SOFT-MODE PHONONS in SrTiO₃ THIN FILMS STUDIED by FAR-INFRARED ELLIPSOMETRY and RAMAN SCATTERING

A. A. SIRENKO *, C. BERNHARD **, A. GOLNIK **, I. A. AKIMOV *†, A. M. CLARK *, J.-H. HAO *, and X. X. XI *

* Department of Physics, the Pennsylvania State University, University Park, PA 16802, *sirenko@phys.psu.edu*

** Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany

† A. F. Ioffe Physico-Technical Institute, St. Petersburg 194021, Russia

ABSTRACT

We report the experimental studies of the vibrational spectra of SrTiO₃ films with the thickness of 1 μm grown by pulsed laser deposition. Fourier-transform infrared ellipsometry between 30 and 700 cm⁻¹ and electric field-induced Raman scattering techniques have been utilized for investigation of the phonon behavior. These results can be used for comparison with the low-frequency measurements of the static dielectric constant. The soft mode in the films reveals hardening compared to that in bulk crystals. This observation is in agreement with the Lyddane-Sachs-Teller formalism.

INTRODUCTION

Ferroelectric materials possess an electric polarization and the direction of this polarization can be reversed by an external electric field. At the temperature above the paraelectric-to-ferroelectric phase transition, these materials are characterized by extremely high values of the dielectric constant (of the order of 30000). Application of a moderate external electric field, which is usually much lower than the breakdown value, results in a dramatic change, or tuning, of the dielectric constant. These properties of ferroelectrics became very promising for practical application after development of modern thin film deposition techniques, which satisfy the requirements of the compact size and compatibility with the planar technology. Recently, ferroelectric materials have been widely utilized in microelectronics as a base for capacitor structures, high density random access memories (DRAMs), nonvolatile ferroelectric memories (FRAMs), hydrogen sensors, optical switches, filters, and waveguides (see Ref. [1] for more detail).

One of the incipient ferroelectrics, which have recently renewed great interest in their fundamental properties, is SrTiO₃ (STO). Several growth techniques, such as pulsed laser deposition (PLD) [2,3], rf magnetron sputtering [4], and molecular beam epitaxy [5] have been utilized to produce high quality STO thin films on different substrates with the thicknesses ranging from a few monolayers to a few microns. Although the crystalline quality of available epitaxial STO films is high, which is usually reported based on the result of x-ray diffraction, it has been demonstrated that at low temperatures STO films have much lower static dielectric constant ε_0 and higher losses compared to that of STO single crystals. The typical low temperature values of ε_0 vary from about 10^3 [2,3] to 5×10^3 [4] depending on the thin film growth technique. At present, the cause of this difference, i.e. the so-called "size effect", is not well understood. One of the models which have been offered to explain this effect, proposes the existence of a "dead layer" with a low dielectric constant located at the interfaces of the films [6,7]. In another approach, the size effect is explained as a consequence of the structural defects in the films induced by impurities and oxygen vacancies or strain due to the lattice mismatch

with the substrate [8]. Whether the poorer film properties are related to the bulk film material or are mostly determined by the interface quality and local-field effects has remained an open question. The answer is considered to be the key issue for optimization of the dielectric properties of STO and a number of other ferroelectric thin films. As it will be shown further, the understanding of this problem is impossible without detailed experimental studies of the vibrational spectra in these materials.

SOFT MODES in SrTiO$_3$

The phonon behavior is of the central importance for the theory of ferroelectricity. When the temperature of the ferroelectric phase transition T_c is approached, the zone-center frequency of the so called "soft mode", which is the lowest frequency transverse optical phonon, falls to zero:

$$\omega_{TO}(T) = const \times |T - T_c|^{1/2}. \tag{1}$$

For ferroelectrics this instability in the spectrum of the optical phonons was predicted by Fröhlich [9] and later was theoretically studied using lattice dynamic calculations [10] and a microscopic approach [11]. The Lyddane-Sachs-Teller (LST) relationship for a crystal with N infrared-active optical modes ($N = 3$ for STO) connects the frequency of the soft mode to the static ε_0 and high frequency ε_∞ dielectric constants:

