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Photoluminescence induced by thermal annealing in SrTiO₃ thin film

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We have grown SrTiO₃ thin films by rf-sputtering and studied its photoluminescence (PL) property after postannealing treatments. While the as-grown film does not show any PL signal, visible frequency PL emissions are induced by high temperature ($T > 550$ °C) annealing. When subsequent low-T (50 °C) and long term (>8 months) annealing was made, the PL-spectra evolved into another pattern in which four distinct luminescence peaks appear simultaneously at $\lambda = 1.8, 2.2, 2.7,$ and 3.1 eV. We propose that these remarkable room temperature PL effects are due to both metastable and energetically stabilized defect states formed inside the band gap. © 2009 American Institute of Physics. [doi:10.1063/1.3275707]

SrTiO₃ (STO) is a simple cubic perovskite oxide with a wide band gap ($E_g = 3.2$ eV). The dielectric constant of STO is large ($\epsilon \sim 300$) and exhibits the quantum paraelectricity at low-T.^{1,2} By electron-doping, STO becomes metallic and even superconducting at low temperature. A high mobility electron gas emerges when STO forms a thin film superlattice with another insulator LaAlO₃.³⁻⁵ In technological application, it is used as ideal substrate for high-T superconductor epitaxial film growth. The use of Nb doped STO as a field-effect transistor and resistance switching memory device has been demonstrated.⁶

Photoluminescence (PL) is another important aspect of STO. It has been known for long time that undoped STO shows the low-temperature PL ($T < 110$ K) at green ($\lambda \sim 540$ nm) (Refs. 7 and 8) and infrared ($\lambda \sim 800$ nm) frequency.⁹ Recently D. Kan *et al.*¹⁰ showed that room-temperature blue-PL can be induced when STO crystal is irradiated by Ar⁺ ion beam. The blue-PL appears also by chemical substitution such as Sr⁺² → La⁺³ or Ti⁺² → Nb⁺³.¹¹

In general context PL emission is derived from defect electronic states inside the band gap due to atomic vacancy or impurity.^{12,13} In STO, a single vacancy of Sr, Ti, and O can be the defect sources whereas the O-vacancy is most common one. In addition, two O-vacancies can bind together to form a cluster. Depending on the cluster configuration the defect energy changes,¹⁴ O-vacancy may also bind with Sr-or Ti-vacancy in various forms of defect clusters.¹⁵ Therefore, the defect states available in STO can be far more abundant and one should be able to extract much richer PL emissions than previously demonstrated. In this work we have grown highly oriented STO thin films and post annealed them in various thermal environments. Thermal annealing is the most common and easy way to induce vacancy defects in thin films. We find that, depending on the annealing conditions, a series of visible PL peaks can be induced at room temperature.

We have deposited STO thin films on thermally oxidized silicon substrates (SiO₂ thickness 200 nm) by sputtering an STO target (2 inch diameter). Applied rf power was 100 W and substrate temperature was fixed at 550 °C. Base pressure of the system was 1×10^{-6} Torr and working pressure was 1.5×10^{-2} Torr. An O₂/Ar flow ratio of 90/10 was maintained during the deposition for 4 h. These as-grown samples were subsequently annealed in either a UHV chamber at 10^{-7} torr or ambient pressure air for 2–6 hours. Four different temperature-pressure conditions used in the thermal treatment are summarized in Table I. Structural properties of the thin film were investigated by high resolution x-ray diffraction (XRD) (using Bruker-AXS D8 Discover, Goeber mirror) and transmission electron microscope (TEM). The PL spectra were taken using a PL(HORIBA Fluorolog-3) equipped with 325 nm excitation laser (power = 30 mW/cm²).

Figure 1 shows the XRD data (a) and the TEM image (b) of the as-grown STO film. In Fig. 1(a) the dominant peak at 32° corresponds to (110) reflection of the STO lattice consistent with other work.¹⁶⁻²¹ Considering the structural factors of each crystalline planes, volume ratio of (110) planes was estimated to be ~50%. Our STO thin films were dominantly (110) orientation on the SiO₂ surface. Rundqvist *et al.*²² reported that Ba_xSr_{1-x}TiO₃ thin films were textured with a dominant (110) orientation on SiO₂/Si substrates similar to our results. They suggested that such a preferential growth could be due to the lower surface energy of the (110) plane. Figure 1(b) shows that the STO layer (10 nm thick) is well

TABLE I. Four different conditions used in the postannealing of the as-grown STO films.

