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Rutherford backscattering/channelling, XRD, XRD pole figure and AES characterization of $FeTiO_3$ thin films prepared in different ambients by laser ablation

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Abstract. In this work, the stoichiometry, epitaxial relationship, crystalline quality and surface of $FeTiO_3$ thin films prepared in oxygen, argon, vacuum and oxygen–argon mixture as ambients by pulsed laser deposition (PLD) have been characterized by Rutherford backscattering (RBS)/ion channelling, x-ray diffraction (XRD), XRD pole figures and Auger electron spectrometry (AES). We have found the films prepared in pure O_2 are oxygen rich even when the gas pressure is down to 0.001 mbar. Although nearly stoichiometric and crystalline $FeTiO_3$ films can be prepared in vacuum or pure argon environment, RBS and AES analyses show the films prepared in pure argon are titanium deficient and the films prepared in vacuum can be easily contaminated by carbon and other impurities. XRD and XRD pole figures clearly show the films prepared in the gas mixture have a parallel relationship with the substrate at the main plane $FeTiO_3(0006)/\alpha\text{-}Al_2O_3(0006)$ and other planes. The films prepared in oxygen and argon also have epitaxial relationship to the substrate $FeTiO_3(0006)/\alpha\text{-}Al_2O_3(0006)$ at the main plane, but the films prepared in vacuum have an epitaxial relationship to the substrate $FeTiO_3(20\bar{2}2)/\alpha\text{-}Al_2O_3(0006)$. The in-plane pole figures show films prepared in argon, oxygen and vacuum have much poorer crystal quality compared to the film deposited in the gas mixture both in the orientation relationship and the ratio of background to signal. An epitaxial $FeTiO_3$ film with high quality and clean surface can easily be prepared in the mixed gases of argon with 5% oxygen, and it has almost single crystal structure with a small amount of twins (less than 10%). The results show that a gas mixture of Ar and 5% O_2 can not only keep the stoichiometry of $FeTiO_3$ and protect the film from contamination of carbon, but also enhance the crystalline quality of the film, especially developing the tendency of film growth in a parallel direction to the substrate.

1. Introduction

Pulsed laser deposition (PLD) is a comparatively new tool for thin film preparation. Conceptually and experimentally, PLD is extremely simple, probably the simplest among all thin film growth techniques. In contrast to the simplicity of hardware, the laser beam interaction is a very complex physical phenomenon. Theoretical descriptions are multidisciplinary and combine both equilibrium and nonequilibrium processes [1]. The mechanism of this process is far from understood. Even so, laser ablation has already become a widely used technique to grow high quality thin films of great variety of materials: most of them are complex oxides. As the quality of prepared films and the deposition process are very sensitive to the experimental

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conditions, good quality films can only be obtained in a limited range of laser fluency, gas pressure and substrate temperature. In the process of PLD, to keep an appropriate stoichiometry and improve film quality is obviously the key point. Ambient gas is certainly believed to play an important role in the process, so the comparison study of films deposited in different ambients is very helpful to understand the extremely complex process. Although there are already some papers concerning thin films prepared in gas mixtures [2–5], there is still no work on detailed characterization of films prepared in different ambients. Through this study we can compare the structure in detail of films prepared in different ambients and therefore understand why an appropriate gas mixture can be very helpful to prepare stoichiometric, surface clean, high quality films with good reproducibility. We believe that more detailed work is urgently needed to ensure that this is the right direction to prepare a stoichiometric thin film of high quality, especially for multi-element oxides.

The $FeTiO_3$ structure (space group $R\bar{3}$) is derived from α-Fe_2O_3 by replacing every other layer of Fe atoms in (0001) planes by a layer of Ti atoms. High-temperature electrical conductivity [6] and magnetic properties [7, 8] of ilmenite $FeTiO_3$ have been measured. Moreover, it has been also paid a lot of attention because of its potential as a chemical catalyst and photo-catalyst [9, 10]. X-ray photoelectron spectroscopy (XPS) [11], low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) [12] have also been used to characterize the ilmenite surface structure and behaviour under heat treatment in different environments. However most, if not all, of these works used natural $FeTiO_3$ bulk or synthetic bulk materials. Although Phillips *et al* [13] tried to prepare iron–titanium oxide thin film for evaluation of the photoconductive and photoelectrochemical properties, there was still no successful work to prepare stoichiometric and crystalline $FeTiO_3$ thin films until epitaxial crystalline $FeTiO_3$ thin films were prepared by our group [14].

In this paper, $FeTiO_3$ thin films prepared in different ambients including pure oxygen, pure argon, vacuum and a gas mixture of argon with 5% oxygen, are characterized by XRD, XRD pole figures, RBS/channelling and AES to study the epitaxial relationship, film structure, stoichiometry, crystalline quality and film surface.

