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Pyroelectric PZT/PMNZTU composite thick films

R.A. Dorey*, R.W. Whatmore

Nanotechnology Group, School of Industrial and Manufacturing Science, Cranfield University, Building 70, Cranfield, Bedfordshire MK43 0AL, UK

Abstract

Uranium doped lead magnesium niobate–lead zirconate titanate (PMNZTU) composite thick films have been fabricated on silicon substrates using a composite sol–gel technique. A slurry, made up of PMNZTU powder and PZT sol, was spun onto a silicon substrate and fired to yield a porous skeletal ceramic structure. Subsequent sol infiltration and pyrolysis was used to modify the density of the films prior to final sintering at 710 °C.

Pyroelectric and dielectric properties have been measured as a function of sol infiltration. The pyroelectric coefficients ($p_{max} = 2.74\,C\,m^{-2}\,K^{-1}$) of the composite thick films were found to be comparable to tape cast and monolithic ceramics of similar composition (2.8 and $3.0\,C\,m^{-2}\,K^{-1}$, respectively).

Maximum figures-of-merit (FOM) ($F_V = 3.45 \times 10^{-2}\,m^2\,C^{-1}$, $F_D = 1.01 \times 10^{-5}\,Pa^{-1/2}$), calculated using the electrical properties of the thick films, can be compared with those of screen printed thick films ($F_V = 2.7–3.9 \times 10^{-2}\,m^2\,C^{-1}$, $F_D = 0.8–1.1 \times 10^{-5}\,Pa^{-1/2}$) processed at temperatures of approximately 1100 °C. The ability to directly integrate thick pyroelectric films onto substrates at temperatures as low as 710 °C, while maintaining competitive figures-of-merit is of considerable interest for future device applications.

Keywords: Films; Sol–gel processes; Pyroelectric properties; PZT; Sensors

1. Introduction

Pyroelectric materials are of considerable interest for applications involving the detection of infra-red (IR) radiation with wavelengths in the ranges 3–5 and 8–14 μm. IR radiation with wavelengths in these ranges is of interest as it is transmitted through the atmosphere with minimal absorption. Furthermore, the peak in the black body emission spectrum for objects at around 300 K lies in the 8–14 μm wavelength range. Detection of such radiation is, therefore, of interest for applications such as thermal imaging, intruder detection and fire detection.[1]

To provide an indication of the effectiveness of a given material for pyroelectric applications it is useful to define two figures-of-merit (FOM).[2]

$$F_V = \frac{p}{c'\varepsilon_o\varepsilon_r} \tag{1}$$

$$F_D = \frac{p}{c'(\varepsilon_o\varepsilon_r\ \tan\delta)^{1/2}} \tag{2}$$

where ε_o is the permittivity of free space and p, c', ε_r, and $\tan\delta$ are the pyroelectric coefficient, the specific volume heat capacity, the relative permittivity, and the loss tangent of the materials, respectively. F_V is proportional to the device voltage responsivity and F_D to its specific detectivity (assuming that circuit noise is dominated by ac Johnson noise due to the ac conductance of the element).

The use of polycrystalline ceramic pyroelectric materials for the detection of IR radiation in such applications offers advantages over other systems such as photoconductive and photovoltaic systems.[1] Along with the ability to operate devices without cooling, ceramics are cheap to manufacture in large areas, they are mechanically and chemically more robust, have high Curie temperatures for greater stability, and their properties can be readily modified through doping to tailor them for specific applications.

Recently a solid solution of lead zirconate titante and lead magnesium niobate (PMNZT), doped with manganese,[3]

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[*] Corresponding author. Tel.: +44 1234 750111x2505; fax: +44 1234 751346.

E-mail address: r.a.dorey@cranfield.ac.uk (R.A. Dorey).

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chromium,[4] antimony[4] or uranium,[5] has been proposed as an attractive material for applications involving detection of IR radiation due to the high pyroelectric coefficient. Values of room temperature pyroelectric coefficients (p), F_V and F_D are given in Table 1.

