

Crystallization Process of Perovskite Type Oxide Thin Films Deposited by PLD without Substrate Heating: Influence of Sputtering Rate and Densification-Driven High Tensile Strain

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Abstract

Crystallization process in non-heating pulsed laser deposition (PLD) and the following post-annealing route for Perovskite oxide thin film fabrication has been studied. Remarkable influence of sputtering rate on crystallization temperatures is demonstrated for BaZrO₃ and SrZrO₃ thin films in this process. Crystalline nuclei formation occurs randomly in the thin films deposited at a high sputtering rate which leads to the faster crystallization at lower temperature, while it occurs predominantly at the substrate or interlayer interface at higher temperature when the sputtering rate is very low, which is also reinforced by the atomic oxygen irradiation upon deposition. It should be noted that crystalline thin film synthesis of BaZrO₃ is possible at a post-annealing temperature below 200°C when the sputtering rate is relatively high. On the other hand, obtained thin films show high tensile strain which is not related to the difference in thermal expansion coefficient between substrate and thin film, but is found to be due to the densification upon crystallization. The tensile strain is relaxed when the thin films are annealed at 750°C or above, while the strain is very stable at a temperature as low as 600°C for 1 week.

Key words: perovskite; PLD; post-annealing; crystallization; proton conducting oxides; tensile strain;

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1. Introduction

Perovskite oxide based proton conducting ceramics show promising properties as electrolytes for intermediate-temperature fuel cells, steam electrolyzers, membrane reactors, hydrogen sensors, and hydrogen pumps [1]. In such electrochemical devices, dense thin film coating is a key process in order to minimize ohmic loss of the electrolytes. For perovskite oxides of high melting points, physical vapor deposition (PVD) is usually applied. Among PVD, pulsed laser deposition (PLD) is acknowledged as an ideal method to synthesize thin films of complex oxides. PLD process is, therefore, very suitable for proton conducting oxides that are composed of several elements and usually high level of dopants, compared to other tools such as sputtering [2,3]. PLD technique has been utilized to fabricate dense and thin electrolyte layers in electrochemical device applications [4] as well as to synthesize epitaxial thin films and artificially modulated multilayers [5-7].

Although the setup of PLD system is simple in principle, one needs to optimize many controlling parameters of the process. Therefore, obtained perovskite-type thin films are not unique with respect to structure and stoichiometry due to difference in PLD parameters. The deviation in electrical conductivities is possibly originated from the difference in structural parameters, in A-site cation nonstoichiometry [8-11] and/or in the texture of the thin films which may correspond to the grain boundary density [12, 13].

The authors have studied the PLD process for perovskite oxide based proton conductors by the conventional high temperature process [5,6] as well as a non-heating process followed by post-annealing, and their influence on the structural and electrical properties [14-16]. In general, the crystalline thin films are deposited on substrates heated at high temperatures, where they are grown in the crystalline phase. The optimal substrate temperature is usually in the range of 600-900°C for crystalline oxides. It is found that when these oxides are deposited by PLD at room temperature, i.e. without substrate heating, one may obtain amorphous phase and they can crystallize of similar or even higher crystallinity at a lower temperature than the high temperature process [14]. When the substrate is single crystal, a highly epitaxial thin film may be obtained at moderate temperatures. These thin films show, however, significantly lower proton conductivity and even lower than those grown by the conventional high temperature PLD, of which the thin films usually show lower proton conductivity than the bulk crystals [15].

The as-deposited amorphous phase shows little difference in local structural analyses [15], while the

post-annealed crystalline phase differs remarkably in structure and electrical conductivity by PLD parameters. Although the amorphous phase does not show an apparent difference, such differences should be originated in the deposition process. In this paper, therefore, influence of PLD condition, especially of sputtering rate has been investigated and the crystallization mechanism is discussed. In addition, x-ray reflection analysis has been performed and the origin of high tensile strain in the thin films is discussed.

