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Citation: APL Materials 3, 062504 (2015); doi: 10.1063/1.4915486
View online: http://dx.doi.org/10.1063/1.4915486
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Enhanced electrical and magnetic properties in La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films deposited on CaTiO$_3$-buffered silicon substrates


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(Received 24 January 2015; accepted 26 February 2015; published online 24 April 2015)

We investigate the suitability of an epitaxial CaTiO$_3$ buffer layer deposited onto (100) Si by reactive molecular-beam epitaxy (MBE) for the epitaxial integration of the colossal magnetoresistive material La$_{0.7}$Sr$_{0.3}$MnO$_3$ with silicon. The magnetic and electrical properties of La$_{0.7}$Sr$_{0.3}$MnO$_3$ films deposited by MBE on CaTiO$_3$-buffered silicon (CaTiO$_3$/Si) are compared with those deposited on SrTiO$_3$-buffered silicon (SrTiO$_3$/Si). In addition to possessing a higher Curie temperature and a higher metal-to-insulator transition temperature, the electrical resistivity and 1/f noise level at 300 K are reduced by a factor of two in the heterostructure with the CaTiO$_3$ buffer layer. These results are relevant to device applications of La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films on silicon substrates.

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The full spectrum of electronic, optical, and magnetic properties—e.g., insulating, semiconducting, superconducting, ferroelectric, and ferromagnetic effects—is found within the structurally compatible family of perovskite oxides. The integration of these epitaxial functional oxides with silicon substrates offers significant opportunities for applications. Among them are micro-electromechanical systems (MEMS) based on epitaxial piezoelectric layers and suspended bolometers based on epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films. The use of silicon substrates greatly facilitates the fabrication of MEMS and suspended bolometers, where three-dimensional structures can be efficiently realized by volume silicon micromachining using conventional techniques such as isotropic etching in alkaline solutions (KOH, TMAH, etc.) or reactive ion etching. The ideal case

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2166-532X/2015/3(6)/062504/10 3, 062504-1 © Author(s) 2015

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for such silicon-based heterostructures is one in which the functional oxide film can be epitaxially grown directly on silicon. Such direct integration is, however, complicated by the high reactivity of silicon with oxygen and the disruption of epitaxy that results from the presence of the resulting amorphous silicon oxide layer at the surface of silicon wafers. An epitaxial buffer layer is, therefore, a general prerequisite to the growth of epitaxial functional oxides on silicon having high structural perfection. An additional challenge is the large difference in the thermal expansion coefficients between silicon and these functional oxides; the ratio of thermal expansion coefficients is about a factor of three between room temperature and growth temperature.

To fabricate epitaxial structures in which the properties of the underlying silicon and the overlying film both achieve their full potential, control of the silicon-oxide interface is critical. Fundamental considerations that must be taken into account in the selection of appropriate epitaxial buffer layers include chemical and structural compatibilities. For the case of silicon, a comprehensive analysis of its thermodynamic stability in contact with binary oxides has been performed. Reactions leading to the formation of interfacial silicide, silicate, or SiO$_2$ layers have been reported when these oxides are exposed to high temperatures during device processing. A large number of oxides have been grown epitaxially on Si (100) or Si (111). The list includes SrTiO$_3$, SrO, BaO, BaTiO$_3$, CeO$_2$, ZrO$_2$, YSZ, Y$_2$O$_3$, Sc$_2$O$_3$, Pr$_2$O$_3$, Gd$_2$O$_3$, La(Y)$_2$O$_3$, and γ-Al$_2$O$_3$ as reviewed by Reiner et al. In terms of structural compatibility, few oxides are well lattice matched to (100) Si. The lattice match of the small number of oxides with the perovskite structure that has been epitaxially integrated with (100) Si using a thin (as thin as a single monolayer (ML)) binary oxide buffer layer is shown in Fig. 1. These include CaTiO$_3$, SrTiO$_3$, SrZrO$_3$, and SrHfO$_3$. The latter two, SrZrO$_3$ and SrHfO$_3$, with pseudocubic lattice constants of 4.101 Å and 4.070 Å at room temperature, respectively, lie off the top of Fig. 1.

