Buffer electrodes for deposition of lead zirconium titanate films on metallic substrates

T. Maeder, L. Sagalowicz and P. Muralt

Laboratoire de Céramique, Département des Matériaux
Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

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1. Introduction

Thin films of $PbZr_xTi_{1-x}O_3$ (PZT) are the subject of keen interest for the fabrication of micro-sensors, actuators and ferroelectric memories. They are usually deposited onto silicon wafer-based substrates. In this scheme, Si is protected against oxidation by a SiO_2 and/or Si_3N_4 layer, followed by a bottom electrode (usually Pt) and PZT. For some applications, however, such structures are not appropriate. For instance, thin metallic sheets may be better substrates for discrete piezo-electric sensor and actuator applications than micromachined Si membranes, as they are less fragile and require no micromachining.

However, direct deposition of PZT onto base metals[1] or silicon is not possible. Metals degrade readily during the high temperatures (500 to 700°C) and oxidising conditions needed to deposit PZT. Additionally, they can interdiffuse with the PZT and alter its properties. Barriers-bottom electrode combinations are therefore needed. The simple solution of using a noble electrode (Pt) to protect the base metal (Ti) did not succeed[2], as exposure to oxidising atmosphere at high temperature led to excessive diffusion of Ti and oxygen through the Pt. The use of an Al_2O_3 scale-forming Ni alloy[3] is possible, but entails the presence of the small insulating Al_2O_3 layer.

We investigated barriers based on ruthenium dioxide (RuO_2), which is an electric conductor and is considered a good electrode for PZT[4]. Moreover, the use of an oxide electrode provides an oxygen "buffer", moving the oxide-metal boundary away from the PZT-electrode interface, and thus hindering depletion of the PZT in oxygen if limited oxidation takes place. Two schemes were tested. One is the oxide/metal (RuO_2/Ru) stack, where the interface should move by slow oxidation of Ru, leaving the structure essentially unchanged. The other scheme uses RuO_2 on chromium (or on commercial stainless steel). Chromium forms a protective, yet semiconducting, oxide scale in oxidising environments.

The second RuO_2/Cr scheme being successful, we used it to demonstrate protection of a very reactive metal (Zr) for piezo-electric metallic membrane structures. Also, its usefulness as a bottom electrode/barrier on Si for integrated devices was examined.

2. Experimental

For TEM sample preparation and temperature reproducibility purposes, the chemical behaviour of metal substrates was mimicked by depositing thin metal films onto oxidised Si wafers, followed by the barrier layer, and the PZT. Ti, Zr, Nb, Cr and 316 stainless steel (SS) metals were tested. All films were deposited using a Nordiko 2000 magnetron sputtering chamber equipped with 100 mm cathodes. Reactive sputtering in oxygen was used for RuO_2 and PZT. Films were deposited at 500°C, except the PZT, which was put down in-situ at 600°C using a 30 nm thick seed $PbTiO_3$ layer to improve nucleation[5; 6]. The thicknesses of the Ru, RuO_2 and PZT were 125, 350 and 330 nm respectively. Prior to Ru and RuO_2 deposition, a 10 nm Ti adhesion layer was deposited. The different schemes are summarised in table 1.

After PZT deposition, samples were characterised by X-ray diffraction (XRD), dielectric analysis and transmission electron microscopy (TEM).

Table 1: Summary of the different barrier schemes

Barrier	Substrate	Purpose
RuO_2 / Ru RuO_2	Ti, Zr, Nb, Cr and SS on SiO_2 / Si	basic study
RuO_2 / Cr	Zr on Si_3N_4 / Si	piezoelectric sensor/actuator (Zr membrane obtained by micromachining Si)
RuO_2 / Cr RuO_2 / Cr / TiW RuO_2 / Cr / TiN	Si	contact between electronic devices and bottom electrode

3. Results and Discussions

RuO_2/Ru on base metal

After PZT deposition, samples on Ti, Zr and Nb were unusable, showing heavy degradation of the surface (holes, delamination). Also, XRD studies revealed that Ti, Zr and Nb had oxidised. On the other hand, Cr and SS showed no noticeable degradation according to XRD or electrical properties. Therefore, RuO_2/Ru does not seem to act as a barrier against oxidation at the 600°C used to fabricate PZT, as the results obtained rather correlate with the base metals' oxidation resistance (Cr and stainless steel resist high temperature oxidation much better than Ti, Zr and Nb). Apparently, oxygen and/or the base metal films can diffuse through Ru.

RuO_2 onto Cr or SS; protection of reactive Zr film by RuO_2/Cr

No difference was observed by XRD or electrical characterisation when Ru was left out on Cr or SS, confirming that Ru plays little role as an oxygen barrier. As Cr itself may not be an ideal membrane material, RuO_2/Cr was used as a barrier to protect a very oxidation-sensitive metal - Zr, which is more suitable. Again, no degradation was found by XRD and electrical characterisation. The PZT/RuO_2/Cr and PZT/ RuO_2/Cr/Zr on SiO_2/Si were studied in detail by TEM. Part of the multi-layered structure is shown in fig. 1. Energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) were performed with a nominal probe size of 2 nm. No impurities were found in the Zr, the Cr and the RuO_2 layer. In the PZT, diffusion of Cr would affect the electrical properties. Some Cr (0.3±0.2 atom%) is indeed detected by EDS but not by EELS. Since the spatial resolution of the EDS technique is low, the Cr detected may come from the Cr layer itself, and it is concluded that the Cr level in the PZT is probably much lower than what was detected by EDS. Therefore, no significant diffusion has taken place between the layers.