2. Experimental

PLD targets of SrZrO₃ (SZO), SrZr_{0.95}Y_{0.05}O₃ (SZY), BaZrO₃ (BZO) and BaZr_{0.95}Y_{0.05}O₃ (BZY) have been prepared by a solid-state reaction in the form of ceramic pellets. SrCO₃, BaCO₃ (99.99 %, Rare Metallic Co. Ltd., Japan), ZrO₂ (TZ-0, Tosoh, Japan), and Y₂O₃ (99.99 %, Nippon Yttrium, Japan) are mixed in stoichiometric proportions and the mixture is calcined at 1200 °C for 10 h in ambient air. The calcined powder is pressed isostatically into pellets to be sintered at 1600 °C for 10 h in ambient air.

An ArF excimer laser (COMPex 205, Coherent Inc.), wavelength=193 nm, is used for PLD process. The base pressure of the PLD chamber is maintained below 10⁻⁶ Pa. Deposition has been made at a sputtering rate ranges between 1 and 30 nm/ 1000 shots which is tuned by the laser power, substrate–target distance = 30 mm, laser repetition rate of 4 Hz and the oxygen partial pressure=0.3 Pa.

Fused silica glass is used as a substrate (15×15 mm², 0.5 mm thick). Pre-treatment of the substrate is carried out by acetone supersonic cleaning. Prior to the non-heating PLD process, an SrTiO₃ (STO) interlayer of about 50 nm thick is deposited on the substrate (substrate temperature= 800°C, oxygen partial pressure= 0.3 Pa, 1 h post-annealing under the same condition as deposition). The role of this interlayer is to avoid any change of the interface composition between substrate and thin film during annealing. It has been assured that the interlayer does not react with the fused silica substrate at the annealing temperatures. A single crystal of STO (Furuuchi chemical corp., Japan) is used as a target for interlayer deposition. Perovskite oxide layers are then deposited on the STO interlayer or directly on fused silica substrate at room temperature. Atomic oxygen irradiation is made near the substrate interface, i.e. at the beginning of deposition. The density of atomic oxygen is approximately 10¹⁵ atoms/(cm² s) which are generated by a small helicon plasma source (ULVAC Inc.). If deposition atmosphere is not indicated, whole deposition process is under the normal molecular oxygen flow. Crystallographic parameters of the deposited materials are given in table 1.

The crystal structure of thin film is investigated by X-ray diffractometer (PANalytical X'Pert PRO MPD) perpendicular to the substrate surface (out-of-plane). The CuK α line is used for the XRD. Parallel beam geometry by an X-ray mirror is used for high temperature *in-situ* measurements, otherwise conventional Bragg-Brentano geometry is used to obtain XRD patterns. High temperature *in-situ* XRD has been performed using a home-made small heater in ambient air. Microstructures of thin films are observed in cross sections of the thin films by TEM (HF-2000, Hitachi Ltd.).

The X-ray reflectivity measurement was carried out by a high-resolution X-ray diffractometer ATX-G (Rigaku) with X-ray wavelength $\lambda= 0.154$ nm (Cu K α 1) generated from a Cu rotating anode (50 kV, 300 mA). X-rays were collimated by a parabolic multilayer mirror and monochromatized by a Ge (220) monochromator.

Table 1: Structural properties of SrTiO₃, SrZrO₃, and BaZrO₃

Material	Crystal system	Lattice constant (Å)	Density	TEC ($\times 10^{-6}$ K ⁻¹)
fused silica	(amorphous)			0.5
SrTiO ₃	cubic	a=3.905	5.12	9.4
SrZrO ₃	orthorhombic	a=8.196, b=5.792, c=5.814	5.46	9.8
BaZrO ₃	cubic	a=4.193	6.23	7.1

