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Multi-target reactive sputtering—A promising technology for large-area $Pb(Zr,Ti)O_3$ thin film deposition

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Abstract

Beyond target diameters of 100 mm, multi-target reactive sputtering becomes a promising technology for ferroelectric thin film deposition. The main advantages of multi-target sputtering technology are: (i) thin films with precise composition control, (ii) stoichiometric variations on the target surface during repeated use are prevented by target preconditioning and operation in the metallic mode, and (iii) higher deposition rate due to sputtering from metals in the metallic mode. The latter requires a much greater precision in control of the partial pressure of oxygen, e.g., by a plasma emission monitor. In this work, $Pb(Zr,Ti)O_3$ thin film deposition on 150 mm silicon wafers by an industrial system is demonstrated. This technology can be easily scaled-up for larger silicon wafers and is compatible with standard semiconductor technology. Films deposited onto ZrO_2 buffer layers were polarized in-plane and they are suitable for piezoelectric MEMS application.
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1. Introduction

Modern fabrication of devices comprising ferroelectric thin films like nonvolatile memory elements, high volumetric efficiency capacitors, waveguide devices, nonlinear optical elements, electromechanical actuators for microelectromechanical systems (MEMS), pyroelectric detectors, etc., requires a cost-effective deposition technique which is compatible with silicon technology. In-plane polarized ferroelectric thin films on ZrO_2 buffered silicon substrates which are required for high-sensitivity devices were previously deposited by chemical solution deposition (CSD) and a subsequent high temperature annealing.[1–3] In order to improve film quality, the ZrO_2 buffer layer was manufactured also by pulsed laser deposition.[4] However, the thickness of ferroelectric films deposited by a one-cycle CSD process is about 50–100 nm. Therefore, devices fabrication requires a multi-layer deposition process. Moreover, to improve interface properties, the ZrO_2 buffer layer and the ferroelectric thin film should be deposited without any process interruption. Thus, thin film sputter deposition is a proper choice for industrial-scale device production. On the other hand, ceramic targets beyond diameters of 100 mm are difficult to fabricate. They often crack during high-power sputtering due to local heating. Due to the preferential sputtering phenomenon, they also fail to retain their original surface composition after repeated use.[5,6] Hence, film stoichiometry can be provided only by selecting very sophisticated combinations of deposition parameters, especially if volatile components like lead are included.[7] In contrast, metal targets are available with higher purity and large diameters.[8] Additionally, due to the higher heat conduction of metals, the targets can be used at a higher power density in comparison to a ceramic target.[9] Reactions of sputtered metal atoms with the reactive gas, i.e., reactive sputtering in the transition mode before the target is completely oxidized, provides compound film growth more easily. Therefore, it is favored for low-temperature, high-rate and large-area deposition.[8,10,11] Reactive sputtering can be performed either with single targets composed of Ti, Zr, and Pb, or by using multiple, independently powered targets.[10] Also, PbO is used as the lead source of $Pb(Zr,Ti)O_3$ films due to its higher melting point than metallic lead.[11,12] In the case of multi-component targets, the target design is generally correct for only a limited range of sputter conditions. For instance, the applied power must be greater than the threshold below which the target is oxidized for all of the components in order to maintain constant sputtering conditions and hence uniform composition in the final film.[10] Moreover,

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Zr/Ti film deposition is obtained on the PbO lead source due to a potential difference between the lead oxide sector and the Zr/Ti sectors in metallic mode.[11]

Multi-target reactive sputtering is a simple thin film deposition technique which meets requirements of device fabrication on an industrial scale and which has been applied for $Pb(Zr,Ti)O_3$ deposition for more than 20 years.[9,10,12,13] The main advantages of multi-target sputtering are:

(i) thin films with precisely controlled composition can be obtained, the stoichiometry of the films can be easily varied by changing the power to the target, e.g., possible loss of lead due to the elevated temperatures can be compensated in this way,
(ii) stoichiometric variations on the target surface during repeated use can be prevented by target preconditioning and operation in the transition mode,
(iii) sputtering from metals in the transition region where the target racetrack is in the metallic mode and the metal is oxidized by the reactive gas on the way to the substrate provides a higher deposition rate,
(iv) compatibility with current silicon technology.

