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Citation: Applied Physics Letters **88**, 142903 (2006); doi: 10.1063/1.2187439
View online: http://dx.doi.org/10.1063/1.2187439
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/88/14?ver=pdfcov
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Substrate-induced strain effects on the transport properties of pulsed laser-deposited Nb-doped $SrTiO_3$ films

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(Received 31 August 2005; accepted 17 February 2006; published online 4 April 2006)

Thin films of Nb-doped $SrTiO_3$ (NSTO) are grown via pulsed laser deposition (PLD) on $LaAlO_3$ (LAO,001), $MgAl_2O_4$ (MAO,001), $SrTiO_3$ (STO,001), and Y-stabilized ZrO_2 (YSZ,001) substrates. The effects of the film-substrate lattice mismatch, film thickness, and substrate temperature during growth on the film properties are investigated. The electrical transport in NSTO films is shown to exhibit a strong sensitivity to strain, which is suggested to arise from the dependence of carrier mobility on bond distortions/stretching and related changes in phonon modes. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2187439]

$SrTiO_3$ (STO) is a unique dielectric material with an interesting set of physical properties. Its semiconducting/metallic versions,[1–5] achievable by appropriate type and level of doping or reduction, are also of great interest to the emerging field of oxide electronics[6] due to its lattice compatibility to a number of functional oxides. However, in any application, the modifications of the physical properties by strain are required to be known, since strain is known to influence the properties of functional oxides dramatically.[7–11] In this letter we address the strain-property issue for the case of Nb-doped STO (NSTO) films. Although useful and interesting work has been done on the growth and properties of NSTO films,[4,12–25] to our knowledge no systematic analyses of strain effects have thus far been reported.

In our experiments, commercially procured (Crystek) high quality single-crystalline $SrTiO_3$ (STO,001), $LaAlO_3$ (LAO,001), $MgAl_2O_4$ (MAO,001), and Y-stabilized ZrO_2 (YSZ,001) substrates were used for film growth. The 0.3 wt % Nb-doped $SrTiO_3$ targets used for pulsed laser deposition (PLD) were made by a standard solid-state sintering technique. A pulsed excimer laser (KrF, $\lambda=248$ nm) was used for ablation. The corresponding energy density and pulse repetition rate were 1.8 J/cm^2 and 10 Hz, respectively. The films were characterized by x-ray diffraction (XRD), Rutherford backscattering (RBS) channeling, atomic force microscopy (AFM), and four-probe electrical measurements. Indium contacts were made to NSTO to ensure ohmic contact characteristics.

The NSTO films grown on STO, LAO, and MAO substrates at 800 and 870 °C showed high quality (001)-oriented growth. The films grown on YSZ, however, exhibited (011) and (001) mixed variants along with a small contribution of even (111). The near homoepitaxial NSTO film growth on STO showed the expected high epitaxial quality (hence XRD not shown), with the film peaks replicating the substrate peaks exactly, but with a tiny shift, reflecting a tiny compressive stress as seen by others as well.[19,22,26] In Figs. 1(a) and 1(b) we compare the main XRD signatures for NSTO films on (001) LAO and (001) MAO substrates grown at 800 °C. The features, which show the gradual evolution of out-of-plane lattice parameter with film thickness, were nominally similar for the films grown at 870 °C with slightly smaller linewidths. The full widths at half maximum (FWHM) of the rocking curves for 1400 Å NSTO film on LAO and MAO are 0.20° and 0.29°, respectively. These represent fairly high quality growth in spite of a significant value of stress in the two cases. The lattice constant (thermal expansion coefficient) for NSTO, LAO, and MAO are 3.914 Å (10.3×10^{-6}/K), 3.79 Å (tetragonal c axis=13.11 Å, 9.2×10^{-6}/K), and 8.083 Å (7.45×10^{-6}/K), respectively. Thus for the NSTO film on (001)LAO the *compressive* strains at 800 and 25 °C are 3.337% and 3.27%, respectively. For the NSTO film on (001) MAO the (half cell) a tensile strains at 800 and 25 °C are 2.959% and 3.155%, respectively. Although the magnitude of strain is comparable in the two cases, their sign is different and the strain decreases (increases) upon cooling from the growth temperature down to room temperature in the case of LAO (MAO). AFM data (not shown) revealed that NSTO film on LAO is very smooth, while that on MAO shows in-plane extended defect network, which could arise from the tensile strain and its increase upon cooling.

In Fig. 1(c) we give the RBS channeling data for a typical 1000 Å NSTO film on LAO, which shows the minimum channeling yield of 7%, which is excellent given the high degree of compressive strain. This can be compared, of course, with that for the nearly homoepitaxial case of NSTO on STO, which is about 1%–2%. The minimum yield for NSTO film on MAO was, however, substantially higher, which can be attributed to the intrinsic random tilts of planes associated with the process of introduction of in-plane defects. The yield was also higher for the film on YSZ due to multiple variants. The inset in Fig. 1(c) shows the connection between the surface roughness and χ_{min}%.

