Structural Characterization of Ar^+-Irradiated $SrTiO_3$ Showing Room-temperature Blue Luminescence

$SrTiO_3$ is a transparent insulator and is widely used as an artificial gem. Recently we found that oxygen-deficient metallic $SrTiO_3$ shows blue (430 nm) emission at room temperature. This is not observed for stoichiometric $SrTiO_3$ [1]. The blue luminescence originates from radiative recombination of conduction electrons and excited holes located in the band gap. Thus, the electron carriers doped by the oxygen deficiency play an important role in this emission. Oxygen vacancies can be introduced into the $SrTiO_3$ crystal by Ar^+-irradiation, resulting in the blue luminescence. We investigated structural changes of an Ar^+-irradiated $SrTiO_3$ single crystal by analyzing the intensity of the X-ray diffraction pattern, and propose a model where the lattice constants are modified by the oxygen deficiency [2].

The Ar^+-irradiation was performed at room temperature at 500 V and an Ar gas flow of 3 cc/min for 10 min. The irradiated crystal showed the room-temperature blue luminescence as well as metallic conductivity. X-ray diffraction measurements on stoichiometric and Ar^+-irradiated $SrTiO_3$ crystals were performed, at room temperature, with a four-cycle diffractometer installed at beamline **BL13XU**. An X-ray beam with a photon energy of 11.9 keV (0.104 nm) and a size of 0.1 × 0.1 mm was incident on the samples.

Figure 1(a) shows the reciprocal-lattice map around (114) $SrTiO_3$ Bragg reflection, on a logarithmic intensity scale, for the non-irradiated crystal. Crystal truncation rod (CTR) scattering is visible along the [11*L*] direction due to the highly two-dimensional (i.e., atomically flat) surface structure. After the Ar^+-irradiation, Fig. 1(b), the sample showed additional intensity in the lower *L* direction region of the (114) reflection. This additional intensity was not observed for the non-irradiated $SrTiO_3$, suggesting that the surface layer modified by the Ar^+-irradiation gave rise to slight lattice expansion along the *c*-axis due to the oxygen-deficiencies in the $SrTiO_3$. Note that the in-plane lattice constant of the Ar^+-irradiated $SrTiO_3$ was fixed by the non-irradiated region so that the surface layer was under compressive strain.

As shown in Fig. 2(a), (00*L*) scans around the (002) Bragg reflection of the Ar^+-irradiated $SrTiO_3$ shows an asymmetric profile. This asymmetry is explained by the surface-lattice structure expansion model illustrated in Fig. 2(b). In the model, the following form for the distribution in the lattice parameter of the *k*-th Ar^+-irradiated tetragonal region ($Z > 0$) along (00*L*) is introduced.

$$c(k) = 3.905 + \Delta c(k) = 3.905 + \alpha \cdot \exp(k/\beta) \quad (k \geq 1).$$

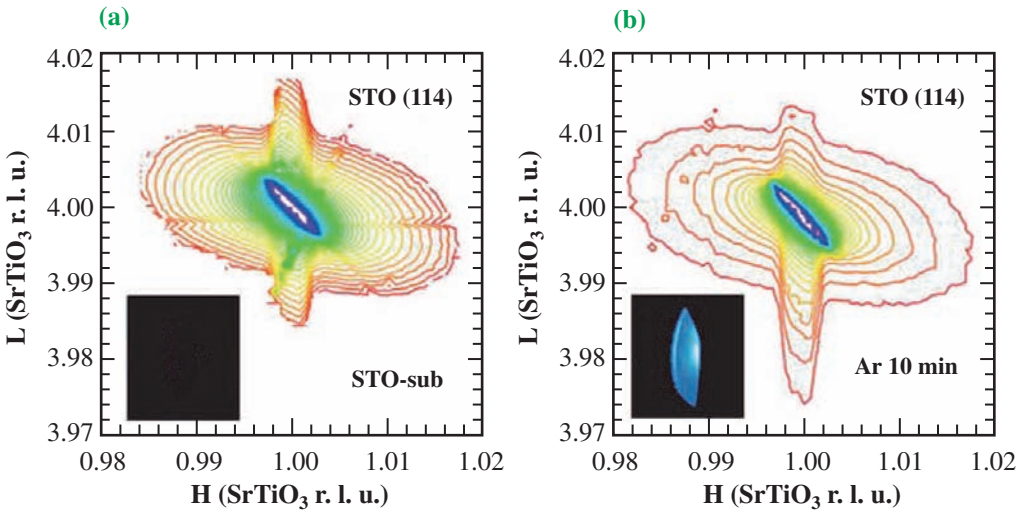

Fig. 1. Logarithmic intensity reciprocal-lattice map around (114) $SrTiO_3$ Bragg reflection for **(a)** non-irradiated and **(b)** Ar^+-irradiated crystals. Inset is a photo of luminescence from each crystal.

