$Pb(Zr,Ti)O_3$ Thin Films on Zirconium Membranes for Micromechanical Applications

T. Maeder, P. Muralt, L. Sagalowicz, I. Reaney[a], M. Kohli, A. Kholkin and N. Setter

Laboratoire de Céramique, Département des Matériaux, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

Original version:
http://hdl.handle.net/10.1063/1.116529

Abstract

An efficient, electrically conductive, chemical barrier for the integration of piezoelectric $Pb(Zr,Ti)O_3$ (PZT) films on reactive metal substrates has been developed, opening new possibilities for PZT integration on micromechanical and semiconductor devices, Very reactive zirconium films have been taken in order to test the quality of the specially designed RuO_2/Cr buffer under the condition of in situ sputter deposition of PZT at 600°C. The PZT/RuO_2 interface was found to be free of intermediate phases. A PZT activated metallic micromechanical element was demonstrated with a thin film Zr membrane.

1. Introduction

Piezoelectric films on structures such as membranes are of keen interest for the fabrication of sensors and actuators such as micromotors [1], micropumps [2] and microphones. Recently, ferroelectric films such as lead zirconium titanate (PZT) have provided a high performance alternative to non-ferroelectric piezoelectrics [3].

However, PZT thin film processing requires temperatures in the 550 to 700°C range in oxidizing conditions. Significant interdiffusion with the substrate materials can occur, mainly oxidation and lead diffusion. These degrade adhesion, electrode conductivity, PZT composition and phase purity [4-9], and hence the functional performance.

Up to now, silicon is the most used substrate for micromechanical applications. Silicon is very well protected against oxidation by its oxide or even by high quality Si_3N_4. However, for some applications, one wishes to avoid micromachining and brittle silicon structures, which may be a problem when assembling hybrid devices such as a micromotor. For simple industrial sensors, metallic substrates provide an interesting alternative, especially since micromachining can be avoided by using thin metallic sheets.

Conductive barriers between PZT and metallic substrates are desired, as they obviate the need for thick electrodes required to drive large areas at high frequency. The same challenge arises for memory applications, where the ferroelectric capacitor has to be preferentially contacted directly to the drain.

Early work of PZT films on base metal films [4] was not successful, as the films oxidized. Moreover, protection of a base metal (Ti) by a noble electrode (Pt) does not succeed [6], as interdiffusion of the Ti and the Pt in the presence of oxygen led to the appearance of considerable TiO_2 on the Pt, leading to excessive reaction with PZT. Another possibility is the use of a Ni alloy [5], which prevents any further oxidation once a 10-20 nm insulating Al_2O_3 oxide scale has formed. However, this work was done on $PbTiO_3$, and may not be satisfactory for PZT, which demands higher processing temperatures (making interdiffusion more likely), and, with a higher permittivity, is more sensitive to the presence of low permittivity layers.

[a] Permanent address: Department of Engineering Materials, University of Sheffield, Sheffield, UK.

In order to avoid an oxygen deficient PZT interface and the growth of an insulating layer by oxidation between the PZT and the electrode, we used an oxide electrode, thus moving the oxygen boundary away from the PZT-electrode interface. RuO_2 is considered a good electrode for PZT [10], and can act as an oxygen "buffer": any oxygen consumed by the underlying metal being supplied by the RuO2, which can partially convert to Ru, leaving the PZT largely unaffected. Since some oxygen will pass through the RuO2, we introduced chromium, which forms a protective, yet semiconducting oxide scale, thus inhibiting oxygen diffusion. Commercial stainless steel ("diluted Cr") worked as well. For the present study, in order to facilitate the composition analysis, it is more practical to use pure Cr.

2. Experiments and results

All films were deposited in a Nordiko 2000 magnetron sputtering chamber equipped with 100 mm cathodes, applying reactive processes with metal targets for the oxides. The PZT was grown in-situ [11] at 600°C, using a 30 nm thick seed $PbTiO_3$ (PT) layer to improve nucleation [12], and the membrane and buffer films at 500°C. Fig. 1 shows the deposited layers, together with the expected oxygen activity profile during PZT deposition. The very thin Ti film served as adhesion layer for RuO_2.

With an efficient barrier scheme, one should see no difference in electrical properties for PZT on the RuO_2 electrode, be it on the stable thermally oxidized SiO_2/Si wafers or on Cr/Zr/SiO_2/Si. For this purpose, the influence of Zr and Cr layers was assessed by comparing the full RuO_2/Cr/Zr sequence with RuO_2/Cr and RuO_2 on SiO_2/Si. For all three metallizations, no significant difference in electrical behavior was found (Table I), indicating that any possible diffusion was not relevant to dielectric properties. The scatter of the measured permittivity can be ascribed to thickness variations in the sputtered PZT.

