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Piezoelectric effect in RF sputtered ferroelectric thin films

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Abstract

Thin ferroelectric films of $BaTiO_3$, $LiNbO_3$, and $Pb(Zr_{0.53}Ti_{0.45}W_{0.01}Cd_{0.01})O_3$ have been grown on different substrates. Processing conditions for the thin film preparation by RF sputtering were optimised to assure the composition transfer between the target and the thin film. Structure of the films was investigated by X-ray diffraction. The basic dielectric and piezoelectric properties were studied and the processing-structure perfection–property relationships of oxide thin films have been revealed. The piezoelectric charge coefficient d_{33} was determined. Self-induced polarisation of the thin films as well as stress-induced polarisation ascribed to reversible displacement of 90° domain walls was taken into account to explain experimental results. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

All materials undergo a small change in dimensions when subjected to an electric field.[1] Some materials show the reverse effect — the development of electric polarisation when they are strained through an applied stress. These are said to be piezoelectric. To a first approximation, the polarisation is proportional to the stress and the effect is said to be direct. Piezoelectric materials also show a converse effect, i.e. the development of a strain directly proportional to an applied field.

Piezoelectric properties are often described in terms of piezoelectric charge coefficients[2] (d_{33} d_{31} and d_{15}) that relate the strain of a piezoelectric sample to an externally applied field and thus describe the electromechanical parameters of the piezoelectric material.

Lithium niobate ($LiNbO_3$) is one of the most important ferroelectric materials and produces strong pyroelectric, photorefractive, and piezoelectric effects. $LiNbO_3$ thin films are especially attractive, as they facilitate step-index profiles, dopant introductions, and multilayer structures.[3] The unique dielectric and electro-optical properties of barium titanate ($BaTiO_3$) make this material particularly attractive for a number of electronic and optoelectronic applications.[4] Lead zirconate titanate (PZT) systems, near the morphotropic phase boundary composition, have been investigated because of their excellent piezoelectric properties in e.g. electro-acoustic transducers.[5]

The objective of the present paper was to obtain ferroelectric thin films of $LiNbO_3$, $BaTiO_3$, and $Pb(Zr_{0.53}Ti_{0.45}W_{0.01}Cd_{0.01})O_3$ (PZT) by RF sputtering, and to investigate their structure as well as basic dielectric and piezoelectric properties.

2. Technology and experimental

In the present work thin ferroelectric films of $LiNbO_3$, $BaTiO_3$, and PZT have been grown on metallic substrates (platinum, stainless steel foil or nickel). The RF sputtering technique was utilised and a customised vacuum system URM-3279014-type was used. Details of the system used have been published recently.[6] However, it is worth noting that pure oxygen plasma was exploited at relatively high pressure of oxygen ($p_{o_2} = 30-80$ Pa).

Structure of the thin films was studied by X-ray diffraction (Dron-4; $CuK_{\alpha_{1,2}}$). The microstructure of the thin film surfaces was investigated by electron microscopy using one-step platinum–carbon replicas. The mean crystallite size D and mean microdeformations $<\Delta d/d>$

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were determined from X-ray patterns.[7] In this connection is should be noted that the microdeformation $<\Delta d/d>$ is the mean of the relative changes in interplanar distance d_{hkl} inside crystallites; single crystal was assumed as a standard.

For electrical measurements silver electrodes of $\varnothing = 1$ mm in diameter and $h = 0.3$ μm in thickness were deposited on the upper side of the thin film by vacuum evaporation. Capacitance (C) and dielectric loss tangent (tgδ) were measured by a bridge technique ($\nu = 1$ kHz) and the dielectric permittivity (ε) was calculated.

$BaTiO_3$ thin films were poled by heating to a particular temperature T and subsequent applying of an electric field for a period of time t_1. The films were then cooled to room temperature (RT) during time t_2.

