Pyroelectric and piezoelectric properties of thick PZT films produced by a new sol–gel route

M. Es-Souni∗, M. Kuhnke, A. Piorra, C.-H. Solterbeck
University of Applied Sciences, Institute for Material and Surface Technology (IMST), Kiel, Germany

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Abstract
The pyroelectric and piezoelectric properties of thick PZT films processed via a new sol–gel method are being investigated. The films were deposited on gold-coated alumina substrates. The pyroelectric properties are being evaluated using pyrodynamic measurements with either a laser or thermoelectric heat source. The pyroelectric coefficient is obtained from pyroelectric current measurements. The piezoelectric properties are being measured using a laser vibrometer-lock-in amplifier set-up. It is shown that the pyroelectric coefficient obtained with laser heating lies in the range of 108 /H9262°C/m 2 K, whereas heating from the rear of the specimen with the thermoelectric element lead to a value of in the range of 350 /H9262°C/m 2 K. These results are explained in terms through thickness temperature gradients. The piezoelectric displacement amplitude versus applied voltage shows a no-linear behaviour, which is explained in terms of materials chemistry. The maximum effective piezoelectric coefficient, d33, is obtained as 340 pm/V, and is superior to the values known for ferroelectric thin films.
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1. Introduction
The use of ferroelectric materials in low-cost infrared detection and thermal imaging systems as well in high power piezoelectric applications, e.g. sensors and actuators, is well established.1–3 The materials of choice for such applications are based on the PbTiO3–PbZrO3 (PZT) solid solution system in bulk ceramic form. In the last years, however, ferroelectric thin films are being intensively investigated for micro-actuators, micro-electromechanical-systems4 (MEMS) and thin film IR-sensor arrays.5 The films can be processed cost-effectively at temperatures far below those required for bulk ferroelectrics. Furthermore, compatibility with silicon technology presents the advantage of active film deposition directly on read-out circuitry which can result in cheap devices.5 A versatile method for the processing of thin films is via solution deposition which allows films of up to 1 /H9262 m thickness to be fabricated in a cost-effective way. Thicker films can be achieved by spin-coating a sol filled with fine dispersion of ceramic particles.6,7 In recent work7 we showed that it is possible to process thick, crack-free and dense PZT films using this processing route. The purpose of this work is to investigate the pyroelectric and piezoelectric properties of these films deposited on gold-coated alumina substrates.

2. Experimental details
Ferroelectric films of 5 /H9262 μm thickness were prepared using a propriety method.2 Milled powders of PZT (PZ21 Ferromerm, DK) were mixed with a PZT52/48 sol and spin-coated on gold-coated alumina (alumina 99.6%, CeramTech, Germany) substrates. The gold coating was also performed using spin-on technique. After pyrolysis and sintering for 30 min at 800 °C, the films were infiltrated with the PZT52/48 sol and annealed at 700 °C for 30 min to give a dense film. The microstructure of the film, including surface topography and cross section, was investigated by means of scanning electron microscopy (SEM). Pt top electrodes were sputtered onto the film surface to provide the electrical front contacts. For piezoelectric and pyroelectric measurements, the front elec-

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* Corresponding author. Tel.: +49 431 210 2660; fax: +49 431 210 2661.
E-mail address: mohammed.es-souni@fh-kiel.de (M. Es-Souni).
trodes with an area of 6.69 mm$^2$ consisted of a central circular pattern with four adjacent contact pads. The samples were measured in the corona poled states (15 kV was applied for 20 min at 150 °C, and the specimens were cooled down under bias).

The impedance measurements were performed in the frequency range from 100 Hz to 1 MHz with a computer controlled impedance analyser. The Curie temperature $T_C$ of the film was measured on cooling at a frequency of 1 kHz.

Pyrodynamic and bolometric measurements were made using a self-made experimental set-up. The thermal excitation is done sinusoidally with a thermoelectric heater/cooler element (Peltier element) or a near-infrared laser ($\lambda = 681.8$ nm, output power amplitude: 9.6 mW). Mean temperature of all measurements was room temperature.