The sensitivity of IR detection systems can be increased by employing thin sections of ceramic 10–20 μm thick.[6] Such thicknesses represent a compromise between increased sensitivity (thinner films) and higher signal to noise ratio and voltage output (thicker films).[7] Hence, despite high FOMs exhibited by monolithic ceramics, the advantages of increased sensitivity combined with good signal to noise ratios and high voltage output mean that thick films are of significant interest for pyroelectric applications.

It is time consuming, expensive, and technically challenging to machine monolithic ceramic components to dimensions of 10's of micrometers. Further, the associated material wastage would be large. One route to produce thinner structures is to use tape-casting techniques. Tape cast uranium doped PMNZT materials,[8] 100–300 μm thick, have been shown to exhibit room temperature pyroelectric coefficients, which compare favourably with that observed in monolithic ceramics (Table 1). Despite achieving relatively thin sections using tape casting, further reductions in thickness would necessitate the use of a support structure. In this instance, the required high processing temperatures (1200–1300 °C) become unattractive as such temperatures would damage the (required) substrates[9] and would make it very difficult to accurately control the composition of the material due to excessive lead loss.[6]

Films between 10 and 20 μm thick, on a variety of substrates, can be readily produced using screen-printing techniques. Pyroelectric PZTZN[6] and PLZT[10,11] materials were deposited onto refractory substrates and fired at 1100 °C. These materials exhibited room temperature pyroelectric coefficients and figures-of-merit in the ranges shown in Table 1. The properties of the screen-printed films were reported to be lower than those of bulk ceramics of comparable composition. This was attributed to effects associated with the clamping of the substrate, diffusion of impurities into the films and loss of lead at the high sintering temperatures. However, it was felt that the use of screen printed films was still of value as the increase in sensitivity compensated for the reduction in pyroelectric response.[6]

Table 1
Reported pyroelectric properties of doped PMNZT monolithic ceramics, tape cast PMNSTU, and screen printed PZTZN and PLZT films

	p ($\times10^{-4}$ C m^{-2} K^{-1})	F_V ($\times10^{-2}$ m^2 C^{-1})	F_D ($\times10^{-5}$ Pa$^{-1/2}$)
Mn doped PMNZT	3.5	7.1	3.6
Cr Doped PMNZT	2.5	4.5	1.5
Sb doped PMNZT	2.5	3.2	1.1
U doped PMNZT	3.0	6.6	4.7
Tape cast PMNZTU	2.8	5.2	3.1
Screen printed films	1.2–1.5	2.7–3.9	0.8–1.1

To overcome this problem of lead loss at high processing temperature and to allow silicon substrates to be used the use of a low temperature composite sol–gel technique[12] for producing PMNZT type films will be investigated. In this process, a ceramic producing sol and a ceramic powder are mixed together to produce a slurry, which is then spun onto a substrate. Subsequent firing, at much reduced temperatures (550–800 °C), converts the sol to an oxide ceramic to form a thick film. Intermediate sol infiltration and pyrolysis can be used to vary the density of the films. To demonstrate the use of the composite sol–gel technique for producing thick pyroelectric films it was decided to utilise a simplified sol composition ($Pb_{1.05}(Zr_{0.825}Ti_{0.175})O_3$) due to the difficulties associated with obtaining a perovskite, lead magnesium niobate–lead zirconate titanate (PMNZTU) material using the sol–gel process. The composition of the PMNZTU powder was maintained at $Pb_{1.01}(Zr_{0.825}Ti_{0.175})_{0.9687}(Mg_{1/3}Nb_{2/3})_{0.025}U_{0.0063}O_3$.

2. Experimental

The PZT producing sol was produced using lead acetate trihidrate (Fisher), zirconium *iso*-propoxide (Aldridge) and titanium *n*-propoxide (Aldridge) as starting reagents and 2-methoxyethanol as the solvent. The PMNZTU powder was produced using a mixed oxide route. Fig. 1 shows a schematic of the sol–gel and PMNZTU powder preparation route. The