Note that the (iii) requires a much greater precision in control of the partial pressure of oxygen. For this purpose, the plasma emission monitor (PEM) technique can be employed which is already well established as a process control tool for large-area reactive sputter deposition.[14–16]

In this work, we demonstrate for the first time the multi-target reactive sputter deposition of a ZrO_2 barrier layer and a PZT thin film in one process run onto a 150 mm oxidized silicon wafers. The PZT film may be polarized in-plane and is thus suitable for piezoelectric application.

2. Experimental

Multi-target reactive sputter deposition was performed in a LS730S sputtering system. The computer controlled system is equipped with a process chamber and a load-lock, both evacuated by turbomolecular pumps. The process chamber consists of four 8 in. metal targets, 3 pulsed dc (30 kHz, duty cycle ∼90%) and 1 RF magnetrons, 2 stationary radiation heaters and a wafer carousel holding four 150 mm silicon wafers (Fig. 1). Additional oxygen gas channels, which are controlled by piezoelectric valves, were introduced near the target surfaces. The gas flow of one channel is controlled by a close-loop feed back circuit of the PEM.

The 150 mm silicon wafers were covered with a 500 nm thermally grown SiO_2 layer. Both ZrO_2 (thickness 220 nm) and PZT films (thickness 350–2000 nm) were sputtered in an argon/oxygen mixture at a total pressure of 5×10^{-3} to 7×10^{-3} mbar. The substrate temperature was kept at about 550 °C for ZrO_2 and at about 580 °C for PZT. Argon flow was kept at 75 sccm (standard cubic centimeters per minute, 1 sccm ≅ 10/6 Pa l/s) while oxygen flow was controlled by PEM. Based on PZT deposition process peculiarities, the oxygen supplies to both of the Pb and Zr targets were fixed at 10 sccm. The

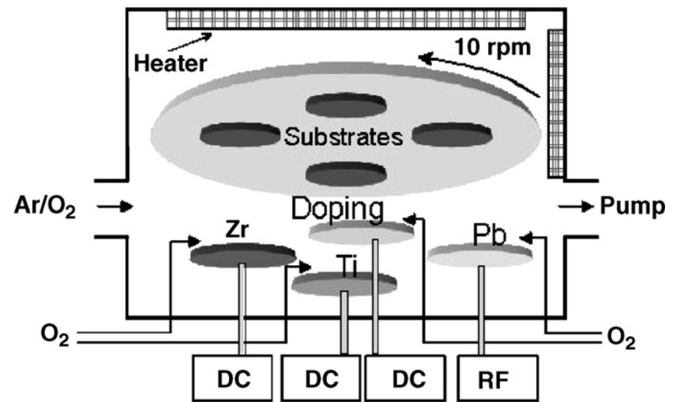

Fig. 1. Schematic diagram of the multi-target-sputter-deposition facility LS730S.

oxygen supply to Ti target was controlled by a piezoelectric valve of close-loop feedback system. This close-loop feedback system makes use of the Ti spectral line intensity of $\lambda = 453$ nm.[17] The wafer carousel was revolving at 10 rpm to ensure layer by layer growth.

