# Hydrothermal growth of BaTiO$_3$ thin films on printed circuit boards for integral capacitor applications

**C. K. Tan · Gregory K. L. Goh · D. Z. Chi · Albert C. W. Lu · B. K. Lok**

**Abstract** Polycrystalline BaTiO$_3$ films were hydrothermally grown on Ti-coated substrates from 80°C to 200°C. Films grown at 200°C exhibited the lowest dielectric loss of around 0.1. Proton incorporation was more severe for the 80°C film resulting in higher dielectric losses and leakage currents about two orders of magnitude higher. Post deposition oxygen plasma treatment removed incorporated protons and reduced the loss tangent but did not reduce defect density. As such, the leakage current of the 80°C film remained high. The films had dielectric constants of 275 to 675 from 100 Hz to 100 kHz and a value of 67 from 100 MHz to 3 GHz.

**Keywords** BaTiO$_3$ · Hydrothermal · Integrated passives · Dielectricity · Leakage current

## 1 Introduction

Integration of passive components into printed circuit boards (PCB) offers the promise of better performance, greater robustness and higher parts efficiency. Not only does direct growth of passives onto boards do away with solder interconnects and optimize area utilization, it also allows for higher feature resolution and greater flexibility in exploring novel architectures in electronic design for optimized performance. Thin perovskite films grown directly on circuit boards have the potential to achieve high capacitance density and replace current soldered-on discrete ceramic capacitors. The challenge lies in ensuring that film fabrication temperatures remain low for process compatibility with polymer-based boards.

Hydrothermal deposition is an attractive method for its low-temperature solution processing, as well as its relatively low operation and startup costs as compared to other film growth methods. It has been demonstrated [1–3] that in a sufficiently alkaline solution of Ba$^{2+}$ ions, substrates covered with Ti-containing precursors can be made to react chemically to form a BaTiO$_3$ film. Depending on the nature and concentration of the precursors, crystalline film formation can be achieved at temperatures as low as 40°C [4].

Growth at low temperatures (<100°C) routinely leads to higher than acceptable dielectric losses and is attributed to the presence of high levels of hydroxyl incorporation and accompanying defects in the films. Oxygen plasma treatment [5] and heat treatment [6–7] and have been used to remove the hydroxyl groups to improve dielectric loss. Most of the prior studies report dielectric properties up to 1 MHz, but integral capacitor applications operate in the microwave range (~GHz) and only one group [5] has reported the dielectric properties of hydrothermal BaTiO$_3$ films in the GHz range. Therefore, there is need for further study of the electrical properties of hydrothermal BaTiO$_3$ films in this frequency range.

In this study, polycrystalline BaTiO$_3$ thin films were grown on Ti-coated PCB substrates at temperatures below the $T_g$ of the polymer-based substrates (<200°C) to demonstrate the compatibility of the process in patterning desired architectures of integrated capacitors on the PCB. Oxygen plasma as a post deposition treatment in lieu of conventional heat treatments at 300°C was investigated as a potential method to improve dielectric and leakage current performance. The dielectric performance of the film in the microwave range (100 MHz to 3 GHz) was also studied.

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## 2 Experimental

Hydrothermal film growth on PCB substrates (copper cladded BT 832 epoxy laminate) was conducted in 40 ml Teflon-lined acid digestion bombs (Parr). The PCB substrate was coated with a 1 $\mu$m thick titanium layer on one side of the substrate by DC magnetron sputtering. 1 cm square substrates were suspended 20 mm from the liner base (with the Ti facing down) using custom Teflon holders. 25 ml of $Ba^{2+}$ precursor was prepared by dissolving appropriate amounts of Reagent grade $Ba(OH)_2$ (Alfa Aesar) in boiling, nitrogen-aerated water to give a 1 M solution. The bombs were sealed immediately after addition of the solution and placed in convectional ovens at reaction temperatures of 80°C, 150°C and 200°C for 24 h. After reaction and cooling to room temperature, the films were cleaned in warm acetic acid to remove any surface carbonates. Selected films grown at 80°C were subjected to oxygen plasma treatment in an Oxford RIE system at 300 mTorr, 300 W for 15 min.

X-ray diffraction (XRD) studies were done using Cu$K\alpha$ radiation on a Bruker D8 GADDS diffractometer equipped with an area detector. The microstructure and morphology of the $BaTiO_3$ films were examined by scanning electron microscopy (JEOL JSM6700F). The average thickness of the films was obtained by step measurement of lithography-patterned and etched features of equivalent films grown on smooth $Al_2O_3$ or Si substrates.

