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Red photoluminescence in praseodymium-doped titanate perovskite films epitaxially grown by pulsed laser deposition

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Intense red photoluminescence (PL) under ultraviolet (UV) excitation was observed in epitaxially grown Pr-doped $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ perovskite films. The films were grown on SrTiO_3 (100) substrates by pulsed laser deposition, and their epitaxial growth was confirmed by x-ray diffraction and reflected high-energy electron diffraction. The observed sharp PL peak centered at 610 nm was assigned to the transition of Pr^{3+} ions from the $^1\text{D}_2$ state to the $^3\text{H}_4$ state. The PL intensity was markedly enhanced by postannealing treatments at 1000 °C, above the film-growth temperature of 600 or 800 °C. Because the excitation and absorption spectra are similar to each other, it was suggested that the UV energy absorbed by the host lattice was transferred to the Pr ions, resulting in the red luminescence. © 2006 American Institute of Physics. [DOI: 10.1063/1.2424438]

Thin films of oxide phosphors have attracted considerable attention for their application to flat-panel displays, such as field-emission displays and electroluminescent (EL) devices, not only because oxide phosphors have the potential advantage of chemical stability against high vacuum and electron bombardment but also thin-film phosphors offer a high image resolution and a strong adhesion to substrates. Attempts have been made to prepare thin films of oxide phosphors by using several techniques, such as evaporation, sputtering, sol-gel processing, and chemical vapor deposition. However, the apparent luminescence intensity of thin-film phosphors is usually less than that of powder phosphors. One reason for the low luminescence intensity in thin-film phosphors is that the emitted light cannot be emanated effectively from the films because of the large difference in refractive index between the thin-film phosphors and air or substrates. Another reason is that the emission efficiency of thin-film phosphors is intrinsically low because their crystallinity is often much poorer than that of powders prepared at high temperatures. Whereas the former problem is one that is inherent to thin-film phosphors, the latter problem can be overcome by synthesizing thin films with a high crystallinity; such films are also essential for developing an understanding of the original luminescence properties of thin-film phosphors. A difference in the photoluminescence (PL) properties between an epitaxial film on a single-crystal substrate and a polycrystalline film on a glass substrate has been reported for the case of Mn-doped ZnGa_2O_4 thin-film phosphors.¹

Recently, the development of oxide phosphors with a perovskite-related structure has been revitalized by the discovery of several materials. $\text{CaTiO}_3:\text{Pr}^{3+}$ and $\text{SrTiO}_3:\text{Pr}^{3+}-\text{Al}$ were reported as potential red phosphors

for display applications for low-energy electron excitation, such as field-emission displays and vacuum-fluorescent displays.²⁻⁵ The chemical composition of Pr-doped ATiO_3 ($A=\text{Ca}$, Sr , or Ba) was optimized as $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$ in the alkaline-earth titanate system.⁶ $\text{Sr}_3\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ was found to show the maximum red luminescence among Pr-doped $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ ($n=1, 2, \infty$) compounds with a perovskite-related structure.⁷ $\text{SrHfO}_3:\text{Tm}^{3+}$ has been proposed as a blue phosphor and its optimized chemical composition was examined in Tm-doped ATiO_3 ($A=\text{Ca}$, Sr , or Ba) by the combinatorial technique.^{8,9} $\text{CaSnO}_3:\text{Tb}^{3+}$ and BaSnO_3 have been identified as green and infrared phosphors, respectively.^{10,11} In addition, intense luminescence of several colors has been found in alkaline-earth stannate systems with perovskite-related structures.¹² Because these phosphors all form perovskite or perovskite-related structures, the arrangements of ions in their lattice and their lattice parameters are similar to those of commercially available perovskite substrates. We therefore expected that thin films of these perovskite-related oxide phosphors could be grown with a high crystal quality on single-crystal perovskite substrates such as SrTiO_3 or LaAlO_3 .

