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Textured $PbTiO_3$–Al_2O_3 composite films prepared by chemical solution deposition

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Abstract

$PbTiO_3$–Al_2O_3 composite films were prepared by chemical solution deposition on silica glass substrates using dip-coating and lead acetate trihydrate, titanium butoxide and aluminum isobutoxide as precursors. The phase composition, preferred orientation and crystallite dimension were determined by powder X-ray diffraction methods. The Al_2O_3 phase seems to be amorphous because of the absence of its diffraction peaks. The presence of this phase affects the preferential orientation of $PbTiO_3$ crystallites. For the molar ratio $n_{Pb}/n_{Al} = 2{-}4$ most films show a strong texture of $PbTiO_3$ crystallites with the a-axis oriented almost perpendicularly to the film plane and the c-axis oriented randomly in the film plane. The texture is much weaker in pure $PbTiO_3$ films. The texture may originate from the minimization of surface and interface energies and from tensile stresses induced during film preparation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Composites; Perovskites; Sol–gel processes; Texture

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1. Introduction

Composites are defined as a mixture of two or more interacting phases. They are called nanocomposites if at least one of the phases has the nanometer size range in at least one dimension.[1] The phases can influence each other in such a way that their properties cannot be simply predicted from those of single isolated phases. Therefore, the nano- and microcomposites are worth not only experimental but also theoretical studying.[2]

In our previous paper[3] we showed that the presence of the Al_2O_3 phase in $PbTiO_3$–Al_2O_3 composite thin films with the composition $p = n_{Pb} / n_{Al} = 1$ suppresses the crystallization of $PbTiO_3$ even at the temperature of 800°C, whereas pure $PbTiO_3$ films were already crystallized at 400°C. The objective of the present paper is to study the effect of Al_2O_3 phase at lower Al_2O_3 concentration ($p > 1$) and to show that its presence can significantly enhance the preferred orientation of the $PbTiO_3$ crystallites. The knowledge of the growth of the oriented perovskite thin films by chemical solution deposition (CSD) is important for applications.[4] For example, thin films with a-axis oriented perpendicular to the substrate with low refractive index such as fused silica may be favorable for waveguides.[5,6] a-Oriented films are also suitable for high capacitive elements in dynamic random access memories (recall that the high dielectric dispersion is along the a-axis in tetragonal ferroelectric).[6] For other applications c-oriented films are needed.[6]

2. Experimental

Pure $PbTiO_3$ and composite $PbTiO_3$–Al_2O_3 thin films were prepared by the CSD technique (sol–gel process). Lead acetate trihydrate, titanium butoxide and aluminum isobutoxide were used as precursors, all the procedures were done under dry nitrogen. Lead acetate trihydrate was dissolved in 2-ethoxyethanol and water was removed by distillation. After cooling to 70°C, titanium butoxide

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was added to the solution. Ten per cent excess of Pb acetate was used in order to compensate lead loss during annealing of films. The solution was then refluxed for 1 h to allow the formation of the Pb–Ti heteroalkoxide. The concentration of the Pb–Ti stock solution was adjusted to 1 M Pb. For the preparation of $PbTiO_3$–Al_2O_3 sols, a 0.8 M stock solution of aluminum isobutoxide in isobutyl alcohol was prepared. A given amount of Pb–Ti solution was mixed with a calculated amount of Al solution, stirred 30 min on an ultrasonic bath and subsequently 2,2-diethanolamine (DEA, $n(\mathrm{DEA})/n(\mathrm{alkoxide})=1$) was added as a stabilizer slowing down the hydrolysis. After 30 min stirring, a calculated amount of water-isobutyl alcohol solution ($n(\mathrm{water}):n(\mathrm{alcohol})=1:3$ to 1:6, $n(\mathrm{water}):n$ (alkoxide) = 1 to 2) was added dropwise. The resulting sol was filtered through porous 0.45 μm poly(tetrafluorethylene) membrane and used immediately for the film deposition.

Silica glass plates (10×25 mm^2, 0.35 mm thick) thoroughly cleaned were used as substrates. After deposition by dip-coating (withdrawal speed 6 cm/min), the films were kept in air at least 5 minutes to allow the hydrolysis-polycondensation reactions to complete. Then they were dried (110°C/10 min) in air, and heat-treated (450°C/15 min). This process was repeated until films with desired thickness were obtained. The resulting films were calcined in air at temperatures 450°C for several hours to ensure complete pyrolysis and then heat-treated at temperatures 500–800°C (2°C/min).

