Wafer level integration of epitaxial piezoelectric thin films for novel NEMS, MEMS and MOEMS applications

M. Dekkers[*], M. Nguyen[*], N. Hildenbrand[*], S. Abel[**], F. Eltes[**], J. Fompeyrine[**], P. Wittendorp[***]

[*]Solmates BV, Drienerlolaan 5 (building 46), 7522 NB, Enschede, The Netherlands
[**] IBM Research GmbH, Zurich Research Laboratory, Säumerstrasse 4, CH-8803 Rüschlikon, Switzerland
[***] SINTEF Digital, MiNaLab, Oslo, Norway

ABSTRACT

$Pb(Zr,Ti)O_3$ (PZT) and $(PbMg_{1/3}Nb_{2/3}O_3)_{2/3}$-$(PbTiO_3)_{1/3}$ (PMN-PT) thin films are epitaxially deposited on 200 mm wafers using Solmates' Pulsed Laser Deposition (PLD) platform. Epitaxy is achieved using an optimized TiN template layer on the lattice mismatched silicon. $SrTiO_3$ was used as buffer layer and $LaNiO_3$ as oxide bottom electrode after which PZT and PMN-PT were deposited. A fully epitaxial thin film stack was confirmed by XRD analysis and the degree of epitaxy was found to be homogeneous across the wafer. The ferro- and piezoelectric properties were measured and found to be stable upon 10^{11} switching cycles.

Keywords: pulsed laser deposition, PZT, PMN-PT, MEMS, Piezoelectric memory.

1 INTRODUCTION

It is well known that Pulsed Laser Deposition (PLD) is a very flexible and versatile technique allowing fast optimization of new and complex material thin films. The unique features of PLD allow for the integration of "Beyond Moore" materials in CMOS and new devices. Among these are PZT, PMN-PT, KNN, $BaTiO_3$, $LiNbO_3$ and other materials of interest for applications in ferroelectrics.

High strain and long term stability of the piezoelectric material are key ingredients for successful commercialization of the thin film piezoelectric MEMS and NEMS applications. These properties are generally achieved in epitaxial films of PZT or PMN-PT [1]. In this contribution the use of epitaxial piezo thin films for Piezoelectronic Transduction Memory Devices is evaluated. This novel Piezoelectric Transduction Memory (PETMEM [2]) device uses a radically different switching mechanism in order to go beyond the power limits of current devices. Integration of epitaxial piezo layers on silicon forms therefore an essential ingredient for the realization of these memory devices.

The common routes for epi- perovskite on silicon need improvement.The deposition of $SrTiO_3$ on Si by MBE yields very good results in terms of epitaxy. However, it is a delicate and slow process. Another route is the deposition of YSZ/CeO_2/Perovskite by PLD. But this is a high temperature process (>700 °C) and yields a high interface roughness [3].

An alternative route is the use of a thin TiN template layer. TiN (001) thin films can be grown on lattice mismatched silicon by domain epitaxy [4]. The lattice mismatch between the Si and TiN unit cell amounts up to about 22%. Domain matching of 4 TiN unit cells onto 3 Si unit cells reduces this mimatch to only about 4%.

Using Solmates PLD platform, wafer-level integration of epitaxial thin films on silicon using TiN template layer is demonstrated and subsequent deposition of epitaxial PZT and PMN-PT thin is presented. The piezoelectrical and piezomechanical properties in relation to their crystalline quality will be discussed. The results of this work are the first milestone in the development of the piezoelectric memory.

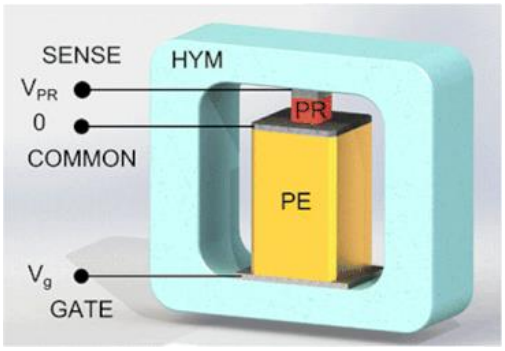

Figure 1: The piezoelectronic transistor (PET) is a transduction device not subject to the voltage limits of field-effect transistors.