Surface temperature measurements were performed using the front electrode as a bolometer. The lock-in amplifier was employed to monitor the bolometric voltage variation. The Pt electrode is contacted with two needles and the current and voltage is supplied and measured separately at the two needles (4-wire sense). An evaluation method using the two first order Fourier coefficients of the temperature and voltage signals is applied to determine the amplitudes. From the amplitudes the calibration coefficient is calculated. The bolometric calibration was done twice and the coefficients values of 0.6131 and 0.6162 °C/mV obtained were close to each other. The dependence of surface temperature on the modulation frequency of thermal excitation is computed from the measured bolometric voltage amplitude and the above-mentioned coefficient. For the Peltier element the frequency was in the range from 30 to 200 mHz and for the laser in the range from 100 mHz to 1 kHz.

The piezoelectric properties were done using a self-made experimental set-up including a computer controlled laser interferometer (Polytec OFV 353 sensor head and OFV 3001 vibrometer controller), DSP lock-in amplifier, frequency generator and voltage source. The vibrometer was operated in the most sensitive velocity range (1 mm/s/V). The position of the laser spot was in the centre of investigated front electrode.

3. Results and discussion

3.1. Microstructure

The surface topography of the PZT films (not shown) shows a crack-free bimodal structure consisting of fine grains and rosette-like coarse grains. The XRD-patterns (not shown) reveal phase pure perovskite without pyrochlore. The cross-section microstructure of the film shown in Fig. 1 reveals quite compact films. It should be pointed out that the processing method outlined above leads to reproducible film microstructures both on platinized silicon, reported in a previous work, and gold-coated alumina.

$$p_i(\omega) = \frac{\Delta p_i(\omega)}{m A}$$

where $p_i(\omega)$ is the pyroelectric coefficient, $\Delta p_i(\omega)$ the amplitude of the pyroelectric current, $\Delta T(\omega)$ the amplitude of the temperature modulation and $A$ the area of the front contact. It is assumed that the temperature variation is homogenous in the ferroelectric film and hence equal to the surface temperature of the film.

In Fig. 2 the magnitudes of the effective bolometer voltage and surface temperature using the sinusoidally modulated laser and the Peltier element as heat sources are shown. Multiplying the magnitude by $\sqrt{2}$ and 0.6162 °C/mV (calibration factor, see above) gives the peak amplitude of the surface temperature. As expected, the surface temperature decreases with increasing frequency. At $f > 3$ Hz an enhanced decrease of the surface temperature is observed.
The dielectric, pyroelectric and piezoelectric properties of the investigated PZT film and a standard PZT ceramic from literature are listed in Table 1. Using the Peltier element as a heat source the surface temperature increases with decreasing frequency because of the slow response of the Peltier element. The figures-of-merit of response $F_D$ and detectivity $D^*$ for a detector element are listed in Table 1 using a volume specific heat capacity $c' = 2.5 \text{ J/cm}^3/\text{K}$. The figures-of-merit agree reasonably with the values obtained from literature for sol–gel films (data compiled in reference). Only the high loss tangent and the high dielectric constant of the ferroelectric films obviously degrades $F_D$, and devices built with this material are supposed to have a higher dielectric-loss generated Johnson noise than one reported for modified PZT ceramics.

