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Homoepitaxial $Sr_{1+x}TiO_{3+\delta}$ films with $-0.2 \leq x \leq 0.25$ grown by reactive molecular-beam epitaxy on $SrTiO_3$ (001) substrates have been studied by ultraviolet Raman spectroscopy. Non-stoichiometry for strontium-deficient compositions leads to the appearance of strong first-order Raman scattering at low temperatures, which decreases with increasing temperature and disappears at about 350 K. This indicates the appearance of a spontaneous polarization with a paraelectric-to-ferroelectric transistion temperature above room temperature. Strontium-rich samples also show a strong first-order Raman signal, but the peaks are significantly broader and exhibit a less pronounced temperature dependence, indicating a stronger contribution of the disorder-activated mechanism in Raman scattering.

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$SrTiO_3$ is a well known incipient ferroelectric, and in bulk remains paraelectric down to 0.3 K.[1] Slight perturbations in the lattice structure can, however, break the delicate balance of forces and lead to the appearance of ferroelectric polarization. This perturbation can come from various sources such as strain,[2–5] doping,[6–8] or even oxygen isotope substitution.[9] Here we focus on the effect of Sr/Ti non-stoichiometry in homoepitaxial $SrTiO_3$ thin films. Specifically of interest is how variation in stoichiometry affects the phonons and their activity in Raman spectra resulting from the ferroelectric phase transitions. Raman spectroscopy is a powerful tool for probing lattice vibrations. For thin films of wide band gap materials such as $SrTiO_3$, excitation using ultraviolet (UV) light is preferable, since UV light with energy above the band gap (3.2 eV for $SrTiO_3$ at 300 K)is absorbed, and therefore the substrate signal is strongly suppressed allowing measurement of spectra from ferroelectric films as thin as a few nanometers.[10,11] In this paper, we apply UV Raman spectroscopy to study ferroelectricity in non-stoichiometric (both strontium-rich and strontium-deficient) homoepitaxial $SrTiO_3$ films.

The 100 nm-thick films were grown by molecular-beam epitaxy (MBE) on stoichiometric, TiO_2-terminated (001) $SrTiO_3$ substrates at 650°C in a background pressure of 5.0×10^{-7} Torr of ultra-high purity molecular oxygen. Growth was monitored by reflection high-energy electron diffraction. Six $Sr_{1+x}TiO_{3+\delta}$ films were studied; nominal compositions x varied from -0.2 to 0.3, including a stoichiometric film, $x = 0$. The Sr/Ti concentration ratios $(1 + x)$ were determined by Rutherford backscattering spectrometry (RBS) to be 0.786, 0.905, 0.97, 1.02, 1.19, and 1.24, resulting in x values -0.214, -0.095, -0.03, 0.02, 0.19, and 0.24 ($\pm$0.04), close to the nominal ones. There may be a certain amount of oxygen non-stoichiometry δ, but the oxygen concentration in the films is difficult to determine by RBS due to the low atomic mass of oxygen. The details of growth and structural characterization by x-ray diffraction (XRD) and scanning transmission electron microscopy (STEM) have been reported elsewhere [12]. According to STEM images, the strontium deficient films appear to have a disordered structure (randomly distributed defects); no secondary phases like TiO_2 were detected. In the strontium excess films, the Ruddlesden-Popper planar faults appear.[12] Both Sr-deficient and Sr-rich films have shown an expansion along the c axis; the c lattice parameters determined by XRD were 3.94, 3.915, 3.905, 3.92, 3.96, and 4.02Å, respectively, for the compositions listed above.[12] Since the films were homoepitaxial, any effect of substrate-induced strain should be negligible. Also, spectra of nominally stoichiometric $SrTiO_3$ films grown by pulsed-laser deposition (PLD) on $SrTiO_3$ substrates with and without $SrRuO_3$ buffer layers were measured. The PLD growth details were reported elsewhere.[13]

Raman spectra were recorded using a Horiba Jobin Yvon T64000 triple spectrometer equipped with a liquid-nitrogen-cooled multichannel charge-coupled device de-