After poling the piezoelectric charge coefficient d_{33} was measured by a quasi-static method.[8] The alternating uniaxial mechanical stress, not exceeding a value of $T_{\sim} = 3\times10^5$ N/m^2 was acting on the "background" of a static compressive stress of $T_{-} = 7\times10^5$ N/m^2. The dynamic head of 10GD-30E-type generated the alternating stress and the stress was applied to the sample by means of a ceramic pipe terminated with a steel hemisphere of $\varnothing = 4$ mm in diameter. The head was fed by the function generator of frequency $\nu = 30$–50 Hz. Value of the piezoelectric charge was calculated based on the voltage, which appeared on the high capacity standard capacitor connected in parallel to the sample of investigation or was measured by the charge amplifier directly.

The piezoelectric elements with known piezoelectric charge coefficient d_{33} were used to verify and check the correctness of operation of the measuring system. Detailed description of the measuring system has already been published.[8]

3. Film structure and properties

3.1. $LiNbO_3$ thin films

It was found from X-ray diffraction patterns that $LiNbO_3$ thin films exhibit a polycrystalline structure with no preferred orientation of the crystallites in relation to the substrate. The average grain size was within the range $\bar{r} = (0.1-0.2)\times10^{-6}$ m. It was observed to increase with an increase in the substrate temperature (T_s) and oxygen pressure (p_{o_2}) in the discharge chamber. The parameters of the hexagonal elementary cell of the thin film at RT ($a_H = 0.5146\times10^{-9}$ m; $c_H = 1.3813\times10^{-9}$ m; $c_H/a_H = 2.69$) were similar to those of the ceramic target ($a_H = 0.5150\times10^{-9}$ m; $c_H = 1.3816\times10^{-9}$ m; $c_H/a_H = 2.69$) as well as to single crystals ($a_H = 0.51483\times10^{-9}$ m; $c_H = 1.38631\times10^{-9}$ m; $c_H/a_H = 2.69$).

The dielectric constant of the $LiNbO_3$ thin films having thickness $d_f = (1$–$10)\times10^{-6}$ m was within the range $\varepsilon = 30$–50 (Fig. 1) whereas the loss tangent tg$\delta = 0.05$–0.07 (measurement field $E^{o}_{\sim} = 10^4$ V/m, frequency $\nu = 1.6\times10^3$ Hz, RT).

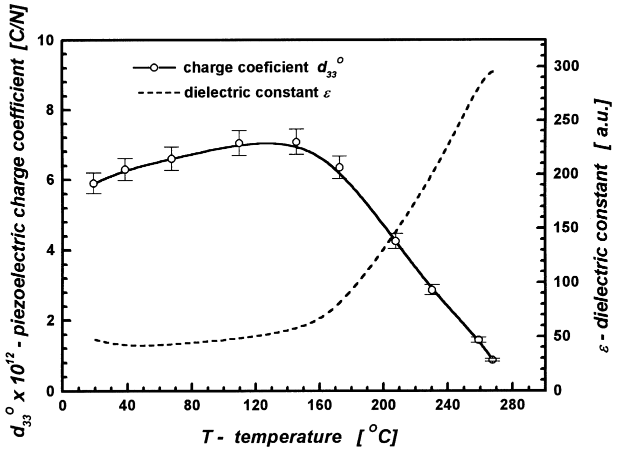

Fig. 1. Dependence of the piezoelectric charge coefficient (d_{33}^{o}) and dielectric constant (ε) on temperature T for the $LiNbO_3$ thin film ($d_f = 2\times10^{-6}$ m; stainless steel substrate).

All $LiNbO_3$ films deposited on metallic substrates showed self-induced piezoelectric activity. In other words, they exhibited piezoelectric properties although they had not been poled in an external electric field. The piezoelectric modulus of the non-poled thin film measured along the OX_3 axis normal to the substrate was $d_{33}^{o} = (6$–$8)\times10^{-12}$ C/N at RT, so it was slightly smaller than d_{33} for poled ceramic samples $d_{33} = (10$–$12)\times 10^{-12}$ C/N.

The dependencies of $d_{33}^{o}(T)$ and $\varepsilon(T)$ for $LiNbO_3$ thin film of thickness $d_f = 2\times10^{-6}$ m, deposited on the stainless steel substrate, are shown in Fig. 1.