3. Results and discussions

In-situ XRD pattern is recorded at each temperature and then the temperature is increased by a heating rate of 6°C/min. Figure 1 shows examples of high temperature *in-situ* XRD results for BZO and BZY thin films. The time shown in figure 1 includes both heating and recording time. The deposition rate of these thin films is 1 nm /1000 pulse. Obvious difference is noted in the temperature at which diffraction peaks appeared between BZO and BZY. The diffraction peaks appeared at 500°C for BZO, while the temperature is 70°C lower for BZY. Similar reduction of the crystallization temperature has also been found in the case of SZO and SZY on MgO single crystalline substrate [14]. This phenomenon is well explained by crystal nuclei formation that may have occurred at lower temperature with yttrium dopant. The diffraction intensity increases with annealing time, which is corresponding to the crystalline phase growth, at higher increasing rate at a higher temperature. There seems no clear difference of the increasing rate between BZO and BZY at the same

temperature. This fact indicates that the crystallization process in these thin films is dominated by the crystal nuclei formation.

On the other hand, it is notable that out-of-plane lattice spacing is close to that of the bulk crystal at the beginning of crystallization, while it decreases monotonically as the crystalline phase grows. Such a short out-of-plane lattice constant is commonly observed in *ex-situ* XRD measurements of these thin films. This demonstrates that the thin film has a significant tensile stress. The difference in thermal expansion coefficients (TEC) between substrate and the thin film may explain such a tensile strain, since TEC of fused silica is significantly smaller than the perovskites (table 1). However, this may not be the case for these thin films. If the difference in TEC accounts for the strain, it is induced when the thin film is cooled from a high temperature where it is crystallized. The fact that the lattice spacing decreases monotonically at a constant temperature suggests a different origin of the strain. The origin of the strain is discussed later.

The as-deposited thin films have been post-annealed at several temperatures for 10 h to find a temperature at which the thin film begins to crystallize (T_{cryst}). Note here that T_{cryst} is not necessarily a critical temperature of crystallization, but is defined for comparison in a limited annealing time. T_{cryst} of SZY and BZY is summarized in Fig. 2. Annealing time is 10 h except for BZY at the highest sputtering rate (~30 nm/ 1000 shot) which has been annealed for 210 h. It is obvious that T_{cryst} decreases with increasing sputtering rate both for SZY and BZY thin films. It is clear that T_{cryst} of SZY is higher than that of BZY. This might be explained by the difference in the crystallographic symmetry; i.e. the cubic structure of BZY is easier to align periodically than the orthorhombic structure of SZY. T_{cryst} seems slightly higher when atomic oxygen is irradiated upon deposition than deposited in molecular O₂, but the trend is not very clear. Our recent study has demonstrated that the crystallization occurs randomly in thin films when the sputtering rate is high, while nucleation at the substrate or interlayer interface is predominant when the atomic oxygen is irradiated upon deposition [16]. This is consistent with the case of MgO single crystal substrate, on which epitaxial crystallization is predominant when the sputtering rate is low and atomic oxygen is irradiated. Another factor for the crystal nuclei formation is sputtering rate. Apart from the influence of the dopant, the sputtering rate may predominantly influence on the crystal nuclei formation at post-annealing. Though there seems no difference in the amorphous phases, the clear trend of T_{cryst} suggests that the amorphous phase should differ with different PLD conditions. A possible explanation is cluster formation at the deposition. The difference of

sputtering rate is equivalent to the difference in density of a laser plume if the laser repetition rate is constant. Deposition from a plume of different density may induce some difference in amorphous phase. Such a difference in amorphous phase may not be in the short range order, as no difference is found in XANES spectra [15], but probably in the medium range order to form a cluster like region. If the crystal nuclei formation is related to the size or the character of the cluster, cluster like structure in the amorphous phase may account for the difference in crystallization process. The proposed crystallization process of the different PLD condition, i.e. sputtering rate and atmospheric condition at deposition, is summarized.

At a high sputtering rate, in O₂ atmosphere;

- (1) Relatively large clusters are formed in the amorphous phase.
- (2) In the post-annealing process at a high temperature, crystal nuclei are formed randomly in the thin film and the thin film crystallizes at a relatively low temperature. Since the crystal nuclei are oriented randomly, polycrystalline phase is dominated even on the single crystal substrate.

