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Strain Effects in Artificially Layered $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ Superconductors

T. Hatano, A. Ishii, S. Labat, S. Arisawa and K. Togano,
National Research Institute for Metals, Sengen 1-2-1, Tsukuba, Ibaraki, 305-0047 Japan
FAX: 81-298-59-2301, e-mail: hatano@nrim.go.jp

Artificially layered and superlattice films of bismuth-based oxide superconductors, for instance $Bi_2Sr_2Ca_3Cu_4O_{12}$, $Bi_2Sr_2Ca_4Cu_5O_{14}$, $Bi_2Sr_2Ca_5Cu_6O_{16}$, $(Bi_2Sr_2Ca_3Cu_4O_{12})_1(Bi_2Sr_2Ca_1Cu_2O_8)_1$ and $(Bi_2Sr_2Ca_4Cu_5O_{14})_1(Bi_2Sr_2CuO_6)_1$, have been synthesized by sequential sputter deposition of bismuth-oxide, strontium-copper-oxide and calcium-copper-oxide monolayers. Crystal structures, superconducting transition temperatures and hole concentration of the films were studied by x-ray diffraction, Meissner effect and Hall effect measurements. As the number of CuO_2 layers per unit (n) increases, the hole concentration per Cu atom is found to decrease inversely proportional to the square of n. Therefore, the hole supply per unit is not independent of n. It is suggested that the amount of excess oxygen, which is the resource of the holes, decreases inversely proportional to the n as n increases. It was observed that the superconducting transition temperatures were enhanced by forming superlattice films of over doped ($Bi_2Sr_2Ca_1Cu_2O_8$, $Bi_2Sr_2CuO_6$) and under doped ($Bi_2Sr_2Ca_3Cu_4O_{12}$, $Bi_2Sr_2Ca_4Cu_5O_{14}$) phases. The results can be understood by stress induced changes in the hole concentration between the over and the under doped phases originated from the epitaxial (lattice matching) formation of the superlattice films.

Keywords: superconductor, BiSrCaCuO, thin film, superlattice, hole concentration, charge transfer, strained superlattice

1. INTRODUCTION

Layer-by-layer deposition techniques have been applied to the synthesis of layered oxide high-T_c superconductors, especially to the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ compounds which have a homologous structure series [1]-[11]. The thermally equilibrium phases having 1 to 3 CuO_2 planes in a unit structure (one half of the body-centered orthorhombic unit cell) and the artificial phases having 4 to 12 CuO_2 planes have been synthesized successfully. The layered $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ structure can also be considered as an alternating blocks of rock salt-type slabs (BiO-BiO) and perovskite slabs [SrO-CuO_2-(n-1)$CaCuO_2$-SrO]. The *in-plane* lattice constants of the rock salt and the perovskite slabs are 0.342 nm and 0.3874 nm, respectively. Because of the large mismatch between their *in-plane* lattice constants, the BiO layers are expanded along the *a-b* plane. As the result, a periodically introduced yielding, namely sausaging, of the $(BiO)_2$ planes is observed in the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ ($n \geq 2$)structure along the *b*-axis with the modulation period of about 2.6 nm (4.8 times of the *b*-axis length). The extra oxygen is introduced into the elongated part of the $(BiO)_2$ planes so as to fill the extra volume formed by the sausaging in the $(BiO)_2$ planes, which results in reservoir of the carriers in the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ superconducting compounds. Since the hole concentration in the CuO_2 plane is a key parameter of the high-T_c superconducting compounds, it is meaningful to study how the hole concentration changes by the increase of n. Furthermore, by the increase of n, the stress which works between the slabs changes. The amount of excess oxygen in the sausaging part of the $(BiO)_2$ planes would change by the increase of n. Therefore, it is worthwhile to study the effect of strains in these slabs by changing the thickness of the perovskite slabs (number of the CuO_2 layers). It is expected that the ***in-plane a,b*** lattice constants increase as n increases, because the ***in-plane a,b*** lattice constants of the perovskite slabs is larger than those of the $(BiO)_2$ planes.

