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Watanabe, Yukio
Mitsubishi Chemical Yokohama Research Center

Tanamura, Mitsuru
Mitsubishi Chemical Yokohama Research Center

Matsumoto, Yasuaki
Mitsubishi Chemical Yokohama Research Center

Asami, Harumi
Mitsubishi Chemical Yokohama Research Center

他

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Ferroelectric/$(La,Sr)_2CuO_4$ epitaxial heterostructure with high thermal stability

Yukio Watanabe, M. Tanamura, Y. Matsumoto, H. Asami, and A. Kato
Mitsubishi Chemical Yokohama Research Center, Yokohama, 227, Japan

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Three-dimensionally aligned epitaxial $(Pb,La)(Zr,Ti)O_3/(La,Sr)_2CuO_4$ multilayers were grown on $SrTiO_3$ (100) single crystals by pulse laser deposition. A cube-on-cube epitaxial relationship of these multilayers was confirmed by the θ-2θ diffraction profile and the pole figure. The stability of their interfaces was confirmed by depth profiles and x-ray diffractometry of the as-deposited and the annealed multilayers having 100–300-Å-thick $(La,Sr)_2CuO_4$ layers. The results suggest that the multilayers can be applied to the ferroelectric field-effect transistor. © *1995 American Institute of Physics.*

Epitaxial ferroelectric/conductive perovskite multilayers have recently received a considerable interest. An example of this structure was a $SrTiO_3$/cuprate superconductor to modulate the superconductivity by the field effect.[1] Another was $YBa_2Cu_3O_7$ $(Bi_2Sr_2Ca_{n-1}Cu_nO_x$ $n=1,2)$ /ferroelectric/ $YBa_2Cu_3O_7(Bi_2Sr_2Ca_{n-1}Cu_nO_x$-$n=1,2)$,$(La,Sr)CoO_3$/ferroelectric/$(La,Sr)CoO_3$ or $SrRuO_3$/ferroelectric/$SrRuO_3$ for a ferroelectric capacitor structure.[2–5] These results have shown that unique properties could be achieved using novel epitaxial structures. The multilayers are also useful to study basic physical problems such as size effect on ferroelectric and dielectric properties.[6]

However, ferroelectric/conductive perovskite multilayers using $La_{2-x}Sr_xCuO_4$ (LSCO) have not been reported to our knowledge. We have found that LSCO films were chemically stable in lithography processes, and that their conductivity could be controlled well down to $x=0.01$ or less, which is suitable for the ferroelectric field-effect transistor.[7] In this letter, we report the growth of the multilayer having good crystallographic properties and superior interface stability. We have chosen $Pb_{1-y}La_yZr_xTi_{1-x}O_3$ ($x=0$, 0.15, 0.25, $y=0.05$, 0.1) (PLZT) as the ferroelectric. The estimated lattice mismatch between a-axis of LSCO and that of PLZT ranged from 3% to 4% at room temperature, depending on the La and Zr concentration.

PLZT/LSCO multilayers were grown *ex situ* and *in situ* on $SrTiO_3$ (STO) (100) single crystal by pulsed laser deposition using an ArF excimer laser. The surface of the substrate heater was maintained at 720–730 °C for LSCO film and 580 °C for PLZT film (520 °C for some PLZTs with $x=0$). The laser power densities on the target were about 0.7 J/cm^2 for the LSCO target and 2 J/cm^2 for the PLZT target. The deposition was carried out in an oxygen pressure of 1–50 mTorr for LSCO and 200–300 mTorr for PLZT. The thicknesses of the LSCO and PLZT layers were 100–1000 Å and 2000–4000 Å, respectively. No post-annealing was performed. Average composition of the film was analyzed by x-ray fluorescent spectroscopy which was calibrated by the inductively coupled plasma spectroscopy. Ferroelectric remnant polarization measured using a Sawyer–Tower circuit was typically ± 3–8 μC/cm^2.

The T-phase (hole-type conduction, Ln_2TO_4:Ln =rare-earth metal, T=3d metal)[8] is known to be stable in a low oxygen environment since the discovery of the cuprate superconductor.[9] Indeed, we obtained La_2NiO_4 films using sintered $LaNiO_3$ targets, when the ambient oxygen pressure was below 30 mTorr. Moreover, LSCO films without impurity phases were formed in oxygen pressure of 0.1–100 mTorr at substrate surface temperatures of 700–750 °C. These observations suggest a good thermal stability of the T-phase films. Additionally, particulates, which are often observed in laser-deposited films,[10] were hardly observed by a scanning electron microscope (SEM) in surface areas of 1