Among these materials, SrTiO$_3$ (cubic cell with $c = 3.905$ Å) has been the most widely pursued perovskite buffer layer, but due to the large lattice mismatch with Si (1.7%), SrTiO$_3$ begins to relax for thickness beyond a few nanometers in thickness, drastically degrading the crystalline quality of the SrTiO$_3$ buffer layer. CaTiO$_3$ (orthorhombic unit cell with $a = 5.3789$ Å, $b = 5.4361$ Å, and $c = 7.6388$ Å at room temperature), yielding a pseudocubic lattice constant of 3.822 Å, has an excellent lattice match to (100) Si (cubic cell with $c = 5.431$ Å) as is readily apparent from Fig. 1. This makes it an obvious candidate as a buffer layer. Thick, commensurate CaTiO$_3$ layers on (100) Si should be in principle realizable. The excellent lattice match should greatly reduce the in-plane and out-of-plane rotation variation achievable in epitaxial perovskite layers on (100) Si. Although

FIG. 1. Temperature dependence of the lattice constants of the perovskites CaTiO$_3$, SrTiO$_3$, and BaTiO$_3$ compared to the lattice parameter of silicon. The lattice parameters of silicon (and germanium) are divided by $\sqrt{2}$ as is relevant for the in-plane epitaxial alignment of (100)$_p$ ATiO$_3$/[100] Si with [011]$_p$ ATiO$_3$ $\parallel$ [001] Si, where the subscript $p$ denotes pseudocubic indices. The pseudocubic lattice parameter $a_p$ of CaTiO$_3$ is plotted.
reported, the potential of CaTiO$_3$ as a buffer layer to transition from (100) Si to functional oxides with the perovskite structure has been largely ignored.

In this paper, we show that the mineral perovskite, CaTiO$_3$, can be used as a buffer layer in the epitaxial transition from (100) Si substrates to perovskite functional oxides, such as La$_{0.7}$Sr$_{0.3}$MnO$_3$. We demonstrate here that La$_{0.7}$Sr$_{0.3}$MnO$_3$ films deposited on CaTiO$_3$/Si indeed showed enhanced electrical properties (e.g., lower electrical resistivity and $1/f$ noise, and high temperature of the metal-to-insulator transition) as well as enhanced magnetic properties (higher Curie temperature) compared to other epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films deposited on buffered silicon substrates.

We grew epitaxial CaTiO$_3$ thin films on (100) Si by reactive molecular-beam epitaxy (MBE). The native SiO$_2$ layer was removed from the (100) Si substrate using a strontium assisted process. Two monolayers of strontium metal (corresponding to $1.2 \times 10^{15}$ atoms/cm$^2$) were deposited at a substrate temperature of $T = 600^\circ$C. Then, the substrate temperature was increased to $T = 800^\circ$C. At this temperature, the silicon dioxide layer was removed by the formation and evaporation of SiO$_x$, and a single crystalline reflection high-energy electron diffraction (RHEED) pattern with a double-domain 2$\times$1 100 Si reconstruction was observed.

CaTiO$_3$ films were grown using a codeposition technique in a manner analogous to the leading technique for producing the highest quality SrTiO$_3$/Si films. Calcium was evaporated from an effusion cell and titanium from a Ti-Ball$^\text{TM}$ sublimation source. The fluxes of the constituent elements, calcium and titanium, were measured using a quartz crystal monitor and typical values for each element were around $1 \times 10^{13}$ atoms/cm$^2$ s. A substrate temperature of 330 $^\circ$C was used to grow the first 2.5 MLs at a background partial pressure of molecular oxygen of $7 \times 10^{-9}$ Torr. Figure 2(a) shows the RHEED pattern after the deposition of 2.5 MLs of CaTiO$_3$. To improve the crystallinity of the films, the oxygen valve was closed and the substrate temperature was increased, in

![RHEED patterns at various times during the growth of a 50 nm La$_{0.7}$Sr$_{0.3}$MnO$_3$/20 nm CaTiO$_3$/Si heterostructure.](image)