2 EXPERIMENTAL

The 200 mm Si (001) wafers are HF-treated before the deposition in order to remove the native oxide. A thin film stack of TiN, $SrTiO_3$, $LaNiO_3$ and PZT or PMN-PT were subsequently deposited using Solmates' SIP-700 platform. The robust and reliable hardware allows uniform thin film deposition up to 200 mm diameter with high process reproducibility [5]. This pulsed laser deposition (PLD) platform uses an integrated KrF excimer laser operating at

wavelength of 248 nm. The deposition parameters of the TiN epitaxial template layer are optimized to achieve the best epitaxy and morphology. The deposition parameters of the other layers were kept constant and are described elsewhere [6].

Figure 2: Solmates SMP-800 platform. Automated PLD system for stable deposition up to 200 mm wafers.

For the TiN the deposition temperature was changed between 600 – 750 °C and the laser fluency was set for low kinetics (<3 J/cm^2) and high kinetics (>5 J/cm^2). to find the optimum settings for epitaxy.

Crystallographic properties of the epitaxial layers were analyzed by Theta-2Theta scans and Phi scans using a PANalytical X'Pert MRD X-ray Diffraction (XRD). Scanning electron microscopy (SEM) for thin film cross sectional imaging was performed using a Zeiss-1550 HRSEM. In addition the backscattering electron detector (EBS) showed the compositional contrast. Atomic force microscopy (AFM) was used on full wafers to measure the surface roughness of the deposited thin films (Veeco Dimension Icon SPM).

For electrical measurements, 300x300 µm^2 capacitors were patterned by a standard photolithography process and structured by argon-beam etching of the 50 nm sputtered top Pt electrodes and wet-etching (HF-HCl solution) of the PZT and PMN-PT films to expose the bottom oxide $LaNiO_3$ electrodes. The polarization hysteresis (P-E) loop measurements were performed with the ferroelectric mode of the aixACCT TF-2000 Analyzer using a triangular ac-electric field of ±200 kV/cm at 1 kHz scanning frequency. The longitudinal piezoelectric coefficient d33,f of the piezoelectric thin-film capacitors was measured by a Double Beam Laser Interferometer (aixDBLI) method with a driving voltage ac signal of ±20 V and 1 kHz.

3 RESULTS

For domain epitaxy of TiN it was found experimentally that the growth kinetics are crucial. TiN deposited with different kinetic energy settings on HF- treated 200 mm Si (001) wafers showed that epitaxy is achieved at 600 °C at high kinetic energy. Low kinetic energy settings for the TiN resulted in poor epitaxy as can be observed from the Phi scan in figure 3. In contrast to the data (blue) for TiN deposited at high kinetics and 600 °C, the 4 reflections are poorly visible (red).

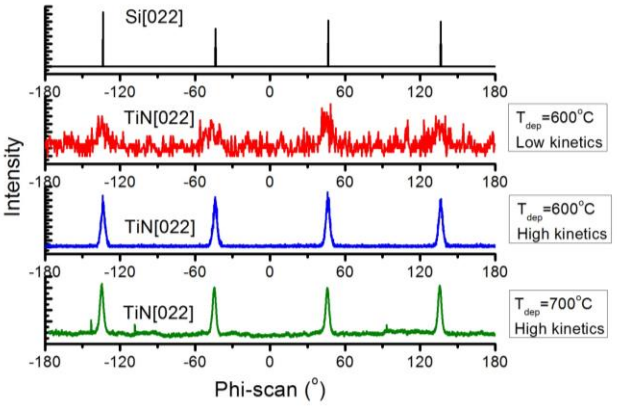

Figure 3: Phi scan of (022) reflection the silicon substrate (black), and the TiN template layer deposited using deposition conditions as indicated (red, blue and green)..

