Atomic arrangement and magnetic properties of $LaFeO_3$-$LaMnO_3$ artificial superlattices

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Artificial superlattices of $LaFeO_3$-$LaMnO_3$ were formed on $SrTiO_3$(111), (100), and (110) substrates with various stacking periodicity using a pulsed laser deposition technique, and their magnetic properties were controlled by altering the ordering of magnetic ions (Fe or Mn). For superlattices constructed on the (111) plane, all the superlattices showed ferromagnetic (or ferrimagnetic) behaviors and the same Curie temperatures (T_C) at 230 K. The magnetization was reduced as the stacking periodicity of the superlattices decreased. On the other hand, in the case of superlattices formed on (110) or (100) substrates, the increase of the spin frustration effect at the $LaFeO_3$-$LaMnO_3$ interface with decreasing the stacking periodicity caused a reduction of T_C and magnetization. In particular, spin-glass-like behavior was observed in superlattices of less than 3/3 stacking periodicity. [S0163-1829(99)50442-6]

Materials that do not exist in nature can be created artificially using the method of depositing superlattices with the layering of different materials on an atomic or molecular scale. The method can be applied to a wide range of fields such as the fabrication of new superconductors, magnetic and ferroelectric materials, etc. New materials with unique physical properties are constantly being created.[1–3] However, the atomic order can only be controlled in the direction parallel to the film plane (i.e., one-dimensional control), and current techniques do not support three-dimensional control of the atomic order.

In an earlier study, we demonstrated that the control of the arrangement of magnetic ions, i.e., the spin order, could be controlled by constructing artificial superlattices with various stacking directions and periodicity.[4–5] Pseudo three-dimensional control of the atomic order was achieved by the method.

In this paper, $LaMnO_3$-$LaFeO_3$ artificial superlattices were formed on $SrTiO_3$ (111), (100), and (110) planes with various stacking periodicity, and their magnetic properties were controlled by managing the ordering of the Mn and Fe ions. $LaFeO_3$ is antiferromagnetic (Fe^{3+}-O-Fe^{3+} superexchange interaction) and has a *G*-type magnetic structure (inter- and intralayer spin coupling are antiparallel).[6–7] On the other hand, $LaMnO_3$ films exhibit ferromagnetic behavior with a Curie temperature of 130 K for La deficiency ($La_{1-\delta}MnO_3$).[8] In this paper, the ferromagnetic $La_{1-\delta}MnO_3$ is noted as $LaMnO_3$.

For artificial superlattices constructed on the (111) plane, ferromagnetic interactions should be introduced at the Mn-Fe interface because the Fe^{3+}-O-Mn^{3+}superexchange interaction is considered to be ferromagnetic according to the theory of Goodenough-Kanamori.[9,10] As a result, ferromagnetism should appear in the superlattice with one-layer by one-layer (1/1) stacking periodicity (see Fig. 1).

On the other hand, for superlattices constructed on (100) and (110) planes, a spin frustration effect occurs at the $LaMnO_3$-$LaFeO_3$ interface because the $LaMnO_3$ film is ferromagnetic[8] and $LaFeO_3$ is antiferromagnetic with a *G*-type spin structure[6–7] (Fig. 1). The spin frustration effect increases as the stacking periodicity decreases. The spin frustration effect of (111) superlattices becomes larger than that of the (100) superlattices in terms of their spin structure. This method even allows a spin frustration effect to be introduced artificially into the system. The $LaMnO_3$-$LaFeO_3$ artificial superlattices were formed according to these concepts.

