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Second-harmonic Generation of Treated-STO Surface

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ABSTRACT

In order to investigate the surface SHG, (110) pure STO single crystals were exposed to a reducing atmosphere to induce the reduction of the Ti ion and the release of oxygen from the lattice compensating the reduction of the Ti ions. The anisotropy and asymmetry of SHG intensity explains a slight shrinkage. The incoming fundamental wave was polarized either in the *p*-in or *s*-in to the plane of incidence for the reflection geometry. The SH polarization diagram could be described by the electric dipole and/or quadrupole contribution of reduced STO single crystal surface.

Keywords : Reduction, Single crystals, Surface second-harmonic generation (SHG), Polarization diagram

1. Introduction

A detailed characterization of the surface properties of $SrTiO_3$ (STO) single crystals is of fundamental importance in many interesting research fields[1-5]. The most used crystallographic orientations of the STO surface are (100) and (110). The (100) STO is terminated by two undisturbed atomic layers, i.e., the SrO or TiO_2 plane. Most applications of STO demand an extremely accurate control of surface structure and chemistry. In addition, the role of oxygen vacancies in ferroelectric perovskite oxides is thought to be important in fatigue[6-8]. The interesting phenomenon in titanium-rich materials is the small shrinkage during reduction, although an expansion is expected because of the increased cation radius.

The nonlinear optical technique of surface second-harmonic generation (SHG) has proved to be a powerful tool for surface analysis. Its strength relies on the fact that the second-order optical nonlinear processes are forbidden in the bulk of center-symmetric materials. This symmetry breaking occurs in the first few atomic layers in the case of ionic or covalent crystals, making second-harmonic generation highly surface specific. Since the early SHG observation of time-resolved laser-induced silicon melting, SHG has been applied successfully for studying surface reconstructions, phase transitions in molecular monolayers, the ferromagnetic-paramagnetic phase transition in a magnetic thin film, and observation of a near-surface structural phase transition[9-13].

The aim of this work is to perform experimental investigations on reduced STO surfaces with different terminations and orientations by means of surface SHG. In order to obtain the maximum information on the surface symmetries, we measure the surface SHG signal at different polarization combinations of both the input pump-beam and output second-harmonic beam, and at different azimuth angles respective to the surface normal.

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2. Experiment Precedure

In order to investigate the surface SHG, (110) pure STO single crystals with 2 sides epi-polished (Ra < 7 Å) were used. (MTI Inc.) For the measurement of the STO single crystal in the oxidized state, a transparent colorless crystal with dimensions of $5 \times 5 \times 0.5$ mm^3 was used. The crystal was exposed to a reducing atmosphere H_2(5%) + N_2(95%) at 1000°C to induce the reduction of Ti^{4+} to Ti^{3+} and the release of oxygen from the lattice compensating the reduction of the Ti ions. The crystal was heat treated for 8 h.

We used a Q-switched Nd-YAG laser with a high peak power as the fundamental light source, with 20 ns pulse width and 200 mJ pulse energy. This equates to a peak pulse power of around 10 MW, in a beam of 6 mm diameter, or around 3.5×10^7 W cm^{-2}. A 20 cm focal length lens was used to focus the beam to a spot size of around 100 μm on the (110) STO sample. The sample was held on a rotational stage which allowed the sample to rotate around its surface normal. The incident angle of the beam, θ, was set to be 45°. The plane of polarization of the input fundamental beam was controlled by rotating the half-wave ($\lambda/2$) plate. The SHG signal generated in reflection was filtered by color filters and detected by a photomultiplier tube. Polarization of the second-harmonic wave was analyzed by rotating an analyzer around its normal.

3. Results and Discussion

Fig. 1 shows the experimental set-up used for the surface

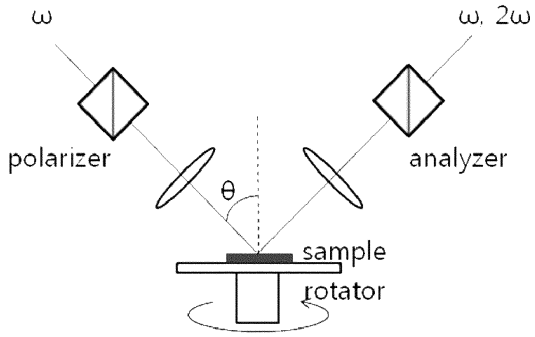

Fig. 1. The experimental set-up used for the surface SHG. $\theta = 45^{o}$ is the incident angle.

