Microstructure and properties of sol–gel processed Pb$_{1-x}$La$_x$(Zr$_{0.52}$, Ti$_{0.48}$)$_{1-x/4}$O$_3$ thin films. The effects of lanthanum content and bottom electrodes

M. Es-Sounia,*, M. Abeda, A. Piorraa, S. Malinowskia, V. Zaporojtchenkob

*a University of Applied Sciences, Surface and Thin Film Technology, Kiel, Germany
bFaculty of Engineering, Multicomponent Materials, Christian-Albrechts University, Kiel, Germany

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Abstract

PLZT (lanthanum doped PZT [Pb(Zr$_{0.52}$, Ti$_{0.48}$)O$_3$]) thin films with 5, 8 and 10 mol% lanthanum were processed via chemical solution deposition on (111)-Pt/TiO$_2$/SiO$_2$/Si (100) and LaNiO$_3$ (LNO)/(111)-Pt/TiO$_2$/SiO$_2$/Si (100). The thin films were investigated in terms of the influence of lanthanum content and substrate heterolayer structure on the microstructure and dielectric properties. It is shown that deposition on (111)-Pt leads to a (100)/(111) preferred texture and a coarse grained microstructure with PbO depleted areas. Deposition on LNO results in a randomly oriented, fine grained microstructure. The dielectric constants decrease with increasing lanthanum content and are higher for the films deposited on Pt. They take values between 1630 (0.05 mol La$^{3+}$) and 865 (0.1 mol La$^{3+}$) for deposition on Pt and between 1090 and 808 for deposition on LNO. The fatigue properties depend also on the lanthanum content and substrate type. The PLZT thin films with lanthanum concentration above 0.05 deposited on LNO show no fatigue. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Scanning electron microscopy; X-ray diffraction; Dielectric properties; Solution deposition

1. Introduction

Ferroelectric ceramic thin films based on the oxides Pb(Zr$_{0.52}$, Ti$_{0.48}$)O$_3$ (PZT) with a perovskite-like structure have been shown to be of major technological interest for many sensor and actuating applications due to their piezoelectric properties [1,2]. In addition, the ferroelectric properties and the relatively high dielectric permittivity make PZT a promising material for thin film based capacitors in ferroelectric based non-volatile memories [3,4]. Many processing routes for thin film PZT, including laser ablation, sputter techniques, CVD and solution deposition methods have been reported [5]. Sol–gel processing with polymeric gels constitutes certainly the method of choice for processing PZT and PLZT thin films with controlled stoichiometry and microstructure (see the review article by Tuttle and Schwarz [6]). Additional advantages lie in the relatively low processing temperatures, the quite simple and cost effective preparation methods, as well as versatile laboratory equipment.

The substrate heterolayer structures usually used for all deposition processes are based on Pt/TiO$_2$/SiO$_2$/Si. However, it has been shown [7–12] that the electrode materials influence dramatically the microstructure and dielectric fatigue behaviour of PZT. Particularly Pt bottom and top electrodes were reported to lead to degradation of dielectric properties under alternating electric fields. The degradation mechanisms, reviewed by W.L. Warren et al. [11], appear to be mainly due to the pinning of domain walls as a result of the accumulation of oxygen vacancies near

* Corresponding author. Tel.: +49-431210-2660; fax: +49-43121062660.
the electrodes during cycling. The ability of the electrode materials to act as a sink for oxygen vacancies seems to control the degree of degradation. In this respect, electrode materials based on metallic oxides such as (La,Sr)CoO$_3$ and RuO$_2$, which act as sinks for oxygen vacancies, have been reported to improve the fatigue properties of PZT thin films.

In a recent work [13], we have demonstrated that it is possible to process high quality sol–gel PZT thin films with high permittivity values in the range from 2900 to 4000 depending on the substrate type. However, although some improvement of fatigue resistance could be obtained by using a buffer layer of the conductive oxide LaNiO$_3$ (LNO), the thin films have been shown to be prone to severe dielectric fatigue. One of the alternatives to improve the resistance to fatigue is doping with A(Pb)-site donors like La$_3$$. The ferroelectric thin films thus obtained are expected to be less prone to domain wall pinning due to oxygen vacancies [14].