The thickness of the films was measured by a stylus profilometer. The surface morphology was studied by optical, scanning electron and atomic force microscopes. The composition of the films was determined by electron probe microanalysis (EPMA) and Rutherford backscattering. X-ray powder diffractometry (Bragg-Brentano, ω-scan, ϕ-scan) was used to describe the phase composition, cell parameters, crystallite dimension and degree of texture. Far infrared transmission using a Fourier transform spectrometer was measured for the evaluation of the soft mode frequency of $PbTiO_3$ phase.

3. Results and discussion

The films were usually compact in appearance and transparent, nevertheless thin cracks were observed in a few cases. Their thickness was typically 500 nm but thinner and thicker samples were prepared as well. The average size, normal to the film plane, of the $PbTiO_3$ crystallites (coherently diffracting regions) in the $PbTiO_3$–Al_2O_3 composites determined from the broadening of X-ray diffraction lines using profile fitting (Pearson VII function) and integral breadth method[7] was between 20 and 50 nm. The lateral size of grains (which can, however, contain one or more coherently diffracting domain) observed by AFM on the surface of the films was about 80 nm. The Pb/Al ratio determined by EPMA in several places (8 or 3) of a sample was quite constant; the relative deviation from the average value was usually equal or smaller than 4%. Taking into account that the analyzed region has the diameter and depth of about 1 μm, we can suppose that the distribution of the $PbTiO_3$ crystallites in the Al_2O_3 matrix is quite homogeneous.

The X-ray powder diffraction patterns for pure $PbTiO_3$ and $PbTiO_3$–Al_2O_3 composites ($p=n_{Pb}/n_{Al}$) obtained by the symmetrical Bragg–Brentano geometry are shown in Fig. 1. The PDF 6-0452 file[8] of tetragonal perovskite $PbTiO_3$ phase (macedonite) is shown for comparison. The Al_2O_3 phase seems to be amorphous, its diffraction peaks are absent for all the composite compositions. It is seen that the composites with $p=2$ and 4 have very pronounced diffraction peaks of $PbTiO_3$ (100) and (200) planes in comparison with other reflections. The (300) peak is also visible. It indicates that $PbTiO_3$ crystallites in these composite films have a strongly preferred orientation (texture) with the (h00) planes

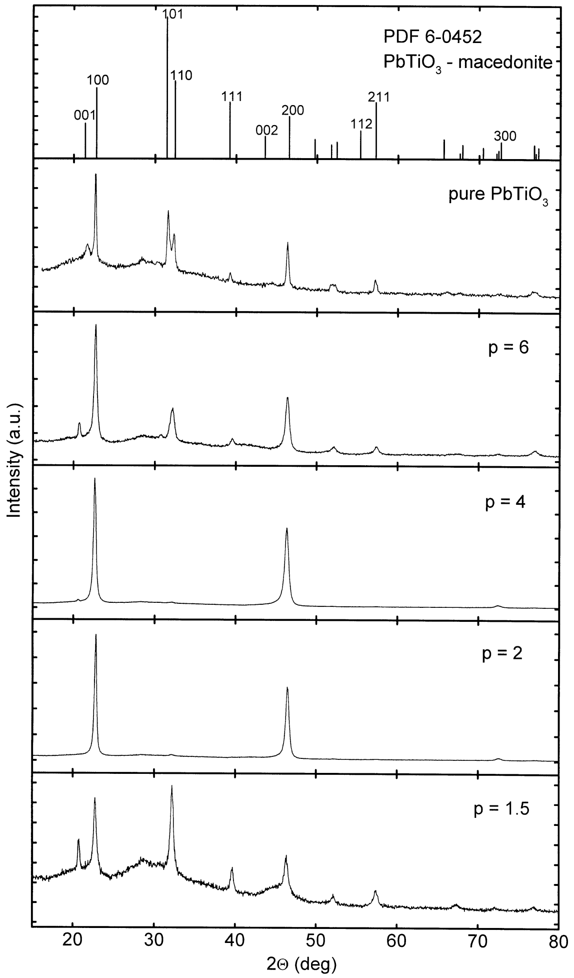

Fig. 1. X-ray powder diffractograms using Bragg–Brentano geometry and CuK_α radiation for pure $PbTiO_3$ and $PbTiO_3$–Al_2O_3 composites ($p=n_{Pb}/n_{Al}$, final annealing was 700°C/3 h for $p=1.5$, 4 and 6, 800°C/1 h for $p=2$, and 700°C/2 h for pure $PbTiO_3$).

