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Infrared phonon spectroscopy of a compressively strained (001) SrTiO₃ film grown on a (110) NdGaO₃ substrate

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Abstract
Polarized infrared reflectivity was measured between 5 and 300 K on a 17 nm thick, 1.1% compressively strained epitaxial (001) SrTiO₃ film and the orthorhombic (110) NdGaO₃ substrate upon which it was grown. A strong in-plane infrared anisotropy of the NdGaO₃ substrate was observed and polar modes with B₁u-and a mixture of B₂u+B₃u-symmetry were seen. At low temperatures three new modes arose in the 90–130 cm⁻¹ range, which we assigned to 4f Nd electronic transitions. The in-plane SrTiO₃ film phonons showed strong stiffening compared to the phonon frequencies of bulk unstrained SrTiO₃, particularly the soft mode, and the in-plane phonon peaks were found to split. No anomalies were detected as a function of temperature in either the infrared response or lattice parameters of the compressively strained SrTiO₃ film, providing an absence of evidence for the out-of-plane ferroelectric phase transition predicted by theory.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

After more than two decades of intense research it has become clear that dielectric properties, as well as many other properties of ferroelectric and related materials, differ significantly from bulk intrinsic properties when in thin film form [1–6]. This occurs for both polycrystalline and epitaxial films. In high-quality epitaxial films the dominant effect is from stress in the film caused by the lattice mismatch between the film and substrate or, in the case where this misfit strain is larger, by the difference in thermal expansion of the film and substrate. The theories based on the Landau–Ginzburg approach to ferroelectric phase transitions, first-principles calculations, and experiments show that the dielectric properties in high-permittivity materials are extremely sensitive to such strains. For instance, the ~1% in-plane tensile strain in a SrTiO₃ film on a DyScO₃ substrate induces a ferroelectric phase transition near room temperature [7] in coexistence with the antiferrodistortive phase below ~180 K, while no ferroelectric phase exists in the unstrained bulk incipient ferroelectric SrTiO₃ [8, 9]. The strain-induced spontaneous polarization Pₛ lies in the film plane in the former case.

Many device applications in nanoelectronics require polarization switching involving an out-of-plane polarization, Pₛ. Theories [4–7, 10–13] predict that this could be induced in SrTiO₃ films by a compressive in-plane stress. Studies have been performed on compressively strained SrTiO₃ epitaxial films on several substrates, including (110) NdGaO₃, (001) (LaAlO₃₀.₂₉₋₋₈(SrAl₁₂Ta₁₂O₃₀.₇₁) (LSAT), and silicon. Films on NdGaO₃ displayed evidence of a ferroelectric phase transition near 150 K using infrared (IR) spectroscopy [14]. SrTiO₃ on LSAT was studied by SHG
and dielectric measurements [15, 16], but no evidence of a ferroelectric phase transition was found [17, 18]. Recently, SrTiO$_3$ films grown directly on (001) Si by molecular-beam epitaxy (MBE) were shown to be ferroelectric up to room temperature [19]. Due to the large compressive strain of $\sim$1.7%, only films of thickness below $\sim$3 nm were shown to be commensurate and ferroelectric up to room temperature. The $\sim$8 nm thick SrTiO$_3$/Si film was relaxed and did not display ferroelectricity [19]. Two recent papers [16, 20] reported out-of-plane ferroelectricity up to room temperature in thicker SrTiO$_3$ films of thicknesses $\sim$60 nm and $\sim$100 nm, respectively. The 100 nm thick film was grown on a single-crystal SrTiO$_3$ substrate by pulsed-laser deposition (PLD) in reduced oxygen atmosphere. Its remnant polarization $P_r$, which survived from low temperatures up to 300 K, was of the order of several $\mu$C cm$^{-2}$ and increased with increasing oxygen deficiency. It has been suggested [21] that the origin of the ferroelectricity in such homoepitaxial films is due to correlated defect complexes, in this case a Sr vacancy adjacent to an oxygen vacancy producing a SrO vacancy. The 60 nm thick SrTiO$_3$/NdGaO$_3$ film grown by PLD showed a very smeared $P_r$, which increases steeply to several $\mu$C cm$^{-2}$ only below $\sim$100 K and shows a very narrow hysteresis loop. These features together with the typical dielectric dispersion below $\sim$150 K were assigned to relaxor ferroelectric behavior [16]. Very recently [22], long-range ferroelectric order below $\sim$700 K with an out-of-plane $P$ has been observed also in a compressively strained (2.1%) 9 nm thick KTaO$_3$ film grown by PLD on a conductive SrTiO$_3$ substrate. Bulk KTaO$_3$ is another classic incipient ferroelectric without a ferroelectric transition down to 0 K.