Magnetic artificial superlattices were constructed by stacking $LaMnO_3$ and $LaFeO_3$ layers on (111), (100), and (110) $SrTiO_3$ substrate using a multitarget pulsed laser depo-

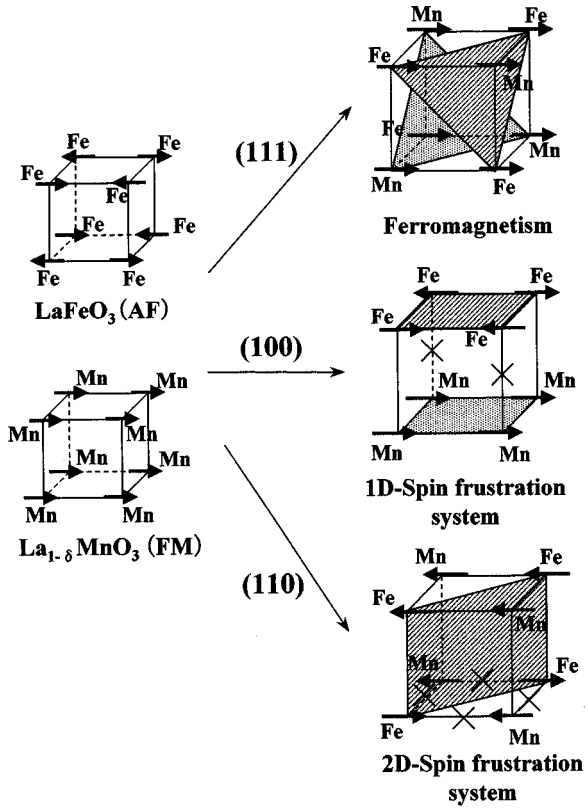

FIG. 1. Schematic models of spin structures in $LaMnO_3$-$LaFeO_3$ artificial superlattices grown on (111), (100), and (110) surfaces. Here AF and FM means antiferromagnetic and ferromagnetic, respectively. For (100) and (110) superlattices, the × signs show the interactions where the spin frustration effect occurs.

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sition (PLD) technique.[4–5] $LaMnO_3$ and $LaFeO_3$ targets were prepared using standard ceramic techniques. All the films were formed at 590 °C in an oxygen/ozone (8%) ambient pressure of 1×10^{-3} Torr with an energy density of 0.5~1 mJ/cm^2. The deposition rate was 10–20 Å/min. The total thickness of the films was 800–1000 Å. The thickness of individual layers were controlled by the number of laser pulses. (The deposition rate from $LaFeO_3$ and $LaMnO_3$ targets were calibrated against the number of laser pulses.) The structure of the lattices was characterized by x-ray diffraction (2θ–θ scan) using a Cu-K_α source (Rigaku:RINT 2000). Surface morphology was observed by atomic force microscopy (AFM) (Digital Instruments–Nanoscope III). Magnetic measurements were performed using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S) with the magnetic field applied parallel to the film plane.

The crystal structures of the $LaMnO_3$-$LaFeO_3$ superlattices on $SrTiO_3$(111), (100), and (110) were studied using x-ray diffraction. All the films showed a single phase and had a preferred orientation normal to the surface of the substrate. Typical features of superlattices were observed. In particular, for a superlattice formed on a (111) substrate with a one-layer by one-layer (1/1) stacking periodicity, small peaks were observed at $2\theta=19.8°$ and 61.6° due to the double perovskite features. The reflection high-energy electron diffraction (RHEED) patterns show streaks which also indicate that the superlattices are epitaxially formed on the (111), (100), and (110) surfaces. The results of the x-ray diffraction and the RHEED measurements indicate that the $LaMnO_3$-$LaFeO_3$ superstructures were sufficiently well formed.

In addition, the morphology of the superlattice on the (111) substrate was observed using an AFM. The average roughness (R_a) and mean-square roughness (R_{MS}) of the film surface (area: 1 μm×1 μm) were found to be 1.7 and 2.2 Å (i.e., less than one layer), respectively, indicating that the artificial superlattice was well formed at the atomic level.

Magnetization versus temperature curve (M-T curves) of $LaMnO_3$-$LaFeO_3$ artificial superlattices (1/1-30/30 sequence) on $SrTiO_3$(111) are shown in Fig. 2(a). A magnetic field of 0.1 T was applied parallel to the film surface, The magnetic property of the 30/30 superlattice resembles that of the original $LaMnO_3$ film. The properties of $LaMnO_3$ and $LaFeO_3$ can be observed independently in superlattices with stacking periodicity greater than a 30/30 sequence, and the property of $LaMnO_3$ was strongly apparent in the temperature 5–400 K because the magnetization of $LaMnO_3$ is much larger than that of the $LaFeO_3$.