One of the main problems of $Pb(Zr,Ti)O_3$ thin film deposition is the lead deficiency in film stoichiometry which is due to PbO volatility[18] and preferential resputtering of lead from the growing film surface atoms by negatively charged oxygen ions.[5,20] As a result, grains with insufficient Pb content nucleate at the initial stage of film deposition even under lead excess conditions. Most of these grains crystallize into a fluorite (pyrochlore) phase. The fluorite grains continue to grow until the Pb/(Ti + Zr) ratio reaches a sufficient value for perovskite grains to be formed. By this way, a non-ferroelectric interface layer with a thickness of up to 100 nm is formed.[21] By using a thin TiO_2 seed layer, we have significantly reduced Pb loss at the initial deposition stage. In this way, we exploit the decreased PbO vapor pressure in the $Pb(Zr,Ti)O_3 + TiO_2$ system compared to $Pb(Zr,Ti)O_3 + PbO$ by about one order of magnitude.[18] A TiO_2 seed layer with an optimal thickness of a few nanometers is totally consumed during the subsequent perovskite phase formation. At higher seed layer thicknesses, a thin non-ferroelectric interface layer remains. The deposition of the film bulk is performed under lead excess conditions. In this case, a lead excess surface layer is formed which reduces the crystallization temperature required to achieve good electrical properties. Thus, the films grow *in situ* in the ferroelectric perovskite phase, i.e., no thermal treatment after deposition is needed. The PZT deposition conditions are summarized in Table 1.

The thickness of the deposited film was determined by ellipsometry. Crystalline phases and orientation have been analyzed by means of a Siemens D5000 X-Ray Diffractometer (Co Kα radiation) in θ–2θ mode. Film microstructure characterization was performed by XRD, AFM, and electron microscopy. Composition analysis included XPS and glow discharge optical emission spectroscopy (GD-OES). NiCr interdigital electrode arrays (finger width 5 μm, finger gap 5, 10, and 20 μm, corresponding number of fingers 119, 89 and 48, respectively, overlapping length 1500 μm) were deposited on the upper surface of the $Pb(Zr,Ti)O_3$ films and patterned using a conventional

Table 1
Deposition conditions of PZT films

Target diameter (mm)	200
Target-substrate distance (mm)	65
RF power at Pb (W)	450
dc pulsed power at Zr (W)	800
dc pulsed power at Ti (W)	2000
Total gas pressure (mbar)	6×10^{-3}
Argon flow (sccm)	75
Oxygen flow for Pb, Zr, Ti (sccm)	0–20
Substrate temperature (°C)	520–580

lift off process. The dielectric properties and the ferroelectric polarization were examined by measuring *C–V* characteristics and *P–E* hysteresis loops. The dielectric constant, the effective electrode distance, and the polarization value corresponding to the measured charge were extracted using a Mathematica program based on Gevorian's model.[19]

3. Results and discussion

As-grown *in situ* crystallized perovskite films deposited without any post-annealing process were investigated. The film deposition rate was 7–10 nm/min in good agreement with previous work.[9] $Pb(Zr,Ti)O_3$ films deposited as described above were of single-phase perovskite comprising randomly oriented grains characterized by a Debye–Scherrer coherence length of 20–40 nm and by fractions of 71% (1 0 0), 6% (1 1 0), and 23% (1 1 1) orientation calculated as[22]

$$f_{hkl} = \frac{(I/I^*)_{hkl}}{(I/I^*)_{l00} + (I/I^*)_{00l} + (I/I^*)_{110/101} + (I/I^*)_{111}} \quad (1)$$

where *I* represents the integrated intensity of a peak and *I** is its counterpart in a powder sample. Electron diffraction pattern in the transmission electron microscope were assigned to PZT (1 0 0), (1 1 0), (1 0 1) and (1 1 1). They were in good agreement with XRD data. The rms roughnesses determined by AFM at the as-grown surface amounted to 38 nm for a perovskite/fluorite film and to 45 nm for a single-phase perovskite film. The film compositions determined by GD-OES were $Pb(Pb_{0.31}Zr_{0.28}Ti_{0.41})O_3$ and $Pb(Pb_{0.13}Zr_{0.35}Ti_{0.52})O_3$, respectively. The excess lead content in the films is in good agreement with the recently proposed phase diagram of the $PbPbO_3$–$PbTiO_3$–$PbZrO_3$ solid solution[23] and also with the lead excess required for single-phase perovskite films deposition.[20] Fig. 2 illustrates the $ZrO_2/Pb(Pb_{0.13}Zr_{0.35}Ti_{0.52})O_3$ interface. The *P–E* hysteresis obtained for different electrode gaps and a film thickness of 600 nm is presented in Fig. 3. The values of induced charge and applied voltage were converted into polarization and electric field neglecting fringing fields associated with finger termination. The obtained *in-plane* dielectric constants of the films were $\varepsilon_r = 700$–800 giving evidence of a high film quality. Both the dielectric constant and the saturated polarization P_s are linearly related to the longitudinal piezoresponse through:

