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PZT thick films for sensor and actuator applications

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Abstract

PZT thick films with thicknesses between 5 and 150 μm are of great interest for microsystems applications where direct coating onto microelectronic substrates and high electromechanical performance are required. Dense PZT thick films have been obtained by combining a PZT-PMN powder with a low melting point glass and the eutectic forming oxides Bi_2O_3 and ZnO. Densification is due to transient liquid phase formation with additional incorporation of cations into the growing PZT grains during sintering. PZT thick films prepared by this method show excellent dielectric, ferroelectric and piezoelectric properties. They have been applied on various substrates, like Al_2O_3, ZrO_2, Low Temperature Cofired Ceramics (LTCC) and silicon wafers which are basis materials for microsystems technology. The influence of the substrate material on the PZT thick film properties and the role of buffer layers will be discussed.

Keywords: PZT; Films; Actuators; Sensors; Dielectric properties

1. Introduction

Lead zirconate titanate (PZT, $Pb(Zr,Ti)O_3$) is the most common piezoelectric material used for sensor and actuator applications because of its unique ferroelectric and electromechanical properties.

PZT thick films with thicknesses between 5 and 150 μm fill the gap between PZT thin films ($t = 100$ nm–2 μm) and bulk materials ($t > 200$ μm). They are of great interest for microsystems applications where direct coating onto microelectronic substrates and high electromechanical performance are required.

Sintering of PZT thick films turned out to be very difficult due to the following restrictions:

- Densification of the PZT green layer during sintering is hindered due to lack of lateral material transport.
- PbO evaporation during sintering at temperatures >850 °C causes degradation of material properties.
- Thermal expansion mismatch of the PZT thick film and the substrate material will lead to crack formation and/or delamination.
- Reactivity with substrate material restricts possible material combinations.

Normally, sintering of PZT materials takes place at temperatures of 1100–1300 °C. Extended research has been carried out during the last 15 years to lower sintering temperature of PZT materials down to 800–950 °C.[1–8]

The present investigation is based on the addition of a low melting point glass and a eutectic forming oxide. Thereby sintering temperature could be reduced down to 900–950 °C.

Screen printing is a very flexible and cost effective technology for producing functional layers on green and fired substrates. For screen printing, powders have to be modified and dispersed into an organic binder to form a printable paste. The paste can than be readily deposited as patterns, which represents a great advantage compared to spin coating or dip coating processes.

2. Experimental

Experiments were based on a PZT-PMN formulation with a high sintering temperature $T_s = 1240$ °C. Sintering temperature was reduced to 900–950 °C by the addition of Bi_2O_3 and ZnO and a borosilicate glass as described elsewhere.[3,7,8] For preparation of the thick film paste the powder was mixed with an organic vehicle and screen printed on electroded substrates.

To avoid open porosity in the PZT thick film and to reduce PbO loss during sintering a double layered sinter arrangement in the green ceramic state as described in Refs.[1,3,9] was found to be advantageous. Therefore, a secondary thick film based on

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the eutectic mixture (Bi_2O_3/ZnO) was screen printed on top of the green PZT thick film. During sintering, the eutectic mixture penetrates the PZT thick film and assists densification by liquid phase formation. During growing of the PZT grains atoms of the eutectic oxides Bi_2O_3 and ZnO are incorporated into the PZT lattice.

Sintering was performed at 950 °C/5 h with shrinkage of approximately 45% in the thickness direction. Lateral shrinkage was suppressed and no cracks were generated.

Thick films with sintered thicknesses between 20 and 150 μm have been applied by repeated screen printing on various substrates like ZrO_2, Al_2O_3, silicon and LTCC. For application on LTCC substrates a fired LTCC Du Pont 951 tape was used.

The substrate material as well as the composition of the electrode has an important influence on the dielectric and ferroelectric properties of the PZT. For ZrO_2 and Al_2O_3 a commercial Au electrode (Heraeus 5789) fired at 1030 °C/2h has been used. For silicon and LTCC substrates a special Au electrode was developed.