For the 1/1-9/9 sequences, the magnetization increases as the stacking periodicity decreases. It must be noted that all the superlattices show the same Curie temperatures (T_C) of 230 K. The change of magnetization and the same T_C value may be explained as follows. Figure 2(b) shows that the ratio of spins which contribute to the magnitude of magnetization increases as the stacking periodicity decreases, i.e., an increase of the number of Fe-Mn interfaces, because the spins of the magnetic ions (Fe^{3+} or Mn^{3+}) on each (111) plane are aligned in the same direction. As a result, the magnetization increases when the stacking periodicity is reduced. Ferromagnetic (or ferrimagnetic) behavior in particular is observed in the 1/1 superlattice. The saturation magnetization (M_S) of the superlattice was measured to be about 30 emu/g ($\fallingdotseq 1.3\mu_B$/site) from the hysteresis curve measured at 6 K [Fig. 3(a)]. However, the value of M_s is estimated to be 103 emu/g ($=4.5\mu_B$/site) for the $Mn^{3+}(d^4)$-O-Fe^{3+}-(d^5) state theoretically. The measured value, therefore, is relatively small compared with the above estimate. We suppose that the reduction of M_s is caused by the complex effect arising from the partial displacement between Fe and Mn ions, charge separation and/or disproportion between Fe and Mn as seen in $LaMn_{0.5}Co_{0.5}O_3$ (or $LaMn_{0.5}Ni_{0.5}O_3$) ordered perovskites[11–12] and the deviation from stoichiometry due to the La and/or oxygen deficiency. In the first case, a 10% displacement of Fe by Mn ion causes the value of M_S to be 80% of the theoretical value. When charge separation between Fe and Mn ions ($Fe^{3+}+Mn^{3+}\rightarrow Fe^{2+}+Mn^{4+}$)occurs, as described in the second case, M_S becomes 80 emu/g ($=3.5\mu_B$/site). Annealing of the 1/1 superlattice was performed at 500 °C (less than deposition temperature) with O_2 flowing to remove the oxygen deficiency. The magnetic behavior after annealing did not change from that seen before.

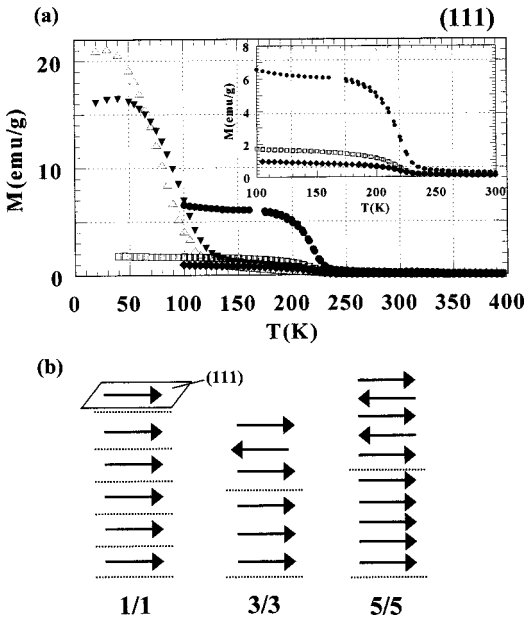

FIG. 2. (a) Temperature dependence of magnetization for $LaMnO_3$-$LaFeO_3$ superlattices formed on $SrTiO_3$ (111) with various stacking periodicity (1/1-●, 5/5-□, 9/9-◆, and 30/30-▼), and for the $LaMnO_3$ film (△) in a magnetic field of 0.1 T. The inset shows an enlargement of the M-T curves of (111) superlattices with 1/1, 5/5, and 9/9 sequences. (b) Schematic spin structures of the $LaMnO_3$-$LaFeO_3$ superlattice with 1/1, 3/3, and 5/5 sequence on a (111) plane. Each arrow shows the synthesis of the spin moment of magnetic ions in each (111) surface.

