Self-tuning MOCVD Approach to the Growth of Very Smooth $La_{1-x}Pb_xMnO_3$ and $PbTiO_3$ Epitaxial Thin Films

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The approach to the growth of stoichiometric lead-containing complex oxide films was developed. It was successfully used for the MOCVD of $La_{1-x}Pb_xMnO_3$ ($x = 0.1-0.6$) and $PbTiO_3$ films on perovskite substrates and MgO at a deposition rate of $\approx 1\ \mu$m/h. The grown films were of a good epitaxial quality with rather low mean surface roughness, $S_a < 2$ nm (for the film thickness $\geq 250-600$ nm). The grown manganite layers were metallic at room temperature with a T_c above 300 K. Such films are suitable for the fabrication of low-field tunnel magnetoresistance devices and thin film capacitors.

I. Introduction

Complex oxides with the perovskite structure demonstrate an impressive range of electrical and magnetic properties: superconductivity, colossal magnetoresistance, ferroelectricity, metallic conductivity, and others. Lead-containing ferroelectric perovskites, $PbTiO_3$, $PbTi_{1-y}Zr_yO_3$, and $Pb_{1-x}La_xTi_{1-y}Zr_yO_3$, are among the most important and most studied perovskite materials now.

The growth of the lead-containing oxide films is usually performed at temperatures of about 500−700 °C to prevent the loss of highly volatile lead oxide from the film. The high volatility of PbO is evidently the reason there are not so many examples of the successful film growth of other lead-containing complex oxides. For example, the literature about thin films of Pb-based high-temperature superconductors is very scarce.[1,2] On the other hand, the volatility of lead oxide provides one very important advantage: as it was observed for $PbTiO_3$ growth, under certain conditions the film adopts exactly that amount of lead that is needed for a stoichiometrical compound, while the excessive lead oxide evaporates.[3−8] For instance, for the growth of $PbTO_3$ the partial pressure of PbO must be between the equilibrium pressures of PbO above $PbTiO_3 + TiO_2$ and $PbTiO_3 + PbO$ phase mixtures. (Throughout this paper we use $PbTiO_3$ notation to denote the lead titanate, though the possibility of the $Pb_{1-x}TiO_3$ solid solution formation should be kept in mind.[9]) At the typical growth temperatures this range expands roughly over 2 orders of magnitude[9] and this makes the synthesis of phase-pure $PbTiO_3$ films rather easy. The same effect is to be expected for other systems containing volatile components (Tl_2O, Bi_2O_3, HgO, and others) and it was experimentally observed for the growth of $Bi_2Sr_2CuO_y$[10] and $Bi_4Ti_3O_{12}$[11] thin films. For this phenomenon (in relation to MBE) Theis and co-workers[8,11] suggested the definition “adsorption-controlled growth”.

Another important feature is the low melting points of PbO and some lead-containing complex oxides. Due to this fact, surface diffusion during the film growth is very high, which may cause an increase of the epitaxial quality of the films and a smoother surface.[12,13] In this paper, we suggest the use of the above-mentioned peculiarities of the lead-containing systems for the MOCVD of phase-pure epitaxial $La_{1-x}Pb_xMnO_3$ and $PbTiO_3$ films with very low surface roughness. For this purpose, we have developed and studied the impulse MOCVD procedure carried out under conditions of relatively high and constant pressure of the volatile oxide, PbO.

