Combinatorial Synthesis of Thin Mixed Oxide-Films and Examinations of Their Piezoelectricity by Ultrasonic Piezo-Mode Imaging

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Abstract. The development of an automated production of thin films and the characterization of their piezoelectric properties in high-throughput is described. A library of 50 undoped as well as doped lead zirconate titanate $Pb(Zr,Ti)O_3$ (PZT) coatings was produced by sol deposition. Afterwards, the piezoelectric properties of the library films were analyzed by automated atomic force microscopy employing the ultrasonic piezo-mode.

Keywords: PZT, combinatorial chemistry, high throughput, sol-gel synthesis, AFM.

1 Introduction

There is in increasing interest in thin films of ceramics with defined mechanical, magnetic or electro-active properties with applications ranging from protective coatings, magneto-optical image storage devices, and micro-electro-mechanical systems (MEMS). A new approach using high-throughput technology to discover materials having defined ferroelectric properties is presented. For the investigation of new piezoelectric materials a lead zirconate titanate $Pb(Zr,Ti)O_3$ (PZT) sol-gel-synthesis was applied, which can be modified in a combinatorial way. The use of an acidic sol-gel-recipe allows a broad variation in composition and doping with many elements.

2 Synthesis

Single-element precursor solutions were mixed by a pipetting robot to form 17 undoped PZT sols of different composition by varying the ratio of lead to zirconium to titanium as piezoelectric reference materials and 33 PZT sols (Pb1.1 Zr0.58 Ti0.42) doped with 6 mol-% of different elements. Subsequently, the precursor solutions were deposited onto a pre-structured silicon wafer **(Figs. 1 & 2)** by chemical solution deposition (CSD) /1/.

P. Perner and O. Salvetti (Eds.): MDA 2006/2007, LNAI 4826, pp. 80–83, 2007.

Fig. 1. Schematic view of the spread of the liquid on a structured substrate /2/

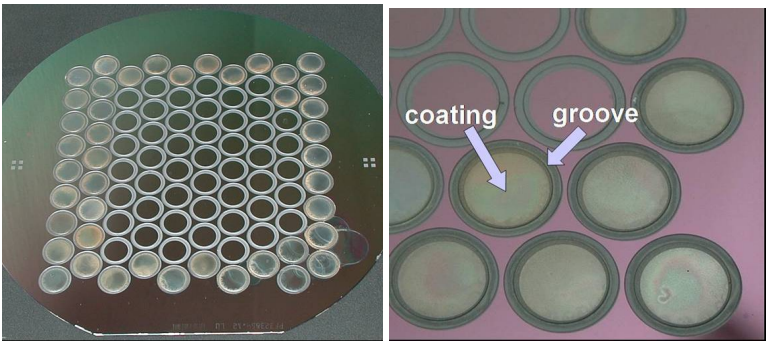

Fig. 2. (a) Micrograph of chemical solution deposition of a thin-film library on a structured 6"-silicon wafer, and (b) an enlarged image (3 × 3.5 cm²) of this library

3 Measurement Technique

The piezoelectric properties of the films on the library were automatically investigated by atomic force microscopy (AFM) employing the ultrasonic piezo-mode /3/. A sinusoidal voltage is applied between an electrically conductive cantilever and a base electrode below a piezoelectric sample **(Fig. 3)** /4/. The localized electric field emanating from the sensor tip of the AFM induces a deformation on a local scale due to the inverse piezoelectric effect. The ac frequency corresponds to the contact resonance of the conductive cantilever. The amplitude and phase of the induced surface displacement is sensed by the tip. The library was analyzed by the AFM tool "programmed move", which allows the cantilever to be positioned automatically to every of the samples on the library. The ultrasonic piezo-mode is an acoustic near-field technique which has been extensively discussed for example in a special session of the International Symposium on Acoustical Imaging (AI27) which was held in Saarbrücken in 2003 /5/.

