PROCESSING SOL-GEL PZT THIN FILMS FOR MICROACTUATORS

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Abstract

Sol-gel derived lead zirconate titanate (PZT) thin films are being investigated for micromechanical applications. A synthesis technique which involves the spin coating of several thin layers followed by rapid thermal annealing to crystallize the perovskite phase and repetition to achieve thicker films is described. Methods of improving the PZT-PZT interfaces between subsequently annealed layers are described. Specifically, the effects of introducing thin (~15 nm) Pb or Ti-rich layers at the PZT-PZT interfaces were investigated by transmission electron microscopy (TEM). Both the Pb and Ti-rich interlayers are shown to yield films of improved microstructure compared to films prepared without such compositional modifications.

1. Introduction

Research in the preparation of PZT thin films of thicknesses greater than 1 micron is driven by interest in the fabrication of piezoelectrically actuated micromechanical devices such as micro-pumps and micro-motors. in order to achieve high yield and reproducible device characteristics, the films must be continuous and of uniform thickness. Initial results indicate that these conditions can be successfully met using a sol-gel method for the PZT film preparation [1,2].

Films in the thickness range of 0.5 to 2.0 microns were tested for ferroelectric and piezoelectric properties with results comparable to those reported in the literature for thinner films [3-5]. The film preparation technique employed involves deposition of several layers by spin coating followed by annealing and repetition of the whole process. By TEM analysis. nanocrystals (< 25 nm) of pyrochlore were observed at the PZT-PZT interfaces probably due to Pb-loss during the rapid thermal annealing. The occurrence of pyrochlore can be expected to diminish the piezoelectric response of the films. However, perhaps a more important problem from a technological standpoint is that during structuring of the films by wet chemical etching, these interfaces tend to etch preferentially, thus reducing the precision achievable in etched features. In this paper, the effects of incorporating either Ti or Pb-rich layers at the PZT-PZT interfaces on the resulting film microstructure is discussed.

2. Experimental

Sol-Gel derived PZT thin films were prepared using a multiple layer spin casting deposition technique. The precursor solution was prepared from Pb acetate tri-hydrate, Ti-isopropoxide and Zr-n-propoxide and formulated to contain 10% excess PbO [l]. The solution preparation procedure, which includes the use of the solvent 2-methoxyethanol, is similar to that originally published by Budd [6]. The following example is illustrative of the film preparation technique. Using a 0.2 molar PZT solution. layers of approximately 30 nm are deposited by spin-coating at 2000 rpm for 40 s. After each deposition, the film is dried at 150°C for 15 s and pyrolyzed at 350°C for 15 s. This process is repeated 8 times and the film rapid thermal annealed at 600°C for 1 minute. This entire process is then repeated three additional times to yield a film of 1 micron

thickness, for example. This process was modified by either using a 15 % excess Pb precursor solution or a solution of composition 40/60, Zr/Ti ratio, as the final layers before the annealing treatments. The films were analyzed by TEM and XRD.

3. Results and Discussion

The general procedure outlined above yields a PZT film which contains nanocrystals of pyrochlore at the PZT-PZT interfaces. as shown in Fig. 1(a) and discussed in more detail in [3]. The occurrence of pyrochlore at the surface of chemically prepared PZT films is known to occur either because of Pb loss during annealing or as a result of insufficient annealing time/temperature to completely transform the transient pyrochlore phase, which is part of the amorphous to pyrochlore to perovskite crystallization path [1,7]. The addition of 10 % excess PbO is typically reported for the preparation of PZT films by MOD or sol-gel techniques.

The first experiments involved the incorporation of thin 40/60. Zr/T": ratio. PZT layers at the interfaces, i.e. as the last layer in each case before annealing (note that the remainder of the film is of 53/47 composition). This technique was chosen because it is known that the pyrochlore phase becomes less stable with increasing Ti content and thus the transformation to perovskite should be facilitated. The second technique involves the incorporation of thin layers which were prepared from a 53/47 PZT precursor solution formulated to contain 15% excess PbO (compared to the 10% used in all other cases herein). The justification here was that often the surface of the PZT films are Pb-deficient due to lead loss during annealing.

In order to study the effect of introducing a thin layer (~15 nm) of slightly Ti-rich (40/60: Zr:Ti ratio) PZT as the final layer before annealing, a film was prepared as follows. First. a thin layer (15 nm) of 40/60 PZT was deposited by spin coating, drying and pyrolysis. Next, 6 layers (~ 30 nm each) of 53/47 PZT were deposited followed by the deposition of another layer of Ti-rich PZT identical to the first layer. The film was then rapid thermally annealed at 650°C for 1 min. After annealing, only perovskite phase was observable by XRD analysis. The above series of layer depositions were then repeated, and the film annealed again using the same heating profile. A BF TEM image of this film is shown in Fig. l(b). The interface (arrowed) which results from the intermediate annealing is observed as a slight change of diffraction contrast. highlighted by the two beam imaging conditions. In high resolution, it is observed that the lattice fringes are continuous through the interface. This can be compared to the TEM image shown in Fig. 1(a) in which no compositional modifications were made at the interfaces. and in which the presence of pyrochlore crystals at the interface(s) is clearly evident.