It is worth noting that the self-induced piezoelectricity of the as-deposited thin films of $LiNbO_3$ is a very stable phenomenon. The value of d_{33}^{o} measured at RT does not change after applying a strong depolarising field ($E_{dep} \approx 10^7$ V/m) to the thin films or heating them up to $T = 450°$C many times.

3.2. $BaTiO_3$ thin films

Results of investigations of the chemical composition of the $BaTiO_3$ thin films by means of X-ray microanalysis have shown that the deposition technique used ensures the composition transfer between the target and the thin film. The thin films were deposited simultaneously on the front side and on the backside of the substrate (on-axis geometry). In such a way the thin films of types I and II, respectively, were grown. Microscopic studies have shown that the $BaTiO_3$ thin films are polycrystalline. It has been also revealed that the average grain dimensions are within the range $\bar{r} = (0.05-0.5)\times10^{-6}$ m and depend on the deposition conditions.

It was found by X-ray investigations that $BaTiO_3$ thin films of the type I exhibited much smaller perfection of the crystalline structure than the films of the type II.

With an increase in mean crystallite size D and decrease in mean relative lattice strain $<\Delta d/d>$, the degree of perfection of the crystalline structure of $BaTiO_3$ thin films increases. These two quantities were calculated based on the broadening of diffraction peaks in the X-ray spectrum.[6,7] For the thin films of the type I the following values were obtained: $D=(20–40)\times10^{-9}$ m and $<\Delta d/d>=0.006–0.015$, whereas, for the thin films of the type II: $D>100\times10^{-9}$ m and $<\Delta d/d>=0.007–0.003$.

In Fig. 2 typical characteristics of $\varepsilon(T)$ for the thin films of both types are shown. One can see that $BaTiO_3$ thin films with large deformation (type I) exhibit broad diffuse phase transition. Unlike the $LiNbO_3$ thin films, the $BaTiO_3$ ones deposited on stainless steel or platinum show a weak self-induced piezoelectric activity. The piezoelectric modulus $d_{33}^{o}=(5-12)\times10^{-12}$ C/N, however, is far smaller than the one for polarised $BaTiO_3$ ceramics $d_{33}=(180–200)\times10^{-12}$ C/N.

To determine optimal conditions of polarisation, various film-processing conditions were investigated and the results are shown in Fig. 3. We have found that the $BaTiO_3$ thin films of the type I are optimally poled under the following conditions: $T=(150–160)$°C, $E=(30–35)\times10^{5}$ V/m; $t_1=(15–25)$ min; $t_2=(50–60)$ min, whereas for the type II $BaTiO_3$ thin films, $T=(150–160)$°C, $E=(15–20)\times10^{3}$ V/m; $t_1=(15–25)$ min; $t_2=(50–60)$ min. Results shown in Fig. 3 are related to the films deposited on platinum substrates.

As a result of the heating of poled thin films the process of depolarisation takes place (Fig. 4). The piezoelectric modulus d_{33} changes monotonically during heating and the maxima in the vicinity of $T_c\approx120$°C, typical for $BaTiO_3$ ceramics have not been found. It should be noted that the piezoelectric effect has been observed at temperature much higher than $T_m=126$°C. The last is an evidence for the broad ferroelectric phase transition. After cooling to RT the thin films exhibited weak piezoelectric activity related to their self-induced polarisation.

