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Room temperature visible electroluminescence from $SrTiO_3/p^+$–Si heterostructure

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Visible electroluminescence has been achieved from a device based on the $SrTiO_3/p^+$-Si heterostructure, in which the $SrTiO_3$ film is deposited by a sol–gel process on silicon substrate. When applied with sufficient forward bias with the positive voltage connecting to the p^+-Si, broad visible emissions peaking at ~550 nm occur. The self-trapped excitons relevant to oxygen vacancies in $SrTiO_3$ are proposed to be responsible for the visible emissions from the $SrTiO_3/p^+$-Si heterostructured device.

Keywords: Thin films; Perovskite; Luminescent materials; Heterostructures

Great research efforts have been undertaken worldwide to achieve efficient light emission from silicon-based optoelectronic devices in order to realize the integration of silicon-based electronic circuits with optoelectronic functionalities [1,2]. Light-emitting diodes (LEDs) based on the III–V semiconductors have already been commercially realized, but their availability is limited by the need for sophisticated preparation equipment as well as the scarcity of Ga resources in the long run [3,4]. Clearly, exploring other cost-effective semiconductors for silicon-based LEDs is worthwhile. $SrTiO_3$ is a perovskite-structured transition-metal oxide with a broad bandgap of about 3.27 eV, which has long attracted considerable attention due to its excellent piezoelectric, dielectric and photoelectric properties [5–12]. Almost all previous research on the luminescence properties of $SrTiO_3$ has focused on the photoluminescence (PL) performance. It is reported that room temperature (RT) blue PL can be excited from $SrTiO_3$ crystal irradiated by an Ar^+ ion beam [13]. The blue PL can also be elicited from $SrTiO_3$ crystals modified by chemical substitution such as $La^{+3} \rightarrow Sr^{+2}$ or $Nb^{+5} \rightarrow Ti^{+4}$ [14]. However, it should be noted that electroluminescence (EL) from LEDs based on $SrTiO_3$ film, which is indispensable for practical applications, has not been achieved to date.

In this work, we have achieved visible EL from a $SrTiO_3/p^+$-Si heterostructured device in which the $SrTiO_3$ film is deposited by a simple sol–gel process. This EL is ascribed to the radiative recombination of trapped electrons and holes through the oxygen vacancy-related energy levels. We believe that this work opens up a new possibility to develop silicon-based LEDs using cost-effective oxide semiconductors, which is of significance for illumination and silicon-based optoelectronics.

The $SrTiO_3$ films were deposited by a sol–gel process on $\langle 100 \rangle$-oriented heavily boron-doped silicon (p^+-Si) substrates with a resistivity of ~0.001 Ω cm and a size of $1.5 \times 1.5\ cm^2$. All analytical grade chemicals were used without further purification. Strontium nitrate ($Sr(NO_3)_2$) and tetrabutyl titanate ($Ti(OC_4H_9)_4$) acted as the solutes, while ethylene glycol ($HOCH_2CH_2OH$), acetyl acetone ($CH_3COCH_2COCH_3$) and 2-methoxyethanol ($CH_3OCH_2CH_2OH$) were used as the solvents. $Sr(NO_3)_2$ was initially dissolved in deionized water and then mixed with $HOCH_2CH_2OH$ and $CH_3OCH_2CH_2OH$. $Ti(OC_4H_9)_4$ was mixed with $CH_3COCH_2COCH_3$ and $CH_3OCH_2CH_2OH$, then added dropwise to the above-mentioned $Sr(NO_3)_2$ solution with constant stirring. Afterwards, this precursor solution was stirred for 6 h, resulting in a stable and transparent yellow sol. All these procedures were performed at RT. The volume ratio of $HOCH_2CH_2OH$:$CH_3COCH_2COCH_3$:$CH_3OCH_2CH_2OH$ was set at 1:1:12 and the concentra-

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tion of Sr or Ti in the precursor solution was ~0.36 mol l^{-1}. To prepare a $SrTiO_3$ film, the resulting precursor sol was spin-coated on the p^+-Si substrates for three cycles, each spun at 3000 rpm for 30 s. The spin-coated sol film was immediately baked on a hot plate at 80 °C for 15 min in air to form the gel films after each spin-coating cycle. Subsequently, the gel film was annealed in air at a temperature of 350–500 °C for 5 h to remove the organics in the gel film and enable crystallization of the film. In order to form the device based on the $SrTiO_3/p^+$-Si heterostructure prepared by the aforementioned procedures, ~150 nm thick indium tin oxide (ITO) film was deposited onto the $SrTiO_3$ film by direct current sputtering and ~150 nm thick Al film was subsequently deposited on the backside of the p^+-Si substrate by thermal evaporation. Herein, both the ITO and Al electrodes were patterned to be circular with a diameter of 1.0 cm. The $SrTiO_3/p^+$-Si heterostructured devices with $SrTiO_3$ film annealed at different temperatures were prepared according to the above procedures. The current–voltage (*I–V*) characteristics of the devices were measured using a Keithley 4200 semiconductor characterization system. To activate EL from each device, appropriate forward bias was applied with the positive voltage connecting to the p^+-Si substrate. Note that no EL could be detected from each device under reverse bias. Moreover, PL from each film was excited by a 325 nm He–Cd laser. All the PL and EL spectra were recorded at RT using an Acton SpectraPro 2500i spectrometer.