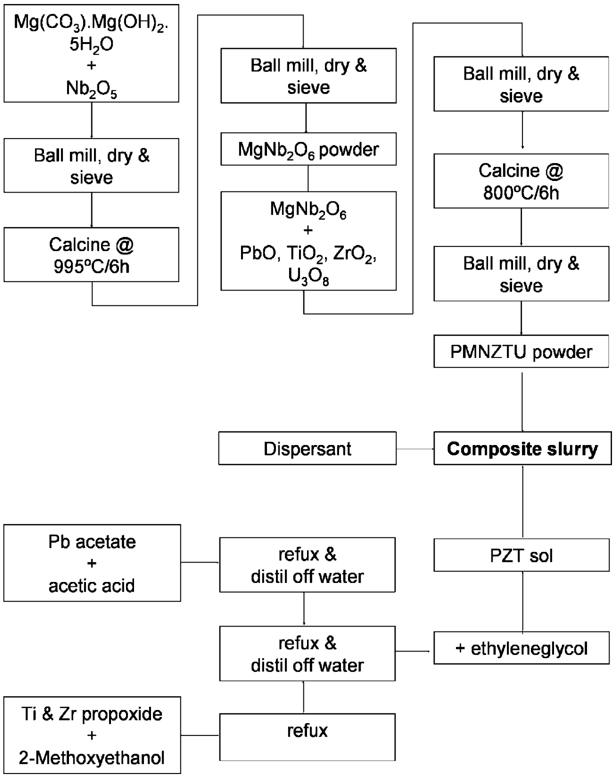

Fig. 1. Schematic of the route used to prepare the PZT/PMNZTU composite slurry.

composite slurry was produced by mixing 30 ml of sol, 45 g of PMNZTU powder, and 0.9 g of dispersant (KR55, Kenrich Petrochemicals).[12] The slurry was ball milled in a N_2 atmosphere (to prevent hydrolysis of the sol) for 24 h prior to use to ensure a homogenous mixing.

Prior to the deposition of the ceramic film, a ZrO_2 diffusion barrier (to prevent the diffusion of lead into the underlying substrate) and Ti/Pt back electrode were deposited onto the silicon substrate. The diffusion barrier was deposited by spinning a solution of zirconium *iso*-propoxide in ethanol onto the silicon wafer. The solution was dried and pyrolysed at 450 °C. In total three layers were deposited prior to crystallising the film at 700 °C. Following the deposition of the 40 nm ZrO_2 layer, 8 nm of titanium and 200 nm platinum were deposited using RF and dc magnetron sputtering.

The ceramic films were deposited by coating the wafer with the composite slurry and spinning the wafer at 2000 rpm for 30 s. The slurry was then dried at 200 °C and pyrolysed at 450 °C. The resultant porous structure was infiltrated with pure sol, dried and pyrolysed. This sol infiltration/pyrolysis was conducted 1, 2, 3 or 4 times. Once the required number of sol infiltration/pyrolysis stages had been completed further composite layers were then deposited (each infiltrated and pyrolysed the appropriate number of times). Four composite layers were deposited to achieve a final film thickness of approximately 9 μm. The films were then subjected to a final sintering regime at 710 °C in air to develop the perovskite structure and to enhance the density of the film.

Two millimetres diameter circular Cr/Au top electrodes were deposited by evaporation and the samples poled at 130 °C for 5 min using a field of $8\,\mathrm{V}\,\mu\mathrm{m}^{-1}$. The field was maintained until the samples had cooled to below 100 °C. Dielectric properties were measured after poling using a Wayne Kerr precision component analyser (6235B) at 30 Hz (close to the expected frequency of operation). The pyroelectric current response for each sample was measured by varying the temperature of the sample by ±2.5 °C about a mean temperature of 25 °C. The samples were isolated from surrounding thermal fluctuations by conducting the tests in a vacuum chamber. The resultant pyroelectric currents were measured using a Kiethley 6517 electrometer and used to calculate the pyroelectric coefficient using Eq. (3).

$$I = Ap\frac{\mathrm{d}T}{\mathrm{d}t} \tag{3}$$

where A is the area of the electrode, $\mathrm{d}T/\mathrm{d}t$ the rate of change of temperature with respect to time and I the measured pyroelectric current.