High resolution transmission electron microscopy (HR-TEM) observations revealed a PZT/RuO_2 interface free of second phases, as shown by the high-resolution micrograph in Fig. 2, whether the Zr and Cr layers were present or not underneath. This indicates little or no out-diffusion from the Cr or Zr. As expected, some reactions have happened at the RuO_2/Ti/Cr interlayer, resulting in a thin 20 nm thick, probably oxidized, Cr-Ti mixture. At the Zr/Cr interface, only a thin (<10 nm) reaction layer has formed. The low level of reaction can be explained by the high melting points (T_m =1860,1850°C for Cr and Zr resp. [13]), leading to low diffusivity at the 600°C deposition temperature. The sequence as seen from scanning electron microscopy (SEM) cross-section is shown in Fig. 3.

Metallization	ε_r (1 kHz)	D (1 kHz) [%]
RuO_2	460-560	4
RuO_2/ Cr	480-500	5
RuO_2/ Cr / Zr	430-450	5

TABLE I. Electrical characterization: permittivity ε_r and loss D (Ti adhesion layer omitted in description).

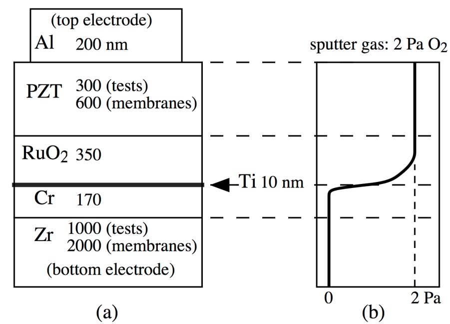
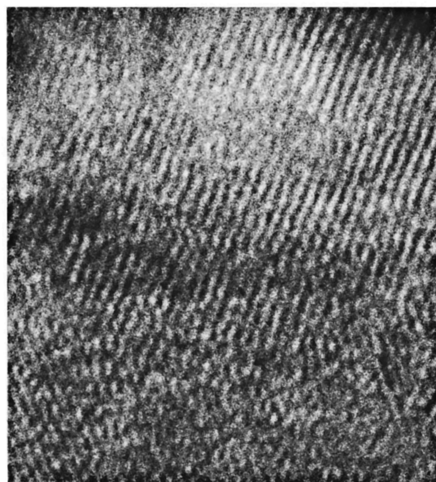


FIG. 1. (a) Deposited sequence. (b) Expected oxygen activity profile throughout the structure. Oxygen diffusion is stopped by the protective chromium oxide scale formed during exposure to oxygen at high temperature (RuO_2 and PZT growth).



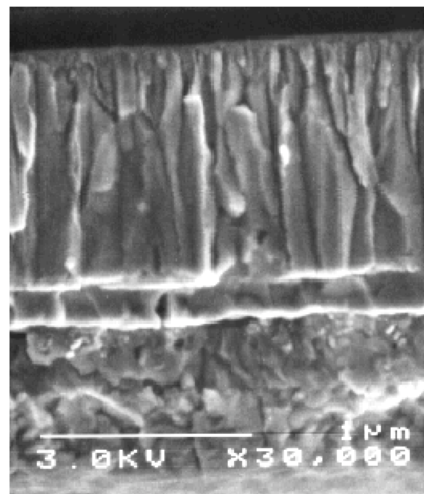


FIG. 2. HR-TEM of PZT/RuO_2 interface. The interface is almost parallel to the electron beam.

FIG. 3. Full metal-barrier-PZT sequence (upside-down), as seen by SEM.

Energy dispersive and electron energy loss spectroscopy (EDS and EELS) were performed on a Hitachi HF 2000 FEG and with a nominal probe size of 2 nm. These measurements were done to quantify interdiffusion between the layers and in particular to check if some Cr has dissolved in the PT and the PZT. The layers are found in the same sequence as that of the deposition, except that a mixed, probably oxidized, Cr-Ti layer has formed at the place of the Ti layer. No impurities were found within the Zr, the Cr and the RuO_2 layer. Some Cr (0.8±0.4%, without considering the oxygen) is detected by EDS both in PT and PZT, but this may come from neighboring regions and is probably not significant. EELS, whose spatial resolution is much higher, was also applied to the PT and the PZT. No Cr could be detected within our detection limit of less than 2%. This confirms that Cr diffusion into PT and PZT is very low or absent.

In order to demonstrate the piezoelectric activity of the PZT on a metal membrane, a circular 4 mm diameter (with 2 mm top electrode) thin film membrane, whose layer sequence is shown in Fig. 1, was micromachined out of the silicon substrate. The piezoelectric deflection vs. frequency spectrum was measured by laser interferometry[14] (Fig. 4). The resonance frequencies agree roughly with those of a thin stretched membrane with an average tensile film stress of 100 MPa, which is explained by the thermal mismatch between silicon and Zr.