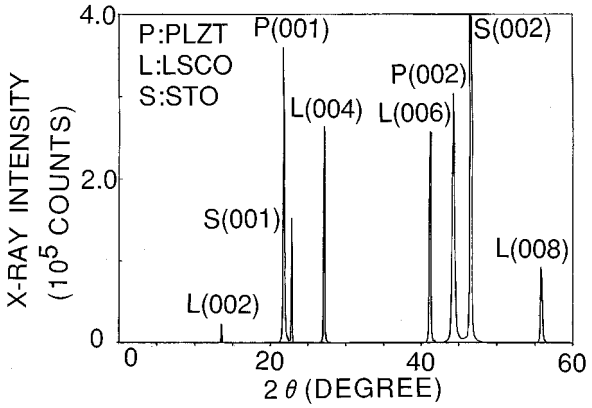

FIG. 1. $\theta/2\theta$ x-ray diffractometer profiles of a $Pb_{0.95}La_{0.05}Zr_{0.2}Ti_{0.8}O_3/La_{1.99}Sr_{0.01}CuO_4$ multilayer grown *ex situ*.

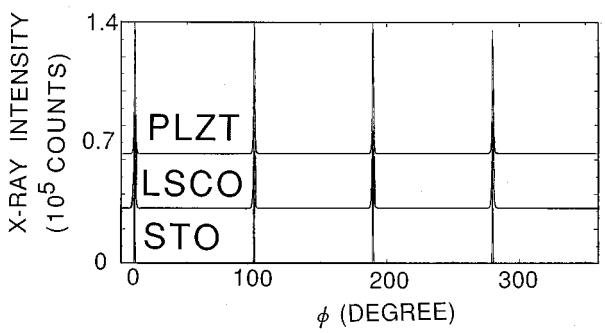

FIG. 2. ϕ x-ray diffractometer profiles of the multilayer shown in Fig. 1.

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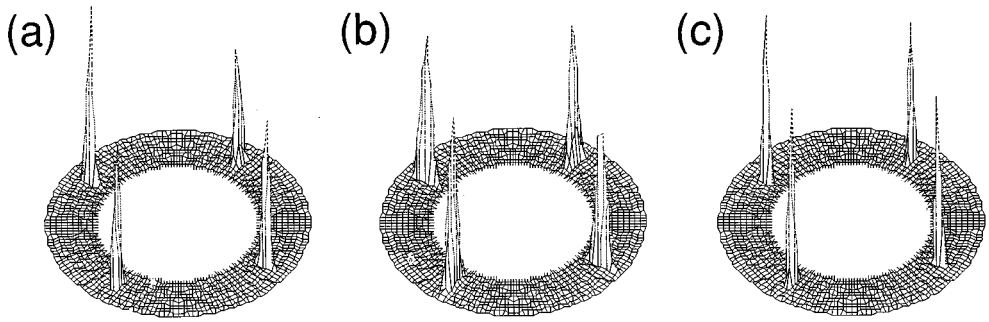

FIG. 3. X-ray diffractometer pole figures of PLZT (a), LSCO (b), and the substrate (c) of the multilayer shown in Fig. 1.

mm^2 of the LSCO films. The film surface was also smooth at an SEM magnification of 100 000. These results were consistent with the fact that more than 8 of 10 capacitors made on the PLZT/LSCO multilayers with an electrode area of 1 mm^2 showed resistance over $0.1G\ \Omega$ at 0.1 V.

An x-ray diffractometer scan for the multilayer showed peaks only from the $(h00)$ and the $(00l)$ families of planes of PLZT and peaks from the $(00l)$ families of planes of LSCO. The $(h00)_{PLZT}$ peaks were observed for $x \geqslant 0.3$ or $y \geqslant 0.1$ in the formula of $Pb_{1-y}La_yZr_xTI_{1-x}O_3$. Figure 1 shows x-ray $\theta/2\theta$ scan diffractometer pattern from a $Pb_{0.95}La_{0.05}Zr_{0.2}Ti_{0.8}O_3$ (2400 Å)/$La_{1.99}Sr_{0.01}CuO_4$ (1200 Å) multilayer. All of the diffraction peaks observed can be indexed as the $(00l)$ peaks from PLZT, LSCO, or the substrate. There was a possibility that the small $(h00)_{PLZT}$ was hidden in the $(00l)$ peaks from the substrate. According to Ref. 11, the integrated intensities of the $(002)_{PLZT}$ and $(200)_{PLZT}$ peaks depend mainly on the multiplicity factor, and thus the volume fraction of the c-axis-oriented PLZT in Fig. 1 was estimated to be more than 99%. The c-axis lattice constant of the PLZT layer estimated from $(00l)$ peaks was 4.10 Å. The sharp peaks in the ϕ scan plots in Fig. 2 show excellent in-plane alignment of these materials. Figure 3 shows the (202) pole figures of the PLZT and the substrate, and the (103) pole figure of LSCO. The full widths at half-maximum (FWHM) in β scan (azimuthal direction) in the pole figures of the PLZT and LSCO layers, and the substrate were 1.2°, 1.2°, and 0.5°, respectively. However, the FWHMs in α scan (radial direction) in the pole figures were 2.6°, 5.5°, and 2.5° for the PLZT and LSCO layers, and the substrate, respectively. The widths reduced in the multilayer having a PLZT composition of $Pb_{0.95}La_{0.05}TiO_3$ and a shorter PLZT a-axis lattice constant. The large widths observed for the single crystal substrates suggest that they were increased by the divergence of the x-ray beams. The dependence of the widths and the lattice mismatch on the ferroelectric composition is summarized in Fig. 4. The effect of the mismatch on the widths in the β scan was evident, while the width of the PLZT peak in the α scan was the same as that of substrate and unchanged. For multilayers having a relatively thick LSCO layer (>500 Å), the above results were the same for *in situ* and *ex situ* grown films.