In this paper we report on a study of an epitaxial (001) SrTiO$_3$ film grown by MBE on a (110) NdGaO$_3$ substrate, using a novel IR reflectance technique to study the temperature behavior of the in-plane polar phonons, including the soft mode [9, 14, 17]. The reason for this study is because of the strong anisotropy in the IR range due to structure of the (110) NdGaO$_3$ substrate, which had not been fully characterized in previous IR reports on NdGaO$_3$ single crystals [23–25] and was neglected in the previous SrTiO$_3$/NdGaO$_3$ film study [14].

In the past, IR and THz transmission spectroscopy was successfully used for characterizing the polar phonons in ferroelectric thin-films, particularly for the soft mode studies in SrTiO$_3$ films [26–31]. The IR reflection technique, which has been more used recently [9, 14, 17], has some advantages over the transmission measurement mode in that it characterizes a broader spectral range, since in most cases it can be used in a broad spectral range where the substrate is opaque. It enables the characterization of all polar phonon modes, and the sensitivity is in many cases enhanced compared to transmission due to an effectively thicker optical path of the multiple reflected beams from both surfaces of the film. It must be noted, however, that the sensitivity depends on a nontrivial way on the optical parameters of the substrate, whose dielectric spectrum varies quite strongly in the reststrahl region. We have also revealed that metallic substrates with a negative permittivity in the IR range strongly diminish the accuracy of determining the phonon parameters of the film. Therefore dielectric substrates without electrodes are preferred for this technique.

2. Experiment and data evaluation

The SrTiO$_3$ film was grown on a (110) NdGaO$_3$ single-crystal substrate in a Vecco 930 oxide MBE system at a substrate temperature of 650 °C in a background pressure of $5 \times 10^{-7}$ Torr of O$_2$ with 10% O$_3$. The details of the growth process are outlined elsewhere [32].

The deposited (001) SrTiO$_3$ film was characterized by x-ray diffraction. The out-of-plane lattice parameter was investigated as a function of temperature using Cu K$_\alpha$ radiation in a PANalytical two-circle diffractometer with a parabolic mirror on the incident beam path. The sample was mounted inside an evacuated chamber and heated up to 770 K by a radiant heater while diffraction was measured using a position-sensitive detector. Room-temperature in-plane lattice parameters were investigated using a four-circle diffractometer. Data indicate that the SrTiO$_3$ film is commensurately strained to the (110) NdGaO$_3$ substrate with in-plane lattice parameters $a = b = 3.863(5)$ Å and out-of-plane lattice spacing $c = 3.941(5)$ Å. The compressive in-plane strain was +1.1%.

Second-harmonic generation measurement of another SrTiO$_3$/NdGaO$_3$ film [15] revealed a signal below 400 K indicating symmetry breaking and the formation of the ferroelectric phase. In a compressively strained film the spontaneous polarization should arise perpendicularly to the film plane and some anomalous temperature dependence of the $c$ lattice parameter could be expected [4]. Figure 1 shows the temperature dependence of the obtained out-of-plane lattice parameters of the (110) NdGaO$_3$ substrate and the (001) SrTiO$_3$ film. Circles denote measurements done while heating up the sample, squares correspond to cooling down. The data show no anomalies in the explored temperature region so that our data give no support to any sharp phase transition above 300 K. This is in agreement with the aforementioned recent findings on PLD-grown SrTiO$_3$/NdGaO$_3$ films [16].