parallel to the surface (a-axis of the cell perpendicular to the substrate plane). This was confirmed by the ω-scans (rocking curves) of (200) planes (Fig. 2). Their maxima are very close to those of (100) diffraction peaks in Fig. 1, i.e. the direction of the preferred orientation in these films is nearly perpendicular to their surface. The ϕ-scans (incidence angle of 4°) for the same samples are shown in Fig. 3. They indicate that the preferred crystallite orientation is quite symmetrical, i.e. close to a fibre texture. This means that there is no significant ordering of the c-axis in the surface plane of the textured films. The correction for the diffraction peak shifts was performed for (h00) planes ($h=1$, 2, 3) using the linear dependence of $d_{\mathrm{hkl}} \cdot h$ vs. $\cos\Theta \cdot \mathrm{cotg}\Theta$ (d_{hkl} denotes lattice plane spacing). It gave the value of $a=3.911$ Å for highly textured composite films with $p=2$ and 4. For the other 10 samples with p between 1.5 and 6 and a different degree of texture we obtained the average value of $a=3.913$ Å (minimum 3.909 Å, maximum 3.921 Å; no internal standard was used). These values are in a good agreement with the known crystal structure of tetragonal (perovskite) $PbTiO_3$ ($a=3.902(3)$ Å, $c=4.156$ (3) Å)[9] and different from the value of $a=3.978$ Å found in a metastable cubic phase[10]. The c/a ratio found for textured samples was found to be about 1.03 (i.e. less than 1.06 in pure $PbTiO_3$ single crystals or powders), fitting to a cubic structure gave no satisfactory results. It means that the textured "cubic-like" phase is still tetragonal. The X-ray data ($\sin^2\psi$ method) indicated the existence of tensile stress of 0.5–1 GPa in most films. However, the published elastic constants necessary for the stress calculation show large differences.

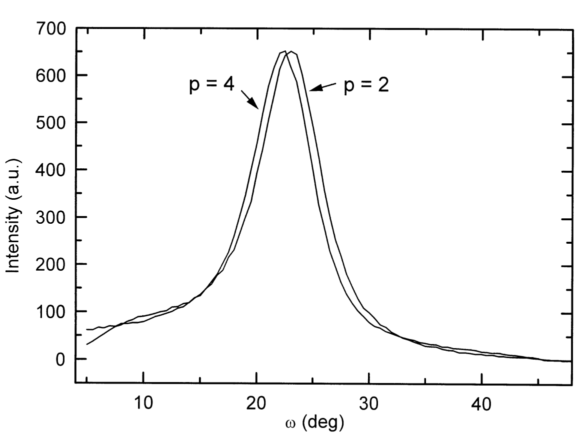

Fig. 2. ω-Scans of $PbTiO_3$ (200) planes for composites with $p=2$ and 4.

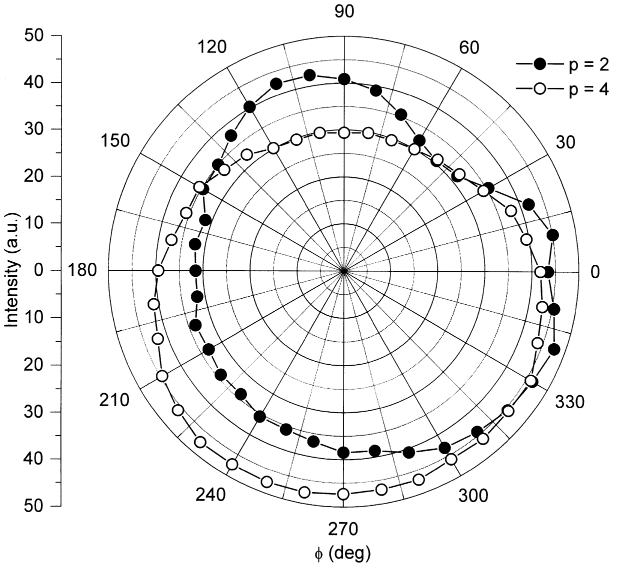

Fig. 3. ϕ-Scans for $PbTiO_3$ (200) planes of composites with $p=2$ and 4. The incidence angle was 4°.

