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Ferromagnetic Characteristics of a Perovskite Type of (La, Sr)MnO₃ Films Deposited by Kr Sputtering

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Abstract. La_{1-x}Sr_xMnO₃ films about 4000 Å thick were deposited by sputtering from the targets with composition of La_{0.76}Sr_{0.24}Mn_{0.78}O_{3.0-y} in the gas mixture of Kr and O₂. Although the orientation of (110) in which metallic ions are most closely packed was preferential for films deposited in the gas mixture of Ar and O₂, the orientation of (111) in which large ions such as O²⁻, La³⁺ and Sr²⁺ are most closely packed was also observed in the X-ray diffraction diagrams. The maximum saturation magnetization of the as-deposited films in Kr and O₂ was 0.17 kG and it increased up to 2.4 kG for the film post-annealed at 1000°C for 3 hours in oxygen atmosphere. This value was larger than that of the film deposited in Ar and O₂ and annealed under the same condition. It seemed that the recoiled particles to the growing film surface and the atoms incorporated into the film were decreased in sputtering process by using Kr and therefore, larger 4πM_s was obtained.

1. INTRODUCTION

Since perovskite oxides such as (La, Sr)MnO₃ and (La, Bi, Sr)MnO₃ possess very attractive properties such as electrical conductivity, ferromagnetism and magneto-optical Kerr effect^{[1][2]}, the deposition of perovskite films have also been attempted. However, it has been difficult to prepare highly crystallized films with good magnetic characteristics by sputter-deposition. It seemed to be attributed not only to their complicated crystal structure, but also the bombardment of the recoiled Ar to the growing film surface. The atomic weight of Ar which is commonly used as sputtering gas, is 39.9 and it is likely to be recoiled by heavy atoms such as La and Sr with atomic weights of 138.9 and 87.6, respectively, and they may bombard to the growing film surface and are easily incorporated into the film. Therefore, in this study, heavier noble gas Kr was used for the deposition of La_{1-x}Sr_xMnO₃ films and their crystallite orientation and magnetic characteristics were investigated.

2. EXPERIMENTAL PROCEDURE

All specimen films were deposited by the facing targets sputtering (FTS) apparatus. This apparatus can confine the discharge plasma in the space between its two facing targets by applying the magnetic field perpendicularly to the target planes, the growing film and the substrate can avoid the plasma damage, i.e., the bombardment of hot-γ electrons and negative oxygen ions with high energy^[3]. Si wafers with thermally oxidized surface layer were used as substrates. Since this surface layer is amorphous and has a very smooth surface, adatoms are able to diffuse on it for a long time and the most closely packed structure is easily formed. A pair of targets with same composition of La_{0.76}Sr_{0.24}Mn_{0.78}O_{3-y} were prepared by dry ceramic technique. They were pre-sintered from the starting mixture of La₂O₃, SrCO₃ and MnCO₃ powder at 1000°C for 1 hour and 1100°C for 2 hour and finally sintered at 1200°C for 4 hour. Sintered targets possessed the saturation magnetization M_s of 38.5 emu/g and it was smaller than 40 % of M_s of perfect single crystal with same composition (about 100 emu/g^[4]). The vacuum chamber was evacuated by the diffusion pump and the average background pressure was 8.7×10⁻⁷ Torr. Kr and O₂ gases were introduced independently and total and oxygen gas pressure P_{total} and P_{O₂} were in the range of 1.0~4.0 and 0.0~0.8 mTorr, respectively. The substrate temperature T_s was in the range of 330~600°C. DC current supply was used for sputtering and the current was set at constant value of 0.2 A. The discharge voltage was depended on P_{total} and P_{O₂}, and it was in the range from 240 to 330 V. Film thickness was set at about 4000 Å.

Film composition was analyzed by the induced coupled plasma spectroscopy (ICPS). Crystallite orientation was evaluated on X-ray diffraction (XRD) diagram and saturation magnetization was measured by using the vibrating sample magnetometer (VSM).

3. RESULTS AND DISCUSSIONS

The orientation of (110) in which metallic ions are most closely packed was preferential for the film deposited in the gas mixture of Ar and O₂. Although each peak intensity became smaller as a whole, the orientation of (111) in which large ions such as O²⁻, La³⁺ and Sr²⁺ are most closely packed was also preferential for the film deposited in the gas mixture of Kr and O₂ in the X-ray diffraction diagrams as shown in Fig.1. It seemed that, since the network of oxygen ions with very light weight were not so seriously damaged during deposition because the number and energy of recoiled particles were fairly decreased for the deposition in Kr + O₂, (111) orientation could also be observed.

The resistivity of the as-deposited films at room temperature without applied field were in the range from 1.8 to 2.6 Ω·cm and these value were considerably higher than those of 3.5×10^{-2} Ω·cm which were reported by other researchers^{[5][6]}. Since the crystallinity of the as-deposited films was insufficient and the regular arrangement of Mn³⁺ and Mn⁴⁺ was not fully enough, the as-deposited films showed quite high resistivity.

Figure 2 shows the dependence of saturation magnetization $4\pi M_s$ on substrate temperature T_s for the as-deposited films and the films post-annealed at 1000°C for 3 hours in oxygen atmosphere. Although $4\pi M_s$ of as-deposited films were almost constant and at most 0.17 kG, i.e. about 1/30 of the $4\pi M_s$ of the sintered bulk La_{0.76}Sr_{0.24}Mn_{1.0}O_{3-y}, it increased up to 2.4 kG after the annealing process. Since $4\pi M_s$ of the films deposited in Ar+O₂ and annealed at the same conditions was smaller than 1.6 kG^[7], it seemed that the decrease of bombardment to the growing film surface and the atoms incorporated into films were fairly decreased by using heavier Kr and therefore, larger $4\pi M_s$ was attained by using Kr as sputtering gas. However, this value was only half of bulk value and the film surface had irregularities due to excessive growth of crystallites. In addition to that the annealed films had quite high resistivity, almost insulator, due to the cracks of film surface.

Further modifications of deposition conditions, such as use of Xe as sputtering gas, seemed to be required to decrease the preparation temperature and to increase the magnetization.

Fig.1 XRD diagrams of (La,Sr)MnO₃ films as-deposited in Ar+O₂ and Kr+O₂, and schematic illustration of (110) and (111) plane of unit cell.

Fig.2 T_s dependences of $4\pi M_s$ of as-deposited films and annealed at 1000°C for 3 hours in oxygen atmosphere.

4. CONCLUSION

La_{1-x}Sr_xMnO₃ films were sputter-deposited in the gas mixture of Kr and O₂ using FTS apparatus. The orientation of (111) in which large ions such as O²⁻, La³⁺ and Sr²⁺ are most closely packed was also observed as well as (110) orientation in which metallic ions are most closely packed. The saturation magnetization of the as-deposited films at 550°C was at most 0.17 kG and it increased up to 2.4 kG after annealing in oxygen atmosphere. It seemed that the bombardment to the growing film surface and the atoms incorporated into films were fairly decreased by using heavier Kr and therefore, larger $4\pi M_s$ was attained by using Kr as sputtering gas.

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