Using high kinetic energy settings the influence of temprerature is then further investigated. Only TiN (002) fractions were found in XRD from T > 600 deg C. Further, the TiN (002) intensity increases with deposition temperature (not shown). In figure 4 it can be observed that the FWHM of TiN (002) rocking curve decreases with temperature, indicating that crystallinity is improved as the mosaic spread is reduced. The surface morphology of the TiN template layer is also dependant on temperature. The surface roughness decreases up to 700 deg C, followed by a sharp increase at 750 deg C as obtained from AFM measurements (not shown). This is in line with the observation that the TiN (002) FWHM reflection sharply decreases, indicating enhanced grain size. Since subsequent layers will be deposited on the TiN epitaxial template, a smooth interface is preffered. For the aforementioned reason the deposition temperature of the TiN template layer was therefore fixed at 700 °C at high kinetics.

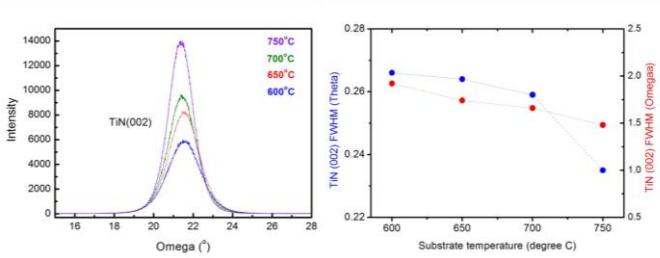

Figure 4: Rocking curves of TiN(002) thin film deposited at different temperatures (left) and FWHM of ω-scan and θ-scan.

It must be noted that for the TiN deposition no low base pressure was required (P-base = 5.10^{-6} mbar) to achieve epitaxy. After the deposition the 50 nm TiN films have a "golden appearance", indicating that they are low on oxygen content. The resistivity was measured using 4-point probe resulting in a fair sheet resistance of about 200 µOhm.cm homogeneous across the wafer. This is still higher than pure TiN indicating that some surface oxidation may have occurred. For ohmic contact to silicon, values as low as 15 µOhm.cm are reported [4].

After the TiN template layers the integration of perovskites needs to be facilitated. With nitride layers, high temperature in combination with high oxygen pressure should be avoided. The direct growth of conductive $LaNiO_3$ on TiN has not been successful yet. Therefore $SrTiO_3$ is selected as interlayer between TiN and oxide electrode. This material is easily grown in a low oxygen environment and acts as buffer layer between the nitride and oxide films. After the $SrTiO_3$, the oxide electrode and piezoelectric films are deposited. The total thin film stack is: 50 nm TiN / 50 nm $SrTiO_3$ / 50 nm $LaNiO_3$ / 1000 nm PZT (or PMN-PT).

The XRD of the film stack was measured at different positions on the 200 mm wafers. In figure 5 it is seen that for all thin films, only the (00l) out-of-plane orientations are visible. Moreover the crystallinity is homogeneous across the wafer as the XRD spectra of measurements on different radii of the wafer are similar. The rocking curves of the PZT (002) reflections completely overlap, indicating similar mosaic spread for different locations on the wafer. An average FWHM of 1.94° was found for PZT (002), which is close to the 1.75° FWHM of TiN (002), indicating that the low masaic spread is maintained throughout the complete layer stack.