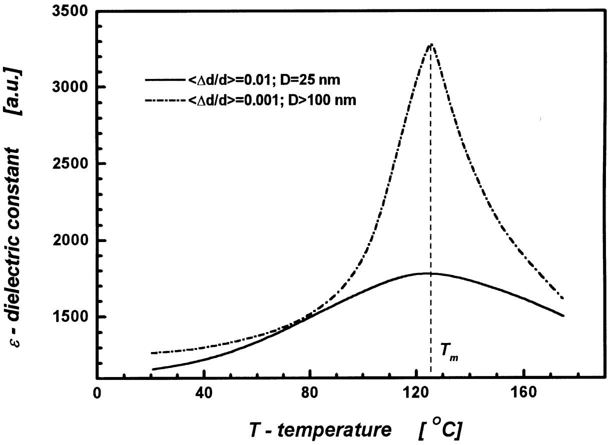

Fig. 2. Dependence of dielectric constant $\varepsilon(T)$ for the $BaTiO_3$ thin films with different degree of structural perfection (platinum substrate; $d_f=3\times10^{-6}$ m; $T_{S}=650$°C; $h_{s-t}=7\times10^{-3}$ m; $p_{O_2}=78$ Pa): 1– $<\Delta d/d>=0.01$; $D=25\times10^{-9}$ m; 2. $<\Delta d/d>=0.001$; $D>100\times10^{-9}$ m.

3.3. PZT thin films

The polycrystalline thin films of $Pb(Zr_{0.53}Ti_{0.45}W_{0.01}Cd_{0.01})O_3$ exhibiting a perovskite-type structure and thickness within the range $d_f=(3–4)\times10^{-6}$ m were deposited on 45×10^{-6} m thick stainless steel substrates. It was found that such films exhibited the self-induced polarisation.[9] The direction of polarisation was from the lower to the upper electrode, i.e. that which would be expected by poling with a negative voltage on the upper electrode of the film. Because of such a polarisation,

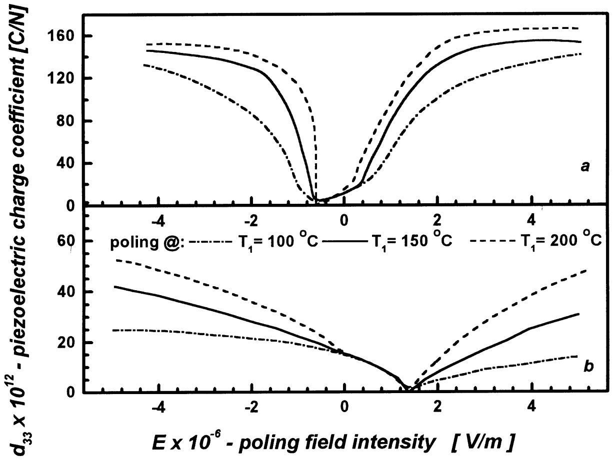

Fig. 3. Dependence of the piezoelectric charge coefficient d_{33} measured at RT, on the poling conditions ($E=(0–5)\times10^{6}$ V/m; $T_1=100$°C, $T_2=150$°C 423 K, $T_3=200$°C, $t_1=12\times10^{2}$ s, $t_2=30\times10^{2}$ s) of the $BaTiO_3$ thin films exhibiting (a) small microdeformation: $<\Delta d/d>=0.002$; $D>100$ nm; $d_f=3.2\times10^{-6}$ m and (b) large microdeformation: $<\Delta d/d>=0.012$; $D\approx40\times10^{-9}$ m; $d_f=2.8\times10^{-6}$ m.

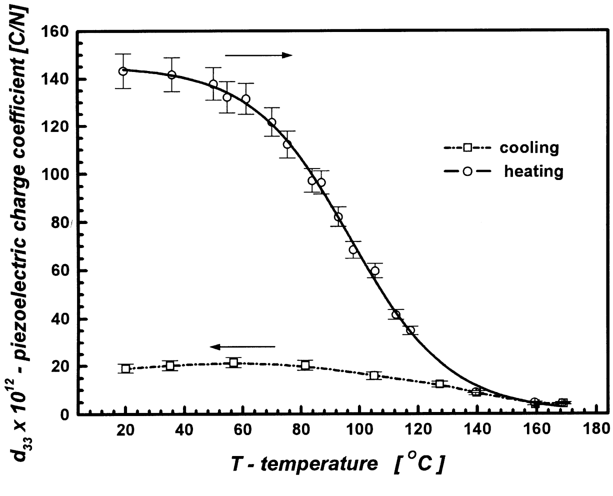

Fig. 4. Dependence of the piezoelectric modulus d_{33} of the $BaTiO_3$ thin films on temperature T (platinum substrate; $d_f=3\times10^{-6}$ m).

