La$_{1-x}$Sr$_x$MnO$_3$ Thin Films on Silicon Prepared by Magnetron Sputtering: Optimization of the Film Structure and Magnetic Properties by Postdeposition Annealing

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Herein, a systematic study of postdeposition annealing for La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) films regarding their structural, electronic, (magneto-)optical, and magnetic properties is presented. The samples are prepared by magnetron sputtering at room temperature on silicon (111) substrates with native oxide and are annealed in ambient atmosphere for 12 h in a temperature range from 600 to 875 °C. The stoichiometry of the films is investigated by X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy is utilized to investigate the vibrational modes of the films. The diagonal and off-diagonal components of the dielectric tensor are investigated by variable-angle spectroscopic ellipsometry and magneto-optic Kerr effect (MOKE) spectroscopy, respectively. The remanence and the coercive field of the layers are characterized by superconducting quantum interference device (SQUID) magnetometry. The magnetic properties are found to improve with increasing annealing temperature up to 850 °C, whereas the resistivity remains within a range between 0.5 and 2 Ωcm. The highest suitable annealing temperature for applications is, however, 775 °C due to the formation of a diffusion layer between LSMO and silicon oxide at higher temperatures.

1. Introduction

Manganites crystallizing in the perovskite structure have attracted significant attention in the past years. In particular, the La$_{1-x}$Sr$_x$MnO$_3$ compounds are very interesting for fundamental research and practical applications, as their magnetic and electric properties are tunable by the concentration of strontium. Out of this family, La$_{0.66}$Sr$_{0.34}$MnO$_3$ is often used as electrode material for spintronic applications due to its almost 100% spin polarization at the Fermi level and high Curie temperature well above room temperature. To achieve a high degree of crystallinity and high Curie temperature, the LSMO electrode layers are typically deposited by pulsed laser deposition (PLD) on single-crystalline substrates with similar lattice constants, e.g., SrTiO$_3$ (STO).

Silicon, one of the most common substrate materials in semiconductor technology, has a different thermal expansion coefficient and lattice constant compared with LSMO. Therefore, LSMO layers deposited onto Si(111) with native oxide are expected to exhibit in the best case a polycrystalline structure. This is probably the reason why LSMO on Si is less investigated than single-crystalline layers deposited on lattice-matched substrates such as LaAlO$_3$ or STO. In most of the reported studies the LSMO layers were fabricated on substrates kept at elevated temperatures independently of the substrate used.

When LSMO deposition was conducted on substrates kept at room temperature, a subsequent annealing step of the samples in oxygen atmosphere or in ambient conditions was necessary to promote the LSMO crystallization. Thermal annealing treatments in pure flowing oxygen were conducted at high temperatures, for example, up to 1200 °C on STO substrates. For silicon, it is very likely that thermal annealing at 800 °C or above results in a reaction between the substrate and the film as known for other materials (e.g., YBa$_2$Cu$_3$O$_7$ on Si) as well as for spin-coated La$_{0.7}$Sr$_{0.3}$MnO$_3$.[21] The highest annealing temperature $T_A$ for a rapid thermal annealing treatment of LSMO on silicon was found to be 800 °C due to the diffusion of silicon into the LSMO layer at 850 °C. This aspect has not yet been considered in all LSMO/Si studies, although annealing temperatures up to 1000 °C were reported. It is therefore important to systematically investigate the structural and magnetic properties of LSMO films on silicon with particular emphasis on the interface properties as a function of the annealing conditions to identify the temperature window, in which high-quality polycrystalline ferromagnetic LSMO films can be obtained.

In this study, we utilized the magnetron sputtering technique to prepare amorphous LSMO films at room temperature on Si(111) substrates covered with native oxide and subsequently annealed the films under ambient conditions. Optical and photoelectron spectroscopy methods, as well as magnetic...
characterization methods, were applied to assess the correlation between the annealing temperature and the structural and magnetic properties of the films.

2. Results and Discussion

2.1. Raman Spectroscopy

The Raman spectra of the substrate, of the as-deposited film, and of the films annealed at 600 and 625 °C are shown in Figure 1c. The Raman modes at 300, 440, 520, 620, and 680 cm⁻¹ belong to the silicon substrate. In addition, a broad Raman band of amorphous LSMO can be seen at 630 cm⁻¹. This band is forbidden in LSMO bulk and can occur due to symmetry lowering. With increasing annealing temperature $T_A$, the intensity of this band decreases, while new modes appear at 423 and 190 cm⁻¹. These modes were already observed for LSMO and LCMO and are claimed to stem from vibrations of the manganese oxide octahedron in the perovskite crystal. From the spectral evolution with $T_A$, one can conclude that the crystallization of sputtered LSMO layers on silicon starts in the temperature range between 600 and 625 °C.

