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Direct patterning of photosensitive chemical solution deposition PZT layers

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Abstract

A highly concentrated solution for producing photopatternable layers of lead zirconate titanate (PZT) was prepared by dissolving into acrylic acid an amorphous PZT powder which was obtained by a sol-gel process. The solution was found to be suitable for spin-coating PZT layers that are photosensitive to UV radiation. After deposition and subsequent exposure the PZT film showed a decreased solubility in several organic compounds. These properties were exploited to create features on platinised silicon (Si) substrates. A thermogravimetric analysis was performed on the solution to determine the best thermal profile for the burn out of the organics. PZT features up to 2 μm thick were obtained after the firing process.

Keywords: Drying; Films; Photopatterning; PZT; Sol-gel process

1. Introduction

Chemical Solution Deposition (CSD) has several advantages over other fabrication methods. It permits coating of complex geometries and offers a very good control of the material composition. Ceramic films have been deposited in a single layer with sol-gel techniques up to about 1 μm thick.[1] Thicker films are normally produced by successive coatings.[2] With a ceramic/sol-gel composite route[3] the thickness achievable by a single deposition step is usually greater than 1 μm but the resulting film is very porous and needs to be infiltrated with sol to increase the density and to improve the electrical properties.[4] In both cases a long time is required to finish the whole process; therefore the manufacture of a dense thick layer in one stage would offer great time savings. In most practical applications it is also necessary to pattern layers by conventional lithography. This usually entails the deposition and exposure of a photoresist layer followed by development and chemical etching. It would be highly desirable if the PZT layer could be patterned directly by UV exposure, both because it would eliminate the need for further lithographic processing and because PZT materials are quite difficult to etch. The development of such a process is one of the objectives of the research described here. A further significant issue related to the thick film manufacture is the cracking that occurs during the thermal treatments for drying and firing. The shrinkage that takes place when the organics are removed from the film creates a stress that is released by the formation of cracks. In order to exploit the desired properties of the ceramic, it is naturally essential that the ceramic film should be crack-free. The production of small patterned areas on the substrate by direct patterning offers a possibility for reduction of the stresses associated with shrinkage and thus cracks elimination.

This paper reports a method for the production of directly patterned features up to 1.9 μm thick using a single deposition step with highly concentrated lead zirconate titanate photosensitive solutions. The films were patterned with UV light before any firing process. High concentrations were used in order to reduce the organic loss during the thermal treatments and the subsequent shrinkage.

2. Experimental

An amorphous PZT powder was prepared by a sol-gel process. An ethanol-based sol used in this route

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gives a PZT powder with composition $Pb_{1.1}[Nb_{0.02}(Zr_{0.52}Ti_{0.48})_{0.98}]O_3$. The starting materials were lead acetate trihydrate, titanium iso-propoxide, zirconium n-propoxide and niobium ethoxide.

The lead solution was prepared with 10 mol% excess lead by dehydrating lead acetate and dissolving it in ethanol. Mono-ethanolamine was then added and the mixture was gently heated in a nitrogen atmosphere to help the complete dissolution of the lead acetate. The weighing and the mixing of the precursors of titanium, zirconium and niobium were carried out under nitrogen to prevent the moisture sensitive stock solutions from being hydrolysed. The precursors were dissolved in ethanol and refluxed under nitrogen for 1 h previous addition of acetic acid. The lead solution and the mixture of titanium, zirconium and niobium precursors were then mixed together and refluxed under nitrogen for 2 h in order to obtain a PZT sol of concentration 0.58 M. When the sol was cool it was filtered and stabilised by the addition of ethylene glycol. 0.5 wt.% of water was added to the sol to start the hydrolysis reaction and after 20 h of ageing a light yellow gel was obtained. The gel was then dried in a reduced atmospheric pressure environment to remove the solvents and to obtain the organic powder.

The powder was found to be shelf stable and highly soluble in few organic solvents. Among these solvents acrylic acid plays an important role in our study because of its photosensitivity.