PZT films were prepared using the processing sequence described above with the exception that the Ti-rich layers were replaced by 15% PbO-rich layers. In Fig. l(c) and 1(d), TEM images are presented which show the PZT-PZT interface due to the subsequent annealings. In this case, the interface is more distinct than in the Ti-rich case, Fig. l(b), yet improved over the case where no interfacial modification was used, Fig. 1 (a). The contrast at the interface is believed to originate from the presence of retained PbO rather than pyrochlore, however reliable quantitative EDS analysis of Pb concentration was not possible due to their small size.

4. Conclusions

To summarize, two methods have been described to control the microstructure of PZT films prepared by a multiple deposition/annealing process. Both the introduction of thin T1 or Pb-rich layers at the PZT-PZT interfaces showed improvements over films prepared without such local compositional modifications. Further measurements and analysis is required to determine effects of such processing modifications on the piezoelectric properties of the films.

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6. References

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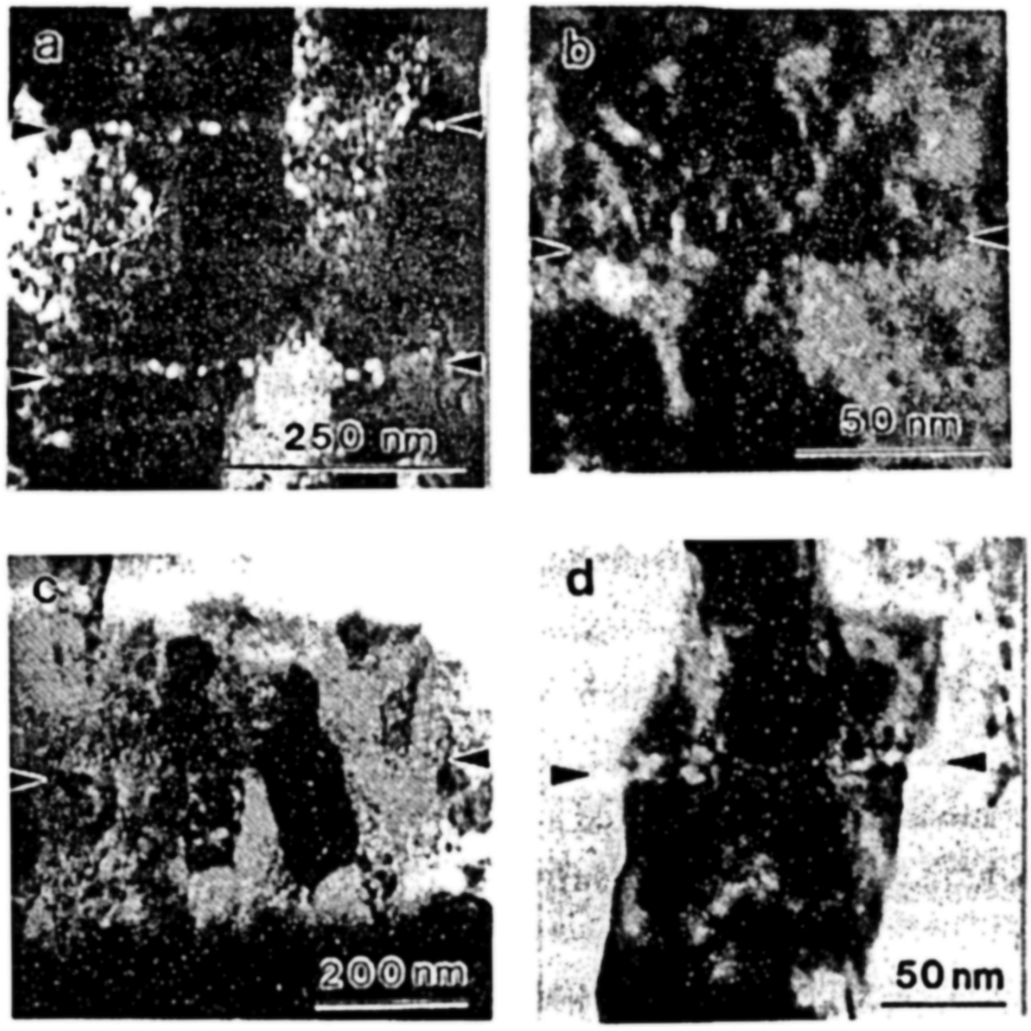

FIGURE 1 TEM images of transverse sections of PZT thin films showing PZT-PZT interfaces due to the multiple annealing process; (a) with no compositional modification at interface (Dark Field), (b) with 40/60 Zr/Ti interfacial layers, (c) and (d) with 15% PbO rich interfacial layers. The interfaces are indicated by arrowheads (See text for further details, b-d are bright field images).