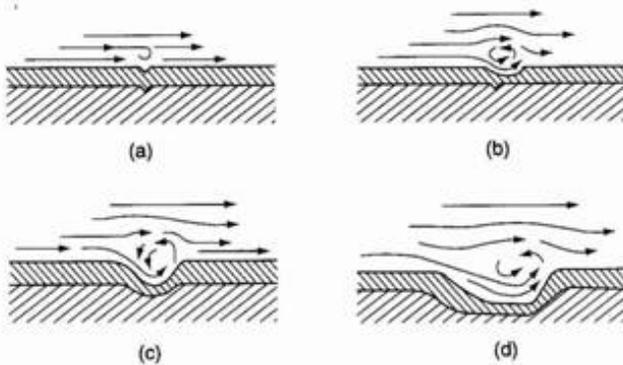


Figure 1. Schematic of turbulent eddy mechanism for downstream undercutting of erosion-corrosion pits [10]. Defects in the coating surface allow turbulent eddies to form (a), which results in undercutting of the protective films (b-d) [9].

C. Atomic Layer Deposition

Atomic layer deposition (ALD) is a well-developed deposition process capable of depositing uniform ceramic thin films, including alumina, zirconia, hafnium oxide, titanium nitride and aluminum nitride. This deposition process is a result of a chemical reaction between two precursor chemicals and the substrate material. The precursor chemicals are in the gaseous phase, allowing uniform coatings to be deposited on surfaces with high aspect ratio features, such as copper MCCs.

ALD is commonly used to deposit oxides and nitrides. This is done by introducing the molecular precursors into the ALD reactor separately. Typically, the first precursor chemical is a volatile molecule consisting of a metal element attached to a ligand. This molecule chemically bonds to the active sites on the substrate surface. This reaction is complete when the metal-ligand gas has reacted with all of the active sites on the surface. To remove any by-product gases, this step is followed by an inert gas purge. After the gas purge, a second precursor chemical is introduced. This reaction is also self-limiting, and completes once it has reacted with all of the metal-ligand molecules. At the end of this reaction a single monolayer film is deposited and the surface chemistry is restored to its initial state. This allows the two-step reaction to be repeated multiple times, each time creating only a single layer. Since each cycle results in a single layer, the thickness of coatings created with ALD can be controlled very precisely by controlling the number of cycles.

An ALD coating process of particular interest for Ni/Au MCCs is alumina (Al₂O₃), shown in Fig. 2. To begin ALD of Al₂O₃, the surface must first be functionalized with hydroxyl (OH) groups (Fig. 2a).

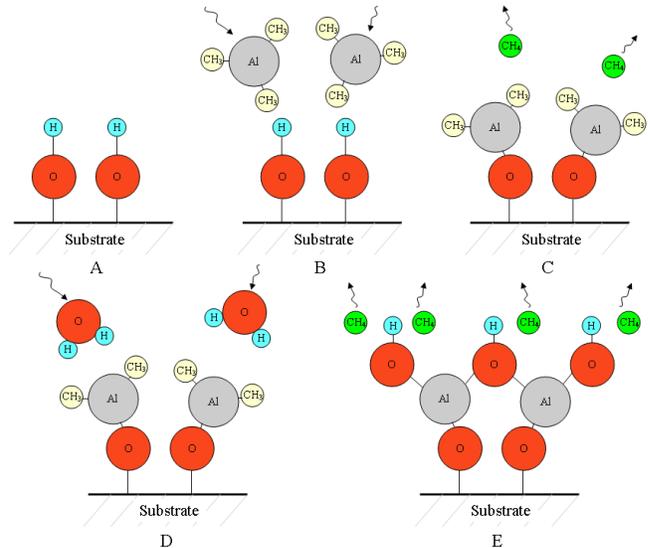
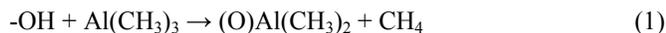


Figure 2. Atomic Layer Deposition Process of Al₂O₃. For Al₂O₃-ALD to begin, the substrate must be prepared with OH groups (A). The first reaction in Al₂O₃-ALD uses Al(CH₃)₃ (B), which reacts with the hydroxyl groups and releases CH₄ (C). The second reaction in Al₂O₃-ALD uses water vapor (D). The water reacts with the remaining methyl groups, releasing more methane, and restores the surface chemistry to the initial OH condition (E).