The IR reflectance measurements under near-normal incidence of the polarized light were performed using a FTIR Bruker IFS 113v spectrometer equipped with a He-cooled (1.5 K) Si bolometer over the 5–300 K temperature range. The
bare NdGaO$_3$ substrate and 17 nm thick SrTiO$_3$ film deposited on the same substrate were measured in two polarizations ($E \parallel [001]$ and $E \parallel [110]$) with respect to the (110) NdGaO$_3$ substrate at the same conditions on cooling down to 5 K in an Optistat CF cryostat (Oxford Instruments). The thick polyethylene windows used permit IR measurements only up to 650 cm$^{-1}$.

The dielectric response of the bare substrate was evaluated from fitting the IR reflectivity spectra

\[ R(\omega) = \left| \frac{\sqrt{\varepsilon^*(\omega) - 1}}{\sqrt{\varepsilon^*(\omega) + 1}} \right|^2 \]  

with the factorized form of the complex permittivity [33]

\[ \varepsilon^*(\omega) = \varepsilon_\infty \prod_j \frac{\omega^2_{\text{TO}j} - \omega^2 + i\omega\gamma_{\text{TO}j}}{\omega^2_{\text{TO}j} - \omega^2 + i\omega\gamma_{\text{TO}j}}. \]  

$\omega_{\text{TO}j}$ and $\gamma_{\text{TO}j}$ are the frequencies of the $j$th transverse optic (TO) and longitudinal optic (LO) polar mode, respectively, $\gamma_{\text{TO}j}$ and $\gamma_{\text{LO}j}$ are their damping constants and $\varepsilon_\infty$ is high-frequency (electronic) contribution to the permittivity.

The obtained fixed parameters were used for fitting the IR reflectance spectra of the SrTiO$_3$/NdGaO$_3$ sample as a two-slab system, by assuming the dielectric function of the SrTiO$_3$ film to have the form of a sum of $n$ independent damped harmonic oscillators

\[ \varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^n \frac{\Delta\varepsilon_j \omega^2_{\text{TO}j}}{\omega^2_{\text{TO}j} - \omega^2 + i\omega\gamma_{\text{TO}j}} \]  

representing the in-plane TO phonon modes of the film, where $\Delta\varepsilon_j$ is the dielectric strength of the $j$th mode.

3. Results and discussion

3.1. IR spectroscopy of the (110) NdGaO$_3$ substrate

The previously reported IR reflectivity [23, 24] and THz transmission data [25] on NdGaO$_3$ single crystals have been obtained in unpolaredized light, neglecting the in-plane anisotropy of the orthorhombic slab. We have revealed that the IR anisotropy of such a (110) plate is quite pronounced and influences the evaluation of the film phonon parameters on such a substrate. Because of this anisotropy we first measured the temperature dependent IR reflectivity of the bare (110) NdGaO$_3$ substrate in polarized light, which allowed us to determine the $E \parallel c$ and $E \parallel [110]$ response (in the orthorhombic axes notation), since the wavevector $k$ of our probing (transverse) IR wave is almost normal to the sample slab. Factor-group analysis for the NdGaO$_3$ with the space group $Pbnm$ (number of formula units in the unit cell $Z = 4$) yields for the Brillouin-zone center ($\Gamma$-point) the following phonon modes [34]:

7A$_{1g}$($aa, bb, cc$) + 5B$_{1g}$($ab$) + 7B$_{2g}$($ac$) + 5B$_{3g}$($bc$) + 8A$_{1u}$($-$) + 10B$_{1u}$($c$) + 5B$_{2u}$($b$) + 10B$_{3u}$($a$).