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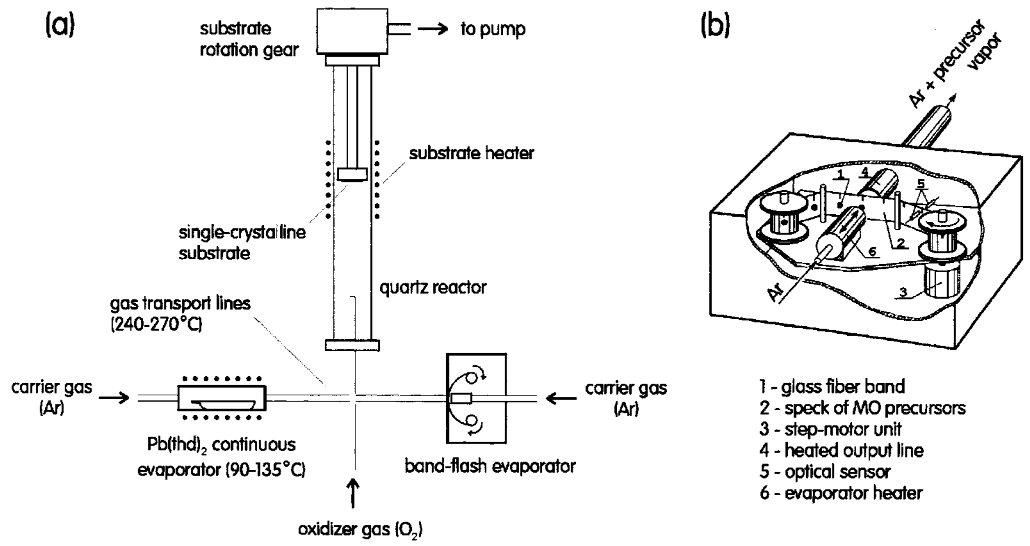

Figure 1. (a) Scheme of the experimental MOCVD setup; (b) details of the band-flash evaporator system used.

Table 1. Conditions of the Film Growth (Total Pressure of 13 mbar and $p(O_2) = 2$ mbar)

system	temp (°C)	deposition time (min)	film thickness (nm)	saturation ratio of PbO, α_{PbO}[a] (%)
La−Pb−Mn−O	680−750	30	400−600	7−30
Pb−Ti−O	680−750	30	250−1000	1−100

[a] The ratio of PbO vapor pressure to the equilibrium PbO vapor pressure at the given temperature (see the Experimental Section for an explanation).

II. Experimental Section

Thin Film Preparation. The important feature of our experimental MOCVD setup (Figure 1) is the separate continuous evaporator for the $Pb(thd)_2$ precursor (thd = 2,2,6,6-tetramethylheptandionate). The other precursors were supplied with the flash evaporator from a glass fiber band.

$Ti(i\text{-}PrO)_2(thd)_2$ (i-PrO = isopropylate), $Mn(thd)_3$, and $La(thd)_3$ were used as other precursors. The conditions of the film growth are listed in Table 1. Polished single-crystalline $LaAlO_3$, $NdGaO_3$, and MgO cut in the (001) plane and $SrTiO_3$ substrates in (001) and (110) orientations were used. Typical substrate dimensions were 5 × 10 × 0.5 mm^3.

The partial pressure of lead oxide, p(PbO), was derived from the mass loss of the $Pb(thd)_2$ precursor and the relevant process parameters (gas flows, total pressure, and deposition time). The evaporation rate of $Pb(thd)_2$ was found to be reproducible in the interval of ±10% of its value over the evaporation temperature range used (90−135 °C). For a simplicity of presentation, we used the ratio

$$\alpha_{PbO} = p(PbO)/p_{satur}(PbO) \times 100\%$$

where p_{satur}(PbO) is the equilibrium vapor pressure of PbO at the deposition temperature. The value of p_{satur}(PbO) was taken from the data of Knacke and Prescher:[14,15]

$$\log\,[p_{satur}(PbO),\ \mathrm{mbar}] = -(13\,566/T) + 11\,374$$

To ensure the reliability of the p_{satur}(PbO) value taken from the literature, the depositions of PbO were performed at 670 °C. PbO crystals could be observed with an optical microscope on the substrates surface for α_{PbO} values of 200% and larger. This fact can be explained by a supersaturation needed to start the condensation or the uncertainty of the actual deposition temperature (it was measured with a thermocouple mounted inside the steel substrate holder). According to refs 14 and 15, for the temperature range used the 2-fold increase in α_{PbO} corresponds to the 20 °C increase of temperature.

