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PREPARATION OF PT AND PZT FERROELECTRIC THIN FILMS BY SOL-GEL METHOD AND THEIR PROPERTIES STUDY

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Abstract. The stable lead zirconate titanate(PZT) complexes were obtained by Schlenk reaction, using the new Zr precursors. Stability of the partially hydrolyzed solutions (polymeric gels) has been studied. Behavior of "Sol-Gel" systems for lead titanate and lead-zirconate-titanate in 2-methoxyethanol, butanol and iso-butanol solutions was investigated. The strong trend to gelation was found in the case of butanol and iso-butanol systems. Processing characteristics for preparation of crystalline thin films of $PbTiO_3$ and $Pb(Zr_xTi_{1-x})O_3$ with perovskite structure, where x=0.5-0.6, have been determined. The method developed allows to produce smooth and transparent crystalline films with preferential crystallographic orientation and also to control the composition. Both substrate and lead titanate (PT) interlayer influences on structure and crystallographic orientation of lead zirconate titanate (PZT) films have been shown. By thermal, X-ray analysis, optical microscopy the gel-powders and morphology of the films have been studied. The value of spontaneous polarization, as well as the rate of domain walls movement of PZT films has been evaluated.

Introduction

The structure of complexed alkoxides in the solution has significant influence on PT and PZT gels stability in sol-gel method of ferroelectric film preparation. The proper selection of the alkoxides and complex forming solvents makes it easy not only to control the stoichiometry of the thin films but also facilitates the crystalline phase growth on a selected substrate [1].

The objective of the present work is to study stability of PT and PZT gels in various solvent systems as well as to study processing characteristics of preparation of crystalline $PbTiO_3$ and $Pb(Zr_xTi_{1-x})O_3$ thin films formation with perovskite structure.

Results and Discussions

For deposition of ferroelectric thin films the sols, containing the zirconium and titanium precursors, were prepared. Lead titanate zirconate (PZT) sols were prepared by multistage procedure according to Schlenk technique [2]. First $Pb(CH_3COOH)_2$ $3H_2O$ was dehydrated by water azeotrope distillation. Then zirconium tetrakis(acetylacetonate) was treated by corresponding alcohol[3]. Further reaction of $Pb(CH_3COO)_2$ with titanium alkoxide and the zirconium complex resulting in the formation of PZT sol takes place.

$$Pb(CH_3COO)_2 + nZr(OR)_4 + (1-n)\,Ti(OR)_4 \longrightarrow PbO_2\{Zr(OR)_2\}_n\{Ti(OR)_2\}_{1-n} + 2CH_3COOR$$

$$n=0\div1$$

The final concentrations for lead titanate (PT) and PZT complexed alkoxides are 0.5 M for films and 1.0 M for bulk ceramic. The final concentrations of the hydrolyzed solutions (gels) are 0.15M for PT and 0.20M for PZT. The $PbZr_xTi_{1-x}O_3$ compositions where x=0.5-0.6 were prepared.

2-Methoxyethanol and certain aliphatic alcohols were used as the environment. Since lead titanate(n=0) gels in 2-methoxyethanol PT-(A) are very stable in the presence of the hydrolysis solution, containing H_2O-HNO_3 and can be kept without significant changes, gels based on butanol PT-(B) are very susceptible to hydrolysis and they are decomposed immediately in the presence of HNO_3, however, they are relatively stable, when the amounts of hydrolytic water do not exceed 0.5 M per mole of the complexed alkoxide. Such gels can be kept for about 4 days, they have excellent tendency to gelation and capable to form smooth crystalline films, when applied on substrate surfaces with microstructure close to that of the films grown from 2-methoxyethanol based gels.

Lead-zirconate-titanate gels show similar behavior but their gels, including butanol based PZT-(B) ones, are more stable though the latter systems immediately decompose in the presence of HNO_3, but they are stable enough in the presence of 1:1 molar ratio of water. It has been found that PZT gels based on isobutanol are rather more stable than the butanol containing gels though, as in the case of butanol, they also don't abide the presence of nitric acid. So, the following order for tendency to gelation: butanol> isobutanol>> 2-methoxy-ethanol was observed.

Different structural features and reactivity of the precursors in the corresponding medium can explain the different behavior of gels observed. GLC analysis data show that the exchange of the alkoxide groups in the initial metal alkoxides with molecules of the alcohol proceeds rapidly. And since 2-methoxyethanol has tendency towards formation of intramolecular complexes, metal 2-methoxyethanolates and also their polymeric gels are less susceptible to further hydrolysis at room temperature and are less viscous.

The hydrolyzed complex alkoxide solutions (gels) were applied on sapphire (110) and nickel substrate surfaces by microsyringe after filtration through glass filter. The substrates were spun at 3000-rpm speed. After each spin-coating deposition the substrates were placed on a hot plate at 300°C for 5 min and 10 min for PT and PZT films, respectively. Coating-drying procedures was repeated from 1 to 4 times for PT films and 4-8 times for PZT films at 500-700°C for one hour. After it the samples were annealed in flowing oxygen or in air.

