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Review

Post-buckling design of thin-film electrolytes in micro-solid oxide fuel cells

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HIGHLIGHTS

- Buckling analysis combined with experiments enabled to fabricate stable YSZ membranes.
- Effective residual stress in a free-standing YSZ film was estimated by a new method.
- Comparisons between simulations and experiments show excellent agreement.
- Novel post-buckling design space for thin electrolyte fabrication has been set up.

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ABSTRACT

The buckling behavior of a thin-film electrolyte of a micro-solid oxide fuel cell is investigated based on experimental measurements, analytical estimations and numerical simulations. An energy minimization procedure is applied in combination with the Rayleigh–Ritz method to represent the buckling modes, evaluate the buckling amplitude and determine the threshold values for instability transitions in the system. The residual stresses in the film deposited on a silicon substrate are evaluated based on wafer curvature whereby nanoindentations tests are applied to estimate the Young's modulus of the deposited film. The partial release of residual stresses in the film during free etching of the substrate is estimated by a new method combining pre-etching optical measurements with posteriori stress analysis. The energy interpretation of the obtained deflection shape is discussed. Comparisons between simulation results and experimental data show the efficiency of this method to predict various buckling stages of free-standing thin films. A post-buckling design space for thin-film electrolyte fabrication is presented by applying a stress-based failure criterion.

1. Introduction

Micro-solid oxide fuel cells (μSOFC) are currently receiving increasing attention as promising electrochemical energy converter devices. The high conversion efficiency, the high power density, the fast start-up times and the low operational temperature (350–550 °C) make this a suitable power source for small portable electronic applications. Before reaching the promised potential of this technology, some challenges need to be overcome like, in particular, the thermomechanical stability during fabrication stages and under operational conditions. A μSOFC is built of a multi-layered structure of ceramic and metallic plates. Although these structures exhibit advantageous properties such as a favorable strength-to-weight ratio, a high fatigue endurance, and a strong corrosion resistance, they may exhibit some functional problems. For example, such a structure has a low resistance towards peeling stresses at the interface between different layers where delamination may occur. In addition, these films are subjected to in-plane stresses associated with both the thermal expansion mismatch and the fabrication process. This may induce either membrane buckling [1] under compression or membrane fracture under tension. Both buckling and cracks reduce the load carrying capacity of the structure [2]. Further, crack propagation can lead to complete failure limiting the operating time of the fuel cell.

The present work deals with the mechanical stress analysis and the design implications for the fabrication of thin films in μSOFCs. The fabrication of μSOFC membranes involves several steps of film deposition and layer etching as depicted in Fig. 1 see Refs. [3] and [4]. After the etching of the silicon substrate (Fig. 1 (c)), the membranes are free-standing and the mechanical system in Fig. 1(g) is found to be a model of three-layer clamped plate which consists of: a top electrode, the electrolyte made of YSZ (as described in Ref. [3]) and a bottom electrode. The stability of such a system should be

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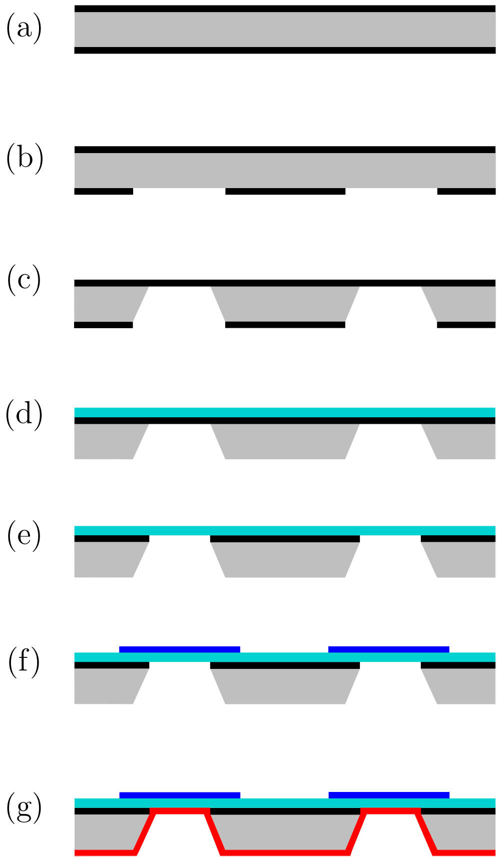


Fig. 1. The fabrication steps of μSOFC membranes. (a) Silicon wafer double side coated with Si_3N_4. (b) Backside photolithography, and reactive ion etching of Si_3N_4 (LPCVD). (c) Wet etching of Si in 20% aqueous KOH. (d) YSZ deposition by PLD onto free-standing Si_3N_4 membrane. (e) Reactive ion etching of Si_3N_4 membrane. (f) LSC Cathode deposition. (g) Anode deposition by platinum sputter-coating.

guaranteed under both fabrication and operation conditions at temperatures between 400 and 500° C.