$$\varepsilon_0 = \varepsilon_\infty \prod_{j=1}^{N} \frac{\omega_{LOj}^2}{\omega_{TOj}^2}, \tag{2}$$

where ω_{LOj} and ω_{TOj} are eigenfrequencies of the longitudinal and transverse optical phonons, respectively. It is generally found that the eigenfrequencies of the phonons other than the soft mode exhibit no sizable variation with temperature and, hence, the temperature variation of the soft mode frequency and the static dielectric constant are connected as follows:

$$\varepsilon_0(T) \propto \omega^{-2}_{TO1}(T), \tag{3}$$

which is consistent with the Curie-Weiss law for the temperature dependence of the static dielectric constant:

$$\varepsilon_0(T) = const \times |T - T_c|^{-1}. \tag{4}$$

In bulk STO crystals, the experimental data for the soft modes and static dielectric constant obey Eqs.(1) and (4) above 50 K (with T_c=32 K) but deviate from the Curie-Weiss law at low temperatures [12]. This deviation was theoretically understood in terms of zero-point lattice fluctuations of the Ti atom with respect to the oxygen octahedral [13] and, consequently, hardening of the soft modes, which never reach zero frequency, was attributed to their strong coupling with transverse acoustic phonons. As a result, at normal conditions STO does not reveal a ferroelectric phase transition even at very low temperatures. However, a strong variation of the soft mode frequency from 90 to 13 cm^{-1} with decreasing temperature from room to the liquid helium value, respectively, is consistent with dramatic increase of the static dielectric function at low temperature ($\varepsilon_0 \cong 24000$ at T= 4 K). Before proceeding to the experimental methods of the soft mode studies in STO thin films we will briefly describe basic properties of the optical phonons.

In the cubic bulk STO crystals with a perovskite structure every atom in the primitive cell is at center of inversion and consequently the optical phonons are of the odd symmetry. Three phonon branches of the F_{1u} symmetry are infrared active and one branch of the F_{2u} symmetry (so called "silent mode") is not infrared nor Raman active. The crystal field splits phonons into longitudinal and doubly degenerated transverse

modes, which are usually labeled in literature according to an increase of their frequency: ω_{LOj} and ω_{TOj} with $j = 1,2,3,4$. The soft mode is the TO_1 optical phonon. At low temperatures, below the structural cubic-to-tetragonal phase transition, which takes place in the bulk at about T_a=105 K, the infrared-active optical phonons split into modes of the A_{2u} and E_u symmetry remaining infrared active. The A_{2u} and the doubly degenerate E_u phonons are polarized along and perpendicular to the tetragonal axis, respectively. The splitting of the optical phonons in the tetragonal phase imply an anisotropy of the dielectric function tensor. In contrast to the cubic phase where the dielectric function tensor is degenerate into a scalar, in the tetragonal phase it has two different components, $\varepsilon_{0\parallel}$ and $\varepsilon_{0\perp}$, for electric field directed along and perpendicular to the tetragonal axis, respectively. The frequencies of the splitted components of the soft mode are still connected to the corresponding components of the dielectric function tensor by the LST relationship. The second group of the phonons of interest is the structural, or R modes. The softening of these phonons at T_a=105 K, when their frequency drops to zero, results in the cubic-to-tetragonal structural phase transition, which in contrast to, e.g. $BaTiO_3$, is not associated with the appearance of a ferroelectric phase. The doubling of the primitive sell in the tetragonal phase leads to the folding of the R phonons into the zone center and splitting into two Raman active mode of the A_{1g} and E_g symmetry.

EXPERIMENTAL TECHNIQUES for the SOFT MODE STUDIES in SrTiO₃

The aforementioned specifics of the optical phonons in STO determine the experimental techniques, which can be utilized for their studies. Phonon spectra in STO bulk crystals have been investigated for many decades using far infrared (IR) spectroscopy [12], neutron scattering [14], Raman scattering [15], and hyper-Raman scattering [16]. Further we will consider the applicability of these experimental methods to the phonon studies in STO thin films.

