

Oriented Films of LaNiO_3 and Other Members of the $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ Series, $\text{LaCuO}_{3-\delta}$ and $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, Obtained by Nebulized Spray Pyrolysis[†]

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The technique of nebulized spray pyrolysis has been explored to find out whether oriented films of certain important oxides can be produced on single-crystal substrates by this relatively gentle method. Starting with acetylacetonate precursors, oriented films of metallic LaNiO_3 containing nearly spherical grains (30 nm) have been obtained. Films of near-stoichiometric $\text{La}_4\text{Ni}_3\text{O}_{10}$ and $\text{La}_3\text{Ni}_2\text{O}_7$ showing metallic conductivity have been obtained by this method. This is indeed gratifying since it is difficult to prepare monophasic and stoichiometric bulk samples of these materials. Films of La_2NiO_4 show the expected semiconducting behavior. In the La–Cu–O system, starting with acetylacetonates, we have obtained films mainly comprising semiconducting $\text{La}_2\text{Cu}_2\text{O}_5$, which is generally difficult to prepare in bulk form. More interestingly, nebulized spray pyrolysis gives excellent stoichiometric films of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ consisting of nearly spherical grains (30 nm) which show ferroelectric behavior. The present investigation demonstrates that nebulized spray pyrolysis provides a useful and desirable route to deposit oriented films of complex oxide materials on single-crystal substrates.

Introduction

There has been extensive effort in the past few years to prepare thin films of oxide materials with different electrical properties, starting from highly insulating dielectric films of lead titanates at one end and superconducting films of cuprates at the other. To deposit such oxide films, radio-frequency (RF) sputtering, pulsed laser deposition (PLD), and metal–organic chemical vapor deposition (MOCVD) have been generally employed.^{1–4} Oxide films obtained by such methods, especially by RF sputtering, do not always give stoichiometric compositions of the oxides. For example, films of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) produced by RF sputtering are often found to be deficient in Pb. Pulsed laser deposition has been quite successful in producing good oxide films, although one does not exactly understand why the technique works so well.⁴ Thus, epitaxial films of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ have been obtained by PLD.^{4,6} PLD has also been employed to prepare films of perovskite oxides such as LaNiO_3 .⁷ We considered that it would be most worthwhile to explore whether simple and gentle chemical routes would provide alternative or even better means of

depositing oriented films of novel complex oxides. With this in mind, we have employed nebulized spray pyrolysis⁸ of organometallic precursors to deposit films of a few novel oxide systems on single-crystal substrates.

In nebulized spray pyrolysis, a solution containing the organic derivatives of the relevant metals in a suitable solvent is atomized by making use of a PZT transducer. The atomized spray is slowly deposited on a solid substrate at an appropriate temperature, with sufficient control of the rate of deposition. Nebulized spray pyrolysis is a gentle method since the decomposition of the atomized spray to yield the oxide occurs at sufficiently low temperatures to be favorable to maintain the desired stoichiometry. Although oxide films of polycrystalline nature have been prepared by spray pyrolysis,^{9–11} the method has not been explored to obtain oriented films of complex oxides such as LaNiO_3 and PZT for possible application in microelectronics and dielectrics.

LaNiO_3 is a metallic conductor¹² with electronic properties somewhat similar to those of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the normal state and has a potential use in solid state electronics. LaNiO_3 is the $n = \infty$ member of the $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ family,¹³ the other important members being La_2NiO_4 ($n = 1$), $\text{La}_3\text{Ni}_2\text{O}_7$ ($n = 2$) and $\text{La}_4\text{Ni}_3\text{O}_{10}$ ($n =$

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3). La_2NiO_4 is a quasi-two-dimensional oxide and has been a subject of many recent investigations^{14,15} because of its interesting structure as well as magnetic and electrical properties. With the increase in the number of perovskite layers in $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$, the material becomes more three-dimensional and metallic. It is difficult to prepare monophasic bulk samples of $\text{La}_3\text{Ni}_2\text{O}_7$ and $\text{La}_4\text{Ni}_3\text{O}_{10}$, since they tend to contain intergrowths of other members of the family,¹³ in addition to having a tendency to lose oxygen.¹⁶ There are indications that stoichiometric samples of the $n = 3$ member is metallic, but there is some disagreement with respect to the electrical properties of the $n = 2$ member.^{13,16,17} While the resistivity of LaNiO_3 is higher than that of $\text{La}_3\text{Ni}_2\text{O}_7$, the oxygen stoichiometry seems to determine whether it is metallic or not. Thus, according to Zhang et al.,¹⁶ $\text{La}_3\text{Ni}_2\text{O}_7$ is metallic, but Sreedhar et al.¹⁷ report semiconducting behavior in samples of unknown oxygen content. It was our desire to prepare thin films of stoichiometric compositions of the different members of the $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ family ($n = 1-3$ and ∞) by nebulized spray pyrolysis.