2. Experiment: sample preparation and characterization

PLD (pulsed laser deposition) was performed by using a second harmonic of a Q-switched Nd:YAG laser of 532 nm, 145 μs in pulse width and 10 Hz in frequency. The average laser density of 2.5 J cm^{-2} was used for deposition. The laser beam was focused on a rotating disclike target within a 2–3 mm diameter. The base pressure was in the range of 10^{-7} Torr at room temperature, and the base pressure at deposition temperature (usually at around 450 °C or higher) was in the range of 10^{-6} Torr. The sapphire substrates were located at a distance of 5.0 cm from the target and they were heated during the deposition. In the deposition the $FeTiO_3$ target was rotated by a motor, and the partial gas pressure was controlled automatically using an MKS250 pressure controller by adjusting the in-flow gas flux. The temperature of the substrate was measured with a thermo-couple affixed to the substrate directly. The temperature fluctuation during deposition can be controlled with an accuracy of 2 or 3 degrees, and the pressure fluctuation during deposition is less than 1%. The general deposition rate under the above conditions is around 40 Å min^{-1}, and the general ablation time is around 30–50 minutes. As soon as deposition was completed, the temperature was reduced slowly to room temperature in several hours. During the processes of decreasing temperature, the films were kept under the same partial pressure as that under which they were deposited. The details of pulsed laser deposition can be seen in a recent paper [14]. Four kinds of thin film are prepared respectively in pure oxygen, pure argon, vacuum and a gas mixture of Ar with 5% oxygen

on *c* plane sapphire (0006) substrates. For comparison, the laser fluency for preparing all these films was same, around 2.5 J cm^{-2}. The gas pressures for different ambients, including pure argon, pure oxygen and the gas mixture are already optimized separately, and they are 0.045 mbar for pure argon, 0.001 mbar for pure oxygen and 0.01 mbar for the gas mixture. For vacuum the base pressure is higher than 10^{-7} Torr, and the pressure in the deposition is around 10^{-5} to 10^{-6} Torr. All results in this article are exclusively from these four samples prepared in pure oxygen, pure argon, vacuum and the mixture of gases. X-ray diffraction and XRD pole figures were explored for crystallographic characterization of all films, and the films were then analysed by RBS/channelling to find the hetero-epitaxy from α-Al_2O_3(0001). An x-ray diffractometer (Rigaku; Cu Kα; 40 kV; 30 mA) was used for XRD analysis, and XRD pole figure measurement was also used to characterize the structure of laser ablated FTO films. RBS/channelling analysis was carried out using 2.0 MeV $^4He^+$ ions from a 3 MV single stage accelerator at TIARA in JAERI Takasaki. RBS/channelling spectra were detected by a detector set at 165°. AES was used to characterize the stoichiometry of the films more directly and accurately, because the RBS technique is not so sensitive with light elements, such as oxygen, carbon and nitrogen. At the same time, AES is also sensitive to surface impurities, so we can find impurities on the film surfaces. A 3000 eV electron beam was used in AES measurement. The conditions for film preparation in different ambients are listed in table 1.

Table 1. The experimental conditions for $FeTiO_3$ film preparation in different ambients.

	Laser: Q-switched Nd:YAG 532 nm, 145 μs in pulse width and 10 Hz in frequency 2.5 J cm^{-2} Base pressure: 10^{-6}–10^{-7} Torr			
	O_2	Ar	Vacuum	Ar + 5%O_2
Gas pressure	0.001 mbar	0.045 mbar	10^{-5}–10^{-6} Torr	0.01 mbar
Deposition time (min)	30	30	30	30

3. Results and discussions

The x-ray diffraction intensities versus incident angle of different $FeTiO_3$ films on *c* plane α-Al_2O_3 (0001) substrates prepared in different ambients are shown in figure 1. We can see the film deposited in 5% oxygen and argon mixed ambient of 0.01 mbar at 450 °C for 30 minutes shows the highest x-ray intensity and a narrow half-width. The figure shows only (000*l*) peaks for $FeTiO_3$ and from sapphire substrate, suggesting that the film growth is epitaxial. We will show the epitaxial relationship in detail later in figure 5. The high intensity, as high as 400, and narrow half-width, 0.188, of the (0006) peak of the $FeTiO_3$ film suggest the film has high quality. The film deposited in vacuum orientates mainly on $(20\bar{2}2)$ with a small amount of (0006) direction. It should be mentioned that there is still around 1 degree difference between the standard $(20\bar{2}2)$ peak and the peak in the spectrum. At the same time, the peak is quite wide, showing the quality is not good. The film deposited in Ar gas mainly orientates in the (0006) direction too, but the intensity of x-rays is still not high. At the same time, the film prepared in oxygen environment only shows a little orientation tendency in the (0006) direction. From this figure, we can clearly see the gas mixture can greatly improve the orientation of $FeTiO_3$ in an appropriate pressure. It should be noted that the *y*-axis scale in figure 1 for the gas mixture, 500, is much higher than those prepared in other ambients, 100.