For frequencies up to 100 kHz, the dielectric properties of the films were determined with an impedance analyzer (HP4194A). Gold electrodes of 1 mm diameter were deposited via a shadow mask onto the film. The unreacted Ti served as the bottom electrode in this parallel plate capacitor configuration. High frequency dielectric characteristics from 100 MHz to 3 GHz were extracted from scattering parameter measurements using a network analyzer. Integral capacitors were fabricated using the hydrothermal film and sputtered copper electrodes. The floating capacitor configuration was adopted to achieve ultra-low parasitic self-inductance for enhanced broadband performance. Leakage current measurements were determined from I-V testing using the same capacitor structure and gold electrodes with a pico-ammeter (HP4140B) that also served as a DC voltage source.

## 3 Results and discussion

### 3.1 Film structure and morphology

From XRD studies (Fig. 1), it was observed that the $BaTiO_3$ films were not only polycrystalline, but also had a cubic structure, instead of the thermodynamically stable tetragonal phase, irrespective of the growth temperature. The lattice pa-

**Table 1** Lattice constants and thicknesses of hydrothermal $BaTiO_3$ films grown at different temperatures

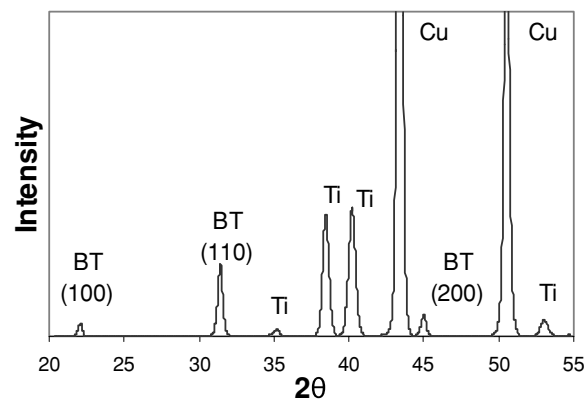| Deposition Temp. (°C) | Lattice parameter (Å) | Film thickness (nm) |
|---|---|---|
| 80 | 4.040(2) | 260 |
| 150 | 4.034(2) | 200 |
| 200 | 4.018(2) | 155 |
| Plasma | 4.039(2) | 260 |



**Fig. 1** XRD pattern of $BaTiO_3$ film grown at 80°C for 24 h.

rameter of the films calculated from the (200) peak position, summarized in Table 1 (which also shows the film thicknesses), showed that the cubic lattice parameter decreased with increasing growth temperature. Using the lattice parameters from Table 1 to calculate the unit cell volume, it is seen that the volume reduces from 65.9 Å$^3$ for the 80°C film to 64.9 Å$^3$ for the 200°C film, approaching the value (64.4 Å$^3$) for that of the ideal unstrained $BaTiO_3$ tetragonal phase. This result is consistent with observations for hydrothermally synthesized $BaTiO_3$ powders where the lattice parameter increased with increasing concentrations of defects like cation vacancies and hydroxyl groups as the growth temperature was reduced [8]. It has been proposed that these defects reduce the long-range attractive Coulomb forces, leading to the expansion of the lattice and loss of tetragonality [9]. Therefore, this indicates that the film grown at 80°C contained more defects than the film grown at 200°C and it is not surprising that tetragonal $BaTiO_3$ can been grown hydrothermally at 220°C when the defect level is even lower [10].