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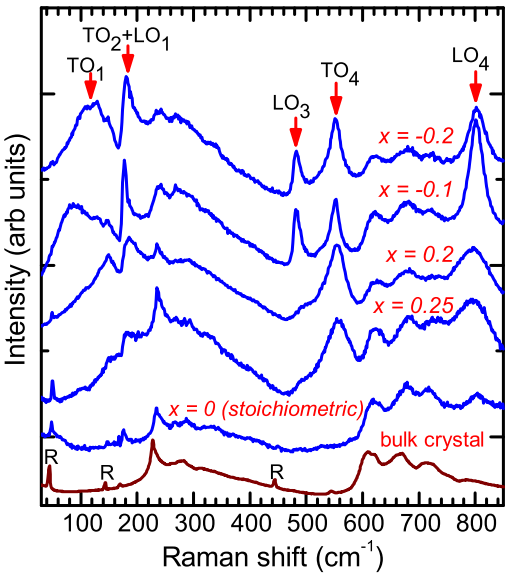

FIG. 1. (Color online) Raman spectra of $Sr_{1+x}TiO_{3+\delta}$ films and a bulk $SrTiO_3$ crystal at 10 K. Arrows mark the first-order $SrTiO_3$ phonon peaks. Symbols "R" label the structural modes due to the rotation of the Ti-O octahedra

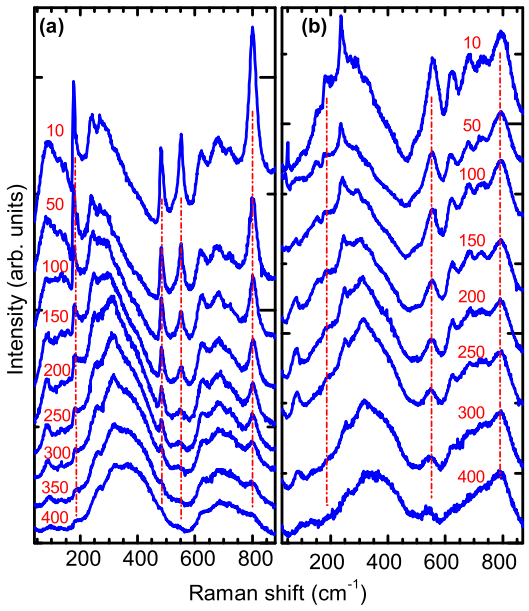

FIG. 2. (Color online) Variable-temperature Raman spectra of a Sr-deficient $Sr_{0.9}TiO_{3+\delta}$ film (a) and a Sr-rich $Sr_{1.25}TiO_{3+\delta}$ film (b). Numbers above the spectra indicate temperatures in K. The vertical dashed-dotted lines are guides for the eye showing the first-order $SrTiO_3$ phonon peaks.

tector. Spectra were recorded in backscattering geometry in the temperature range 10–450 K using a variable temperature closed cycle He cryostat. For excitation, the 325 nm He-Cd laser line was used with a power density of 0.5 W/mm^2 at the sample surface, low enough to avoid any noticeable local heating.[14]

$SrTiO_3$ is a cubic perovskite-type crystal having 12 optical phonon modes. All phonons are of an odd symmetry with respect to the inversion, hence inactive in the first-order Raman scattering. Raman spectrum of bulk $SrTiO_3$ contains only the second order (two-phonon) features.[15] A breakdown in the inversion symmetry of the crystal (e.g., due to a ferroelectric distortion) leads to the appearance of the first-order peaks Raman spectra.

Figure 1 shows Raman spectra of a bulk $SrTiO_3$ crystal, the MBE-grown stoichiometric film, and non-stoichiometric films at 10 K. The stoichiometric film's spectrum is similar to bulk $SrTiO_3$ with broad second order peaks. The structural modes at 44, 144, 445 cm^{-1} (labelled R in Fig. 1) present in the low-temperature spectra are due to the antiferrodistortive cubic-tetragonal phase transition, which occurs at 105 K and involves the rotation of the Ti-O octahedra.[16] The resulting tetragonal structure $4/mmm$ is still centrosymmetric and the fundamental $SrTiO_3$ phonons remain Raman inactive. In contrast, the non-stoichiometric films exhibit intensive first-order peaks of the fundamental $SrTiO_3$ phonons, indicative of a breakdown in inversion symmetry. The spectral features that we focus on are TO_1 (the soft mode) at 85–120 cm^{-1}, and the hard modes TO_2+LO_1 (these two modes have very close frequencies), LO_3, TO_4, and LO_4 at 180, 480, 550, and 800 cm^{-1}, respectively.