We investigated the high-quality epitaxial growth of Pr-doped alkaline-earth titanate films on SrTiO_3 (100) substrates by pulsed laser deposition, and we examined their red PL properties. The target chemical composition of the films was $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$, which gives the maximum luminescence in Pr-doped ATiO_3 ($A=\text{Ca}$, Sr , or Ba).⁶ No other dopant for charge compensation was added into $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$ because the charge compensation is considered to occur spontaneously between the doped Pr ions and cation vacancies probably generated during heat treatment under adequate oxygen partial pressure. Although $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$ is an orthorhombic system, the lattice parameter reduced to an ideal cubic perovskite lattice

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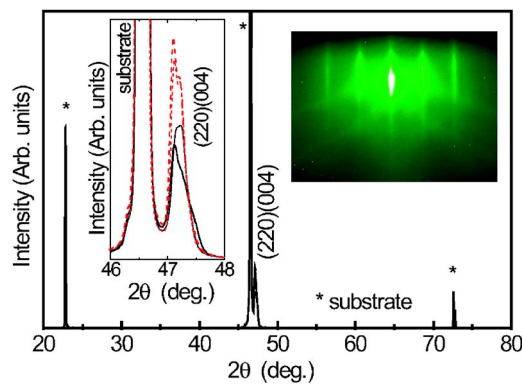


FIG. 1. (Color online) XRD pattern of $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$ film grown at 600 °C (film A) on a SrTiO_3 (100) substrate along with the image of its RHEED pattern. The left inset shows XRD patterns of as-grown (thick line) and annealed (thin line) films for film A (solid line) and film B (dashed line).

was $a_p=0.3860$ nm, which is approximately a 1% lattice mismatch against SrTiO_3 as a substrate. In addition to the film growth, the effect of postannealing treatments on the PL properties was investigated in an attempt to increase the PL intensity of the films.

The films were grown on SrTiO_3 (100) substrates by pulsed laser deposition using a single-phase $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$ polycrystalline target. The single-phase $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$ powders and polycrystalline targets were prepared by a conventional solid-state reaction method. The details of the target-preparation process have been described in a previous report.⁶ During film growth, the SrTiO_3 substrates were heated to 600 °C for film A or 800 °C for film B, and the oxygen partial pressure was controlled at 100 Pa. An ArF excimer laser ($\lambda=193$ nm) was used that had a repetition rate of 4 Hz and a fluence of ~ 1.2 J cm^{-2} pulse^{-1} at the target surface. These film-growth conditions were selected on the basis of previous experience in the epitaxial growth of $\text{SrTiO}_3/\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films on SrTiO_3 substrates.¹⁵ All the films in this study were approximately 300 nm thick. Postannealing treatments were performed at 1000 or 1100 °C in air. As-deposited films were quickly placed in the heated furnace, kept there for 1 h, and then promptly removed. Taking account of diffuse coefficients of cations in typical ionic oxides, the diffusion of Pr ions primarily occurs within the films and the diffusion into substrates is negligible under this postannealing condition. The phase and crystallinity of the films were examined by x-ray diffraction (XRD) and reflected high-energy electron diffraction (RHEED). Their PL properties were evaluated by means of PL emission and excitation spectra measured with a conventional fluorescence spectrophotometer (Hitachi F-4500) at room temperature.

The epitaxial growth of $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$ films on SrTiO_3 (100) substrates was confirmed by the XRD and RHEED patterns. The XRD pattern of a $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$ film grown at 600 °C (film A) is shown in Fig. 1. Film B, grown at 800 °C, also gave a similar pattern, and these patterns were not markedly changed by the postannealing treatments, as shown in the inset. The ($hh0$) or ($00l$) reflections, which correspond to ($00l$) reflections in an ideal perovskite lattice, appeared exclusively in these patterns, suggesting that $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$ films were grown epitaxially. The RHEED pattern of film A is also shown in the inset to Fig. 1. The clear streaky RHEED

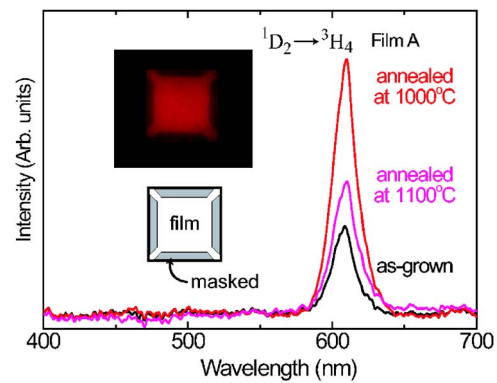


FIG. 2. (Color online) PL spectrum of $\text{Pr}_{0.002}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.997}\text{TiO}_3$ film grown at 600 °C (film A) under UV excitation ($\lambda_{\text{ex}}=254$ nm) and its variation after postannealing treatment. The photograph is the UV-excited film after postannealing at 1000 °C.

pattern indicates a very high crystal quality of the epitaxial film.

