Effects of the Printed Wiring Board Process on Ceramic Thin-Film Capacitors Integrated into Printed Wiring Boards

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Abstract: Most research in integrating thin-film ceramic capacitors layers directly into printed wiring boards (PWB) has focused on forming capacitors on metal foil at relatively high temperatures. An equally significant challenge however, resides in the PWB embedding process. In this process, the capacitor may be subjected to aggressive processes and chemicals that may affect its mechanical or chemical integrity. This work investigates effects of some of the PWB chemical processes. Thermodynamic predictions suggest that acid-based systems are deleterious to barium titanate. Exposing barium titanate thick-film capacitors to the various etching chemistries confirmed that barium titanate is not completely stable in these solutions. Acid-based solutions aggressively dissolve the barium titanate but alkaline-based solutions are more benign. Thin-film capacitors were then formed on smooth copper foil to a thickness of approximately 700 nanometers. The capacitors were electrically characterized and then exposed to the chemistries used in the PWB process. Exposure to the acid etching solution had very severe effects on the electrical properties.

Key words: thin-film, embedded ceramic capacitors, printed wiring board, etching.

1. INTRODUCTION

Integrating decoupling capacitors into printed wiring boards frees up surface real estate, allowing additional board space for more silicon and other devices. The ability to locate devices immediately above decoupling capacitors shortens interconnect distances, which decreases the lead inductance and increases the maximum frequency of operation (1,2). One crucial packaging need, however, is high capacitance density. Considerable effort has been applied in recent years to create robust films with capacitance densities greater than 1μF/cm². Recently such films on copper foil have been achieved by chemical solution deposition approaches using barium titanate based compositions (3,4,5).

One proposed process flow (6) for integrating thin-film ceramic capacitors into printed wiring boards comprises forming a thin-film capacitor structure on copper foil. The thin-film capacitor layer is prepared by chemical solution deposition and sintered to yield a high capacitance density dielectric. A top electrode is deposited over the entirety of the dielectric by a variety of technologies, such as sputtering, thermal vacuum evaporation or electroless plating of platinum, nickel or copper.

Following this, the foil is laminated to a laminate prepreg structure used to fabricate inner layers for multilayer printed wiring boards. A combination of etching steps is then undertaken to form the final capacitor structure. The inner layer containing the capacitors may then be incorporated inside a multilayer printed wiring board using standard PWB processes. In this and in other proposed process flows that integrate thin-film capacitors into PWBs, the ceramic dielectric is exposed to some or all of the solution chemistries used in the printing wiring board process.

1. PWB PROCESS AND CHEMISTRIES

TABLE 1: Chemicals used in the PWB Process

Copper Etching	Ferric chloride in hot hydrochloric acid Cupric chloride in hot hydrochloric acid Cupric chloride in hot ammonium hydroxide
Photoresist stripper	Hot potassium hydroxide
Copper adhesion treatment	Hydrogen peroxide in dilute sulfuric acid followed by alkali cleaners

Table 1 lists the various processes and chemicals used in the printed wiring board process. For example, etching copper may expose the dielectric to ferric chloride in 2N hydrochloric acid at 70ºC or cupric chloride in 20% ammonium hydroxide at 50ºC. Removal of the photoresist may expose the dielectric to hot potassium hydroxide. The foil may also have a treatment consisting of exposure to dilute hydrogen peroxide in dilute sulfuric acid to enhance its adhesion to prepreg.

2. THERMODYNAMIC PREDICTIONS

Thermodynamic analysis of the effects of etching solutions and the copper adhesion treatment on barium titanate were undertaken using a program specifically designed to predict and calculate the concentrations of the equilibrium species. Figure 1 shows the predicted outcome of barium titanate exposed to 2.4 M hydrochloric acid containing 0.8 moles of ferric chloride at various temperatures. The analysis predicts that barium titanate is unstable in hydrochloric acid-based etching solutions reacting to form barium chloride and titanium dioxide.