The aim of the present work is to investigate the effects of La$_3$$ on the dielectric and fatigue properties of sol–gel processed PZT with a composition near the morphotropic phase boundary [Pb(Zr$_{0.52}$, Ti$_{0.48}$)$_3$O$_3$]. For this purpose, La$_3$$ was added in variable concentrations of 0.05, 0.08 and 0.1 mol on Pb sites. In order to study the effects of bottom electrode on the microstructure and properties of the PLZT thin films, deposition was conducted on (111)-textured Pt/TiO$_2$/SiO$_2$/Si and on sol–gel processed LNO buffer layer. Microstructural and dielectric characterization including polarization fatigue are reported for different capacitor configurations.

2. Experimental

The PLZT stock solutions were prepared from 1.1 mol Pb (II)-acetate trihydrate, lanthanum nitrate hexahydrate, 0.52 mol tetrapropyl-zirconate, 0.48 mol tetra-isopropylorthotitanate to give the desired nominal compositions. The solutions were diluted in 10 mol of 2-methoxyethanol and stabilised with 3 mol acetyl acetone and 3.33 mol acetic acid. An excess of 0.1 mol PbO with respect to the nominal compositions was adopted in order to compensate for preferential PbO evaporation during firing.

Depositions were achieved on pre-annealed substrates via spin coating at 800 rpm for 9 s (pre-coating) and 5000 rpm for 20 s. The films were either directly deposited on highly (111)-textured Pt bottom electrode on TiO$_2$/SiO$_2$/Si or on a sol–gel processed LNO buffer layer [13]. The coated substrates were pre-fired on a hot plate at 350°C for 30 min before additional coating sequences were performed. Final firing was conducted in two steps: 15 min at 500°C followed by 40 min at 750°C under flowing oxygen. The specimens were introduced into the furnaces preheated to the required temperatures.

The thin films were characterized by means of X-ray diffraction (XRD) using Cu Kα radiation and analytical scanning electron microscopy (SEM). In order to show the effects of the LNO buffer layer on the surface and on the PLZT/substrate interface morphology, atomic force microscopy (AFM) investigations were conducted on the 111-Pt film heat treated at 700°C for 40 min and on (111)-Pt coated with two LNO layers and fired at 500 and 750°C under the same conditions as for PLZT film processing. The polarization hysteresis curves were determined on capacitors obtained by sputtering Au top electrodes of $600 \times 600 \, \mu\text{m}^2$ area using a shadow mask. For electrical contact a corner of the Pt bottom electrode was left uncoated. The measurements were made on a commercial ferroelectric testing system (RT6000S, Radiant) at a frequency of 500 Hz and variable voltage amplitudes. The dielectric fatigue tests were performed at 5 V and a frequency of 500 Hz.

3. Experimental results

3.1. X-Ray diffraction

Fig. 1 shows XRD patterns of sol–gel PLZT with different La$_3$+ contents deposited on textured (111)-Pt and annealed in O$_2$ atmosphere for 40 min at 750°C. For comparison, the XRD diagram of the substrate heat treated at 750°C at ambient atmosphere is also shown. It can be seen that in all cases the 100 peak has the largest intensity among the perovskite PLZT peaks. However, with increasing the lanthanum content, the ratio of the intensity of the 100 to the 111 peaks also increases and the 110 peak gains in intensity. Using the same substrate type and similar firing conditions, it has been shown [13] that PZT (0 mol La$_3$+) develops a 100 preferred texture and evidence of the 111 peak could not be found. Increasing the La$_3$+ is therefore responsible for the increase in the 111 peak intensity. The addition of lanthanum appears, therefore, to promote a polycrystalline structure with the predominance of 100 and 111 textures. These observations agree to some extent with previous work where a 111 preferential texture of PLZT films with similar compositions deposited on (111)-Pt was reported [15,16].

The presence of the LNO buffer layer on the (111)-Pt electrode changes the PLZT crystallographic orientation to more random ones. The ratio of the intensity of the 100 to the 110 decreases with increasing lanthanum content and is minimum for 0.1 mol. The absence of the 111 line should also be noticed, Fig. 2. Similar results were also obtained on PZT deposited on LNO [13].
Fig. 1. XRD diagrams of the substrate (a), the PLZT with 0.05 mol La\(^{3+}\) (b), 0.08 (c) and 0.1 (d). The peaks designated hkl are perovskite peaks.