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_x$ (°C)</th>
<th>$e'$</th>
<th>$\tan \delta$</th>
<th>$p$ (μC/cm²)</th>
<th>$T_c$ (°C)</th>
<th>$e'$</th>
<th>$\tan \delta$</th>
<th>$P_0$ (mC)</th>
<th>$P_0$ (μC/°C)</th>
<th>$d_{33}$ (pm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT film</td>
<td>21–23</td>
<td>528</td>
<td>0.022</td>
<td>352</td>
<td>240</td>
<td>516</td>
<td>0.0027</td>
<td>386</td>
<td>2.5 $\times$ 10⁶</td>
<td>2.8 $\times$ 10⁻³</td>
</tr>
<tr>
<td>PZT ceramic</td>
<td>–</td>
<td>200</td>
<td>–</td>
<td>–</td>
<td>220</td>
<td>2.5 $\times$ 10⁶</td>
<td>2.8 $\times$ 10⁻³</td>
<td>1.4 $\times$ 10⁻⁵</td>
<td>540</td>
<td></td>
</tr>
<tr>
<td>PZT thick film</td>
<td>–</td>
<td>900</td>
<td>–</td>
<td>–</td>
<td>420</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Modified PZT ceramics (PZFNTU).  
$^b$ Sintered PZT21 ceramics (materials data sheet, Ferroperm).
the powder, which constitute two phases with different sto-
ichiometries and therefore different piezoelectric properties.

The values of $d_{33}$ are lower than those of sintered PZT21
ceramics reported in the materials data sheet (Ferroperm
Piezoceramics A/S) but are superior to those reported
for PZT thin films. Barrow et al. report a $d_{33}$ value of
325 pm/V on a 20 µm PZT thick film, which is close to that
of the present work. The piezoelectric hysteresis loop can
be seen in Fig. 4b. An almost square hysteresis loop is obtained
with a high remnant strain. This behaviour is usual for soft,
I.e. donor doped, PZT ceramics. However, it can also be
seen that the hysteresis loop is asymmetric both in the strain
and field axis which is indicative of an internal bias field.

Although the present results can be first considered as pre-
liminary, and need complementary investigations, e.g. deter-
mination of the in-plane piezoelectric coefficient $d_{31}$, they
nevertheless show the promising potentials of these films in
micro-actuator applications.

4. Summary and conclusion

For the determination of the pyroelectric coefficient of
a ferroelectric film from pyrodynamic measurements the
pyroelectric current is more suitable than the pyroelectric
voltage, since the uncertainty in the film capacitance is
avoided. Also a thermal excitation of the sample from the
rear side, using a thermoelectric heater/ cooler or Peltier
element, which ensures a homogeneous heating of the
ferroelectric film, is necessary. The 5 µm thick PZT film
prepared with the powder-sol method is a suitable ferro-
electric material for infrared detection at room temperature.
The dielectric and pyroelectric properties of the ferroelectric
film given in Table 1 agree reasonably with the values from
literature. The relatively large dielectric loss of this thick
film (tan δ = 0.022) in comparison with other PZT films
may be due to relaxation phenomena both at the powder/sol
interfaces, since they are of different stoichiometries, and at
the film-electrode interface. However, the pyroelectric coeffi-
cient $p = 352 \mu C/K/nm$ obtained is large for a PZT film. The
high relative permittivity $\varepsilon' = 558$ of the investigated PZT
film suggest an application for small area detector elements,
E.g. an array of detector elements for thermal imaging. The
figure-of-merit of voltage response $F_v = 2.8 \times 10^{-2} m^2/C$ is
similar to other PZT films but smaller than that of modified
PZT ceramics. This also holds for the figure-of-merit of spe-
cific detectivity $F_D = 14 \times 10^{-6} Pa^{-1/2}$ which is by a factor 4
smaller compared to modified PZT ceramics, and hence the
detector has a higher dielectric-loss generated Johnson noise.

The piezoelectric properties of the films are promising for
micro-actuator applications. They can be further improved by
choosing a sol stoichiometry closer to that of the PZT powder
material.

In conclusion, the present work shows that it is possible
to obtain good quality thick PZT films via spin-coating a
colloidal sol-powder solution. This processing route allows
such films to be obtained in few coating sequences. It offers
a good control of film thickness and microstructure, and is in
this respect superior to the screen-printing method. As can be
inferred from pyroelectric and piezoelectric measurements,
the films can be used both in pyroelectric and piezoelectric
applications.

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