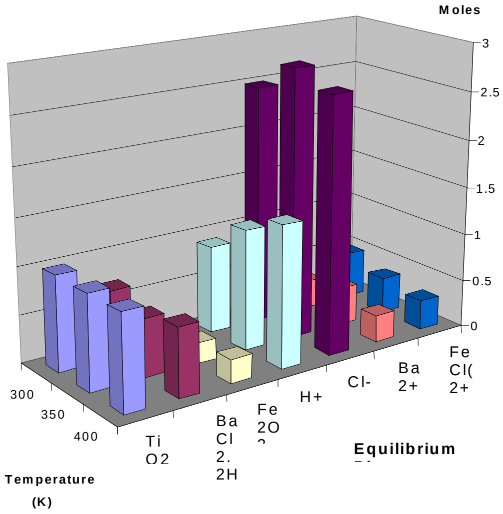

FIGURE 1: Acid Corrosion Products of Barium Titanate at Various Temperatures

Figure 2 shows the expected outcome of barium titanate exposed to 0.67 moles ammonium hydroxide containing 0.39 moles ammonium chloride at 50ºC. As can be seen, barium titanate is predicted to be much more stable in alkali than the hydrochloric acid-based etching system reacting to form small quantities of barium chloride and titanium dioxide.

Figure 3 shows the expected outcome of exposing barium titanate to 5% hydrogen peroxide in a dilute solution of sulfuric acid. As can be seen from the predicted products, barium titanate appears to be very unstable in this solution reacting to form titanium dioxide and barium sulfate.

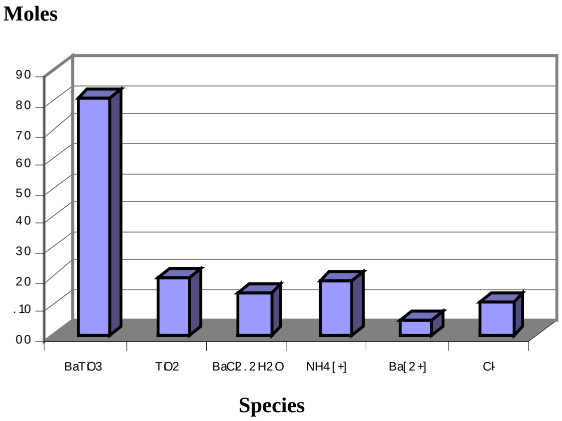

Figure 2: Alkali Corrosion Products of Barium Titanate

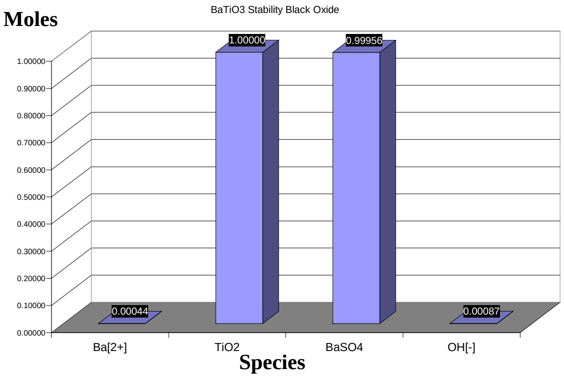

FIGURE 3: Stability of Barium Titanate in Sulfuric Acid containing Hydrogen Peroxide

3. KINETIC MEASUREMENTS

While the thermodynamics suggest that exposing barium titanate to the printed wiring board chemistries is unfavorable, the process may be feasible if the rate of reaction is slow enough. A series of experiments were