Differential thermal (DTA) and differential thermogravimetric(DTG) analyses data for PZT gel-powders in the temperature interval of 100-700°C show three areas relating to the weight losses with minimums on the DTG curves, the two of them are accompanied by exothermic reactions, which can be observed on the DTA curve. The samples of gel-powders were dried at 120°C for 2h. In spite of this, within 110°C-130°C temperature range the weight loss of about 4% takes place, which probably can be related to evaporation of the remains of the solvent. Further temperature rise reveals the two processes. The first one, which takes place at 190°C-400°C, can be explained by decomposition and evaporation of organic components accompanied probably by the formation of the low-valence oxides, e.g. PbO. The second process begins at 430°C-440°C and can be related to the formation of the lowest valence oxides and crystallization of pyrochlore structure and further crystallization of perovskite phase at 490°C-510°C.

According to the XRD patterns perovskite structure of PT is formed at the temperatures nearby 450°C. The characteristic lattice parameter data are the followings: a ≈3.886Å, c ≈ 4.128 Å, c/a ≈ 1.0623. The two series of peaks performing in XRD patterns of $PbTiO_3$films can be related to the first and second orders of reflection from the surfaces of (100) and (001) of perovskite structure. This fact is the evidence of the formation of the azimuth oriented unlimited axis texture of (100) type [4]. It has been shown that PT crystalline film growth both in the case of 2-methoxyethanol and butanol doesn't depend either on nature or orientation of substrate used. This fully justifies the use of PT as interlayer for producing the PZT thin films. XRD patterns of PZT gel-powders obtained at different temperatures are given in Figure 1. The curve (a) shows XRD patterns for sample fired in air at 500°C for 1 h. The curve (b) shows XRD patterns for the sample fired at 480°C in oxygen flow for 1h. The XRD patterns (c) were obtained for the sample, which passed differential thermogravimetric analysis (20°C-700°C, 10°/min.in air). Analysis of the experimental data obtained shows the reduction of temperature of formation of perovskite phase on firing the samples in oxygen flow. At temperatures close to 700°C the influence of oxygen on the process of structure formation is insignificant. The close picture is observed for PZT films fired at 700°C in air (Figure 2). The temperature dependencies of XRD patterns given in Figure 2 comply with DTA and DTG data and are the good evidence of the fact of formation of perovskite phase over the temperature range around 500° C.

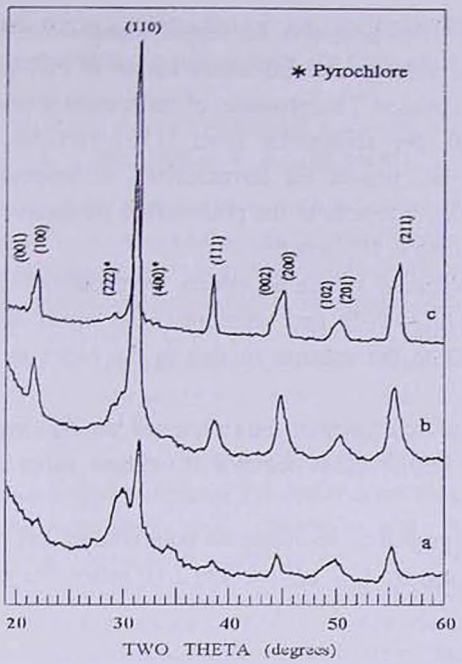

Figure 1. X-ray diffraction patterns of PZT-(A) gel powders.

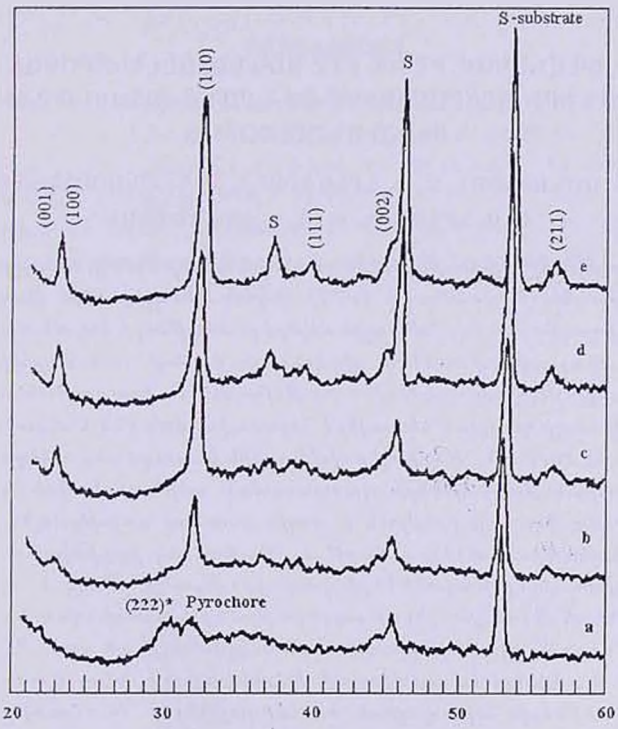

Figure 2. X-ray diffraction patterns of PZT-(A) films obtained on nickel substrate at a) 500°C; b) 550°C; c) 600°C; d) 650°C; e) 700°C.