At a low sputtering rate, in O₂ atmosphere or with atomic oxygen irradiation;

- (1) Clusters may be formed in the amorphous phase but they may be too small and it is more homogeneous.
- (2) Crystallization occurs at a higher temperature as the crystal nuclei are not easily formed in the thin film. Crystal growth starts predominantly at the interface, therefore, they may grow epitaxially on a single crystal substrate or locally on a crystalline phase.

The BZY thin film thicknesses of as-deposited and post-annealed thin films of the same batch are determined to be 53 and 43 nm, respectively, by TEM observation (Fig. 3). Note that there may be thickness distribution of the thin films, therefore, TEM observation has been made at the corresponding part of as-deposited and post annealed specimens. The post-annealing has been made at 550°C in ambient air for 48 h, to assure full crystallization of the thin films. Such a thickness change by post-annealing has been commonly observed in the non-heating PLD process, which may possibly be due to change in density from the amorphous to the crystalline phase. In order to determine the densities of thin films, x-ray reflection measurements have been performed on the same specimens and the reflection profiles have been analyzed as-deposited and post-annealed BZY thin films on fused silica substrates. The obtained profiles show obviously that there are

several layers in both thin films, from which the absolute density of each layer is difficult to be analytically determined. We have made, therefore, more qualitative analyses to confirm whether the change in film thickness is due to change in density. The Fourier transforms of the reflection profiles give the total thicknesses of as-deposited and post-annealed thin films to be in the range of 63–64 nm and 51–52 nm, respectively, when the density value is in between $6\text{--}5\text{ g cm}^{-3}$. The thickness values are different from TEM observation. The disparity may come from the difference in observation due to thickness distribution of the specimens. The thickness ratios of as-deposited and post-annealed thin films are 1.23 in both TEM and x-ray reflection analyses. On the other hand, the simulation of the density values using the critical angles of reflection demonstrated that the density ratio between these thin films are about 1.26, which is very close to the thickness ratio. This fact ensures the change in the density by crystallization on the premise that the weight of the thin film is constant. Such a densification on a substrate should cause the significant tensile strain that leads to the remarkable decrease of out-of-plane lattice parameter, as observed also in *in-situ* XRD measurements at a constant temperature (Fig.1). Such an influence of densification on strain is also reported for YSZ thin films [17].

Kushima and co-workers have demonstrated by first-principle calculations that tensile strain affects the defect chemistry such as the active formation of oxygen vacancies in these perovskite-systems [18]. Except for few cases, the thin film proton conductivity of these perovskite oxides is remarkably lower than the bulk ceramics. The columnar structure of typically less than 100 nm results in high grain boundary density in a conventional physical vapor deposition process, such a low proton conductivity is mostly explained by the grain boundary contribution. The fact of even lower proton conductivity in the case of epitaxial SZY thin films in non-heated PLD and post-annealing process suggests the importance of strain effect since it has less grain boundary density but remarkable tensile strain.

In addition to the densification, the X-ray reflection analyses revealed that several layers of different densities are formed upon deposition at room temperature with the same PLD condition, some of which may be split into more layers of different densities when crystallized at a high temperature, though the difference in density values may not be large. Although the as-deposited thin film seems homogeneous, contrast difference of the layers is clearly noted in the post-annealed thin film, among which the first 10 nm is the most significant (Fig. 3). Such a phenomenon has not been observed when the thin films are deposited and

crystallized upon deposition at a high temperature. This fact suggests the PLD plume may be changed during deposition either due to change of laser beam pattern or due to change in the target surface condition since the nominal laser power is kept constant.