Rutherford backscattering spectrometry measurements were taken to determine the film stoichiometry and thickness. Ion channelling was used to check the crystalline quality of these

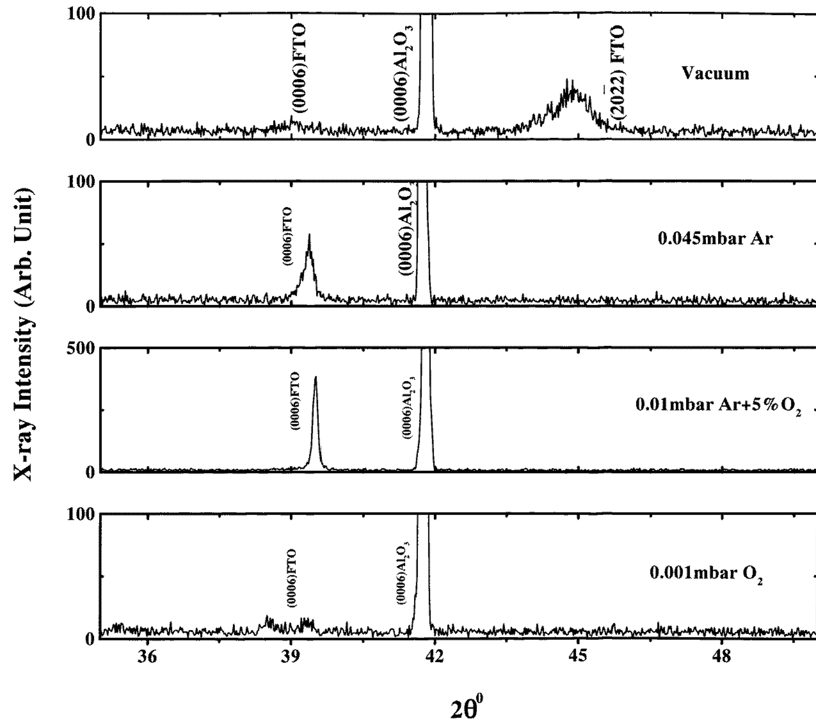


Figure 1. X-ray diffraction intensity versus incident angle plot from $FeTiO_3$ films on α-Al_2O_3 (0001) substrate prepared in pure O_2, pure Ar, vacuum and a gas mixture of Ar and 5% O_2. It should be noted that the y-axis scale is different in the case of gas mixture of Ar with 5% O_2.

films, and even to estimate the aligned level of each element roughly. RBS/channelling analyses show the films prepared in pure oxygen environment under pressure 0.001 to 0.04 mbar are oxygen rich and almost amorphous. The RBS spectrum of the film prepared in pure O_2 is not shown here to save space. The simulated result from RUMP [18] is given in table 2 with the results of other films. Figure 2 shows the aligned and random RBS spectra of $FeTiO_3$ thin film prepared in pure argon environment and the spectrum from the RUMP simulation. From RUMP simulation of the RBS spectrum, we can find the atomic ratios of Fe:Ti:O are 1.05:0.95:3.0, i.e., the film is non-stoichiometric, short of titanium. The reason is the mass difference between titanium and iron, and similar results have already been reported [19]. The minimum backscattering yield analyses show iron and titanium are better orientated than oxygen too.

The aligned and random RBS spectra of the $FeTiO_3$ film prepared in vacuum with that from RUMP simulation was shown in figure 3. We can see from RBS analysis that the film is almost stoichiometric, and the film quality indicated by the minimum backscattering yields in the aligned spectrum is also good, around 20% for iron and titanium. However the orientations of oxygen atoms are not good, and we can see that clearly from the slope of oxygen on the surface part. If we combine the RBS result with that of XRD analysis, we can conclude that the films prepared in vacuum are orientated mainly in the $(20\bar{2}2)$ direction and the oxygen atoms are not well oriented. There is a little Ar (less than 1%) in the film, which can be seen from the small peak in the RBS spectrum, and it is attributed to the Ar gas that we used before the deposition in vacuum.

Table 2. The film thickness and stoichiometry by RBS and χ_{min} analytical results for different elements by channelling.

	O_2	Ar	Vacuum	Ar + 5% O_2
Film thickness (Å)	1800	1450	820	1280
Growth time (min)	30	30	30	30
Atomic ratios of Fe:Ti:O	1.0:1.0:3.2	1.05:0.95:3	1.0:1.0:3.0	1.0:1.0:3.0
χ_{min} for Fe (%)	amorphous	37	23	14
χ_{min} for Ti (%)		50	24	19
χ_{min} for O (%)		57	38	34

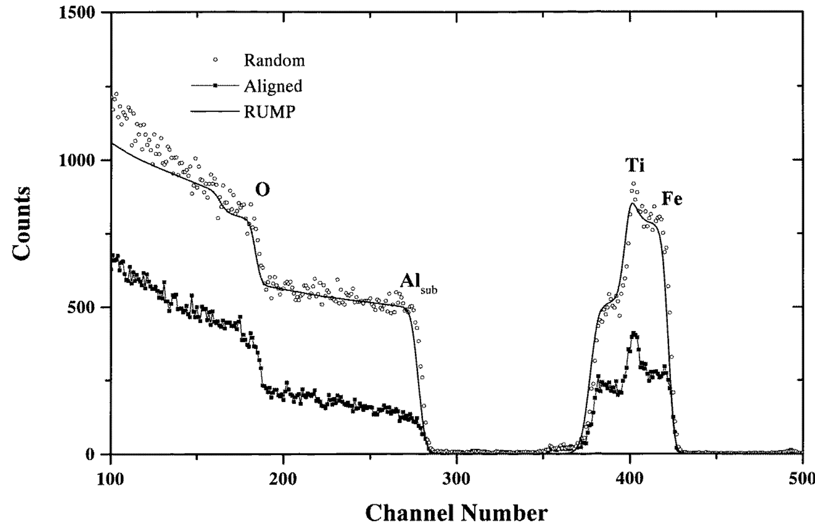


Figure 2. The aligned and random RBS experimental spectra with that from RUMP simulation of the film prepared in 0.045 mbar pure Ar ambient gas.