Examination of the surface morphology of the films revealed that there was a significant difference between the films grown at 80 and 150°C and that of the film grown at 200°C. As shown in Fig. 2, nucleation and growth of the films was continuous, with the larger grains in Figs. 2(a) and 2(b) being islands that nucleated earlier. At the 200°C growth temperature, the film had the most uniform grain size distribution because the nucleation rate was the highest, as would be expected for the highest growth temperature. These
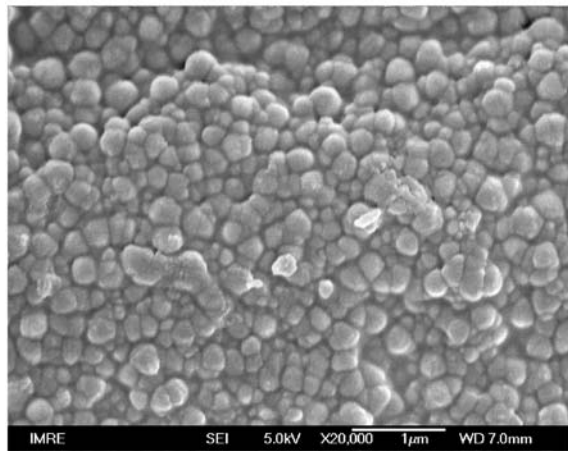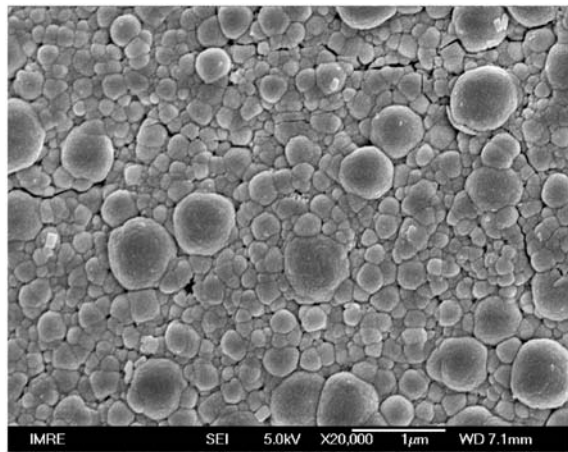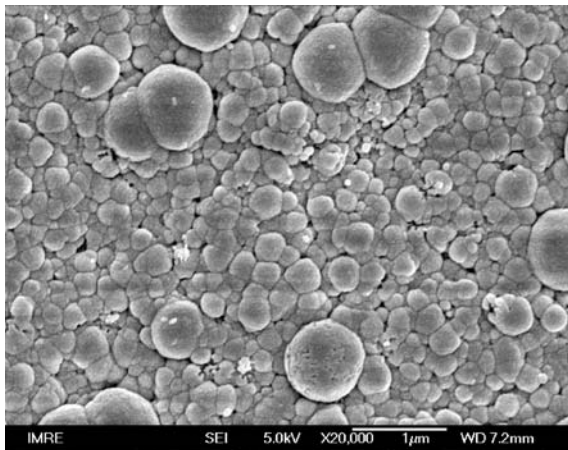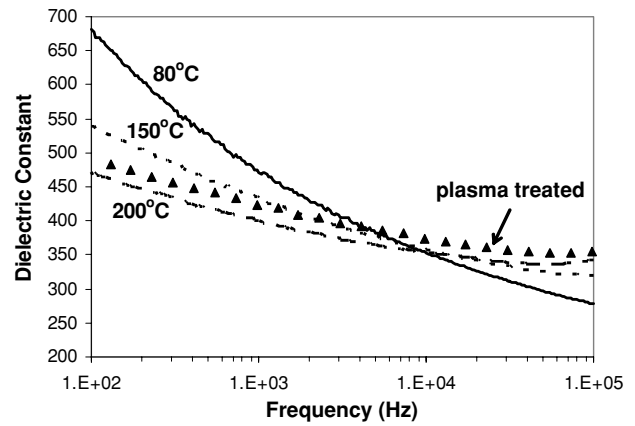
**Fig. 2** SEM of surfaces of BaTiO$_3$ films grown at (a) 80°C, (b) 150°C, and (c) 200°C
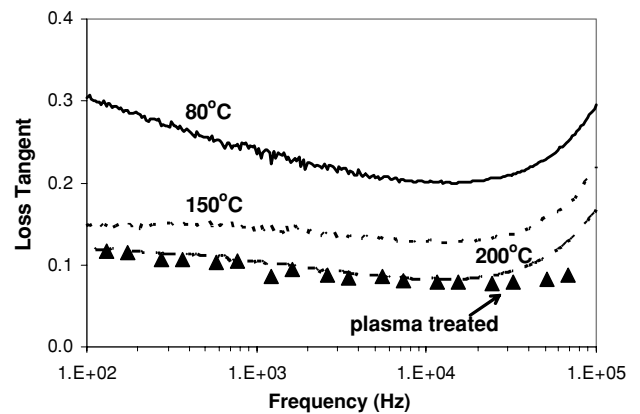
observations are consistent with Avrami-type continuous nucleation and growth [4].

