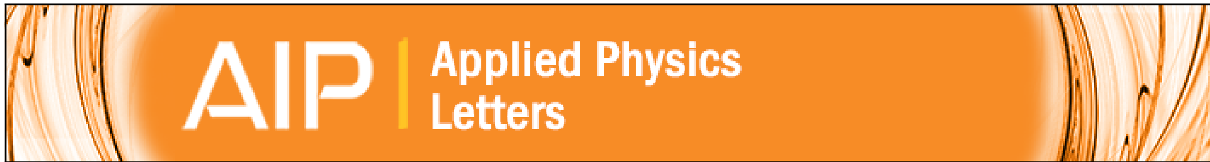

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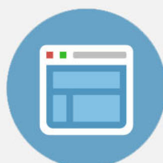

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Very large dielectric constant of highly oriented $Pb_{1-x}Ba_xTiO_3$ thin films prepared by chemical deposition

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Highly (100) oriented $Pb_{0.8}Ba_{0.2}TiO_3/LaNiO_3$ structures were grown on $LaAlO_3(100)$ substrates by using a wet, soft chemical method and crystallized by the microwave oven technique. The Au/PBT/$LaNiO_3/LaAlO_3$ capacitor shows a hysteresis loop with remnant polarization, P_r, of 15 $\mu C/cm^2$, and coercive field, E_c, of 47 kV/cm at an applied voltage of 3 V, along with a dielectric constant over 1800. Atomic force microscopy showed that $Pb_{0.8}Ba_{0.2}TiO_3$ is composed of large grains about 300 nm. The experimental results demonstrated that the microwave preparation is rapid, clean, and energy efficient. Therefore, we demonstrated that the combination of the soft chemical method with the microwave process is a promising technique to grow highly oriented thin films with excellent dielectric and ferroelectric properties, which can be used in various integrated device applications. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1637150]

The development of ferroelectric thin film technology has been receiving great investments due to the possibility of achieving a greater miniaturization of the integrated electronic circuits used nowadays.[1] Many thin films with a perovksite-type structure have been extensively investigated for a variety of integrated device applications. However, it is a generally acknowledged fact that ferroelectric oxide thin films with perovskite-type structure, deposited on $Pt/Ti/SiO_2/Si$ substrates, present serious fatigue problems after a great number of polarization switching cycles.[2] Therefore, much research has been extensively undertaken in order to achieve not only fatigue-free ferroelectric thin films, but also films with high dielectric constant. In order to achieve these characteristics, electrodes based on metallic oxides such as $LaNiO_3$, $SrRuO_3$, $BaPbO_3$, and $YBa_2Cu_3O_{7-x}$, replacing the electrodes based on noble metals like platinum, and the growth of epitaxial or highly oriented thin films, are an alternative approach to reach better properties.[3,4] Among them, the most widely used metallic oxide used in electrodes has been $LaNiO_3$.[5,6] The current interest in ferroelectric thin films, epitaxially or highly oriented grown, is due to the fact that they present better properties than polycrystalline thin films.[7,8] In addition, attempts have been made to enhance the crystallization ability of ferroelectric thin films and metallic oxide electrodes. This has stimulated a search for other techniques for the annealing process, in which conventional annealing (furnace) and rapid thermal annealing processes are utilized nowadays. Another approach utilizes the microwave frequency source of energy that is being developed as a way to process materials and has opened an opportunity to enhance crystallization with a lower annealing processing time, since it decreases the interfacial reactions between ferroelectric thin films and electrodes and also improves the control over the crystallographic orientation of the thin films.[9–11]

Several synthesizing methods are available for the growth of ferroelectric thin films and metallic oxide electrodes, such as metalorganic chemical vapor deposition,[12] pulse laser deposition,[13] magnetron sputtering,[14] and the most common of them involves chemical methods such as sol–gel.[15] Among those methods, wet soft chemical methods have a better potential for technological applications, because of their precise control of composition and homogeneity, and good conformality.[16,17] Bao *et al.*[18] reported $LaNiO_3$ thin films grown on thermally oxidized silicon substrates by the sol–gel technique with the subsequent deposition of $(Pb,La)TiO_3$ thin films also prepared by sol–gel. Wang *et al.*[19] reported the preparation of the highly (100) oriented $Ba_{0.9}Sr_{0.1}TiO_3/LaNiO_3$ heterostructure grown on Si(100) by chemical solution routes. However, there is no report on $Pb_{0.8}Ba_{0.2}TiO_3$ thin films on $LaNiO_3$ bottom electrodes. Moreover, in this current work both $Pb_{0.8}Ba_{0.2}TiO_3$ and $LaNiO_3$ thin films are highly oriented.