Figure 4 shows the aligned and random RBS spectra of the $FeTiO_3$ film on α-Al_2O_3 (0006) substrate prepared in the gas mixture of 5% oxygen with argon and the spectrum from RUMP simulation. The low aligned yields χ_{min}, around 15%, for iron and titanium mean the film has a high quality. Anyway the higher interface part than the surface peak suggests that epitaxy is superior at the surface compared to the interface. The lower quality of the near-interface region is likely related to a high density of misfit locations arising from the lattice mismatch of about 7–8%. From the spectra we can see oxygen is also well aligned, which is shown clearly by the smooth oxygen depth distribution in the aligned spectrum. However, compared to iron, titanium is not so well located, which can be seen clearly by its comparatively higher aligned backscattering yields. The reason here is likely due to the different element mass too, as is oxygen. The simulated film thickness is around 1300 Å with atomic ratios of Fe:Ti:O = 1.0:1.0:3.0. The result suggests a stoichiometric film within the error range of RBS having been prepared by PLD. However, relative amounts of oxygen in the film cannot be determined exactly because the Rutherford scattering cross section is dependent on the ratio of the square of the atomic number of the target elements. The estimation of roughly 10% accuracy is reasonable in this situation.

A relation between the crystal axes of FTO and the in-plane vectors of the sapphire substrate can be obtained from x-ray diffraction pole figures. FTO has a crystal symmetry of $R\bar{3}$, so

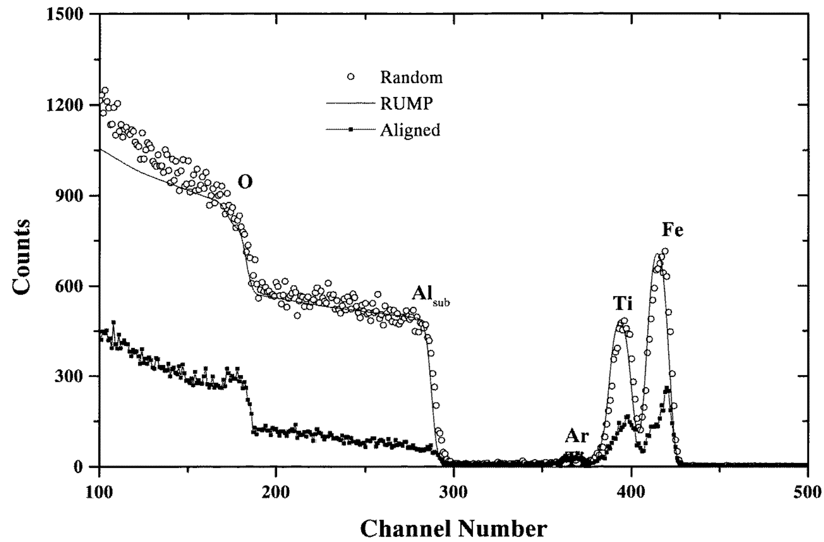


Figure 3. The aligned and random RBS experimental spectra with that from RUMP simulation of the film prepared in vacuum.

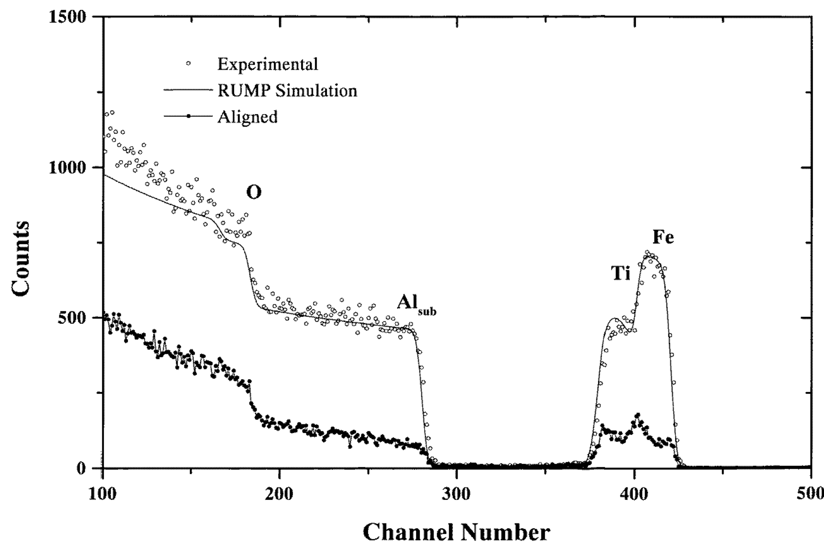
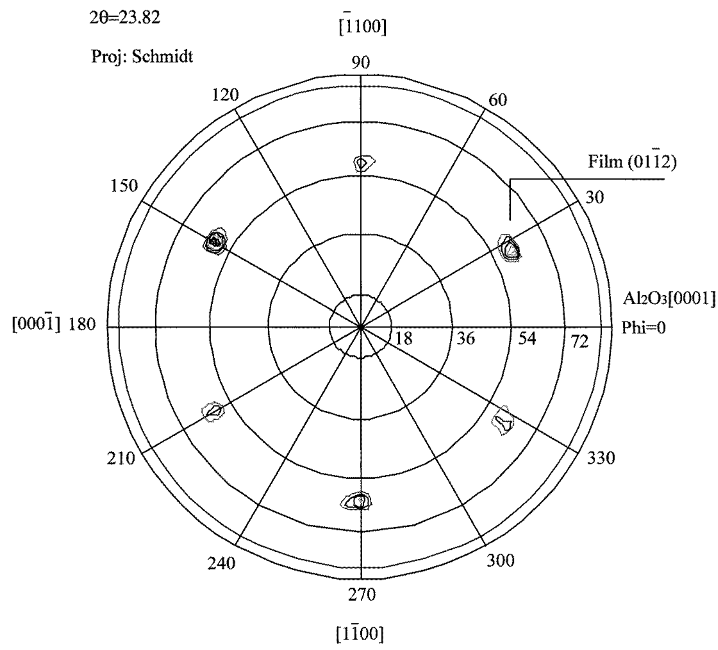