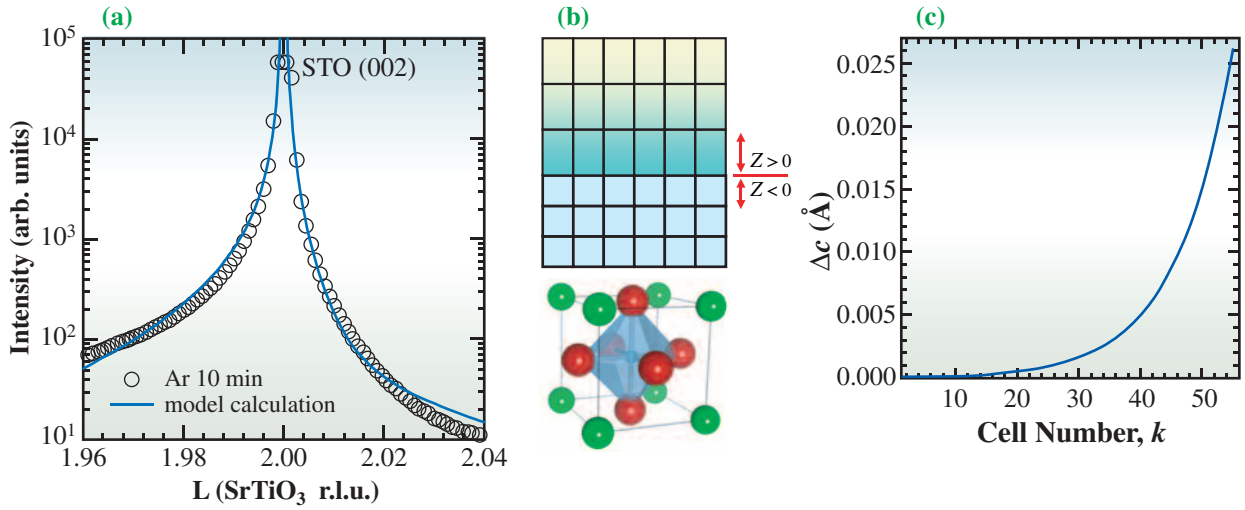

Fig. 2. **(a)** (00*L*) scan around (002) $SrTiO_3$ Bragg reflection of Ar^+-irradiated crystal and the result of the model calculation. **(b)** Schematic illustration of a structural model. **(c)** Variation of the lattice parameter *c* in the surface layer.

By using the atomic positions along the *z* axis for the constituent atoms and atomic scattering factors, the structure factors of the Ar^+-irradiated region, $F_{Ar\text{-}ir}(00L)$ ($Z > 0$) and the non-irradiated bulk region, $F_{Non\text{-}ir}(00L)$ ($Z \leq 0$), are given by

$$F_{Ar-ir}(00L) = \sum_{k=1}^{n}\left[f_{Sr}\exp(-2\pi iLc^*(Z_1(k)-c(k)/2))+f_{Ti}\exp(-2\pi iLc^*Z_1(k)) + f_O\left\{2\exp(-2\pi iLc^*Z_1(k))+\exp(-2\pi iLc^*(Z_1(k)-c(k)/2))\right\}\right],$$

and

$$F_{Non-ir}(00L) = \left[f_{Sr}\exp(-2\pi iLc^*(-a_0/2)) + f_{Ti}+f_O\left\{2+\exp(-2\pi iLc^*(-a_0/2))\right\}\right]\sum_{k\leq 0}^{-\infty}\exp(-2\pi ikLc^*a_0),$$

respectively. Thus the scattering intensity $I(00L)$ should be

$$I(00L) = A\cdot\left|F_{Ar-ir}(00L)+F_{Non-ir}(00L)\right|^2,$$

where the coefficient *A* is a scale factor.

With this model, the observed Bragg peak is well reproduced with α = 0.00006, β = 9.05, and n = 55. Figure 2(c) shows the results of variation in $c(k)$ as a function of k. The number of cells, n = 55, corresponds to the total thickness of the Ar^+-irradiation modified region of about 21 nm. The maximum lattice expansion reached about 0.67%. Our finding shall give a better understanding for the mechanism of room temperature blue luminescence from oxygen deficient surface layer of $SrTiO_3$ and may lead to novel high performance photo device.

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References

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