Monitoring of Longitudinal-Wave Velocity and Attenuation of $SrTiO_3$ at Low Temperatures Using Picosecond Ultrasound Spectroscopy

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We measured the longitudinal-wave velocity and its attenuation in $SrTiO_3$ between 20 and 300 K using picosecond ultrasound spectroscopy. From the temperature dependence of the velocity and attenuation, we monitored the cubic-tetragonal phase transition of $SrTiO_3$ near 100 K, whereas no more transitions were indicated below 100 K. From the measured attenuation coefficients, we estimate the relaxation time τ. Because of the ultrahigh frequency measurements, the product $\omega\tau$ is larger than unity, where the traditional theory for phonon-phonon interaction fails to explain the relaxation time. We then derived the relationship between the relaxation time and attenuation for $\omega\tau > 1$.

1. Introduction

$SrTiO_3$ exhibits a perovskite structure and is widely used as a substrate for superconducting thin films. Its low-temperature behaviors have been intensively studied and many anomalies are indicated below 70 K. However, their mechanisms are still unrevealed. In 1964, Lytle[1] reported a cubic-tetragonal phase transition at 100 K and also suggested that $SrTiO_3$ showed other phase transitions at 65 and 10 K. The cubic-tetragonal phase transition was confirmed by many experiments with abrupt changes in sound velocities[2] and internal friction.[3,4] However, other phase transitions still remain unclear, while many anomalies have been reported for the temperature range lower than 100 K. For example, Ledbetter and coworkers[5,6] observed the temperature dependence of permittivity and elastic moduli at various frequencies, and found unusual behaviors below 65 K. They concluded that these anomalies were caused by dynamic effects such as optical mode crossing and domain wall mobility.[5–7] Although they argued that the second sound, which is a wave-like propagation of entropy or temperature,[8] is neither necessary nor sufficient to explain such anomalies, the second sound in $SrTiO_3$ was indicated by Brillouin light scattering.[9–11]

In this study, we monitored the longitudinal-wave velocity and attenuation of $SrTiO_3$ at low temperature using picosecond ultrasound spectroscopy. The attenuation is more sensitive to phase transitions at higher frequencies[3,4] and Ang *et al.* found that low-temperature anomalies are highly frequency dependent with the low-frequency range (from 1 kHz to 220 MHz measurements).[6] Picosecond ultrasound can excite sub-terahertz ultrasounds without any contact, which should show a much higher sensitivity to phase transitions. This method can measure the longitudinal-wave elastic constant of ultrathin films[12–15] and that of oxides and semiconductors[16] with high precision. Low-temperature measurements also have been performed,[17,18] while phase-transition monitoring has not been reported so far. Considering that sub-terahertz ultrasound is expected to be sensitive to phase transitions, we perform phase transition monitoring in $SrTiO_3$ by picosecond ultrasound spectroscopy to determine whether the other phase transitions are indicated or not.

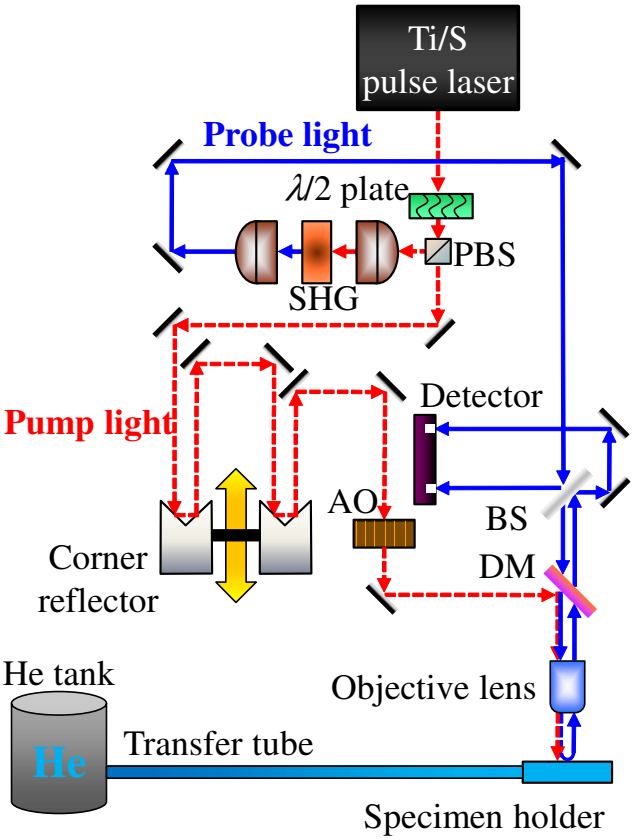

Fig. 1. (Color online) Developed optics. Dashed lines show a wavelength of 800 nm and solid lines show a wavelength of 400 nm.