Figure 4. The aligned and random RBS experimental spectra with that from RUMP simulation of the film prepared in 0.01 mbar gas mixture of 5% oxygen with argon. The minimum yields suggest that epitaxy is superior at the surface compared to that of interface.

an untwinned single crystal should show threefold symmetry in the pole figure. Figure 5(a) shows the pole figure of $(01\bar{1}2)$ in-plane of c axis oriented $FeTiO_3$ film deposited in the gas mixture of argon and oxygen on α-Al_2O_3 (0001) substrate. It shows two groups of FTO $(01\bar{1}2)$ poles; one group located at $\phi = 30°$, $150°$ and $270°$, and the other group at $\phi = 90°$, $210°$ and $330°$. This suggests that the c axis oriented film is grown epitaxially; however, there are two kinds of twin that are rotated by $60°$ about the film normal. It should be noted that the relative



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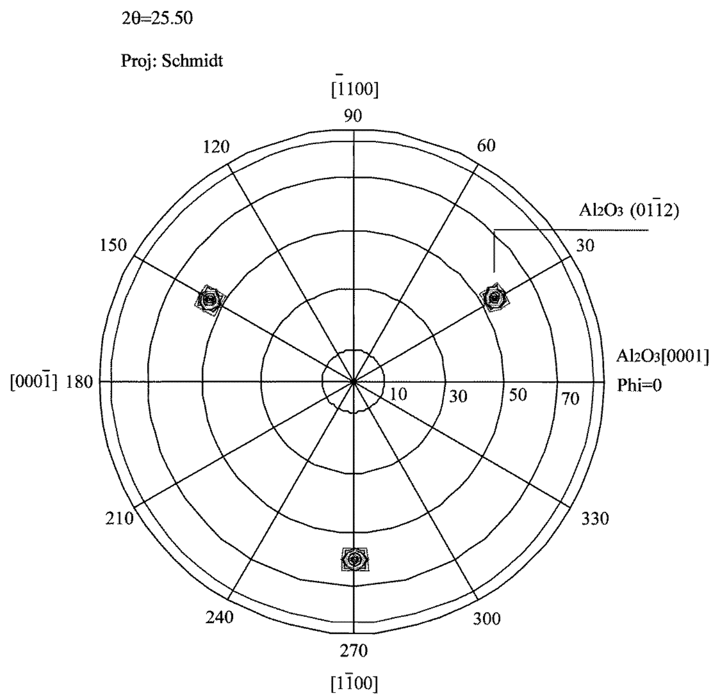


(*b*)

Figure 5. (*a*) (01$\bar{1}$2) pole figure of *c* axis oriented $FeTiO_3$ film deposited in the gas mixture of argon with 5% oxygen on α-Al_2O_3 (0001) substrate. (*b*) (10$\bar{1}$4) pole figure of *c* axis oriented $FeTiO_3$ film prepared in the gas mixture of argon with 5% oxygen on α-Al_2O_3 (0001) substrate.

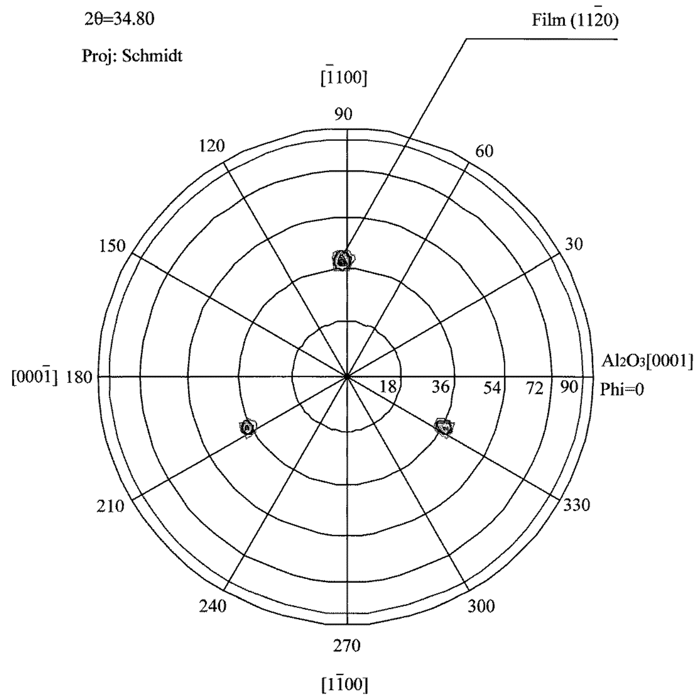
intensities of these two groups are quite different, and the intensity of the group at $\phi = 90^\circ$, 210°, 330° is only around 20% of the other group at $\phi = 30^\circ$, 150°, 270°. This means the film is nearly single crystal, with only a small amount of twins. The $(10\bar{1}4)$ pole figure of the same sample is also shown in figure 5(*b*). The x-ray diffraction pole figure measurements of other axes show similar results, i.e., the laser ablated FTO film is nearly single crystal with small amount of twins. The relative pole figures of the substrate measurement show the parallel relationship of the film to the sapphire substrate at both the main plane and in-planes. The pole figures of substrates are not shown here to save space.