Condition	Temperature (°C)	Pressure (Torr)	Time (hour)
1	550	760	6
2	550	10^{-7}	2
3	750	760	6
4	750	10^{-7}	2

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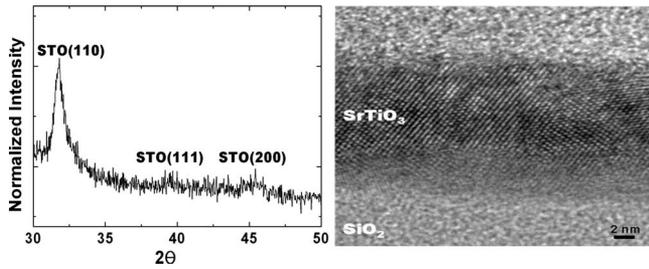


FIG. 1. High resolution XRD data (a) and TEM image (b) of the as-grown STO film.

crystallized and oriented along the growth direction. For the annealed samples, the XRD and TEM data were identical with the as-grown one without showing any notable change.

Figure 2 shows PL spectrum of the annealed samples 1 through 4 and the as-grown samples. In the sample 3 (750 °C-760 Torr annealed, Table I), a prominent PL peak is observed at $\lambda=420$ nm. It corresponds to the blue-luminescence and is similar to the blue-PL induced by Ar-irradiation ($\lambda=420-430$ nm). In the sample 1, the PL peak appears at $\lambda=505$ nm whereas in the samples 2 and 4, it is at $\lambda=630$ nm. These correspond to the green and red-orange emissions, respectively. The as-grown, nonannealed STO does not show any PL signal. We note that single crystal STO close to the ideal stoichiometric ratio (Sr:Ti:O = 1:1:3) also shows no PL emission at room temperature.^{7,10}

The insets in Fig. 2 show the actual PL image recorded with a digital camera during the laser illumination. It is very interesting to note that these PL colors we have induced are in fact the three primary-colors used in the display industry. It is also noteworthy that these colors can be induced in single material STO by the relatively easy processing technique of thermal annealing.

We have repeated the complete experimental sequence, film growth \rightarrow thermal annealing \rightarrow PL measurement, several times to check the reproducibility of the PL effect. In some cases, the blue- and green-peaks appeared simultaneously in samples 1 and 3. The red-PL in sample 4 had higher reproducibility. To test possible influence of the buffer layer on the PL effect, we have annealed the bare SiO₂/Si substrate with-

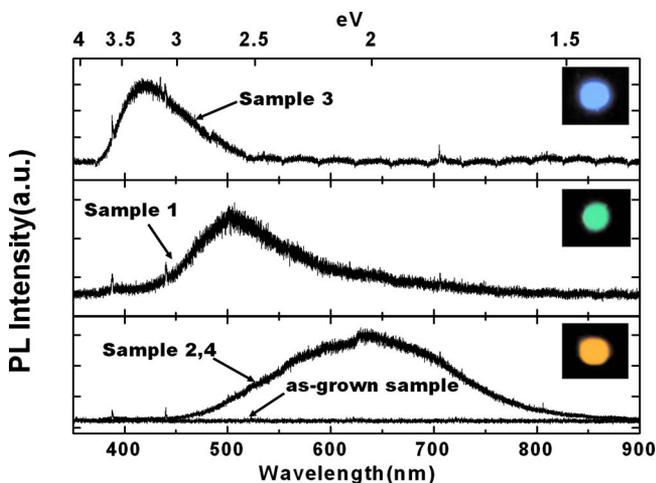


FIG. 2. (Color online) PL spectrum of the postannealed STO films taken at room temperature. PL data of the as-grown film is shown together. The insets in the three panels show the PL images taken with a digital camera during the laser excitation.

