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Constrained sintering of alumina stripe patterns on rigid substrates: Effect of stripe geometry

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Abstract

The sintering behaviour of alumina stripes deposited on sapphire substrates by micromolding in capillaries – a soft lithographic method – with lateral dimensions from 10 to 500 μm and thicknesses between 7 μm and 32 μm was studied. Unlike in continuous films, the lateral sintering strain is not negligible, thus reducing the constraint imposed by the substrate. Lateral shrinkage depends on the stripe width and thickness. The degree of constraint exerted on alumina stripes by a rigid sapphire substrate was investigated by comparing the lateral and vertical strains and is found to be dependent on stripe geometry. The formation of a delaminated, highly dense edge zone was observed at the free boundaries. Its influence on overall densification and local density distribution depends on its extension compared to the total film width. A gradient in local density was found that varied both with stripe thickness and width as predicted by finite element and discrete element simulations.

Keywords: Thick film; Simulation; Micromolding in capillaries; Constrained sintering; Alumina

1. Introduction

Patterned films are the basis of many applications such as ceramic gas sensors.[1–4] Micro-electromechanical systems,[5] and complex 3D microelectronic components based on the low temperature cofired ceramics (LTCC) technology. In practice, challenges arise from the co-sintering of these layered systems due to the geometrical constraint imposed by adjacent layers that densify at a different rate, or not at all in the case of rigid substrates. This constraint impedes the lateral shrinkage during sintering, which generates stresses and causes the overall densification to slow down compared to free sintering.[6] On the microstructural scale, the constraint may result in anisotropy along the thickness direction, showing density gradients or oriented and elongated pores.[7] Furthermore, damage in the form of cracking around pre-existing flaws in the film, debonding along interfaces or delamination of the film from the substrate can occur.[8] These phenomena have been extensively studied in continuous systems, such as symmetric or asymmetric laminates with layers made of different ceramics materials or ceramic layers on rigid substrate.[9,10]

In real film–substrate systems, the degree of constraint depends on the adhesion of the film to the substrate, which in turn is determined by the properties of the latter. Well-bonded interfaces are expected to inhibit the lateral shrinkage, while poorly bonded films may slip or delaminate during sintering, causing a non-zero lateral shrinkage. Metal substrates may accommodate the shrinkage of a ceramic film by their ability to deform plastically at elevated temperatures.[11] Furthermore, the lateral feature size is supposed to influence adhesion, as critical phenomena such as debonding frequently occur near the edges and may become dominant in patterned films of reduced width.[12]

However, theoretical analyses of sintering films on rigid substrates do not incorporate all of the above mentioned effects. The first analyses of continuous sintering films that have been carried out within the framework of continuum mechanics used the isotropic constitutive laws and the viscoelastic analogy.[13,14] The assumption of perfect constraint and the neglect of substrate

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deformation result in a complete inhibition of the lateral shrinkage, and all shrinkage is predicted to take place in the thickness direction.[15,16] However, the results of this simplified approach do not match the observed deformation, clearly overestimating the densification in many systems, especially for those sintering by solid state mechanisms.[17] The anisotropy of the sintering material has later been taken into account in an anisotropic constitutive model whose predictive capabilities proved to be much more accurate.[6,18]

On the other hand, much effort has been put into the development of simulation techniques that allow the modelling of densification and shape distortion of real sintering films. FEM simulations predict significant edge effects such as local shape distortion and density gradients along the film width and thickness[19] and some of these effects have been confirmed by experiments.[20] However, conventional FEM modelling does not assess the changing microstructure. This drawback has been compensated for in a multiscale approach that integrates kinetic Monte–Carlo model for microstructure evolution into the continuum theory of sintering.[21] In recent years, discrete element simulation methods have been developed, providing an interesting tool to investigate the behaviour of patterned films.[22] Here, too, a non-zero lateral shrinkage in the top part of the film and a non-uniform vertical shrinkage near the film edges were predicted. Also, edge delamination was modelled by DEM and confirmed by accompanying experiments.[12] DEM simulations have also been recently used to study crack growth in constrained films and its effect on fracture toughness.[23]

Despite the relevance of substrate properties and edge effects on applications, systematic experimental studies of the influence of finite feature size on the constrained sintering are lacking. This knowledge, however, is necessary to develop design rules for patterned films, as edge effects are likely to become significant in small structures. The same holds true for the influence of the film/substrate interface properties that must be understood to estimate the degree of constraint and the resulting lateral shrinkage. In a previous publication,[12] ceramic stripes with widths ranging from 10 to 100 μm were sintered and edge effects were found to depend on the stripe dimensions. This leads to the assumption that the densification behaviour of narrow stripes is likely to be dominated by the edge effects, while wide stripes would behave like continuous films with negligible contribution of the edge effects.