Figure 6(*a*) shows the in-plane $(11\bar{2}0)$ pole figure of $(20\bar{2}2)$ oriented $FeTiO_3$ film deposited in vacuum on α-Al_2O_3 (0001) substrate. It shows only three peaks of FTO $(11\bar{2}0)$. This suggests that the atomic arrangement in the $(11\bar{2}0)$ direction is quite good even without twins. The ratio of background to signal is less than 10%. That is the reason why we can get a small minimum yield in the aligned RBS spectrum shown in figure 3. However the $(30\bar{3}0)$ pole figure (figure 6(*b*)) shows twinned structure with other unknown peaks. At the same time, the ratio of background to signal in figure 6(*b*) is as high as 30%.

The $(01\bar{1}2)$ in-plane pole figure of *c* axis oriented $FeTiO_3$ film deposited in pure argon on α-Al_2O_3 (0001) substrate is shown in figure 7(*a*). It also shows two groups of FTO $(01\bar{1}2)$ poles; one group located at $\phi = 0^\circ$, 120° and 240°, and the other group at $\phi = 60^\circ$, 180° and 300°. This suggests that the *c*-axis oriented film ablated in pure argon is grown epitaxially; however, there are two kinds of twin that are rotated by 60° about the film normal. The relative intensities of these two groups are almost same, and it means the film has a twinned structure. The ratio of background to signal, as high as around 30%, suggests the poor quality of the film. Figure 7(*b*) shows the $(01\bar{1}2)$ in-plane pole figure of $FeTiO_3$ film deposited in pure oxygen on α-Al_2O_3 (0001) substrate. It shows three groups of FTO $(01\bar{1}2)$ poles; one group located at $\phi = 0^\circ$, 120° and 240°, the second group at $\phi = 60^\circ$, 180° and 300° and the third group at $\phi = 90^\circ$ and 180°. This suggests poor quality of the film.

AES was also used to characterize these films prepared in different ambients. Figure 8 shows the Auger electron spectroscopy spectrum from the $FeTiO_3$ film prepared in the ambient mixture of Ar with 5% oxygen of 0.01 mbar. The spectrum only shows iron, titanium and oxygen signals without any distinguishable impurity. The 3000 eV electron beam was used in the AES measurement. By Auger analysis, we can see it clearly that the film prepared in a vacuum environment contains a certain amount of carbon. The impurity carbon does not only exist on the surface; it also exists at depth. Figure 9 shows the AES spectrum of the film prepared in vacuum after 15 minutes sputtering using argon. From RBS (figure 3) and AES (figure 9) analyses, we can see the film prepared in vacuum can be easily contaminated by carbon and other impurities. Carbon contamination is a 'common' problem in most techniques for film preparation, because a small amount of carbon does exist in a vacuum system. However in the case of the gas mixture, a high gas pressure makes the small amount of carbon 'invisible'. However, the accurate determination of stoichiometry from the Auger electron spectrum is still difficult.

The reason why the gas mixture can greatly enhance the (0006) orientation is possibly because the argon fraction in the gas mixture can not only decrease the oxygen part which contributes to oxygen richness, but also activate the oxygen. Therefore oxygen in the plume can have higher energy, which will make the film growth preferred in the (0006) direction. We will report our research in another paper that the increase of laser fluency will also enhance the orientation of the (0006) direction [15] for the same reason. A similar result was also found in $LiNbO_3$ [16] and $Ba_2NaNb_2O_{15}$ [17]. It also should be noted that the reproducibility of film preparation in the gas mixture is very high, i.e., we can easily reproduce a film with the high quality that is quite difficult in other environments. The reason maybe is the low fraction of O_2 with high amount of Ar can not only keep a higher pressure that is necessary to prepare a