LaCuO_3 is a metallic perovskite and can be prepared only at high oxygen pressures.¹⁸ Efforts to deposit LaCuO_3 films have generally yielded $\text{La}_2\text{Cu}_2\text{O}_5$ ¹⁹ which is in itself difficult to prepare in bulk form. We have examined La-Cu-O films obtained by nebulized spray pyrolysis. Another oxide system that we have investigated is $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT). Thin films of PZT and such lead-based titanates have attracted much attention recently because of their useful ferroelectric and piezoelectric properties with applications in microelectronics and other devices.²⁰⁻²⁴ Although several methods have been employed to deposit PZT films, there appears to be a need for a relatively easy method of depositing films of the stoichiometric oxides with proper orientation for use in devices.

Experimental Section

We have carried out nebulized spray pyrolysis by employing a simple, locally fabricated apparatus described in Figure 1. The dimensions of the transducer were 20 mm diameter and 1 mm thick while the operating frequency was 1.72 MHz. In the setup employed by us the transducer was in contact with the liquid, and this helped to minimize the power required and to reduce the temperature. The height of the geyser was controlled by means of the acoustic intensity. The atomized spray which goes up in the column was deposited on a hot substrate which was then heat treated to get the proper film.

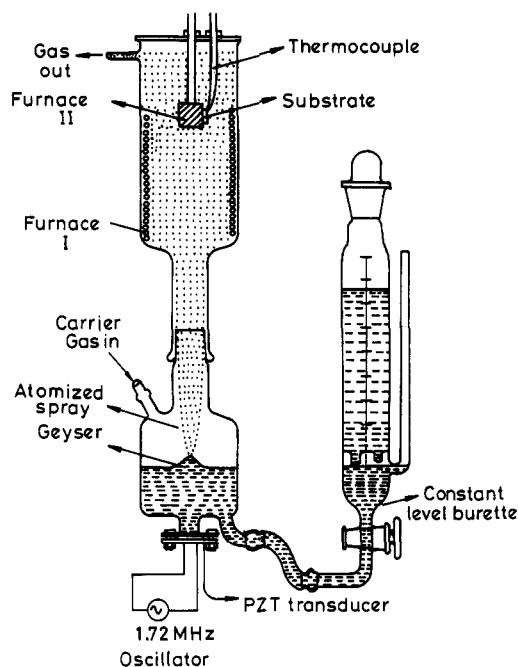


Figure 1. Schematic diagram of the apparatus used for ultrasonic nebulized spray pyrolysis.

The rate of deposition was controlled by means of the flow rate of the carrier gas used, the temperature of the substrate, and the concentration of the organometallic derivatives. For depositing the films, we have employed Si(100), Si(111), MgO (100), and SrTiO_3 (100) as substrates.

The oxide films were characterized by X-ray diffraction and scanning electron microscopy, energy-dispersive X-ray analysis, dc conductivity and atomic force microscopy. A Philips X-ray powder diffractometer PW 1050/90 fitted with PW 1140/70 goniometer was employed for X-ray diffraction studies. A Cambridge S-360 scanning electron microscope was used for microstructure studies, along with a Link AN10000 energy-dispersive X-ray analyzer with ZAF4/FLS software for quantitative elemental analysis. Nanoscope II fitted with AFM was used to study the surfaces of some of the films. Four-probe conductivity measurements were carried out down to 15 K by using a Lakeshore closed-cycle cryostat and Lakeshore constant-current source. Ohmic gold contacts were employed by sputtering gold on to the films through a mask. Ferroelectric hysteresis loop measurements were carried out by using a home built modified Sawyer-Tower circuit.

To assess the quality of the oxide films produced by nebulized spray pyrolysis, we first deposited ZnO films starting with zinc acetate solution in methanol (0.1 mol %) on glass substrates. In Figure 2 we show the X-ray diffraction pattern of ZnO film deposited at 600 K for 4 h on a glass substrate. We see that even on a glass substrate, the ZnO film is reasonably oriented, showing (002) orientation. With the increasing deposition temperature, the ZnO films became better oriented. We could get oriented films of ZnO on MgO (100) and SrTiO_3 (100) substrates as well. The scanning electron micrograph of a ZnO film obtained is shown as the inset in Figure 2. The micrograph shows that the average grain size is around 30 nm. In Figure 3, we show the X-ray diffraction pattern of a NiO film [(200) oriented] deposited on SrTiO_3 (100) substrate at 625 K by using nickel acetylacetonate in methanol (0.1 mol %). The scanning electron micrograph shown in the inset of Figure 3 indicates that the average grain size is 30 nm.

