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On the porosification of LTCC substrates with sodium hydroxide

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ABSTRACT

Outstanding material properties of low temperature co-fired ceramics (LTCC) make them the technology of choice when targeting the realization of robust, highly integrated substrates or packaging solutions for micromachined devices. However, the relatively high permittivity limits their utilization in high-frequency applications, as in addition defined areas with reduced permittivity in one single LTCC layer would be most beneficial. The wet-chemical porosification method under alkaline conditions is a novel and most advantageous approach which can be applied for permittivity reduction through locally embedding air into the LTCC surface in its *as-fired* state with low impact on the surface characteristics. The resulting porosity of the LTCC substrates after the etching process is strongly affected by the LTCC tape composition as well as the etch parameters. Since the chemical composition of the tape is desired to be unaltered, optimizing the etching parameters, namely etchant concentration, etching time, and bath temperature is a reasonable procedure which allows tailoring the porosification process for the LTCC tapes in their *as-fired* state.

In this work the etching behavior and surface morphology of the LTCC substrates have been studied, both qualitatively and quantitatively, and detailed gravimetric and roughness measurements, as well as porosification depth investigations, were carried out. The conducted analyses suggest a dominating reaction-controlled mechanism for the etching process. In addition to generating a tailored porosity in the surface-near region, overall thickness reduction of the LTCC through the overall dissolution of the LTCC surface under a defined etching condition was also possible. The experimental results were finally fitted into a nonlinear polynomial model for providing an experimental basis in order to identify the most crucial parameters to achieve a tailored porosity.

1. Introduction

Low temperature co-fired ceramics (LTCC) are composites of glass and ceramics which can be most beneficially used for the realization of miniaturized devices and robust substrates [1–5]. LTCC technology allows the combination of individual layers with different functionalities such as high permittivity and low dielectric loss into a single multilayer laminated package and thereby to achieve multi-functionality in combination with a high integration and interconnection level. In addition, it also provides the possibility to fabricate three-dimensional, robust structures enabling in combination with thick film technology the integration of passive, electronic components, such as capacitors, resistors, and inductors into a single device [6–11].

The attractive thermal, mechanical, and dielectric properties of LTCC materials, as well as their compatibility with thick films of high electrical conductivity, such as silver or gold, make them most suitable for various applications such as in wireless communication or in automotive radar systems [12–16].

However, the relatively high permittivity of LTCC materials limits their application in high-frequency devices and the integration of radiating elements such as patch antennas requiring defined regions of low permittivity to achieve optimized radiation performance.

In order to overcome this problem, several approaches have been already examined. A straightforward approach for lowering permittivity is the addition or replacement of some LTCC constituents with low permittivity materials. These materials are mainly introduced to LTCC green tapes before the firing process. Therefore, several novel compositions for LTCC substrates have been developed to reduce the permittivity of LTCC [17–20].

Another approach is reducing the permittivity by introducing air as a very low permittivity material ($\varepsilon_r = 1$). Basically, air can be implemented into the LTCC through different methods. For example lowering the firing temperature by reducing the densification process and hence, the bulk density of the LTCC, results in a decreased permittivity. Another approach for introducing air is the so-called sacrificial template technique, in which a “pore former” material is mixed

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with the slurry before the tape casting process and then eliminated during the firing process leaving porosity in the sintered LTCC. Different kinds of pore former materials including ploy (methyl methacrylate), graphite, and carbon black have been reported in literature [21–23]. However, all the above-mentioned methods are pre-firing processes which require alteration of the LTCC tape composition or fabrication process, and cannot be applied to commercially available LTCC tapes.

Another porosification method based on pore-formers comprises debinding the LTCC into powder, mixing the powder with slurry additives and ploy (methyl methacrylate) microspheres and then tape casting, laminating and firing [24]. Although this method can be applied to commercially available LTCC substrates, it is a multi-step fabrication method which entail additional costs and efforts. Also, due to the overall distribution of the pores in the LTCC bulk this method may also result in poor mechanical properties of the substrate. Another drawback associated with all these approaches is that they reduce the permittivity throughout the whole substrate and obtaining areas with different permittivity is still a major challenge.

Employing a combination of different substrate materials e.g. polymer and LTCC, is another option. However, this approach besides increased manufacturing costs, leads to intrinsic disadvantages such as bond wires introducing parasitic inductances as well as different coefficients of thermal expansion which result in local strain and thereby a reduced lifetime [24–27]. The addition of hallow glass microspheres in polyimide films deposited on the surface of the LTCC reduces the permittivity even further. However, these approach also suffers from locally inhomogeneous thermomechanical properties of the LTCC surface as well as a strongly undulated surface topography due to the integrated glass microspheres [28].