Fig. 2. XRD diagrams of LNO on 111-Pt/TiO\(_2\)/SiO\(_2\)/Si (a) and deposited PLZT thin films with 0.05 mol La\(^{3+}\) (b), 0.08 (c) and 0.1 (d).

3.2. Microstructures

Fig. 3 shows AFM images of the substrates used. The thin film Pt electrode shows a high roughness and numerous surface discontinuities which probably result from coarse clusters. The rms values obtained vary between 21 and 76 nm. Coating with a LNO buffer layer leads to a fairly smooth surface with rms values in a narrow range from 5 to 17 nm. PLZT thin films deposited on Pt, therefore, show higher roughness than those deposited on LNO. Values of rms of approximately 59 and 5.5 nm were obtained for PLZT/Pt and PLZT/LNO/Pt, respectively.

Figs. 4–6 show the surface morphologies obtained on both substrates. It can be seen that the bottom electrode type and the lanthanum content influence the microstructure of the thin films. The PLZT thin films deposited on (111)-Pt usually show a two phase microstructure consisting of relatively coarse grains surrounded by a dark contrast second phase. In this case, increasing the lanthanum content leads to increased grain size and area fraction of the second phase (compare Fig. 4a,b,c). Both for 0.08 and 0.1 La\(^{3+}\) PLZT films deposited on Pt the grains with a rosette-like structure suggesting a radial growth from a centre ‘seed’, e.g. Fig. 4d, were observed. The morphology of these grains show many ‘arms’ on the whole periphery and suggest that growth occurs by expanding these arms in the matrix, probably pyrochlore, accompanied by the preferential partitioning of Pb in the perovskite phase. EDX mappings, Fig. 5, reveals in fact that the dark contrast areas are depleted in Pb whereas the silicon signal (from the matrix) is higher, which indicates a preferential evaporation of PbO. In contrast, PLZT deposition on LNO leads to a finer polycrystalline structure with a homogeneous composition, as exemplified in Fig. 6.

Examination of cross sections reveals compact thin films in all cases, as exemplified in Fig. 7 for 0.08 La\(^{3+}\) PLZT on 111-Pt and LNO/(111)-Pt.
3.3. Dielectric properties

All thin films show well defined and shallow ferroelectric hysteresis curves. The dielectric constants were obtained from a total of 50 capacitors at a voltage amplitude of 5 V. The thin films directly deposited on Pt have been found to have the highest number of electrical shortings (8% of the capacitors showed electrical shorting) whereas no electrical shorting occurred for thin films deposited on the LNO buffer layer. Fig. 8 illustrates the ferroelectric hysteresis curves for the different thin films investigated, and Table 1 shows the values of the dielectric constants for the indicated thin film thickness. The values compare favourably with those reported for similar compositions in the literature [15–17], where values between 700 and 1000 were obtained for 0.05 mol La$_3^+$ films on Pt. Mean values of the coercive field and remnant polarisation are also shown.

The ferroelectric and dielectric properties depend both on the lanthanum content and bottom electrode: increasing the lanthanum content leads to decreased property values; and deposition on Pt results in a relatively higher dielectric constant, coercive field and remnant polarisation. The effects of La on the dielectric properties are, however, more pronounced for direct deposition on Pt. Deposition on LNO results in higher saturation voltages and a narrow variation range of the dielectric properties (Fig. 8b and Table 1).

The effects of the applied voltage amplitude on the ferroelectric behaviour of the PLZT thin films are shown in Fig. 9a–d for two different La$_3^+$ concentrations and substrates. As can be seen, increasing the lanthanum content leads in general to a shift of the hysteresis saturation towards higher voltages. The use of the LNO buffer layer results for all compositions in shallow hysteresis curves with relatively small variations of remnant polarisation and coercive field with the applied voltage.

The fatigue properties are illustrated in Fig. 10 as normalised remnant polarisation $P_r/P_{r0}$ ($P_{r0}$ is the remnant polarisation before cycling) vs. the number of switching cycles $N$.