To deposit the films of LaNiO_3 and other members of the $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ family, we have employed acetylacetonates of lanthanum²⁵ and nickel.²⁶ An appropriate mixture of the two acetylacetonates was taken in methanol solvent (0.1 mol %)

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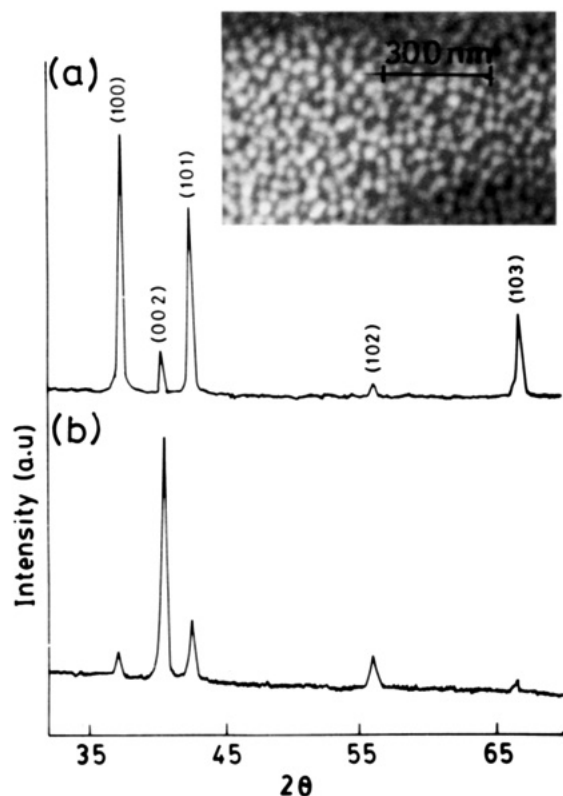


Figure 2. X-ray diffraction patterns of (a) polycrystalline ZnO and (b) of the ZnO film deposited on a glass substrate at 600 K. Inset shows the scanning electron micrograph of the ZnO film.

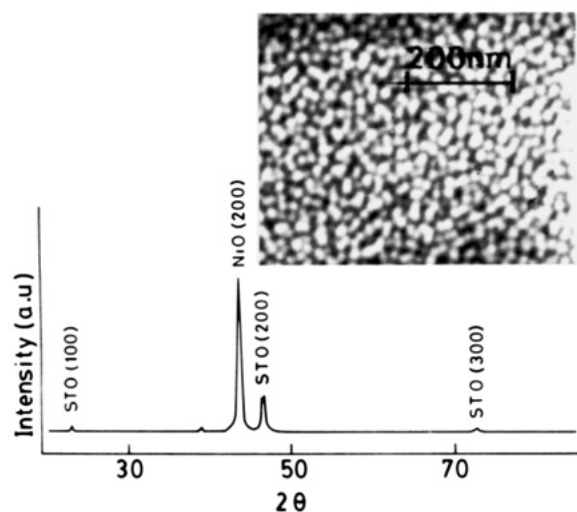


Figure 3. X-ray diffraction pattern of the NiO film deposited on $\text{SiTiO}_3(100)$ at 625 K for 1 h. Inset shows the scanning electron micrograph of the NiO film.

for the purpose of deposition. Methanol was found to be a better solvent than acetylacetonate for depositing the nickelates. We could also deposit films of these nickelates without any solvent, but it was difficult to control the rate of deposition under such conditions. The rate of deposition of the nickelate was primarily controlled by the concentration of the precursors in the solvent. To deposit the films of LaNiO_3 , $\text{La}_4\text{Ni}_3\text{O}_{10}$, $\text{La}_3\text{Ni}_2\text{O}_7$, and La_2NiO_4 , the molar ratios of lanthanum acetylacetonate and nickel acetylacetonate employed are 1:1, 4:3, 3:2, and 2:1, respectively. For depositing $\text{LaCuO}_{3-\delta}$ films, we employed acetylacetonates of lanthanum²⁶ and copper²⁷ (in a

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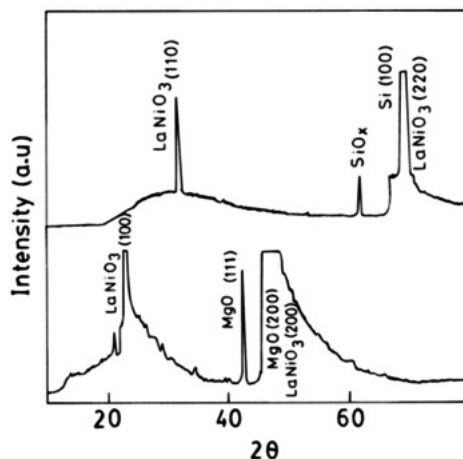


Figure 4. X-ray diffraction patterns of LaNiO_3 films deposited on $\text{Si}(100)$ and $\text{MgO}(100)$ at 675 K (deposition time, 1 h).

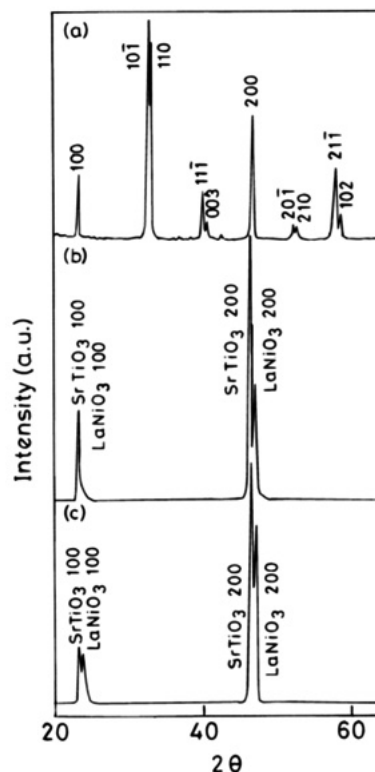


Figure 5. X-ray diffraction patterns of (a) polycrystalline LaNiO_3 and LaNiO_3 films deposited on $\text{SrTiO}_3(100)$ substrate at 675 K for (b) 1 h and (c) 4 h.

