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Chemically processed Nb-doped $SrTiO_3$ films and properties*

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Abstract: Homogeneous, crack-free $SrNb_xTi_{1-x}O_3$ thin films on (110) silicon substrates were successfully fabricated by sol-gel processing. The optimum route and conditions were systematically investigated. $Sr(OAc)_2$ glacial acetic acid solution, after being refluxed and reacted with tartrate, formed $Sr(OAc)_2(C_4H_6O_6)_2$; $Ti(OBu)_4$ formed $Ti(OAc)_{4-x}(AcAc)_x$ after having the ligand partially exchanged with AcAc, while $Nb(OC_2H_5)_5$ formed $(OAc)_2Nb(AcAc)$ $(C_4H_6O_6)$ by exchanging of ligand in glacial acetic acid with $(CH_3CO)_2O$. All the metal species after undergoing partial hydrolysis and polymerization with hydroxyl or oxygen, formed $SrNb_xTi_{1-x}O_3$ cluster sol. Methyl cellulose (MCL) caused $SrNb_xTi_{1-x}O_3$ sol to have polymeric structure and easily form films. $SrNb_xTi_{1-x}O_3$ films with perovskite were subsequently formed after being annealed at 650~750 °C for 60 min in 25% N_2+75% H_2 (volume ratio) atmosphere. Resistivity of the $SrNb_{0.1}Ti_{0.9}O_3$ films at room temperature was 64 μΩ·cm, a particular T^2 temperature dependence of the resistivity, from 25 K up to room temperature, was observed.

Key words: $SrNb_xTi_{1-x}O_3$ (SNTO) film, Sol-gel technique, Donor-doping-semiconductor
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INTRODUCTION

Perovskite-type oxides have attracted considerable interest regarding their various electronic, magnetic and optical properties, such as superconductivity, colossal magnetoresistance and ferroelectricity caused by strong interactions of their charge, spin and lattice characteristics (Millis, 1998; Wu *et al*., 2000; Gariglio *et al*., 2001). Currently, many investigations are underway to harmonize these properties and create new functional materials for applications to oxide electronics. Among a number of perovskite oxides, $SrTiO_3$ is one of the most important materials because of its application for standard substrates of functional materials, including superconductor films, magnetoresistance films and ferroelectric films (Wu *et al*., 2000). It is now possible to take advantage of the diverse behavior in epitaxial heterostructure, and the highly electrical conductivity. Perovskite heterostructure films have been found useful for oxide electronic devices (Pan *et al*., 2004; Contreras *et al*., 2003). An example is epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3/SrRuO_3$ heterostructures (Sugiura *et al*., 2001; Ahn *et al*., 1997). For opening novel applications to electronics, it is necessary to fabricate n-type $SrNb_xTi_{1-x}O_3$ (SNTO), as such electron doped $SrTiO_3$ is known to transform insulating $SrTiO_3$ into a metallic state based on the cubic perovskite with the space group pm3m, where Ti and Nb atoms are located at the cube corner, Sr atoms at the cube centers, and O atoms at the edge centers (Wu *et al*., 2000; Sugiura *et al*., 2001).

The present study aimed at fabricating low-resistivity n-type SNTO films without an argon-filled or inter-atmosphere glove box. SNTO sol precursor was successfully prepared with $Nb(OC_2H_5)_5$, $Ti(OC_4H_9)_4$ and $Sr(OAc)_2·2H_2O$, SNTO films on Si(110) fabricated at reasonably low processing temperatures.

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Glacial acetic acid as solvent made the compounds change into acetates, which play the role of the corresponding alkoxides; $(CH_3CO)O$ removes crystallized H_2O and makes the ligands exchanged under anhydrous conditions.

The $Sr(OAc)_2$, combining with tartrate, formed $Sr(OOCCH_3)_{2-x}(C_4H_6O_6)_{x/2}$, which was hydrolyzed as

$$Sr(OOCCH_3)_{2-x}(C_4H_6O_6)_{x/2}+(2-x)H_2O =Sr(OH)_{2-x}(C_4H_6O_6)_{x/2}+(2-x)CH_3COOH. \quad (1)$$

When $(OC_4H_9)_4Ti$:AcAc>1:2 (mol/mol),

$$Ti(OOCCH_3)_4+2AcAc\rightarrow Ti(OOCCH_3)_2(AcAc)_2+2HOOCCH_3, \quad (2)$$

$$Ti(OOCCH_3)_2(AcAc)_2+2H_2O\rightarrow Ti(OH)_2(AcAc)_2+2HOOCCH_3. \quad (3)$$

While Nb(V) of $Nb(OC_2H_5)_5$ as center metal ion reacted with AcAc and $C_4H_6O_6$ formed $Nb(AcAc)_2(C_4H_6O_6)_2$ by ligand exchanging, under anhydrous conditions,

$$Nb(OC_2H_5)_5+2HOOCCH_3+AcAc+C_4H_6O_6= Nb(OOCCH_3)_2(C_4H_6O_6)(AcAc) \quad (4)$$

synchronized the effect between the $C_4H_6O_6$ and AcAc makes

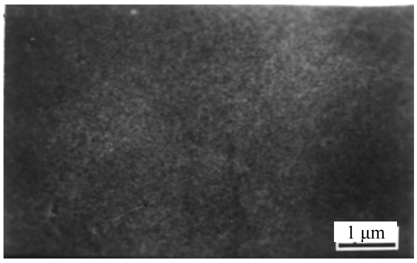
$$(OOCCH_3)_2Nb(C_4H_6O_6)(AcAc)+2H_2O= (OH)_2Nb(C_4H_6O_6)(AcAc)+2HOOCCH_3. \quad (5)$$