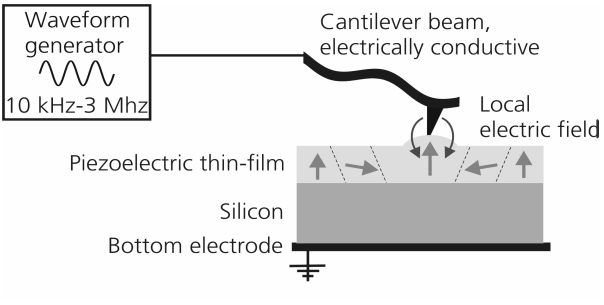

Fig. 3. Principle of the AFM ultrasonic piezo-mode

4 Results of Automated Analysis Using Ultrasonic Piezo-Mode

A topography image of the surface was acquired simultaneously with the acoustic image. The ultrasonic piezo-mode images of 17 piezoelectric reference films as well as 15 of the 33 doped PZT- films revealed dark and bright areas corresponding to high and low local vibration amplitudes. The samples doped with the following elements showed a contrast in the ultrasonic piezo-mode image: Ba, Ce, Co, Cu, Li, Sr, Na, K, La, Pr, Rb, Ag, Te, V(III), and V(V) indicative of piezoelectric properties. **Fig. 4** illustrates examples of topography images of three different samples ((a), (c), and (e)) together with their corresponding ultrasonic piezo-mode images ((b), (d), and (f)) /1/.

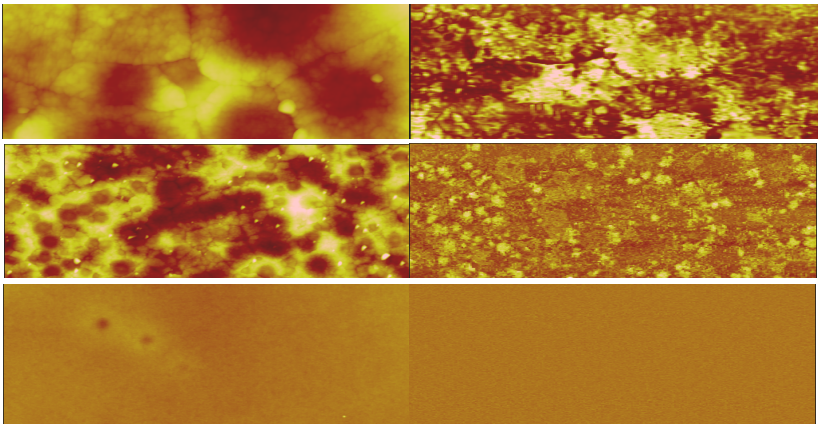

Fig. 4. (a), (c), and (e): Topography images of three different samples doped with Ba, Sr and Er, respectively. The image size is 10×3 µm². The scale covers 50 nm difference in height. (b), (d), (f): Corresponding ultrasonic piezo-mode images of the same surface areas as shown in (a), (c), and (e). The amplitude range of the ultrasonic piezo-mode images is 1.5 V.

The contrast in the ultrasonic piezo-mode image is caused by ferroelectric domains, but false positives resulting from variation of film roughness cannot yet be excluded. To exclude such topography effects, the samples have been examined by impedance spectroscopy as well yielding ε. For the PZT coating doped with Sr an ε-value of 194.36 was obtained which is typical for perovskites. These results confirm the ultrasonic AFM piezo-mode measurements.

5 Conclusion

We have described the development of an automated production of thin films and the characterization of their piezoelectric properties in high-throughput. A library of 50 undoped as well as doped lead zirconate titanate $Pb(Zr,Ti)O_3$ (PZT) coatings was produced by sol deposition. Afterwards, the piezoelectric properties of the library films were analyzed by automated atomic force microscopy employing the ultrasonic piezo-mode. The results show that the piezoelectric properties can be determined by

using the atomic force microscopy employing the ultrasonic piezo-mode. For the automatic determination of the piezoelectric properties an image processing procedure is needed that will be developed in future.

Acknowledgements

This work was supported by grants from the German Science Foundation through the "SFB 277" as well as the "Graduate College 232 "Materials for efficient energy use". The authors thank B. Wessler from Siemens AG for the supply of structured wafers.

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