Three of these modes, 1B$_{1u}$ + 1B$_{2u}$ + 1B$_{3u}$ are acoustic modes and the remaining modes are optic. In the parentheses the Raman and IR activities are denoted, $a$, $b$, and $c$, describe the direction of the electric dipole moment of the IR-active mode and $ij$ ($i, j = a, b, c$) denotes the Raman activity (direction of $E$ in the incident and scattered wave, respectively). Therefore the IR selection rules predict 9B$_{1u}$ modes for $E \parallel c$ and the mixture of 7B$_{2u}$ and 9B$_{3u}$ modes for the $E \parallel [110]$ polarization with half of their oscillator strengths compared to the IR response in the principal $E \parallel b$ and $E \parallel a$ directions, respectively. The A$_{1u}$ modes are optically inactive (silent). The selection rules should be independent of temperature from $\sim$10 up to $\sim$1200 K because the space group of NdGaO$_3$ does not change [35, 36] even if some weak dielectric anomalies near $\sim$240 K and weak magnetic anomalies near $\sim$190 K (without long-range magnetic ordering) were observed [37].

In figure 2 we present the polarized IR reflectivity spectra for selected temperatures at 5–300 K in the 30–650 cm$^{-1}$ spectral range. In the low-frequency range below $\sim$100 cm$^{-1}$ the sample becomes partially translucent at low temperatures so that the increase of the reflectivity at the low-frequency end is due to multiple reflections from both sample surfaces. This part was not considered for the fitting, which assumes reflection from a semi-infinite surface.

In figure 3 we plot the calculated complex dielectric functions $\varepsilon_\infty(\omega)$ at several temperatures from the fits of the $E \parallel c$ reflectivity spectra, which represent the response function of the B$_{1u}$ modes. It is clearly seen that at low temperatures all the predicted modes are revealed, but with
Table 1. Parameters of the B1u polar modes in NdGaO3 obtained from the fit of polarized $E \parallel [001]$ IR reflectivity at 300 and 5 K. Frequencies $\omega_{TO,j}$ and $\omega_{LO,j}$ and dampings $\gamma_{TO,j}$ and $\gamma_{LO,j}$ of modes are in cm$^{-1}$, $\Delta \varepsilon_j$ is the dielectric strength and $\varepsilon_\infty = 3.93$.

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Figure 3. Real and imaginary part of the $\varepsilon^c_\omega(\omega)$ dielectric function of the (110) NdGaO3 substrate obtained from fitting its $E \parallel [001]$ polarized IR reflectivity spectra.

Increasing temperature the mode at 131 cm$^{-1}$ effectively vanishes. It appears that this mode could be of electronic origin (crystal field splitting of the 4f$^3$ Nd levels of the 4I$_{9/2}$ multiplet), as observed in Raman scattering and deduced from optical absorption [38, 39]. Parameters of the fit at 5 and 300 K are shown in table 1 along with the calculated dielectric strengths of the polar phonons (their contributions to static permittivity) [33]

$$\Delta \varepsilon_j = \frac{\varepsilon_\infty}{\omega_{TO,j}^2} \prod_k (\omega_{OK}^2 - \omega_{TO,j}^2) \prod_{k \neq j} (\omega_{OK}^2 - \omega_{TO,k}^2)$$

In figure 4 we plot the calculated dielectric function $\varepsilon_{ab}(\omega)$ in the $E \parallel [110]$ direction while the fit parameters are listed in table 2. Again a low-frequency doublet (at 91 and 109 cm$^{-1}$) out of the 17 fitted modes vanishes on heating, which can also be assigned to the 4f Nd electronic transitions. The remaining 15 modes are in a good agreement with the 16(B$_{2u}$ + B$_{3u}$) predicted modes. As also appears from the tables 1 and 2, only modes below 200 cm$^{-1}$ are appreciably temperature dependent. We have plotted their temperature dependent TO frequencies in figure 5.
Table 2. Parameters of the \((B_{2u} + B_{3u})\) polar modes in \(\text{NdGaO}_3\) obtained from the fit of polarized \(E \parallel [110]\) IR reflectivity at 300 and 5 K. Frequencies \(\omega_{TOj}\) and \(\omega_{LOj}\) and dampings \(\gamma_{TOj}\) and \(\gamma_{LOj}\) of modes are in \(\text{cm}^{-1}\), \(\Delta \varepsilon_j\) is the dielectric strength and \(\varepsilon_\infty = 3.2\).