SHG. The incoming fundamental wave was polarized either in the plane (*p*-in) or perpendicular (*s*-in) to the plane of incidence for the reflection geometry. The fundamental beam reflected from the bottom surface, due to the small thickness (0.5 mm), generated a secondary SHG signal. Due to multiple reflections, this contribution from the secondary SHG signal was larger than the primary SHG, as observed via reflection SHG. This secondary SHG signal was minimized by roughening the bottom surface of the crystal with sandpaper.

The optical transmittance spectra for the pure and reduced (110) $SrTiO_3$ single crystals in the wavelength region 190 to 1100 nm are shown in Fig. 2. The optical band gap of the crystals was determined from the optical transmittance spectra. The edge of fundamental absorption was near 395 nm for both pure and reduced $SrTiO_3$ single crystals. From the well-known formula between the absorption coefficient and the optical band gap, the value of E_g was about 3.15 eV.

The anisotropy shown in the polar diagram can be explained when we assume the point group to be mm2. Point group mm2 have d_{131}, d_{223}, d_{311}, d_{322}, and d_{333} tensor components. Then the anisotropy of SHG intensity is expressed as

$$I^{2\omega} \propto \left| E_{out}^{2\omega} \right| = \{(2d_{15}+d_{31})\cos\phi(\sin\phi)^2 + d_{31}(cos\phi)^3\}^2$$

The result for reduced STO is shown in Fig. 3. Reduced STO was investigated in more detail by XRD. Lattice parameters of oxidation and reduction for STO were 3.992 Å and 3.904 Å, respectively. It shows that no significant atomic displacement can be observed. This indicates that the amount of reduced Ti ions and released oxide ions is too small to be explained by XRD. However, the optical SHG could investigate the shrinkage after reduction of the STO. The anisotropy and asymmetry of SHG intensity in Fig. 3 explains a slight shrinkage. Considering the enhancement of induced surface dipoles and the enlargement of disordering of the treated STO surface, the anisotropic enhancement of the second-order nonlinear polarization with SHG coefficient d_{ijk} can be understood. The SHG coefficient d_{ijk} is proportional to the ensemble average of $r_i r_j r_k$, with r_i being

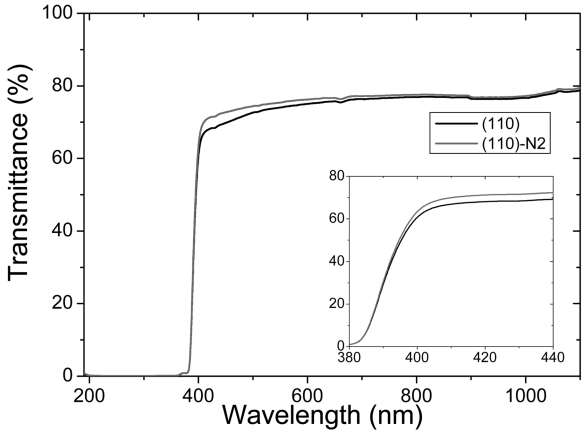

Fig. 2. Transmittance spectra for pure and reduced (110) $SrTiO_3$ single crystals.

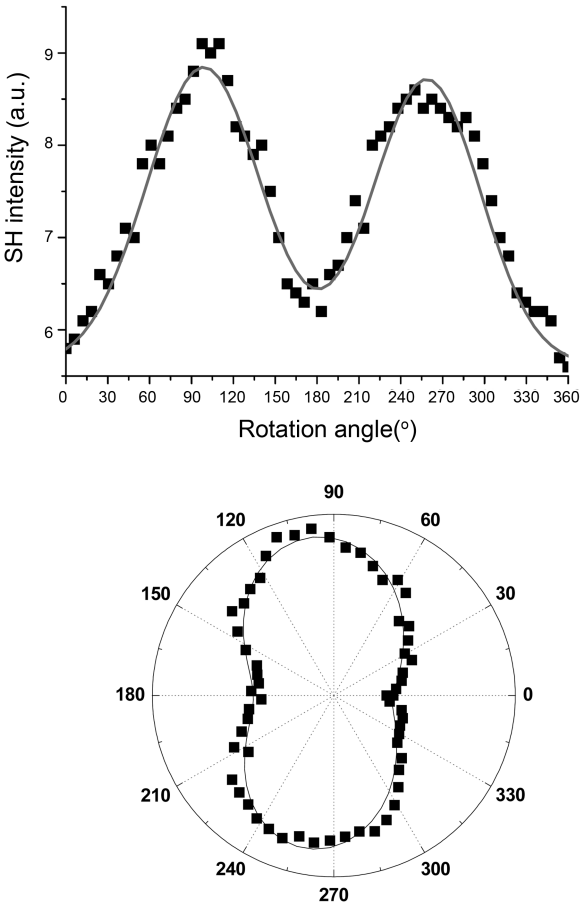

Fig. 3. Fundamental incidence angle dependence of the SH intensity of reduced (110) STO single crystals.

the dipole moment operator in the *i* direction.

