Rare-earth ions doping effects on the optical properties of sol–gel fabricated PbTiO_3 thin films

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1. Introduction

For last decades ferroelectric materials are being considered for application in different kinds of devices, such as storage information and photonic devices, piezoelectric actuators and infrared sensors. Utilization of ferroelectrics in the form of thin films is even more attractive since it allows their integration into existent semiconductor circuit technology and creation of new types of the devices. In particular, solid solutions of PbZrO_3-PbTiO_3 system are the most prominent candidates for such applications due to high remnant polarization, piezoelectric coefficient and low coercive field. Moreover, ferroelectric, dielectric and optical properties of these materials can be tuned by appropriate doping. The analysis of available literature shows that the properties of lead based perovskite thin films are very sensitive to doping with elements of the lanthanide series (Ln). There is a large number of papers devoted to doping effects in PZT (lead zirconate titanate) and PT (lead titanate) thin films which, however, cannot be reviewed in this brief report. Systematic investigations of lanthanide ions doped PLZT (lead lanthanum zirconate titanate) and PZT ceramics were undertaken by Park et al. [1] and Tan et al. [2]. Boyle et al. [3] investigated doping effects on PZT thin films with emphasis on the effects of doping and deposition conditions on microstructure, dielectric and ferroelectric properties. Effects of Ln doping on the optical properties were not addressed and experimental data are scarce in the literature. Chang and Desu [4] reported on the dependence of the refractive index of Pb(Zr_0.5Ti_0.5)O_3 (PZT50/50) thin films on doping with up to 6 mol.% of La and Nd, and showed a tendency of the refractive index to increase with increasing dopant concentration. In view of the fact that lanthanide elements doped materials are of great importance for photonic applications [5], an attempt is made in this paper to trace the effects of Ln ions doping on refractive index (n) and extinction coefficient (k) of PbTiO_3 thin films.

2. Experimental details

The sol–gel method was utilized to process Ce, Sm, Dy, Er and Yb doped PbTiO_3 thin films with doping
element concentrations of 0, 2, 5 and 8 mol.% according to the stoichiometry \((\text{Pb}_{1-x}\text{Ln}_x)\text{TiO}_3\). The precursor solutions were prepared from lead acetate, lanthanide acetates and titanium iso-propoxide. Lead and lanthanide acetates were dissolved in 3 mol of acetic acid; excess of 10 mol.% lead excess was added into solution to compensate for PbO volatility during high temperature treatments. Titanium iso-propoxide was stabilized with 2 mol of acetylacetone. The two parts were then mixed at room temperature and subsequently dissolved in 2-methoxethylacetone to achieve a final solution concentration 0.4 mol/l. Thin films were prepared by spin-coating on commercial \((111)\text{Pt/Ti/SiO}_2/\text{Si}\) substrates at 3000 rev./min for 30 s. Each coating was then dried on the plate at 340 °C for 5 min and pyrolized at 500 °C for 5 min. Four successive coatings were deposited. The specimens were finally annealed in a pre-heated furnace at 700 °C for 5 min in air.

The optical properties of the films were investigated by means of ellipsometry using a HeNe-laser source \((\lambda = 632.8 \text{ nm})\). The ellipsometric film thickness and complex refractive index are obtained from a fit to the measured data, applying the Fresnel equation and a model for the layered system [6]. Here we will deal with the components of the complex index of refraction \(N\), which is expressed as

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N = n - jk
\]

where \(n\) is the real part of the refractive index, \(j\) is the imaginary operator and \(k\) is the imaginary part of the refractive index or the extinction coefficient. Very often the value of \(n\) is treated as the refractive index that is, of course, acceptable only in case of loss-free materials.

Considering data for various angles from 30 to 85°, an over determined system was achieved, which allowed for cross checking, increased resolution and testing the employed model. As a measure of the resolution the change in the thickness due to changes in \(n\) by 1% is noted. Ellipsometric thicknesses of prepared samples were found to be in the range from 200 to 300 nm.

Additionally, X-ray photoelectron spectroscopy (XPS, Omicron Full Lab system, monochromated Al \(K_α\) soft radiation source) investigations were conducted on selected films. Measurements were performed on as-deposited film and after Ar ion cleaning at 1 keV and 70 nA for 2 min.

3. Results and discussion

The results presented below were obtained on films processed under the same conditions and exhibiting very similar surface topography and microstructure with a mean grain size in the vicinity of 100 nm.

Fig. 1 shows the dependence of the refractive index \(n\) (a) and the extinction coefficient \(k\) (b) of \(\text{PbTiO}_3\) films doped with 2 mol.% of Ln on the nature of doping element in comparison to the non-doped specimen. A high value of \(n\) (2.73) was obtained for pure lead titanate thin film. For doped films one can note some decrease in \(n\). Moreover, with the exception of Ce, the trend of \(n\) to decrease from 2.69 to 2.57 when the atomic number of the element changes from 62 (Sm) to 70 (Yb) can be observed. With respect to \(k\), while Ce and Sm lead to the lower values in comparison to non-doped film, Dy, Er and Yb doping results in higher values. The smallest value of \(k\) (2.11×10^{-4}) was found for the film doped with 2 mol.% of Ce.