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3.2. IR spectroscopy of the \(\text{SrTiO}_3\) film

In figure 6 we plot the polarized reflectance of our \(\text{SrTiO}_3/\text{NdGaO}_3\) sample, which differs from the bare substrate reflectivity in several spectral regions, mainly below \(\sim 150\) and near \(560\ \text{cm}^{-1}\). The spectral fit of the two-layer system using the known bare \(\text{NdGaO}_3\) substrate fit parameters enables us to obtain both the \(\varepsilon_c(\omega)\) and \(\varepsilon_{ab}(\omega)\) dielectric functions of the \(\text{SrTiO}_3\) film, as shown in figures 7 and 8 respectively. This is shown only below \(200\ \text{cm}^{-1}\) as the high-frequency \(\text{TO4}\) mode doublet at \(561 + 563\ \text{cm}^{-1}\) does not show any appreciable
Figure 7. Complex dielectric function of the SrTiO$_3$ film obtained from fitting the $\mathbf{E} \parallel [001]$ polarized IR reflectance of the SrTiO$_3$/NdGaO$_3$ system. Static permittivity obtained from the fit as a function of temperature is shown in the inset.

Figure 8. Complex dielectric function of the SrTiO$_3$ film obtained from fitting the $\mathbf{E} \parallel [110]$ polarized IR reflectance of the SrTiO$_3$/NdGaO$_3$ system.

Figure 9. Temperature dependences of the in-plane TO1 mode doublet of the 17 nm SrTiO$_3$ film on the NdGaO$_3$ substrate from the polarized reflectance spectra in comparison with the TO1 mode from the unpolarized IR reflectance spectra of the 50 nm SrTiO$_3$ film on the same substrate [14].

Figure 10. Complex dielectric function of the SrTiO$_3$ film obtained from fitting the $\mathbf{E} \parallel [001]$ polarized IR reflectance of the SrTiO$_3$/NdGaO$_3$ system.
films with the nearly in-plane isotropic LSAT substrate do not, however, indicate any ferroelectric transition from our IR data [17]. From the present studies, the suggested ferroelectric transition near 150 K on the basis of the previous IR studies of SrTiO3/NdGaO3 film in unpolarized light, showing the appearance of the very weak silent TO3 mode [14], appears to be an artifact of evaluation that neglected the strong substrate anisotropy. Also the strongly stiffened TO2 mode parameters is not possible due to strong phonon dispersion in the substrate reflectivity in this frequency range. Summarizing, there is neither IR nor XRD evidence for the out-of-plane ferroelectric phase transition in the compressed SrTiO3 films and further studies are needed.

4. Conclusions

In this study polarized IR reflectance spectroscopy was used to study the in-plane phonon response of a very thin (∼17 nm) epitaxial compressed SrTiO3 film deposited by MBE on an orthorhombic (110) NdGaO3 substrate. The strong in-plane IR anisotropy observed for the bare NdGaO3 substrate was fully explained by the corresponding phonon and electron excitations of B1g and mixed (B2g + B3g) symmetries determined from 300 to 5 K. By using these data we were able to study the temperature dependences of the in-plane TO1 and TO4 modes of the SrTiO3 film and reveal their in-plane anisotropy. Appreciable stiffening of all the observed phonons compared to the strain-free bulk samples was found. No indication of any theoretically expected out-of-plane ferroelectric phase transition was found, in accordance with the recent findings [16] from second-harmonic generation and remnant polarization measurements, which show only a very smeared relaxor-like ferroelectric transition below ∼150 K.

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References


Figure 10. Temperature dependences of the polar modes from the polarized IR reflectance spectra of our SrTiO3/NdGaO3 film in comparison with other compressively strained SrTiO3 films [14, 17] and bulk ceramics [40].


[40] Petzelt J et al 2001 *Phys. Rev.* B **64** 184111