

# Photoelectrochemical activity of co-doped SrTiO<sub>3</sub>

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## 1. Introduction

Water splitting on the surface of a photoelectrode can be used to convert sunlight energy into clean and storable hydrogen fuel for a future hydrogen-powered society (Fig.1). Since SrTiO<sub>3</sub> is a chemically stable oxide semiconductor with a band structure that is suitable for decomposing water, it appears to be a suitable material for use as a photoelectrochemical electrode in a water splitting cell. However, since the band gap of SrTiO<sub>3</sub> is 3.2 eV, it shows photocatalytic activity only under ultraviolet light. Therefore, studies have been conducted on doped SrTiO<sub>3</sub> to develop a water-stable semiconductor that can absorb visible light. The strategy is to use transition metal doping that forms an in-gap impurity level close to the top of the valence band without shifting the conduction band edge. It has been found that Rh-doped SrTiO<sub>3</sub> shows photocatalytic hydrogen evolution activity under visible light[1]. However, the photocatalytic activity of Rh:SrTiO<sub>3</sub> depends on the Rh valence state. Rh would normally be expected to substitute Ti at the Ti<sup>4+</sup>-site while the Rh valence of either Rh<sup>3+</sup> or Rh<sup>4+</sup> is determined by the presence of oxygen vacancies. Rh<sup>4+</sup>:SrTiO<sub>3</sub> shows lower activity than Rh<sup>3+</sup>:SrTiO<sub>3</sub> because, Rh<sup>4+</sup>:SrTiO<sub>3</sub> has an unoccupied in-gap level that promotes rapid trapping and recombination of photocarriers (Fig.2). It is thus necessary to stabilize the Rh<sup>3+</sup> valence state to improve the energy harvesting efficiency of a photoelectrode.

In previous studies, the Rh<sup>3+</sup> valence state has been stabilized in epitaxial Rh:SrTiO<sub>3</sub> thin film photoelectrodes by growing films in reducing conditions (700°C, 10<sup>-6</sup> Torr) by pulsed laser deposition (PLD) [2]. However, the lattice defects associated with the oxygen vacancy clusters and Rh-V<sub>O</sub> clusters also work as photocarrier trapping centers that lead to a decrease in photocatalytic activity. In particular, carriers from deeper parts of the photoelectrode cannot reach the electrode surface before trapping. Therefore, the Rh<sup>3+</sup> dopant valence must be stabilized without forming oxygen vacancies or other types of lattice defects that give rise to shallow electron trap states close to the conduction band edge.

In this study, two methods were tried for the purpose of fixing the Rh<sup>3+</sup> valence without causing Rh clusters, Rh-V<sub>O</sub> clusters or V<sub>O</sub> clusters to form. One way is to reducing Rh<sup>4+</sup>:SrTiO<sub>3</sub> by annealing in vacuum. This technique prevents Rh clustering and may avoid the formation of Rh-V<sub>O</sub> clusters. Another way is to use co-doping, specifically to substitute La<sup>3+</sup> at the Sr<sup>2+</sup> site and thus control the Rh valence without oxygen vacancy doping.

## 2. Experiment

All epitaxial photoelectrode films were grown by PLD. The sintered ceramic targets for PLD film growth were prepared by standard solid state synthesis. The Rh doping level was 5%. A Rh 5at% SrTiO<sub>3</sub> target with

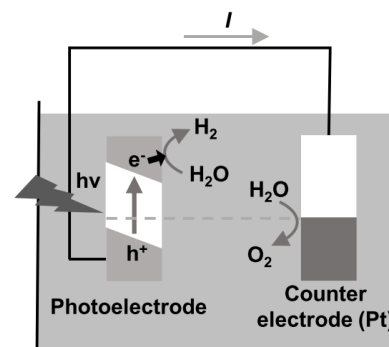


Fig 1. Energy conversion system from sunlight to hydrogen in a photoelectrochemical cell.

