Transactions of the Materials Research Society of Japan 24 [1] 13-18 (1999)

Creation of Novel Properties on Ferromagnetic・Ferroelectric Superlattices

Hitoshi Tabata, Kenji Ueda, Yuji Muraoka and Tomoji Kawai
Institute of Scientific and Industrial Research, Osaka University
8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
FAX: 81-6-6875-2440, e-mail: tabata@sanken.osaka-u.ac

We have constructed ferroelectric and/or ferromagnetic superlattices by a layer-by-layer successive deposition technique with a laser MBE. An ideal hetero-epitaxy can be obtained due to the similar crystal structure of the perovskite type ferroelectric $BaTiO_3$, $SrTiO_3$, PZT and ferro- or antiferromagnetic $LaFeO_3$, $LaCrO_3$, $LaMnO_3$. In both superlattices, strain effect plays an important role for deterring their physical properties. In the Bi-base layer structured superlattices, we have controlled dielectric constant and ferroelectric properties. And we also control the spin order on $LaFeO_3/LaCrO_3$ and $LaFeO_3/LaMnO_3$ superlattices formed on $SrTiO_3$(111), (110) and (100) substrate. Such a spin structure(ferromagnetic order) can not be realized in bulk samples.
Key words: superlattices, ferroelectrics, ferromagnetics, laser MBE

1. INTRODUCTION

Transition metal oxides have a lot of interesting potential for the functional electric devices. Early transition metal oxides, such as PZT and $BaTiO_3$, show ferroelectric and dielectric properties corresponding to their band insulative characters. They are also expected to large piezoelectric and electro-strictive effect. Magnetic character is interesting on the middle transition metal oxide group (Mn, Fe, Co etc.) with increasing the number of spins.

Until now, the materials researches tend to be performed independently on magnetic and ferroelectric field. We have constructed hetero-structures with combination of ferroelectric- ferromagnetic materials by a laser MBE technique. An ideal hetero-epitaxy can be obtained owing to the similar lattice parameter of ferroelectric $BaTiO_3$, PZT and antiferro- or ferro-magnetic $(La,Sr)MnO_3$, $LaMnO_3$, $LaCrO_3$ and $LaFeO_3$.

We can introduce the lattice stress easily by applying voltage for the piezoelectric compounds(Fig.1). The CMR effect of $(La,Sr)MnO_3$ layer is strongly affected by the lattice stress due to the piezoelectric properties of PZT layer. In the FET-type devices consisting of ferromagnetic /ferroelectric hetero-structure show interesting phenomena. Electro-magnetic properties of ferromagnetic layer can be controlled by changing the lattice distortion and induced charge via changing of applied voltage for the ferroelectric layer. Furthermore, new spin order and spin frustration are expected competing with ferromagnetism of self-doped $LaMnO_3$ and anti-ferromagnetism of $LaFeO_3$ on $SrTiO_3$(111) and (100) surface. Spin glass phase transition (casp shape in magnetization vs. temperature measurements) is observed actually at around 50K in the 1/1 - 3/3 superlattices. In case of $LaMnO_3/LaFeO_3$ superlattices on (111) surface, on the other hand, spin glass does not occur. Furthermore, Curie temperatures maintain almost same value from 1/1 to 9/9 periodic sequences. This behavior is quite different from non-doped $LaFeO_3/LaCrO_3$ superlattices.

