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DOPING EFFECTS IN PZT THIN FILMS PREPARED ON DIFFERENT SUBSTRATES

VPLIV DOPIRANJA NA TANKE PZT-PLASTI, PRIPRAVLJENE NA RAZLIČNIH PODLAGAH

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There are only a small number of publications on the subject of the dopant solid-solubility limit in lead-zirconate-titanate (PZT) ceramics, and in only a few publications is the dopant solid-solubility limit in PZT thin films mentioned. In this work, an attempt is made to study the dopant solid solubility in PZT thin films. Iron-doped as well as undoped PZT thin films were prepared on different substrates ($Pt/TiO_x/SiO_2/Si$, sapphire, $SrTiO_3$ and MgO) using a chemical-solution-deposition (CSD) method. The films were deposited on substrates using a spin-coating process. A composition with a Zr/Ti ratio of 50/50 and a tetragonal perovskite phase structure was chosen for this study. The mol fraction of an excess 10 % PbO with respect to the nominal composition was added to compensate for PbO losses due to volatilization during the crystallization anneal. The compositions of the iron-doped PZT thin films were $Pb(Zr_{0.5}Ti_{0.5})_{1-x}Fe_xO_{3-x/2}$ + 10 % PbO (mol fraction) excess (x = 0.02, 0.05, and 0.5). We have studied the effect of iron on the phase-formation behaviour, the microstructure and the electrical properties.

The crystallization of the obtained thin films was found to depend strongly on the substrate used. It is known that the solid solubility of acceptors (such as Fe) in PZT ceramics is limited to a few percent; however, according to the X-ray data, the solid solubility of iron in PZT thin films is much higher. Secondary phases are not observed in undoped and Fe-doped PZT thin films deposited on $SrTiO_3$, even at very high Fe concentrations (up to 50 %).

Key words: PZT thin films, iron doped, chemical solution deposition, different substrates

Relativno majhno število publikacij obravnava trdno topnost dopantov v keramiki svinčevega cirkonata titanata (PZT) in samo nekaj člankov omenja topnost dopantov v tankih PZT-plasteh. V tem prispevku smo predstavili rezultate raziskav tankih PZT-plasti, dopiranih z železom. Tanke PZT-plasti brez dopantov in PZT-plasti, dopirane z železom, smo pripravili na različnih podlagah ($Pt/TiO_x/SiO_2/Si$, safirju, $SrTiO_3$ and MgO) s sintezo iz raztopin (*CSD - chemical solution deposition*). Tanke plasti smo nanesli na različne podlage z metodo vrtenja (*spin coating*). Raziskovali smo tanke PZT-plasti z razmerjem Zr/Ti = 50/50 ki imajo tetragonalno perovskitno strukturo. Zaradi odparevanja PbO med žganjem smo k začetni sestavi dodali molski presežek PbO 10 %. Sestava z železom dopiranih tankih PZT-plasti je bila $Pb(Zr_{0.5}Ti_{0.5})_{1-x}Fe_xO_{3-x/2}$ + 10 % PbO (molski delež) kjer je x = 0,02, 0,05 in 0,5. Raziskovali smo vpliv železa na fazno sestavo, mikrostrukturo in električne lastnosti dopiranih tankih PZT-plasti.

Kristalizacija pripravljenih vzorcev je bila močno odvisna od vrste podlage. Iz literature je znano, da je trdna topnost akceptorjev (na primer Fe) v PZT-keramiki omejena na nekaj odstotkov. Glede na rezultate rentgenske analize je topnost železa v tankih PZT-plasteh veliko večja. Nedopirane PZT- in z železom dopirane tanke PZT-plasti, pripravljene na $SrTiO_3$, so bile enofazne tudi pri zelo visoki koncentraciji železa (do 50 %).