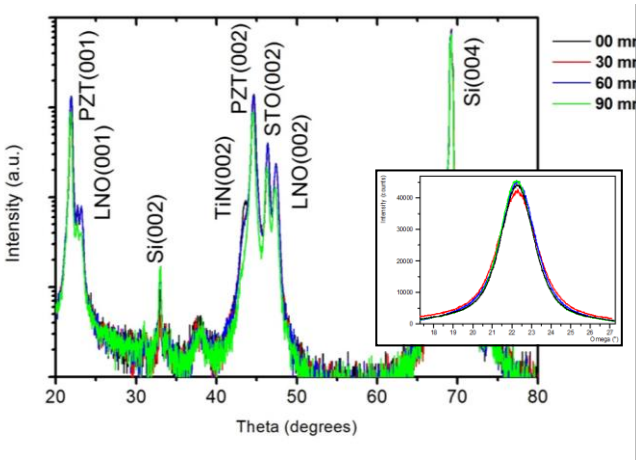

Figure 5: XRD spectrum of 50 nm TiN / 50 nm $SrTiO_3$ / 50 nm $LaNiO_3$ / 1000 nm PZT on different radial positions of the 200mm Si(001) wafer. The inset shows the PZT (002) rocking curve on the same positions.

In the XRD a low intensity peak is visible at about 38°. This is an indication that oxidation of TiN has occurred, likely during the deposition of $SrTiO_3$. However, this has not degraded the epitaxial relation between the TiN and $SrTiO_3$ as can be concluded from the Phi scan in figure 6. The data shows epitaxial relationship of all induvidual layers, as all (101) are aligned and 90° seperated. This confirms the following epitaxial relation: Si (001) ‖ 50 nm TiN (001) ‖ 50 nm $SrTiO_3$ ‖ 50 nm $LaNiO_3$ ‖ 1000 nm PZT (or PMN-PT, not shown).

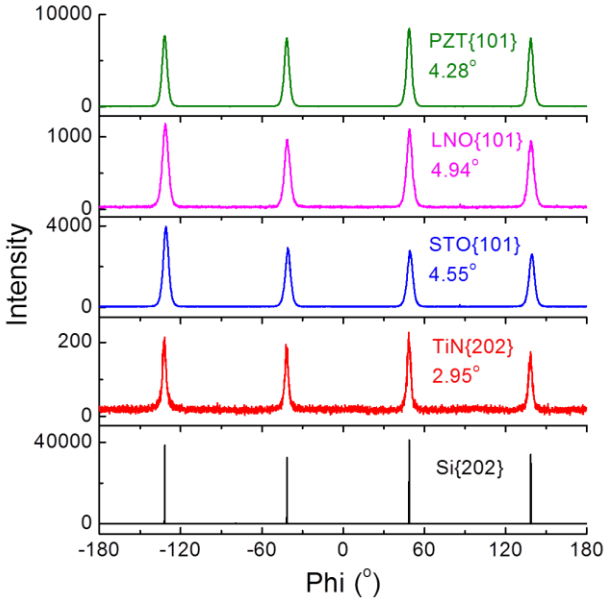

Figure 6: XRD spectrum of 50 nm TiN / 50 nm $SrTiO_3$ / 50 nm $LaNiO_3$ / 1000 nm PZT on different radial positions of the 200mm Si(001) wafer. The inset shows the PZT (002) rocking curve on the same positions.

The left side of figure 7 shows the cross section SEM of the epitaxial layer stack. The film grows smooth and coherent as it is difficult to distinguish the individual layers. When the EBS detector is used, one can discriminate the layers based on their chemical composition (right side of figure 7). Here sharp and smooth interfaces become visible.

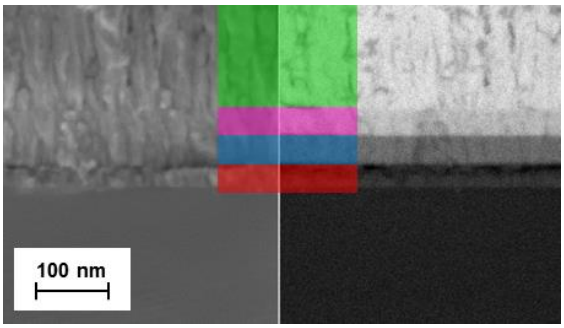

Figure 7: SEM cross section using standard and EBS detector. The overlay colours indicate the TiN (red), $SrTiO_3$ (blue), $LaNiO_3$ (purple) and PZT (green) layers.