Wet-chemical etching is an unconventional post-fired approach for locally decreasing the permittivity through modification of surface near regions of the LTCC by embedding air on a micro or even sub-microscopic scale. This approach was first reported for DuPont 951 LTCC tape using orthophosphoric acid solution as etchant [29]. Subsequently, the porosification of various LTCC systems with the same etchant solution was investigated in more detail [30,31]. This process leads to channel-like, statistically distributed and interconnected open meso-to macropores which cause a reduction in permittivity without the need to alter the tape composition or the firing process. The main concern associated with this method is the increased roughness due to the etching process which is a challenge for further metallization. Since the patch antennas operated at high frequencies typically are placed on the surface of substrates and the electromagnetic field density is strongest at the outer shell of the conductors, the so-embedded air is most effective surface-near when directly arranged below the radiating elements [32]. Therefore, it is crucial to preserve the LTCC substrate topography after the etching process, especially when targeting in these areas the realization of thin film structures such as patch antennas or planar conductors with a high lateral resolution down to the µm-range [33]. Most recently, we reported an alternative approach for the porosification of Ceramtape GC LTCC [34] demonstrating, that in comparison with the acid-based etching, the use of an alkaline etchant offers the potential for a better surface quality with a suitable bearing plane for further metallization lines.

Furthermore, by introducing structural defects e.g. through the porosification process, physical properties of LTCC such as thermal, and mechanical properties are influenced [13,35,36]. Therefore, controlling the degree of porosification to the favorable extend is of great importance. However, for tailoring the porosity and hence, the permittivity of LTCC substrates with their well-balanced fabrication parameters, a controlled porosification process is a prerequisite [37]. Thus, the present study aims towards a detailed investigation of the recently introduced alkaline porosification process on a commercially available LTCC tape (Ferro L8) and consequently, on the identification of the etching conditions needed to achieve the pre-defined porosification results. Due to its dielectric constant $\varepsilon_r = 7.3 \pm 0.2$ and loss tangent of < 0.18% at 3 GHz Ferro L8 is suitable for cost-sensitive low-to mid-frequency telecommunications, automotive, and medical modules, components, and sensors as well as higher frequency aerospace, satellite, and other applications requesting high reliability [38–40]. To the best of our knowledge, the porosification of this tape has not been reported in the literature so far.

2. Experimental details

Basic information about the material properties of the Ferro L8 and the individual fabrication process can be found in the corresponding datasheet [38]. For porosification, the desired amounts of sodium hydroxide (NaOH) pellets (99%, from VWR) were dissolved in deionized water and served as etchant solution.

The investigated Ferro L8 substrates were square in shape, with an edge length of approximately 10 mm and a thickness of about 190 µm. The wet-chemical etching experiments were carried out in aqueous NaOH solutions at constant temperatures below 100 °C with varying concentration between 0.5 to 6 mol L^{-1}. In order to inhibit water evaporation and thus the increase of the NaOH concentration during etching, all experiments were carried out in a custom-built batch reactor. The LTCC substrates were flushed in propan-2-ol prior to the etching experiments and were held in position by a fixture made of polytetrafluoroethylene (PTFE). Prior to and after the etching process, the LTCC substrates were washed with deionized water and propan-2-ol. By the end of the etching process, the LTCC samples were dried at 110 °C in air.

Gravimetric studies were conducted by use of a Sartorius R200D microbalance with a standard deviation in the range of ≤0.02 mg where the LTCC substrates were weighed prior and after the etching process. The mass removals were normed to the initial weight of the *as-fired* substrates and stated in %.

The effects of all wet chemical etching process parameters were studied using Design-Expert® Software. Central Composite Design (CCD), was used to create an experimental design plan. The ANOVA analysis uses the entered experimental data and fits them into a mathematical model. By doing so, the results from experimental conditions which are not studied can be estimated, and the overall experimental effort can be reduced significantly. The response parameters for modeling were chosen by assessing gravimetric results and corresponding scanning electron microscope (SEM) micrographs in terms of mass removal, porosification depth (d_p), and thickness reduction.

Fracture planes after breaking and surface morphology of the *as-fired* and etched substrates were evaluated using a Hitachi SU8030 SEM applying the secondary electron (SE) detector. The micrographs of the samples were taken without any metal coating at an operating voltage of 2 kV in the charge suppression scanning mode. Further investigations on the surface topography of the LTCC substrates were conducted via 2-D surface roughness measurements using an optical profilometer (FRT MicroProf., Fries Research & Technology GmbH) with an x–y-resolution of 1 µm and a z-resolution of 3 nm.

To gain information on the porosified LTCC substrates, mercury intrusion porosimetry measurements were conducted. Mercury intrusion curves were recorded on a PASCAL 140/440 setup (Thermo Scientific) up to a maximum pressure of 400 MPa, corresponding to a minimum pore opening diameter of 4 nm. Additionally, in order to get information about the pore structures, the extrusion curves during pressure release were recorded. A minimum number of 35 specimens were tested in each run. As the flat specimens are aligned such to form stacks in the sample holder, increased volumes are found due to the intrusion of the interstitial space between individual LTCC substrates in the stack at intrusion pressures below 400 kPa. In order to correct for this phenomenon, a non-porosified stack of *as-fired* samples was tested in addition to the etched samples. Furthermore, a double intrusion treatment was conducted in the low-pressure region (< 400 kPa), only