2. Experimental Methods

Picosecond ultrasound spectroscopy uses an ultrafast pump light pulse to excite ultrasound and a probe light pulse to detect it.[19,20] Figure 1 is a schematic of the optics we developed. We use a titanium-sapphire pulse laser of 140 fs pulse duration, 80 MHz repetition rate, and 800 nm wavelength. We divided the source light pulse into pump and probe light pulses by a polarization beam

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splitter (PBS) and their power ratio is adjusted by a $\lambda/2$ plate.

The pump light is reflected by two corner reflectors, which control the delay time to the probe light, and is modulated at 100 kHz by an acousto-optical (AO) crystal. We distinguish pump light from probe light by a sharp color-cut dichroic mirror (DM), which reflects 800-nm-wavelength light and transmits 400-nm-wavelength light. The pump light is reflected by the DM and incident to the specimen surface. Ultrasound is then excited through the ultrafast thermal expansion and shrinking at the specimen surface.

The probe light's frequency is doubled by a second-harmonic-generator (SHG) crystal. Part of the probe light enters a balance detector as a reference, and the major part is perpendicularly incident to the specimen with the pump light. The amplitude and phase of the probe light reflected from the specimen will change from those of the reference light owing to the strain pulse ultrasound excited by the pump light. Therefore, we can detect the ultrasound by extracting the changes in the reflectivity by the balance detector and a lock-in amplifier. We used a cryostat as a specimen holder to control the temperature between 20 and 300 K. The specimen was attached on a Cu heat exchanger cooled by liquid He. To measure the specimen temperature, we used a semiconductor thermometer attached to the heat exchanger at 10 mm from the specimen.

If the specimen is not an opaque material, the ultrasound works as a diffraction grating for the probe light. Diffracted probe light and reflected probe light at the surface interfere with each other. We can observe an oscillating signal in the reflectivity as the ultrasound propagates. This is Brillouin oscillation,[21,22] and its frequency f is well approximated by the Bragg's condition of backward diffraction,[23] that is

$$f = \frac{2nv}{\lambda_{probe}}, \tag{1}$$

where n is the refractive index, v is the longitudinal sound velocity, and λ_{probe} is the wavelength of the probe light. By ellipsometry, n can be precisely measured, so that we can determine v through f. We used 99.99%-purity (100) $SrTiO_3$ single crystals grown by the Bernoulli method at Furuuchi chemical corporation. They include impurities such as Ba, Al, Ca, and so on, but their concentrations are less than 50 ppm at most. We deposited a 17-nm-thick Pt thin film on the surface as a sound generator.

3. Results and Discussion

3.1 Cubic-tetragonal phase transition

The Brillouin oscillations observed between 20 and 300 K were exponentially damped, as shown in Fig. 3. We succeeded in monitoring the changes of attenuation and sound velocity with high precision, as shown in Fig. 2. We calculated the attenuation coefficient α by fitting the exponential function to the envelope of the decaying oscillation and determined the frequency by fast Fourier transform. We assumed that the refractive index would proportionally decrease with temperature.[24]

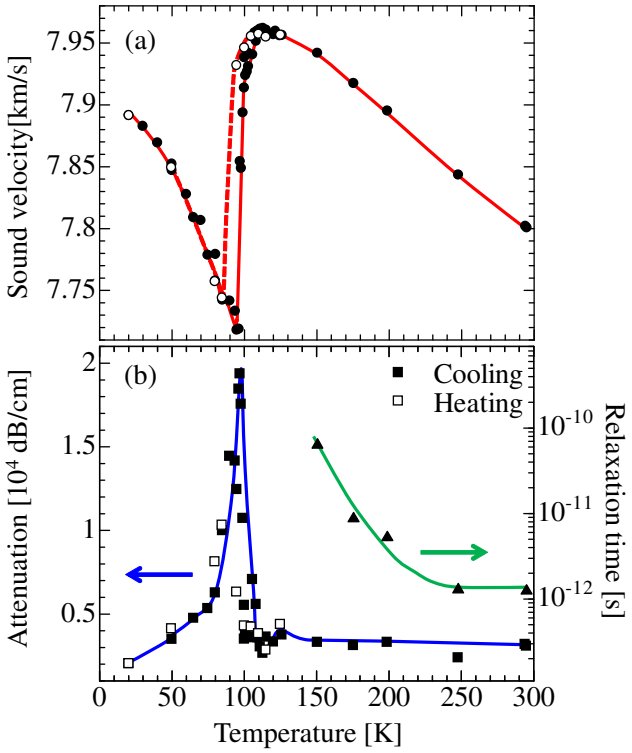

Fig. 2. (Color online) Exponentially damped Brillouin oscillations in $SrTiO_3$ at typical temperatures. Dashed lines denote the fitted exponential functions.

