

## Epitaxial하게 증착된 rutile-TiO<sub>2</sub>와 anatase-TiO<sub>2</sub> 박막의 구조적 성질과 광전 성질에 대한 연구

### Structural and photovoltaic properties of epitaxial rutile and anatase films

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#### Abstract

Epitaxial rutile-TiO<sub>2</sub> and anatase-TiO<sub>2</sub> films were grown at 800 °C on Al<sub>2</sub>O<sub>3</sub> (1102) and LaAlO<sub>3</sub> (001), respectively, using pulsed laser deposition. The formation of different phases on different substrates could be qualitatively explained by the atomic arrangements at the interfaces. We also successfully deposited epitaxial rutile-TiO<sub>2</sub> and anatase-TiO<sub>2</sub> films on conductive RuO<sub>2</sub> and La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> electrodes, respectively. Using a Kelvin probe, we measured the photovoltaic properties of these multilayer structures. A rutile-TiO<sub>2</sub> film grown on RuO<sub>2</sub> showed a very broad peak in the visible light region. An epitaxial anatase-TiO<sub>2</sub> film grown on La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> showed a strong peak with a threshold energy of 3.05 eV.

**Key Words :** Rutile-TiO<sub>2</sub>, anatase-TiO<sub>2</sub>, pulsed laser deposition, Kelvin probe, photovoltaic property

#### 1. 서 론

Crystalline TiO<sub>2</sub> films with rutile or anatase phases are found in many applications, such as solar energy conversion devices,[1] photocatalysts in waste water treatment,[2] insulators in metal-oxide-semiconductor (MOS) devices,[3,4] storage capacitors in dynamic random access memories (DRAM),[5] waveguides,[6] and optical coatings.[7] The rutile-TiO<sub>2</sub> (rutile) phase has a tetragonal structure whose *a*- and *c*-axes lattice constants are 4.59 Å and 2.96 Å, respectively. Since bulk rutile has dielectric constant values of 170 parallel to the *c* axis and 89 perpendicular to the

*c*-axis,[8] applications of rutile films to the MOS devices or DRAM have been investigated.[3-5] The anatase-TiO<sub>2</sub> (anatase) phase also has a tetragonal structure whose *a*- and *c*-axes lattice constants are 3.79 Å and 9.51 Å, respectively. Since bulk anatase has a higher photovoltaic conversion efficiency, or photocatalytic activity, anatase films have been studied for the applications of solar energy conversion devices or photocatalysts.[9,10]

There have been many reports on the structural, optical, and electrical properties of TiO<sub>2</sub> films.[1-7,9,10] In these studies, rutile phase has received the most attention, since it is very stable and it is the most abundant TiO<sub>2</sub> polymorph in nature. Anatase films, on the other hand, have not been widely studied, since the anatase phase is less stable than rutile

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phase. Anatase phase is easily transformed to rutile phase at growth temperatures over than 400 °C.[11] Although it is of great technical significance to study epitaxial rutile and anatase films on conductive electrodes, this has not been performed due to the lack of an electrode material which has structural compatibility with TiO<sub>2</sub>.

In this paper, we report our efforts to control the phases of epitaxial TiO<sub>2</sub> films by selecting certain substrates or bottom electrode materials. Epitaxial rutile and anatase films can be grown on LaAlO<sub>3</sub> (001) and Al<sub>2</sub>O<sub>3</sub> (110<sub>2</sub>) substrates, respectively. We have also deposited epitaxial rutile and anatase films on conductive RuO<sub>2</sub> and La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> (LSCO) electrodes, respectively.

## 2. 실험

RuO<sub>2</sub>, LSCO, and TiO<sub>2</sub> films were grown using pulsed laser deposition. Epitaxial RuO<sub>2</sub> electrodes were deposited on Al<sub>2</sub>O<sub>3</sub> (110<sub>2</sub>) substrates under 0.5 mTorr oxygen at 700 °C. Epitaxial LSCO electrodes were deposited on LaAlO<sub>3</sub> (100) substrates under 200 mTorr oxygen at 700 °C. All the TiO<sub>2</sub> films, except for those on RuO<sub>2</sub>, were grown at the same conditions, *i.e.* under 200 mTorr oxygen at 800 °C, irrespective of the substrates or the bottom electrodes. TiO<sub>2</sub> films on RuO<sub>2</sub> were grown at 750 °C since RuO<sub>2</sub> was not stable at deposition temperatures above 800 °C.[12] Following the depositions, the films were cooled in an oxygen pressure of 300 Torr without any further thermal treatment.