The interfaces between the different layers were also studied. Although the RuO_2 and PZT appear to be free of second phases in the dark field image of fig. 1 as well as in high resolution TEM [7], a reaction layer (<10 nm) is present between Cr and Zr. More interesting is the presence of a 20 nm thick reaction layer between the Cr and RuO_2. EELS (fig. 2) reveals that it is composed of Cr and Ti, and that it is probably oxidised. Since the thickness of the TEM foil used for the analysis is very

small, it cannot be certain that the oxide found does not come from an oxidation at the surface of the TEM film. The high resolution image of fig. 3 reveals that this oxide has a crystalline structure. This layer is probably very important since it protects Cr against further oxidation and ensures that almost no Cr is diffusing through the RuO_2 to the PZT. Macroscopic measurements show also that it does not constitute an insulating layer.

RuO_2/Cr barrier on Silicon

Finally, the possibility of making direct contact between the PZT / bottom electrode stack and a Si device was assessed. Additional barrier layers had to be designed, however, as Cr reacts with Si at 450°C [8] to form a silicide. Experimentally, our Cr layers deposited directly onto Si spalled off due to this reaction. We therefore tried 2 barriers, which are standards in the microelectronics industry: titanium nitride (TiN), or tungsten with 10% weight titanium (TiW). About 100 nm of TiN or TiW were sputtered onto Si, followed by the usual PZT/RuO2/Cr. Both barriers appear to work at our temperature range (no intermixing by XRD, normal PZT electrical data), although more characterisation (TEM and contact resistance measurements) need to be done.

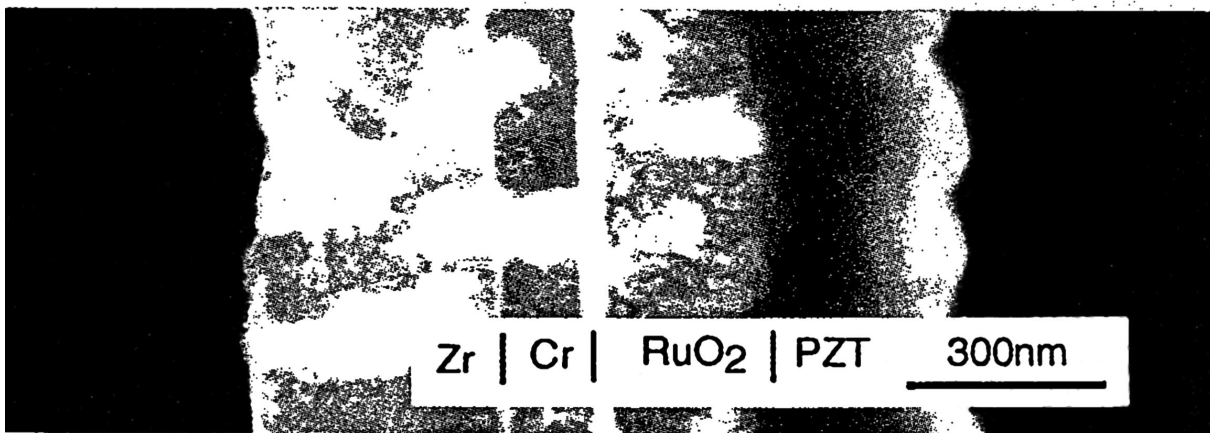

Figure 1: Dark field TEM image of a part of the multi-layered structure.

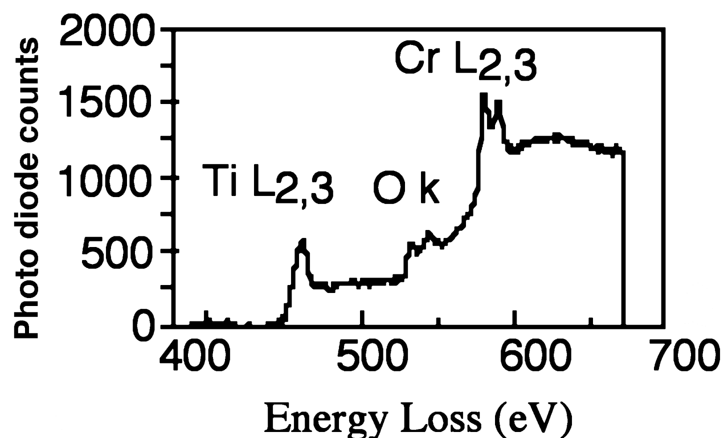

Figure 2: EELS spectrum of the interdiffusion layer between the Cr and the RuO_2 layers. This spectrum was obtained with a HF2000FEG microscope equipped with a Gatan 666 parallel detection located at the CIME (EPFL). It shows that the layer contains Ti, Cr and is probably oxidised.

Figure 3: High resolution TEM image of the interdiffusion layer (in the middle) between the Cr and the RuO_2.

Conclusion

The RuO_2/Ru sequence was not useful as a barrier to protect base metals against oxidation during PZT deposition, as only those with good oxidation resistance (Cr and stainless steel) withstood the PZT fabrication stage. In the case of Cr and SS, the 20 nm thick oxidation product is sufficient to protect these metals against ulterior degradation. Moreover, this thin protective layer is not insulating, allowing electrical contact between electrode and substrate.

Finally, we successfully applied the RuO_2/Cr barrier to a very reactive metal (Zr), and, with the help of TiW or TiN, to Si. Deposition of PZT on metallic foils for micromechanics and on Si-based integrated microelectronic devices is now possible with electrical contact and without degradation.

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