Figure 4 demonstrates the annealing effect on the tensile strain after the post-annealing (=crystallization process). As we have described above, the tensile strain is caused by the densification of the thin film. Therefore, the strain depends on the degree of crystallization, as observed in figure 1. In order to assure that the thin films are fully crystallized, the first post-annealing is made at 750°C for 10 h both for (a) and (d). Remarkable shift of the diffraction peak positions of BZY thin film is observed from (a) through (c). It demonstrates a decrease in out-of-plane lattice parameter due to tensile strain caused by densification in crystallization process. Note that the STO interlayer shows also a slight shift upon annealing at 750°C or above. This is because small tensile strain caused by the difference in thermal expansion coefficient between substrate and STO interlayer since the STO layer is crystallized upon deposition. Side inclination XRD stress analyses confirmed the high tensile strain of the BZY thin film after the crystallization and its relaxation after the annealing at 750°C or above.

On the other hand, when the annealing temperature is as low as 600°C, the tensile strain would not be relaxed at this temperature even after 1 week. It should be noted that the lattice parameter of (d) is larger than that of (a). The difference in the lattice parameter is possibly due to partial relaxation of the thin film (d) which occurs during the post-annealing for crystallization. Since thin films (a) and (d) are deposited at low and medium sputtering rate, respectively, the crystallization temperature of the thin film (d) is much lower than that of (a), which is demonstrated in figure 2. The thin film (d) is, therefore, fully crystallized much earlier than (a) during 10-hour post-annealing, and it is already partially relaxed in the post-annealing process. However, the lattice parameter does not change when it is annealed at 600°C for 1 week and is still smaller than that of (c). This fact assures that the lattice relaxation of these thin films may not occur at 600°C.

Though the influence of the sputtering rate on crystallization is clearly observed and the origin of the strain can be explained well, PLD is still a complicated process with a lot of parameters. There are still many uncertain phenomena to be clarified for better synthesis of perovskite oxide proton conducting thin films. The densification of the thin film may not be avoidable in this route, but the advantage for highly epitaxial thin film synthesis on a single crystal substrate could be profitable; for example, when the process is used to form

thin epitaxial buffer layers or to deposit thin films on a substrate which shrinks in the similar rate as the thin film by post-annealing.

4. Conclusions

BZO, BZY and SZY thin films have been synthesized in non-heating PLD and post-annealing process and their crystallization behavior is studied. The crystallization process may possibly be explained by the cluster formation at deposition, which controls crystal nuclei formation for long range ordering at a high temperature. At a high sputtering rate, polycrystalline thin films are easily obtained at remarkably low temperatures, especially when the material has high crystal symmetry, while epitaxial crystallization is possible at a low sputtering rate and/or with atomic oxygen irradiation on a single crystal substrate. Densification from amorphous to crystalline phase induces high tensile strain in this process, which will be relaxed by annealing at 750°C or above.

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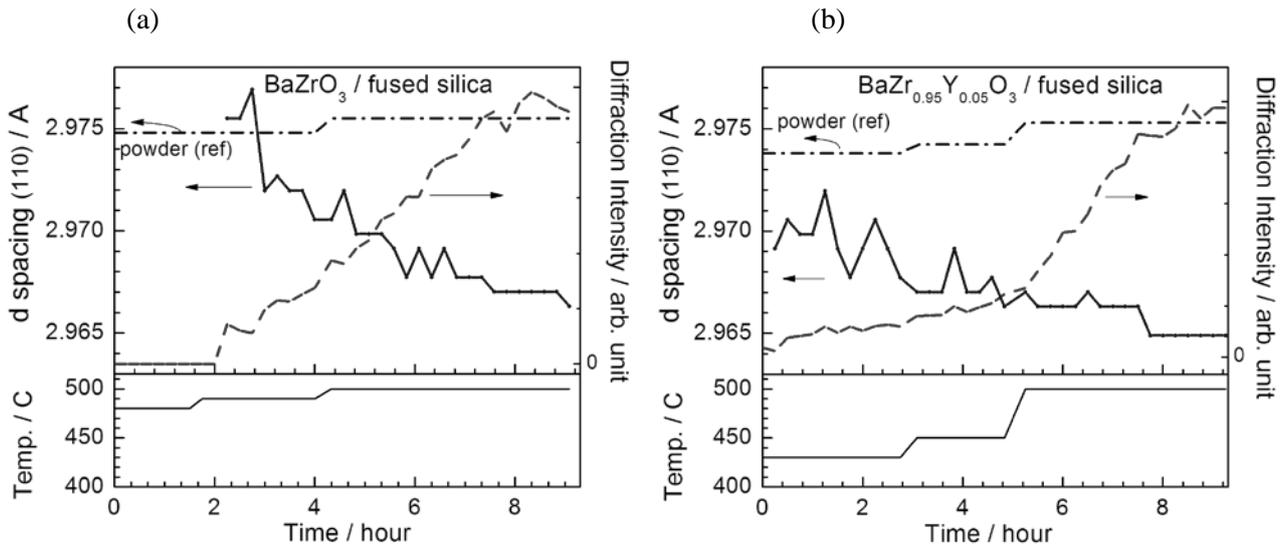


