

THIN PIEZOELECTRIC LAYERS OF $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ OBTAINED BY THE SOL-GEL METHOD

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In the paper the method of obtaining of thin layers of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ceramics and the results of their preliminary investigations are presented. The layers have been obtained by the sol-gel technology. They were deposited on anodized surfaces of plates, parallelepipeds and cylinders of Al. The existence of ferroelectric (hysteresis loop) and piezoelectric (in poled layers) properties has been ascertained. The possibility of the application of those layers as ultrasonic transducers in the range of high frequencies has been proved using them for generation and reception of pulses of ultrasonic longitudinal waves.

1. Introduction

Thin films of piezoelectric materials are widely used as ultrasonic transducers in the frequency range above 100 MHz, as elements of acoustoelectric, acoustooptic and electrooptic devices and as active layers in sensors and actuators. Thin films of piezoelectrics of simple chemical composition are obtained using classical vacuum technologies – two-source evaporation (CdS), reactive evaporation (AlN) or cathode sputtering (ZnO). These methods are useless for the most often applied piezoelectric materials – LiNbO_3 and PZT-type ceramic ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, with additives if needed). Thin layers of LiNbO_3 with the properties comparable to those of monocrystals have not been obtained as yet in spite of many works done at various research centres. Thin layers of the PZT ceramic are produced by magnetron sputtering dc or rf in oxygen or in an oxygen-argon mixture [3]. Multielement targets (Pb, Zr, Ti) or sintered ceramic targets are sputtered. An expensive and complicated equipment is necessary and the deposition process is time-consuming (the deposition rate is about 0.1 nm/s). Therefore chemical methods are developed, e.g. chemical vapour deposition [14]. In this method vapours of compounds containing Pb, Zr, Ti are carried by a stream of an inert gas (usually Ar) and deposited on heated substrates. Thin layers of PZT can be also obtained by laser ablation [6]. Ion-beam deposition [1] or electron-beam evaporation [11] have minor practical applications.

Recently a sol-gel (solution-gelation) method or its modification MOD (metallo-organic decomposition) are most often used to obtain thin layers of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ [7]. In this paper the authors present the results of investigations of PZT thin layers obtained by the sol-gel method.

To master the technology of PZT thin layers of high quality is very important for many practical applications. Recently many papers have been published concerning the application of PZT thin layers as elements of RAM memory [10]. This is a return to the old idea of the ferroelectric memory. The sol-gel technology makes it possible to produce very thin ferroelectric layers of high quality. Their polarization can be switched by low voltages ($\leq 5 \text{ V}$) and their properties do not change up to over 10^{11} cycles write/read. Those layers can be integrated with electronic IC's.

Piezoelectric ceramics are widely used in sensors and actuators, e.g. in the so-called intelligent structures [2] applied for the detection and compensation of deformations and vibration of elements, e.g. in aeronautics. Unfortunately it is impossible to produce very thin (thickness of several μm) ceramic plates. A similar problem exists in the construction of piezoelectric bimorphs applied in sensors for surface investigations [12]. PZT thin layers produced by the sol-gel method should be useful in both cases [8].

2. Sol-gel technology

The sol-gel technology permits to control the composition of the obtained layers (Zr-Ti ratio, additives), to deposit layers on large surfaces (also non-planar) and it is more simple and less expensive than the vacuum deposition techniques. The necessary temperatures are lower than in the classical technologies of PZT ceramic production (high temperature sintering of metal oxides – up to 1500°C , often under high pressure). The layers have a homogeneous structure and their grains can have dimensions of $\sim 1 \mu\text{m}$. This is important for applications in the frequency range above 100 MHz.

The $\text{Pb}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$ layers described in this article were obtained by chemical sol-gel process [16] using dip coating. The stock solution was prepared from lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ dissolved in glacial acetic acid, zirconium propoxide $\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$ and titanium isopropoxide $\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4$. Distilled water and propanol were used as solvents to regulate the wettability. The addition of ethylene glycol was necessary to prevent cracking and to improve the surface smoothness of the films. The film thickness was controlled by the concentration and the viscosity of the solution of metallo-organic compounds. The hydrolysis and polycondensation of alkoxides produce an amorphous network in the solution. The shelf life of the solution at the room temperature was long. The solution was well fitted for use for at least several months.