The Curie temperature of superlattices with 1/1-9/9 sequences is constant [Fig. 2(a)]. The fixed T_C of 230 K can be explained based on the fact that T_C is determined by the average of all magnetic interactions. For a superlattice with 3/3 sequences, the total magnetic interaction (J_{total}) is expressed by the following relation because $J_{Fe\text{-}Fe}$, $J_{Mn\text{-}Mn}$, and $J_{Fe\text{-}Mn}$ each accounts for 1/3 of all the magnetic interactions [see Fig. 2(b)]:

$$3/3: J_{total}=[(J_{Fe\text{-}Fe}+J_{Mn\text{-}Mn})+J_{Fe\text{-}Mn}]/3,$$

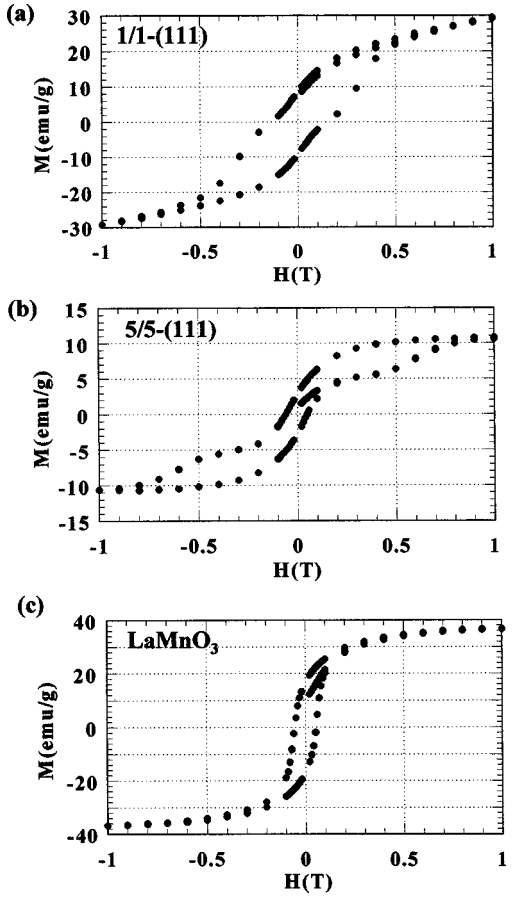

FIG. 3. Hysteresis curves of $LaMnO_3$-$LaFeO_3$ superlattices formed on $SrTiO_3$ (111) with (a) 1/1 and (b) 5/5 stacking periodicity, and (c) that of the $LaMnO_3$ film at 6 K.

where $J_{\text{Fe-Fe}}$, $J_{\text{Mn-Mn}}$, and $J_{\text{Fe-Mn}}$ represented the magnetic interactions between Fe^{3+}-Fe^{3+}, Mn^{3+}-Mn^{3+}, and Fe^{3+}-Mn^{3+} ions, respectively. For superlattice with 5/5 and 7/7 stacking periodicity, the total magnetic interactions are given as follows based on the same concept.

$$5/5{:}J_{\text{total}}=[2(J_{\text{Fe-Fe}}+J_{\text{Mn-Mn}})+J_{\text{Fe-Mn}}]/5,$$

$$7/7{:}J_{\text{total}}=[3(J_{\text{Fe-Fe}}+J_{\text{Mn-Mn}})+J_{\text{Fe-Mn}}]/7.$$

From these results, the total magnetic interactions can be generally expressed as a function of the stacking periodicity as follows:

$$\text{N/N}{:}J_{\text{total}}=\frac{[(N-1)(J_{\text{Fe-Fe}}+J_{\text{Mn-Mn}})+2J_{\text{Fe-Mn}}]}{2N}, \quad (1)$$

where N indicates the stacking periodicity of artificial superlattices.

Factors that weaken superexchange interactions, such as interfacial imperfections characteristic of artificial superlattices,[13–15] and oxygen and La deficiency, must be considered in order to calculate the values of the magnetic interaction precisely. The parameters α and β are added to Eq. (1) to take the effects into account. Equation (1) is transformed into Eq. (2) by the procedure.