(a) After the growth of 2.5 MLs of CaTiO$_3$ at $T = 330^\circ$C viewed along the [100]$_p$ azimuth of CaTiO$_3$. (b) After the growth of 2.5 MLs of CaTiO$_3$ after annealing in vacuum at $T = 600^\circ$C viewed along the [100]$_p$ azimuth of CaTiO$_3$. (c) After the growth of 20 nm of CaTiO$_3$ viewed along the [100]$_p$ azimuth of CaTiO$_3$. (d) After the growth of 50 nm of La$_{0.7}$Sr$_{0.3}$MnO$_3$ completing the heterostructure viewed along the [100]$_p$ azimuth of La$_{0.7}$Sr$_{0.3}$MnO$_3$. This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://aplmaterials.aip.org/about/rights_and_permissions
vacuum, to 580 °C for 15 min (as shown in Fig. 2(b)). Next, the sample was cooled down to 330 °C to grow a second 2.5 MLs of CaTiO₃ under the same growth conditions as the first 2.5 MLs. Again the sample was annealed in vacuum at T = 580 °C for 8 min. At this temperature, the calcium, titanium, and oxygen shutters were opened simultaneously, and with the oxygen background pressure at 1 × 10⁻⁷ Torr, the thickness of the epitaxial CaTiO₃ layer was grown to 20-40 nm. Figure 2(c) shows the RHEED pattern at the end of the growth of the 20-nm thick CaTiO₃ layer. Rutherford backscattering spectrometry/channeling (RBS/C) utilizing He⁺ ions with an energy of 1.4 MeV was applied to investigate the composition and crystalline quality of the films. The computer software RUMP was employed to analyze the RBS data. The films have a Ca:Ti composition ratio of 1.05 ± 0.05. A RBS/C minimum yield χ_{min} = 12% was observed.

Following the growth of the CaTiO₃ film, 50 nm of La₀.₇Sr₀.₃MnO₃ was deposited on it. The La₀.₇Sr₀.₃MnO₃ film was grown at a substrate temperature of 670 °C by co-deposition in a distilled ozone background pressure of 5 × 10⁻⁷ Torr. The RHEED pattern at the completion of the 50-nm thick La₀.₇Sr₀.₃MnO₃ layer completing the La₀.₇Sr₀.₃MnO₃/CaTiO₃/Si heterostructure is shown in Fig. 2(d).

Film structural properties and morphology were investigated by X-ray diffraction (XRD) and by atomic force microscopy (AFM) in tapping mode (Digital Instruments—Nanoscope III). Cross sectional transmission electron microscopy (TEM) specimens were prepared by mechanical grinding and polishing, followed by argon ion milling (Gatan model 691 Precision Ion Polishing System) to electron transparency. The samples were examined using a JEOL 3011 high resolution TEM, operated at 300 kV.

In Fig. 3(a), a θ-2θ x-ray diffraction scan of the La₀.₇Sr₀.₃MnO₃/CaTiO₃/Si heterostructure is shown. The labels indicate the h00 series of CaTiO₃ and La₀.₇Sr₀.₃MnO₃ peaks. As expected, the La₀.₇Sr₀.₃MnO₃ film grows under compressive strain which results in a larger out-of-plane lattice constant c = 3.905 Å compared to bulk La₀.₇Sr₀.₃MnO₃, which has a pseudocubic lattice spacing of 3.876 Å. Figure 3(b) shows the rocking curve in ω of the 200p reflections of the CaTiO₃ and La₀.₇Sr₀.₃MnO₃ layers of the heterostructure. They have full width at half maximum (FWHM) of 0.67° and 0.71°, respectively. The epitaxy was verified by off-axis φ scans of the 110p CaTiO₃ peak as shown in Fig. 3(b). The peak has a FWHM of 0.86° in φ. A smooth surface with a root mean square (RMS) roughness of 0.5 nm was measured over a 1 μm × 1 μm region by AFM (see Fig. 4). This is the lowest value reported for manganite films of comparable thickness grown on silicon substrates.