Ključne besede: tanke PZT-plasti, dopirane z železom, sinteza iz raztopin, različne podlage

1 INTRODUCTION

The most common ferroelectric compositions in current use are lead zirconate titanate $Pb(Zr_{1-x}\ Ti_x)O_3$ and its many variations. Depending on the Zr/Ti ratio and introduced dopants, these materials can be used for ferroelectric (PZT, PT, PLZT, PNZT, etc.)[1,2,3], pyroelectric (PZT 15/85, $PbTiO_3$, $Pb_{1-x}La_xTiO_3$, $Pb_{1-x}Ca_xTiO_3$)[1,4] and piezoelectric (PZT 45/55, PZT 53/47)[1,5] applications. Ferroelectric PZT thin films are promising candidates for non-volatile memory devices. The intensive research associated with such thin films raised a number of questions of both fundamental and applied nature. These questions had to be solved to ensure the overall success of ferroelectric thin-film technology. PZT thin films exhibit significant differences in their electrical properties and microstructure when compared to bulk ceramics.[6,7,8] It is not clear whether "size effects" or the different structural properties of PZT thin films have an influence on the ferroelectric properties.

PZT ceramics are almost always used with a dopant to improve and optimize their basic properties for specific applications. Equal concentrations of different dopants have not yielded similar property modifications in PZT thin films.[8,9,10] Higher concentrations, however, have been reported to yield inferior properties when compared to undoped films.[8] While there have been substantial improvements in many of the properties of PZT using acceptor and donor dopants, it is important to achieve a greater understanding and control over the properties of ferroelectric materials. In particular, we are interested in understanding how dopants affect the crystallization, the orientation, the microstructure and consequently the electrical properties of PZT thin films.

2 EXPERIMENTAL

A sol-gel process was used to prepare undoped PZT 50/50 and Fe-doped PZT thin films. High-purity lead acetate [$Pb(CH_3COO)_2$], zirconium n-butoxide [$Zr(C_4H_9O)_4$], titanium n-butoxide [$Ti(C_4H_9O)_4$], and, in the case of doped PZT thin films, iron (III) acetylacetonate [$Fe(C_5H_7O_2)_3$] were used as starting materials for preparing the spin-on solutions. 2-methoxyethanol [$CH_3OC_2H_4OH$] was used as a solvent. The precursor solutions were based on the following stoichiometries: $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $Pb(Zr_{0.5}Ti_{0.5})_{1-x}Fe_xO_{3-x/2}$, where x = 0.02, 0.05 and 0.50. To compensate for the volatility of PbO during the final annealing process an excess of 10 % PbO (mol fraction) was added to all the solutions. The required starting materials were dissolved in 2-methoxyethanol upon heating and mixing. Further refluxing for 22 h with one distillation resulted in a stock solution. The final concentration of the solution was adjusted to 0.5 M by the addition of 2-methoxyethanol. A 4% (volume fraction) of formamide [$CHONH_2$] was added to the freshly prepared sols at room temperature as a drying-control additive.

For thin-film deposition $Pt(111)/TiO_2/SiO_2/Si$, sapphire (0001), $SrTiO_3$ (100) and MgO (100) substrates were used. The solutions were passed through a 0.2-μm filter prior to use and spin coated by spinning the sol for 30 s at 3000 r/min using a photo-resist spinner (1-EC101D-R485), Headway Research, Garland, TX. After the deposition process, the coated film was dried on a hot plate at 200 °C for 2 min and pyrolysed at 350 °C for 1 min to evaporate and burn out the organic. The deposition, drying and pyrolysis were repeated three times before further heat treatment. The films were crystallized at 650 °C for 15 min in air using a rapid-thermal-annealing quartz-lamp furnace. The final film thickness depends on the composition, and it ranges from 0.13 μm to 0.17 μm.

The crystal orientation of the obtained thin films was analyzed using X-ray diffraction (XRD) with Cu-K_α radiation (Philips PW 1710). Scanning electron microscopy (SEM) (JEOL JXA 840A) was used to examine the microstructure of the films. The grain size was determined by method of intercepts. The film thickness was measured using a Rank Taylor Hobson profilometer.

For the electrical characterization of thin films, gold top electrodes were applied to the surface of the films using a shadow masking-sputtering method. The area of the gold electrodes was 0.24 mm^2. A portion of PZT thin film was etched away with a mixture of $HCl/H_2O/HF$ to expose the bottom Pt electrode. The P-E hysteresis loops of the samples were measured at 12 V and 100 Hz (triangular wave) by a FE thin-film tester (AixACCT).