In the $T_A$ range from 650 to 750 °C, the Raman spectra of the LSMO films undergo no visible changes (Figure 1b), indicating that the structural ordering in LSMO does not change significantly in this temperature range.

When $T_A$ exceeds 775 °C (Figure 1a), the mode at 190 cm⁻¹ decreases in intensity and it disappears at $T_A = 800$ °C, whereas new modes appear at 145, 178, 490, 590, 610, and 667 cm⁻¹. Their intensities increase with annealing temperature. These new bands occurring in the Raman spectra are an indication of pronounced structural changes in the film. The layer annealed at 875 °C showed in X-ray photoelectron spectroscopy depth profiling (XPS-DP) (see Section 2.2) a complete intermixing of the LSMO film with silicon oxide, leading to the conclusion that the Raman modes mentioned earlier are due to a diffusion layer at the interface.

2.2. XPS-DP and Reflective Electron Energy Loss Spectroscopy

The technique of XPS-DP includes repetitive XPS scans after ion beam etching steps eroding the sample surface. This makes it possible to investigate the sample layer by layer with a resolution determined by the escape depth of the investigated electrons, of around 10 nm. To determine the composition of the film it is necessary to fit the XPS spectra (see Figure 2).

The stoichiometry was determined from the peak areas, calculated in a fitting procedure using Thermo Fisher-adjusted element sensitivity factors first discussed by Scofield and additional information about the instrument (e.g., the transmission function). The total peak area for an orbital of one element was calculated by adding the areas of photoelectron peaks and the satellites of the photoelectron peaks while excluding loss features. A loss feature is a peak in the spectrum caused by photoelectrons losing a certain amount of energy due to scattering. To identify the loss features, reflective electron energy loss spectroscopy (REELS) was conducted. For this, the sample was exposed to electrons with a kinetic energy of 1000 eV and elastic as well as inelastically scattered electrons were measured. The so-created spectrum has no satellites and it is, therefore,
straightforward to identify electron energy loss features, EELF, or plasmons in the spectrum. The loss spectrum of the sample annealed at 775 °C is shown in Figure 3. The inelastically scattered electrons are presented in a 50× magnified scale. The spectrum shows three features at 5, 14, and 28 eV. Broad peaks in the XPS spectrum having a binding energy which is close to these values but higher than the binding energy of a photoelectron peak can be considered as loss features; see, for example, Figure 2: the broad peak at 117 eV has a binding energy, which is about 14 eV higher than the La 4d photoelectron peak and can therefore be considered as an electron energy loss peak of this peak.

An exemplary XPS spectrum of the layer annealed at 775 °C after an Ar⁺ sputtering time of 96 min is shown in Figure 2 as an example for the fitting procedure. The Mn 3s, La 4d, Si 2p, Sr 3d, and Si 2s orbitals were fitted with 2, 3, 2, 2, and 2 components, respectively. The full width at half maximum, FWHM, was kept identical for both components of one doublet.

It is well known that the Mn 3s peak splits into two peaks with one corresponding to the core level and the other to a satellite feature. The La 4d deconvolution into three doublets was conducted according to the work by Sunding et al. The doublet with the lowest binding energy originates from La atoms in the ground state, whereas the other two doublets are strong satellites due to excited atoms with electrons in the 4f band. During the DP procedure, Si 2s and Si 2p peaks appear in the spectra. The area of the Si 2p peak overlaps with the La 4d peak and it was fit by coupling its intensity to the free-standing Si 2s peak, whereas the FWHM was constrained to the value of silicon dioxide. This gives a good measure for the area of the Si 2p peak. The splitting of the Si 2s peak in two components might be caused by two different chemical environments, one due to SiO₂ and one due to a diffusion layer between LSMO and SiO₂. The same splitting into two features was also considered during the fitting procedure for the Si 2p feature. At a binding energy of 117 eV, which is 14 eV higher than that of the La 4d peak, a broad feature is visible. After cross checking with the REELS spectrum, this feature was identified as an EELF.

The Sr 3d orbital splits in two doublets. This might be explained by 1) different chemical environments of the surface and bulk atoms (a surface core-level shift[21]; 2) different chemical environments due to Mn⁺ and Mn⁴⁺ ions[21]; or 3) the existence of a ground state and a satellite peak.