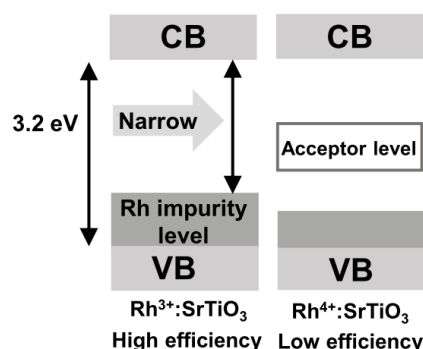


Fig 2. Schematic illustration of SrTiO<sub>3</sub> band gap narrowing by Rh doping.

7% excess Sr was used for Rh:SrTiO<sub>3</sub> thin film growth. Another target with Rh at 5% and La at 5% doping and 7% Sr excess was used for (La, Rh) co-doped SrTiO<sub>3</sub> films growth. The growth rate of the films was measured by reflection high-energy electron diffraction (RHEED) and the film thickness was controlled by calculating an appropriate deposition pulse number from the measured growth rate. The *c* axis length and crystallinity of the thin films were analyzed by thin film X-ray diffraction and rocking curve measurement. The valence state of Rh was evaluated by X-ray photoelectron spectroscopy (XPS) and UV-Vis-NIR optical absorption measurement. The XPS measurements were done with a 1486.6 eV x-ray source in Photon Factory. Cyclic voltammetry measurements in a 0.1 M KOH electrolyte solution were used for evaluating the photocatalytic activity of the thin films. The thin films for XPS analysis were grown on conducting Nb(0.05wt%):SrTiO<sub>3</sub> substrates to prevent charge-up. For other measurements, a non-doped SrTiO<sub>3</sub> substrate was used. For cyclic voltammetry analysis, an epitaxial Sr<sub>2</sub>RuO<sub>4</sub> thin film was grown as a bottom electrode between the photoelectrode thin film and the SrTiO<sub>3</sub> substrate.

### 3. Results and discussion

The valence of Rh of the thin films was determined by X-ray photoelectron spectroscopy and UV-Vis-NIR measurement. A Rh:SrTiO<sub>3</sub> film grown at 700°C and 10<sup>-1</sup> Torr showed an absorption peak at around 560 nm, which is a signature of the presence of Rh<sup>4+</sup> (Fig. 3a). As a result of annealing this thin film for 3 hours in vacuum (10<sup>-6</sup> Torr, 800°C), the film was reduced and the 560 nm peak disappeared. However, XPS showed the presence of Rh<sup>4+</sup> in both as-grown and vacuum-annealed films, which means that the surface of the film to a depth of several nm was always re-oxidized by exposure to air (Fig. 4). A Rh:SrTiO<sub>3</sub> film grown at reducing conditions (Fig. 3b) was in a pure Rh<sup>3+</sup> state that could not be fully converted to a Rh<sup>4+</sup> state by air annealing, indicating that defect clusters are present in the film. Fig. 3c shows optical absorption spectra of a (La, Rh) co-doped SrTiO<sub>3</sub> film grown at 10<sup>-1</sup> Torr. A perfect Rh<sup>3+</sup> state is evident and the absorption spectrum does not change after an air anneal (400°C, 6 hours) which means that oxygen vacancies are not necessary for Rh valence control in a co-doped film. Even upon air annealing, Rh was not converted to the Rh<sup>4+</sup> state, as shown by the lack of the