The texture was observed in all films with the p-value between 2 and 4 which were thinner than 1 μm and annealed above 600°C (one textured sample was obtained even after 500°C annealing; this was the minimum temperature necessary for $PbTiO_3$ crystallization). It seems that the texture decreases rapidly as the thickness increases above 1 μm. However, more samples should be studied to verify it. Fig. 1 also shows that slight (h00) texture is present also in pure $PbTiO_3$ film.

The room-temperature far infrared transmission measurements were performed on composite films with $p=1.5$, 2 and 6. After smoothing out the interferences in spectra, the soft mode frequency of $PbTiO_3$ phase was determined at 76 ± 1.5 cm^{-1}. The same value (≈ 76 cm^{-1}) was found in the composite film with $p=1$, where the crystallization of the $PbTiO_3$ phase was suppressed and the soft mode in the IR spectra was not distinct but visible.[3] However, the soft mode frequency in the pure $PbTiO_3$ films (annealing temperatures 400, 700 and 800°C) was significantly higher, about 82 cm^{-1}.[3] The shift of the soft mode frequency to lower values could be assigned to compressive internal stresses.[3]

A question emerges, what can be the origin of the preferred orientation of the crystalline phase in the two-phase composite film if the substrate and the second phase are amorphous. We have not found any papers dealing with a texture origin in such systems. For single-phase films the published papers show that a lot of factors can influence the texture formation. It could be the kind of precursors used,[11,12] usage of various stabilizers[13], withdrawal speed,[13] thickness of the layer,[5] heat treatment,[5,13–16] intrinsic stresses[5,17] and others. Regarding the intrinsic stresses in multideposited $PbTiO_3$ films, the crystallization of the perovskite phase from an amorphous oxide gradually changes the stress state from tension to compression on cooling to room temperature.[18] A plausible explanation of the texture formation on an amorphous substrate seems to be the so called self-textured growth when the plane with the lowest surface energy (F-face) grows parallel to the substrate.[19] The F-face is the crystallographic face which contains two or more "periodic bond chains" defined as an uninterrupted array of the strongest bonds between the building blocks in the structure.[20] It is the {100} plane for cubic titanium perovskites[19], but the differences between the surface energies of the $(100) \equiv (010)$ and (001) planes in tetragonal $PbTiO_3$ are probably not significant ($c/a = 1.06$, in our case 1.03). It is obvious that not only surface energy but also interface energies at the substrate surface and between the crystallites of the same phase or of the different ones (in the case of composites) can play a role in the self-textured growth. The slight (h00) texture observed in $PbTiO_3$ films on SiO_2 glass substrates was explained by self-textured {100} face growth at 650°C and then, on cooling, by a tensile stress preferring the (h00) domains to (00l) ones at the cubic-tetragonal phase transition at 490°C.[5,21]

An analogous two-stage scenario can be outlined for our case. The tetragonal $PbTiO_3$ perovskite phase crystallizes from the amorphous dried gel during the pyrolysis ($T = 450°C$). Here the self-textured growth of crystallites with one of F-faces (100) and (001) parallel to the film surface is preferred. At final heating ($T > Tc = 490°C$) the tetragonal phase transforms into the cubic one. During reversed transformation on cooling the formation of (h00) domains is preferred due to supposed tensile stresses. Both consecutive stages (the F-face self-textured growth and stress affected cubic-tetragonal transformation) can be influenced by the presence of the amorphous Al_2O_3 phase. The first stage can be affected by the presence of $PbTiO_3$–Al_2O_3 interfaces changing the total interface energy, the second one can be influenced by the existence of additional stresses due to Al_2O_3 matrix. These effects can depend on the concentration of Al_2O_3 in the composite. However, detailed experimental studies of the film structure, e.g. by transmission electron microscopy, are necessary for better understanding of the texture origin in the $PbTiO_3$–Al_2O_3 composites.

4. Conclusions

The presence of an amorphous Al_2O_3 phase affects the preferential orientation of $PbTiO_3$ crystallites in the $PbTiO_3$–Al_2O_3 composite films prepared by the sol–gel method using the dip-coating technique on silica glass substrates. Pronounced (h00) texture was observed in films with $n_{Pb}/n_{Al} = 2$–4. Two main factors seem to be responsible for the texture formation: a self-textured {100} face growth due to minimization of surface and interface energies and a tensile stress induced during film preparation preferring the (h00) domains against (00l) domains at the cubic-tetragonal phase transition.

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