We detected an abrupt change of sound velocity and an attenuation increase at approximately 95 K, which were attributed to the cubic-tetragonal phase transition. However, the transition temperature is lower than the reported value by 10 K.[1–6] This result may suggest that the structural phase transition occurs near 95 K. Another possibility includes the temperature increase by the laser-beam irradiation; the energy of pump and probe lights is approximately 40 mW, so about a half nJ energy is incident to the specimen by a single pulse. In the case of perpendicular incidence, the reflectivity R of light energy is given by

$$R = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2}, \tag{2}$$

where n and k are the refractive index and extinction coefficient, respectively. To simplify, we assumed that $(1-R)E$ is absorbed in the Pt thin film and causes the temperature increase there, where E is the energy of a single pulse. The spot diameter at the specimen is approximately 50 μm and the film thickness is about 17 nm, and we considered this region as the absorption volume. The temperature increase ΔT is then given by

$$\Delta T = \frac{(1-R)E}{\rho C_{\mathrm{Pt}} V}, \tag{3}$$

where ρ is the mass density, C_{Pt} is the specific heat, and V is the absorption volume.

We calculated the temperature increases in the surface thin film using reported values of n, k,[25] and C_{Pt},[26] and

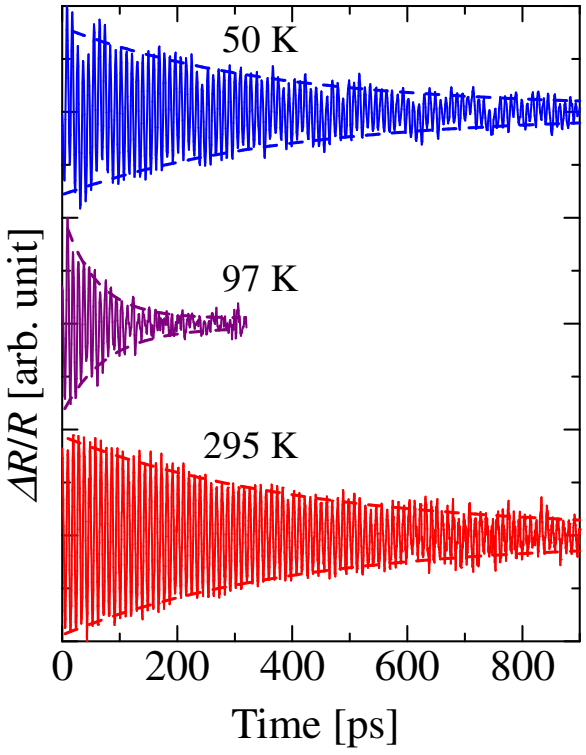

Fig. 3. (Color online) Temperature dependence of (a) sound velocity (circle symbols) and (b) attenuation coefficient (square symbols) and relaxation time (triangle symbols). Closed and open symbols denote the measurements in cooling and heating processes, respectively. The horizontal axis shows the temperature measured by the semiconductor thermometer, which might be lower than the specimen temperature owing to the laser-beam irradiation.

found that they are less than a few kelvins between 50 and 300 K. There thus might be a difference between the temperature measured using a semiconductor thermometer and the specimen temperature.

3.2 Low-temperature anomalies

In our measurements, low-temperature anomalies such as those reported by Ang *et al.*[6] were not observed. Our observations indicated that the reported anomalies did not stem from structural phase transition. Picosecond ultrasound spectroscopy can measure sound velocity with high precision, and small changes in sound velocity due to structural phase transition could be well detected. Since we measured sound velocity and attenuation in a small region, our measurement would not reflect domain wall effects, which are considered as one of the causes for low-temperature anomalies, leading to normal behaviors.