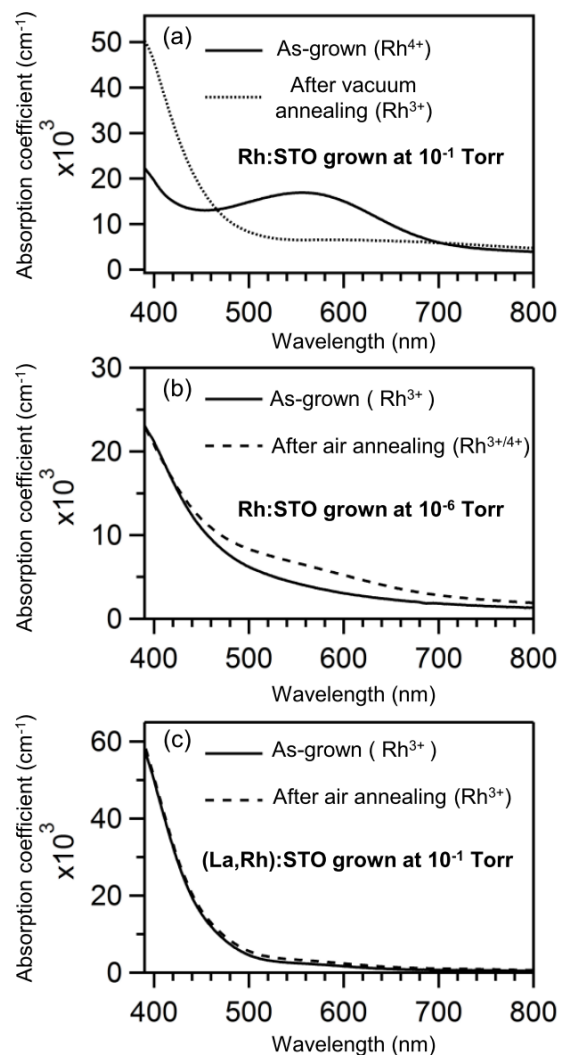


Fig 3. UV-Vis-NIR absorption spectra of (a) Rh:SrTiO<sub>3</sub> grown at 10<sup>-1</sup> Torr, 700°C and annealed in vacuum (b) Rh:SrTiO<sub>3</sub> grown at 10<sup>-6</sup> Torr, 700°C, and annealed in air, and (c) (La,Rh):SrTiO<sub>3</sub> grown at 10<sup>-1</sup> Torr, 700°C and annealed in air. Air annealing was done at 400°C, 6h.

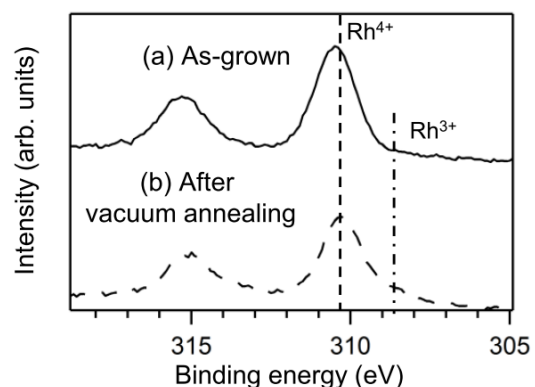


Fig4. XPS result of as-grown and vacuum annealed Rh:SrTiO<sub>3</sub> films.

560 nm absorption peak in Fig. 3c. Co-doping with La can be concluded to be effective for controlling the Rh valence in Rh:SrTiO<sub>3</sub>. The presence of cluster defects can be detected by the expansion of the lattice constant [3]. Since all films were grown on the STO substrate, ideally the XRD patterns of the substrate and the film should overlap. The peak of Rh:SrTiO<sub>3</sub>(002) grown at 10<sup>-1</sup> Torr almost perfectly overlapped with the STO substrate peak position (Fig. 5a), means that the film is nearly free of defects. However, the film peak position shifts to the lower angle (larger lattice constant) after vacuum annealing due to the presence of oxygen vacancies. Lattice expansion was also observed in Rh:SrTiO<sub>3</sub> grown at 10<sup>-6</sup> Torr and (La, Rh):SrTiO<sub>3</sub>. Clusters are thus present in the film grown at 10<sup>-6</sup> Torr. Since the ionic radius of 12-coordinates Sr is larger than La, the XRD peak shift of the co-doped sample indicates that defects may still be present in the film.