Characterization. X-ray diffraction (XRD) study of the films was performed with DRON 3M and SIEMENS D5000 diffractometers with Cu Kα and Cr Kα radiation. Scanning electron microscopy (SEM) and energy-dispersive X-ray quantitative analysis (EDX) were carried out with a CAMSCAN 4M electron microscope equipped with a EDX 9800 analyzing system. Atomic force microscopy (AFM) was performed on clean samples' surfaces with a Solver P4-SPM-MDT (NT-MDT, Russia) atomic force microsope. Cation composition and thickness of the films as well as homogeneity of the components' distribution and ion channeling were investigated by Rutherford Backscattering Spectrometry (RBS). A collimated beam of 1.1 MeV He^+ ions ~0.5 mm in diameter was used. For the channeling investigations on the epitaxial films, the [001] film axis was first aligned parallel to the incident beam direction. Transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM) studies were performed on the films cross sections prepared by ion milling, with the film facing away from the ion gun. A Philips CM30UT electron microscope equipped with the field emission gun operating at 300 kV and the Link EDX element analysis system was used. The measurements of the electric resistance of manganite films were made with a two-contact scheme in the range of 77−450 K. Silver paste contacts were used.

III. Results and Discussion

La−Pb−Mn−O Films. To obtain the single-phase $La_{1-x}Pb_xMnO_3$ film, the growth must be performed in a window of p(PbO) to avoid the crystallization of PbO (i.e., $\alpha_{PbO} < 100\%$, see the Experimental Section) and to prevent the decomposition of the $La_{1-x}Pb_xMnO_3$ solid solution with the loss of PbO (Figure 2). The high-temperature boundary of $La_{1-x}Pb_xMnO_3$ stability is not known, but we observed no signs of $La_{1-x}Pb_xMnO_3$ decomposition or any cation nonstoichiometry for $\alpha_{PbO} \geq 7\%$. The presence of the third temperature-independent boundary is caused by simple stoichiometrical relations: the formation of single-phase $La_{1-x}Pb_xMnO_3$ solid solution is no more possible if the vapor phase does not contain enough lead precursor. So the position of this boundary, that is, p(PbO), depends directly on the ratio of La and Mn precursors and the rate of their supply. Under the conditions denoted in Figure 2 with

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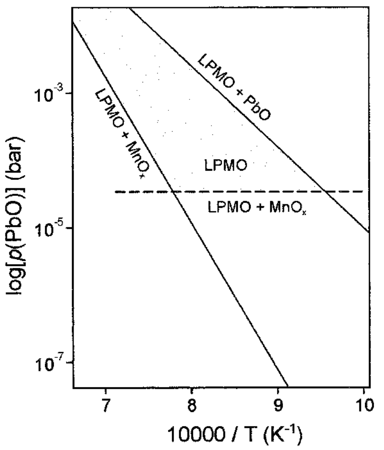

Figure 2. Area of the self-tuning growth mode of the phase-pure $La_{1-x}Pb_xMnO_3$ film (marked with gray color). The approximate numerical values of p(PbO) and T are given. “LPMO” is $La_{1-x}Pb_xMnO_3$.

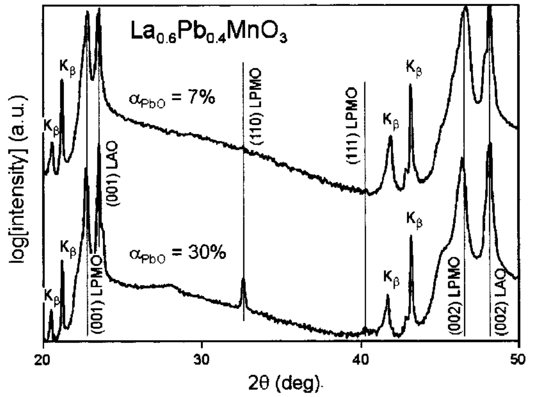

Figure 3. XRD $\theta-2\theta$ scans of $La_{1-x}Pb_xMnO_3$ films grown at various α_{PbO} values.