Neutron scattering: The geometrical factor restricts this very powerful method since it usually requires several grams [17]. of the solid state sample. Thus, the conventional neutron scattering cannot be directly applied to the phonon studies of STO films with the typical thickness less than 1 μ m. Recent development of neutron scattering allows studies of ultrasmall samples with the weight of about 5 mg, which though requires very thick freestanding STO films and at present this method is not of the practical interest.

Hyper-Raman scattering: This technique can, in principle, provide useful information about the infrared-active optical phonons [16]. However, these experiments utilize very high excitation laser power density and only transparent in the infrared spectral range samples can be studied by the conventional hyper-Raman scattering with a pulsed Nd:YAG laser excitation. Special efforts should be made to choose the right transparent substrate with no hyper-Raman response in the frequency range of the STO optical phonons. Our preliminary results on hyper-Raman scattering demonstrated that the defect-induced absorption of the exciting laser usually results in a damage of the studied STO films. Moreover, the STO films grown on conducting substrates, which are of the practical interest, can by no means be studied with hyper-Raman scattering because of the strong absorption in the substrate layer and a consequent damage of the whole sample.

Infrared spectroscopy: In bulk STO this method allowed measurements of the dielectric function in the far-infrared spectral range and determination of the frequencies of the infrared-active optical phonons. To obtain real and imaginary parts of the dielectric

function in reflection or transmission experiments, it requires application of the Kramers-Kronig transformation. The uncertainties of this approach limit the accuracy of the measurements. Far-infrared ellipsometry provides the same kind of information but without relaying on the Kramers-Kronig transformation, since both the real and imaginary parts of the dielectric function are measured at the same time. Recently we have applied the Fourier transform infrared (FTIR) ellipsometry to thin STO films using synchrotron radiation [18]. The high brightness of the synchrotron light source allows us to probe thin films with a small in-plane area, thus minimizing the effects of the film thickness fluctuations.

Raman scattering: The conventional Raman scattering is limited in bulk STO by the odd parity of the optical phonons since at the normal conditions they are not Raman but infrared active. First order Raman scattering has been studied in bulk STO only in the cases of ferroelectricity induced by application of hydrostatic or uniaxial stress, or when the central symmetry of the system has been broken by impurities. Application of external electric field also removes the center of inversion and makes all the optical phonons Raman active [15]. Our previous studies of thin STO films [19] demonstrated the observation of the zone center optical phonons in the Raman scattering experiments. The possible reason for that is the existence of the local polarization due to the presence of oxygen vacancies [8]. In the same manner as external electric field, this polarization removes the center of inversion in STO films. Raman scattering in STO thin films under application of external electric field (see Ref. [8] for more detail) is of the special interest since it allows measurements of the soft mode frequency tuning. These experiments will be described below along with the results of the FTIR ellipsometry measurements.

EXPERIMENT

STO film with the thickness of 1μm was epitaxially grown using PLD on a single crystal [001]-oriented STO substrate. A conductive $SrRuO_3$ (SRO) buffer layer with the thickness of 0.35 μm was inserted between the film and the substrate to screen the optical signal from bulk STO. The SRO buffer layer also serves as the bottom electrode. To apply an external electric field normal to the STO film plane, a transparent indium-doped tin oxide (ITO) layer was deposited on top of the STO film at 200 C^o in 16 mTorr oxygen, resulting in high conductivity of ITO. The lattice constant mismatch between SRO and STO (~0.64%) results in slight tensile in-plane stress in the STO films. X-ray diffraction [20] and Raman scattering by R phonons [8] demonstrated that STO films grown in the same conditions have a cubic structure at high temperatures with a transition to a tetragonal structure at about 125 K, which is higher than that in the bulk (T_a^{bulk} =105 K). Narrow full width at half maximum (FWHM) is found in both the Bragg peaks (~0.1^o) and the rocking curves (~0.16^o).