In the present work, we report on the preparation of highly (100) oriented $Pb_{0.8}Ba_{0.2}TiO_3$ and metallic oxide $LaNiO_3$ thin films with excellent structural, microstructural, dielectric, and ferroelectric properties on $LaAlO_3$ substrates by the soft chemical method, and a domestic microwave oven was used to crystallize these thin films.

The $LaNiO_3$ and $Pb_{0.8}Ba_{0.2}TiO_3$ thin films were prepared by a wet, soft chemical method, as described elsewhere.[17,20] The $LaNiO_3$ thin films were spin coated on (100) $LaAlO_3$ substrates by a commercial spinner operating at 7200 revolutions/min for 30 s (spin coater KW-4B, Chemat Technology). Each annealing layer was dried at 150 °C for 5 min, and then prefired at 300 °C for 6 h in a conventional oven. After the prefiring, each layer was crystallized in a microwave oven at 700 °C for 10 min. Using the same procedure, the $Pb_{0.8}Ba_{0.2}TiO_3$ thin films were deposited by spinning the precursor solution on the $LaNiO_3/LaAlO_3$ structure. In this case, the thin films were annealed at 600 °C for 10 min in the microwave oven. Through this process, we have obtained thickness values of about 250 nm for $LaNiO_3$ and 300 nm for

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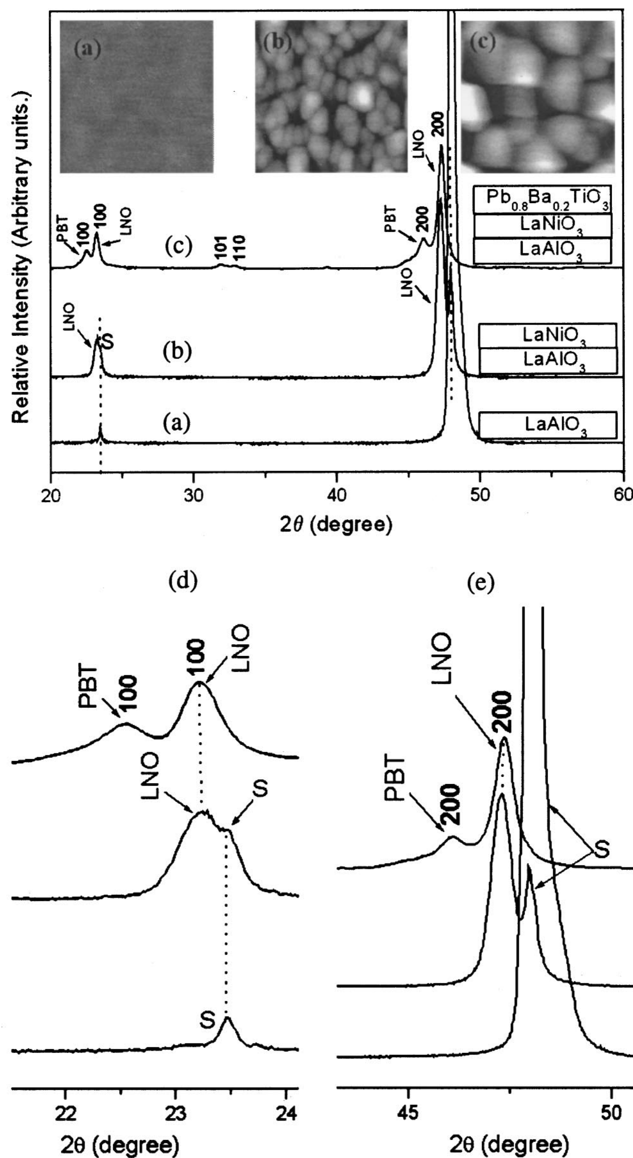

FIG. 1. X-ray diffractograms of (a) the $LaAlO_3(100)$ substrate; (b) $LaNiO_3$ thin film on the $LaAlO_3(100)$ substrate; and (c) the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film on $LaNiO_3/LaAlO_3(100)$. Inset shows the AFM micrographs (1×1 μm) of the (a) substrate; (b) $LaNiO_3$ thin film; and (c) $Pb_{0.8}Ba_{0.2}TiO_3$ thin film. S = Substrate peak. Magnified sections of the x-ray diffractograms, emphasizing the peaks (d) in the 2θ region from 22° to 24° (e) in the 2θ region from 45° to 50°.

$Pb_{0.8}Ba_{0.2}TiO_3$, reached by repeating the spin-coating and heating treatment cycles. The microwave oven used was a simple domestic model similar to that described in Ref. 9.