It is known that visible light interacts with matter via the polarizability of the valence electrons [7]. Following Hench and West [8], the index of refraction depends on the polarizability of the material, which in turn is determined by the sum of ionic refractions \(R_i\). In crystal compounds the value of \(R_i\) depends upon: (i) the electronic polarizability which increases as the number of electrons in the ion increases; (ii) the coordination number of the ion; (iii) the polarizability of the first neighbor ions coordinated with it; and (iv) the field intensity \(z/a^2\) where \(z\) is the valence of the ion and \(a\) is the distance of separation [8]. With respect to rare-earth elements doped lead titanate, some of the factors listed above may be neglected. In fact, partially filled 4f valence levels of Ln-elements are shielded from the external field with 5p^2 and 5p^{6} states. In this case, it is assumed that rare-earth elements will affect optical properties of our films mainly through the polarizability of the valence shells and the field intensity \(z/a^2\). Therefore, it is expected that the index of refraction would change smoothly while the electronic configura-
The oxidation changes from [Xe]4f^5d^6s^2 (Ce) to [Xe]4f^4s^2 (Yb). This assumption is to some extent consistent with the experimental results presented in Fig. 1, with the exception of Ce, which requires some additional discussion. A possible explanation of particular behavior of Ce-doped film can be proposed considering specific oxidation states of Ce in the PbTiO₃ lattice. It is well known that unlike the usual +3 oxidation state peculiar to the elements of Ln-series, Ce may also take +4 oxidation state. To our knowledge experimental investigations of the oxidation state of Ce in lead based perovskites are still lacking. In the present work Ce-doped PbTiO₃ film was investigated by means of X-ray photoelectron spectroscopy (XPS) which is sensitive to the oxidation states of elements via peak position shifts. Fig. 2a shows XPS spectra of PbTiO₃ thin film doped with 5 mol.% of Ce. Dashed line represents the spectra taken for as-deposited film. The XPS spectra of the same sample measured after Ar ion cleaning is shown by solid line. The Ar ion cleaning did not lead to noticeable modification of the spectra. Only the 1s peak of C, attributed to surface contamination, disappeared. Detailed structure of the peak designated Ce 3d₅/₂ is shown separately in Fig. 2b. The values of binding energy obtained by Gaussian fitting (881 and 877 eV) indicate the presence of Ce in +4 oxidation state [9].

The refractive indices and extinction coefficients of Sm, Dy and Er doped films are plotted vs. doping level in Fig. 3. For both Sm and Dy some decrease in the index of refraction is observed (Fig. 3a) which is in contradiction to the results reported by Chang and Desu [4] for La and Nd doped PZT thin films. It is thought that the increase of the concentration of Sm and Dy is accompanied with some decrease in the density of the material and, as a result, decrease in the refractive index (p. 347 in Ref. [8]). At the same time, doping with Er up to 8 mol.% did not affect significantly the refractive index of PbTiO₃ film and no explanation can be proposed at the moment. The imaginary part of the refractive index of Sm, Dy and Er doped films revealed complex behavior with respect to doping level. While for all concentrations investigated, Dy and Er doped films show nearly linear increase of k when the doping level increases, (Fig. 3b), doping with Sm leads to opposite effect—the extinction coefficient, which is, in fact, loss of the light intensity, was slightly decreased for x<5 mol.%. Further increase in Sm content caused an abrupt increase in k.

Fig. 2. XPS spectrum of PbTiO₃ thin film doped with 5 mol.% of Ce (a). Here the peaks denoted as: a and b–Ce 3d₅/₂, c–Ce Auger, d–Pb 4p₁/₂, e–Pb 4p₃/₂, f–Ti 2p, g–O 1s, h–Ti 2p₃/₂, 2p₁/₂, i–Pb 4d₅/₂, j–Pb 4d₃/₂, k–C 1s, l–Pb 4f₁/₂ and m–Pb 4f₃/₂. The spectrum of as-deposited film is shown by dashed line. Solid line represents the spectrum taken after cleaning of the surface with Ar ions at 1 keV, 70 nA for 2 min. Detailed structure of the peaks attributed to 3d of Ce is shown separately in (b). The experimental data are shown by circles; the result of the Gaussian fitting is represented by solid line.

Fig. 3. Values of the refractive index (a) and extinction coefficient (b) of Sm, Dy and Er doped PbTiO₃ thin films plotted vs. concentration of doping element. Solid line is a guide for the eye.
4. Conclusions

In conclusion, Ce, Sm, Dy, Er and Yb doped lead titanate thin films on (111)Pt/Ti/SiO$_2$/Si substrates were processed via sol–gel technique. Ellipsometric investigations were conducted to obtain real and imaginary parts of the refractive index. For all lanthanide elements investigated, reduction in $n$ in comparison to pure lead titanate thin film was obtained (the case of 2 mol.% of Ln-elements doped films). Furthermore, apart from Ce-doped films, a continuous decrease in $n$ with increasing the atomic number of doping elements was observed. Ce doping leads to an abrupt reduction of $n$ and might be explained by the +4 oxidation state of this element (deduced from XPS data). At the same time a significant increase in the imaginary part of the refractive index with increasing atomic number of doping elements was found.

The level of doping is also shown to affect $n$ in the case of Sm and Dy while Er doping did not produce any noticeable change. As to the extinction coefficient $k$, a general tendency to increase with increasing doping concentration could be noticed, although the mechanisms of light loss in rare-earth elements doped perovskite materials are worth original investigations.

References