The crystal structures of the films were determined by X-ray diffraction (XRD) performed on a Rigaku D/max-gA X-ray diffractometer with graphite-monochromatized Cu K_α radiation ($\lambda = 1.54178$ Å). The morphologies of the films were observed by field emission scanning electron microscopy (FESEM, Hitachi S-4800).

The surface and cross-sectional FESEM images of the $SrTiO_3$ film annealed at 400 °C are shown in Figure 1a and b, respectively. As can be seen, the densely packed nanocrystals form a flat film with a number of cracks. The $SrTiO_3$ film is ~120 nm thick and the interface between the $SrTiO_3$ film and silicon substrate is distinct. It should be mentioned that the annealing temperature has no significant affect on the morphology of the films. Figure 1c shows the XRD patterns of the films annealed at different temperatures. There are no prominent diffraction peaks in the XRD pattern of the film annealed at 350 °C, indicating an amorphous structure. As for the films annealed at 400 or 500 °C, the diffraction peaks can be indexed to perovskite $SrTiO_3$, featuring a polycrystalline structure without preferential orientation. The nanosized crystal grains of the $SrTiO_3$ film, as shown in Figure 1a, lead to the somewhat broad diffraction peaks. Moreover, the more intense diffraction peaks in the XRD pattern of the film annealed at 500 °C indicate a better crystallinity, which accords with the fact that the higher annealing temperature promotes crystallization.

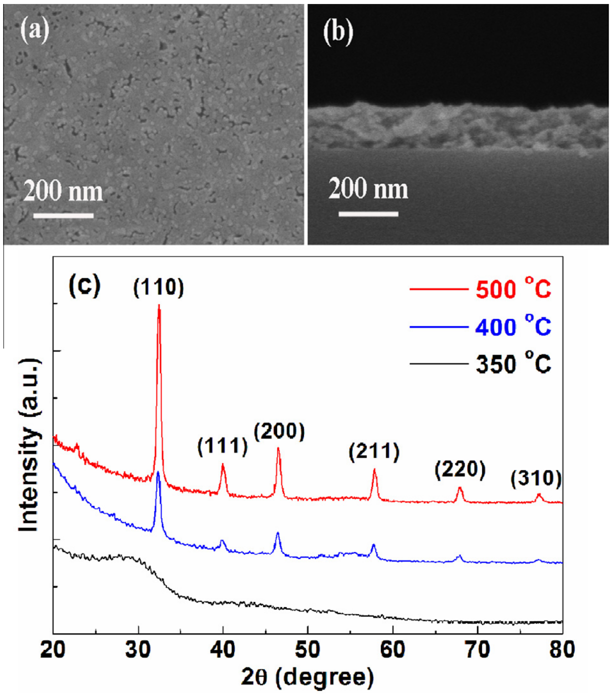

Figure 1. (a) Surface and (b) cross-sectional FESEM images of the $SrTiO_3$ film annealed at 400 °C. (c) XRD patterns of the $SrTiO_3$ films annealed at different temperatures.

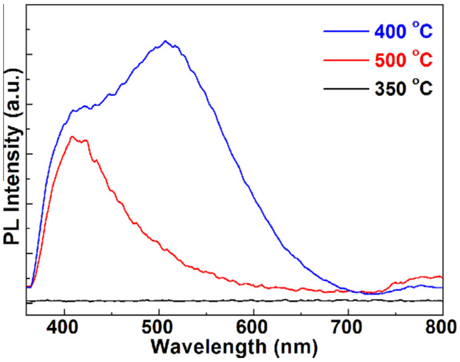

Figure 2. PL spectra of the $SrTiO_3$ films annealed at different temperatures, excited by the 325 nm He–Cd laser.

Figure 2 shows the visible PL spectra of the $SrTiO_3$ films annealed at different temperatures. The amorphous $SrTiO_3$ film annealed at 350 °C exhibits no PL. The PL spectrum of the $SrTiO_3$ film annealed at 400 °C contains a broad emission band centered at ~520 nm, together with a shoulder located at ~410 nm. In comparison, the $SrTiO_3$ film annealed at 500 °C exhibits only one broad emission band peaking at ~410 nm. Accordingly, it is known that the luminescence properties of the $SrTiO_3$ films are closely related to the lattice structures. For the indirect bandgap semiconductors the luminescence mostly originates from the defect electronic states in the bandgap related to the atomic vacancies or impurities [15,16]. In $SrTiO_3$, the oxygen deficiency generally induces oxygen vacancies and Ti^{3+} ions. Herein, the former are probably shallow electron traps and the latter act as deep hole traps [17]. Moreover, oxygen-deficient complex clusters can occur, resulting in slight lattice rearrangement and localized electronic levels in the bandgap which are critical for the luminescent recombination [16]. In view of the previous reports [13–15,18], the ~410 nm emission band in our $SrTiO_3$ films could