

Notes

Patterning of Rare-Earth Manganate Thin Layer Using Self-Assembled Organic Thin-Film Templates

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Received May 29, 1999

$\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ compounds, where Ln is rare earth and A is divalent element such as Ca, Sr, Ba and Pb, are promising cathode materials in solid oxide fuel cells and catalysts in the oxidation of hydrocarbons or carbon monoxide.¹ Recently, giant magnetoresistance effect (GMR) have been reported in these rare-earth manganates,² which not only drives great fundamental interest in the mixed oxidation states of manganese but also has opened up the possibility of their use as read heads for magnetic sensors.³

The application of these manganates requires preparation of the thin films with particular physico-chemical properties. Cheap and versatile alternatives to physical methods based on evaporation would be the solution techniques which are particularly suitable for large-scale production and coatings. Some methods based on the chelating ligands have been reported but a drawback of deposition processes is that the rheology of the solutions requires repeated coatings and intermediate calcinations to obtain films with a relatively thick films of 100 nm. Therefore, we here describe a new solution method to deposition of thicker films by spin-coating. We have investigated the transport property of the $\text{La}_{0.66}\text{MnO}_3$ thin layer after heat treatment which is particularly sensitive to densification of the film.

For many applications, the ability to pattern films into useful device architectures is a key consideration. The inherent chemical stability and refractory nature of oxide materials often present difficulty in this regard, resulting in requirements for several conditions to effect the patterning of the films, by either chemical etching or ion milling, thus increasing the complexity of any manufacturing process. Recently, self-assembled monolayers (SAMs) have begun to be explored for applications in microfabrication, including microcontact printing ($\mu\text{-CP}$).^{4,9} The patterned SAMs were used as thin resists, to transfer patterns onto thin-films, either by selective chemical etching or by selective deposition. For example, applications of selective chemical etching of the patterned octadecyltrichlorosilane (OTS) layer demonstrate the facile fabrication of elastomeric light valve⁴ and micro-coils on capillaries for high resolution proton nuclear magnetic resonance on nanoliter volumes.⁵ In earlier reports for selective deposition, it has been shown that patterned SAMs of OTS, can be utilized as molecular resists and templates for directing the deposition of thin-films. Patterned metal

thin-films of Cu,¹⁰⁻¹¹ Pt,¹² Pd¹² have been deposited by metal-organic chemical vapor deposition. Patterning of oxide thin-films including LiNbO_3 ,¹³ $(\text{Pb},\text{La})\text{TiO}_3$,¹³ and Ta_2O_5 ,¹⁴ $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ⁸ has been carried out by sol-gel method. Self-assembled monolayers are used in this work to functionalize surfaces with robust hydrophilic thin films, thereby influencing the strength of the interactions of the substrate with reagents used in the sol-gel deposition process. We employ the $\mu\text{-CP}$ to create micrometer scale patterns of organosilane monolayers on the substrates.

The current study extends these earlier works to develop the utility of $\mu\text{-CP}$ method to prepare the rare-earth manganate with giant magnetoresistant property on the single crystal oxide substrate such as LaAlO_3 . A key challenge exists in the patterning of thin films of these oxide materials since both substrate and thin-films oxides display widely disparate dry and wet chemical etch rates.¹⁵ We described here a novel method for patterning the oxide thin layers by selective functionalization of the substrate surface with a printed organic thin-film template.

Experimental

Selective sol-gel deposition of oxide thin films consists of three steps (i) microcontact printing of hydrophobic monolayer patterns on a substrate, (ii) solution (sol-gel) deposition of oxide thin films on the top of patterned functionalized substrate, and (iii) mild, non-abrasive polishing using wet cotton felt.

The substrate surface was patterned with SAMs of OTS by $\mu\text{-CP}$. To do this, the LaAlO_3 substrate had been washed with deionized water, acetone, and 2-propanol and dried with a stream of argon. A similar procedure has been used to pattern the OTS monolayer, with dimensions from 4 μm to 300 μm .⁸

Sol-gel precursor solution was synthesized from metal alkoxides in 2-methoxyethanol solution. Lanthanum methoxyethoxide, lead acetate, and manganese acetate (La : Pb : Mn = 2 : 1 : 3) were dissolved in 2-methoxyethanol, and heated under flowing dry nitrogen. Volatiles were removed by distillation until the condensing vapors reached the boiling point of 2-methoxyethanol. The solution was then diluted with 2-methoxyethanol, and the distillation was

repeated twice. This procedure was necessary to remove water and acetic acid from the precursor solution, which enhanced subsequently combination among Pb, La and Mn alkoxide species. During the final distillation, the precursor solution was concentrated to 1M, based Mn content.