The photosensitive PZT solutions were obtained by mixing the powder produced by the procedure described above with acrylic acid (Aldrich; 99% purity) and stirring for 3–4 h to produce a clear, viscous solution (35 wt.%). 3 wt% of a sensitiser was then added to the mixture to enhance its photosensitivity. A more concentrated PZT solution (40 wt.% powder, 3 wt.% sensitiser) was then prepared in order to increase the thickness of the film. A thermogravimetric analyisis coupled with mass spectrometry (TGA-MS) was performed on the solution to have information on the release of the organics during the thermal treatments. In order to identify the evolution of the volatile compounds a few m/q (ion mass over ion charge) values were plotted as a function of time. Dry air as carrier gas at a flow rate of 50 ml/min and a heating rate of 2 K/min were the experimental conditions applied to perform the analysis.

The prepared solutions were deposited on platinised silicon substrates using a spin coater in a clean room environment. All the samples were prepared using the same spinning conditions: 3000 rpm for 30 s. The as-obtained "wet" samples were then prebaked at 70 °C for 25 min to permit contact between the films and the patterning mask and then patterned using UV light from a mercury lamp source (radiance power: 13.4 mW/cm^2). The effect of different exposure times (5, 10, 15, 20 and 25 min) was studied.

The decreased solubility in several organic compounds shown after exposure to UV light was exploited to develop the photopatterned samples. Once developed the films were then thermally treated in a furnace using a ramp of 2 K/min with a dwell of 20 min at 170, 382 and 465 °C.

Parameters such as the quality of the film and the thickness before and after the firing process were taken into account to evaluate the best exposure time. The thickness and width of the features obtained following the procedure described above were determined using a profilometer (Dektak-3-ST).

3. Results and discussion

Fig. 1 shows the result of the thermogravimetric analysis performed on the solution. The results are expressed in terms of weight loss (% of mass) versus temperature of the PZT solution. The derivative of the TG curve is also shown to highlight the temperatures at which the major weight losses occur. The coupling of TGA with mass spectroscopy allowed the volatile compounds to be identified in the four main steps.

The decomposition of the PZT solution is initially dominated by the release of acrylic acid (mass losses from room temperature up to ca. 200 °C). This is supported by the observation on the mass spectrum of two specific ions for the acrylic acid (m/q = 55 and 72). The acrylic acid is released in two different steps (around 50 and 170 °C) indicating that it might be present in two different forms: as a pure solvent and as a chelating agent. A plateau is then found at ca. 50% weight loss. The decomposition increases again above approximately 315 °C. Two more steps (at around 380 and 465 °C) result in a final sample weight of 26.7% of the initial weight. In these two final steps the organics contained in the powder and more acrylic acid are released. In the final decomposition step the oxygen level decreases below the background level of dry air, which indicates that combustion is taking place.

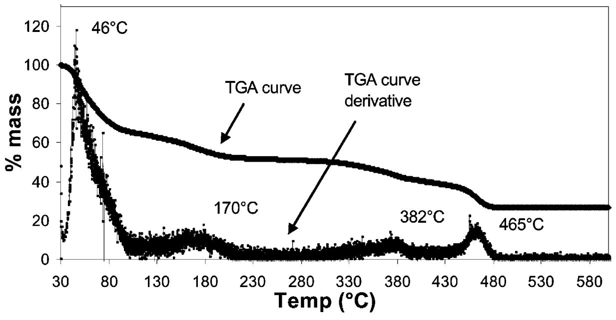

Fig. 1. Results of TGA on PZT solution; the green curve is the derivative of the weight loss as a function of the temperature.

The clear solution was deposited on the Pt/Si substrates leading to transparent films with a "wet" appearance. Following the prebaking and the exposure steps the films appeared transparent and glassy. In Fig. 2 a schematic of the film processing is reported.