The PZT layers were deposited on anodized surfaces of plates, parallelepipeds and cylinders of Al. The anodization process was carried on aluminium samples which were immersed into a H_2SO_4 bath of concentration of 1.5 M. Hard and transparent aluminium oxide films of fine porosity were obtained as a result. The increase of the film thickness was regulated by the parameters of the anodization process. The current density ranged

from 1 to 2 A/dm² at a voltage of 12–20 V. The process was conducted at the ambient temperature and with intensive mixing. Three or four PZT layers were subsequently deposited on the substrate surface. After deposition of every layer, the prepolymerized coating in the form of a metallo-organic gel was dried in air at room temperature, then further polycondensation took place at a higher temperature and finally an inorganic oxide structure was formed.

During the drying stage the wet film was converted into a hard coating and a considerable shrinkage of the coating occurred. Thus it was more effective to prepare thinner layers than a thicker one. The next stage was to fire the samples in a furnace at 400° C for 15 minutes. During the firing the following processes went on: evaporation of the solvent residues, decomposition of the organic compounds, removal of residual –OH and –O – C₃H₇ groups, pyrolysis of the organic compounds or groups into carbon and progressive densification of the film. At the end of this stage the metallo-organic film changed to a fine mixture of lead, titanium and zirconium oxides and free carbon. At higher temperatures the free carbon oxidized and carbon dioxide was removed from the surface. The yellowish mixture of the oxides was transformed to an amorphous PZT film that became milky and translucent. After final firing the samples were immersed in a metallo-organic solution to deposit another layer and the procedure was repeated.

In order to achieve a complete crystallographic structure, the fired films were annealed. The purpose of annealing was to change the amorphous structure into the perovskite one. This process was performed according to the following temperature-time program. At first the annealing temperature was progressively raised, then maintained at 600° C for 6 h and subsequently it was progressively reduced to the room temperature. During firing film crystal nuclei were formed and next, during the annealing, the growth of the crystals and phase transformation continued.

For the measurements upper Ag or Al electrodes were deposited on PZT by the vacuum evaporation.

3. Investigations of the ferroelectric properties of the $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin layers

The existence of a hysteresis loop is the basis criterion to confirm the ferroelectric properties of the material [5]. Measurements have been done by the standard method in the Sawyer–Tower circuit [4]. Figure 1 presents the hysteresis loops of PZT thin layer deposited by the sol-gel method on an Al parallelepiped. Figure 1 a – the unpolarized layer, Figure 1 b – the polarized layer. The measurements have been done for $f = 10$ kHz and the voltage $U_x = 50$ V. The characteristic asymmetry of the hysteresis loop is visible in the case of the polarized layer.

The shape of the loop and the way of its change with the increase of the applied voltage testify that it is caused by the ferroelectric hysteresis and not, for example, by the nonlinear conductivity of the non-ferroelectric material [5].