The XPS-DP raw data are shown in Figure 4. The spectral intensity is plotted here in color scale with respect to the binding energy and the etching time. For all graphs, the LSMO/air interface of the sample is at the top and the silicon is at the bottom. For the samples annealed at 800, 825, and 875 °C, the Ar⁺ etching process was stopped when the SiO₂ layer was reached. It is clearly visible that the interface LSMO to SiO₂ is sharp for the sample annealed at 625 °C. By increasing the annealing temperature to 750 °C, the SiO₂ layer grows and interdiffusion of silicon into the LSMO layer occurs. Furthermore, after etching the sample for ∼50 min, the Sr 3d, La 4d, and Mn 3s peaks shift toward lower binding energies. This might be caused by the growth of the silicon oxide layer fed by oxygen atoms from the LSMO layer. Such a process would lead to a reduction of the metals in LSMO and therefore in a shift toward lower binding energies. The interdiffusion is even more pronounced at 775 °C, though it increases significantly at 800 °C, where half of the layer thickness shows a Si signal. The DP from the sample annealed at 875 °C shows a complete intermixing of the SiO₂ substrate layer with the LSMO film which means that the LSMO layer was destroyed.

As reported earlier by, for example, Leufke et al.[22] for LSMO magnetron-sputtered thin films, the stoichiometry of the layers differs from that of the target. This can be easily seen comparing the XPS spectra of the film annealed at 750 °C and target shown in the Supporting Information (Figure S1). It is clearly visible that the Mn-to-La ratios are quite similar in film and target, whereas the concentration of Sr is significantly reduced in the film. The stoichiometry of the target was determined to be in good agreement with the specification of 61.4% (60%) oxygen, 19.3% (20%) manganese, 13.6% (13.3%) lanthanum, and 5.7% (6.6%) strontium, with each value having a statistical uncertainty of 2%.

The stoichiometry profiles of the layers annealed at 625, 750, 775, and 800 °C are shown in Figure 5 as a function of Ar⁺ etching time. The experimental etching time was not converted into values of film depth in nanometers because the films show a different layer thickness before and after annealing. As the initial layer thickness was the same, the films should have different densities due to crystallization so that each film has a different etching rate in depth. Furthermore, the sputtering yields are different for different elements.

The stoichiometry evaluation of the DP is strongly influenced by the monoatomic Ar⁺ etching procedure in a way that the stoichiometry changes during the Ar⁺ etching process (Figure 5). With increasing etching time, an increase in the La and a decrease in the O content are observed. This is caused by the known side effect of monoatomic Ar⁺ etching[24] to induce a change in the oxidation state of metals and change the stoichiometry due to different sputtering yields of elements. Nevertheless, the concentration of Sr with respect to Mn and La is lower than expected, even before the DP procedure. In addition, the data show a rather slow decrease in La content with respect to Mn at the LSMO/SiO₂ interface indicating that the sputtering yield of this compound is lower for La atoms than for all other atoms. The interface can be considered sharp in

![Figure 3](link) REELS spectrum for the film annealed at 775 °C. Electron energy loss is defined as excitation energy minus measured kinetic energy. The excitation energy was 1000 eV.
the case of annealing temperatures of 625 and 750 °C. The gradual concentration change of the LSMO layer content at the interface with SiO₂ can be explained by the electron escape depth of around 10 nm at a kinetic energy of about 1350 eV. Furthermore, a spatially nonhomogeneous erosion by the ion beam could explain the additional broadening of the stoichiometry profile, but as the etching crater was chosen to be five times larger than the X-ray spot, this influence should be negligible. Even though the XPS-DP technique with monoatomic Ar⁺ ions has some drawbacks in terms of preserving the stoichiometry, one can rely on the determined properties of the interface because the small ion energy does not induce a pronounced intermixing. For the layers annealed at 750 and 775 °C, small amounts of silicon are detectable after 70 min Ar⁺ etching time and the silicon concentration increases more significantly after additional 20 min. However, the concentration of La and Mn decreases much slower with respect to the etching time for the sample annealed at 775 °C compared with the sample annealed at 750 °C. This
indicates the growth of a silicon oxide layer at the interface accompanied by an interdiffusion between the thermally grown silicon oxide and LSMO. This effect is drastically increased if $T_A$ is increased to 800 °C. Here the Si 2s and Si 2p core-level peaks are already visible in the XPS spectrum after 60 min Ar⁺ etching and the La concentration is close to 0 after ~160 min Ar⁺ etching instead of 140 min for the sample with $T_A = 775$ °C. The existence of the diffusion layer is responsible for the new intense Raman modes at 590 and 667 cm⁻¹ for $T_A$ higher than 775 °C. This is proven by the fact that the layer annealed at 875 °C appeared to be entirely intermixed with silicon (see Figure S2 of the Supporting Information). In addition, the results show that the etching time for the silicon oxide layer increases with $T_A$. This indicates that during the annealing procedure, oxygen from the ambient atmosphere diffuses through the LSMO layer to feed the growth of the silicon oxide at the interface. It is, thus, crucially important to take the growth of SiO₂ into account when calculating the dielectric function of the LSMO films on silicon (see next section).