The precursor solution (1 M of Mn) was spun atop OTS patterned LaAlO_3 for 30 seconds at 3000 rpm. After the deposition sample were heated on the hot plate at 200 °C. During pyrolysis, regions of amorphous layers above the OTS functionalized regions were severely cracked and showed poor adhesion. In contrast, well-bound, continuous layers were formed above underivatized regions. The loosely adhered layers were selectively removed by mild mechanical abrasion with cotton felt wetted with 2-propanol. We note that this is but one method which effectively removes the non-adherent materials. Other methods, including hydrothermal treatment, are under investigation. The sample was heated at 900 °C for 1 hour in the oxygen atmosphere to evaporate lead oxide and to obtain sintered $\text{La}_{0.67}\text{MnO}_3$ thin layer.

X-ray diffraction (XRD) data was obtained with a Rigaku D-max IIIA diffractometer (Cu target), while the effect of magnetic field strength on electrical transport was investigated using a Quantum Design SQUID magnetometer in fields ranging up to 7T and temperatures from 5 to 350 K. A standard four-point probe technique was used to determine the resistivity at 1 mA.

Results and Discussion

Selectivity of the deposition is clearly demonstrated by the optical microscopy and the energy dispersive line scan made across the imaged region. Figure 1 shows selectively patterned 100 μm wide $\text{La}_{0.67}\text{MnO}_3$ bars on LaAlO_3 single crystal substrate by hydrophobic OTS-SAMs. The stability of patterned self-assembled films of OTS formed by contact printing has been reported.^{16,17} The resulting films have sig-

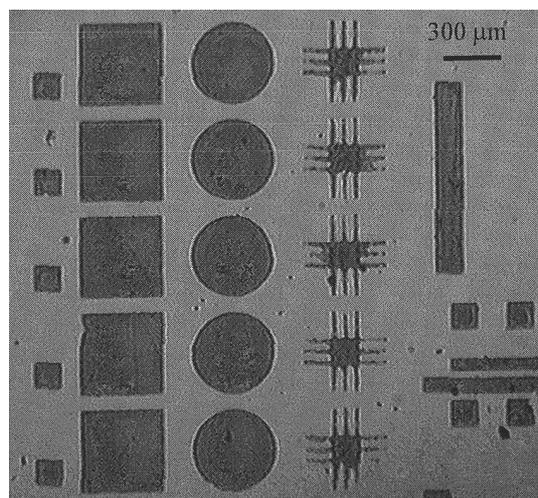


Figure 1. Rare-earth manganate layer spin coated on monolayer-functionalized LaAlO_3 after nonabrasive polishing to remove nonadherent oxide above hydrophobic monolayer.

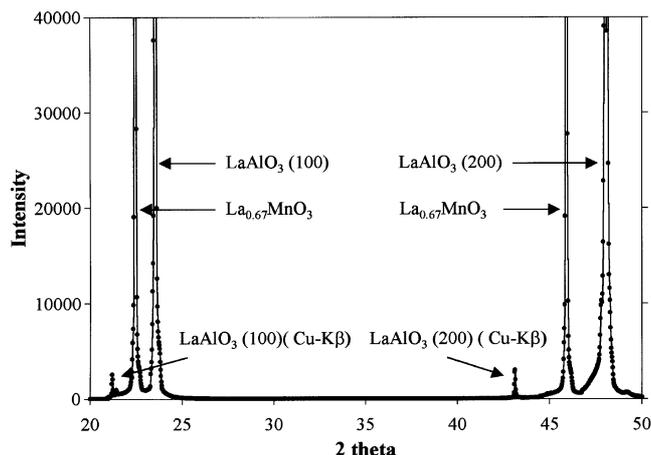


Figure 2. XRD data recorded for $\text{La}_{0.67}\text{MnO}_3$ thin layer crystallized at 900 °C.

nificant mechanical, thermal, and chemical stability enough to apply the sol-gel deposition. It is generally believed that the adsorption of alkytrichlorosilane and other alkylsilanes with hydrolyzable bonds proceeds on hydrated surfaces via the formation of silanols as intermediates, which then react in turn laterally or with surface OH groups to form a network polymer which is covalently bound to the surface in some degree.^{18,19} In this work, the adsorption of OTS on single crystal oxide substrate of LaAlO_3 has been successfully obtained for the patterning of perovskite manganate thin layer.