### 3.2 Dielectric properties

As shown in Fig. 3, the dielectric constant of the BaTiO$_3$ films at frequencies lower than 10 kHz increased with de-





**Fig. 3** (a) Dielectric constant, and (b) dielectric loss of BaTiO$_3$ films grown at different temperatures and for one film subjected to oxygen plasma treatment after growth at 80°C

creasing growth temperature, but converged to a common range between 275 and 350 as the frequency increased beyond 10 kHz. The dielectric loss was also strongly frequency dependent (note that the upward curve of the loss after 10 kHz is due to the imminent resonance of the capacitor setup and is a limitation due to design rather than material property). Such dielectric behavior has been linked with proton incorporation as hydroxyl groups in the perovskite lattice due to incomplete dehydroxylation during hydrothermal growth [5–7]. The hydroxyl groups contributed to the overall polarization of the film via dipole polarization resulting from reconfiguration of the hydroxyl group [7] and interfacial polarization (space charge) due to proton hopping [6].

For all growth temperatures, a gradual reduction of the dielectric constant with increasing test frequency was observed instead of a sharp drop-off at a specific frequency. To account for this, it has been proposed that not all the hydroxyl groups are equivalent, being located not only in the lattice, but also at the surface and grain boundaries [7]. The different relaxation frequencies of the hydroxyl groups at these non-equivalent sites would then overlap, leading to the gradual decline. The

present authors believe that in addition to this, an overlap of the relaxation frequencies also occurred between the interfacial polarization mechanism and the dipole polarization mechanism. As indicated earlier by the smaller lattice expansion, the films grown at higher temperatures had smaller dispersions in the dielectric constant as they had fewer incorporated protons and therefore fewer hydroxyl groups. As such, the 200°C film had the lowest dielectric constants and loss tangents.

The dielectric loss over the range 100 Hz to 100 kHz was also lower for films grown at higher temperatures. Dielectric loss in hydrothermal films has been attributed to both the time lag between the hydroxyl dipole switching rate and the frequency of the applied ac field [7] and migration losses due to proton hopping [6]. Again, since the concentration of hydroxyl groups decreased with increasing growth temperature, such losses would necessarily be lower as the deposition temperature employed was raised.

Typically, post deposition heat treatments of around 300°C or higher are employed to remove the incorporated protons and lower the dielectric losses (not unexpectedly, the dielectric constant also falls) [6, 7]. Such high temperatures are not compatible with polymer based PCBs. Balaraman and co-workers observed that the use of oxygen plasma as a post-deposition treatment (without the application of a heat source) lowered the dielectric losses from 28% to 6% at 100 kHz [5]. In this study, Fig. 3 shows that the post-deposition oxygen plasma treatment of a film grown at 80°C lowered the dielectric constants and loss tangents to values similar to the 200°C film, indicating that the proton concentration had been reduced to levels similar to that in the 200°C film.

The extracted dielectric constant from scattering parameter measurements of the integral capacitor grown at 80°C (but not subjected to oxygen plasma treatment) is shown in Fig. 4. It was observed that resonance occurred above 1.5 GHz as a
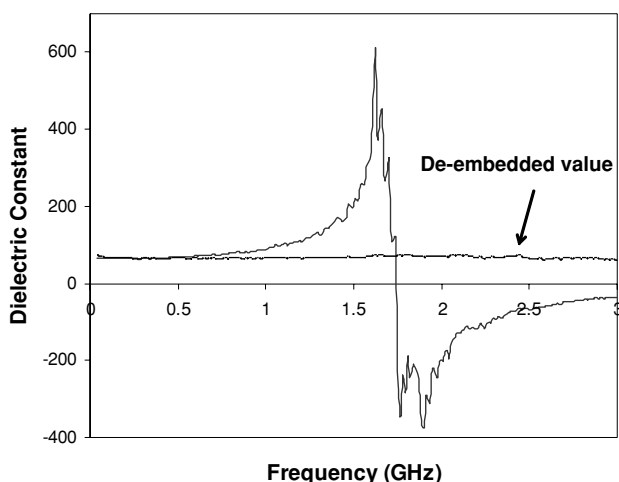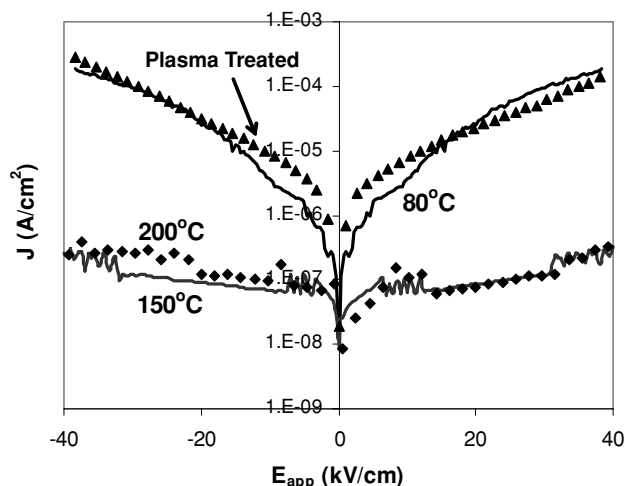