3 RESULTS AND DISCUSSION

After annealing at 650 °C for 15 min the PZT and Fe-doped PZT thin films deposited on MgO and sapphire (0001) substrates were not well crystallized (**Figure 1**). The perovskite phase (Pe) of the films was randomly oriented and the positions of the peaks were shifted with increased iron concentration. Such shift to higher angles indices on reduction of *d*-spacing and consequently of cell size with iron doping.

The XRD profiles of the crystallized Fe-doped PZT thin films deposited on $Pt/TiO_2/SiO_2/Si$ and $SrTiO_3$ substrates are shown in **Figures 2 and 3**, respectively. All the patterns show the perovskite structure. The results are different from those observed with bulk PZT ceramics. As known from bulk ceramics, the off-valent acceptors (such as Fe^{3+} replacing Zr^{4+} or Ti^{4+}) are compensated by oxygen vacancies and have only limited solubility in the lattice. It has been reported that the solid

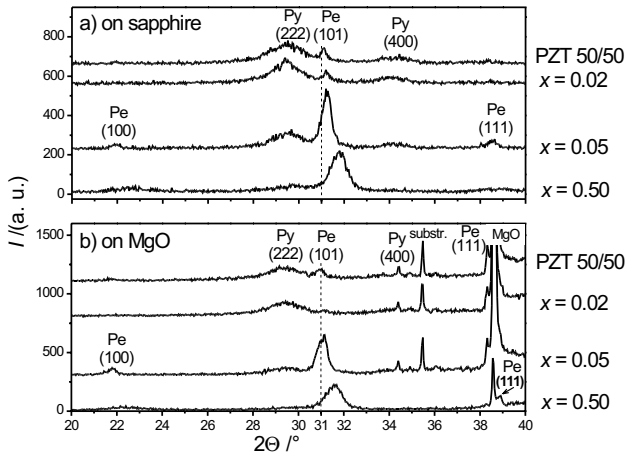

Figure 1: X-ray diffraction patterns of undoped and Fe-doped PZT thin films deposited on (a) sapphire and (b) MgO substrates

Slika 1: Difraktogrami nedopirane tanke PZT-plasti in z železom dopiranih tankih PZT-plasti, nanesenih na podlago iz safirja (a) in MgO (b)

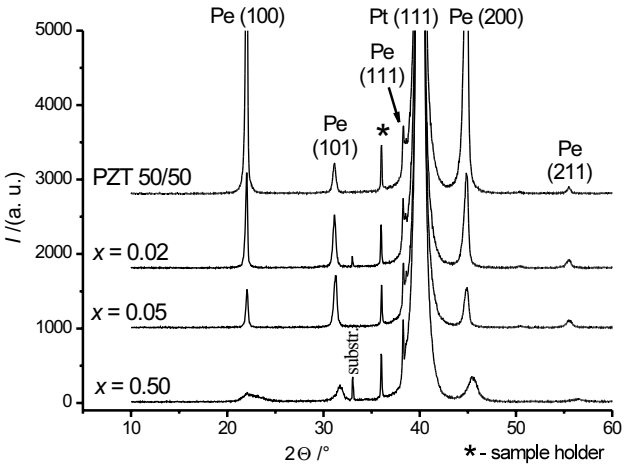

Figure 2: X-ray diffraction patterns of undoped and Fe-doped PZT thin films deposited on $Pt/TiO_2/SiO_2/Si$ substrate

Slika 2: Difraktogrami nedopirane tanke PZT-plasti in z železom dopiranih tankih PZT-plasti, nanesenih na $Pt/TiO_2/SiO_2/Si$ podlago

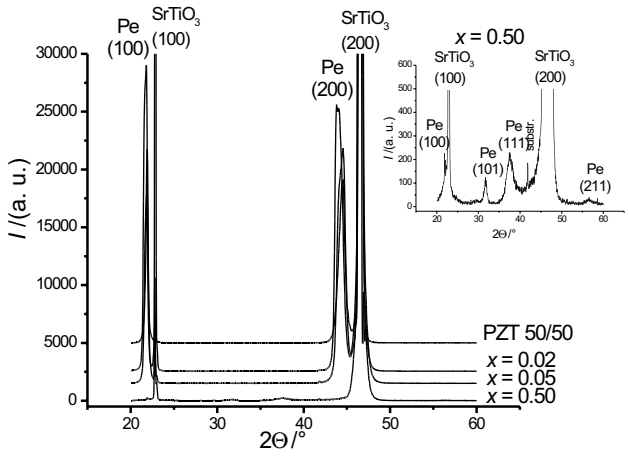

Figure 3: X-ray diffraction patterns of undoped and Fe-doped PZT thin films deposited on $SrTiO_3$ substrate

