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Low-temperature deposition of high-response piezoelectric thin films

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Strontium-doping of the popular lead zirconate titanate results in improved piezoelectric response characteristics. The synthesis of these thin films at a low temperature of 300 °C on silicon substrates is demonstrated. High response with an estimated piezoelectric coefficient (d_{33}) value of 892 pm V^{-1} was measured. Microstructural characterization results showing strong *c*-axis texture and lattice guiding effects are also presented.

Keywords: Thin films; Electromechanical properties; Crystalline oxides; High-resolution electron microscopy

Lead zirconate titanate (PZT) thin films are reputed for their relatively high piezoelectric performance [1,2], based on value of the piezoelectric response coefficients such as the piezoelectric charge coefficient d_{33}. Reported values of d_{33} for PZT thin films vary from ~100 to 400 pm V^{-1}. This relatively high response, often unmatched by other piezoelectric materials, has led to the widespread use of PZT thin films in electronic devices for sensing and actuation, but often with processing capabilities limited by the high deposition temperature required (600–700 °C).

The ability to synthesize successfully high-performance piezoelectric thin films at lower temperatures provides the capability for more versatile integration with microelectronics, expanding the range of potential applications. In order to achieve this objective, the theoretical basis, synthesis and characterization of low-temperature-deposited, high-piezoelectric-response thin films are described in this paper.

While PZT displays excellent piezoelectric response, it has been found that substituting strontium for a small percentage (~1.6%) of lead atoms at the 'A'-site of the perovskite ABO_3 structure of PZT enhances the piezoelectric response [3–7]. Thin films of PSZT (1.6 μm thick) were deposited on metal-coated silicon substrates by RF magnetron sputtering under the conditions given in Table 1. The silicon (1 0 0) substrates were first dipped in hydrofluoric acid to remove the native oxide layer. A diffusion barrier of 200 nm silicon dioxide was deposited, following which the gold electrode layer 150 nm thick was coated with the aid of a 15-nm titanium adhesion layer. All three layers were sequentially deposited by electron beam evaporation without breaking vacuum (at room temperature and under a vacuum of 1×10^{-7} torr). Following this, sputtering was carried out, with the samples placed on a 3-in. resistive substrate heater, which was compatible with deposition in an oxygen atmosphere [8]. Very accurate control of temperature was achieved using a Eurotherm Controls Model 808 temperature controller programmer. The post-deposition cooling rate was found to influence the degree of perovskite orientation in the thin films [9], based on which a cooling rate of 5 °C min^{-1} was chosen. The deposited thin films were extensively characterized using a combination of X-ray diffraction (under conditions as in Ref. [10]) and transmission electron microscopy (under conditions described in Refs. [11] and [12]).

Piezoelectric response measurements on PSZT thin films samples were carried out using a nanoindenter (Fig. 1) to estimate the piezoelectric charge coefficient d_{33}, using the technique described in Ref. [7]. This technique was rigorously tested during development to ensure that the values obtained were quantitatively accurate by ascertaining that similar values were obtained using both the nanoindenter and an atomic force microscope under the same testing arrangement [7,13]. Control samples consisting of amorphous silica thin films (no PSZT) were tested, demonstrating no response under an applied electric field. Moreover, substrate

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Table 1. RF magnetron sputtering conditions for PSZT.

Target	$(Pb_{0.92}Sr_{0.08})(Zr_{0.65}Ti_{0.35})O_3$
Target diameter	100 mm
RF power	100 W
Target to substrate distance	70 mm
Process gas	10% oxygen in argon
Base pressure	9.0×10^{-6} torr
Sputtering pressure	1.0×10^{-2} torr
Substrate temperature	300 °C
Temperature ramp-up rate	10 °C min^{-1}
Temperature ramp-down rate	5 °C min^{-1}
Sputtering duration	4 h

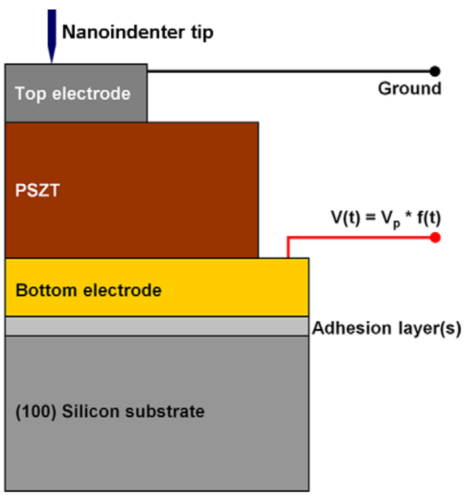

Figure 1. Schematic representation of the nanoindentation-based piezoelectric response measurement arrangement.

bending did not influence the results obtained, as no force was applied on the films during testing; identical values were obtained for films deposited on silicon and alumina substrates. The samples were studied under the influence of the inverse piezoelectric effect by applying an electric field and observing the variation in film thickness. More than one top electrode was defined on samples of interest to study the uniformity of the piezoelectric response in different regions of the samples. The response variations (as peak-to-peak changes in film thickness) over an 8 × 8-μm region under an applied electric peak-to-peak voltage of 32.8 V for a 1.6-μm-thick PSZT thin film sample is shown in Figure 2. This figure shows bands of piezoelectric response variations which corresponded to a minimum peak-to-peak thickness variation of 24.0 nm and a maximum of 29.3 nm, which correspond to d_{33} values of 732 pm V^{-1} and 892 pm V^{-1}, respectively. These piezoelectric response values were extracted from the raw data, consisting of sinusoidal variations of the film thickness, averaging the measurements over five cycles.