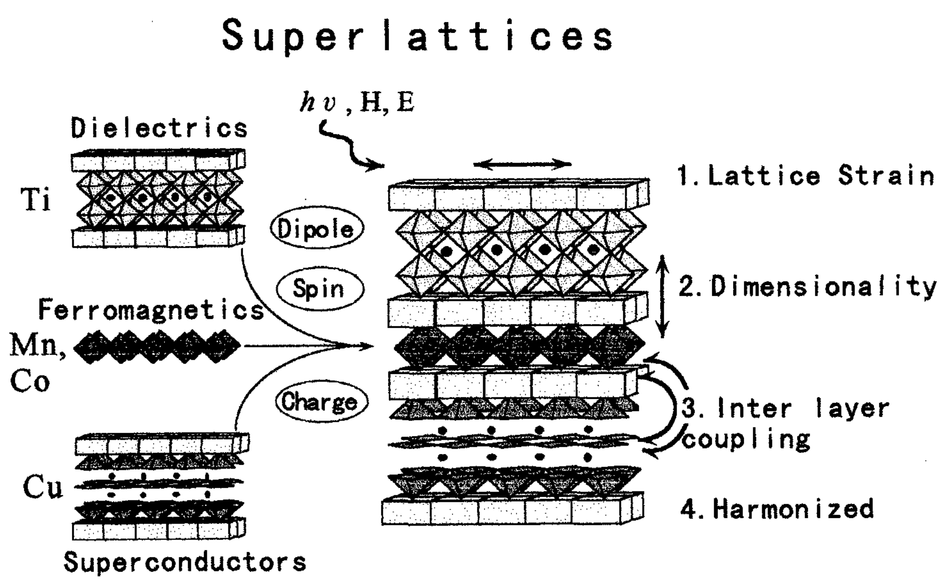

Fig. 1 Schematic model of the superlattices

2. SPIN CONTROL

A magnetic interaction between two magnetic ions via a nonmagnetic ion (such as oxygen) was first proposed by Kramers (1) and was systematized by Anderson (2). Later, this so-called superexchange interaction, was refined by Goodenough (3) and Kanamori (4) at a level so that this theory can be applied to various magnetic materials. According to their rules, we can estimate and predict whether a magnetic interaction thorough superexchange interaction between two spins is of a ferromagnetic or antiferromagnetic character. A lot of researchers have used this idea as a starting point for synthesizing ferromagnets. Based on these rules, the 180° superexchange interaction in a metal dimer via oxygen which has a d^3-d^5 electron state (∠M-O-M=180 ° , M=Fe^{3+},Cr^{3+}etc) is predicted to be ferromagnetic (4). The most typical and still unachieved combination is Fe-O-Cr systems. It is expected that if Fe^{3+} and Cr^{3+} ions are introduced alternately in the B site of perovskite-type transition metal oxides (ABO_3), the synthesis of ferromagnetic materials can be achieved. Although some attempts to synthesize such materials have been made by the sintering methods, the atomic order of Fe-O-Cr has not been achieved due to a phase separation into Fe-oxide and Cr-oxide phases (5). As a result a ferromagnetic ordered phase has not been obtained, and the materials have shown antiferromagnetic character (6-7).

The single phase $LaCrO_3$ and $LaFeO_3$ have G-type magnetic structures and Neel temperatures (T_N) of 280K and 750K, respectively (8-10). When the artificial superlattice of $LaCrO_3$-$LaFeO_3$ is synthesized by depositing several layers of $LaCrO_3$ and $LaFeO_3$ on $SrTiO_3$(111), there is the possibility of forming films that have various magnetic properties by controlling the stacking periodicity. Ferromagnetism can especially occur in the case of one layer by one layer stacking on the (111) surface because Fe^{3+} and Cr^{3+} ions are bridged by oxide ions alternately in the film (Fig. 2).

In this research, we have succeeded in synthesizing a new ferromagnetic artificial superlattice for the first time by alternately stacking one unit layer of $LaCrO_3$, $LaMnO_3$ and $LaFeO_3$ on $SrTiO_3$(111) single crystal using a laser MBE method (Fig. 2). Such materials cannot be obtained in the conventional bulk phase because they are not stable from a thermodynamic point of view (5-7). Furthermore, even in the case without phase separation (randomly mixing of Fe^{3+} and Cr^{3+} ions), antiferromagnetic interaction is dominant in the material since Fe-O-Cr ordered phase could not be achieved statistically. An artificial superlattice is a powerful tool for synthesizing these new materials (11). Actually, this artificial superlattice has been successfully applied to synthesize superconducting and dielectric superlattices.