3. Conclusions

In conclusion, an electrically conductive buffer layer scheme for PZT deposition on reactive metal substrates was developed and successfully tested. Clean interfaces were obtained, and piezo-electric activity on Zr membranes was demonstrated. Deposition of PZT on metallic foils is now possible without risk of interdiffusion.

Acknowledgements

This work is funded by PPM, the Swiss priority program for materials research. The SEM work of Mr. Jacques Castano is also gratefully acknowledged. The microscopy work was done at the CIME at the EPFL.

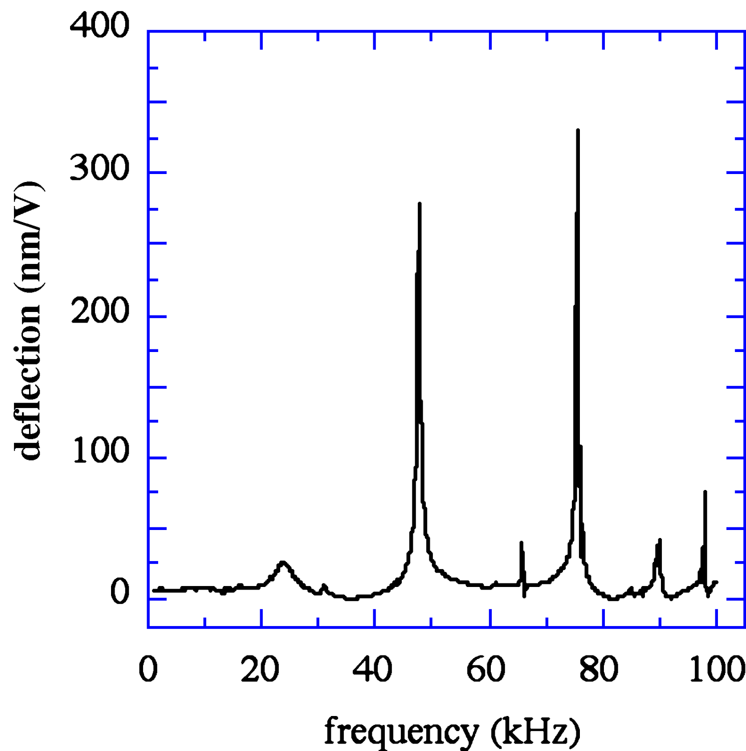


FIG. 4. Piezo-electric response of the Zr membrane activated by PZT.

Bibliography

1 G.-A. Racine, R. Luthier, and N. F. de Rooj, in Micro Electro Mechanical Systems, Fort Launderdale, USA, 1993 (IEEE), p. 128-132.

2 K. Brooks, D. Damjanovic, A. Kholkin, I. Reaney, N. Setter, P. Luginbuhl, G.-A. Racine, N. F. de Rooij, and A. Saaman, Integrated Ferroelectrics 8, 13-23 (1995).

3 P. Muralt, M. Kohli, T. Maeder, A. Kholkin, K. G. Brooks, and N. Setter, Sensors and Actuators 48, 157-165 (1995).

4 S. A. Myers and E. R. Myers, in Materials Research Symposium Proceedings, Vol. 243, 1992 (MRS, Pittsburgh), p. 107-112.

5 T. Ogawa, Integrated Ferroelectrics 1, 99-110 (1992).

6 K. Sreenivas, I. Reaney, T. Maeder, N. Setter, C. Jagadish, and R. G. Elliman, J. Appl. Phys. 75, 232-239 (1994).

7 K. Abe, H. Tomita, H. Toyoda, M. Imai, and Y. Yokote, Jpn. J. Appl. Phys. 30, 2152-2154 (1991).

8 D. Barrow, C. V. R. V. Kumar, R. Pascual, and M. Sayer, in Materials Research Symposium Proceedings, Vol. 243, 1992 (MRS, Pittsburgh), p. 113-122.

9 R. Bruchhaus, D. Pitzer, O. Eibl, U. Scheithauer, and W. Hoesler, in Materials Research Symposium Proceedings, Vol. 243, 1992 (MRS, Pittsburgh), p. 123-128.

10 D. P. Vijay and S. B. Desu, J. Electrochem. Soc. 140, 2640-2645 (1993).

11 R. Bruchhaus, H. Huber, D. Pitzer, and W. Wersing, Ferroelectrics 127, 137-142 (1992).

12 T. Maeder and P. Muralt, in Materials Research Society Symposium Proceedings, Vol. 341, San Francisco, USA, 1994 (MRS, Pittsburgh), p. 361-366.

13 R. C. Weast, Handbook of Chemistry and Physics, 64th ed. (CRC Press, Boca Raton, Florida, 1984).

14 Q. M. Zhang, W. Y. Pan, and L. E. Cross, J. Appl. Phys. 63, 2492 (1988).