The superlattice films of the members of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ [22(n-1)n in an abbreviated form] series are also studied. Because of the lattice mismatch between the series members, the superlattices are also a kind of strained superlattices. The authors have recently reported that the enhancement of T_c is observed in the superlattice films consisting of the under doped 2234 (2245) units and the over doped 2212 (2201) units [12,13]. They concluded that the charge transfer from the over doped unit to the under doped unit can explain the observed T_c enhancements. To explain the results in the previous studies, it is necessary to investigate the mechanism of the charge transfer from the over doped phase to the under doped phase. In this paper, the artificial 22(n-1)n films, the $(2234)_1(2212)_1$ and the $(2245)_1(2201)_1$ superlattice films are examined in detail by x-ray diffraction (XRD) especially ***in-plane***. We report and discuss the effects of the change in the *in-plane* lattice constants by artificial lattice layering of the phases like 2234, 2245, etc. and by the superlattice formation. In the latter case, it would result in the transfer of the holes from the over doped unit to the under doped unit due to the lattice mismatch in the *a-b* planes.

2. EXPERIMENTAL

The details of deposition condition using the *off-axis* three target RF magnetron sputtering apparatus were described elsewhere [12-16]. For the synthesis of the 22(*n*-1)*n* single phase films, sequence of layering on MgO single crystal (001) substrates heated at 700-710 °C was $BiO\text{-}SrCu_{0.5}O_{1.5}\text{-}(n\text{-}1)CaCuO_2\text{-}SrCu_{0.5}O_{1.5}\text{-}BiO$. For the synthesis of the $(2245)_1(2201)_1$ superlattice film, for instance, the sequence of layering was $BiO\text{-}SrCu_{0.5}O_{1.5}\text{-}4CaCuO_2\text{-}SrCu_{0.5}O_{1.5}\text{-}BiO\text{-}BiO\text{-}2SrCu_{0.5}O_{1.5}\text{-}BiO$. The deposition sequence of a unit was repeated 32 times for the single phase films and 16 times for the superlattice films. The thickness of the single phase films was designed to have the same number of molecular layers as the superlattice films and is 39 nm for 2201 and 78 nm for 2245, respectively. The thickness of the superlattice films of $(2234)_1(2212)_1$ and $(2245)_1(2201)_1$ is 59 nm.

The crystal structures of the films were measured by an x-ray diffractometer equipped with rotating anode. The details of x-ray diffraction measurement conditions were described in our previous papers [12-16]. The *in-plane a,b* lattice constants were directly measured using Philips Material Research Diffractometer. A grazing incidence x-ray beam, 0.5° from the film surface, was employed for the measurements of the *in-plane* (200) and (220) diffraction from the strongly *c*-axis textured films.

The hole concentration in the films was measured by the Hall effect experiment. The measurement was done at 140K (normal state) with current (1 mA) parallel to the film surface (*a-b* plane) under a magnetic field of 0.6 T applied perpendicularly to the film surface (parallel to the *c*-axis).

The T_c was measured by a superconducting quantum interference device (SQUID) under the magnetic field of 10 Oe applied perpendicularly to the film surface.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction of artificial phases

Fig. 1 shows the x-ray θ/2θ diffraction (XRD) spectra of the 2234, 2245 and 2256 artificially layered films. These films were synthesized under the similar conditions except the deposition time of $CaCuO_2$ layers. Only the (00ℓ) diffraction lines are observed from the superconducting phases indicating that the layered oxide films have almost complete *c*-axis textures. Only the even ℓ peaks in (00ℓ) diffraction lines are observed because of the body-centered orthorhombic symmetry in the crystal structure of the artificial phases. The position of the (00ℓ) diffraction lines are analyzed in detail by the lattice constant precision plot [16]. The accuracy of *n* is within ±0.01 for the films plotted in Fig.1. The intensities of the (0,0,2(n+3)) line decrease as n increase because the CuO_2 layers interleave halfway between the average lattice of BiO-SrO-Ca-Ca-Ca· · -SrO-BiO.