3. Measurement equipment

PZT films were poled at room temperature at 20 kV/cm, 5 min previous to measurement of the dielectric properties. Measurement of the parameters was done at least 24 h after poling.

The dielectric constants were measured at 1 kHz, using a Hewlett Packard 4194A Impedance Analyzer.

The measurement of the piezoelectric coefficient d_{33} was performed at the Department of Physics of the Martin-Luther-University Halle at 130 Hz, using equipment based on a capacitive detector.[10]

A modified Sawyer-Tower circuit was used to determine ferroelectric hysteresis loops. Internal resistance was measured by a Hewlett Packard 4339A High Resistance Meter.

For determination of the deflection and the blocking force, LTCC bending elements were clamped into a fixture at one side. The measurement of deflection and force takes place on the free end of the bending element using laser triangulation (Micro-Epsilon) and a load cell (Kistler® Typ 9207), respectively. The force measurement is aligned with the deflection measurement and is extreme stiff related to the bending stiffness of the bending element. Therefore, the block force can be determined directly. All data (temperature, driving voltage, displacement and force) were collected by a special software tool running on a PC.

4. Results and discussion

Sintering of the PZT thick films prepared by the introduced method results in PZT thick films with thicknesses between 20 and 150 μm. Fig. 1 shows a typical SEM micrograph of a PZT thick film on an Al_2O_3 substrate.

For being able to prepare integrated functional components in planar design, specific material problems have to be solved. The reaction between SiO_2 and PbO is relevant for PZT films on Si containing substrates like 96% alumina, Si wafer and LTCC. We considered this problem in detail in connection with the development of integrated PZT thick film devices.

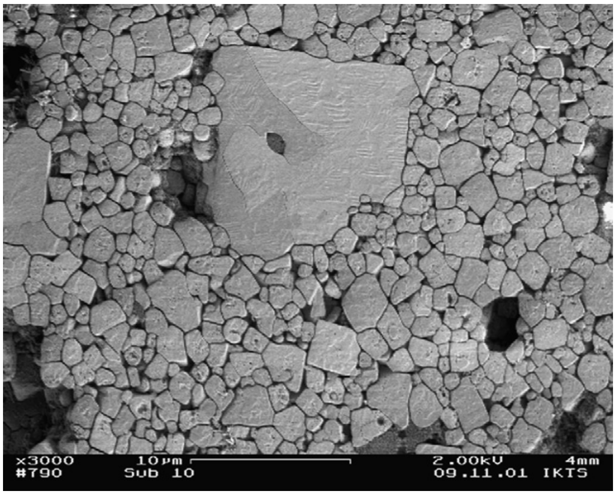

Fig. 1. SEM micrograph of a polished and etched cross section of a PZT thick film.

Table 1
Properties of PZT thick films

Substrate	Al_2O_3 (99.7%)	LTCC (DP 951)
Sinter temperature	950 °C/5 h	900 °C/5 h
Permittivity $\varepsilon_{33}^T/\varepsilon_0$ (1 kHz)	1600–2000	1200–1400
Dielectric loss tan δ (1 kHz)	<0.04	<0.04
Piezoelectric coefficient d_{33} [pC/N]	150–210	140
Remnent polarization P_r [μC/cm^2]	12–16	9–13
Coercive field E_C [kV/cm]	12–13	11
Internal resistance R_{is} [Ω]	>10^{10}	>10^6

The existence of silicon or silicon oxide in the substrate and the electrode material causes the diffusion into the PZT thick film and therefore the reaction to lead based silicates, which deteriorate the ferroelectric behaviour of the PZT thick film.

Best results have been obtained using pure Al_2O_3 (99.7%) and ZrO_2 substrates with Au electrodes. Table 1 gives a summary on results measured on a 100 μm PZT thick film on 99.7% Al_2O_3.