2.3. (Magneto)-Optical Spectroscopy

2.3.1. Variable-Angle Spectroscopic Ellipsometry (VASE)

The variable-angle spectroscopic ellipsometry (VASE) data modeling of the as-deposited layers was conducted simultaneously for six samples with thicknesses in the range between 80 and 100 nm using an optical multilayer model. The dielectric functions of the layers were assumed to be optically isotropic due to their amorphous structure. The model took into account the dielectric functions of silicon from the study by Veis et al.[27] (with a thickness of 1 mm) and of silicon oxide from the study by Calderon et al.[28] (with a thickness of 2 nm). A general oscillator layer with variable thickness was applied to account for the LSMO layer. This allows the determination of the dielectric function, on the one hand, and of the layer thickness of the amorphous LSMO, on the other hand. To fit the data of the samples annealed at temperatures higher than 625 °C, it was necessary to fit the increased layer thickness of the silicon oxide below the LSMO layer. As indicated by the XPS results, the silicon oxide layer thickness increased during the annealing process, most likely due to a diffusion of oxygen through the LSMO layer.

It should be noted that upon annealing the LSMO layer thickness decreases. Therefore, we will consider in the further discussion the relative thickness change (RTC), defined as the difference between the thicknesses after and before annealing divided by the thickness before annealing. Its evolution with annealing temperature is shown in Figure 6, while the absolute thickness values can be found in the Figure S3, Supporting Information. It can be seen that the RTC (i.e., the LSMO layer thickness) decreases with increasing annealing temperature until it reaches a plateau of 37% in the temperature range between 725 and 775 °C. This change may be explained by crystallization of LSMO as observed in other reports with a reduction of 16% for sputtered and annealed La₀.₅₆Li₀.₃₃TiO₃ layers[25] and up to 31% for dip-coated Lu₂O₃:Eu³⁺, Tb³⁺ films[26]. For the layer...
annealed at 800 °C, the XPS-DP results showed a strong interdiffusion between LSMO and silicon oxide. In this case, the RTC value is not trustable because the ellipsometry model does not take into account the diffusion layer. The implementation of the inhomogeneous diffusion layer in the ellipsometric data modeling was not considered because the diffusion is undesirable and hence an annealing at 800 °C should be avoided in technological applications.

The diagonal components $\varepsilon_{xx} = \varepsilon_{xx1} + i\varepsilon_{xx2}$ of the dielectric tensor $\varepsilon$ obtained from the modeling of the ellipsometry data are shown in Figure 7. The real part $\varepsilon_{xx1}$ is a measure of the polarizability of the material, whereas $\varepsilon_{xx2}$ is the imaginary part related to the dielectric losses of the material. The dielectric functions of the as-deposited layer and the layer annealed at 600 °C are very similar (Figure 7), indicating no major structural changes at this $T_A$. The absorption of the layer annealed at 625 °C shows an additional feature in the low-photon-energy range (Figure 7). This feature increases with $T_A$. In addition, the absorption feature occurring at around 3.5 eV for the as-deposited film shifts to 4.0 eV starting with a $T_A$ of 625 °C. This feature remains at the same energy and its intensity increases only slightly with increasing $T_A$ (Figure 7).

The line shape and the values of the dielectric function are consistent with those of LSMO deposited on STO as reported by Veis et al.\cite{27} but they differ significantly from the dielectric function of LSMO films grown on Si(100) reported by Calderón et al.\cite{28} This discrepancy can be explained by the fact that Calderón et al. annealed the LSMO films at 900 °C. This may have caused the growth of SiO$_x$ and an interdiffusion between silicon oxide and LSMO, which were not accounted for in their calculation of the dielectric function.

We should note here that the VASE data of the layers annealed at temperatures higher than 800 °C could not be fitted with the optical model described in the beginning of this section. The dielectric function determined for the layer annealed at 800 °C should be considered with care due to the occurrence of the diffusion layer, as already discussed in the Raman spectroscopy and XPS-DP sections. This dielectric function should be understood as an effective dielectric function of LSMO with a diffusion layer.

Figure 6. Relative LSMO layer thickness change (RTC) versus annealing temperature. RTC is defined as the difference between the thicknesses after and before annealing divided by the thickness before annealing.