3. EXPERIMENTAL

The present magnetic superlattices have been constructed in the following way. The $LaCrO_3$ and $LaFeO_3$ layers are stacked by using multi targets pulsed laser deposition (PLD) technique. (Fig. 2.) An ArF excimer laser pulse is focused on the targets to induce ablation, and the ablated atoms and ions are deposited on the $SrTiO_3$(111) substrate. The PLD technique is such a fine method that the spatial and time condition can be controlled. An atomic scale control of the crystal growth can be driven by the PLD method combined with RHEED observations (11, 12). Targets of $LaCrO_3$ and $LaFeO_3$ were synthesized by mixing La_2O_3 with Cr_2O_3, and La_2O_3 with α-Fe_2O_3, respectively at a mole ratio of 1:1 and sintering them at 1000℃. The distance between the Fe and Cr layers was varied from 2.3Å (1 unit layer) to 16.1Å (7 unit layers), and the total thickness of the superlattices was 600~1100Å. Solid solution $LaCr_{0.5}Fe_{0.5}O_3$ films were also formed as reference samples. The films were formed at 580℃ in an oxygen/ozone(8%) ambient pressure of 1mTorr. The deposition rate was 10 Å/min. All magnetic measurements were performed using a SQUID magnetometer (Quantum design MPMS-5S) with the magnetic field applied parallel to the film plane.

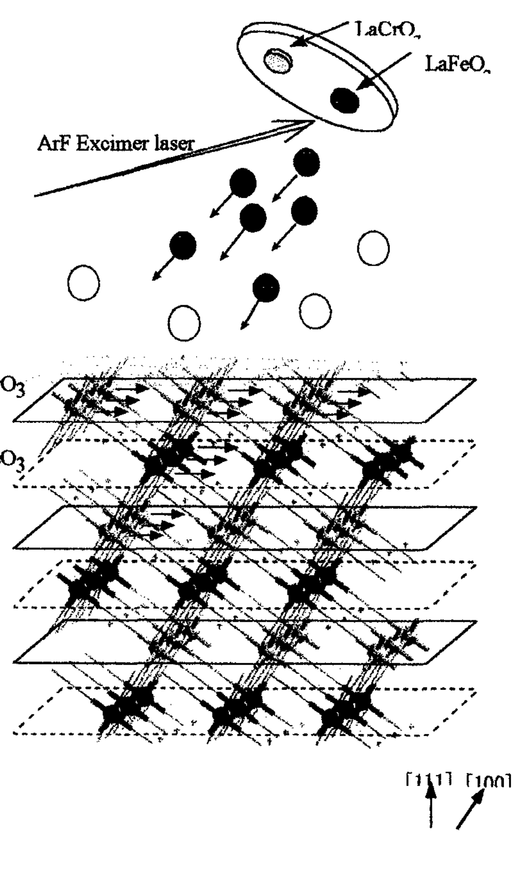

Fig. 2 : A schematic diagram for the construction of the $LaCrO_3$-$LaFeO_3$ superlattice on () surface by the laser MBE method. CrO layer and FeO layer are stacked alternately.

4. RESULT AND DISCUSSION

4.1 $LaFeO_3$/$LaCrO_3$ superlattices

X-ray diffraction measurements of $LaCrO_3$-$LaFeO_3$ superlattices in each stacking periodicity exhibit characteristic of artificial structures (Fig. 3). The distance of periodic layers (corresponding to the distance of FeO-CrO layer) is 2.29Å, and the FWHM (Full Width of Half Maximum) is 0.28~0.2° which indicates that our sample is well constructed as we desire. The RHEED measurements of the $LaCrO_3$-$LaFeO_3$ artificial superlattices on $SrTiO_3$(111) substrate showed a streaked patterns, indicating that the films are formed epitaxially and was well crystallized up to the topmost surface.

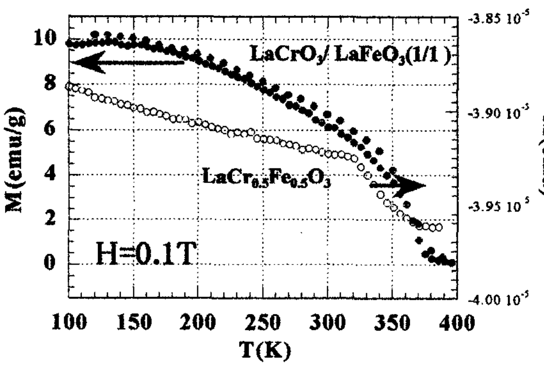

Fig. 3 : Temperature dependence of magnetization of $LaCrO_3$-$LaFeO_3$ superlattice on (111) (●) and that of $LaCr_{0.5}Fe_{0.5}O_3$ solid solution film (○) which are measured in a 0.1T field applied parallel to the surface of the substrate.