The OH groups provide active sites for the metal-ligand molecule tri-methyl-aluminum ($\text{Al}(\text{CH}_3)_3$) to bond, resulting in the following reaction (1) (Fig. 2b):



At the end of this reaction, the methane (CH_4) is removed via inert gas purge (Fig. 2c), and the remaining $\text{Al}(\text{CH}_3)_2$ provides the necessary surface chemistry for the next reaction. Water vapor (H_2O) is flowed into the ALD chamber creating the following reaction (2) (Fig. 2d):



The H_2O in this reaction reacts with the $-\text{CH}_3$ sites that remain from the initial precursor. The reaction self-saturates once all the $-\text{CH}_3$ sites have reacted. At the end of this reaction, a single ALD cycle is complete, and the density of surface hydroxyl group is restored to the original state (Fig. 2e) [11].

ALD is identified as a coating process capable of producing highly uniform thin films. Since the deposition process uses gaseous precursor chemicals, ALD has the ability to deposit material on substrates with high surface aspect ratio features, like copper MCCs. The self-limiting nature of ALD allows coatings of precise thickness to be deposited. ALD works especially well at depositing ceramics, like Al_2O_3 . Since ceramics are naturally electrically insulating and hard, they will provide excellent corrosion and erosion protection in Ni/Au plated copper MCCs.

D. Self-Assembled Monolayers

The surface chemistry of the substrate plays an important role in coating adhesion. A specific chemistry is required for bonding during ALD deposition where the surface must be hydrophilic to ensure the first step in the cyclic ALD process occurs. Any imperfections on the substrate surface will also limit deposition, and result in pinholes. Self-assembled monolayers (SAMs) were chosen as a surface treatment method that is compatible with ALD, is capable of providing hydrophilic, defect free surfaces for initial deposition.

The SAM technique involves chemically reacting molecules with a short polymer chain to a surface, as illustrated in Fig. 3. The chemicals used in these types of surface preparations are typically polymer chains approximately 8-20 molecules long. On one side of the polymer chain is a reactive functional group, capable of forming a chemical bond with a surface. In this effort a thiol ($-\text{SH}$) functional group capable of creating a chemical bond with gold or copper was used. It should be pointed out that the “coating” used in this process is more than just paint, as the chemical bond between the molecule and the metal surface is of a permanent nature. The other end of the polymer chain is a hydroxyl ($-\text{OH}$) surface group that will form a chemical bond with the precursors used in the ALD process. Although other functional groups are possible, the hydroxyl group will form the strongest bond with the ALD treatment. The self-

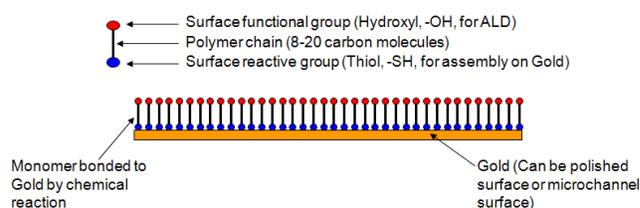


Figure 3. Illustration of hydrophilic surface preparation using self-assembled monolayer technique. While one end of the molecule chemically reacts with the surface, the hydrophilic side of the molecule points away from the surface creating a surface that is ready for ALD treatment.

assembly process is naturally self-extinguishing after one layer of molecules assembles on the surface, since only one of the functional groups on the polymer chains reacts with the gold or copper surface while the other functional group is non-reactive. Furthermore, the reactive end group does not react with the surface functional group.