1.1. Design consideration for thin-film manufacturing

When PLD is employed, the deposited film exhibits different responses with respect to the deposition conditions and techniques. A high-temperature deposition may induce a residual compressive stress which drives the membranes to buckle. On the other hand, the deposition at room temperature may initiate, during a subsequent annealing up to 400°C, cracks which propagate in the brittle film causing rupture under tensile stresses as shown in Fig. 3 (see also [3]). The residual stress is then a finger print of the deposition's mechanism type and the related conditions of temperature and pressure, see for example [5]. Another examples of the intrinsic effects are the phase transformation inside the film, the densification, the crystallization, and, the chemical association–dissociation which induces a strain, and subsequently, a chemomechanical stress in the material ([6] and [7]).

In this work, focus is made on the stress analysis and design of YSZ electrolyte fabricated by pulsed laser deposition PLD (see Fig. 1(e) and Fig. 2).

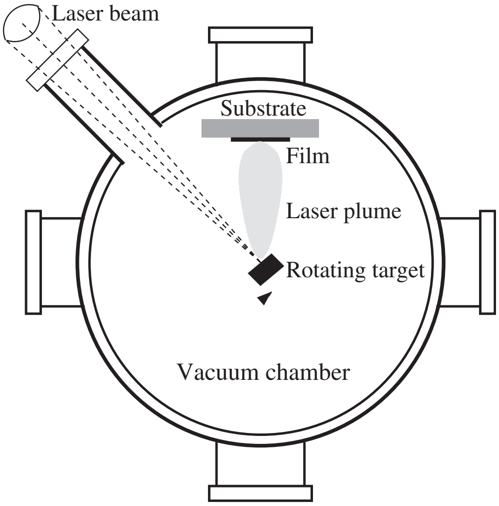


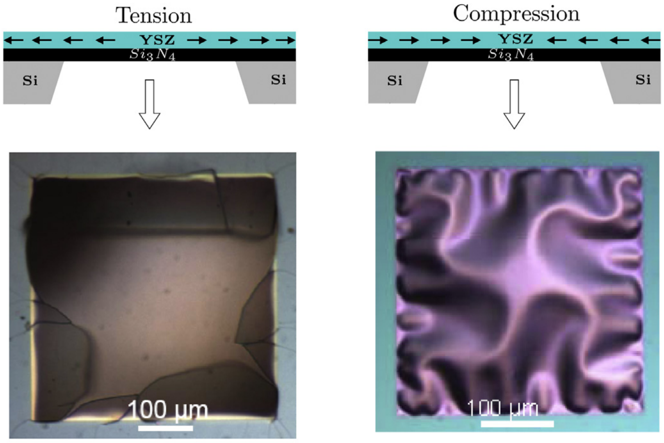
Fig. 2. Schematic representation of PLD techniques used in the fabrication of thin YSZ film deposited onto a silicon substrate.

In the framework of μSOFC, some design concepts are adopting a failure-based buckling criterion, like in Refs. [8], where the use of thick film is recommended to avoid both buckling and fracture. Such a design option suffers from drawbacks which are related to the fabrication costs of the thick deposited films and to the low electrochemical performance attributed to the long transport path in the cross-plane direction of thick membranes.

A "design accepting buckling" is highly important for the fabrication of thin films in many applications where a stress-based failure is adopted. Although the important contribution from Ref. [9] toward a design in post-buckling regime, the application of the energy method in such a work is restricted to the axis-symmetry describing the first buckling where the secondary buckling (second bifurcation) is not captured and then excluded from the design space.

Important simulation results on the buckling of membrane in μSOFC are shown in Refs. [10], however, there is always a need to provide a guideline for membrane designs based on both simulation results and experiments where fabrication and operation constraints in fuel cells are considered.

In the presented study, an advanced exploitation of the energy method is contributed to provide the needed informations on thin-film design in different buckling stages. The numerical results are



(a) (b)

Fig. 3. Two typical results of free-standing YSZ membrane obtained from pulsed laser deposition. (a): YSZ membrane rupture after YSZ deposition at room temperature and annealling up to 400 °C at 3 °C min^{-1}. (b): membrane buckling after PLD deposition at 700 °C. Images are taken at room temperature.