3.2 Hole concentration of artificial phases

The hole concentration per Cu atom is found to decrease inversely proportional to the square of *n* as number of CuO_2 layers increases as shown in Fig. 2. If we could assume that the hole supply per unit is independent of *n*, the hole concentration per Cu atom would decrease inversely proportional to the *n*. The experimental result means that the hole supply per unit depends inversely proportional to the *n*. Although, an accurate evaluation of excess oxygen is not possible for those artificial thin films, it is suggested that the amount of excess oxygen, which is the resource of the holes, decreased inversely proportional to the *n* as *n* increases. As the increase of *n*, the thickness of the perovskite slabs increase. Therefore, it becomes harder to laminate these slabs as *n* increases. Thus the amplitude of modulation decreases which results in the decrease of the excess volume in the BiO planes for the excess oxygen.

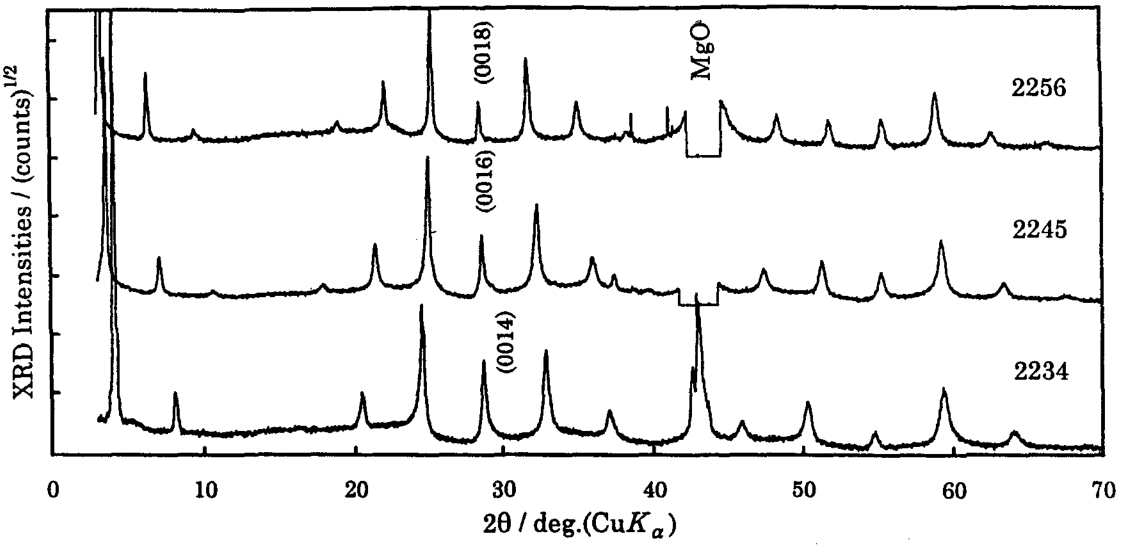

Fig. 1. X-ray θ/2θ diffraction spectra of 2234, 2245 and 2256 films synthesized under the similar conditions except the deposition time of $CaCuO_2$ layers.

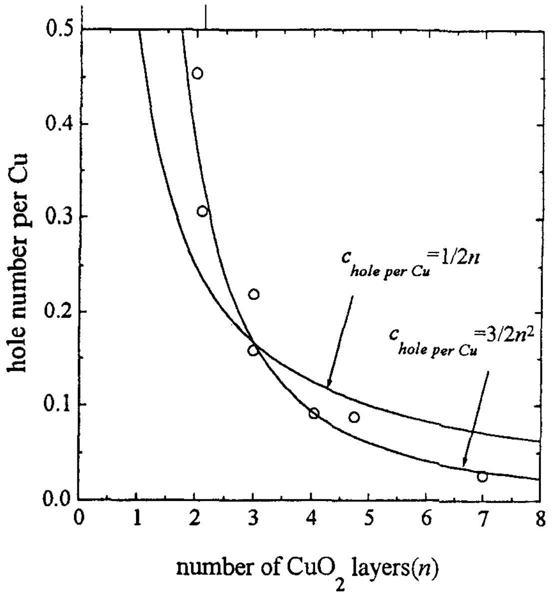

Fig. 2. Hole concentration in the films measured by the Hall effect experiment. The measurement was done at 140K (normal state) with current (1 mA) parallel to the film surface (*a-b* plane) under a magnetic field of 0.6 T applied perpendicular to the film surface (parallel to the *c*-axis).