1:1 molar ratio) in methanol solvent. Films of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ were deposited using lead acetate and the isopropoxides of zirconium and titanium taken in proper proportions in methanol solvent (0.1 mol %). The films of all the above perovskite oxides were ~ 200 nm thick unless specified.

Results and Discussion

In Figure 4, we show the X-ray diffraction patterns of LaNiO_3 films deposited on $\text{Si}(100)$ and $\text{MgO}(100)$ substrates at 675 K for 1 h and annealed in air at the same temperature for 12 h. Films of LaNiO_3 on the Si substrate, distinctly show the (110) and (220) reflections, with the (220) reflection overlapping with the Si(200) reflections. On the MgO substrate, the (100) reflection of LaNiO_3 is seen, but the (200) reflection overlaps with

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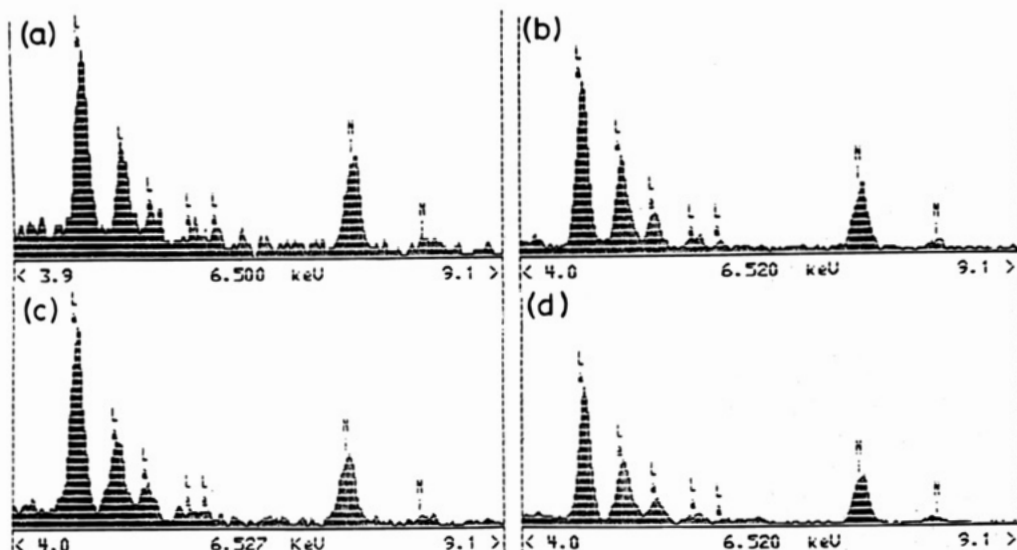


Figure 6. EDX spectra of (a) LaNiO_3 , (b) $\text{La}_4\text{Ni}_3\text{O}_{10}$, (c) $\text{La}_3\text{Ni}_2\text{O}_7$, and (d) La_2NiO_4 films on $\text{SrTiO}_3(100)$ (deposition time, 4 h).

the $\text{MgO}(200)$ reflection. In Figure 5, we show the X-ray diffraction patterns of LaNiO_3 films deposited on a $\text{SrTiO}_3(100)$ substrate for different intervals of time. For the purpose of comparison, we have given the diffraction pattern of polycrystalline LaNiO_3 (Figure 5a). We see indications of the (100) and (200) reflections of LaNiO_3 in a pattern of the film after 1 h of deposition (Figure 5b), but the reflections of the film are not as well delineated from those of the substrate. These reflections are, however, clearly seen in the film deposited for 4 h (Figure 5c), which has a thickness of around $1 \mu\text{m}$. The X-ray diffraction patterns in Figure 5 clearly demonstrate that the LaNiO_3 films are oriented. What is particularly significant is that the orientation obtained by nebulized spray pyrolysis is the same as that obtained by PLD.⁷

In Figure 6 we show a typical EDX spectrum of a LaNiO_3 film (deposited on SrTiO_3) giving a lanthanum-to-nickel ratio of 1:1, thereby confirming the stoichiometry. We have studied the morphology of the LaNiO_3 films deposited on $\text{SrTiO}_3(100)$ substrates by SEM and AFM. We show a scanning electron micrograph in Figure 7a and a surface plot from AFM in Figure 7b. The grains are nearly spherical with good connectivity. The average grain size as shown by SEM is 30 nm. The AFM image shows the presence of particles of 30–40 Å diameter within each grain of 30 nm. Four-probe electrical resistivity measurements (Figure 8) show the LaNiO_3 films deposited on SrTiO_3 to be metallic. The observed resistivity is comparable to the values reported in the literature.^{12,17}