The film exposed for 5 min was completely removed once treated with the developer. This indicates that the exposure time was not long enough to permit the polymerisation of the film and the subsequent change in solubility. The films exposed for 10 and 15 min appeared inhomogeneous and porous (Fig. 3). This is probably due to the inflowing of the developer into the pores of the film which is not yet fully polymerised. The thicknesses before firing were respectively 0.2 and 1.5 μm. The width of the features was found to be 10% larger than the original dimensions on the mask. This effect might be due to polymerisation of the acrylic solution beyond the borders of the mask.

When exposed for 20 and 25 min the films were transparent and uniform in appearance (Fig. 4). Their thicknesses before firing were in both cases 1.9 μm and the dimensions of the features exceeded those on the mask by 5–6%. The measurement of the film thicknesses showed an increase with exposure time going from 0.2 μm (10 min exposure) up to 1.9 μm (20 min exposure). This suggests that the development process might be responsible not only for the removal of the unexposed area but also of a superficial layer from the features.

Fig. 5 shows a scanning electron microscope (SEM) photomicrograph of a circular feature after prebaking and development. The feature was produced using a 35 wt.% PZT solution exposed for 20 min. The circular element is partially detached from the substrate indicating that during processing the developer infiltrated behind the feature releasing film. Shrinkage stresses present in the dried film lead to the bowing observed.

Following developing the samples were fired in a furnace to obtain a ceramic PZT film.

The results obtained from the TG analysis were taken into account when selecting the thermal treatments of the films. The first temperature profile (prebaking at 70 °C on a hot plate) was necessary in order to prevent the "wet" film from sticking to the mask. The subsequent thermal treatments were carried-on on a programmable furnace using dwell times of 20 min at 170, 382 and 465 °C (temperatures at which the weight loss is maximum). This precaution was taken to permit

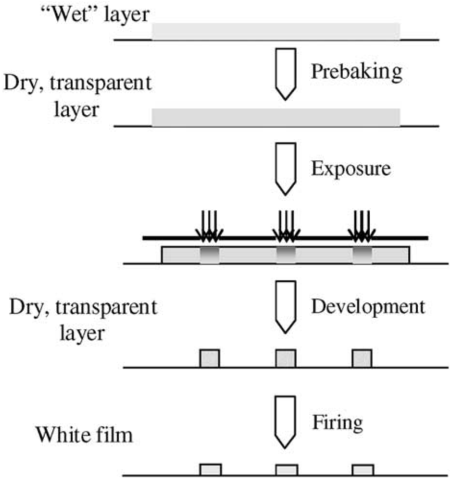

Fig. 2. Schematic of the film processing.

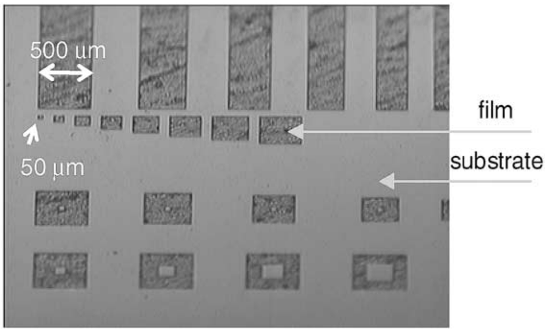

Fig. 3. Appearance of the developed film after 15 mm exposure.

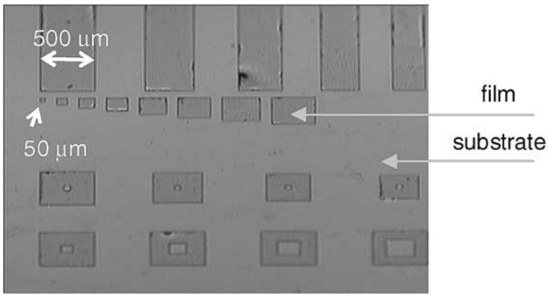

Fig. 4. Appearance of the developed film after 20 mm exposure.