The sample geometry [see insets to Fig. 1(a,b)] allows the ellipsometry, Raman scattering, and low-frequency dielectric measurements to be performed on the same structure. The sample was attached to a cold finger inside an optical He-flow cryostat with a temperature range between 5 and 300 K. Raman scattering measurements were taken in the conventional backscattering and in close-to-90° configurations. The z axis is perpendicular to the film plane, while x and y axes are parallel to the [100] and [010] directions of the cubic STO structure, respectively. The 514.5 nm line of an Ar^+-ion laser was used for excitation. Raman spectra were recorded with a SPEX Triplemate spectrometer equipped with a charge-coupled device (CCD) detector. During the Raman scattering measurements, a dc voltage was applied to the sample providing an electric field inside the STO film up to 30×10^4 V/cm. FTIR ellipsometry experiments have been

carried out at the National Synchrotron Light Source in Brookhaven National Laboratory using synchrotron radiation [21]. No electric field has been applied to the sample during the ellipsometry measurements.

RESULTS AND DISCUSSION

Fig. 1(a) presents an imaginary part of the effective dielectric function, $\varepsilon''(\omega)$, for the 1 μm-thick STO film at 10 K. The soft TO_1 phonon mode is clearly observed along with other TO modes, and their positions are marked in the figure with arrows. The phonon frequencies were determined by the best fit of the experimental spectra to the factorized form of the dielectric function [12]:

$$\varepsilon(\omega) = \varepsilon_\infty \prod_{j=1}^{N=3} \frac{\omega_{LOj}^2 - \omega^2 + i\gamma_{LOj}}{\omega_{TOj}^2 - \omega^2 + i\gamma_{TOj}}, \tag{5}$$

where $\gamma_{TO(LO)j}$ represents damping of the TO_j (LO_j) modes. Note that the LST relation is the $\omega \to 0$ limit of Eq. (5). The peak at 480 cm^{-1} is close to the frequency of the LO_3 phonon and corresponds to the Berreman mode originated from the energy losses at the interface between STO and SRO [22].
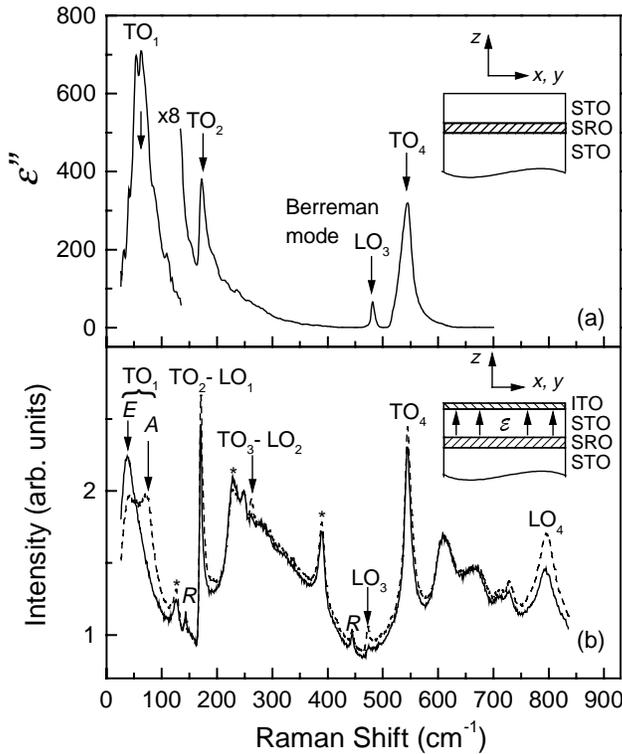
Figure 1.
Ellipsometry and Raman spectra for 1 μm-thick STO film at $T=10$ K. The insets show the schematics of the investigated structure grown on an STO substrate.
(a) The imaginary part of the effective dielectric function. Positions of the optical phonons are marked with arrows.
(b) Raman spectra without (solid line) and in the presence of external electric field of 22×10^4 V/cm directed normal to the film (doted line). The soft mode components are labeled A and E. Structural modes are denoted with R. Optical phonons from the SRO buffer layer are marked with stars.