Figure 7. Real and imaginary parts of $\varepsilon$ for different $T_A$. On the left-hand side are the dielectric functions of the as-deposited layer and the layers annealed between 600 and 675 °C, while the right-hand side shows the dielectric functions of the layers annealed between 700 and 800 °C.
2.3.2. Magneto-Optical Kerr Effect Spectroscopy

To obtain information about the off-diagonal elements $\varepsilon_{xy} = \varepsilon_{xy1} + i\varepsilon_{xy2}$ of the dielectric tensor $\varepsilon$ of the LSMO layers, spectroscopic magneto-optic Kerr effect (MOKE) measurements were carried out. The MOKE spectra recorded for different annealing temperatures are shown in Figure 8 as open symbols together with the modeled data (solid lines).

Due to different silicon oxide layer thicknesses, and thereby different optical interference conditions, the spectra differ significantly from each other. The spectrum of the film annealed at 600 °C shows a signal which is about a factor of 4 smaller than the one for the film annealed at 625 °C, whereas the line shape of both spectra is similar. This is not the case for the spectrum of the film annealed at 775 °C. Even if the order of magnitude of the Kerr angle is the same, the line shape is completely different compared with the films annealed at lower temperatures. The 800 °C annealed film shows an entirely different spectral line shape compared with the previous ones and the signal itself increases by one order of magnitude.

Due to these strong spectral changes, it is difficult to relate the MOKE spectra with the intrinsic magneto-optical signal of the LSMO films. Therefore, it is necessary to model the MOKE spectra to extract the off-diagonal elements of the dielectric tensor. As input parameters for modeling the measured MOKE spectra, the diagonal elements $\varepsilon_{xx}$ of the dielectric tensor and the layer thickness obtained from VASE data modeling were used. The fitting of the MOKE spectra was conducted using WVASE32 software assuming optically isotropic layers. Even though there are some differences between the modeled and the measured data, the line shape agreement is very good.

$\varepsilon_{xy}$ of the LSMO layers obtained from the optical model fits are shown in Figure 9. They are very similar to each other in the $T_A$ regime 625–775 °C despite the difference observed in the corresponding MOKE spectra. This indicates that the effects of optical interference in the LSMO/SiO$_2$/Si heterostructure were properly considered in the optical model fit procedure and the resulting $\varepsilon_{xy}$ represents the intrinsic magneto-optical properties of the LSMO film. The small Kerr angle observed for $T_A = 600$ °C can be explained by incomplete crystallization, leaving large amorphous regions that show no pronounced ferromagnetism, which is in agreement with the Raman, SQUID, and VASE results. The energy dispersion of $\varepsilon_{xy}$ of the layers annealed between 625 and 775 °C is consistent with the one reported by Veis et al.[27] for single-crystalline LSMO films on STO, except for a shift of 0.2 eV toward higher photon energy in our case. This shift might be explained by the different stoichiometry. The discrepancy between the $\varepsilon_{xy}$ of the sample annealed at 800 °C and the other layers must be due to the interdiffusion between silicon oxide and LSMO as discussed earlier.

To identify optical transitions probed by MOKE, it is necessary to consider the complete dielectric tensor $\varepsilon$ with the dielectric function (diagonal component) $\varepsilon_{xx} = \varepsilon_{xx1} + i\varepsilon_{xx2}$ and the off-diagonal element $\varepsilon_{xy} = \varepsilon_{xy1} + i\varepsilon_{xy2}$:

$$
\varepsilon = \begin{pmatrix}
\varepsilon_{xx} & \varepsilon_{xy} \\
-\varepsilon_{xy} & \varepsilon_{xx}
\end{pmatrix}
$$

(1)

The dielectric functions for right- (RCP) ($\varepsilon_+$) and left- (LCP) ($\varepsilon_-$) circular polarized light are calculated as the sum of the
Therefore, the optical transitions induced by RCP and LCP light can be identified by looking at the real part $\varepsilon_{xy1}$ of the off-diagonal element

$$\varepsilon_{\pm} = \varepsilon_{xx1} \mp i\varepsilon_{xy1} + i(\varepsilon_{xx2} \pm \varepsilon_{xy2})$$

(3)

The following considerations should be taken into account: if $\varepsilon_{xy1} = 0$, the RCP and LCP light modes are equally absorbed in the LSMO layer, meaning that there is no magneto-optically active transition with a momentum quantum number ($m_j$) change of $\Delta m_j = 0$ available. If $\varepsilon_{xy1} > (\leq) 0$, RCP (LCP) light is more strongly damped than LCP (RCP) light, meaning that a magneto-optical transition $\Delta m_j = +1 (\pm 1)$ takes place. $\varepsilon_{xy1}$ shows two broad features corresponding to RCP light absorption at 1.7 and 3.5 eV (Figure 9). Toward higher photon energies, LCP light is predominantly absorbed.