In the present work, these open questions are addressed by studying the sintering of alumina stripes with widths ranging from 10 to 500 μm and thickness from 7 to 32 μm to investigate the effect of both stripe width and thickness on the geometrical constraint. The paper is organised as follows: first, a detailed evaluation of SEM cross sections of different stripe geometries is presented to understand the shape distortion and local density distribution brought about by constrained sintering and compared to simulation results existing in the literature. The relative contributions of the edge zones in different stripe geometries are assessed and their influence on the lateral shrinkage and densification is studied. Second, the degree of constraint is quantified by comparing the vertical and lateral strains as function of stripe geometry.

2. Experimental procedure

The aqueous slurry used for the preparation of patterned films on smooth substrates was made of 50 vol% alumina powder with an average particle size of d_{50} = 150 nm (TM-DAR, Taimei Chemicals, Japan) dispersed in deionised water at a pH of 10 (obtained by adding concentrated ammonium hydroxide) using 0.7 mg/m^2 of dispersant (Dolapix CE 64, Zschimmer Schwarz, Germany) per surface area of powder.

A pattern consisting of stripes with widths between 10 and 500 μm was designed using AutoCad 2009 (Autodesk, Germany). The design was then used to fabricate an intermediate mask with electron beam lithography (Institut für Mikrostrukturtechnik, Karlsruhe Institute of Technology, Germany). This mask was used for the fabrication of photo resist-patterned silicon wafers by X-ray lithography. Elastomer stamps were produced by casting liquid mixture of polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning, Midland, USA) with its hardener onto the wafer and subsequent degassing and curing at 80 °C for 4 h. Prior to the casting of PDMS, the wafer was treated with (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (ABCR, Karlsruhe, Germany) to facilitate the separation of the dried stamp. The stamps were then peeled off and subjected to oxygen plasma etching (Polaron PT7100, Quorum Technologies, Sussex, UK) for 60 s at 40 mA. This etching step renders the stamps hydrophilic for 30 min by exchanging surface methyl groups by hydroxide groups, enabling the water-based slurry to wet and penetrate the channels.

A micro drop of slurry was then deposited onto a smooth sapphire substrate (CrysTec GmbH, Berlin, Germany) with an area of 20 mm × 20 mm and a surface roughness of R_a = 0.5 nm. The stamp was manually placed onto the drop with as little pressure as possible and dried in controlled atmosphere (relative humidity 90%, 7 °C) to keep the stamp saturated with water during the hydrophilic stage. This step prevents diffusion of water from the slurry into the stamp to avoid the degrading effect this would have on homogeneity and contour accuracy.[24] After 30 min, the stamps became hydrophobic again and the temperature was raised to 40 °C and the samples were dried in uncontrolled atmosphere to promote drying via diffusion of water through the open channels.

Then the stamp was removed from the substrate, leaving behind alumina patterns on the substrates. The whole pattern consists of a square slurry reservoir from which stripes go out in 4 directions. The total length of the pattern is 14 mm. Only clearly separated stripes (at least fivefold longer than their width) were used for evaluation. This condition was easily satisfied for all stripes with a thickness of 7–16 μm, whereas the stripes with thicknesses of 27 μm and 32 μm could only be deposited with sufficient length for widths between 25 μm and 250 μm due to the high viscosity of the slurry (0.2 Pa s at a shear rate of 50 s^{-1}). In this case, a stripe of 500 μm in width and 500 μm in length was used as a continuous film for comparison with the narrower stripes.

Unless stated otherwise, the samples were all sintered at 1450 °C for 4 h using a heating rate of 25 °C/min up to 1200 °C followed by 10 °C/min up to 1450 °C. Their lateral dimensions