In Fig. 2(a) we compile the evolution of the out-of-plane lattice parameter as a function of film thickness for the cases of NSTO films grown on (001) LAO and MAO substrates. It can be seen that the stress is clearly relaxed gradually with increase in film thickness but not fully, even up to a thickness of 3000 Å. Traditionally, strain relaxation in heteroepitaxial films in the framework of the Matthews and Blakeslee[27] model as refined by Fischer, Kuhne, and Richter,[28] the latter

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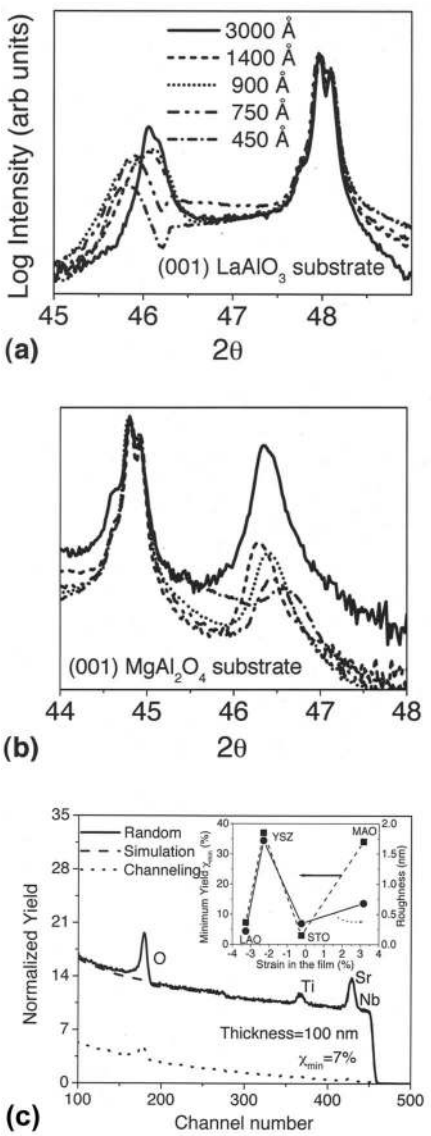

FIG. 1. Film thickness dependence of primary XRD peak for Nb:STO films on (a) (001) LAO and (b) (001) MAO substrates; (c) RBS channeling spectra for Nb:STO film on (001) LAO. The inset shows the strain dependence of minimum channeling yield $\chi_{\min}\%$ and rms surface roughness.

accounting for the interactions between dislocations by employing an image force approach. In the model of Fischer *et al.*, t_{crit} is related to the lattice mismatch strain $\varepsilon[\varepsilon=(a_f-a_s)/a_s]$, a_f and a_s being the film and substrate lattice constants, respectively, according to

$$\varepsilon = \frac{\cos\lambda}{2y}\left[1+(\ln y)\left(\frac{\frac{1-\nu}{4}}{4\pi(1+\nu)\cos^2\lambda}\right)\right],$$

where $y=t_{\text{crit}}/b$, with b as Burger's vector and λ as the angle between Burger's vector and the direction in the interface normal to the dislocation line, while ν is Poisson's ratio. Using appropriate numbers for LAO and MAO, t_{crit} for both cases is $\sim 50-60$ Å. Kim *et al.*[29] have obtained the evolution of the lattice parameter as a function of layer thickness, namely,

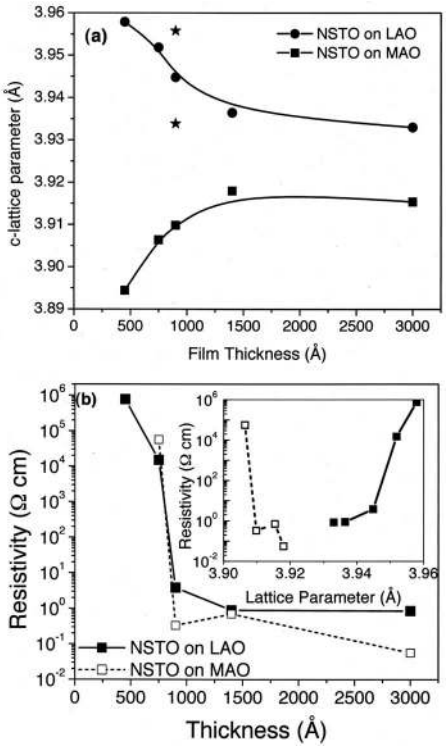

FIG. 2. (a) Film thickness dependence of out-of-plane lattice parameter for Nb:STO films on (001) LAO and MAO substrates; (b) film thickness dependence of the room temperature resistivity for films on (001) LAO and MAO substrates. The inset shows the relation between room temperature resistivity and mean lattice parameter.