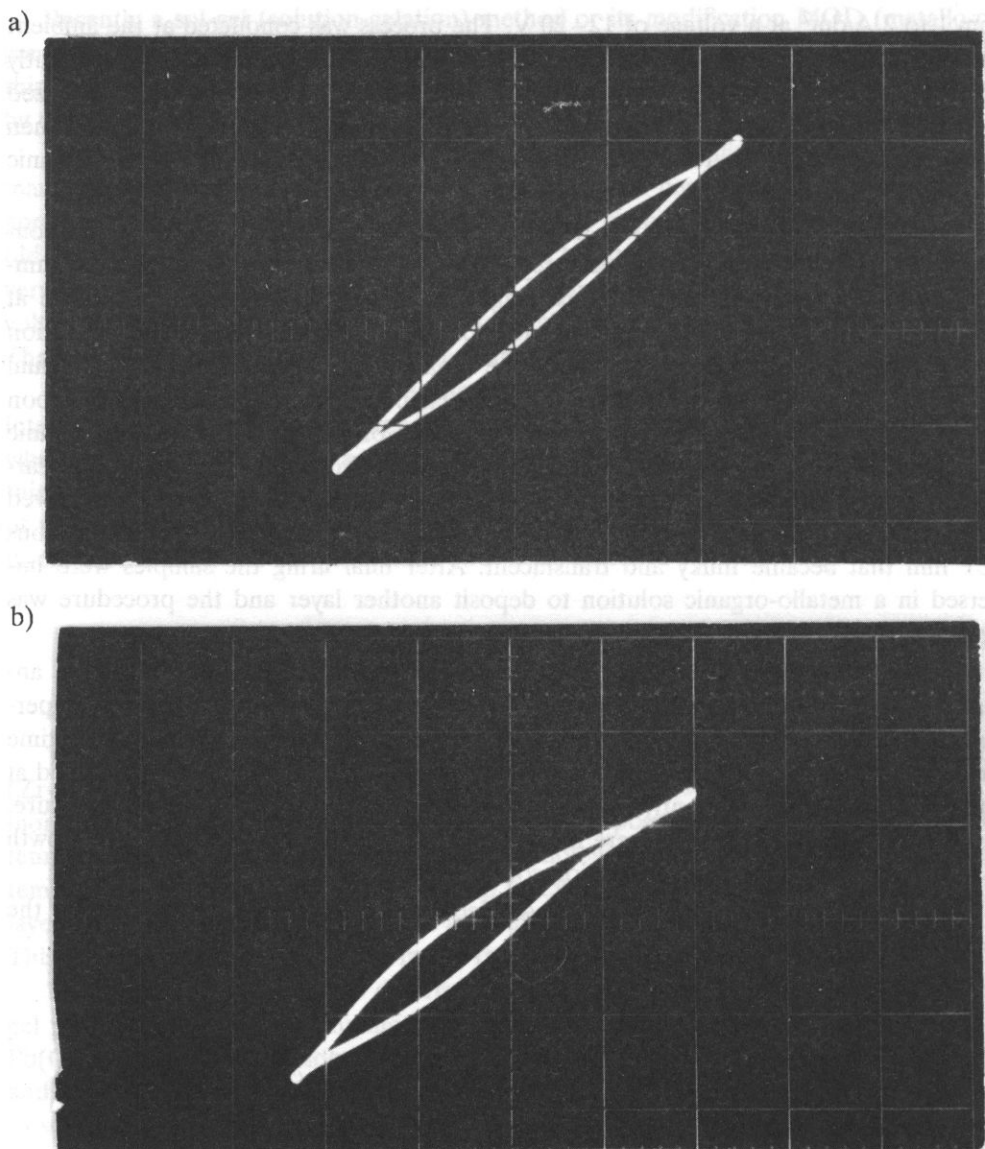


Fig. 1. Hysteresis loop for $\text{Pb}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$ thin layer a) unpolarized layer, b) polarized layer. In this case the characteristic asymmetry of the hysteresis loop is visible.

4. Thin $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ layers as ultrasonic transducers

The obtained PZT thin layers have been polarized and we have verified the possibility to use them as ultrasonic transducers. We have measured the characteristics of the lines in the form of thin layers PZT transducers deposited by the sol-gel method on the surfaces of the parallelepipeds and cylinders of Al. The transducer generated pulses of longitudinal

ultrasonic waves which were received by the same transducer after the reflection at the end surface of the line.

Figure 2 presents insertion loss as function of frequency for the thin layer PZT transducer on the Al parallelepiped of 9 mm length. The measurements were done without electrical matching circuits between transducer and the generator (receiver). A "Matec" apparatus was used as generator and receiver. The curve in Fig.2 is a typical, slightly asymmetric, wide-band characteristic obtained for thin piezoelectric transducer loaded by a solid propagation medium [9].