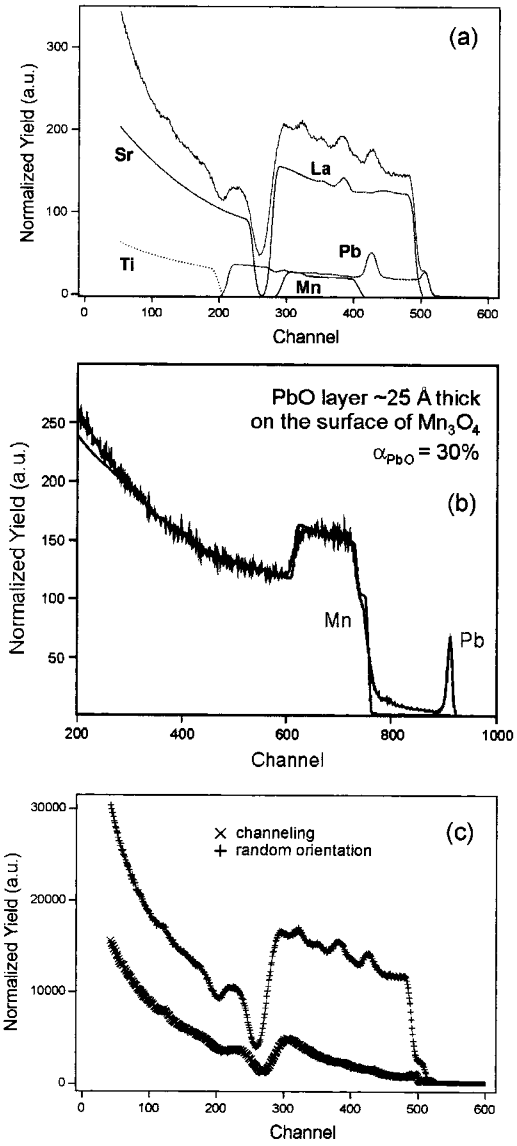

Figure 4. (a) RBS scan taken from the $La_{0.6}Pb_{0.4}MnO_3$ epitaxial film on (001)$SrTiO_3$; (b) RBS spectrum for the Mn_3O_4 film deposited at α_{PbO} = 30%; (c) channeling demonstrating high epitaxial quality of the $La_{0.6}Pb_{0.4}MnO_3$ film (χ = 7.3%).

a gray color, the composition of the $La_{1-x}Pb_xMnO_3$ solid solution could be easily adjusted by changing the ratio of La and Mn precursors supplied into the reactor.

The following parameters were found to have a strong effect on the films’ orientation and morphology: the pressure of lead oxide, the growth rate, and the value of x in the $La_{1-x}Pb_xMnO_3$ solid solution (i.e., the ratio between La and Mn precursors in a vapor phase). The films grow in a (001) orientation on (001) perovskite substrates for α_{PbO} lower than some critical value; for larger α_{PbO} additional (110), (111), and (211) orientations appear, but the (001) orientation is still always predominant (Figure 3). It is noteworthy that the additional orientations grow despite the use of (001) perovskite substrates. The appearance of these orientations was also found to be caused by the increase of the deposition rate and/or the decrease of the x value in $La_{1-x}Pb_xMnO_3$. Two possible explanations for this fact could be suggested:

(1) The increase of α_{PbO} leads to the increase of the thickness of the PbO adsorption surface layer and the appearance of additional orientations may be caused by the crystallization of a polycrystalline material from the liquid phase. RBS spectra of $La_{1-x}Pb_xMnO_3$ thin films quenched from the deposition temperature reveal the presence of a thin surface layer enriched with lead (Figure 4a). By the deposition of Mn_3O_4 films under the same conditions (thus with PbO vapor), it was directly demonstrated that the surface peak observed in the most cases is attributed to the PbO adsorbed layer (~25 Å for Mn_3O_4 film on $LaAlO_3$, Figure 4b).