The ferroe- and piezoelectric properties of the epitaxial PZT and PMN-PT films are measured using the 300x300 μm^2 capacitors. The piezoelectric loop for the PMN-PT is more slender compared to the PZT due to its relaxor like behavior (not shown). The C-V measurements for both film stacks are shown in figure 8. The dielectric constant of the PZT is about 1200, wheras the dielectric constant of PMN-PT exceeds 3000. On the other hand the small signal piezo coefficient d_{33} is not so much different, 50 pm/V to 65 pm/V respectively. These values are not spectacularly high, but it is pointed out here that these films are still clamped to the substrate. For the specific PETMEM application where a high d33 is required, the films will be unclamped by structuring the devices to submicron dimensions. It is expected that this will significantly boost the piezoelectric coefficient [7]

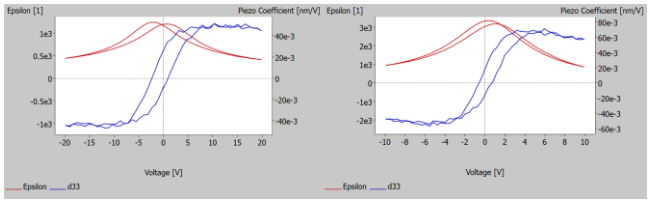

Figure 8: C-V measurements of PZT (left) and PMN-PT (right) thin films yielding dilectric constant (red) and small signal piezo coefficient d_{33} (blue)

As mentioned previously the main driver for epitaxial thin films is the stability. In order to check the long term stability of the PZT and PMN-PT thin films they are exposed to 10^{11} actuation cycles at 10V bipolar switching. The polarization and piezo coefficient response of the epitaxial PMN-PT film are shown in figure 9. As can be observed the responses are very stable up to 10^{11} actuation cycles.

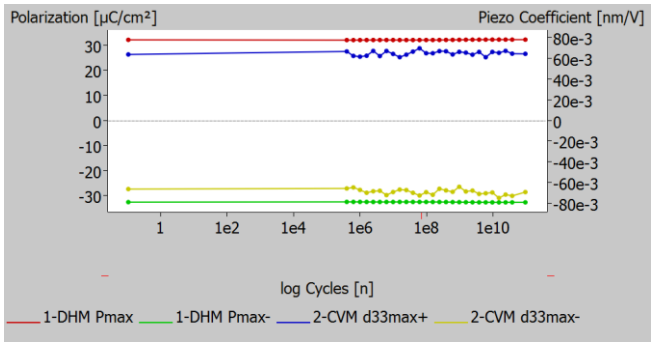

Figure 9: Polarization and d_{33} response of PMN-PT during 10V bipolar switching.

4 CONCLUSIONS

PZT and PMN-PT thin films are epitaxially deposited on 200 mm wafers using Solmates' Pulsed Laser Deposition (PLD) platform. Epitaxy is achieved using a TiN thin film on the lattice mismatched silicon. It is shown that using PLD the best domain epitaxy can be achieved at deposition temperature of 700 °C, as this resulted in the smallest FWHM rocking curve of TiN (002) whilst yielding a smooth interface that allows subsequent growth of epitaxial oxide layers. The high kinetic energy of the ablated species during the growth of TiN is crucial to obtain epitaxy. $SrTiO_3$ was used as buffer layer and $LaNiO_3$ as oxide bottom electrode after which PZT and PMN-PT were epitaxially deposited. From structured capacitors the dielectric constant and piezo coefficients were measured. The results are typical for clamped epitaxial piezoelectric thin films and showed a stable performance upon high number of actuation cycles.

These results indicate that using Solmates'PLD platforms epitaxy on silicon is readily available on wafer level. This will accelarate the commercial uptake of novel MEMS and NEMS devices such as the PETMEM device.

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