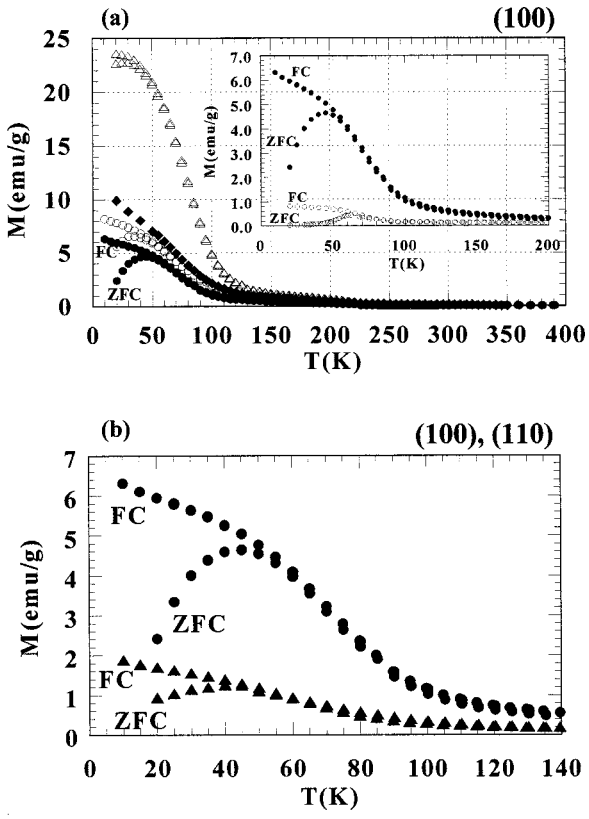

FIG. 4. (a) Temperature dependence of magnetization of the $LaMnO_3$-$LaFeO_3$ superlattices formed on the $SrTiO_3$ (100) with various stacking periodicity (2/2-●,3/3-○,11/11-♦), and for the $LaMnO_3$ film (△) in a magnetic field of 0.1 T with different cooling [zero-field cooling (ZFC) and field cooling (FC)] processes. The inset shows magnetization versus temperature curves of a 2/2 superlattice on (100) substrate with different cooling processes in fields of 0.005 (○) and 0.1 T (●), respectively. (b) Magnetization versus temperature curves of 2/2 superlattices on (100) (●) and (110) (▲) substrates with different cooling process.

$$J_{\text{total}}=\frac{[(N-1)\alpha(J_{\text{Fe-Fe}}+J_{\text{Mn-Mn}})+2\beta J_{\text{Fe-Mn}}]}{2N}. \quad (2)$$

The experimental J values were applied to this equation. The experimental J values were calculated using mean-field approximation (nearest-neighbor interactions were only considered). With $\alpha=0.5$ and $\beta=1$, the experimental values were successfully reproduced, suggesting that the interactions between Fe-Fe and Mn-Mn ions are weakened more significantly than the interaction between Fe-Mn and the interfaces.

Only one T_C is observed when the stacking sequence is short (1/1-9/9), and the T_C originating for the single $LaMnO_3$ phase is observed when the stacking periodicity is large (30/30). (The T_N originating from $LaFeO_3$ in the superlattice with larger sequence is not confirmed because of the temperature limitation of four instrument.) The behavior of these superlattices agrees well with the results from Abarra *et al.*[16] on CoO/NiO superlattices and those of Ramos *et al.*[17] on FeF_2/CoF_2 superlattices.

Furthermore, unusual behavior was observed in the hysteresis curve with 5/5 stacking periodicity [Fig. 3(b)]. Broad hysteresis with a coercive field (H_c) at 0.15 T was observed in a superlattice with 1/1 stacking periodicity [Fig. 3(a)]. The

hysteresis curve for $LaMnO_3$ [Fig. 3(c)], on the other hand, shows the slim shape characteristic of soft magnetic materials. The superlattice of 5/5 stacking periodicity exhibits a complex hysteresis curve such as that produced when the properties of a superlattice with 1/1 stacking periodicity and $LaMnO_3$ are mixed. The hysteresis curve was considered to reflect the properties of both the Fe-Mn interface and $LaMnO_3$. The reason for such unique hysteresis is as follows.