The structure of the $LaNiO_3$ and $Pb_{0.8}Ba_{0.2}TiO_3$ thin films was analyzed by x-ray diffraction in the θ–2θ mode scan, recorded on a Rigaku diffractometer (D/max-2400) using Cu $K\alpha$ radiation. The microstructure and the thickness of the thin films were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa) and scanning electron microscopy (Zeiss, DSM940A), respectively. The electric properties were measured by an $Au/Pb_{0.8}Ba_{0.2}TiO_3/LaNiO_3/LaAlO_3$ capacitor structure. The upper electrodes of Au for the electrical measurements were prepared by evaporation through a shadow mask with 4.9×10^{-2} mm^2 dot area. Dielectric and ferroelectric properties of the capacitor were measured by an HP4192A impedance/gain phase analyzer and a Radiant Technology

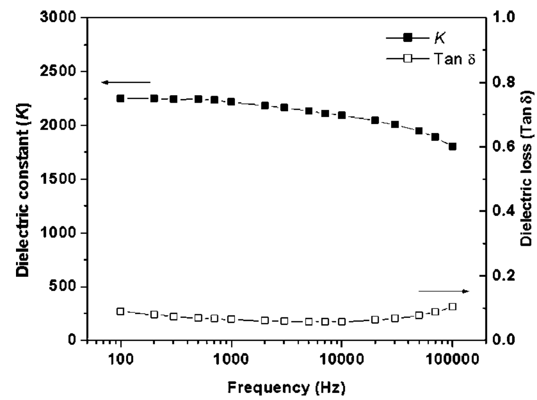

FIG. 2. Frequency dependence of the dielectric constant and dielectric loss of the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film with a $Au/PBT/LaNiO_3/LaAlO_3(100)$ configuration.

RT6000HVS in a virtual ground mode, respectively.

Figure 1 shows the x-ray diffraction patterns for (a) (100) $LaAlO_3$ substrate, (b) $LaNiO_3/LaAlO_3$ structure, and (c) $Pb_{0.8}Ba_{0.2}TiO_3/LaNiO_3/LaAlO_3$ structure. It can be seen that the $LaNiO_3$ thin film electrode annealed at 700 °C for 10 min is highly (100) oriented and crystallizes into the perovskite single phase [Fig. 1(b)]. Figure 1(c) shows the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film deposited on the $LaNiO_3/LaAlO_3$ structure, where the intensities of the (100) and (200) peaks are stronger than those of the (101) and (110) peaks, indicating that the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film is highly (100) oriented and only displays the perovskite phase. Therefore, both thin films are highly (100) oriented, due the following factors; the enhanced crystallization and interfacial growth improvement of the thin films, which were significantly influenced by the microwave treatment, as well as by the matching of the lattice parameters between the $LaNiO_3$ and $Pb_{0.8}Ba_{0.2}TiO_3$ thin films. In Fig. 1(b) the intensity of the (100) peak of the substrate is much weaker than the one related to the (200) peak. This is in agreement with the same order of peak intensity observed in the pure substrate, Fig. 1(a). In Fig. 1(c) there is no substrate peak at all. It may be considered that the thickness of the $Pb_{0.8}Ba_{0.2}TiO_3/LaNiO_3$ structure might play some role in explaining this.

The inset in Fig. 1 shows the AFM surface morphologies obtained in the contact mode of the (a) $LaAlO_3$ substrate, (b) $LaNiO_3/LaAlO_3$ structure, and (c) $Pb_{0.8}Ba_{0.2}TiO_3/LaNiO_3/LaAlO_3$ structure. It was found that the surface of the $LaAlO_3$ substrate is very smooth, with an average surface roughness of 0.07 nm. For the $LaNiO_3$ thin film electrode annealed at 700 °C for 10 min, a smooth, pinhole-free, and continuous surface morphology with no cracks was observed. The average surface roughness value of the $LaNiO_3$ thin film electrode on the $LaAlO_3$ substrate is 10 nm and the average grain size is in the range from 120 to 160 nm [see the inset of Fig. 1 (b)]. The surface morphology of the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film annealed at 600 °C for 10 min on the $LaNiO_3/LaAlO_3$ structure shows large grains with a size of about 300 nm with an average surface roughness of 12 nm [see the inset of Fig. 1(c)].