As the silica content in the substrate material increases the ferroelectric properties of the PZT will decrease as shown in Fig. 2. To overcome this problem a special Au electrode for Si containing substrates was developed. This Au electrode serves

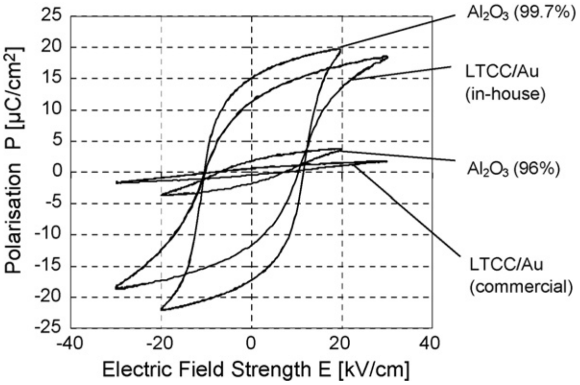

Fig. 2. Ferroelectric hysteresis loops of PZT thick films on different substrates.

as a buffer layer to prevent diffusion of the silica from the substrate into the PZT thick film. With this Au electrode it is possible to apply PZT thick films on Si and LTCC, which are key substrate materials in microsystems technologies. Table 1 gives an overview of performance data of a 100 μm PZT thick film on LTCC.

5. Application of PZT thick films

PZT thick films are of great interest as sensors and actuators for microsystems, optical and smart structure applications. Prototypical developments were part of R&D projects showing the feasibility of the following integrated functions:

- Ferroelectric capacitor as charge and information storage device.
- Piezoelectric actuator elements as basis for micropositioners, micropumps, active optical devices, and high frequency ultrasound transducers.
- Piezoelectric sensor elements, as transducer for pressure, force and strain measurements.
- Piezoelectric generator elements, usable for energy harvesting and battery substitute for low power circuits.

Starting in 1995 with large area PZT thick films on Al_2O_3 substrates for application as information storage material in electrostatic printing machines[1,2] our main focus on functional integration is presently on Si wafers and LTCC as substrate materials.

In view of an adaptive optical mirror for use in the EUV lithography PZT thick films with a thickness of 100 μm have been applied on top of a 4 in. Si wafer. A special in-house developed Au electrode has been chosen as bottom electrode. Forty-two PZT triangles with a side length of 6 mm have been screen printed in a hexagonal arrangement as shown in Fig. 3. During sintering PbO loss of the PZT thick film causes reaction to lead silicates with the surrounding Si which results in the formation of halos around the Au electrode. The properties of the PZT thick film are not influenced by this reaction because of the buffer function of the Au bottom electrode. Because backside of the Si wafer was used as mirror face, the halos had no influence on the reflective properties of the wafer.

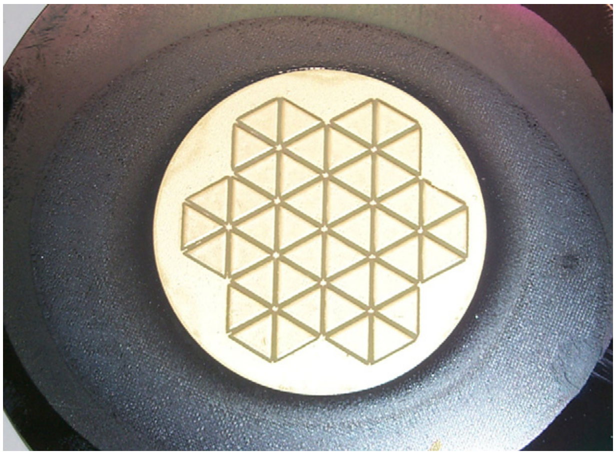

Fig. 3. PZT thick film pattern consisting of 42 triangles (side length $a = 6$ mm) with Au bottom and top electrode on 4 in. silicon wafer.