3. Results and discussion

Fig. 2 shows the variation in relative permittivity and loss (at 30 Hz) as a function of the number of sol infiltration/pyrolysis stages. The relative permittivity can be seen to increase as the number of sol infiltrations is increased. The values of relative permittivity observed in the high density (>2 sol infiltration/pyrolysis stages) thick films were slightly larger than those observed in the tape cast[8] and monolithic PMNZTU ceramics[5] which were in the range 230–300 depending on the processing temperature. This slight increase in the relative permittivity is probably due to the presence of the PZT sol which is expected to have a relative permittivity of approximately 350.[13] The addition of Mn as a doping element has been shown to decrease the relative permittivity of PZT sol–gel films,[14] and the addition the dopants to PMNZT was shown to reduce the relative permittivity in ceramic materials relative to PZT and PMNZT.[3–5] Hence, it is reasonable to assume that doping or a closer matching of the composition of the sol to that of the powder would result in a decrease in the relative permittivity of the films.

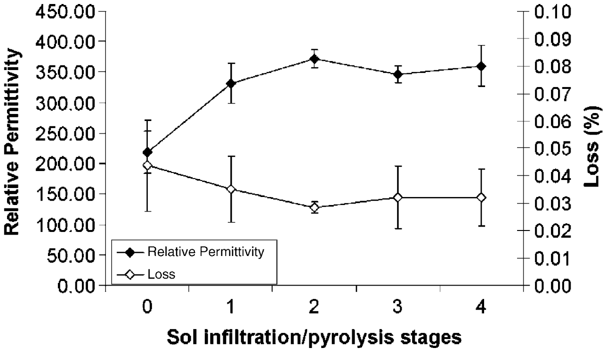

Fig. 2. Variation in value of relative permittivity (at 30 Hz) and loss as a function of the number of sol infiltration/pyrolysis treatments.

The pyroelectric coefficient of the composite sol–gel films can be seen to increase as the level of sol infiltration/pyrolysis increases (Table 2). The maximum pyroelectric coefficients observed are comparable with those observed in the bulk and tape cast materials. The increase in pyroelectric coefficient is thought to be due to the increase in the amount of active material present following the infiltration of the structure.

The figures-of-merit (F_V and F_D) for each of the films are also given in Table 2. They are lower than those for the tape cast and monolithic PMNZTU ceramics due to the higher values of relative permittivity and loss. However, they are comparable to the values previously reported for PZTZN and PLZT thick films. Due to high pyroelectric coefficients exhibited by the material it can be seen that the optimisation of the PZT sol (to decrease the relative permittivity) could result in enhancement to the figures-of-merit such that they

Table 2
Pyroelectric coefficients and figures-of-merit for the PZT/PMNZTU composite thick films

Infiltrations	p ($\times10^{-4}$ $\mathrm{C\,m^{-2}\,K^{-1}}$)	F_V ($\times10^{-2}$ $\mathrm{m^2\,C^{-1}}$)	F_D ($\times10^{-5}$ $\mathrm{Pa^{-1/2}}$)
0	1.50	3.10	0.65
1	1.75	2.39	0.69
2	1.86	2.26	0.77
3	2.50	3.27	1.01
4	2.74	3.45	0.94

approach those of the PMNZTU materials processed at 1200–1300 °C.

It should also be noted that in calculating the FOMs the specific volume heat capacity of the films was assumed to be comparable to that of the monolithic material (i.e. $2.5 \times 10^6\,\mathrm{J\,m^{-3}\,K^{-1}}$). Due to the porous nature of the films this value could be expected to be lower in the thick films, which would result in an increase in the FOMs.

4. Conclusions

A series of PZT/PMNZTU composite thick films were fabricated at 710 °C using a composite sol–gel technique. Pyroelectric coefficients comparable to those of bulk and tape cast components were observed despite the considerable reduction in upper processing temperature. The relative permittivity of the high density composite films was slightly higher than that of the bulk and tape cast materials due to the presence of the sol–gel phase with non-optimised composition. This increased relative permittivity resulted in a reduced FOM relative to that exhibited by tape cast and monolithic PMNZTU. FOMs were comparable to films produced by screen-printing and processed at 1100 °C.

Despite the lower FOMs (relative to tape cast and monolithic materials), the increase in sensitivity associated with the use of thick films and the low processing temperatures make this deposition technique an attractive one for manufacturing pyroelectric sensors.

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