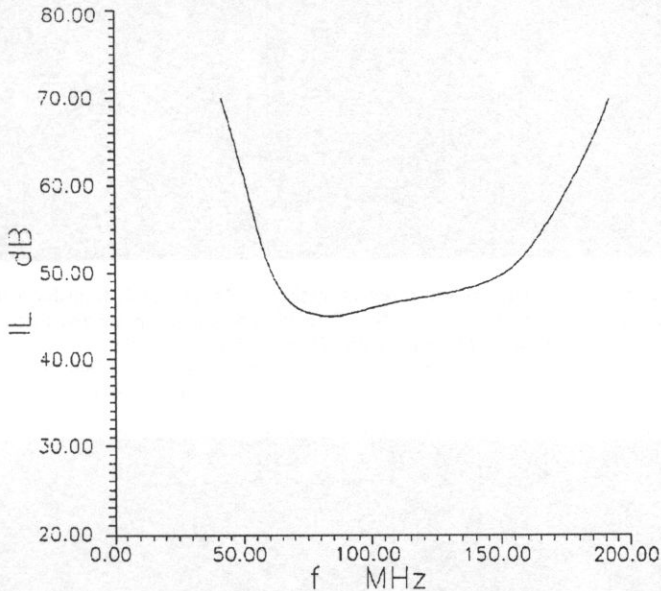


Fig. 2. Insertion loss versus frequency for a line in the form of $\text{Pb}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$ thin layer transducer deposited on the parallelepiped of Al. The wide band-width and slight asymmetry of the curve are typical of thin piezoelectric transducer loaded by a solid propagation medium.

Two examples of the oscillograms of the pulses (after detection by the receiver) for different carrier frequencies are presented in Fig.3 – for 100 MHz and Fig.4 – for 175 MHz. The obtained trains of pulses are typical of the structure of the applied acoustic lines [15]. In Fig. 3 one can see successively: the electric pulse, the first acoustic pulse which returned to the transducer after reflection at the line end, the second acoustic pulse which returned to the transducer after two reflections at the line end and one reflection at the line-transducer boundary, etc. In Fig.4 only one acoustic pulse is visible because the insertion loss for 175 MHz was considerably greater than for 100 MHz – Fig.2. The results obtained for other lines of various dimensions were similar.

The PZT thin layers were also deposited on circular plates of an Al sheet of thickness of 1 mm. These transducers received, among others, pulses of longitudinal waves generated in a parallelepiped of fused quartz. A plate of LiNbO_3 (Y-36 cut) was the transmitting transducer. The plate was indium bonded to the propagation medium and worked in a wide band of frequency.