The results show unambiguously that both the lanthanum content and bottom electrode type affect dramatically the polarisation fatigue behaviour of the PLZT thin films. All PLZT thin films directly deposited on Pt show a drastic decrease in the normalised remnant polarisation with increasing the number of switching cycles, whereas deposition on the LNO buffer layer results in improved fatigue resistance. In this respect, a lanthanum content above 0.05 mol seems to be necessary in order to achieve dielectric integrity over a large number of cycles ($>10^3$). Considering the capacitors Au/0.08La$_3^+$/LNO/Pt and Au/0.1La$_3^+$/LNO/Pt an increase in the remnant polarisation with $N$ of approximately 10 and 5%, respectively, is observed with increasing $N$. This small increase is usually attributed to poling processes of the ferroelectric thin films which

![Fig. 4. Back-scattered electron (BSE) micrographs of the PLZT thin films deposited on (111)-Pt: (a) 0.05 mol La$^{3+}$; (b) 0.08 La$^{3+}$; (c) 0.1 La$^{3+}$; (d) details of Fig. 3c showing a rosette like grains with a centre seed. The micrographs show the perovskite phase grains surrounded by dark contrast second phase areas. Notice the finer grain size of the 0.05 La$^{3+}$ PLZT thin film.](image-url)
lead to the unpinning of ferroelectric domains and increase the remnant polarisation [18].

4. Discussion

4.1. Microstructure development

The results of the X-ray diffraction presented above shows that both the lanthanum content and the bottom electrode type influence dramatically the microstructure development of the PLZT thin films. Deposition on (111)-Pt leads to a (100)/(111) texture of the thin films (with respect to the normally major 110 peak in the perovskite structure). However, with increasing lan-

Table 1
The dielectric properties of PLZT of different La\(^{3+}\) contents deposited on the substrate type indicated*  

<table>
<thead>
<tr>
<th>Capacitor type</th>
<th>d (nm)</th>
<th>(k \pm \sigma)</th>
<th>(E_c) (kV/cm)</th>
<th>(P_r) ((\mu)C/cm(^2))</th>
<th>(R_s) ((\Omega\cdot\text{cm})) \times 10^{10}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/0.05La(^{3+})/Pt</td>
<td>300</td>
<td>1630 ± 50</td>
<td>46</td>
<td>6</td>
<td>8.6</td>
</tr>
<tr>
<td>Au/0.05La(^{3+})/LNO/Pt</td>
<td>300</td>
<td>1090 ± 30</td>
<td>32.7</td>
<td>3.2</td>
<td>18</td>
</tr>
<tr>
<td>Au/0.08La(^{3+})/Pt</td>
<td>310</td>
<td>1119 ± 15</td>
<td>20</td>
<td>3.8</td>
<td>n.d</td>
</tr>
<tr>
<td>Au/0.08La(^{3+})/LNO/Pt</td>
<td>300</td>
<td>909 ± 40</td>
<td>20.2</td>
<td>2.5</td>
<td>8.4</td>
</tr>
<tr>
<td>Au/0.1La(^{3+})/Pt</td>
<td>300</td>
<td>865 ± 45</td>
<td>20</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Au/0.1La(^{3+})/LNO/Pt</td>
<td>320</td>
<td>808 ± 25</td>
<td>12.5</td>
<td>2.5</td>
<td>11.4</td>
</tr>
</tbody>
</table>

*Where \(d\) is the film thickness, \(k\) the dielectric constant, \(E_c\) the coercive field, \(P_r\) the remnant polarization and \(R_s\) the specific resistance. All values were measured at a voltage amplitude of 5 V and a frequency of 500 Hz. The \(\sigma\) is the statistical distribution from 50 measurements.
thanum content, the ratio of the intensity of the 100 to that of the 111 peak decreases and the 110 peak gains in intensity denoting that more randomly oriented films are obtained. It should be pointed out that the microstructure evolution is not due to the thermal treatment conditions since for all thin films the same conditions were applied. The formation of texture in ferroelectric thin films based on PZT is known to be strongly influenced by the bottom electrode and annealing conditions [7,15,16]. A reaction between the Pt electrode and the thin film resulting in a buffer layer of a Pb–Pt intermetallic phase has also been reported to influence film texture [19,20]. Heterogeneous nucleation on highly oriented (111)-Pt electrodes has been reported to favour (111) texture at high annealing rates and temperatures due to lattice matching [7,15,16,19]. At intermediate annealing rates a (100) texture is preferred and arises as a result of the lower nucleation barrier associated with the (100) orientation of PZT [7,8]. The results obtained in the present work suggest that both crystallisation processes are occurring. Until detailed microscopic investigations of the early crystallisation processes have been made we can only speculate in advancing the following crystallisation sequences: First heterogeneous nucleation is expected to occur at the interface with (111)-Pt giving rise to preferential (111) orientation. As crystallisation proceeds, the amorphous/pyrochlore phase is expected to become progressively enriched with excess Pb which may lead to its destabilisation and spontaneous crystallisa-