(2) Another possible explanation is concerned with the structure of various crystal faces of the perovskite material. Pb atoms are present in *every* atomic layer of $La_{1-x}Pb_xMnO_3$ perpendicular to the [110] direction, while only every *second* layer perpendicular to the [001] direction contains lead atoms. If α_{PbO} is high, the surface of the growing film is covered with a relatively thick lead-rich adsorbed layer. This circumstance may cause a nucleation of (110) and other orientations to be more preferable in comparison to the nucleation of grains with a (001) orientation.

These observations are schematically summarized in Figure 5.

A significant decrease of the surface roughness was observed for the films obtained at moderate values of α_{PbO} (from 7 to ~20%), while the high α_{PbO} led to the roughening of the films’ surface (Figure 6). The absolute

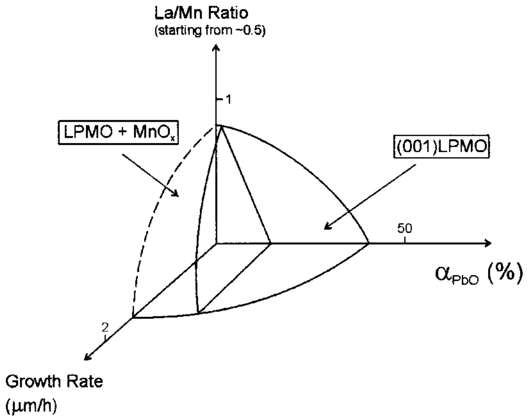

Figure 5. Schematic of the influence of various deposition parameters on the orientation and phase composition of $La_{1-x}Pb_xMnO_3$ films on (001) perovskite substrates for the deposition temperature of about 720 °C. The numbers on the axes are given as approximate values. “LPMO” is $La_{1-x}Pb_xMnO_3$.

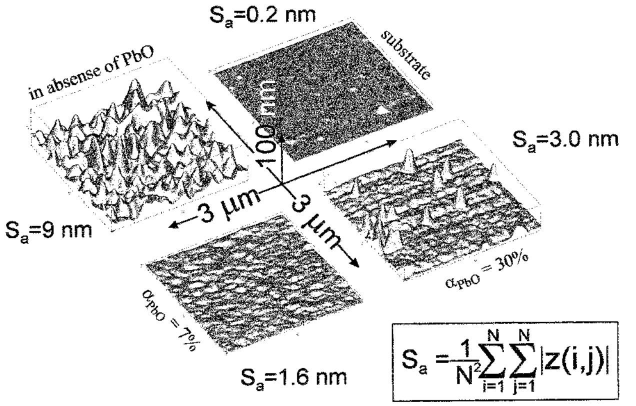

Figure 6. AFM images of $LaAlO_3$ substrate, $La_{0.8}MnO_3$, and $La_{0.6}Pb_{0.4}MnO_3$ films grown at various α_{PbO} values.

value of the surface roughness for the films prepared under optimal conditions was very low ($S_a \sim 1.6$ nm), even for the films 600 nm in thickness deposited with a high deposition rate, which can be important for constructing epitaxial heterostructures. The surface smoothness is believed to be a result of the intensive surface diffusion due to the presence of a quasi-liquid adsorbed PbO layer. The phenomenon was previously observed for the film growth of other complex oxides, like $BaTiO_3$,[12] $LaAlO_3$, $MgAl_2O_4$, CeO_2, and ZrO_2,[13] in the presence of highly volatile oxides with low melting points, PbO and/or Bi_2O_3. The roughening of the films' surface at high α_{PbO} is probably connected with the appearance of additional orientations in the film due to different growth rates of various crystal planes.