Although no anomalies appeared in sound velocity and attenuation, we observed long-periodic vibrational background changes below 120 K and their frequencies are between 3 and 8 GHz. This may be the second sound of $SrTiO_3$. It has been reported that the second sound in $SrTiO_3$ was observed by the light-scattering method and its frequency was on the order of 10 GHz.[9,10] Our results are consistent with this. Because the picosecond ultrasound induces coherent phonons by a pump light, it would be expected that a relationship between pump light energy and the changes in the second sound can be observed.

3.3 Attenuation coefficient

Since picosecond ultrasound spectroscopy is a noncontact measurement and $SrTiO_3$ absorbs almost no visible light,[27] the attenuation is not caused by the measurement system but by the material. Moreover, a single crystal has no grain boundary and diffraction scattering can be ignored because the penetration depth and wavelength are much smaller than the spot diameter. Seki *et al.*[28] theoretically introduced the so-called Seki parameter,

$$\Lambda = \frac{a^2}{\lambda z}, \tag{4}$$

to calculate the apparent attenuation due to the diffraction of ultrasound, where a is the spot diameter, z is the propagation distance of ultrasound, and λ is the wavelength of ultrasound. In our measurements, λ is about 80 nm, leading to $\Lambda \simeq 3 \times 10^{-4}$. This is so small that the diffraction loss can be neglected. This means that we have measured the intrinsic attenuation in $SrTiO_3$ in the sub-terahertz order. The acoustic wave is considered as a macroscopic driving force that modulates the frequencies of the thermal phonons through the mechanism provided by the anharmonicity of the solid. The attenuation of the acoustic wave is then closely correlated to the relaxation time. A theory of this mechanism was first proposed by Akhieser,[29] a simplified version was given by Bömmel and Dransfeld,[30] and a more complete version was derived by Woodruff and Ehrenreich[31] by solving the linearized Boltzmann equation. It takes the form[32]

$$A_{\mathrm{np/cm}} = \frac{CT\gamma^2\omega^2\tau}{2\rho v^3(1+\omega^2\tau^2)}, \tag{5}$$

which is valid when $\omega\tau < 1$. There, $A_{\mathrm{np/cm}}$ is the attenuation ratio per unit cm, C is the specific heat per unit volume, T is the absolute temperature, γ is the Grüneisen parameter, ω is the angle frequency, ρ is the mass density, and v is the sound velocity. We calculated τ using the reported values for C[33] and γ,[34] and measured values for v, ω, and $A_{\mathrm{np/cm}}$. However, the solutions do not satisfy the condition $\omega\tau < 1$. This indicates that the attenuation is mainly caused by the direct interaction of the acoustic wave with individual phonons. Then, we calculated the relationship between the attenuation and relaxation time for $\omega\tau > 1$. Woodruff and Ehrenreich derived the attenuation expression[31]

$$A_{\mathrm{np/cm}} = \frac{CT\gamma^2\omega}{2\rho v^3}\mathrm{Im}\left(\frac{{I_{00}^*}^2}{I_{01}^*} + i\omega\tau I_{00}^*\right), \tag{6}$$

where * indicates the complex conjugate and I_{mn} is

$$I_{mn} = \int_{-1}^{1} \frac{\mu^m(1-\mu)^n}{1-i\omega\tau(1-\mu)}d\mu. \tag{7}$$

In the previous studies, eq. (6) is simplified under the condition of $\omega\tau < 1$. We calculate it without any ap-

proximations and derive the following equation

$$A_{\mathrm{np/cm}} = \frac{CT\gamma^2\omega}{2\rho v^3}\mathrm{Im}\left\{\left[2\omega\tau i + \frac{4\omega^2\tau^2}{2\omega\tau i + \log(1-2\omega\tau i)}\right]^*\right\}. \quad (8)$$

Then, we calculate the relaxation time with eq. (8) above 150 K, as shown in Fig. 2(b), below which no τ satisfies the eq. (8), indicating that an increase in the attenuation owing to a phase transition prevents application of the usual relaxation theory.

4. Conclusions

We succeeded in monitoring a phase transition by picosecond ultrasound spectroscopy. However, the temperature at the laser radiated point might be higher than the temperature measured by a thermometer. This should be carefully investigated, through monitoring other material's phase transitions, for example. In this study, no anomalies of $SrTiO_3$ below 100 K were observed in sound velocity. This indicates that the reported various anomalies were not caused by a structural phase transition but by other dynamic effects. We made a direct measurement of the intrinsic attenuation in an ultrahigh frequency region, which leads to the relaxation time in the $\omega\tau > 1$ region.

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