The temperature dependence of magnetization for the $LaCrO_3$-$LaFeO_3$ artificial superlattices with a stacking periodicity of 1/1 layer on $SrTiO_3$(111) is shown in Fig. 4. In this case, a magnetic field of 1000Oe (H=0.1T) was applied parallel to the surface of the substrate. There is clear evidence of a ferromagnetic transition at a temperature of 375K. The magnetization of the $LaCrO_3$-$LaFeO_3$ superlattices increases with decreasing temperature. A saturated magnetization comes to ~2 emu/g (which corresponds to about 3 μ_B at one site). From the theoretical estimation, the magnetization value of 4 μ_B/one-site would be expected due to the atomic order of $Fe^{3+}(d^5)$-$O^{2-}(2P^6)$-$Cr^{3+}(d^3)$ high spin state. Our experimental results are slightly smaller than the calculated. This is due to imperfections in the crystallinity and the atomic stacking sequence of the superlattices. It must be refined in the more sophisticated experiments. Tendency of magnetization change against measuring temperature can be discussed. The magnetization-temperature curve can be fitted with a relation of

$$M / M_0 = \alpha\left(\frac{T_c - T}{T_c}\right)^{\beta}$$

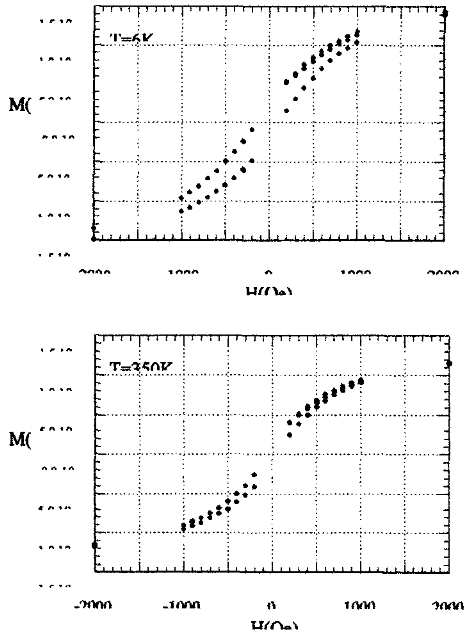

Fig. 4 : Hysteresis curves for $LaCrO_3$-$LaFeO_3$ / $SrTiO_3$(111) at 6K and 350K with the magnetic field applied parallel to the film plane.

where M_0 and T_C are the saturated magnetization and Curie temperature, respectively. In the case of α =1.09 and β =0.33, the curve is well reproduced. The value of β =0.33 is quite similar that of standard Heisenberg-type spin ordered character.

In the case of artificial superlattice with larger (>1unit layer) stacking periodicity, the ferromagnetic interactions are introduced in the interface between Fe and Cr layer. Actually, in the case of 7/7 layer superlattice, ferromagnetic character was also observed, and show magnetization of 1 μ_B/one-site. This is another evidence of ferromagnetic character in our superlattices. As a reference, the M-T curve of the $La(Fe_{0.5}Cr_{0.5})O_3$ solid solution film in 0.1T field is also shown in Fig. 3. It is clearly different from that of the $LaCrO_3$-$LaFeO_3$(1/1) superlattice. A cusp shape is observed at 320K which is a typical feature of antiferromagnetism. A background which increased monotonously with decreases in the measured temperature was caused by the paramagnetic character of the substrate. A ferrimagnetism may also be an acceptable explanation for the M-T character of the $LaCrO_3$-$LaFeO_3$(1/1) superlattice. The magnetization value of 3 μ_B/one-site, however, is too large to attribute to a ferrimagnetic order. It should be concluded that a new magnetic order of Fe-O-Cr has been realized for the first time in the superlattice. The magnetization dependence of the magnetic field (hysteresis curve) of $LaCrO_3$-$LaFeO_3$ artificial superlattice (1/1 sequence) on substrate (111) is shown in Fig. 4. Clear hysteresis was observed in M-H curves in the temperature region from

6K to 350K. The remnant magnetization of the superlattices decreases with increases in temperature up to 375K. Above the T_C (=375K), it shows a paramagnetic character. These are typical feature of ferromagnetic materials. These results provide further evidence that the ferromagnetic spin order is realized in the artificial lattice with a one by one layer stacking combination.