Figure 2 shows the frequency dependence of the dielectric constant and dielectric loss of the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film on the $LaNiO_3$ bottom electrode. The dielectric constant shows a slight decrease and the dielectric loss slowly in-

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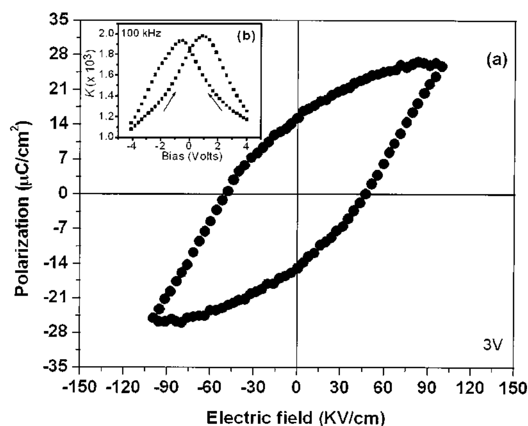

FIG. 3. (a) $P-E$ hysteresis loop and (b) applied voltage dependence of the dielectric constant for the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film with a Au/PBT/$LaNiO_3$/$LaAlO_3$(100) configuration.

creases with increasing frequency. The dielectric constant value at the frequency of 100 kHz is 1804, which is much higher than the one reported by Giridharan and Jayavel,[21] about 118, for sol–gel derived $Pb_{0.8}Ba_{0.2}TiO_3$ thin films on platinum electrodes. In addition, the dielectric constant value obtained in this work is also rather larger than those from other thin films on $LaNiO_3$ bottom electrodes reported in the literature.[22,23] Bao *et al.*[18] reported a dielectric constant value of 1468 at a frequency of 1 kHz and the remnant polarization and the coercive field were about 4.24 $\mu C/cm^2$ and 23.2 kV/cm, respectively, for a $Pb_{0.75}La_{0.25}TiO_3$ thin film prepared by sol–gel on the $LaNiO_3$ bottom electrode. Wang *et al.*[19] related a dielectric constant value of about 650 at a frequency of 1 kHz and the remnant polarization and the coercive field were 10.8 $\mu C/cm^2$ and 96 kV/cm, respectively, for $Ba_{0.9}Sr_{0.1}TiO_3$ thin films on the $LaNiO_3$ bottom electrode. Notice that the dielectric constant value for the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film deposited on the $LaNiO_3$ electrode is much higher than those for films directly deposited on platinum and $LaNiO_3$ bottom electrodes prepared by other techniques. This enhancement may be due to the improvement between the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film and the $LaNiO_3$ electrode interface, which could be a result of the formation of a highly oriented $Pb_{0.8}Ba_{0.2}TiO_3$/$LaNiO_3$/$LaAlO_3$ structure, as well as to the large grain size of the $Pb_{0.8}Ba_{0.2}TiO_3$ thin films. This supports our idea that microwave oven treatments suppress the formation of a very low dielectric constant layer at the thin film/electrode interface, which is the main cause of the lower value of the dielectric constant related to many ferroelectric thin films.[18,24]

$Pb_{0.8}Ba_{0.2}TiO_3$ thin films on the $LaNiO_3$ bottom electrode exhibit ferroelectric characteristics, as can be seen from the hysteresis loop shown in Fig. 3(a). The $Pb_{0.8}Ba_{0.2}TiO_3$ thin film showed good ferroelectricty, and the remnant polarization and coercive field were 15 $\mu C/cm^2$ and 47 kV/cm, respectively. Figure 3(b) shows the electric field dependence of the capacitance or dielectric constant for the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film. A dielectric constant–electric field hysteresis loop is also observed, which reflects the ferroelectric behavior. This corroborates the result of the $P-E$ hysteresis loop in Fig. 3(a). The small value of the coercive field and the high value of the remnant polarization obtained for the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film on the $LaNiO_3$ bottom electrode can be interpreted as the result of highly (100) oriented thin films. However, for achieving these properties, the contribution of the large grain size of $Pb_{0.8}Ba_{0.2}TiO_3$ might also occur, in which the domain walls in the thin films with larger grains are easier to switch under a lower external field, resulting in the small value of the coercive field.

In conclusion, highly (100) oriented $Pb_{0.8}Ba_{0.2}TiO_3$/$LaNiO_3$ structures have been grown on $LaAlO_3$(100) substrates by a wet, soft chemical method and annealed by a microwave oven process. This study indicates that the $Pb_{0.8}Ba_{0.2}TiO_3$ thin film on the $LaNiO_3$ bottom electrode was shown to have excellent structural, microestructural, and electrical properties. The dielectric constant is above 1800, making it a very attractive candidate for many applications. Moreover, the remarkable improvement in all the properties suggests that the wet, soft chemical method, combined with annealing by the microwave oven process, is an alternative approach to obtaining thin films with a quality comparable to the best thin films, suitable for integrated device applications, and processed by conventional methods.

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