$$a_f = a_0 + \frac{t_{\text{crit}}}{t}(a_s - a_0),$$

where a_0 is the bulk lattice constant of the film. Note that for $t<t_{\text{crit}}$, $a_f=a_s$. However, as t increases, a_f begins to recover gradually towards the bulk value a_0. It can be seen that the film thickness required to attain the value $a_f \sim a_0$ is about $10t_{\text{crit}}$. Thus, for NSTO on LAO or MAO, one can expect a substantially relaxed value of the lattice parameter for films thicker than ~ 600 Å, which is observed in Fig. 2(a). The incomplete stress relaxation, even at thicknesses larger than $\sim 10t_{\text{crit}}$, could result in oxide matrices with directional bonds because of the inability of the dislocations to completely overcome the energy barriers and fully propagate towards the interface. This was also observed in the case of Fe_3O_4 films on $MgAl_2O_4$,[30] $Nd_{0.5}Sr_{0.5}MnO_3$ films on $LaAlO_3$,[31] and V_2O_3 films on sapphire.[11] The microstructure of the film in such a case is suggested to be in the form of a dislocation penetrated top region above a uniformly stressed dislocation-free thin bottom layer. It is interesting to point out that for the case NSTO on LAO, the film of about 900 Å shows a double peak structure [strain release bifurcation, as reflected by the star symbols in Fig. 2(a)] although the average lattice parameter follows the gradual trend. It may be noted that the x-ray diffraction technique can probe the whole film including the coherently strained and the partially/fully relaxed layers in thin films.

In Fig. 2(b) we show the thickness dependence of room temperature resistivity of NSTO films on (001) LAO and MAO substrates. For films of NSTO grown on STO, a much lower room temperature resistivity ($\sim 6\times 10^{-5}$ Ω cm, 3000 Å, $T_{\text{sub}}=870$ °C) was obtained. Interestingly, for pure

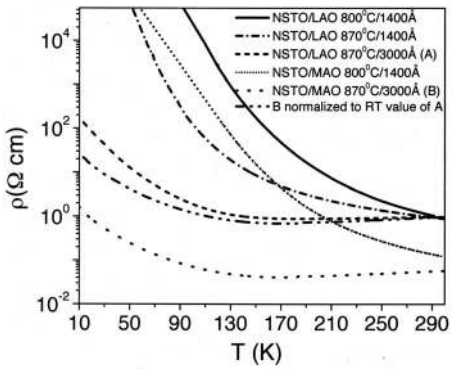

FIG. 3. Temperature dependence of resistivity for some cases of Nb:STO films grown on (001) LAO and MAO substrates.

STO films on STO a low-resistivity state was also seen to stabilize, although this value was somewhat higher than that for NSTO film ($\sim 1.3\times 10^{-4}$ Ω cm, 3000 Å, $T_{sub}=870$ °C). The surface of STO is known to be rendered conductive subsequent to high-temperature processing under reducing ambient due to oxygen vacancies and if one grows an STO cap, the conductivity can be retained. In the inset of Fig. 2(b) we show the same resistivity data as a function of the out-of-plane lattice parameter to bring out the connection with degree of strain. It is clearly seen that for films thinner than about $10t_{crit}$, the resistivity begins to rise rapidly with the decrease of film thickness, implying that the coherently strained portion of the films in both cases of large compressive and tensile strains are highly resistive. Interestingly, the compressive strain in the case of NSTO film on LAO is expected to tilt the Ti–O–Ti bond angle, while the tensile strain in the NSTO film on MAO is expected to linearize but stretch the bond. In either case the *p-d* overlap is negatively affected, reducing the transfer matrix element. Laffez *et al.*[9] have attributed the strain effects in $NdNiO_3$ to the changes in the electronic band structure related to the O–Ni–O superexchange angle. Yonezawa *et al.*[10] have found similar influences of bond distortions on metal-insulator transitions in V_2O_3. The key role of the Mn–O–Mn bond length and angle in the control of electronic phases in colossal magnetoresistive manganites is well known.[7,8] Also, Yamamoto *et al.*[32] have shown that at coherent grain boundaries in Nb:STO, the double-Schottky barriers (DSB) are not formed or their height is very small, while they can be generated at low coherent boundaries. The behavior of the extended defect planes in the case of films on LAO and MAO could also be different.

In Fig. 3 we show the temperature dependence of resistivity for a few cases of NSTO films grown on (001) LAO and MAO substrates. The growth temperature and film thickness are clearly seen to have significant influence on the temperature dependence of resistivity, because both factors relate to the degree of residual strain and the related microstructure. The resistivity for the partially strain relaxed films on MAO (bond stretching case) seems to be considerably lower than that for films on LAO (bond bending case). Since most dopants are expected to be ionized in this temperature regime, and Nb valence is nominally identical, the observed behaviors may originate from the changes in phonon modes, which are suggested to control the temperature dependence of mobility in this system, as discussed earlier.[23–25] Indeed, strain-related asymmetric distortions could lift degeneracies related to such modes thereby affecting the electron-phonon scattering significantly.

In conclusion, substrate-induced strain is shown to have significant influence on the transport properties of Nb-doped STO films grown on different substrates. The coherently strained pseudomorphic films are seen to be non-metallic.

One of the authors (W.R.) thanks the Fulbright commission for support. The authors thank B. Varughese for XPS measurements. This work was also supported under UMD NSF-MRSEC Grant No. DMR 00-80008.

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