The microstructure of the La₀.₇Sr₀.₃MnO₃/CaTiO₃/Si epitaxial heterostructure was studied by TEM. Figure 5(a) shows the overall microstructure of the specimen, including an amorphous SiOₓ layer, which formed in situ by the diffusion of oxygen through the growing epitaxial film and oxidation of the underlying silicon substrate during the film growth. The formation of SiOₓ layers during growth is common in epitaxial oxide on silicon systems when the oxygen partial pressure is high and at the same time, the silicon substrate is hot. The out-of-plane linear defects evident in Fig. 5(a) are rotation domain boundaries, common to CaTiO₃. A typical region of the La₀.₇Sr₀.₃MnO₃/CaTiO₃ interface, exhibiting good epitaxy between the two layers, is shown in Fig. 5(b). A selected-area electron diffraction (SAED) pattern, taken from both film layers simultaneously, is shown in Fig. 5(c). No spot-splitting is evident, consistent with good epitaxy between the two layers.

We have performed electrical and magnetic measurements on this same sample. Electrical resistivity measurements as a function of temperature were performed on unpatterned films by the standard four-probe technique. Magnetization was measured by a superconducting quantum interference device (SQUID) magnetometer. Figure 6(b) reports the magnetization as a function of temperature in a field of 0.01 T. The zero-field-cooled (not shown) and field-cooled magnetizations have been measured. The curve has been fitted by a theoretical standard static Brillouin magnetization function. The La₀.₇Sr₀.₃MnO₃ shows a rapid increase of the magnetic moment below the Curie temperature T_C = 360 K, and the saturated magnetization value at low temperature is 3.5 μB/Mn. These values are similar to the values of bulk La₀.₇Sr₀.₃MnO₃ and the highest reported for thin films grown on silicon substrates. The metal-insulator transition temperature is consistent with the magnetic properties. The temperature dependence of the electrical resistivity is shown in Fig. 6(a). The film shows a metal-insulator transition temperature, T_{MI}, higher than 400 K. This
is the highest value reported for La$_{0.7}$Sr$_{0.3}$MnO$_3$ grown with or without a buffer layer on silicon substrates.\textsuperscript{36–38,44,47,51–55} Moreover, the electrical resistivity value at 300 K is 1.5 m$\Omega$ cm, which is quite similar to bulk La$_{0.7}$Sr$_{0.3}$MnO$_3$.\textsuperscript{56} and lower by a factor 2 compared to what we have obtained in the La$_{0.7}$Sr$_{0.3}$MnO$_3$ films of comparable thickness deposited on SrTiO$_3$/Si by the same MBE technique. We also measured the electrical resistivity of a single CaTiO$_3$ layer on (100) Si substrate to rule out the effect of the oxygen content on the physical properties of CaTiO$_3$.\textsuperscript{21,22} The film was grown under the same conditions as that used for the CaTiO$_3$ part of our La$_{0.7}$Sr$_{0.3}$MnO$_3$/CaTiO$_3$/Si heterostructure whose RHEED patterns are shown in Fig. 2. (b) Rocking curves in $\omega$ of the 200$_p$ reflection of the La$_{0.7}$Sr$_{0.3}$MnO$_3$ and the 200$_p$ reflection of CaTiO$_3$ of the same heterostructure. (c) $\phi$-scan of the 110$_p$ CaTiO$_3$ peak.

FIG. 3. (a) $\theta$-2$\theta$ XRD scans of the same La$_{0.7}$Sr$_{0.3}$MnO$_3$/CaTiO$_3$/Si heterostructure.
heterostructures. The inset of Fig. 6(a) shows the electrical resistance as a function of temperature for a bare 20-nm thick CaTiO$_3$ film on a (100) Si substrate. Insulating behavior over the whole temperature range is observed. This leads us to conclude that both the electrical and magnetic properties are enhanced compared to those reported in high epitaxial quality La$_{0.7}$Sr$_{0.3}$MnO$_3$ films deposited on SrTiO$_3$ buffered Si substrates,$^{39}$ where $T_{MI}$ and $T_C$ values were 350 K and 330 K, respectively. We ascribe the enhancement of these properties to the fact that the La$_{0.7}$Sr$_{0.3}$MnO$_3$ cell is under compressive in-plane strain on CaTiO$_3$/Si as predicted by Millis et al.$^{57}$ and also experimentally observed in Ref. 43.