The degree of magnetic order can be controlled using the surface, (111) or (100) surface, of the substrate properly. F-type magnetic order (ferromagnetic order) is observed on (111) plane in the $LaFeO_3$-$LaCrO_3$ superlattices (1/1 sequence). In contrast, in the case of superlattices on (100) plane surface, antiferromagnetic properties have been expected and actually observed, and the Neel temperatures of the films decrease along with reductions in the stacking periodicity.(Fig. 5) In this case, ferromagnetic order occur in the c-axis direction perpendicular to the (100) plane. However, in-plane (a-b plane) character is antiferromagnetism. Therefore, totally as a whole, C-type antiferromagnetic character is observed and antiferromagnetic order, i.e. Neel temperature, can be controlled in our superlattices. These results will be discussed in detail in other paper (13). It should be noted that magnetic character is able to be changed artificially by a superlattice technique by choosing the substrate with different orientation. Furthermore, a new type magnetic order which are not achieved in bulk materials can be obtained in these superlattices.

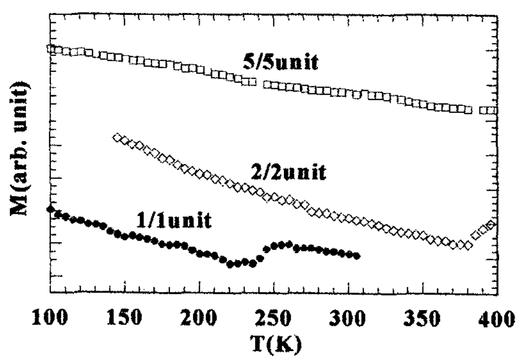

Fig. 5 : Temperature dependence of magnetization of $LaCrO_3$-$LaFeO_3$ superlattice on (100) (●) which are measured in a 0.1T field applied parallel to the surface of the substrate.

4.2 $LaFeO_3$/$LaMnO_3$ superlattices

The temperature dependence of magnetization for $LaMnO_3$-$LaFeO_3$ artificial superlattices (1/1~40/40unit) on $SrTiO_3$ (111) is shown in Fig. 2. The 0.1T field applied parallel to the film plane. In the cases of 1/1~9/9 sequence, the magnetization increases with the shortening of the stacking periodicity, and the Curie temperatures (T_C) are constant in all the superlattices. In the case of superlattice with 40/40 sequence, the magnetic behaviors are very similar to those of $LaMnO_3$ film. For larger stacking periodicity such as 40/40 sequence, the properties of $LaMnO_3$ and $LaFeO_3$ appear independently. The properties of $LaMnO_3$ are appeared strongly in the temperature range from 5 to 400 K On the other hand, in the case of superlattices with small stacking periodicity (1/1-9/9), the changes of the magnetic properties are explained as follows. As is shown in Fig. 6, the rate of spins which contribute to the magnitude of magnetization increase with decreasing the stacking periodicity, that is, increasing the Fe-Mn interface because spins of magnetic ions (Fe^{3+} or Mn^{3+}) are aligned in the same direction in (111) planes. The magnetization increase with decreasing the stacking periodicity by this effect.

Particularly, in the case of 1/1 superlattice, ferromagnetic behaviors are observed. The saturation magnetization (M_S) is estimated to be about 1 μ_B/site from the hysteresis curve measured in the field range from -1T to 1T. M_S is estimated to be 4.5 μ_B/site for $Mn^{3+}(d^4)$-O-$Fe^{3+}(d^5)$ state when Mn^{3+}-Fe^{3+} superexchange interactions are considered to be ferromagnetic from the theoretical estimation. Our result is rather small comparing with the theoretical result. The reducing M_S will be caused by the interfacial imperfection effect, oxygen deficient effect, and hole doping effect for La deficient.

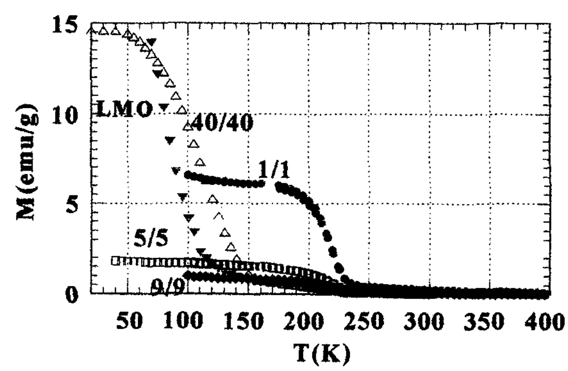

Fig. 6 : Temperature dependence of magnetization of $LaFeO_3$-$LaMnO_3$ superlattice on $SrTiO_3$(111) which are measured in a 0.1T field applied parallel to the surface of the substrate.