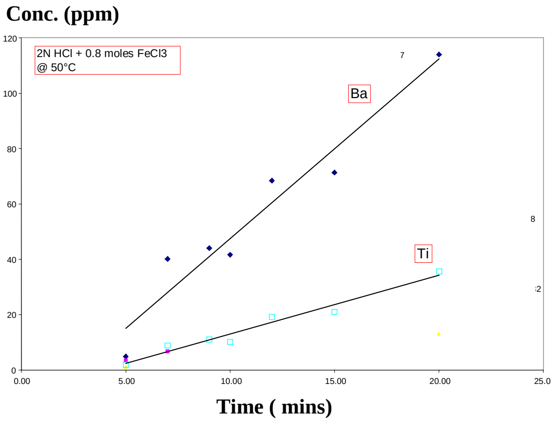

FIGURE 4: Barium Titanate Corrosion in Acid Etch Solution

undertaken to determine the rate of reactions. Figure 4 shows the results of ICP analysis of the corrosion solution after a barium titanate thick-film capacitor had been exposed to the hydrochloric acid etch solution for varying times. As can be seen, there is a selective and rapid removal of barium from the barium titanate. Figure 5 shows the barium titanate corrosion in alkali etch solution. In this case, the rate of loss of barium is 20X slower. Figure 6 shows the results of exposure to hydrogen peroxide in sulfuric acid. This appears to show selective leaching of the titanium from the barium titanate with no evidence of barium leaching. This conflicts with the thermodynamic predictions for this solution.

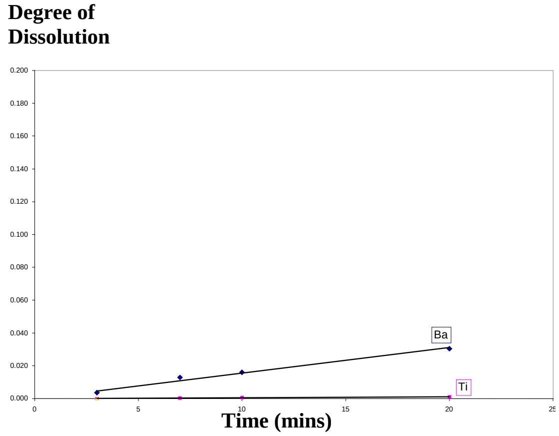

FIGURE 5: Barium Titanate Corrosion in Alkaline Etch Solution

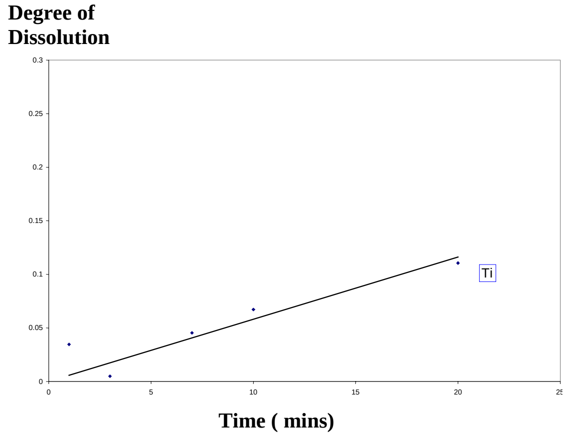

FIGURE 6: Capacitor Corrosion in Hydrogen Peroxide in Sulfuric Acid.

A summery of the data is presented in Table 2

TABLE 2: Summary of Dissolution Mechanism and Reaction Rates

Chemistry	Ba Loss Rate ($mg/cm^2/min$)	Elements Selectively Dissolved
Acid etch	0.17	Ba
Alkaline etch	0.008	Ba
Hydrogen peroxide in sulfuric acid	-	Ti

4. ELECTRICAL RESPONSE TO EXPOSURE

Thin-film barium strontium titanate (BST) layers were fabricated on copper foil by RF magnitron. The dielectric was crystallized at 900ºC under an atmosphere of 10^{-9} atm pO_2 followed by sputtering platinum electrodes onto the BST through a shadow mask. The stack was finally heat treated at 550ºC at $1x10^{-5}$ Torr O_2 to fully oxidize the dielectric. Sputtering was chosen to deposit the dielectric to ensure the dielectric had little or no porosity that might cause measurement errors due to moisture ingress. Samples were then dipped into the acid etching chemistry for various times, rinsed with de-ionized water and dried. Capacitance and loss factor values for zero and 6 minutes are shown in Figures 8 and 9. As can be seen in Figure 8, the original capacitor shows good properties out to 20 volt bias but in Figure 9, after 4 minutes exposure, the dielectric shows increased loss tangent at 7 volts and complete breakdown at 15 volts.