In the ALD process the metal surface needs to be kept very clean so that the chemical bond to the surface is strong. Chemical cleaning methods were used, since mechanical cleaning methods will be difficult on the micro-channel surfaces. The self-assembly process occurs spontaneously on the surface when a solution of the molecules in either a liquid or vapor form comes into contact with the surface. Typical thiol chemistry involves immersing a cleaned surface in an alcohol/SAM reagent mixture to allow the self-assembly process to occur. In this case, a thiol with a relatively long carbon chain was chosen because longer chained SAM molecules tend to pack and organize better than shorter chain SAM molecules. Further, the SAM was terminated with a hydroxyl group to make the surface hydrophilic.

In addition to strong bonding, the SAM covers surface defects on the metal surface, which will insure that a pinhole free ceramic coating is deposited. The elastic properties of the SAM also make the ceramic coating more strain tolerant, reducing stresses caused by mismatch in thermal expansion coefficient between the ceramic coating and metal MCC. Increased compliance also aids erosion protection.

II. COATING IDENTIFICATION

Fig. 4 shows an illustration of the complete coating, including the alumina, SAM, and metal plating layers on the copper MCC surface. It should be noted that the gold layer is not required as the SAM can be deposited directly on copper. However, the SAMs generally bond better to gold than copper and the Ni/Au layer certainly doesn't hamper the passivation protection of the coating.

III. EXPERIMENTAL RESULTS

A. Erosion, Corrosion, Thermal Cycling

Three micro-channel samples were fabricated for each of the passivation tests, including a baseline (all copper), gold plated and an alumina (by ALD) coated sample. The alumina sample was first coated with gold, and a thiol based SAM

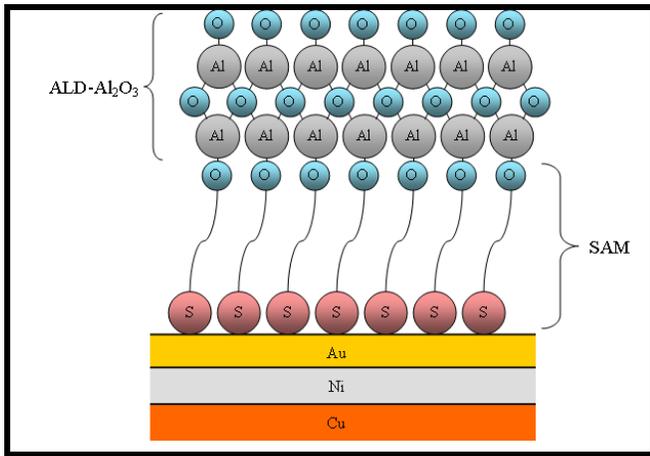


Figure 4. Illustration of coating: alumina coating deposited on a self assembled monolayer on a gold plated copper surface

before 10-100 nanometers of alumina was deposited by ALD. The thickness of the coating results in negligible thermal resistance. Several test apparatus were fabricated for the different passivation processes. In all, 3 different passivation tests were performed, including erosion, corrosion and thermal cycling.

A multipurpose test set capable of high liquid velocities and accelerated electrochemical corrosion was developed to test for erosion and corrosion (Fig. 5). The test article design includes a lid with a step to eliminate flow area above the fins and a means for applying electrical current normal to the surface (Fig. 6). The resulting average fluid velocity through the channels was 1.9 m/s.