For a correlation of the spectral features in the diagonal and off-diagonal elements of the dielectric tensor to the electronic structure, we refer to the schematic density of states in LSMO shown in Figure 10. The orbital energies are based on local spin density approximation (LSDA) + U calculations by Uba et al.[29] and the schematic density of states reported by Takenaka et al.[30] determined by investigations of the optical conductivity of La$_{0.825}$Sr$_{0.175}$MnO$_3$. However, they are refined to fit our results. The schematic density of states also contains the magnetic quantum number $m_l$[31] and the projection of the total angular momentum quantum numbers $m_j = m_l + m_s$ of the orbitals. $m_s$ is $\frac{1}{2}$ if the electron has spin up and $-\frac{1}{2}$ for spin down. These quantum numbers are needed to determine which

**Figure 9.** Real and imaginary parts of the off-diagonal elements of LSMO for different $T_A$.

**Figure 10.** Schematic density of states based on various studies[31,34] with magneto-optical selection rules. The allowed optical transitions induced by linear, left-circular, and right-circular polarized light are represented by black, red dashed, and blue dotted arrows, respectively. Magnetic $m_j$ and projection of the total angular momentum $m_j$ quantum numbers are given for each orbital.
transitions follow the selection rules for linear polarized, RCP, and LCP light. In this picture, RCP transitions have \( \Delta m_j = 1 \) (blue dotted arrows), LCP transitions have \( \Delta m_j = -1 \) (red dashed arrows), and linear polarized transitions have \( \Delta m_j = 0 \) (black solid arrows).

The absorption feature at 0.6 eV (see Figure 7) can be attributed to a transition from O 2p \( \uparrow \) to Mn \( eg \), \( \uparrow \). Additional linear polarized light transitions possibly observed in the dielectric function correspond to O 2p to Mn \( eg \), \( \uparrow \) at 3.1 eV, Mn \( eg \), \( \uparrow \) to Mn \( t_{2g} \), \( \uparrow \) at 3.4 eV, and O 2p \( \uparrow \) to Mn \( t_{2g} \), \( \downarrow \) at 4.0 eV. The optical transitions at higher photon energies could not be verified due to the limited spectral range of the ellipsometry measurements.

The optical transition seen in the off-diagonal element for RCP light is probably Mn \( eg \), \( \uparrow \) to Mn \( t_{2g} \), \( \downarrow \) at 3.4 eV. The transitions excited by LCP light should be O 2p \( \downarrow \) to Mn \( eg \), \( \uparrow \) at 0.6 eV, Mn \( t_{2g} \), \( \uparrow \) to Mn \( eg \), \( \downarrow \) at 1.9 eV, O 2p to Mn \( eg \), \( \downarrow \) at 3.1 eV, O 2p \( \downarrow \) to Mn \( t_{2g} \), \( \downarrow \) at 4.0 eV, and Mn \( t_{2g} \), \( \uparrow \) to Mn \( t_{2g} \), \( \downarrow \) at 5.3 eV. All transitions are shown in Table 1. However, peaks in the dielectric function are only observable for RCP light is probably Mn \( eg \), \( \downarrow \) at 0.6 eV, Mn \( t_{2g} \), \( \downarrow \) at 3.4 eV, and O 2p \( \downarrow \) to Mn \( t_{2g} \), \( \downarrow \) at 4.0 eV.

### Table 1. Assignment of the optical transitions of LSMO: linear indicates linear polarized light transitions and RCP and LCP indicate right-circularly and left-circularly polarized transitions.

| Transition | Energy [eV] | RCP | Linear | LCP |
|------------|-------------|-----|--------|-----|
| O 2p \( \uparrow \) to Mn \( eg \) | 0.6 | X | X | X |
| Mn \( t_{2g} \) to Mn \( eg \) | 1.9 | X | – | X |
| O 2p to Mn \( eg \) | 3.1 | X | X | – |
| Mn \( eg \) to Mn \( t_{2g} \) | 3.4 | X | X | – |
| O 2p to Mn \( t_{2g} \) | 4.0 | X | X | X |
| Mn \( t_{2g} \) to Mn \( t_{2g} \) | 5.3 | X | X | X |
| O 2p to Mn \( t_{2g} \) | 6.5 | X | X | X |