Having obtained good oriented films of LaNiO_3 , we sought to deposit films of the $n = 1, 2,$ and 3 members of the $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ series, starting with the appropriate acetylacetonate mixtures. The substrate temperature and deposition time were 675 K and 4 h, respectively, in all the cases, and the films were annealed at the same temperature for a period of 12 h in air. EDX analysis of the films of these materials (Figure 6) show the lanthanum to nickel ratios to be 1.8:1, 3.1:2, 4:3, respectively, for La_2NiO_4 , $\text{La}_3\text{Ni}_2\text{O}_7$, and $\text{La}_4\text{Ni}_3\text{O}_{10}$. In Figure 9 we show the X-ray diffraction patterns of $\text{La}_4\text{Ni}_3\text{O}_{10}$ on $\text{Si}(111)$ and $\text{SrTiO}_3(100)$ substrates. $\text{Si}(100)$ could not be used as a substrate because of the overlap of its reflections with those of the nickelate. We see that

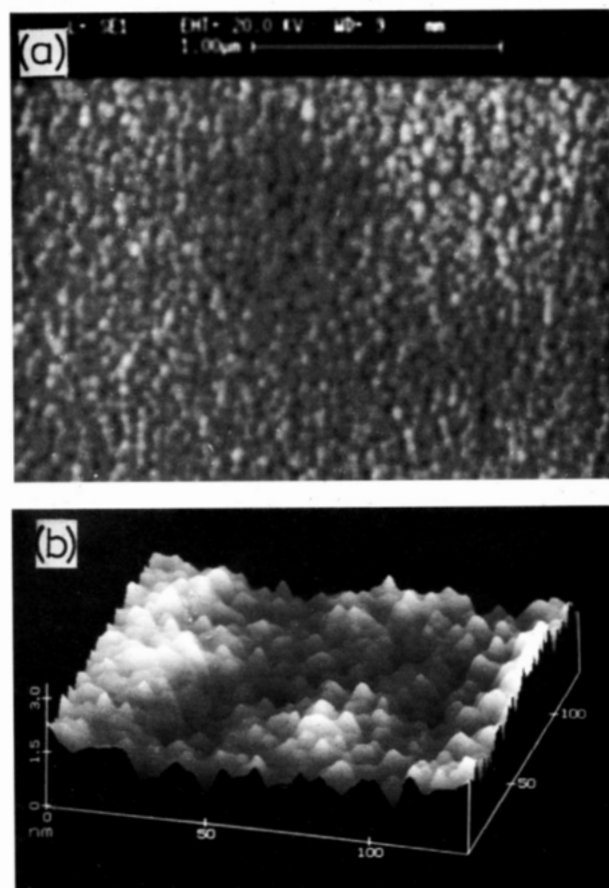


Figure 7. (a) Scanning electron micrograph and (b) AFM surface plot of an LaNiO_3 film deposited on $\text{SrTiO}_3(100)$.

the (008), (0010), (0018) reflections of $\text{La}_4\text{Ni}_3\text{O}_{10}$ on the $\text{Si}(111)$ substrate and the (0014) and (2210) reflections on the $\text{SrTiO}_3(100)$ substrate. The film of $\text{La}_3\text{Ni}_2\text{O}_7$ on $\text{SrTiO}_3(100)$ shows only the (0010) reflection (Figure 8c). There appears to be little doubt that the films of $\text{La}_4\text{Ni}_3\text{O}_{10}$ and $\text{La}_3\text{Ni}_2\text{O}_7$ obtained by us are oriented.

Electrical resistivity data of the $\text{La}_4\text{Ni}_3\text{O}_{10}$ and $\text{La}_3\text{Ni}_2\text{O}_7$ films are shown in Figure 8. $\text{La}_4\text{Ni}_3\text{O}_{10}$ shows the expected metallic behavior, the resistivity being slightly higher than that of LaNiO_3 as reported earlier in the case of bulk samples.¹³ The film of $\text{La}_3\text{Ni}_2\text{O}_7$

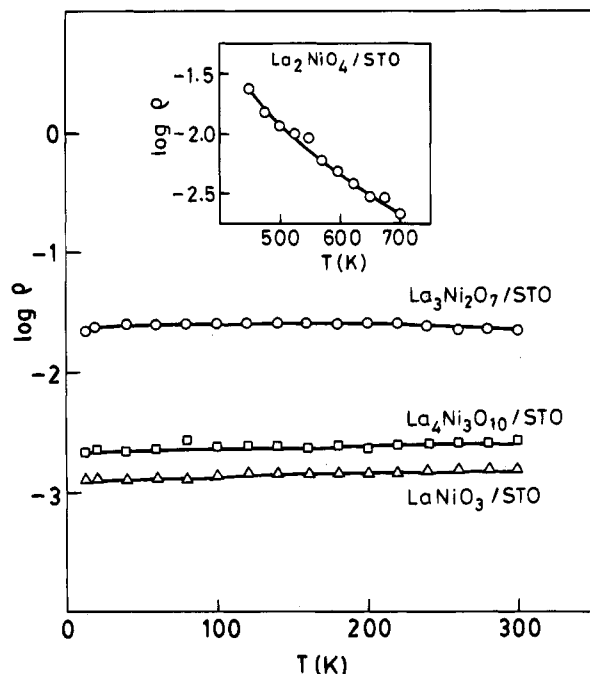


Figure 8. Temperature variation of resistivity ($\Omega \text{ cm}$) of LaNiO_3 , $\text{La}_4\text{Ni}_3\text{O}_{10}$, and $\text{La}_3\text{Ni}_2\text{O}_7$ films deposited on $\text{SrTiO}_3(100)$. The inset shows the behavior of an La_2NiO_4 film.