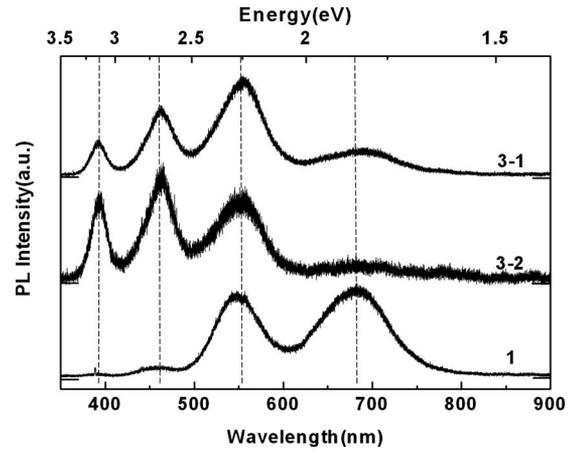


FIG. 3. PL data of the STO films after the low-T (50 °C) and long-term (>8 months) annealing of Sample 1 and two pieces of Sample 3 (3-1 and 3-2). The curves are shifted equally in the vertical axis.

out STO film under the same conditions as for the samples 1-4 and measured PL spectra, but no PL signal was seen. It shows that the PL peaks come indeed from the STO layer.

What are the defect states that give rise to the PL effects? Single oxygen vacancy makes donor level located close the conduction band bottom.^{23,24} A recent LDA+U calculation showed that oxygen vacancies tend to bind together to form two-vacancy clusters.¹⁴ The clustering is accompanied by localization of electron at Ti ion. A localized electron level is formed as a result where the level energy is within the gap, about 0.5-1.5 eV below the conduction band. The oxygen vacancy can bind with Sr vacancy as well where the cluster energy is also within the band gap.¹⁴ If electrons in these in-gap levels recombine with valence band hole, various visible PL lines will appear as we observed.²⁵ In attempt to reveal the defect types in our samples, we tried x-ray absorption spectroscopy and Rutherford backscattering spectrometry (RBS) measurements but could not obtain reliable data due to the ultrathin film thickness.

We have kept the Samples 1 and 3 in moisture-free N₂ atmosphere at 50 °C for more than eight months and remeasured the PL spectra. After this long term storage, the samples exhibited very interesting changes as shown in Fig. 3. In Sample 3, the original blue peak has evolved into the four distinct peaks (3-1 and 3-2). They are seen in Sample 1 as well that had the green PL peak initially, although the high energy peaks are weak. The four peaks are located at $\lambda=392$ nm (3.1 eV), 461 nm (2.7 eV), 555 nm (2.2 eV), and 682 nm (1.8 eV), respectively, which covers the wide colors from red up to deep blue. The PL emission in these cases appears white in color to naked eye. The four peaks are narrower in widths than the initial blue and green PL peaks.

This remarkable PL evolution effect suggests that the defects formed after the high-T short-time annealing are in some metastable states. The long-term, low-T annealing brings them into the energetically stable in-gap states irrespective of their starting metastable states. If we accept the defect cluster picture, the clusters are in some unstable configurations initially and they evolve into stable clusters during the second annealing stage. Perhaps the vacancies rearrange themselves through thermally assisted migration/diffusion. Our results suggest that at least four stable in-gap levels exist and contribute to the PL emission. It will be

important to identify the origins of these defect states through both theoretical and experimental investigation.

In summary, we have shown that rich visible PL emissions can be induced in STO thin films at room-temperature by thermal annealing treatment as follows: an initial high-T annealing and a subsequent low-T long-term annealing. The three primary PL colors (red, green, and blue) emerge from the initial treatment and then evolve into the four distinct and well resolved PL peaks during the latter annealing process. This is a potentially great advantage for applications that require the full color spectrum in one sample at room temperature. One may propose that interdiffusion of atoms at the STO/SiO₂ interface can occur, and causes the PL. However, recently we found that the visible PL emission peaks are seen in STO/Si film (without the SiO₂ layer) and also in single crystal STO sample treated by the first stage high-T thermal annealing. Fundamentally, it is important to understand the in-gap defect states which give rise to the PL emissions. We think that both theoretical calculations and high-resolution experimental probes such as TEM, electron-energy-loss spectroscopy, or RBS are needed in the future study.

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²⁵One may also speculate that Si in the SiO₂ buffer migrates into the STO layer and forms some defect levels. However, we recently observed the visible-PL emissions in thermally annealed single crystal STO, which eliminates this possibility.