The PL spectrum of film A under ultraviolet (UV) excitation ($\lambda_{\text{ex}}=254$ nm) is shown in Fig. 2. The film shows a sharp emission line at 610 nm, as is observed in powder samples. This emission line was assigned to the intraatomic transition from the 1D_2 state to 3H_4 in Pr^{3+} ions. The details of the luminescence mechanism is described in the references.^{3,5} The photograph showing an even red luminescence indicates that Pr^{3+} ions are uniformly distributed in the epitaxially grown thin film. After postannealing at 1000 °C, the peak intensity of the red emission significantly increased; however, postannealing at 1100 °C reduced the emission intensity. It was therefore shown that the red PL intensity is optimized by a postannealing treatment at 1000 °C.

The effect of the film-growth temperatures on the PL intensity is shown in Fig. 3. In the as-grown states, film B showed a brighter luminescence than film A does. Although the PL intensity of both films increased after postannealing at 1000 °C, the PL intensity of film A perceptibly exceeded that of film B. These features of the peak intensity variation are summarized in the inset. Consequently, the maximum red luminescence was obtained in the film grown at 600 °C and postannealed at 1000 °C. The increase in the peak intensity for film A originates from an improvement in crystallinity as a result of postannealing, because the XRD diffraction peaks are clearly sharpened after postannealing, as shown in the

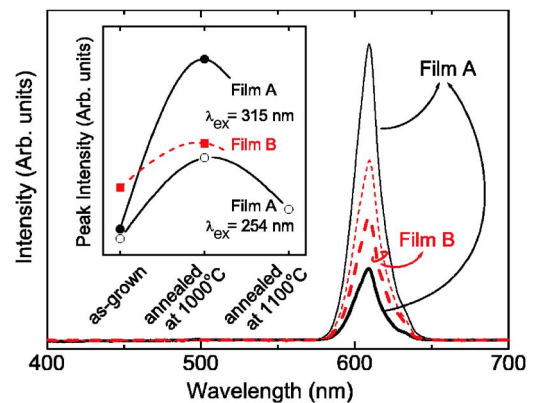


FIG. 3. (Color online) PL spectra of as-grown (thick line) and annealed (thin line) films for film A (solid line) and film B (dashed line) under UV excitation ($\lambda_{\text{ex}}=315$ nm). The variation in the peak intensity is shown in the inset.

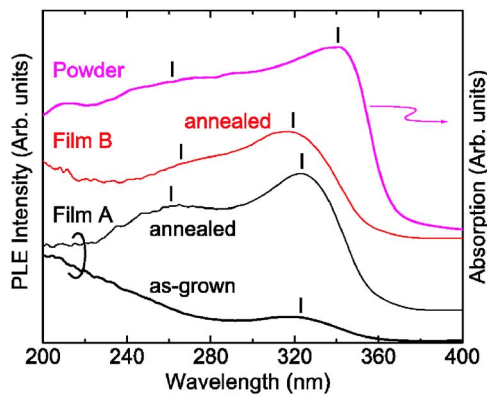


FIG. 4. (Color online) PL excitation spectra of as-grown or annealed films A and B along with the absorption spectrum of a powder sample.

inset of Fig. 1. Although it is not obvious why the annealed film A should surpass the annealed film B in PL intensity, the low-temperature growth may result in not only slightly lower crystallinity but also easier incorporation of the Pr^{3+} ions into the crystal lattice.

The PL excitation spectra of as-grown and annealed films A and B are shown in Fig. 4 along with the absorption spectrum of a powder sample. Annealed films A and B show two peaks at approximately 320 and 260 nm in the excitation spectra, while as-grown film A shows only one peak at 320 nm, probably because of its weak PL intensity. In the absorption spectrum, two peaks at approximately 340 and 260 nm were observed, corresponding to the two peaks in the excitation spectra. Previous analyses of optical absorption in alkaline-earth titanates have shown that these two peaks are mainly to the result of electronic transitions from $\text{O } 2p$ to $\text{Ti } 3d$ states.^{14,15} We therefore consider that the two peaks observed in the excitation spectra are the result of absorption by the host lattices rather than by Pr ions. That is, we suggest that the excitation energy is initially absorbed by the host lattice and then the energy is transferred to the Pr ions, resulting in the red luminescence.

In conclusion, Pr-doped $\text{Ca}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ perovskite films were grown epitaxially on SrTiO_3 (100) substrates and their intense red luminescence was observed at room temperature. The PL intensity was markedly increased by postannealing treatments, and the maximum PL intensity in this study was obtained by the combination of relatively low-temperature film growth at 600 °C and sequential rapid postannealing at 1000 °C. The fabrication of epitaxially grown thin-film phosphors showing intense luminescence may open a path to their application not only in display devices, such as EL devices, but also in light-emitting or lasing devices in future research.

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