Thin films of $(\text{La}_{1-x}\text{Pb}_x)\text{MnO}_3$ have been deposited using 2-methoxyethanol solution. The detailed chemical analysis for the precursor solution is now under investigation. In the preliminary analysis of infrared spectroscopy, acetate group remains in the final precursor solution and is considered to help the adhesion of thin layer on the substrates. The nominal composition of prepared thin film after heat treatment at 900 °C could be written as $\text{La}_{0.67}\text{MnO}_3$ confirmed by semi-quantitative energy dispersive spectra. The residual lead content has been observed as the value less than 1% com-

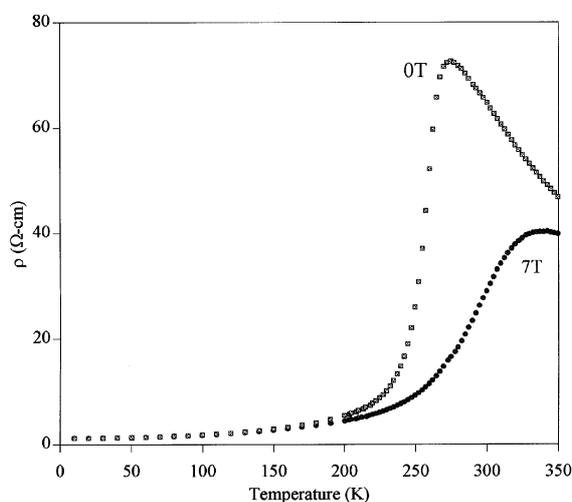


Figure 3. Temperature variation of the magnetoresistance of $\text{La}_{0.67}\text{MnO}_3$ thin layer crystallized at 900 °C.

pared to the initial composition. Phase development of the $\text{La}_{0.67}\text{MnO}_3$ layer, after annealing at 900 in oxygen, was confirmed by examining the X-ray diffraction of the $\text{La}_{0.67}\text{MnO}_3/\text{LaAlO}_3$ (Figure 2). No evidence of secondary phases, such as La_2O_3 and Mn_3O_4 was seen. It is noted that LaAlO_3 (100) substrates yield polycrystalline films with a very strong epitaxial character. The thickness of the deposited oxide layers was obtained as 0.1 μm measured by surface profilometry scan.

The chemical composition of starting materials (La : Pb : Mn = 2 : 1 : 3) was selected by the following synthetic strategy. It has been reported that both $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$ ²⁰ and $\text{La}_{1-x}\text{MnO}_3$ ^{21,22} show GMR effect in the temperature range of 200 to 300 K. It is noted that the deposition of oxide thin layers depends on the internal stress due to the volume changes during the calcination and the crystallization steps. The evaporation of lead oxide at high temperature (900 °C) reduces the stress during the high temperature treatments and enhances the sintering of the perovskite oxide thin layer on the substrate. In the present study, conductive films have been obtained at the temperature as low as 700 °C. Low temperature synthesis allows a higher lead content to give different chemical composition of $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$ with low quality contact between the polycrystallines in the thin film to give higher resistivity.

The resistivity versus temperature at zero field and 7T in the temperature range from 350 K to 5 K for the deposited film is shown in Figure 3. The application of a magnetic field of 7T causes a significant decrease in the resistivity of $\text{La}_{0.67}\text{MnO}_3$ thin film, particularly around room temperature. The curve shows a maximum at 275 K and below that the temperature coefficient of resistivity is positive indicating the metallic nature of the film. This is comparable with the resistivity vs. temperature behavior of the bulk $\text{La}_{1-x}\text{MnO}_3$ samples.²¹ At 300 K, the resistivity of the film was about 60 $\Omega \cdot \text{cm}$ and the magnetoresistance ratio ($\Delta\rho/\Delta\rho_0$) was about 50%, respectively.

In conclusion, microcontact printing of alkylsiloxane monolayers combined with sol-gel processing was found to be effective in producing patterned oxide thin layers on oxide substrate. Continuous oxide thin layer were selectively deposited on area not modified by μ -CP of SAMs. Potential applications were explored by fabrication of $\text{La}_{0.67}\text{MnO}_3$ magnetoresistant materials. Applications as active catalytic membrane and magnetic sensor are envisioned.

Acknowledgment. The research was supported by the National Science Foundation through the Science and Tech-

nology Center for Superconductivity, and by the U. S. Department of Energy, Division of Materials Sciences, through the Materials Research Laboratory.

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