## 3. 결과 및 고찰

Figure 1 shows the XRD  $\theta$ - $2\theta$  scans for TiO<sub>2</sub> films grown on LaAlO<sub>3</sub> (001) and Al<sub>2</sub>O<sub>3</sub> (110<sub>2</sub>) substrates, respectively. On Al<sub>2</sub>O<sub>3</sub> (110<sub>2</sub>) only rutile (011) peaks are observed, indicating that a pure rutile film is formed, and that the film is preferentially aligned. On LaAlO<sub>3</sub> (001),

only anatase (001) peaks are observed, although this anatase film is deposited under the same conditions as those of the rutile film. This indicates that the structural phases, which have different thermodynamic stability, can be manipulated through the selection of substrate materials.

For epitaxial growth of rutile and anatase films on conductive electrodes, it is necessary to

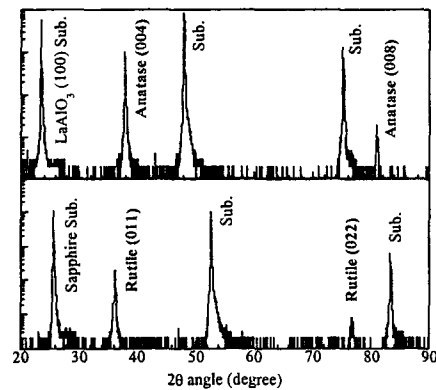


그림 1. 하부전극이 없는 박막의 X 선 회절 패턴.  
Fig. 1. X-ray diffraction patterns for films without bottom electrodes.

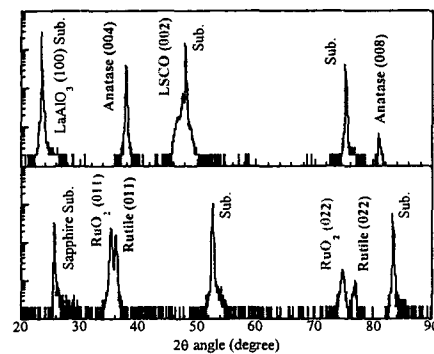


그림 1. 하부전극이 있는 박막의 X 선 회절 패턴.  
Fig. 1. X-ray diffraction patterns for films with bottom electrodes.

consider the lattice structure of the materials. RuO<sub>2</sub> has a tetragonal structure whose a and c

axes lattice constants are 4.50 Å and 3.10 Å, respectively. These values are very close to 4.59 Å (mismatch 2%) and 2.96 Å (mismatch 4.5%) of rutile phase, respectively. On the other hand, LSCO has a cubic structure whose lattice constant is 3.81 Å, which is very close to 3.79 Å (mismatch 0.5%) for the a-axis of anatase. Similar arrangements of O groups are expected between RuO<sub>2</sub> and rutile, and between LSCO and anatase as discussed above. Figure 2 shows the XRD  $\theta$ - $2\theta$  scans for a TiO<sub>2</sub>/LSCO/LaAlO<sub>3</sub>(001) and a TiO<sub>2</sub>/RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>(110<sub>2</sub>), respectively. As expected, only rutile (011) and RuO<sub>2</sub> (011) peaks are observed on an Al<sub>2</sub>O<sub>3</sub> (110<sub>2</sub>) substrate, and only anatase (001) and LSCO (001) peaks are detected on a LaAlO<sub>3</sub> (001) substrate. The epitaxial growth of rutile and anatase films on conducting RuO<sub>2</sub> and LSCO electrodes, respectively, has been confirmed by XRD  $\varphi$ -scans.

Using a Kelvin probe,[14] we could measure contact potential difference (CPD) between a metallic reference probe and the above multilayers, whose electrodes have 100 Å thickness in order to allow the penetration of a monochromatic light. There were no features in the CPD values of the bare RuO<sub>2</sub> and LSCO electrodes. The rutile/RuO<sub>2</sub> showed a very broad peak in the visible light region, whose threshold energy was around 1.7 eV. However, an energy gap of 1.7 eV for our rutile film was much smaller than 3.0 eV, *i.e.* the optical band-gap of a bulk rutile.[15] Further work is necessary to find the origin for the great shift in threshold energy. On the other hand, anatase/LSCO showed a strong peak, whose threshold energy was about 3.05 eV. This value is slightly smaller than 3.23 eV, *i.e.* the optical band-gap of bulk anatase.[16] In addition, there was a broad and small peak in the visible light region. This peak might result from the deep levels due to the defects in the anatase film or at the anatase/LSCO interface.

#### 4. 결론

The structural phase of epitaxial TiO<sub>2</sub> films can be manipulated by varying the substrate or the electrode materials. Photovoltaic properties of epitaxial rutile and anatase films on conductive electrodes were investigated by a Kelvin probe. An anatase film on LSCO has an optical band-gap of 3.05 eV, which is slightly smaller than 3.23 eV for bulk anatase. On the other hand, a rutile film on RuO<sub>2</sub> has a much smaller optical band-gap of 1.7 eV.

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