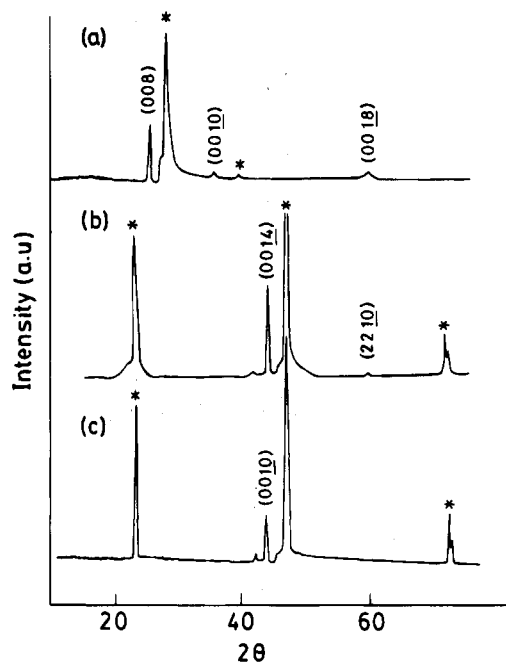


Figure 9. X-ray diffraction patterns of films of (a) $\text{La}_4\text{Ni}_3\text{O}_{10}$ deposited on $\text{Si}(111)$ and (b) on $\text{SrTiO}_3(100)$ and (c) of $\text{La}_3\text{Ni}_2\text{O}_7$ deposited on $\text{SrTiO}_3(100)$. Asterisks indicate substrate reflections.

shows a higher resistivity than that of $\text{La}_4\text{Ni}_3\text{O}_{10}$, but the temperature variation of resistivity is negligible. This behavior is somewhere between that of $\text{La}_3\text{Ni}_2\text{O}_7$ and $\text{La}_3\text{Ni}_2\text{O}_{6.9}$ reported by Zhang et al.¹⁶ The resistivity values obtained by us however differ from these reported by Zhang et al.¹⁶ as well as Sreedhar et al.¹⁷ The latter workers have found $\text{La}_3\text{Ni}_2\text{O}_7$ to be a semiconductor probably because of oxygen deficiency in their sample. It is difficult to prepare good stoichiometric monophasic samples by conventional solid-state routes. The films obtained by us however appears to be nearly stoichiometric with respect to oxygen, probably because

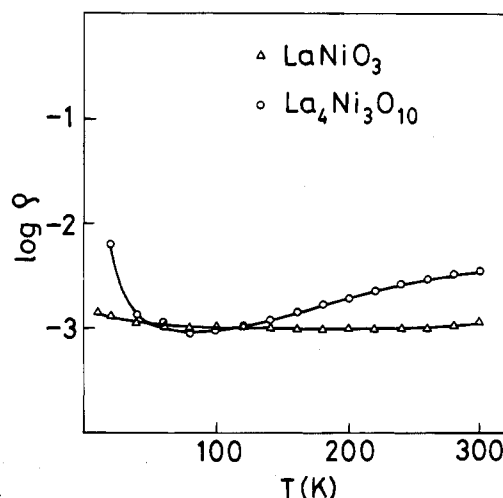


Figure 10. Temperature variation of resistivity ($\Omega \text{ cm}$) of the films LaNiO_3 and $\text{La}_4\text{Ni}_3\text{O}_{10}$ deposited on $\text{Si}(100)$.

of the relatively low temperature involved in the preparation of the films.

We could obtain good films of La_2NiO_4 on $\text{SrTiO}_3(100)$. The resistivity plot of such a film is shown as an inset in Figure 8. The film shows semiconducting behavior at high temperatures consistent with the results of Bassat et al.¹⁵ on bulk samples. $\text{La}_4\text{Ni}_3\text{O}_{10}$ films deposited on $\text{Si}(100)$ substrates show a metal-to-semiconductor transition around 100 K (Figure 10). Sreedhar et al.¹⁷ have found a similar behavior in bulk $\text{La}_4\text{Ni}_3\text{O}_{10}$ around 110 K. The metal-semiconductor transition found by us seems to arise from the depletion of oxygen from the oxide by the silicon substrate. Oxygen deficiency is likely to be responsible for the resistivity behavior of bulk $\text{La}_3\text{Ni}_2\text{O}_7$ reported by Sreedhar et al.¹⁷ as well. Significantly, even the LaNiO_3 film is not really metallic on a silicon substrate (Figure 10).