The lattice parameter of epitaxial $La_{1-x}Pb_xMnO_3$ films grown on $LaAlO_3$ and $SrTiO_3$ substrates were found to differ from each other because of the well-known tetragonal strain effect.[16] Thus, the lattice constant $a_\perp$ of the $La_{0.5}Pb_{0.5}MnO_3$ material in 400-nm-thick films was 3.90(1) and 3.85(1) Å for $LaAlO_3$ and $SrTiO_3$ substrates, respectively. Indeed, the $LaAlO_3$ possesses a smaller pseudocubic lattice constant (3.793 Å) that causes a compressive strain in the (001) plane and a respective expansion of the lattice in the [001] direction. The effect of the $SrTiO_3$ ($a = 3.905$ Å) substrate on the $a_\perp$ lattice parameter of the manganite layer is just the opposite.

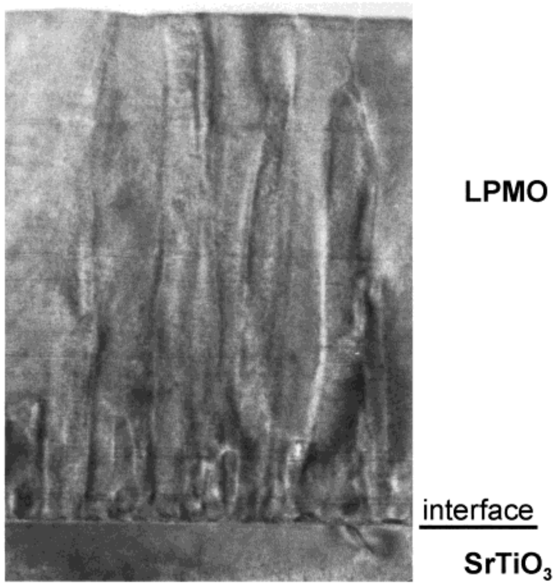

Figure 7. TEM image of the cross-section of the phase-pure epitaxial $(001)La_{1-x}Pb_xMnO_3/(001)SrTiO_3$ film: (010) zone. Film thickness is about 500 nm. “LPMO” is $La_{1-x}Pb_xMnO_3$.

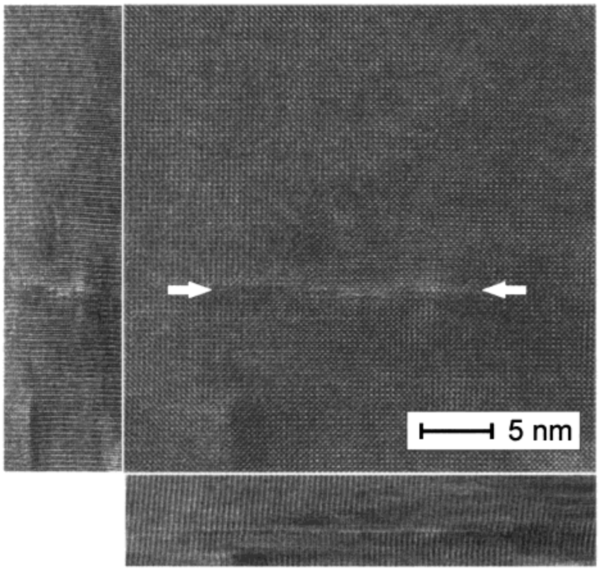

Figure 8. HREM image of the cross-section of $La_{1-x}Pb_xMnO_3$ film containing a K_2NiF_4-type defect (marked with arrows). The (010) zone is shown. The left and bottom images are produced from the original one by compressing them along one direction.

With TEM it was found that the grown single-phase films were free of any precipitates and the perovskite material was of a high epitaxial quality (Figure 7); the film–substrate interfaces were found to be semicoherent. These observations are in accordance with XRD and AFM results described above. The only defects of the crystal structure observed are K_2NiF_4-type intergrowths in $La_{1-x}Pb_xMnO_3$ (Figure 8). Similar but much more extended intergrowths were observed for (La,Nd,Sr)-MnO_3 thin films grown by MOCVD.[16] It is noteworthy that in $(La,Nd,Sr)MnO_3$ films the extra planes are extended for the length of thousands of angstroms, even with total film nonstoichiometry being as low as 1 at.