Electrical low-frequency noise measurements were performed at 300 K in the same way as previously described.$^{39,58,59}$ The La$_{0.7}$Sr$_{0.3}$MnO$_3$/CaTiO$_3$/Si thin film was patterned by UV photolithography and argon ion etching to form a 50 $\mu$m wide and 150 $\mu$m long strip, which includes two gold pads for supplying the current and two gold pads at which the voltage was measured in a four-probe geometry. Figure 7 presents the voltage noise spectral density measured at various
bias currents. We can clearly observe both Johnson (or thermal) noise at high frequency and $1/f$ (or flicker) noise at low frequency. In contrast to Johnson noise, which depends neither on bias current nor on frequency, the latter gives a frequency and bias current dependent contribution to noise, which gives an indication of the material quality.\(^60\) This $1/f$ noise is usually described by the Hooge empirical relation, which does not have any physical basis, but has been shown to agree well with experimental observations for homogeneous samples. This relation is given by the following general formula:\(^61\)

$$
\frac{S_V}{V^2} = \frac{\alpha_H}{n} \times \frac{1}{\Omega \times f},
$$

where $S_V$ is the voltage noise spectral density ($V^2 \text{ Hz}^{-1}$), $V$ is the sample voltage ($V$), $\alpha_H$ is the Hooge parameter (dimensionless), $n$ is the charge carrier density ($m^{-3}$), $\Omega$ is the sample volume ($m^3$), and $f$ is the measuring frequency (Hz). It is very useful to compare the $1/f$ noise magnitude in different materials independent of the sample volume and the bias conditions. In order to estimate the voltage noise spectral density of the material, the noise of the electronic readout and the noise of the voltage contacts were removed. As presented in the inset of Fig. 7, the quadratic dependence of the voltage noise spectral density at 1 Hz and at 300 K versus the sample voltage was verified.

FIG. 6. (a) Resistivity vs. temperature of La$_{0.7}$Sr$_{0.3}$MnO$_3$ grown on CaTiO$_3$/Si. The inset shows the resistivity of a 20-nm thick CaTiO$_3$ buffer layer on silicon. (b) Temperature dependence of the magnetization ($M(T)$) in a magnetic field of 0.01 T of the same heterostructure shown in Figs. 2–4.
FIG. 7. Voltage noise spectral density plots of a 50 µm wide by 150 µm long strip patterned in the same La$_{0.7}$Sr$_{0.3}$MnO$_3$ film of Figs. 2–4 grown on CaTiO$_3$/Si measured at various bias currents. The inset shows the voltage noise spectral density at 1 Hz versus the sample voltage.

within experimental error bars as expected from Eq. (1), thus enabling a correct estimation of $\alpha_H/n$ values. The normalized Hooge parameters $\alpha_H/n$ was then measured to be $(4.2 \pm 0.6) \times 10^{-31}$ m$^3$ at 300 K, which is about two times lower than the one measured in La$_{0.7}$Sr$_{0.3}$MnO$_3$ films of comparable thickness deposited on SrTiO$_3$/Si with $\alpha_H/n$ values of $(9.8 \pm 0.6) \times 10^{-31}$ m$^3$ at 300 K and only two times higher than the one measured in La$_{0.7}$Sr$_{0.3}$MnO$_3$ films of comparable thickness deposited on SrTiO$_3$ single crystal substrates with $\alpha_H/n$ values of $(2.47 \pm 0.6) \times 10^{-31}$ m$^3$.

In conclusion, we have shown the promise of epitaxial (100)$_p$-oriented CaTiO$_3$ as a buffer layer for the integration of functional oxides having the perovskite structure with silicon. Specifically, we have grown high-quality epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$ films on CaTiO$_3$/Si. Both the Curie and the metal-to-transition temperatures are the highest reported values for La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films deposited on buffered silicon substrates. The corresponding electrical resistivity and the 1/f noise level are decreased by a factor of two compared to those measured in high-quality epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films of comparable thickness deposited on SrTiO$_3$/Si. These films exhibit magnetic and electrical properties comparable with bulk La$_{0.7}$Sr$_{0.3}$MnO$_3$, making them of interest for room temperature applications on silicon substrates.

We gratefully acknowledge the financial support of Intel and the National Science Foundation through the MRSEC program (Grant Nos. DMR-1120296 and DMR-1420620), and Grant Nos. ECCS-0708759 and DMR-0315633. This work was performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation (Grant ECCS-0335765).