3.3 *In-plane* lattice constants of artificially layered films and superlattice films

The decrease of hole concentration results in the decrease of the population of Cu^{3+} ions and in the increase of that of the Cu^{2+} ions. Because the radius of the Cu^{2+} ion is larger than that of the Cu^{3+} ion, this results in the increase of the average ionic radius of Cu and may result in the increase of the lattice constants. Therefore, it is necessary to evaluate the *in-plane a,b*-lattice constants of the series structures and to evaluate lattice mismatches between the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ series members in the superlattice films. Fig. 3 shows the *in-plane a,b*-lattice constants measured by the x-ray diffraction at the grazing incidence. Because of the pseudo-Tetragonal structure of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ series members, *a* and *b* lattice constants can not be distinguished. Therefore, the lattice constant of the primitive cell is shown in Fig. 3. It is observed that the *a,b* lattice constants increase monotonically as *n* increases. This result proves that the increase of the population of the Cu^{2+} ions results in the increase of the *in-plane* lattice constants of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ series structures.

The *in-plane a,b* lattice constants of the superlattice films are observed in between those of the single phase films which consist the superlattice. Therefore, the superlattices synthesized here are not simply the alternate layering of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ series structure, but are "strained superlattice" due to the lattice mismatching in the *a-b* planes.

3.4 Charge transfer in the superlattice films

In the case of $(2245)_1(2201)_1$ superlattice formation, a compression stress works in the 2245 units in the *a-b* plane and a tensile stress works in the 2201 units. As the results, the *in-plane a,b*-lattice constants were observed between those of the 2245 and 2201. The stress can be released if the ratios of Cu^{3+}/Cu^{2+} become equal in both the 2245 and 2201 units. It is suggested that the stress in the 2245 and 2201 induces the change in the population of the Cu^{3+} ions in the superlattice consisting of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ series members. The stress releasing in the *a-b* plane might be the driving force of the charge transfer from the over doped unit to the under doped unit which results in the optimization of the hole concentration in the CuO_2 planes and the enhancement of T_c in the over/under doped superlattice films.

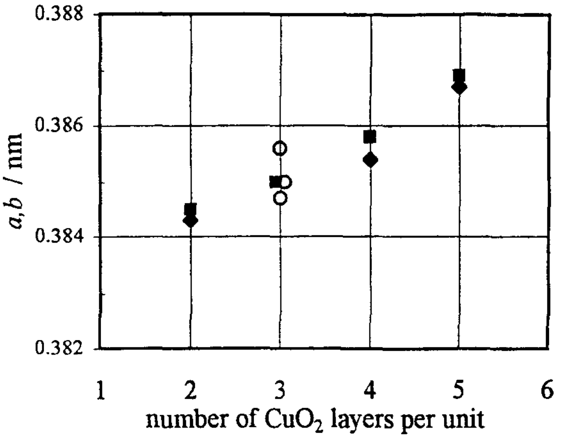

Fig. 3. *In-plane* lattice constants of the superlattice films (open circle) and single phase films (closed squares).

4. CONCLUSION

The hole concentration per Cu atom is found to decrease inversely proportional to the square of *n* as number of CuO_2 layers increases. Therefore, the hole supply per unit is not independent of *n*. It is suggested that the amount of excess oxygen, which is the resource of the holes, decreased inversely proportional to the *n* as *n* increases.

The superlattice films consisting of the alternating molecular layers of 2234 (2245) and 2212 (2201) were examined in detail by the x-ray diffraction especially *in-plane*. The observed superconducting transition temperature in the $(2234)_1(2212)_1$ and $(2245)_1(2201)_1$ superlattice films were higher than those of the 2234 (2245) and 2212 (2201) single phase films. This result can be explained in terms of the charge transfer from the over doped unit (2212, 2201) to the under doped unit (2234, 2245).

Because the *in-plane* lattice constants of the pseudo-Tetragonal 22(*n*-1)*n* differ slightly between the 2234 (2245) (~0.386 nm) and 2212 (2201) (0.384 nm) phases, the superlattice films synthesized here are a kind of strained superlattice. It is suggested that the stress might induces the charge transfer from the over doped layers to the under doped layers so as to release the strains in both over doped (tensile stress) unit and under doped unit (compressive stress) by equalizing the average ionic radius of Cu and the concentration of Cu^{3+} ions in the CuO_2 layers.

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