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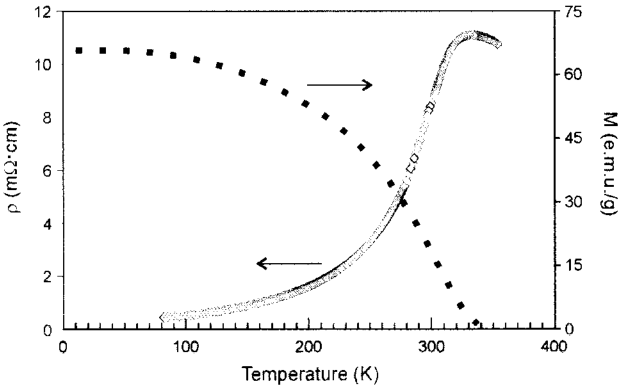

Figure 9. Temperature dependence of the resistivity and magnetization of the $(001)La_{0.6}Pb_{0.4}MnO_3$ film.

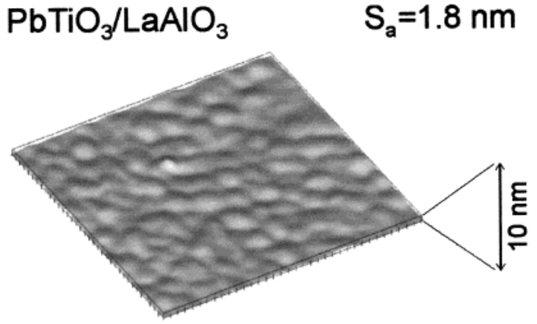

Figure 10. AFM image of $PbTiO_3/(001)LaAlO_3$ film grown at 680 °C, $\alpha_{PbO} = 100\%$. The scan area is $3.5 \times 3.5\ \mu m^2$ and the film thickness is about 250 nm.

%. In the case of $La_{1-x}Pb_xMnO_3$ films the extra planes are rather short (<100 Å), pointing out the stricter composition regulation due to the self-tuning mechanism.

Sharp spectrum edges observed by RBS correspond to a very smooth surface of $La_{1-x}Pb_xMnO_3$ thin films in accordance with AFM and TEM observations. Moreover, the RBS spectra show a rather high degree of composition uniformity, though some fluctuations of the cation composition were detected. This probably comes from the instability of the precursors feeding. Nevertheless, a self-tuning mechanism seems to be very effective in preventing the formation of secondary phases or other extended defects: observed ion channeling minimum yield was as low as ~7.3% (Figure 4c) despite the composition deviations.

The metal−insulator and ferromagnetic−paramagnetic transitions occur for the grown $(001)La_{1-x}Pb_xMnO_3/LaAlO_3$ ($x = 0.1-0.6$) films above 300 K and at room temperature these solid solutions are metallic and ferromagnetic (Figure 9). Thus, the material is a good candidate for fabrication of magnetoresistive devices operating at room temperature. Also, the high electrical conductivity makes these films interesting for application as thin film electrodes in various oxide circuits.

Pb−Ti−O Films. The $p(PbO)-T$ conditions of the growth of stoichiometric $PbTiO_3$ are similar to those of $La_{1-x}Pb_xMnO_3$ described above (Figure 2). The temperature dependencies of the PbO equilibrium partial pressure above $PbTiO_3 + TiO_2$ and $PbTiO_3 + PbO$ phase mixtures were taken from ref 9. Under appropriate conditions single-phase $PbTiO_3$ films were grown on $(001)LaAlO_3$, $(001)SrTiO_3$, $(110)SrTiO_3$, and (001)MgO substrates. $PbTiO_3$ films were found to grow with two types of orientation: with the *a* and *c* axis normal to the (001) plane of the substrate material. AFM study revealed high smoothness of the $PbTiO_3$ layers grown in the self-tuning mode (S_a of lower than 2 nm for the surface area of $10\ \mu m^2$, Figure 10). The surface smoothening can be explained in a way similar to that for the $La_{1-x}Pb_xMnO_3$ films (Figure 5).