The SH polarization diagram for reflection geometry is presented in Fig. 4. The SHG polarization diagrams for an α-polarized fundamental wave can be written as[14]

$$I_{2\omega}^{\alpha} \propto (E_{2\omega}^{a,u})^2 \cos^2\phi + (E_{2\omega}^{a,t})^2 \sin^2\phi - 2(E_{2\omega}^{a,u})(E_{2\omega}^{a,t})\cos\phi\sin\phi\cos\Delta$$

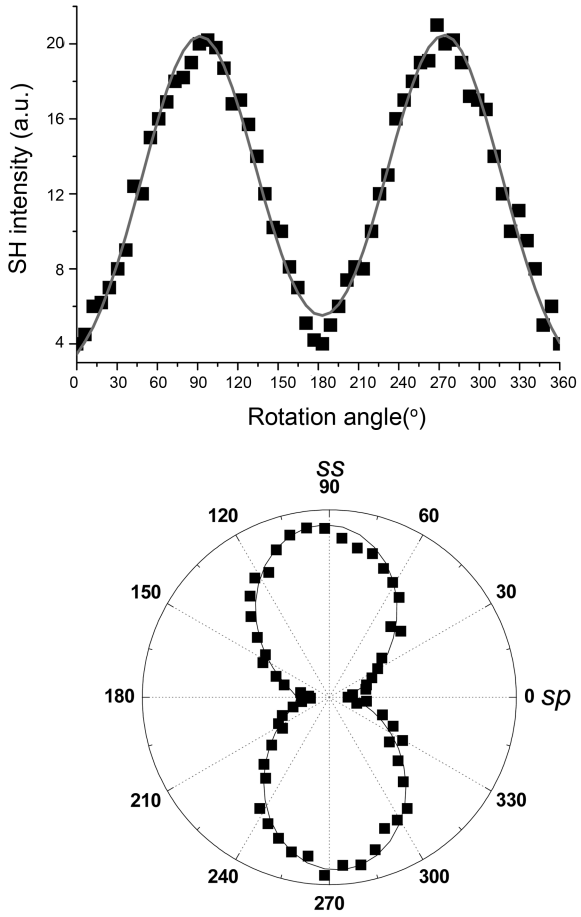

Fig. 4. SHG polarization diagram for reduced (110) STO single crystals for azimuthal angle.

where $E_{2\omega}^{a,u}$ and $E_{2\omega}^{a,t}$ in the reflection geometry are *p*- and *s*-polarized components of the SH field, respectively, $\alpha = p, s$. Δ is the phase difference between $E_{2\omega}^{a,u}$ and $E_{2\omega}^{a,t}$ that may rise due to the complex character of both linear and nonlinear susceptibilities. Optical SHG derives its surface sensitivity from the fact that normally the strongest electric dipole contribution to the SHG response is forbidden in the bulk of centro-symmetric materials, but necessarily allowed at the symmetry breaking surface. High order quadrupole contributions are responsible for the bulk SHG. The ideal (110) $SrTiO_3$ surface consists of alternating positively charged SrTiO and negatively charged O_2 layers. Their relative scarcity is connected to the polar character of the surface: along the [1 1 0] direction, planes of either SrTiO or O_2 composition alternate, with a net dipole moment per unit cell. In the reflection geometry, their contributions to the SHG signal are largely dependent on the Fresnel factors and the coherence length. The reduced surface of crystals becomes dominated by TiO_2-terminated layers that had been inferred from surface sensitive spectroscopy. It is well known that these layers are subject to the additional loss of oxygen, which introduces oxygen vacancies and causes dramatic changes in the electronic structure. This loss of oxygen is also apparent in photoemission data[15].

4. Conclusion

We have reported the observation of a reduced surface variation on a single crystal by means of optical second-harmonic generation by using the intrinsic sensitivity of the SHG technique for inversion symmetry breaking. The amount of reduced Ti ions and released oxide ions are too small to be explained by XRD. The anisotropy and asymmetry of SHG intensity explains a slight shrinkage. The SH polarization diagram could be partially described by the electric dipole and/or quadrupole contribution of the reduced STO single crystal surface.

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