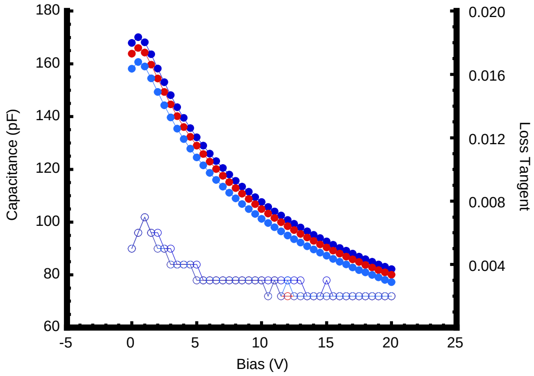

Figure 8: Capacitance and Loss Tangent for a Series of as Made BST Capacitors.

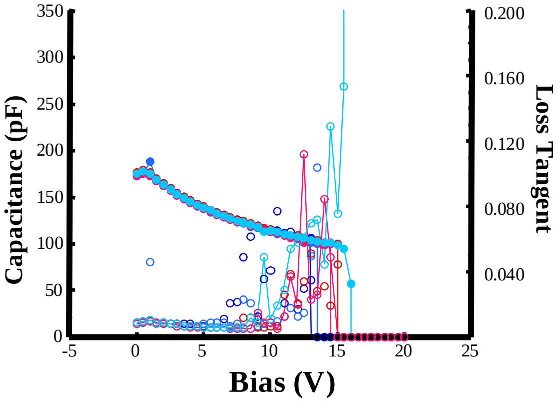

Figure 9: Capacitance and Loss Tangent Values for a Series of Thin-Film BST Capacitors after Exposure to the Acid Etching Solution for 4 Minutes.

Leakage current also proved to be sensitive to chemical exposure to the hydrochloric acid based etching chemistry. As shown in Figure 10, the leakage current showed negligible change for up to 1 minute of exposure but thereafter the leakage current became significantly higher with considerable variations in values.

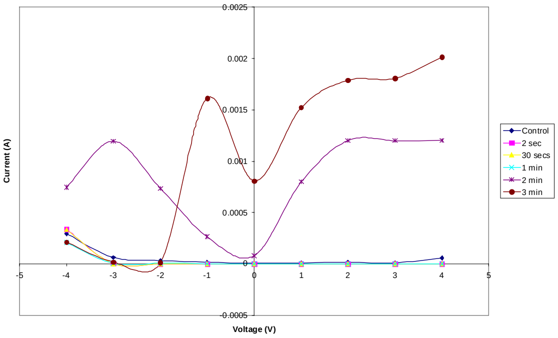

FIGURE 10: Leakage Current as a function of time in hydrochloric acid based etching solution

5. DISCUSSION

It is clear from these initial experiments that fired-on-foil capacitors cannot be incorporated inside a printed wiring board using the traditional acid etching solutions. Alkaline etching solutions, however, may be feasible. It is postulated that the degradation seen in the electrical properties is due to surface deposits of reaction products. These may or may not be removable with the PWB rinsing process. Complete removal of surface deposit may restore the properties to the original values. However, even if this can be achieved, long term reliability will have to be assessed to determine if exposure to any of the PWB chemistries is a major issue.

6. CONCLUSIONS

Embedding thin film fired-on-foil capacitors inside printed wiring boards will require substantial attention to the processes used in the embedding process and a thorough evaluation of long term reliability.

7. REFERENCES

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