The presence of PT as interlayer for sapphire and nickel substrates results in the changes of intensities ratio for the diffraction curves of PZT films, which correspond to (001) and (110) surfaces. The presence of reflections from (001) surfaces, which are comparable with the reflections from (110) surfaces, is the result of the formation of 90^0 twins, typical for ferroelectrics of perovskite structure [5]. The presence of PT interlayer results in the preferential formation of just these 90^0 twins considerably suppressing (110) domains.

Studies of polarization switching effects were carried out on samples of PZT films applied on Si-SiO_2-Ti-Pt and sapphire (110) substrates. Measurements were carried out according to the scheme similar to the Merz method [6]. The impulse duration is 15 μsec.

According to the experimental data obtained the full switching of polarization takes place in about 2 μsec and is detected at voltages value of 1000 v (electric field strength 2.5 10^3 V/cm).

The tentative appraisal of spontaneous polarization and rate of the domain wall movement are equal approx. to 2 $\mu K/cm^2$ and 2 10 m/sec, respectively.

Acknowledgement

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ՋՈԼ–ՀԵԼ ԵՂԱՆԱԿՈՎ PT ԵՎ PTZ ՍԵԳՆԵՏՈԷԼԵԿՏՐԱԿԱՆ ԲԱՐԱԿ ԹԱՂԱՆԹՆԵՐԻ ՊԱՏՐԱՍՏՈՒՄԸ ԵՎ ՆՐԱՆՑ ՀԱՏԿՈՒԹՅՈՒՆՆԵՐԻ ՈՒՍՈՒՄՆԱՍԻՐՈՒՄԸ

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Ցիրկոնիում-տիտանային նոր պրեկուրսորների օգտագործմամբ Շլենկի ռեակցիայով ստացվել են կապարի տիտանիտի ցիրկոնատի (PZT) կայուն կոմպլեքսներ: Ուսումնասիրվել է մասնակիորեն հիդրոլիզված (պոլիմերային հնլեր) լուծույթների կայունություն: Կապարի տիտանիտի եւ կապարի տիտանիտի ցիրկոնատի համար ուսումնասիրվել է զոլ-հնլ համակարգի վարքը մեթիլցելոզոլում, Ն-բուտանոլում եւ իզո-բուտանոլում: Ն-բուտանոլի եւ իզո-բուտանոլի դեպքում նկատվել է հելատաջացման մեծ հակվածություն: Որոշվել են $PbTiO_3$-ի եւ $Pb(Zr_xTi_{1-x})O_3$-ի պերովսկիտային կառուցվածք ունեցող ($x = 0,5-0,6$) բյուրեղական բարակ թաղանթների պատրաստման տեխնոլոգիական պարամետրերը: Մշակված եղանակը հնարավորություն է տալիս ստանալ առավելապես բյուրեղագրաֆիական ուղղվածություն ունեցող հարթ եւ թափանցիկ բյուրեղական թաղանթներ, ինչպես նաեւ վերահսկել թաղանթների բաղադրությունը: Ցույց է տրվել հիմքի եւ կապարի տիտանիտի միջանկյալ շերտի ազդեցությունը կապարի տիտանիտի ցիրկոնատի (PZT) կառուցվածքի եւ բյուրեղագրաֆիական ուղղվածության վրա: Ջերմային, ռենտգենաֆազային անալիզների եւ օպտիկական միկրոսկոպիայի միջոցով ուսումնասիրվել են ստացված թաղանթների մորֆոլոգիան եւ հնլ-փոշիները: Գնահատվել են սպոնտան բևեռացման արժեքները, ինչպես նաեւ PZT թաղանթների համար դոմենյան պատերի շարժման արագությունները:

ПРИГОТОВЛЕНИЕ PZ И PZT СЕГНЕТОЭЛЕКТРИЧЕСКИХ ТОНКИХ ПЛЕНОК ЗОЛЬ-ГЕЛЬ МЕТОДОМ И ИССЛЕДОВАНИЕ ИХ СВОЙСТВ

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Стабильные комплексы титаната цирконата свинца (PZT) получены по реакции Шленка с использованием новых циркониевых прекурсоров. Изучена стабильность частично гидролизованных растворов (полимерных гелей). Изучено поведение золь-гель систем для титаната свинца и цирконата титаната свинца в метилцеллозольве, *н*-бутаноле, *изо*-бутаноле. Сильная склонность к гелеобразованию замечена в случае бутанола и *изо*-бутанола. Определены технологические параметры для приготовления кристаллических тонких пленок $PbTiO_3$ и $Pb(Zr_xTi_{1-x})O_3$ перовскитной структуры, где x = 0,5-0,6. Разработанный метод позволяет получить гладкие и прозрачные кристаллические пленки с преимущественной кристаллографической ориентацией, а также контролировать состав пленок. Показано влияние подложки и промежуточного слоя титаната свинца на структуру и кристаллографическую ориентацию цирконата титаната свинца (PZT). Термическим, рентгенофазовым анализами, оптической микроскопией изучены гель-порошки и морфология полученных пленок. Оценены величины спонтанной поляризации, а также скорости передвижения доменной стенки для PZT пленок.

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