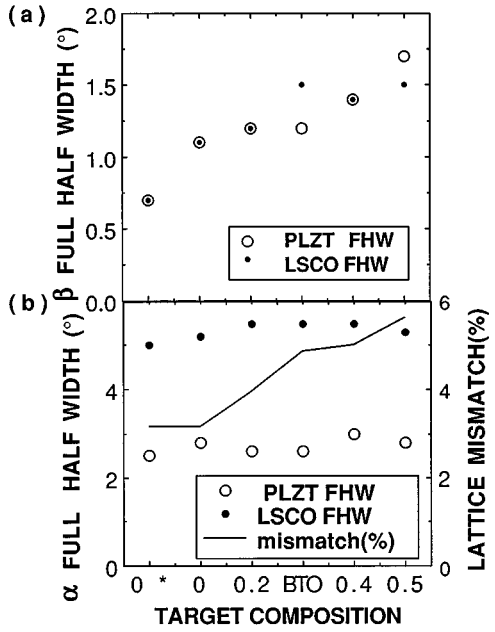

FIG. 4. Dependence of the widths (a,b) in the pole figures and the lattice mismatch (b) between LSCO and ferroelectric on composition. The numbers in the horizontal axis in the figure denote x in the formula of $Pb_{0.95}La_{0.05}Zr_xTi_{1-x}O_3$. The symbol 0* represents the multilayer of which $Pb_{0.95}La_{0.05}TiO_3$ layer was deposited at a lower substrate temperature (520 °C), and the BTO represents the $BaTiO_3$/LSCO multilayer.

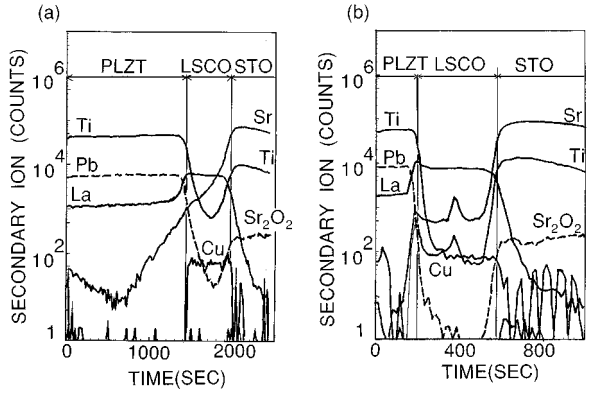

FIG. 5. SIMS depth profiles of PLZT/LSCO (2000 Å)/STO, where PLZT=$Pb_{0.95}La_{0.05}Zr_{0.2}Ti_{0.8}O_3$ (2000 Å) (a) and PLZT=$Pb_{0.95}La_{0.05}TiO_3$ (500 Å) (b).