The photoelectrochemical properties of Rh:SrTiO<sub>3</sub> and (La,Rh):SrTiO<sub>3</sub> were studied by cyclic voltammetry (Fig. 6). All films showed a *p*-type cathodic response under visible light. Vacuum annealed Rh:SrTiO<sub>3</sub>, which contains fewer defect clusters, generated twice the photocurrent of a film grown at 10<sup>-6</sup> Torr., suggesting that reduction of lattice defects is effective for enhancing photoelectrochemical activity. The largest photocurrent was obtained for (La,Rh):SrTiO<sub>3</sub>. This improvement can be attributed to the lack of oxygen vacancies and the related photocarrier trap defects.

## 4. Conclusions

The Rh<sup>3+</sup> state in SrTiO<sub>3</sub> was stabilized by vacuum annealing or co-doping with La. It was found that La co-doping is effective for reducing the number of defect clusters and improving the light harvesting efficiency of the photoelectrode.

## 5. References

- [1] R. Konta et al., *J. Phys. Chem. B*, **108**, 8992 (2004).
- [2] S. Kawasaki et al., *Appl. Phys. Lett.*, **101**, 033910 (2012).
- [3] T. Ohnishi et al., *Appl. Phys. Lett.*, **103**, 103703 (2008).

## 6. Presentations

- [1] Poster presentation, “Reversible Rh valence change in optimized Rh:SrTiO<sub>3</sub> thin films” 第64回応用物理学会春季学術講演会
- [2] Poster presentation, “Observation of Rh valence state in Rh:SrTiO<sub>3</sub> thin films”, 第78回応用物理学会秋季学術講演会.
- [3]Poster presentation, “Enhanced photoelectrochemical activity of a La,Rh co-doped SrTiO<sub>3</sub> photoelectrode” 第65回応用物理学会春季学術講演会

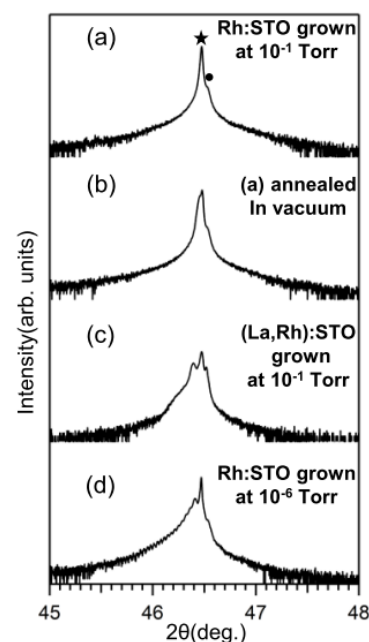


Fig 5. XRD patterns of several typical SrTiO<sub>3</sub> films showing the effect of lattice expansion. The star marks the SrTiO<sub>3</sub> substrate (002) peak. The circle marks the Cu Kα<sub>2</sub> line.

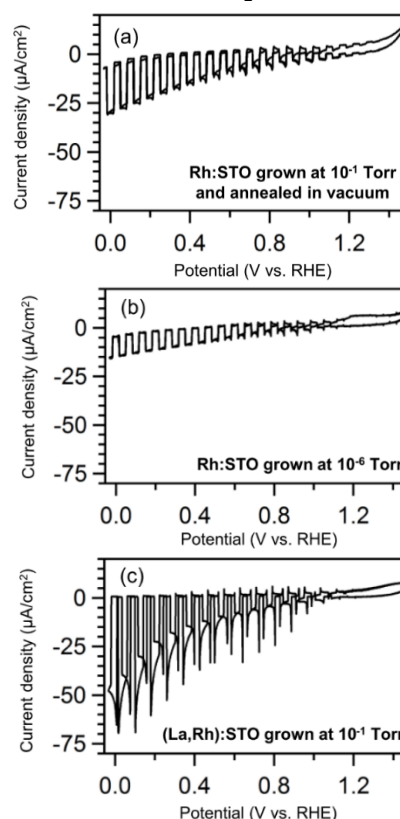


Fig 6. Cyclic voltammogram under visible 400-720 nm chopped illumination. Photoelectrode film thickness was 40 nm. The light source is a 100 W Xenon lamp. Electrolyte is 0.1M KOH aq. (pH 13).