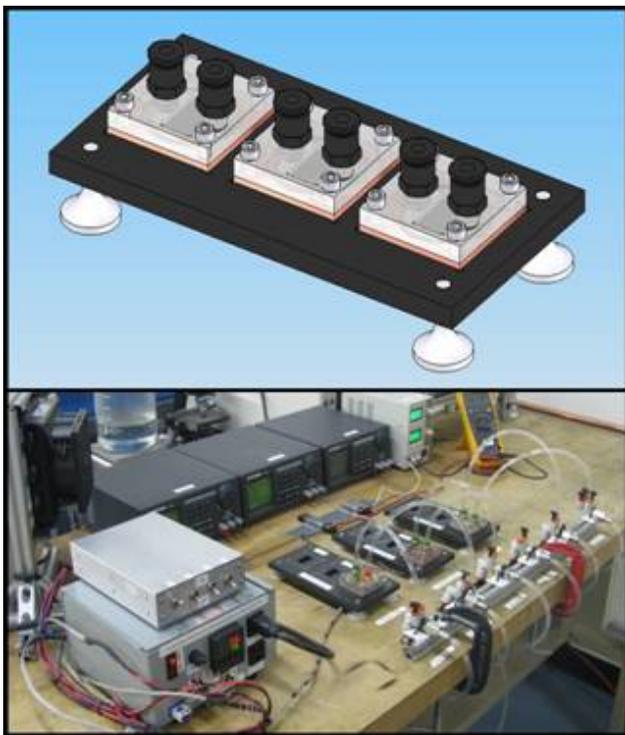


Figure 5. Illustration corrosion and erosion test apparatus.

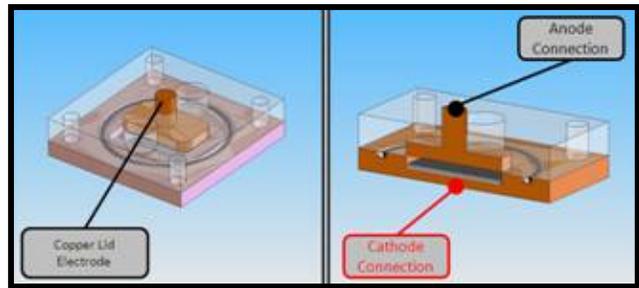


Figure 6. Illustration of corrosion test article.

Currently, Ni/Au thin films are susceptible to erosion, exposing bare copper to the DI-H₂O. Our goal was to show the ceramic coating would be impervious to these effects. Visual inspection was used after high velocity testing, but in all cases including bare copper, there were no detectable traces of erosion. In future work, higher velocities at longer duration will be used.

Several thermal cycling tests were performed to demonstrate the survivability of the alumina coating under thermal stress. The most impressive test involved heating a copper and an alumina coated micro-channel side by side on a hot plate. At temperatures exceeding 300°C, the alumina coated sample showed no oxidation resistance, which would be expected if thermal expansion were to cause delamination of the coating (Fig. 7). The baseline copper sample showed gross oxidation (a form of corrosion) as expected. Other tests were also run where the samples were cycled between room temperature and 100°C in water several dozen times without degradation.

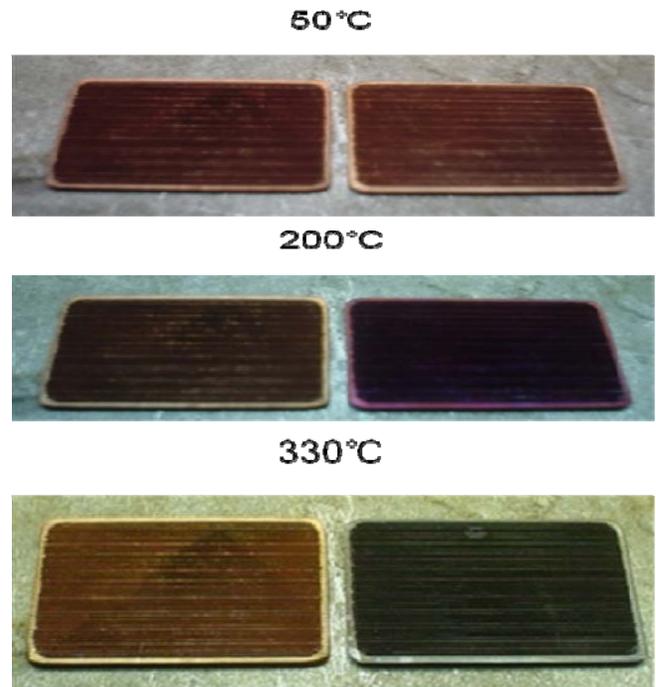


Figure 7. Thermal cycling results for copper and alumina coated samples.

An accelerated corrosion test was also performed where a voltage was applied across the surface through an electrically conductive salt water solution. As expected, the copper (Fig. 8) and gold plated (Fig. 9) samples showed significant, visible corrosion. The alumina (on gold) coated sample showed negligible corrosion (Fig. 10). Future work involves using electrochemical analysis to quantify corrosion rates.