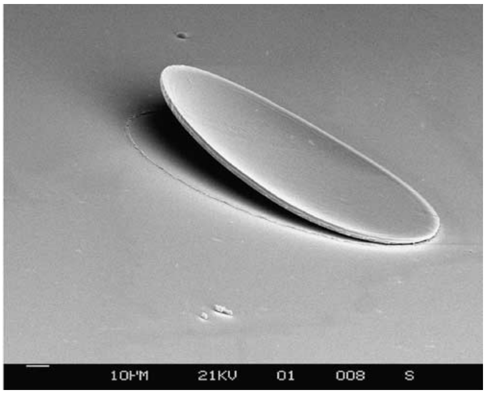

Fig. 5. SEM photomicrograph of a circular feature after prebaking and development. The feature was produced using a 35 wt.% PZT solution.

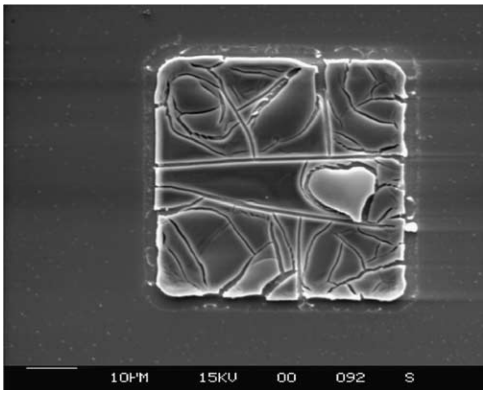

Fig. 6. SEM photomicrograph of a 50 μm feature after firing. The feature was produced by deposition of a 35 wt.% concentrated PZT solution.

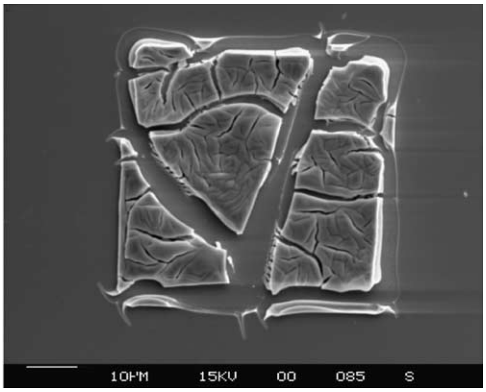

Fig. 7. SEM photomicrograph of a 50 μm feature after firing. The feature was produced by deposition of a 40 wt.% concentrated PZT solution.

a slow release of the organics and to prevent the formation of cracks.

The analysis of SEM photomicrographs of the fired films revealed the presence of a network of cracks. Fig. 6 shows the extent of cracking of a feature approximately 50 μm in size obtained by the deposition of a 35 wt.% concentrated PZT solution. It is possible to observe a residual pattern around the shrunk feature indicating the original feature size prior to the thermal treatments. The scale of the uncracked areas suggests that it may be possible to obtain uniform uncracked structures when the feature size is reduced to below 5 μm. Future work will address the issue of cracking in relation to the dimension of the features.

Firing at 465 °C leads to a reduction in film thickness of approximately 50%. The final film thickness obtained from the low concentration solution was 0.9 μm. A more concentrated PZT solution (40 wt.%) was then prepared in order to increase the thickness of the films. The film obtained spinning this solution on a Pt/Si substrate was prebaked at 70 °C for 25 min and exposed for 20 min under UV light.

The viscosity of the solution resulted in a film thickness of 3.5 μm after the exposure step. Fig. 7 shows a 50 μm feature deposited using the more concentrated solution. It was expected that the higher concentration of the stock solution would reduce the degree of shrinkage and hence the degree of cracking. However, the increased viscosity and subsequent thickness lead to increased stresses and cracking. Following the firing process the thickness decreased by 50% leading to features around 2 μm thick.

4. Conclusions

A photopatternable solution has been developed and spun onto platinised silicon substrates. Optimal experimental conditions were found to prebake and expose the film in order to obtain a good quality pattern and to minimise the exposure time. These conditions were found to be 70 °C prebaking temperature and 20 min exposure time. The concentration of the spun solution was increased to obtain patterned ceramic films up to 1.9 μm thick.

Acknowledgements

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