The magnetization versus temperature curves for $LaMnO_3$-$LaFeO_3$ artificial superlattices (1/1~11/11unit) on $SrTiO_3$ (100) is shown in Fig. 7. We would like to remind you of spin frustration effect caused at $LaFeO_3$-$LaMnO_3$ interface in (100) superlattices. In the case of superlattices with larger stacking periodicity, the properties of $LaMnO_3$ and $LaFeO_3$ appear independently. The properties of $LaMnO_3$ are appeared strongly in the temperature range from 5 to 400 K. The magnetization of superlattices decreases and become unsaturated and T_C decrease with decreasing stacking periodicity. The magnetic properties of $LaMnO_3$ affected by the spin frustration effect at the interface.

Particularly, in the superlattices less than 3/3 stacking periodicity, zero-field cooling and field cooling samples show different magnetic behaviors (inset of Fig. 7).

We think the unusual magnetic behaviors are caused by the appearance of spin glass phase by the spin frustration effect. And, detailed magnetic measurements is performed about the superlattice with 2/2 stacking periodicity.

The magnetization versus temperature curves of superlattice with 2/2 sequence in different fields (50 or 1000 Oe) are shown in Fig. 4(b) and (c). In these figures, ZFC and FC exhibit zero-field cooling and field cooling magnetization respectively. The magnetic behavior differs depending on whether the sample is cooling with (FC) or without (ZFC) field. A sharp cusp at about 65K with ZFC sample is found when the applied field is 50 Oe, but this cusp loses its sharpness and becomes a broad maximum, and at the same time moves to lower temperature with increasing the field. This is one evidence of spin glass materials. The increase of spin frustration effect caused by decreasing stacking periodicity bring spin glass phase into existence.

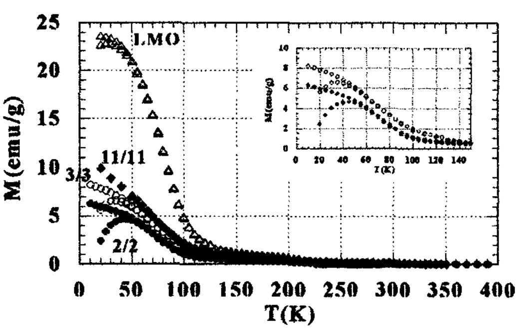

Fig. 7 : Temperature dependence of Magnetization for the $LaMnO_3$-$LaFeO_3$ superlattices formed on $SrTiO_3$ (100) with various stacking periodicity (2/2, 3/3, 11/11, and for $LaMnO_3$ film in the magnetic field of 0.1T. The inset shows the enlargement of magnetization versus temperature curves of 2/2 and 3/3 superlattices in different cooling process. Magnetization versus temperature curves for zero-field cooling (ZFC) and field cooling (FC) process in the field of 50 Oe and 1000 Oe.

As we have demonstrated, superlattices formed on (111), (110) and (100) surface are promising approach to control the three dimensional spin arrangement. The B-site ions are ordered as checkered structure, striped structure and layered structure, respectively.(see Fig.8) New magnetic character is expected corresponding to the B-site ion ordering.