IV. CONCLUSIONS AND FUTURE WORK

Thin film (<100 nanometer) alumina coatings deposited by ALD are promising candidates for passivation coatings in MCCs and other liquid cold plates. In experimental thermal cycling, erosion, and corrosion tests, ceramic ALD coatings outperformed state of the art metallic coatings. Future work involves long duration life testing, more quantitative electrochemical analysis, and exploration of other ALD deposited ceramics, such as hafnia.

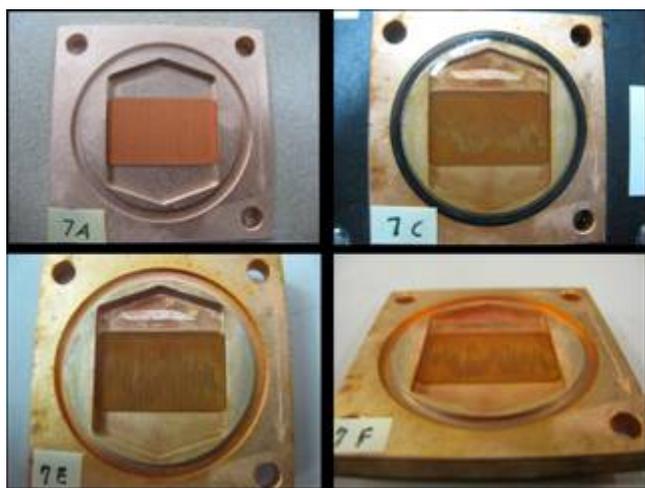


Figure 8. Results for corrosion testing of baseline copper samples are shown. The top left picture is before testing, the others are post testing.

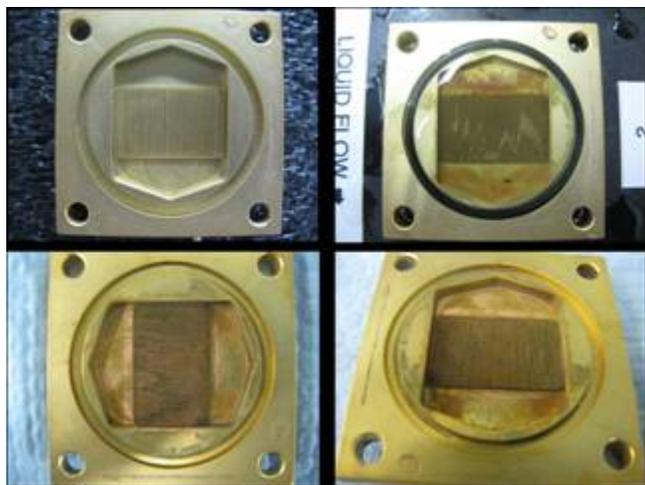


Figure 9. Results for corrosion testing of gold plated samples are shown. The top left picture is before testing, the others are post testing.

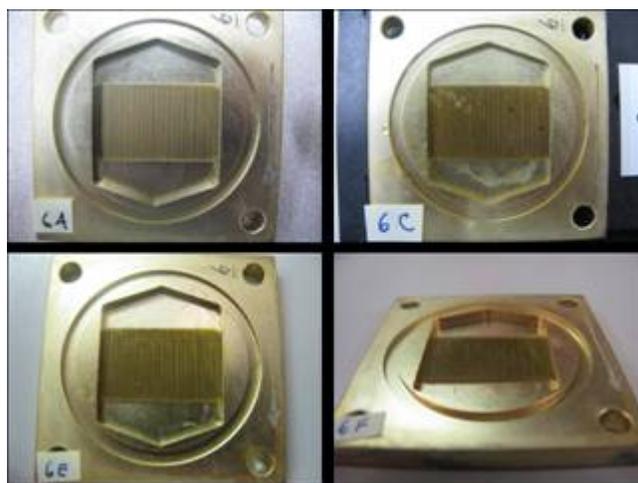


Figure 10. Results for corrosion testing of alumina (by ALD) on gold plated samples are shown. The top left picture is before testing, the others are post testing.

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