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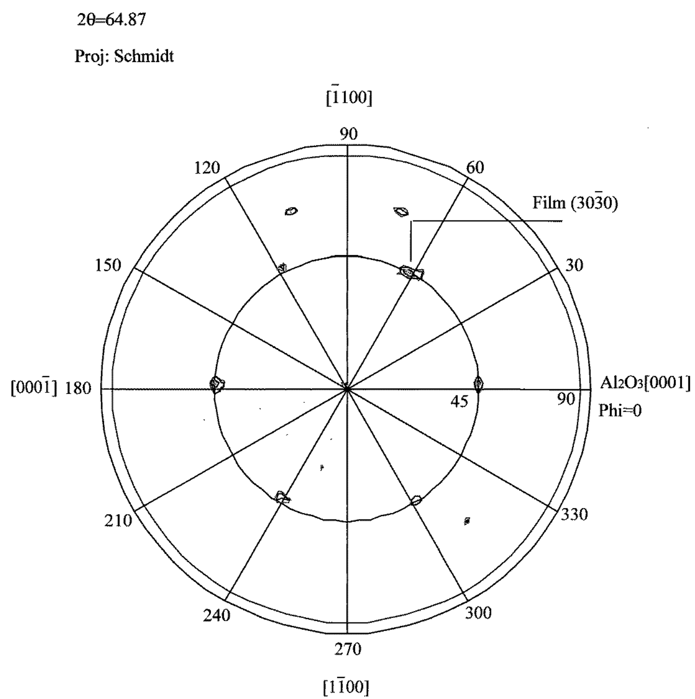
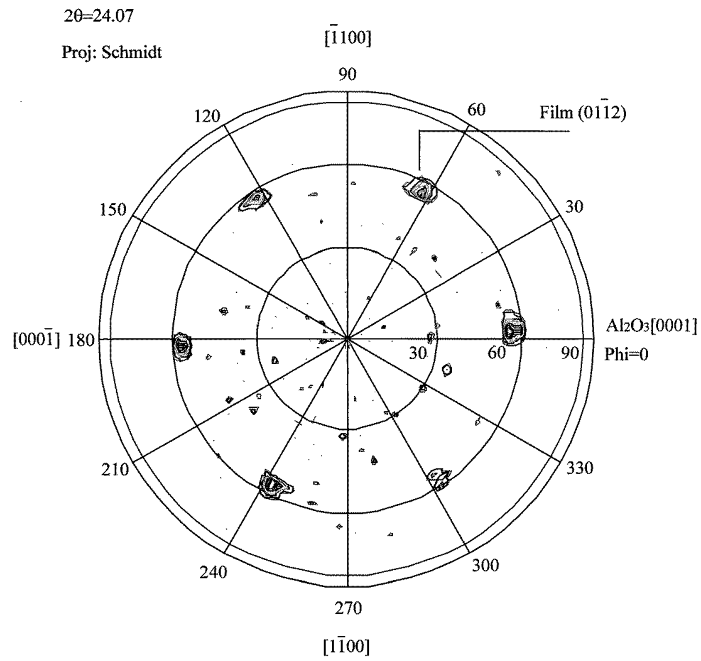


(*b*)

Figure 6. (*a*) (11$\bar{2}$0) pole figure of $FeTiO_3$ film prepared in vacuum on α-Al_2O_3 (0001) substrate. (*b*) (30$\bar{3}$0) pole figure of $FeTiO_3$ film prepared in vacuum on α-Al_2O_3 (0001) substrate.



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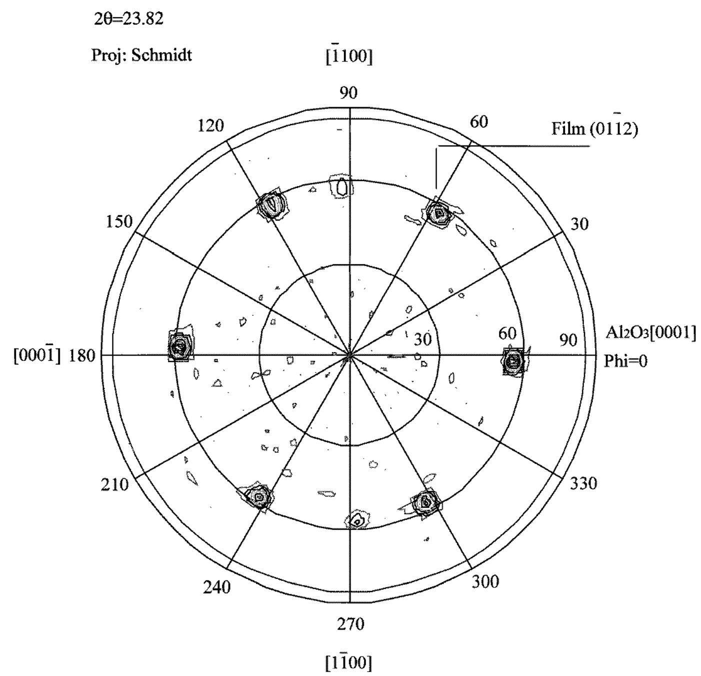

(*b*)

Figure 7. (*a*) (01$\bar{1}$2) pole figure of $FeTiO_3$ film deposited in pure argon on α-Al_2O_3 (0001) substrate. (*b*) (01$\bar{1}$2) pole figure of $FeTiO_3$ film deposited in pure oxygen on α-Al_2O_3 (0001) substrate.