Variable temperature spectra of strontium-deficient films (Fig. 2(a)) showed these peaks decreasing and disappearing at ∼350 K. The complete disappearance of the first-order Raman peaks at higher temperatures indicates that the breakdown of the inversion symmetry selection rules cannot be attributed to lattice defects alone. If the first-order Raman scattering is defect-induced, it should be observed at higher temperatures as well. At higher temperatures (above 350 K), however, the spectra of strontium-deficient films are the same as stoichiometric $SrTiO_3$. The observed behavior indicates the appearance of spontaneous polarization in the strontium-deficient films. Considering the temperature evolution of the spectra of strontium-rich films (Fig. 2(b)), one can notice a different behavior: even at low temperatures the phonon peaks are broad (about twice as broad compared to the strontium-deficient films), and they do not disappear even at high temperatures. This indicates a stronger contribution of the defect-induced mechanism in Raman scattering in the strontium-rich films.

The breakdown of the symmetry selection rules has been previously observed in Raman scattering from $SrTiO_3$ films grown by PLD,[17] and attributed to polar nanoregions associated with oxygen vacancies [17] or dipole moments associated with polar grain boundaries in polycrystalline or textured samples.[18] The samples studied here are single-crystalline films having no grain boundaries, so this effect is not present. Later studies of intentionally oxygen-reduced bulk $SrTiO_3$ showed that oxygen vacancies alone are unlikely to cause the observed effect, and should also lead to the appearance of additional peaks, that are not present in the thin film spectra.[19]

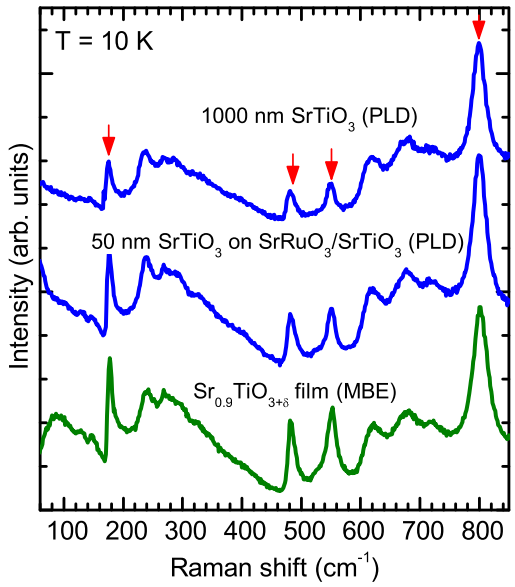

FIG. 3. (Color online) Raman spectra of the strontium-deficient MBE-grown film ($Sr_{0.9}TiO_{3+\delta}$) and two nominally stoichiometric $SrTiO_3$ films grown by PLD on $SrTiO_3$ substrates with and without $SrRuO_3$ buffer layers. Arrows indicate the first-order peaks of the $SrTiO_3$ optical phonons.

Even if oxygen vacancies play a role, it must be in combination with other non-stoichiometry or defects.

Figure 3 shows Raman spectra of strontium-deficient film and two nominally stoichiometric PLD-grown $SrTiO_3$ films on $SrTiO_3$ substrates without and with $SrRuO_3$ buffer layers. The latter films (with $SrRuO_3$ bottom electrodes) were proved to be ferroelectric by a combination of techniques including the polarization hysteresis loops measured by piezoresponse force microscopy.[13] The shape and temperature evolution of Raman spectra from $SrTiO_3$ films with and without $SrRuO_3$ contact layers are essentially the same. This indicates that thin coherently strained $SrRuO_3$ layers following the lattice parameter of the $SrTiO_3$ substrate have no noticeable effect on the properties of $SrTiO_3$ films. The spectra of the strontium-deficient films studied here are remarkably similar to the spectra of the PLD-grown ferroelectric $SrTiO_3$ in terms of both the first-order Raman peaks (which are slightly stronger in the strontium-deficient films) and their temperature evolution (Fig. 3). This result supports the suggestion that relatively small amounts of cation non-stoichiometry, which were demonstrated to occur even in nominally stoichiometric PLD-grown samples,[20,21] can lead to the appearance of polar nanoregions and relaxor-like ferroelectricity, as reported by Jang *et al.*[13]

In summary, Sr/Ti non-stoichiometry in homoepitaxial $SrTiO_3$ films leads to the appearance of first-order peaks in Raman spectra, which are symmetry-forbidden in paraelectric $SrTiO_3$. Strontium-deficient samples, in particular, exhibit a temperature evolution of Raman spectra consistent with a ferroelectric phase transition with the transition temperature ~350 K. Similar spectra have been recorded from nominally stoichiometric PLD samples proven to be ferroelectric. Our results highlight the sensitive nature of the ferroelectric properties of $SrTiO_3$ to stoichiometry and imply that strontium deficiency (probably existing in small amounts even in nominally stoichiometric $SrTiO_3$ films and single crystals) can offer an explanation for the origin of polar nanoregions.

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