All metal species undergo a succession of transformations (Yin *et al*., 2004): (1) hydrolysis of the complexes; (2) polymerization via successive multimolecular of the metal ions by oxo- or hydroxyl- or aqua-bridges; (3) formation of homogenetic and stoichiometric SNTO sol. MCL with hydroxyl and carbonyl group makes the metal hydroxyl complexes polymerized and formed polymeric SNTO sol.

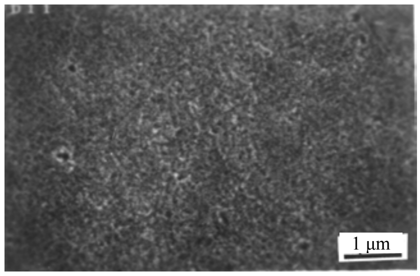
Spin-coating the SNTO sol precursor on silicon at 3000~3500 r/min for 20 s in 100 class clear room, the coated films were annealed at 350 °C for 30 min. The operations were recycled to obtain the desired thickness. The coated films were annealed at appropriate temperature for 60 min in 25% N_2+75% H_2 (volume ratio) atmosphere formed by decomposing NH_3 at annealing temperature.

SEM OF SNTO FILMS

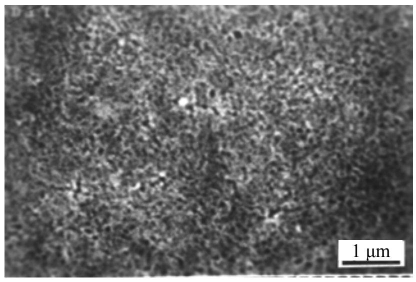
Fig.1 shows the Scanning Electron Microscopy (SEM) images of the SNTO films deposited on Si(110) after being annealed at certain temperatures.



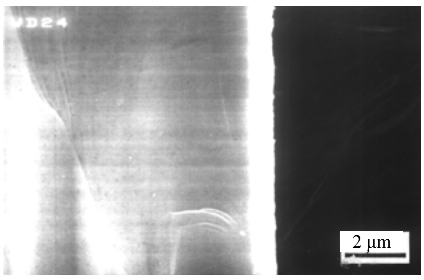
(a)



(b)



(c)



(d)

Fig.1 SEM images of the SNTO film after being annealed. (a) 550 °C, 60 min; (b) 650 °C, 60 min; (c) 750 °C, 60 min; (d) Cross section SEM (750 °C, 60 min)

After being annealed at 550 °C for 60 min, the SNTO film appears as a dense structure composed of metal oxide clusters, while after being annealed at 650 °C for 60 min, the film exhibits typical distinct crystal grains. The morphology appears dense, uniform, and crack-free. The crystal grain sizes increased with increasing annealing temperature. Thickness of the films was about 0.6 μm after being annealed at 750 °C for 60 min depending on the spinning number.

SNTO crystals are readily grown to a size much larger than that of the original particles, but isolation of the hydrous particles upon annealing might limit crystallization from taking places on a large local scale, so that the original nano-scaled microstructure is preserved. Furthermore, crystal growth involves advancing of grain boundaries. Grain boundaries of SNTO films are 'pinned' and their motions are restricted by the hydroxyl or organic additive. So the 'pinning' particles of SNTO crystals are in nano-scales.

CRYSTALLOGRAPHIC MICROSTRUCTURE OF SNTO FILM

The crystallographic microstructures of SNTO films on Si(110) substrates were examined using the X-ray-diffraction (XRD) technique and are shown in Fig.2.

After intermediate annealing at 550 °C, the SNTO film is amorphorous without special diffraction peaks; diffraction peaks (110), (111), (200), (211) appear after annealing at 650 °C for 60 min, the intensity of the diffraction peaks are increased monotonically with increasing annealing temperature. The resultant SNTO films appear polycrystalline as a good-cubic perovskite with (110) orientation.

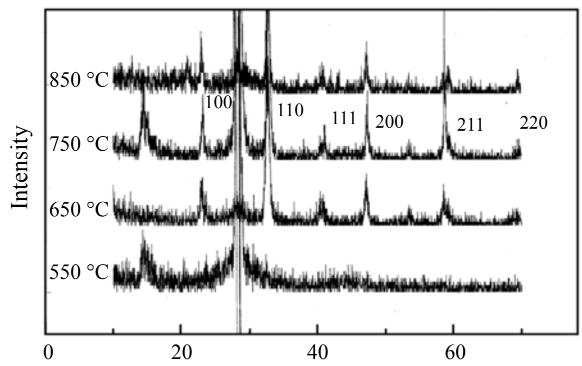


Fig.2 XRD patterns of 0.6 μm thick SNTO films deposited on Si(110) substrates

Fig.3 is the temperature dependence of resistivity of SNTO film measured with the four probe methods.