Slika 3: Difraktogrami nedopirane PZT-plasti in z železom dopiranih tankih PZT-plasti, nanesenih na $SrTiO_3$ podlago

solubility of Fe^{3+} in PZT ceramics is limited to the mol friction 1.5 % (which corresponds to $x = 0.03$); above that value secondary phases are formed.[11] In the case of our thin films deposited on $Pt/TiO_2/SiO_2/Si$ and $SrTiO_3$ substrates the secondary pyrochlore type phase (Py) was not observed, even at very high iron concentrations. All the diffraction lines corresponded to those of the perovskite structure, within the XRD detection limit.

We assume that the difference in the crystal structure and the lattice mismatch between the film and the substrate caused the difference in crystallinity and epitaxy of the films deposited on the different substrates.

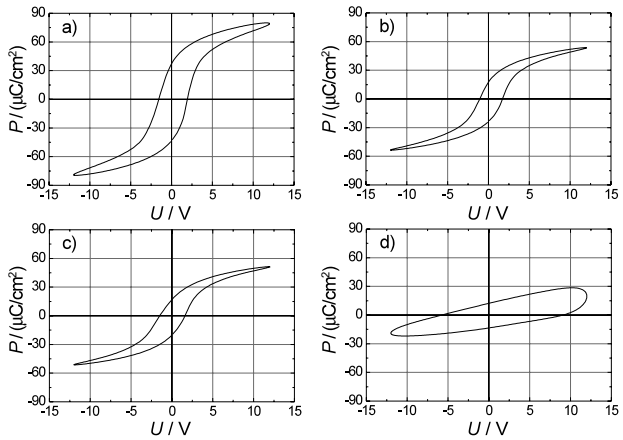

Figure 4: Room-temperature ferroelectric hysteresis loops (P–U) of PZT and Fe-doped PZT thin films: (a) PZT 50/50; (b) $Pb(Zr_{0.5}Ti_{0.5})_{0.98}Fe_{0.02}O_{2.99}$; (c) $Pb(Zr_{0.5}Ti_{0.5})_{0.95}Fe_{0.05}O_{2.975}$ and (d) $Pb(Zr_{0.5}Ti_{0.5})_{0.5}Fe_{0.5}O_{2.75}$ (measured at 12 V, 100 Hz) (P – polarisation)

Slika 4: Feroelektrične histerezne zanke (P–U) tankih plasti, izmerjene pri sobni temperaturi: (a) PZT 50/50; (b) $Pb(Zr_{0,5}Ti_{0,5})_{0,98}Fe_{0,02}O_{2,99}$; (c) $Pb(Zr_{0,5}Ti_{0,5})_{0,95}Fe_{0,05}O_{2,975}$ in (d) $Pb(Zr_{0,5}Ti_{0,5})_{0,5}Fe_{0,5}O_{2,75}$ (izmerjene pri 12 V, 100 Hz) (P – polarizacija)