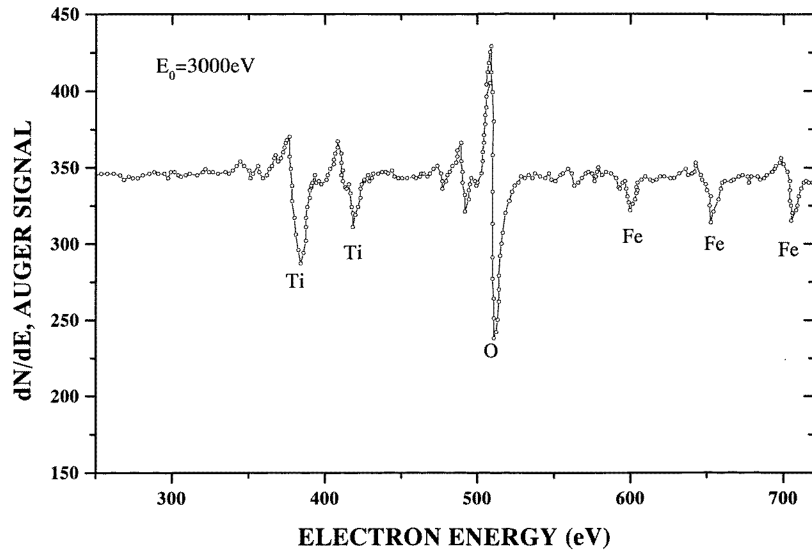

Figure 8. Auger electron spectrum from the $FeTiO_3$ film prepared in a gas mixture of Ar with 5% O_2 on α-Al_2O_3 (0001) substrate.

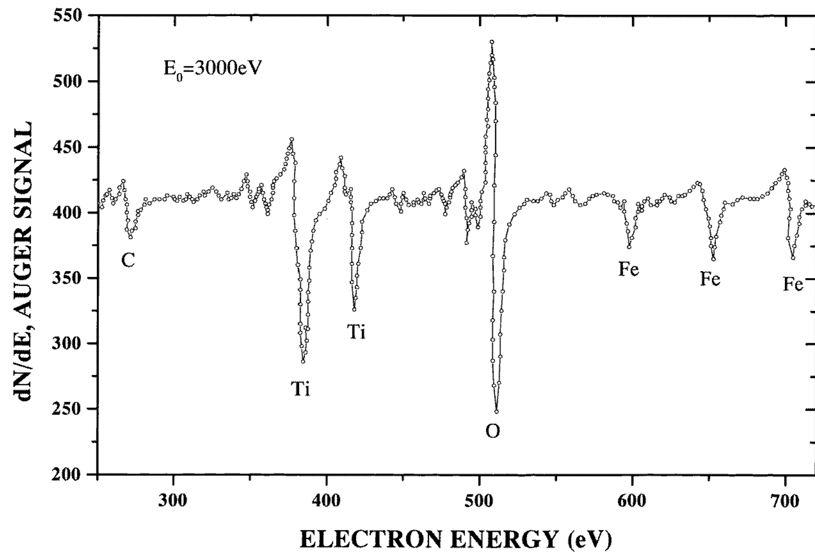

Figure 9. Auger electron spectrum from the $FeTiO_3$ film prepared in vacuum on α-Al_2O_3 (0001) substrate.

homogeneous and pure film, but also the low fraction of O_2 makes the process not so sensitive to the deposition conditions. This can be seen more clearly through comparison of RBS and AES spectra of films prepared in vacuum and gas mixture conditions.

4. Conclusions

In summary, RBS/channelling, XRD, XRD pole figures and AES were used to characterize the $FeTiO_3$ thin films prepared in pure oxygen, pure argon, vacuum and oxygen–argon mixture as ambients by pulsed laser deposition. It has been found that the best films were prepared under a mixed ambient of 5% oxygen and argon gas at 450 °C for 30 minutes. The high XRD intensities with narrow half-width, parallel epitaxial growth relationship to substrate $FeTiO_3(0006)/Al_2O_3(0006)$ both at main plane and in-planes, low aligned channelling yields and clean surface from AES measurement indicate the high quality of the film. The films prepared in pure O_2 from 0.01 to 0.04 mbar are a little rich in oxygen, and we have not obtained a highly crystalline film in a quite wide temperature range. Using pure argon as ambient gas we have obtained a crystalline thin film, but the film is not stoichiometric, and the crystalline quality is not so good which can be seen from the minimum backscattering yields in the Rutherford backscattering spectra. The film prepared in vacuum conditions shows near stoichiometry and low minimum backscattering yields, but the growth relationship to the substrate is $FeTiO_3(20\bar{2}2)/Al_2O_3(0006)$ and the oxygen atoms are not as well aligned as iron and titanium atoms. We can see this clearly by an oxygen slope in the aligned spectrum in figure 4. Also the film prepared in vacuum can easily be contaminated by carbon and other impurities. The other things concerning gas mixture we want to note here are: (1) Compared with other ambients, the reproducibility in gas mixture is quite high, i.e., we can easily prepare a crystalline film with high quality that is normally difficult in other environments, at least in our case. This is possibly because the gas mixture with high content of inactive argon makes the plume interaction with the ambient not sensitive. At the same time, high pressure, a condition for preparing a homogeneous film, is satisfied too. (2) We have also obtained high quality films on other planes of α-Al_2O_3 (0001) substrate using the gas mixture too. A paper concerning the comparison of film deposition on the different planes with different gas pressures and different laser energy densities has been already reported [15]. Maybe we can anticipate that an optimized ambient gas mixture will not only keep film stoichiometry same as the target, but also improve the film quality by activating the reactive gas through inactive gas, such as Ar. We think it works not only on oxides with multi-elements.

Acknowledgments

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