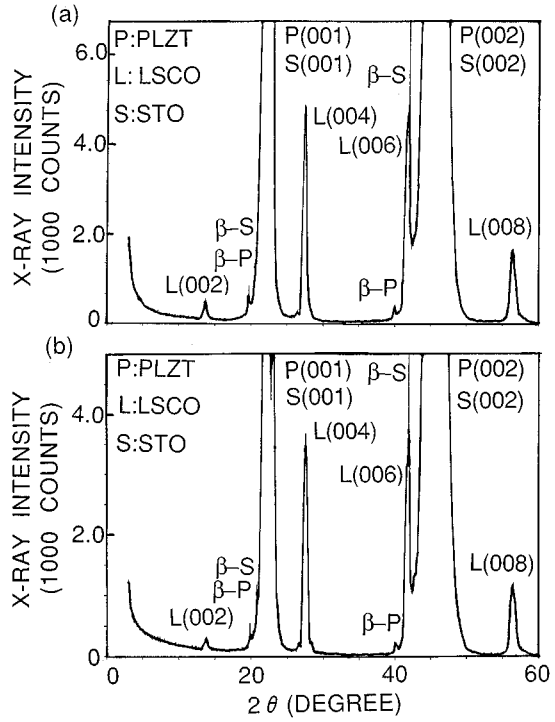

FIG. 6. $\theta/2\theta$ x-ray diffractometer profiles of $Pb_{0.9}La_{0.1}Zr_{0.1}Ti_{0.9}O_3$ (2100 Å)/$La_{1.99}Sr_{0.01}CuO_4$ (150 Å) grown *in situ* before annealing (a) and after annealing (b). The marks *β-P* and *β-S* indicate the $(00l)_{PLZT}$ and $(00l)_{STO}$ diffractions of Cu $K\beta$ irradiation which was reduced by filter.

The compositional depth profile of the multilayers was studied by Auger electron spectroscopy (AES). No interdiffusion of the element was detected in the multilayer, whereas interdiffusion of Si and Ti was detected at the PLZT/Si interface grown in the same condition. Furthermore, formation of the impurity phase at the interface was not detected by the secondary ion mass spectroscopy (SIMS) depth profile. However, we could not exclude the possibility of the subtle interdiffusion of Pb and Ti into LSCO. In the case of the $Pb_{0.95}La_{0.05}TiO_3$ (grown at 520 °C)/LSCO multilayer, no interdiffusion was detected within measurement error [Fig. 5(b)].

In order to examine the stability of the interface during the device fabrication and to detect the interdiffusion at the interface by x-ray diffraction, a PLZT/LSCO multilayer having a 150-Å-thick LSCO layer was grown *in situ*. Figures 6a and 6b show $\theta/2\theta$ x-ray diffraction patterns from the multilayer before and after annealing at 300 °C in pure oxygen for 5 h. The diffraction pattern was unchanged before and after the annealing. All of the diffraction peaks observed were indexed as Cu $K\alpha$ and Cu $K\beta$ $(00l)$ peaks from PLZT, LSCO, or the substrate. Two small shoulders at the $(004)_{LSCO}$ peak were visible in the diffraction patterns before and after the annealing. However, the shoulders were often observed in single layered 100–200-Å-thick LSCO films. Therefore, they were probably not due to the interface reaction. Furthermore, 100–300-Å-thick LSCO films coated *in situ* with PLZT layers showed conductivity comparable or superior to that of single layered LSCO.

In conclusion, we have grown a three-dimensionally aligned epitaxial heterostructure using $La_{2-x}Sr_xCuO_4$ and $Pb_{1-y}La_yZr_xTi_{1-x}O_3$ with a tetragonal crystal structure. The interdiffusion at the interface was well suppressed and the interface was confirmed to be highly stable.

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[1] U. Kabasawa, K. Asano, and T. Kobayashi, Jpn. J. Appl. Phys. **29**, L86 (1990).
[2] R. Ramesh, W. Chan, B. Wilkens, T. Sands, J. Tarascon, J. Keramidas, and J. Evans, Integrated Ferroelectrics **1**, 1 (1992).
[3] R. Ramesh, A. Inum, W. K. Chan, B. Wilkens, K. Myers, R. Remsching, D. L. Hart, and J. Tarascon, Science **252**, 944 (1991).
[4] J. T. Cheung, P. E. D. Morgan, D. H. Lowwndes, X.-Y. Zheng, and J. Breen, Appl. Phys. Lett. **62**, 2045 (1993).
[5] C. E. Eom, R. B. Van Dover, J. M. Philips, D. J. Werder, J. H. Marshall, C. H. Chen, R. J. Cava, and R. M. Fleming, Appl. Phys. Lett. **63**, 2570 (1993).
[6] Y. Watanabe, Y. Matsumoto, H. Kunitomo, M. Tanamura, and E. Nishimoto, Jpn. J. Appl. Phys. **33**, 5182 (1994).
[7] Y. Watanabe, *Extended Abstract of the 1994 International Conference on Solid State Devices and Materials (SSDM'94)* (Japan Society of Applied Physics, Tokyo, Japan, 1994), p. 784.
[8] Y. Tokura, Physica C **185–189**, 174 (1991).
[9] J. G. Bedenorz and K. A. Mueller, Z. Phys. B **64**, 189 (1896).
[10] S.-G. Lee, D.-S. Hwang, Y. K. Park, and J. C. Park, Appl. Phys. Lett. **65**, 764 (1994).
[11] S. G. Ghonge, E. Gao, R. Ramesh, T. Sands, and V. G. Keramidas, Appl. Phys. Lett. **63**, 1628 (1993).