2.4. Magnetic Properties

For the field-cooled magnetization over temperature measurements, the samples were cooled down in a magnetic field of 2 mT from 400 to 4.2 K. Afterward, the measurements were carried out from 4.2 to 400 K with an applied field of 2 mT, while the temperature increased at 3 K min \(^{-1}\). The Curie temperature \( (T_C) \) was then determined from the minimum of the first derivative of the magnetization versus temperature curve. All films exhibit \( T_C \) higher than 300 K. \( T_C \) increases with increasing \( T_A \) with a local maximum at around 650 K followed by a further increase above (Figure 11a). In-plane hysteresis loops were measured at 300 K with a SQUID vibration sample magnetometer (VSM). The magnetization was calculated in two ways: the volume was calculated using the layer thickness determined by ellipsometry after annealing for films annealed up to 800 °C. For films annealed above 800 °C, where we could not evaluate the layer thickness after annealing, the thickness before annealing was used. The magnetization (Figure 11b) shows a strong increase with \( T_A \) between 600 and 650 °C and then it increases slightly up to a \( T_A \) of 775 °C and decreases to almost 0 at a \( T_A \) of 875 °C. This reveals again the impact of the diffusion layer between the silicon oxide and the LSMO starting at 800 °C. Due to the very low coercive field and the “remanent” magnetization of the superconducting magnet\(^{[32]}\) in the SQUID VSM, a magnetic field correction of the hysteresis loops was applied (for details, see Supporting Information, Figure S4, and the corresponding text). The coercive field \( H_c \) (Figure 11c) shows a local maximum at 625 °C of \( (2.3 \pm 0.5) \) mT followed by a minimum of \( (1.0 \pm 0.5) \) mT at 750 °C. Furthermore, \( H_c \) increases until \( (7.5 \pm 0.5) \) mT at 850 °C. Afterward, a strong reduction to \( (3.2 \pm 0.5) \) mT occurs at 875 °C.

In contrast, the remanence at room temperature (see Figure S5 in the Supporting Information) increases up to 825 °C. At 875 °C, we observe an abrupt drop of the remanence from 63% to 16% due to the complete intermixing of the LSMO and silicon oxide layers. Taking additionally the magnetic moment into account one can see that the remanent magnetic moment is highest for the films annealed at 775 and 800 °C.

2.5. Electrical Properties

To determine the electrical resistivity \( \rho \) of the annealed samples, the measured 4pt resistance \( R_{4pt} \) was evaluated using the following equation.

\[
\rho = \frac{\pi}{\ln(2)} \cdot t_{4pt} \tag{4}
\]

This formula was first presented by Albers et al.\(^{[33]}\) and corrects the resistance by the layer thickness \( t \) and accounts also the shape of the sample. It is valid for films with a thickness smaller than half the probe spacing and a lateral sample size of \( \approx 10 \) times the probe spacing, which is the case for our measurements.

Figure 11d shows the resistivity as a function of \( T_A \) calculated for layers annealed above 775 °C with the layer thickness before annealing and for layers annealed below or equal to 775 °C with the layer thickness after annealing as determined by VASE. The results show a rather constant resistivity of about 1 \( \Omega \)cm if the layer thickness after annealing is considered and \( T_A \) is larger than 650 °C. Other groups obtained similar values for sputtered LSMO.\(^{[34,35]}\) Urushibara et al.\(^{[36]}\) reported for \( La_{0.85}Sr_{0.15}MnO_3 \) and \( La_{0.9}Sr_{0.1}MnO_3 \) crystals at 300 K a resistivity of 0.25 and 2 \( \Omega \)cm, respectively.

For annealing temperatures of 825 and 850 °C, the sheet resistivity remains in the same range, but the resistivity values cannot be determined due to the large uncertainty in the LSMO film thickness determination. The sample annealed at 875 °C becomes insulating.

3. Conclusion

We systematically studied the structural, optical, electrical, and magnetic properties of LSMO layers deposited by magnetron
sputtering on Si(111) covered with native oxide at room temperature. To induce crystallization, the films were annealed for 12 h at different temperatures in the range from 600 to 875 °C in ambient atmosphere. To assess the film properties, we used DP by the combination of Ar⁺ etching and XPS, Raman spectroscopy, spectroscopic ellipsometry, magneto-optical spectroscopy, as well as SQUID and MOKE magnetometry. Along with the application of VASE and MOKE spectroscopy for assessing the film quality assessment, we determined the diagonal and off-diagonal elements of the dielectric tensor and we revised the assignment of the optical transitions observed in the spectral range from 0.7 to 5.5 eV.

Our results indicate that the lowest annealing temperature, which should be used for the crystallization of amorphous LSMO layers on silicon, lies between 600 and 625 °C. This is consistent with other reports. The dielectric function (both diagonal and off-diagonal elements) and the Raman spectra show only slight changes in the annealing temperature regime between 625 and 775 °C. Starting with 775 °C, the optical methods and the XPS-DP indicate the diffusion of Si atoms into the LSMO layers. The films become ferromagnetic starting with the lowest annealing temperature, and their magnetic properties, that is, coercive field, remanent magnetic moment, and Curie temperature, improve with the annealing temperature. Taking especially the remanent magnetization and the saturation magnetization at 300 K into account, it turns out that the samples at a \( T_A \) of 775 and 800 °C show the best magnetic properties. Considering also the growth of a silicon oxide layer at the LSMO/Si interface and silicon diffusion into the LSMO films’ trade-off with the magnetic properties, we suggest that the best annealing temperature for amorphous LSMO on silicon substrates is 775 °C.