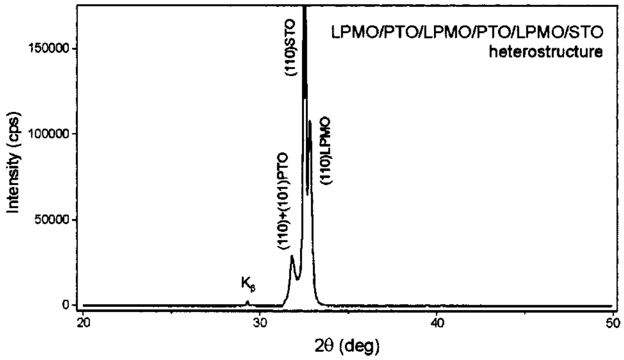

Figure 11. $\theta-2\theta$ XRD scan of the epitaxial $La_{0.6}Pb_{0.4}MnO_3/PbTiO_3/La_{0.6}Pb_{0.4}MnO_3/PbTiO_3/La_{0.6}Pb_{0.4}MnO_3$ five-layer heterostructure grown in situ at 740 °C and $\alpha_{PbO} = 7\%$ on the $(110)SrTiO_3$ substrate.

The deficiency of lead oxide (too low α_{PbO} or too high growth temperature) always led to the growth of the $PbTiO_3 + TiO_2$ phase mixture or even of pure TiO_2. TiO_2 was found to grow epitaxially in a crystallographic form of anatase on (001)-oriented perovskite substrates. The epitaxial relations were as follows,

$$(001)TiO_2 \parallel (001)ABO_3; \quad [100]TiO_2 \parallel [100]ABO_3$$

where ABO_3 denotes $LaAlO_3$ or $SrTiO_3$. This behavior is expected, taking into account the fact that the anatase form of TiO_2 possesses a tetragonal structure with $a = 3.7852$ Å, resulting in a lattice mismatch of lower than 2% with the (001) plane of these substrates. The epitaxial growth of anatase on $(001)SrTiO_3$ has been previously reported[17] and can be described in terms of epitaxial stabilization phenomenon.[18]

La−Pb−Mn−O/Pb−Ti−O Multilayer. The band-flash evaporation MOCVD technique is well-suited for a deposition of multilayers due to the pulse nature of the feeding process: each pulse is produced from a separate speck of the volatile precursor on a moving glass fiber band.[19] We succeeded in growing the five-layer heterostructure containing three $La_{0.6}Pb_{0.4}MnO_3$ films and two $PbTiO_3$ films on the $(110)SrTiO_3$ substrate. The thickness of each layer was about 20 nm. The deposition temperature and α_{PbO} were maintained the same during the growth period ($\alpha_{PbO} = 7\%$ and $T = 740$ °C). The XRD scan of this sample is given in Figure 11. The peaks of the manganite and the titanate layers are clearly seen; both materials grow epitaxially. The profile concentration and cross-section analyses of the grown heterostructure are in progress.

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IV. Conclusions

A self-tuning approach based on a MOCVD technique was developed. It allowed us to grow the phase pure epitaxial films of $La_{1-x}Pb_xMnO_3$, $PbTiO_3$, and heterostructures with a high epitaxial quality. The approach provides a MOCVD route to the phase pure films of many complex oxides, which are otherwise difficult to grow because of unavoidable fluctuations in the films' stoichiometry. A significant improvement of a films' smoothness was achieved, a feature being the key element for the realization of high-capacity ferroelectric memory devices. The layers obtained are suitable for the fabrication of low-field tunnel magnetoresistance devices and thin film capacitors.

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