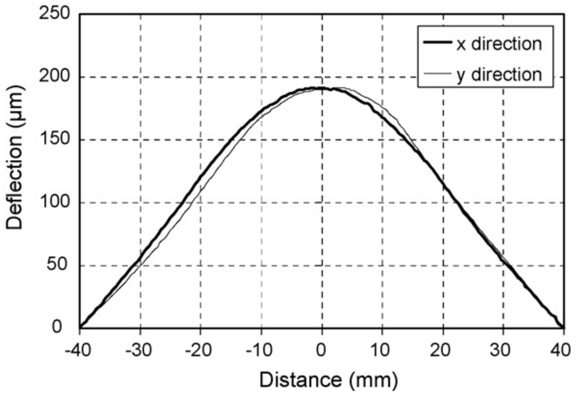

Fig. 4. Static deflection profile of a Si wafer with screen printed PZT thick films (Fig. 3). All PZT elements were parallel connected with each other and simultaneously driven at 20 kV/cm.

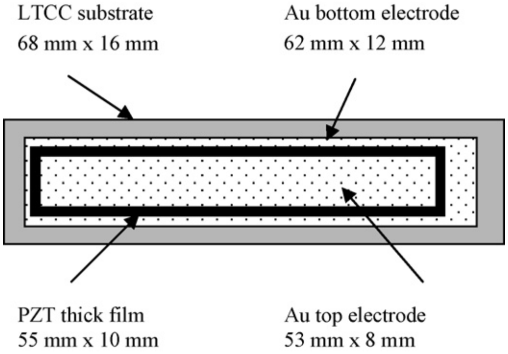

Fig. 5. LTCC bending element with PZT thick film and Au bottom and top electrode (drawing not to scale).

By driving the PZT thick film pattern the Si wafer bends in a parabolic manner. Deflection in x and y direction has been measured and is drawn in Fig. 4. It extends 200 μm at a driving field $E = 20$ kV/cm.

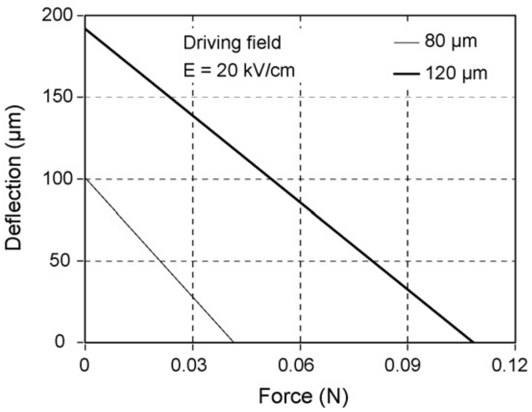

Fig. 6. Working diagram of a LTCC bending element (Fig. 5) driven with $E = 20$ kV/cm.

LTCC is also an interesting substrate material for microsystems technology because of its unique packaging properties. Bending structures based on sintered 0.6 mm thick Du Pont 951 tapes and PZT thick films have been prepared (Fig. 5). Thickness of the PZT thick film was adjusted to 80 and 120 μm.

The bending elements were clamped 5 mm into a fixture on their short side and their working diagrams determined. Performance of the bending elements depends on the PZT thick film thickness and results in blocking forces of $F_B = 0.04$ N and $F_B = 0.11$ N for PZT thick films of 80 and 120 μm thickness on LTCC, respectively (Fig. 6).

The presented results show the feasibility of active structures based on LTCC which open new fields for MEMS applications.

6. Conclusion

PZT thick films based on a PZT-PMN powder have been produced successfully by reducing sintering temperature via liquid phase sintering. Properties of PZT thick films are strongly influenced by the substrate and electrode material composition. To prevent diffusion of silicon or silicon oxides into the PZT thick film a special Au electrode was developed.

PZT thick films with thicknesses between 20 and 150 μm have been applied on different substrates like Al_2O_3, ZrO_2, silicon and LTCC which are basis materials for microsystems technology. They are of great interest as sensors and actuators for microsystems, optical and smart structure applications like, for example, piezoelectric pressure sensors, micropumps, ultrasonic transducers, ferroelectric printing forms and active optics.

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