4. Experimental Section

Si(111) substrates covered with a 2 nm-thick native oxide were cleaned in three steps in an ultrasonic bath with isopropanol, acetone, and de-ionized (DI) water for 5 min each. An Advanced Energy DC pinnacle plus sputtering generator was used for pulsed DC deposition with a pulse frequency of 100 kHz and a reverse bias time of 2 \( \mu \)s, to avoid target charging, at a sputtering power of 30 W. The system was equipped with a planar magnetron sputtering cathode ION X–2 (THIN FILM CONSULTING) with a target slot diameter of 50.8 mm (2 in.). The base pressure of the deposition chamber was \( 3 \times 10^{-5} \) Pa, whereas the deposition of LSMO layers was realized at a pressure of 2 Pa in a flowing oxygen–argon atmosphere with a volume ratio of 2:1. The deposition was conducted with a disk-like SurfaceNet target with a nominal stoichiometry of \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \). The stoichiometry of the target was verified by XPS. The distance between target and substrate was 11 cm. All films were sputtered in one deposition run to achieve films as comparable as possible. Afterward, each sample was annealed for 12 h in ambient atmosphere at a constant temperature \( T_A \) in the range between 600 and 875 °C in Nabertherm L 1/12 oven.

The stoichiometry of the layers was investigated by XPS-DP in a Thermo Fisher ESCALAB 250 Xi setup. The electron excitation was conducted with a monochromated Al Kα X-ray source with an energy of 1486.6 eV. The elliptical X-ray spot was set up to a size of 300 × 100 μm. All spectra were taken with a pass energy of 20 eV. This resulted for the Ag 3d_{5/2} orbital in FWHM of 0.58 eV. To avoid sample charging, a charge compensation with a mixture of low-energy Ar⁺ ions and electrons was utilized. Scanning ion beam etching was conducted with Ar⁺ ions with a kinetic energy of 200 eV to reduce intermixing of the layer. The scanning spot size of the Ar⁺ beam was set to 1.5 × 1.5 mm to prevent edge effects of the etched crater. The spectra obtained were analyzed using...
the Thermo Advantage software by Thermo Fisher Scientific. The spectra were fit with a Shirley[38] background and peak functions defined as a weighted sum of Lorentzian and Gaussian contributions, which is a good approximation for the measured XPS peaks.[29] Furthermore, REELS was conducted to identify loss features in the spectra. The stoichiometry was calculated using the ratios of Si 2s, O 1s, La 4d, Sr 3d, and Mn 3s photo-electron peaks.

Raman spectroscopy data were obtained using a Horiba Labram HR800 Raman spectrometer with a 100×/0.9 NA objective. The excitation light source was a solid-state COBOLD laser with a wavelength of 514.7 nm and a power of 100 μW focused on the sample surface with a surface spot size of ≈1 μm. The Raman signals were collected using diffraction grating with 600 lines mm⁻¹ and a liquid nitrogen-cooled charge-coupled device (CCD). The experimental resolution was 2.3 cm⁻¹.

The layer thickness and the dielectric function of each film (before and after annealing) were determined by VASE with a J. A. Woolam Co., Inc. Ti:Solar ellipsimeter in an energy range between 0.7 and 5.0 eV. The angle of incidence was varied from 50° to 75° in 5° steps. The spectra obtained were modeled with the WVASE software.

Spectroscopic and magnetic field-dependent measurements of the MOKE were carried out with a home-built polar setup similar to the one described by Herrmann et al.[40] in a photon energy range from 1.7 to 5.5 eV and an angle of incidence of ≈1.3°. The maximum applied magnetic field was ±1.7 T. To model the off-diagonal elements of the dielectric tensor in WVASE, both the layer thickness and the dielectric function as determined from VASE data were used. In addition, an out-of-plane hysteresis loop was measured at a photon energy showing a high Kerr rotation in the MOKE spectrum.

A Lucas Labs/Signatone Corp. SP4 4pt-head with a Keithley 2636 source meter was used for four point-resistance measurements of the layers. The probe tips were made of osmium and the tip-to-tip distance was 1.6 mm (1/16 inch).

To determine the Curie temperature, field-cooled magnetization versus temperature scans in a range between 4.2 and 400 K were conducted in a Quantum Design MPMS SQUID–VSM. In addition, in-plane hysteresis loops were measured at 300 K. For the magnetic moment per cm², the area of the sample was measured with a digital microscope VHX-500 (Keyence) at 50× magnification.

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

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