A metallic transport behavior was observed over the whole temperature range of 25~300 K. The temperature dependence of resistivity can fit well the $\rho=\rho_0+AT^2$ relation and be described by the transport behavior of the Fermi liquid model (Shanthi and Sarma, 1998).

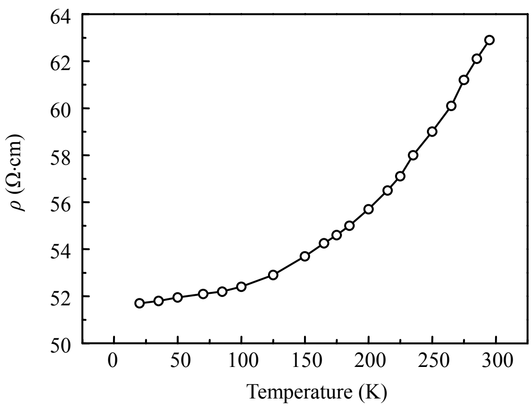


Fig.3 Temperature dependence of resistivity measured for SNTO films

CONCLUSION

Polycrystalline, homogeneous, and crack-free $SrTiO_3$ thin films were successfully prepared by the polymeric precursor method. $Sr(OAc)_2$, $Ti(O_4C_9)_4$ and $Nb(OC_2H_5)_5$ were changed into corresponding metallic complexes by ligand exchanging, and underwent partial hydrolysis and polymerization with hydroxyl or oxygen, formed SNTO polymerized sol. MCL caused the SNTO sol precursor to have heteropolymertic structure and achieve filming easily. The films, deposited on Si(110) substrate using the spin coating technique, were crystallized into cubic perovskite structure after being annealed at 700 °C in 25% N_2+75% H_2 (volume ratio) atmosphere formed by decomposing NH_3 at annealing temperature. Dependence of resistivity could fit well the relationship $\rho=\rho_0+AT^2$.

References

Ahn, C.H., Tybell, T., Antognazza, L., Char, K., Hammond, R.H., Beasley, M.R., Fischer, Φ., Triscone, J.M., 1997. Local nonvolatile electronic writing of epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3/SrRuO_3$ heterostructures. *Science*, **276**(5315):1100-1103. [doi:10.1126/science.276.5315.1100]

Contreras, J.R., Kohistedt, H., Poppe, U., Waser, R., 2003. Resistive watching in metal-ferroelectric-metal junctions. *Applied Phys. Lett.*, **83**(22):4595-4597. [doi:10.1063/1.1627944]

Gariglio, S., Seo, J.W., Fompeyrine, J., Locquet, J.P., Triscone, J.M., 2001. Transport properties in doped Mott insulator epitaxial $La_{1-y}TiO_{3-\delta}$ thin films. *Phys. Rev. B*, **63**(16):161103. [doi:10.1103/PhysRevB.63.161103]

Millis, A.J., 1998. Lattice effects in magnetoresistive mangane perovskites. *Nature*, **392**(6672):147-153. [doi:10.1038/32348]

Pan, F., Olaya, D., Price, J.C., Rogers, C.T., 2004. Thin-film field-effect transistors based on La-doped $SrTiO_3$ heterostructures. *Appl. Phys. Lett.*, **84**(9):1573-1575. [doi:10.1063/1.1651647]

Shanthi, N., Sarma, D.D., 1998. Electronic structure of electron doped $SrTiO_3$: $SrTiO_{3-\delta}$ and $Sr_{1-x}La_xTiO_3$. *Phys. Rev. B*, **57**(4):2153-2158. [doi:10.1103/PhysRevB.57.2153]

Sugiura, M., Uragou, K., Tachiki, M., Kobayashi, T., 2001. Estimation of trap levels in $SrTiO_3$ epitaxial films from measurement of $(LaSr)MnO_3/SrTiO_3/(LaSr)TiO_3$ p-i-n diode characteristics. *J. Appl. Phys.*, **90**(1):187-191. [doi:10.1063/1.1334638]

Wu, W.B., Lu, F., Wang, K.H., Pary, G., Chry, C.L., Zhang, Y., 2000. Epitaxial and highly electrical conductive $La_{0.5}Sr_{0.5}TiO_3$ films grown by pulse laser deposition in vacuum. *J. Appl. Phys.*, **87**(2):700-706. [doi:10.1063/1.373724]

Yin, M.Z., Wang, M.Q., Yao, X., 2004. Fabrication of $LaAlO_3$ films by sol-gel process with corresponding inorganic. *J. Zhejiang Univ. SCIENCE*, **5**(6):696-698. [doi:10.1631/jzus.2004.0696]