Mn layers are pinned by the Fe-O-Mn superexchange interaction at the interface, and the layers become magnetically harder. The effect of the Fe-Mn interaction can reach only the nearest or second-nearest adjacent layers because the magnetic interaction is short range, with the other layers retaining the original $LaMnO_3$ characteristics. From these results, the length for conveying the interactions at the interface, i.e., correlation length of the spin, is supposed to be less than two layers.

The magnetization versus temperature curves for $LaMnO_3$-$LaFeO_3$ artificial superlattice (2/2,3/3,11/1 sequence) on $SrTiO_3$(100) and on the $LaMnO_3$film (LMO) as a reference sample are shown in Fig. 4(a). The inset shows the magnetization versus temperature curves of 2/2 superlattices on the (100) substrate with different cooling [zero-field cooling (ZFC) and field cooling (FC)] processes and different magnetic fields. For superlattices formed on (100) and (110) substrates, the magnetic properties differed significantly from those of (111) due to the spin frustration effect. For superlattices of larger stacking periodicity, the properties of $LaMnO_3$ and $LaFeO_3$ are highly distinct. The properties of $LaMnO_3$ appear strongly in the temperature range of 5–400 K because $LaMnO_3$ shows a larger magnetization than the antiferromagnetic $LaFeO_3$. In contrast to the results from superlattices on $SrTiO_3$ (111) substrates, the magnetization and T_c of superlattices on (100) substrates decreases as stacking periodicity decreases, and the magnetization becomes unsaturated. The ferromagnetic properties of $LaMnO_3$ are weakened by the neighboring $LaFeO_3$ layer because the spin frustration effect occurs at the Mn-Fe interface. To explain this behavior, magnetization versus temperature curves were measured for a 2/2 superlattice at different applied magnetic fields (0.005 and 0.1 T) using different cooling processes [see inset of Fig. 4(a)]. The magnetic behavior differs depending on whether the sample is cooled with (FC) or without (ZFC) an applied field. A sharp cusp at about 65 K is observed in the ZFC sample when the applied field is 0.005 T, but this cusp loses its sharpness and becomes a broad maximum, and moves to a lower temperature when the applied field is increased to 0.1 T. This behavior is one of clear evidences for the spin-glass state. The increased spin-frustration effect caused by the reduced stacking periodicity leads to the formation of a spin-glass-like phase. This is caused by the competition between ferromagnetism in Fe-Mn and Mn-Mn, and antiferromagnetism in Fe-Fe.

The superlattice formed on (110) substrates with 2/2 stacking periodicity also shows spin-glass-like behavior [Fig. 4(b)]. The magnetic field was applied parallel to the [001] direction in the (110) and (100) superlattices to avoid the magnetic anisotropy effects. The magnetization at the glass temperature (T_g) is about 1/3 that of the (100) superlattice. This is caused by the larger frustration effect than that of the (100) superlattices as shown in Fig. 1. The number of bonds where the spin frustration effect occurs in the (110) superlattice is twice as large as that in the (100) superlattice per eight-metal unit cell (Fig. 1), which correlate well with the suppression of the magnetization (1/2∼1/3). In the case of (110) superlattices, the spin frustration effect is twice as great as that of the (100) superlattice.

To summarize, $LaMnO_3$-$LaFeO_3$ artificial superlattices were constructed on $SrTiO_3$ (111), (100), and (110) substrates using laser MBE methods and their magnetic properties were evaluated. The magnetization of superlattices constructed on the (111) plane increases as the stacking periodicity decreases, and the superlattice with 1/1 stacking periodicity exhibited ferromagnetic (or ferrimagnetic) behavior. For (100) and (110) superlattices, on the other hand, the spin frustration effect increases with lower stacking periodicity and spin-glass-like behaviors was observed in superlattices with a stacking periodicity of less than 3/3.

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