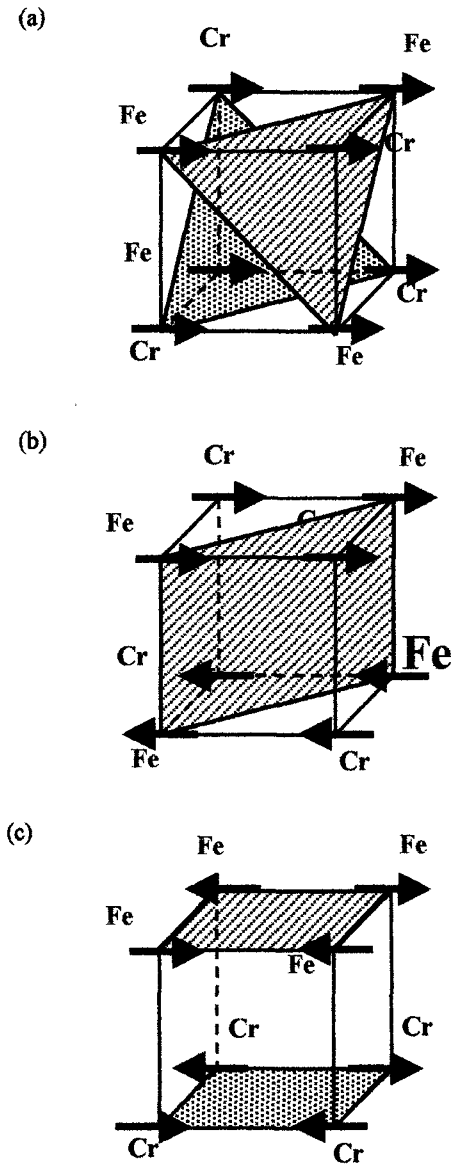

Fig. 8 Schematic model of spin arrangement in the superlattce on the (111), (110) and (100) surface.

5. CONCLUSION.

In summary, $LaFeO_3$-$LaCrO_3$ and $LaMnO_3$-$LaFeO_3$ artificial superlattices are constructed on $SrTiO_3$ (111), (110) and (100) substrates by laser MBE method and their magnetic properties are examined. Ferromagnetism has been revealed for the first time in our $LaFeO_3$/$LaCrO_3$ superlattice with a sequence of one by one unit layer on (111) surface. Magnetization of superlattices constructed on (111) plane increases with reducing stacking periodicity and the superlattice with 1/1 stacking periodicity show ferromagnetic behaviors. In the case of (100) superlattices, on the other hand, the effect of spin frustration increases with decreasing the stacking periodicity and the spin glass like phase have been appeared in superlattices with less than 3/3 stacking periodicity. New materials with Fe and Cr ions arranged alternately were formed by constructing artificial superlattices. $LaMnO_3$-$LaFeO_3$ artificial superlattices are constructed on $SrTiO_3$ (111), (110) and (100) substrates by laser MBE method and their magnetic properties are examined. Magnetization of superlattices constructed on (111) plane increases with reducing stacking periodicity and the superlattice with 1/1 stacking periodicity show ferromagnetic behaviors. In the case of (100) superlattices, on the other hand, the effect of spin frustration increases with decreasing the stacking periodicity and the spin glass like phase have been appeared in superlattices with less than 3/3 stacking periodicity. In this way, by using the method for creating an artificial superlattice based on theoretical consideration, we can control spin structures as we desire and can form materials with various spin structures.

REFERENCES

1. H. A. Kramers Physica **1**, 182 (1934).
2. P. W. Anderson Phys. Rev. **79**, 350 (1950).
3. J. B. Goodenough Phys. Rev. **100**,564 (1955).
4. J. Kanamori J. Phys. Chem. Solids, **10**, 87 (1959).
5. A. Wold and W. Croft J. Phys. Chem. **63**, 447 (1959).
6. A. Belayachi, M. Nogues, J. -L. Dormann, and M. Taibi Eur. J. Solid. State. Inorg. Chem. **t.33**, 1039 (1996).
7. K. P. Belov, M. A. Belyanchikova, A. M. Kadomtseva, T. M. Ledneva, M. M. Lykina, T. L. Ovchinnikova and L. P. Shlyakhina Sov. Phys. - Solid State **14** (1972) 813
8. R. Aleorard, R. Pauthenet, J. P. Rebouillat and C. Veyret J. Appl. Phys. **39**, 379 (1968).
9. W. C. Koehler, E. O. Wollan and M. K. Wilkinson Phys. Rev. **118**, 58 (1960).
10. D. Treves J. Appl. Phys. **36**, 1033 (1965).
11. T. Kawai, M. Kanai and H. Tabata Mater. Sci. Eng. **B41**, 123 (1996).
12. H. Tabata, T. Kawai and S. Kawai Phys. Rev. Lett. **70**, 2633 (1993).
13. K. Ueda, H. Tabata and T. Kawai submitted to Phys. Rev. Lett.

(Received December 11, 1998; accepted February 28, 1999)