![Fig. 8. The polarisation hysteresis curves for the PLZT thin films deposited (a) on 111-Pt and (b) on LNO/(111)-Pt. The capacitor configuration is Au/PLZT/Pt or Au/PLZT/LNO/Pt.](image)

![Fig. 9. The polarisation hysteresis curves at different applied voltages: (a) 0.05 La3+ PLZT on (111)-Pt; (b) on LNO/(111)-Pt; (c) 0.1 La3+ PLZT on (111)-Pt, (b) on LNO/(111)-Pt.](image)
tion of the perovskite with an orientation corresponding to the lowest nucleation barrier, i.e. (100). Perovskite nuclei may form on discrete preferential sites, e.g. inclusions, sites of compositional fluctuations, and grow consuming the amorphous phase, giving rise to the rosette-like morphology with a centre seed, e.g. Fig. 4d. Growth will stop when the second phase is stabilised due to the loss of PbO through evaporation. The resulting microstructure consists then of perovskite grains separated by Pb depleted areas which constitute depressions in the microstructure, e.g. Fig. 5. This crystallisation scheme is similar to that proposed by Cross et al. [16]. However, they omitted in their discussion the (100) preferred orientation which is well visible in their XRD diagrams. The increase of the (111) peak intensity with increasing the lanthanum content may be interpreted in terms of the effects of this element in reducing the tetragonality of the perovskite phase thus increasing the lattice matching with 111-Pt [15].

The microstructures obtained with PLZT deposited on LNO/(111)-Pt present a quite different picture. Although at small La$^{3+}$ concentration we may recognise some tendency for (100) preferred orientation (the 100 peak intensity is somewhat higher than that of 110), a general tendency to form a randomly oriented polycrystalline microstructure is well documented. The resulting microstructure is fine grained and is thought to arise from crystallisation of the perovskite grains from the nano-crystalline pyrochlore phase. This is thought to be favoured by the randomly oriented LNO phase. In all cases the existence of the paraelectric pyrochlore phase in the final microstructures could not be detected via XRD probably because of the low volume fractions involved.

4.2. Dielectric properties

The dielectric properties are also affected by the lanthanum content and substrate type, i.e. microstructure. Increasing the La$^{3+}$ content is expected to lead to excess positive charges which are compensated by $V_{p}^{-}$ vacancies. As a consequence domain mobility is greatly enhanced and lower coercive fields as well as a higher squareness of the hysteresis loops are expected [14]. The present results show, however, that increasing the La$^{3+}$ content leads to lower maximum and remnant polarisation as well as coercive field. Polarisation saturation is also shifted towards higher applied fields. It appears that the positive effects of lanthanum found in bulk ceramics do not fully apply to thin films probably due to residual stresses associated with the mismatch of thermal expansion coefficients between the substrate and the deposited thin film. La is also known to decrease the curie transition temperature thus leading to higher residual stresses (the difference between the annealing temperature and the transition temperature determines the level of residual stresses) which affect the dielectric properties [21]. In the case of deposition on Pt the increase in the volume fraction of the lead-depleted second phase with increasing lanthanum content may also account for the decrease in polarisation properties. Furthermore, it has been shown [13,21] that interfacial reactions between the thin film and the Pt electrode lead to an interfacial, low permittivity layer of approximately 80 nm [13] which is expected to be detrimental to the dielectric properties.