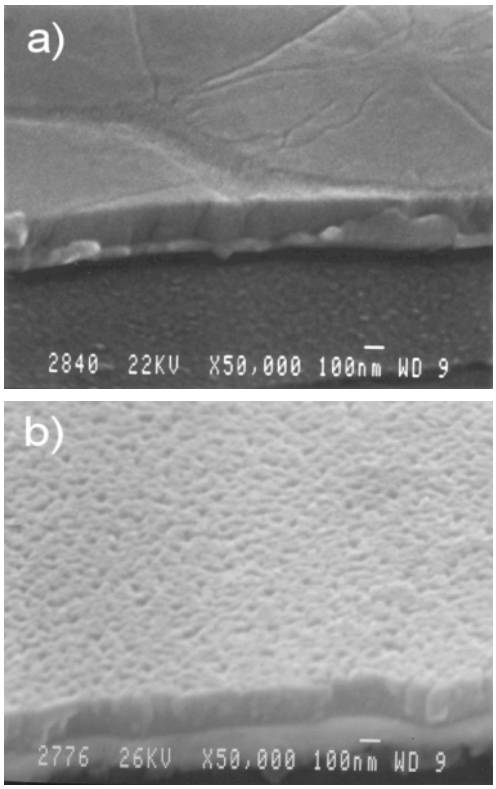

Figure 5: SEM micrographs of (a) PZT 50/50 and (b) $Pb(Zr_{0.5}Ti_{0.5})_{0.95}Fe_{0.05}O_{2.975}$ thin films deposited on $Pt/TiO_2/SiO_2/Si$ substrate

Slika 5: SEM-posnetki mikrostruktur tankih plasti, nanesenih na podlago $Pt/TiO_2/SiO_2/Si$ (a) PZT 50/50 in (b) $Pb(Zr_{0,5}Ti_{0,5})_{0,95}Fe_{0,05}O_{2,975}$

The ferroelectricity of the thin films was investigated by observing the hysteresis loop. All the observed hysteresis loops are slightly unsymmetrical, probably because of the different top (Au) and bottom (Pt) electrodes used, or because of the unsatisfactory adhesion of the top electrodes. The hysteresis loops of the undoped and iron-doped PZT thin films are shown in **Figure 4**. As can be seen, polarisation–electric-field (P-E) hysteresis loops were obtained for all the thin films. The shape of the hysteresis loop, the remnant polarisation and the coercitive field were found to change with the iron concentration. The average remnant polarisations of the thin films with iron content $x = 0$, $x = 2$ and $x = 5$ were 40, 20, and 18 μC/cm², respectively. The measured loop in the case of the thin film with a very high iron concentration ($x = 0.5$) is not a classical ferroelectric hysteresis loop; neither is it a straight line, characteristic of linear dielectrics. The remnant polarisation is much lower and the coercive field is three times higher than in the case of an undoped PZT thin film. The rounded shape of the loop indicates the conductivity of the sample. It is clear that the polarization of the doped PZT thin films with iron contents up to $x = 0.05$ change like with bulk ceramics,

i. e., the remnant polarization decreases with an increase in the iron concentration. However, in contrast to bulk ceramics, the coercive field of iron-doped PZT thin films (x = 0.02 or 0.05) is smaller than that of an undoped PZT thin film.

Microstructure investigations performed with an SEM show that the addition of iron (up to x = 0.05) to PZT thin films deposited on $Pt/TiO_2/SiO_2/Si$ substrates causes a large reduction in the grain size (**Figure 5**). The average grain size of an undoped PZT thin film is 0.91 μm, and the average grain size of the $Pb(Zr_{0.5}Ti_{0.5})_{0.98}Fe_{0.02}O_{2.99}$ and $Pb(Zr_{0.5}Ti_{0.5})_{0.95}Fe_{0.05}O_{2.975}$ thin films is 0.85 μm and 0.04 μm, respectively. This trend is in agreement with the reports for bulk PZT ceramics, which document a decrease of the grain size with the addition of acceptor dopants (for example Fe^{3+}).[12] However, in the case of a heavily Fe-doped PZT thin film (x = 0.5) the grains are much bigger than those of a $Pb(Zr_{0.5}Ti_{0.5})_{0.95}Fe_{0.05}O_{2.975}$ thin film (x = 0.05). The average grain size of a $Pb(Zr_{0.5}Ti_{0.5})_{0.5}Fe_{0.5}O_{2.75}$ thin film is 0.31 μm. More detailed structural studies are in progress.

4 CONCLUSION

The solid solubility of iron in PZT thin films deposited on $Pt/TiO_2/SiO_2/Si$ and $SrTiO_3$ substrates is different from that of bulk ceramics; it extends up to x = 0.5, according to the XRD analysis. The measured hysteresis loops confirm the ferroelectric nature of undoped and iron-doped PZT thin films with concentrations of iron up to x = 0.05.

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