Fig. 1: In-situ high temperature XRD results of BaZrO₃ thin films deposited on fused silica substrates at a low sputtering rate (1 nm/ 1000 pulse) by PLD without substrate heating; (a) non-doped BaZrO₃ and (b) 5mol% Y doped BaZrO₃.

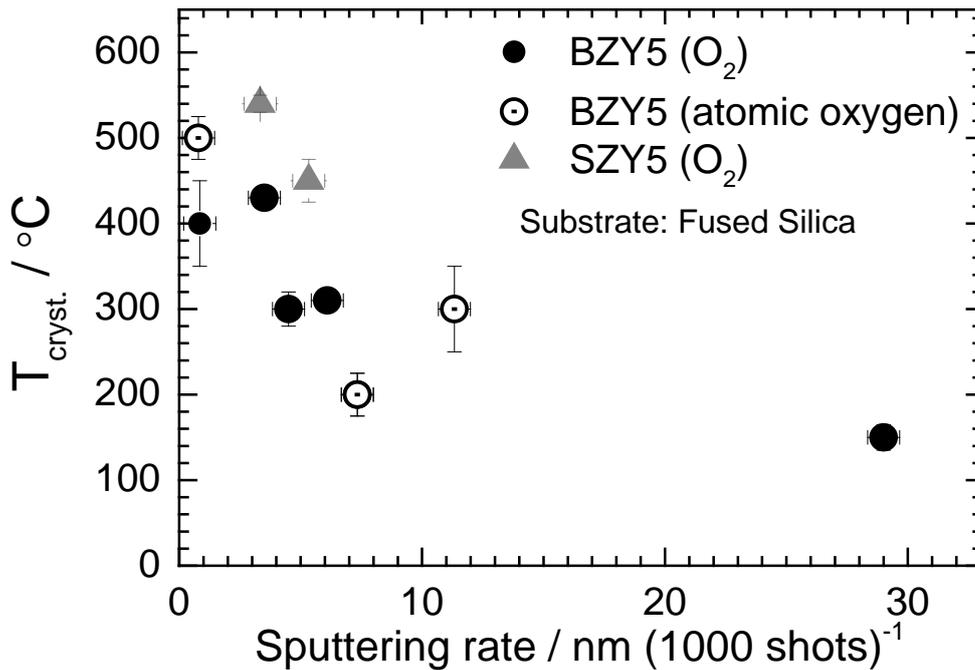


Fig. 2: Crystallization temperature as a function of sputtering rate. Here the temperature is defined as the lowest temperature at which diffraction lines appear in the XRD pattern.