$$d_{33} = 2Q_{11}\varepsilon_0\varepsilon_r P_s \quad (2)$$

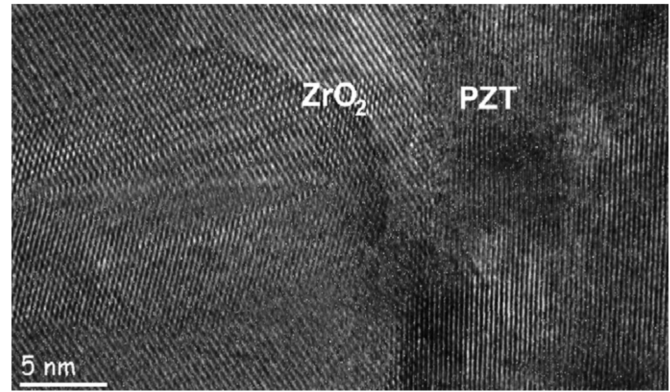

Fig. 2. TEM image of the $ZrO_2/Pb(Pb_{0.13}Zr_{0.35}Ti_{0.52})O_3$ interface.

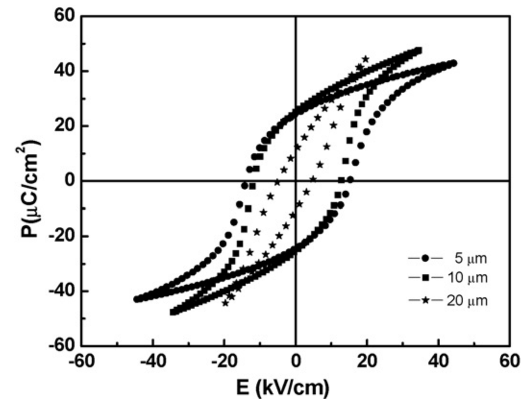

Fig. 3. *P–E* loop of $Pb(Pb_{0.13}Zr_{0.35}Ti_{0.52})O_3$ with IDE electrodes of 5 μm finger width and finger gaps between the adjacent electrodes of 5, 10 and 20 μm.

where Q_{11} is electrostrictive coefficient which amounts to about 0.05 m^4/C^2.[24] Therefore, the longitudinal piezoelectric coefficient d_{33} should exhibit the same trends as the dielectric constant and polarization. Note, that if the $Pb(Zr,Ti)O_3$ film is poled in the plane of the film, the *in-plane* stress and poling direction can be made to coincide. This results in a longitudinal response of $d_{33} = 265$ pm/V where the typical piezoelectric coefficient d_{33} is two to three times larger than the transverse value d_{31}.[1] Thus, this work describes a promising technology for industrial fabrication of piezoelectric MEMS devices.

4. Conclusions

Multi-target reactive sputtering of $Pb(Pb_{0.13}Zr_{0.35}Ti_{0.52})O_3$ thin films is demonstrated. Deposition was performed onto oxidized 150 mm silicon wafers covered with a ZrO_2 buffer layer. This promising technology for large-area deposition is easily scaled-up for larger silicon wafers and is compatible with standard silicon wafer technology. The films were polarized in-plane by biasing an interdigital electrode structure and they are suitable for piezoelectric MEMS applications.

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