Raman spectra obtained at $T = 10$ K with and without application of external electric field $\mathcal{E}$ are shown in Fig.1(b). The phonon frequencies determined by Raman scattering are similar to the results of FTIR ellipsometry. Raman spectrum at $\mathcal{E} = 0$ (solid line) contains a strong peak at about 40 cm^{-1} originated from the E_u component of the soft mode (labeled E). Application of the external electric field [see dotted line in Fig. 1(b)] leads to appearance of the A_{2u} component of the soft mode (labeled A). The selection rules for the A and E peaks change with an increase of the electric field and in the strong field-limit the nonzero components of the Raman tensor are α_{zz} and $\alpha_{xz,yz}$ for the A and

E phonon modes, respectively. The splitting between them at low temperatures and in the absence of electric field is induced by the tetragonal distortion. The soft mode frequency is higher at low temperature than that in bulk STO crystals. This result is in quantitative agreement with the LST formalism.

CONCLUSIONS and ACKNOWLEDGMENTS

We have demonstrated that FTIR ellipsometry and electric field-induced Raman scattering in STO thin film allow experimental determination of the optical phonon frequencies including that of the soft mode. It is possible to measure the temperature and electric field dependencies of the soft mode frequency and the splitting of the soft mode induced by the tetragonal distortion. The details of these studies will be published elsewhere [8,18]. Based on the LST relation, our measurements provide a contactless determination of the static dielectric constant, which can be compared with the experimental values measured in the same sample with, e .g., an LCR meter. Systematic experimental studies of the soft mode behavior will help to find an explanation of the difference between the dielectric properties of the STO films and bulk crystals.

REFERENCES

[1] O. Auciello, J. F. Scott, and R. Ramesh, Physics Today **51**, 22 (1998).
[2] H.-Ch. Li, W. Si, A. D. West, and X. X. Xi, Appl. Phys. Lett. **73**, 190 (1998).
[3] H.-Ch. Li, W. Si, A. D. West, and X. X. Xi, Appl. Phys. Lett. **73**, 464 (1998).
[4] D. Fuchs, C. W. Schneider, R. Schneider, and H. Rietschel, J. Appl. Phys., **85**, 7362 (1999).
[5] R. A. McKee, F. J. Walker, and M. F. Chisholm, Phys. Rev. Lett., **81**, 3014 (1998).
[6] C. Zhou and D. M. Newns, J. Appl. Phys. **82**, 3081 (1997).
[7] C. Basceri, S. K. Streiffer, A. I. Kingon, and R. Waser, J. Appl. Phys. **82**, 2497 (1997).
[8] I. A. Akimov, A. A. Sirenko, A. M. Clark, J.-H. Hao, and X. X. Xi, unpublished.
[9] H. Fröhlich, Theory of Dielectrics (Oxford: Clarendon Press, 1949).
[10] W. Cochran, Adv. Phys. **9**, 387 (1960).
[11] R. A. Cowley, Adv. Phys. **12**, 421 (1963).
[12] J. L. Servoin, Y. Luspin, and F. Gervais, Phys. Rev. B **22**, 5501 (1980).
[13] A. S. Chaves, F.C.S. Barreto, and L.A.A. Ribeiro, Phys. Rev. Lett. **37**, 618 (1976).
[14] J. D. Axe, J. Harada, and G. Shirane, Phys. Rev. B **1**, 1227 (1970).
[15] J. M. Worlock and P. A. Fleury, Phys. Rev. Lett. **19**, 1176 (1967).
[16] H. Vogt, Phys. Rev. B **51**, 8046 (1995).
[17] P. Lindner and G. Wignall, MRS Bulletin **24** (No. 12), 34 (1999).
[18] A. A. Sirenko, C. Bernhard, A. Golnik, A. M. Clark, J.-H. Hao, W. Si, and X. X. Xi, unpublished.
[19] A. A. Sirenko, I.A. Akimov, J.R. Fox, A.M. Clark, H.-Ch. Li, W. Si, and X.X. Xi, Phys. Rev. Lett. **82**, 4500 (1999).
[20] B. O. Wells *et al.,* unpublished.
[21] R. Henn, C. Bernhard, A. Wittlin, M. Cardona, and S. Uchida, Thin Solid Films **314**-**315**, 643, (1998).
[22] D. W. Berreman, Phys. Rev. **130**, 2193 (1963).