We attempted to deposit films of $\text{LaCuO}_{3-\delta}$ by taking an equimolar proportion of lanthanum and copper acetylacetonates in methanol solvent. The films deposited on $\text{SrTiO}_3(100)$ and $\text{MgO}(100)$ substrates at 575 K (for 3 h) and annealed at the same temperature in air for 12 h gave oriented films. In Figure 11a we present the X-ray diffraction pattern of such a film deposited on $\text{SrTiO}_3(100)$ showing the (006), (608), (1114), (4212), and (0022) reflections of orthorhombic $\text{La}_2\text{Cu}_2\text{O}_5$.²⁸ We have also obtained films of only $\text{La}_2\text{Cu}_2\text{O}_5$ on both the substrates by depositing at slightly lower temperatures. This is noteworthy since it is difficult to prepare $\text{La}_2\text{Cu}_2\text{O}_5$ in bulk form.²⁸ In Figure 11a there is a reflection around 2θ of 23.113 which we attribute to the (100) reflection of the tetragonal phase of $\text{LaCuO}_{3-\delta}$. On the MgO substrate, we observe the (006), (604), (312), (3118), and (0022) reflections of orthorhombic $\text{La}_2\text{Cu}_2\text{O}_5$ and the (001) reflection at 2θ of 22.353 of tetragonal $\text{LaCuO}_{3-\delta}$. It is possible that by changing the conditions of deposition and by annealing under high oxygen pressures, one may get films containing a higher proportion of $\text{LaCuO}_{3-\delta}$ ($\delta < 1.1$). The cuprate films obtained by us show semiconducting behavior even after annealing in flowing oxygen at 575 or 775 K for 12 h (Figure 12).

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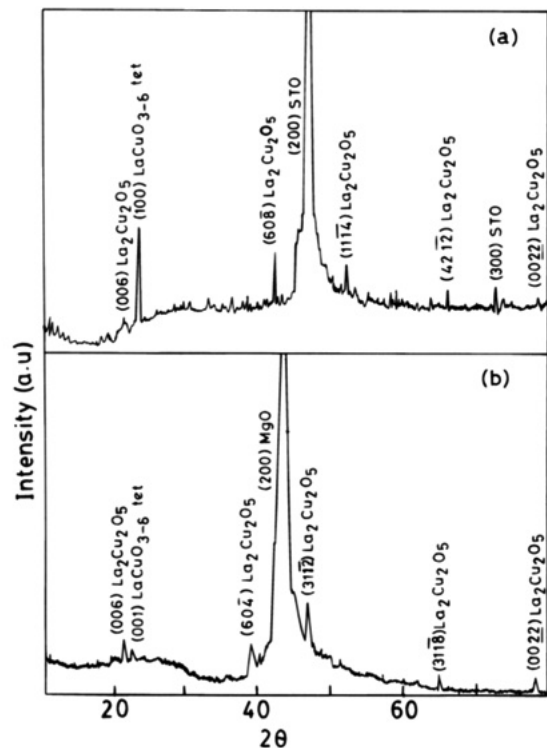


Figure 11. X-ray diffraction patterns of $\text{LaCuO}_{3-\delta}$ films deposited on (a) $\text{SrTiO}_3(100)$ and (b) $\text{MgO}(100)$.

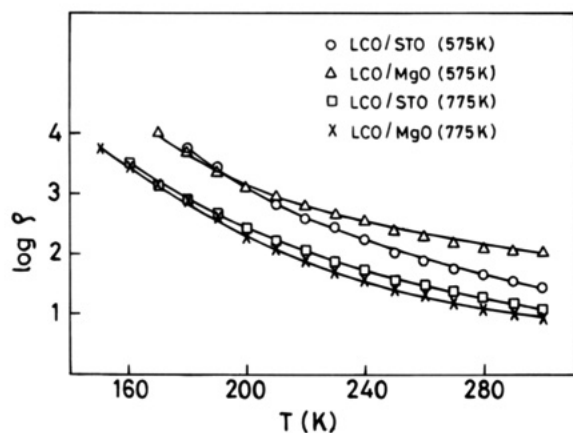


Figure 12. Temperature variation of resistivity ($\Omega \text{ cm}$) of $\text{LaCuO}_{3-\delta}$ films (annealed at 575 and 775 K in oxygen for 12 h) on $\text{SrTiO}_3(100)$ and $\text{MgO}(100)$.

We have successfully deposited films of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ on $\text{SrTiO}_3(100)$ substrates by nebulized spray pyrolysis. In Figure 13 we show the X-ray diffraction pattern of a PZT film deposited by us along with that of a polycrystalline sample. We see that the film shows only the (001) and (002) reflections, indicating that we have a *c*-axis oriented films. The formation of oriented films of PZT by nebulized spray pyrolysis is significant. In Figure 14a we show the scanning electron micrograph of the PZT film deposited on $\text{SrTiO}_3(100)$. The micrograph shows the presence of good connectivity and near spherical grains of $\sim 30 \text{ nm}$. From EDX spectrum of the film shown in Figure 14b, the percentages of Pb, Zr, and Ti were found to be 50, 26, and 24 respectively. The PZT film showed the *P-E* hysteresis loop (Figure 15), characteristic of ferroelectric films with reasonably satisfactory values of the coercive field and remnant polarization.