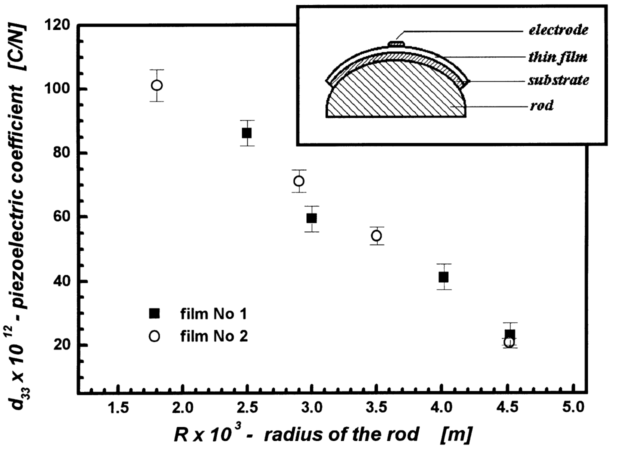

Fig. 5. Dependence of the piezoelectric charge coefficient d_{33} on the radius of bending R for the thin PZT films mounted on the cylindrical rod.

value of the piezoelectric charge coefficient worked out at $d_{33} = (5\text{–}8) \times 10^{-12}$ C/N.

As-deposited films were first cut into chips of dimension 3×4 mm. Secondly, they were bent in a way leaving the thin PZT film on the convex side of the substrate, and then they were mounted by spot welding on the surface of the cylindrical rods (Fig. 5). Diameter of the rods was within the range $\varnothing = 3.6\text{–}9$ mm. Finally, the piezoelectric coefficient d_{33} for such films was measured.

Dependence of the piezoelectric charge coefficient d_{33} on the radius of bending (R) for thin films of $Pb(Zr_{0.53}Ti_{0.45}W_{0.01}Cd_{0.01})O_3$ is shown in Fig. 5. One can see that d_{33} increases markedly with decreasing R. It reaches a value of about $d_{33} = 97 \times 10^{-12}$ C/N. It should be noted that it is about 50% of the d_{33} value typical for the bulk ceramic samples of the same chemical composition. However, it appeared that while bent in the opposite direction (film on the concave side of the substrate) the thin film also showed an increase in the initial piezoelectric coefficient but to a lesser degree (by 20–30%).

Such experimental data one can explain in terms of stresses, and the stress-induced poling characteristics[10,11] can be ascribed to domain reorientation process.[10,12] In the case of bending (PZT film on the convex side of the substrate) the thin film suffered tensile stress that favoured reorientation of 90° domain boundaries between *a*- and *c*-domains. As result of such a reversible movement of 90° *a*–*c*-domain boundaries the volume of polarised part of domains increases.

According to published data[13] exertion of $T = 5.1 \times 10^4$ Nm^{-2} of tensile stress by bending the wafer with (111) oriented poled PZT film resulted in an increase of average domain width by about 1%. Simple estimations have shown[14] that a change of volume of polarised part of domains by about a few-hundredth percent is big enough to obtain the effective value of piezoelectric charge coefficient at the level of $d_{33} = 100 \times 10^{-12}$ C/N or even greater. In this connection it should be noted that the high values of d_{33} did not change for 8 months.

4. Conclusions

By means of selection of processing conditions one can obtain piezoelectric thin films exhibiting a high degree of structural perfection. RF-sputtered $LiNbO_3$ thin films distinguished by stability of self-induced polarisation, which did not disappear either under strong depolarising field or under the influence of high temperature treatment. The $BaTiO_3$ thin films showed weak self-induced polarisation. However, it was found that the $BaTiO_3$ thin films having small microdeformations, have the potential for use as piezoelectric sensors of mechanical quantities within the temperature range not exceeding $T = 80°C$. It has been found that self-induced polarisation of the PZT thin films as well as stress-induced polarisation ascribed to reversible displacement of 90° domain walls can significantly increase the piezoelectric charge.

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