The PLZT deposition on LNO/Pt leads to lower permittivity values, which can be explained by the random orientation and the finer grain size of the thin films; both have been reported to be responsible for higher residual stresses due to the reduction of the density of 90° domains which may lead to a substantial reduction, if not suppression, of the tetragonality of the thin films [14,21]. Furthermore, the effect of lanthanum content on the polarisation properties is much less pronounced than in the preceding case which is an indication that residual stresses due to the fine grain size predominantly affect these properties.

Another effect of lanthanum addition observed in the present work is the overall increase in resistivity in comparison to the values reported for PZT [13]. This is expected to lead to lower leakage currents and has been explained in terms of La$^{3+}$ doping being vacancy compensated with no electronic charge carriers being generated [14,17]. The fact that PLZT deposited on Pt generally shows lower resistivity can be explained by the heterogeneous microstructure obtained and effects of interfacial phases, as discussed above.

Finally dielectric fatigue appears to be influenced by the substrate type, microstructure and lanthanum content.

The thin films deposited on Pt all show an abrupt decrease in the remnant polarisation after approximately $5 \times 10^5$ cycles. Due its relatively homogeneous
microstructure, the 0.05 \(\text{La}^{3+}\) thin film is characterised by a higher fatigue resistance than the thin films of higher \(\text{La}^{3+}\) contents. However, the fatigue properties are still poor using the Pt bottom electrode, although a substantial improvement of the fatigue properties of lanthanum doped PZT over those of undoped PZT [13] cannot be ignored. These results agree well with those reported in previous work, though on other compositions [22]. The degradation mechanisms are usually attributed to domain pinning by space charge due to the accumulation of oxygen vacancies at the ferroelectric/Pt electrode interface. The desirable effect of La as donor dopant leading to a better resistance of PZT against degradation [14] is, therefore, thought to be outweighed by the interactions at the electrode interface. However, microstructure effects, particularly the presence of second phases, seem also to play a substantial role as suggested by the higher degradation of the films containing 0.08 and 0.1 \(\text{La}^{3+}\).

Deposition on the LNO buffer layer results in a pronounced improvement of the resistance to fatigue degradation. As the lanthanum content increases the ratio of remnant polarisation after \(10^9\) fatigue cycles to the initial value increases from 0.8 to 1.1, with the highest value being that of 0.08 \(\text{La}^{3+}\) film. As mentioned above, the increase in remnant polarisation is attributed to poling effects due to the unpinning of domains during fatigue. The improvement of fatigue resistance can be discussed in terms of microstructural homogeneity, suitable interactions at the electrode/thin film interface, where the LNO buffer layer is thought to act as a sink for oxygen vacancies, and the absence of undesirable interfacial interactions. With respect to the latter point, the LNO buffer layer is expected to constitute a barrier layer between PLZT and Pt. It also leads to a substantial smoothing of the interface, e.g. Fig. 3, and thus contributes to a better stability against degradation.

5. Conclusions

The microstructure and dielectric properties of sol–gel processed PLZT (lanthanum doped PZT \([\text{Pb(Zr}_{0.52}, \text{Ti}_{0.48}]{\text{O}}_3]\) thin films have been investigated depending on lanthanum content and substrate heterolayer structure. The following conclusions may be inferred:

- The PLZT thin films deposited on (111)-Pt/\(\text{TiO}_2/\text{SiO}_2/\text{Si}\) show a (100)/(111) texture. This is interpreted in terms crystallisation processes involving heterogeneous nucleation on (111)-Pt due to increased lattice matching and spontaneous crystallisation of the remaining Pb rich phase in the energetically favoured (100) orientation. The microstructure obtained is characterised by coarse grains and the presence of Pb depleted areas.

- The PLZT thin films deposited on \(\text{LaNO}_3(\text{LNO})/(111)-\text{Pt/}(\text{TiO}_2/\text{SiO}_2/\text{Si})\) show randomly oriented, homogeneously distributed fine grains. It is thought these grains crystallise from the nanocrystalline pyrochlore phase.

- The remnant polarisation and coercive field decrease with increasing the lanthanum content. Deposition on LNO generally lead to lower ferroelectric/dielectric properties.

- The fatigue properties depend strongly on the substrate type and lanthanum content. The fatigue resistance is considerably improved by using a LNO buffer layer at lanthanum concentrations higher than 0.05 mol. This is thought to arise from suitable interfacial interactions and homogenous microstructures.

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References