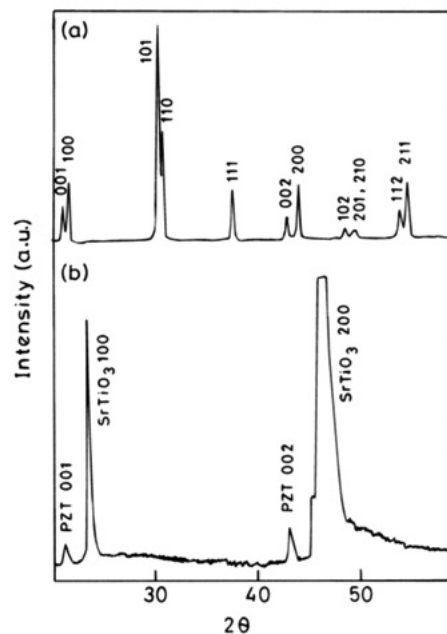


Figure 13. X-ray diffraction patterns of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$: (a) polycrystalline sample; (b) oriented film deposited on $\text{SrTiO}_3(100)$ at 625 K for 3 h.

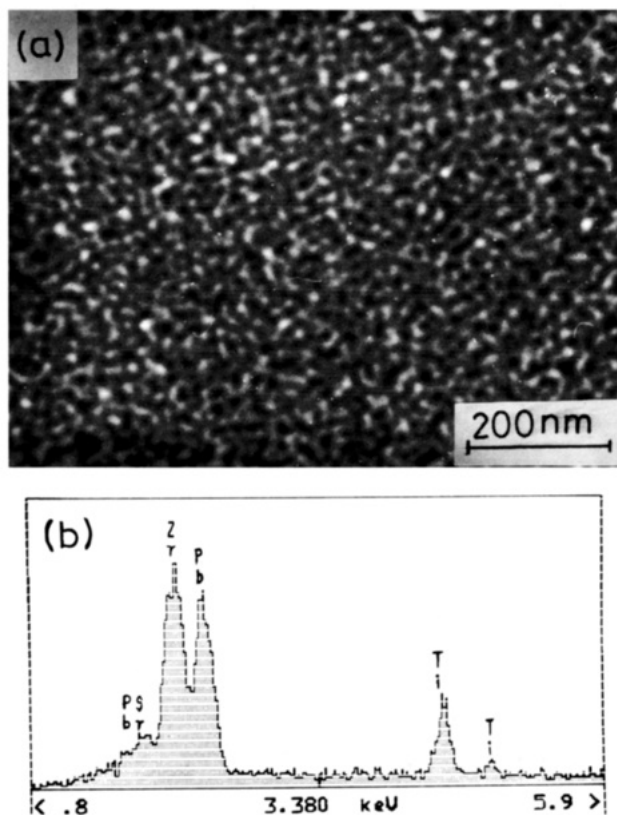


Figure 14. (a) Scanning electron micrograph of a $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ film deposited on $\text{SrTiO}_3(100)$ at 625 K for 3 h and annealed in air for 12 h; (b) EDX spectrum of the same film.

Concluding Remarks

The present study clearly establishes nebulized spray pyrolysis to be a simple and effective route to prepare oriented films of oxide materials on single-crystal solid substrates. A few comments on the mechanism of formation of oriented films would be appropriate.

(i) In the technique employed by us, the dynamics of evaporation as well as of the decomposition of the



Figure 15. Hysteresis loop of the $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ film deposited on $\text{SrTiO}_3(100)$.

precursors determine the nature of the film formed. Generally, high substrate temperature gives thin and more continuous films, but maintenance of stoichiometry, especially in the case of oxides, is unknown. Very low temperatures give films of poor quality. We have made a judicious choice of substrate temperature (neither too low nor too high) to ensure good continuous films which are near stoichiometric as evidenced by transport property measurements in the case of nickelates.

(ii) The heterogeneous nucleation involved in the formation of films is likely to be layer-by-layer growth rather than three-dimensional nucleation and island growth. Almost certainly, the mechanism does not involve the adsorption of the deposited material followed by nucleation. For oriented growth to occur, the initial deposit should be single crystal with a specific plane oriented with respect to the substrate. This is likely to have occurred in the present situation. Furthermore, the nucleation rate for a specific orientation has to be greater under the conditions of deposition. It is likely that the substrate temperature employed by us is favorable for epitaxy. We have, however not been able to establish the epitaxial nature of the films deposited by us. This would require a Φ scan, rocking curves, and HREM.

(iii) The substrate itself has a role in determining the nature of the oriented oxide film. In a pyrolytic reaction of the kind employed here, it is important to have a neutral substrate such as SrTiO_3 , since this does not adversely affect the stoichiometry of the film but favors the oriented film growth. Substrates such as Si are not desirable, since they have a tendency to pick up the oxygen from the oxide film after deposition and create oxygen deficiency in the film.

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