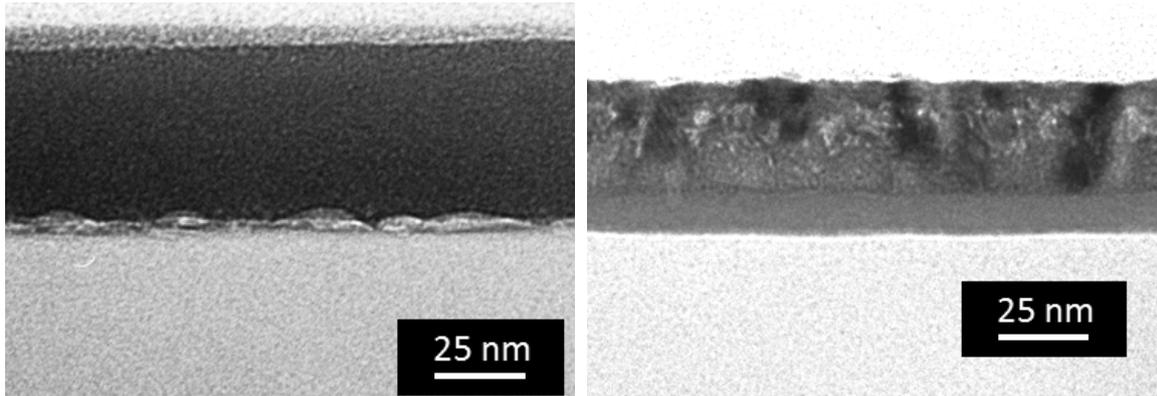


Fig. 3: TEM micrograph of the cross sections of as-deposited (left) and post-annealed (right) BZY thin films of the same batch deposited on a fused silica substrate.

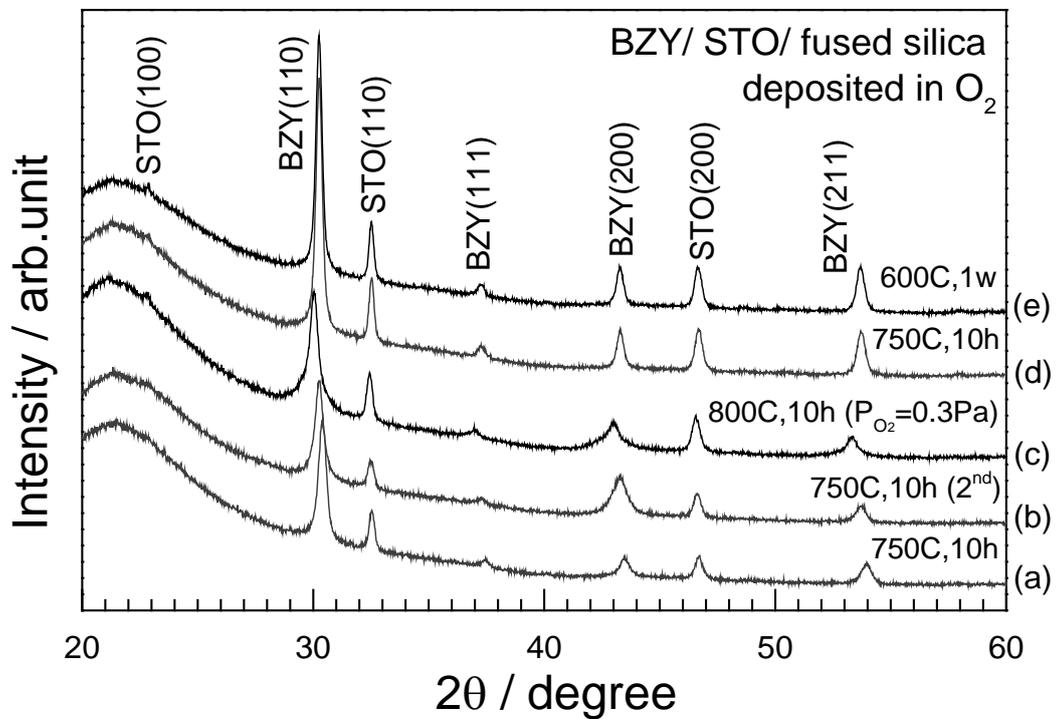


Fig. 4: XRD patterns of post-annealed BZY thin films deposited at low (a)-(c) and medium (d) and (e) sputtering rate on fused silica substrate with STO inter layer. The thin films have been first crystallized at 750°C ((a) and (d)) and there after they are annealed again at the condition for each specimen ((b), (c) and (e)) as indicated in the figure.