**Fig. 5** Leakage current behavior of hydrothermal BaTiO$_3$ films grown at different temperatures and with oxygen plasma treatment

result of a parasitic self-inductance of 13.3 pH. After the de-embedding process, the extracted dielectric constant value of approximately 67 showed good stability up to 3 GHz. Since this value is much lower than the value of ∼275 obtained at 100 kHz, there could have been further dielectric relaxation somewhere between 100 kHz and 100 MHz. Further work is required to confirm this relaxation and understand its cause.

### 3.3 Leakage currents

Current-voltage measurements of the hydrothermally grown BaTiO$_3$ films over the range of ±1 V (Fig. 5) revealed that the leakage currents of the 150 and 200°C films were about two orders of magnitude lower than for the 80°C film. Leakage mechanisms in hydrothermal BaTiO$_3$ films have been linked to defect dependent mechanisms like Schottky-barrier and Poole-Frankel conduction [7, 11, 12]. In hydrothermal films, proton incorporation must be accompanied by cation vacancies to maintain charge neutrality of the lattice. These vacancies are believed to be the defects involved in the leakage current mechanisms. Since proton incorporation in the films grown at higher temperatures was lower, the defect concentration would also be lower and would explain the correspondingly lower leakage currents observed.

Figure 5 also shows that oxygen plasma treated films initially grown at 80°C showed no improvement in leakage current over the as-grown films. It is known that the removal of hydroxyl groups would necessitate the creation of oxygen vacancies for charge compensation according to,

$$2(OH_o^\bullet) \Leftrightarrow V_o^{\bullet\bullet} + O_o + H_2O \qquad (1)$$
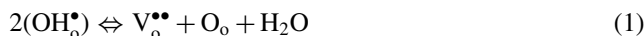
where the water molecules created are removed from the surface first and then followed successively by water molecules



**Fig. 4** Dielectric constant extracted from high frequency impedance characterization of a BaTiO$_3$ film grown at 80°C

further from the surface [13]. Balaraman and co-workers [5] not only demonstrated that the oxygen plasma eliminated hydroxyl groups and lowered the dielectric loss, but also believed that the reactive oxygen species in the plasma compensated for the oxygen vacancies according to,

$$O''(plasma) + 2(OH_o^\bullet) \Rightarrow 2O_o + H_2O \qquad (2)$$
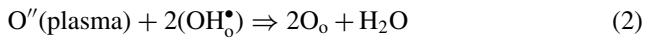
Since the oxygen vacancies are required to balance the presence of the cation vacancies to maintain overall charge neutrality, their elimination would require the removal of the cation vacancies or the formation of some other positively charged defects.

The elimination of hydroxyl defects does not necessarily lead to reduced expansion of the lattice since the cation vacancies also disrupt the attractive forces in the lattice. Table 1 shows that the lattice parameter stay relatively unchanged after oxygen plasma treatment, suggesting that the cation vacancies were still present. This would explain why the leakage current of the 80°C film remained high even after the oxygen plasma treatment.

## 4 Conclusion

Hydrothermal BaTiO$_3$ films were grown on Ti-coated PCBs at 80, 150 and 200°C to study the effect of the growth temperature on the electrical properties. The film grown at 200°C had the least lattice expansion, indicative of the fact that such films had the lowest concentrations of incorporated protons and accompanying cation vacancy defects. Not surprisingly, this film had the lowest loss tangents. Oxygen plasma treatment of the 80°C film was effective in lowering the loss tangents to values similar to the 200°C film but was not able to reduce the leakage current of the 80°C to the values obtained by the 150 and 200°C films that were 2 orders of magnitude lower. This is because the oxygen plasma eliminated hydroxyl groups but did not reduce the overall defect density. The dielectric constant of the 80°C film at 100 MHz to 3 GHz was 67. This was much lower than the values of 275 to 675 obtained for the 100 Hz to 100 kHz region and a dielectric relaxation phenomena is believed to have occurred somewhere between 100 kHz and 100 MHz.

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