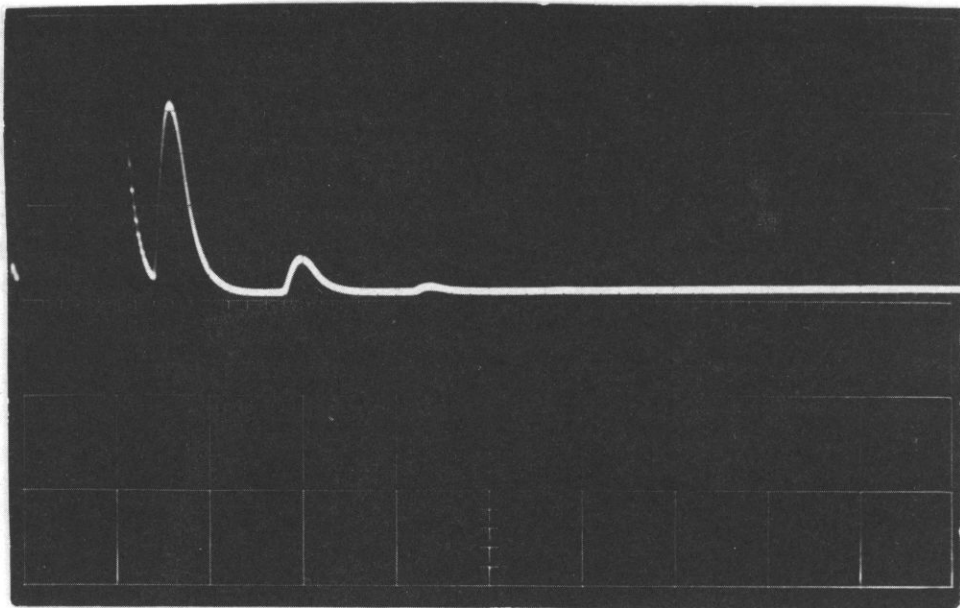


Fig. 3. Oscillogram of pulses generated and received by the $\text{Pb}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$ transducer deposited on a Al parallelepiped with length $l = 9$ mm, $f = 100$ MHz, $2\mu\text{s}/\text{div}$. The electric pulse and three successive acoustic pulses with transit paths $2l$, $4l$ and $6l$ are visible.

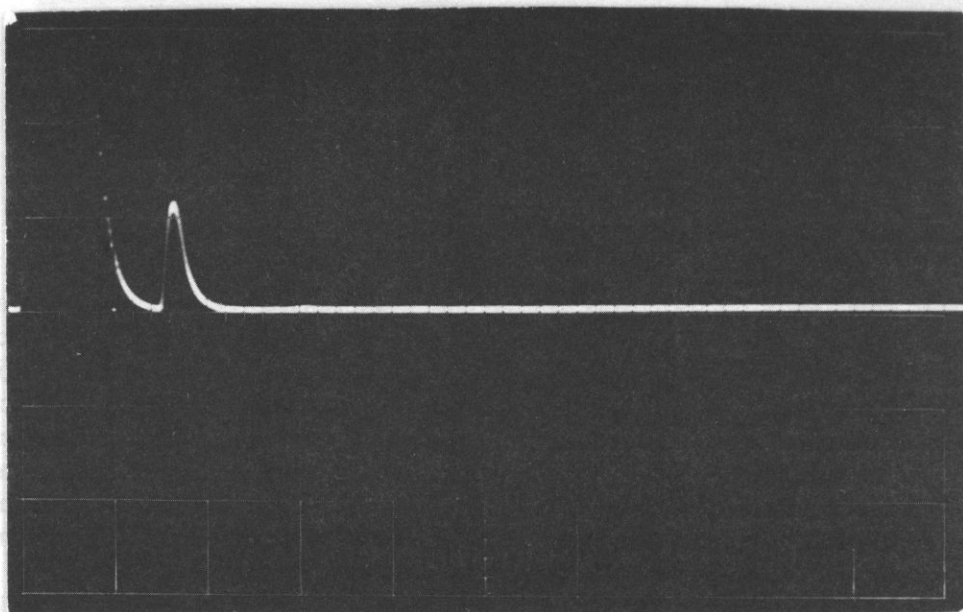


Fig. 4. As Fig.3 $f = 175$ MHz. Only one acoustic pulse is visible because the insertion loss for 175 MHz was considerably greater than for 100 MHz.

5. Conclusion

The presented results of preliminary investigations prove that the obtained $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ layers have ferroelectric and piezoelectric properties. After the polarization they worked as high frequency ultrasonic transducers. Their properties did not differ considerably from the data published by other authors. Therefore it should be possible to apply them in the devices mentioned in the introduction, similarly as the thin layers obtained by the sol-gel method and described in [8, 13].

We have not obtained as yet completely satisfying properties of the thin layers of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$. The microscopic investigations indicate that the grains are larger than $\sim 1 \mu\text{m}$ reported by other authors in previous publications. The uniformity of the layers was not always perfect. A very good furnace was not available. The structure of PZT layers depends on the conditions of firing and annealing. Further works with raw materials of higher quality using an improved furnace and more precise control of the technological processes should obviously allow to improve the quality of the layers.

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