This ultra-high value of d_{33} (a maximum of 892 pm V^{-1}), which is more than twice as high as the maximum value reported for PZT thin films on silicon (419 pm V^{-1}) [14], is an improvement of 50% (one and a half times) on the highest thin film d_{33} value of 608 pm V^{-1} reported previously for PSZT thin films on

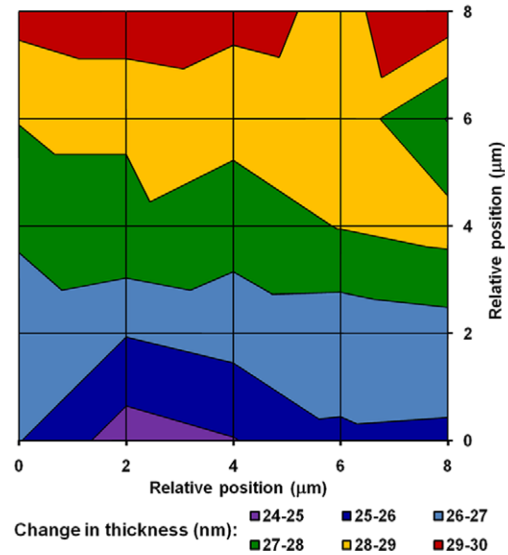

Figure 2. Result from mapping the piezoelectric response over an 8 × 8-μm area on the PSZT thin film surface.

gold [7]. The ultra-high-piezoelectric-response measured for these PSZT thin films can be attributed to three factors. Firstly, the PSZT thin films were deposited under optimized conditions following extensive analysis [8,9,12]. Secondly, the inclusion of the silicon dioxide layer improved the degree of preferential orientation in the PSZT thin films (Fig. 3), apparently caused by the increased guiding effect from the underlying gold layer

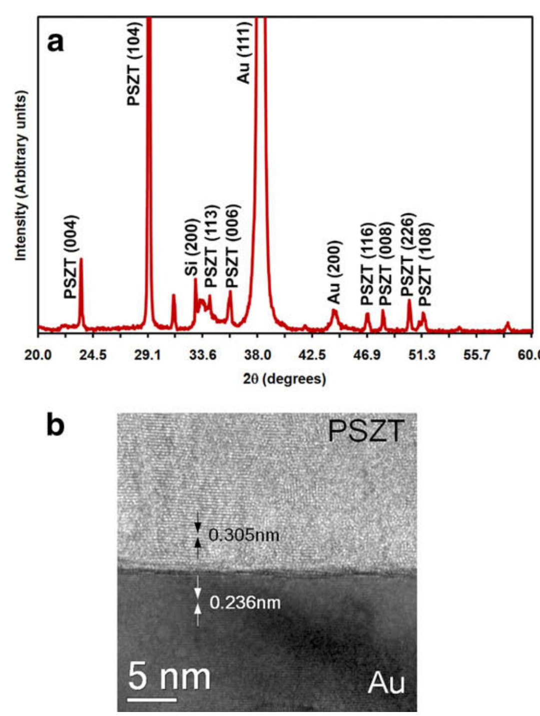

Figure 3. Characterization results for the PSZT thin film samples: (a) X-ray diffractogram showing the strong preferential orientation of PSZT (1 0 4) and Au (1 1 1); and (b) high-resolution transmission electron micrograph showing the guiding effect of Au (1 1 1) on PSZT (1 0 4).

(due to suppression of amorphous layer formation and enhanced gold texturing). Finally, and most importantly, the piezoelectric response observed could be attributed to the modified (and expanded) unit cell of the PSZT thin films under study [10]. This larger unit cell creates more room for atomic displacements under an applied electric field [15], with the capability of causing higher levels of strain in the PSZT thin films.

The values of d_{33} reported are termed 'effective values', as these apply for piezoelectric response measurements carried out on continuous thin films which are two-dimensional (length and width dimensions much greater than the film thickness). Lefki and Dormans [16] and Nagarajan et al. [17] have shown that the piezoelectric response of such films is damped by substrate clamping effects and, in reality, would have a component of error in the results. However, for thin film applications, the results presented in this paper are very relevant.

The only comparable result demonstrating ultra-high-piezoelectric-response thin films with d_{33} values up to 2000 pm V^{-1} was reported by Ouyang et al. [18]. While this result clearly demonstrates the ability to engineer films to attain high-piezoelectric-response, this deposition was carried out at 600 °C on $SrTiO_3$ substrates. The present authors demonstrate comparable high-piezoelectric-response for deposition at 300 °C on metal-coated silicon substrates. This makes the process compatible with microsystem fabrication using widely accepted silicon technology.

In summary, this paper presents results for the piezoelectric response characterization of optimized low-temperature piezoelectric thin films on silicon substrates. High response with a maximum d_{33} value of 892 pm V^{-1} was measured, for the PSZT thin films deposited on metallized silicon substrates at 300 °C. The origin of the ultra-high response can be attributed to optimized deposition conditions, the pronounced preferential texture in the thin films and a modified unit cell structure.

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