Electrochemical Nitrate Reduction to Ammonia on Facet-engineered Epitaxial Perovskite Oxide

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Abstract

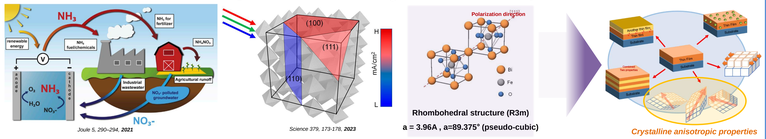
Electrochemical (EC) nitrate reduction to ammonia (NRA) is an attractive "waste-to-wealth" method for sustainable NH_3 synthesis because of its mild operating conditions, which are considered a promising alternative to the industrial Haber-Bosch process. However, developing catalysts with high activities and Faradaic efficiencies for this complicated eight-electron reaction is a great challenge. Recently, in order to solve the above problems, many studies such as doping, nanostructuring, and single atom catalyst have been conducted, but it is difficult to properly understand this reaction due to heterogenetic nature of catalyst materials.

In this regard, the EC NRR properties of $BiFeO_3$ thin-films with different crystallographic orientations and consequent electrochemical properties are investigated. As the crystallographic direction changes from (001) to (110) to (111), the electrochemically active surface area (ECSA) of the epitaxial $BiFeO_3$ thin film changes, and among them, (110) is the highest at 0.62 mF cm^{-2}. Furthermore, (110)-$BiFeO_3$ exhibits superior donor concentration (20.4 10^{24} cm^{-3}) as compare to other planes.

This study strongly suggests that the crystallographic orientation of materials greatly affect to NRR catalysis and facet-engineered perovskite-oxide materials can be used as effective electrochemical catalyst.

Introduction

Facet-engineered $BiFeO_3$ as a model system



❖ Nitrate-containing wastewater streams are used as a nitrogen source for the production of ammonia, a versatile compound that can be used as fertilizer, chemical, or fuel.

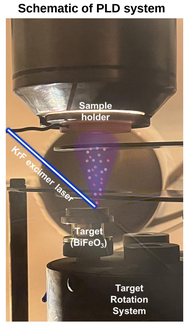
❖ The utilization of facet-engineering strategy has been widely used as a tool to modulate specific catalytic reactions.

❖ Facet-engineered $BiFeO_3$ thin-films were prepared to investigate the relationship between crystallographic orientation and EC NRA catalysts.

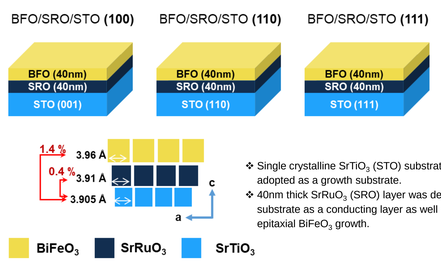
Experiments

Pulsed Laser Deposition (PLD) system

Schematic of PLD system



Sample structure



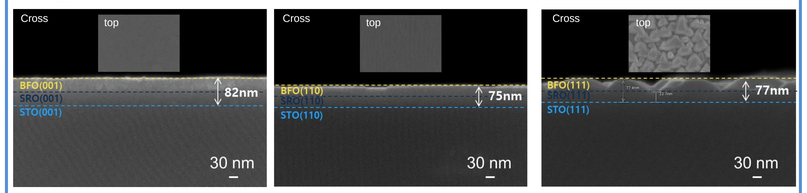
❖ Single crystalline $SrTiO_3$ (STO) substrates (001, 110, 111) were adopted as a growth substrate.

❖ 40nm thick $SrRuO_3$ (SRO) layer was deposited on the STO substrate as a conducting layer as well as a buffer layer for epitaxial $BiFeO_3$ growth.

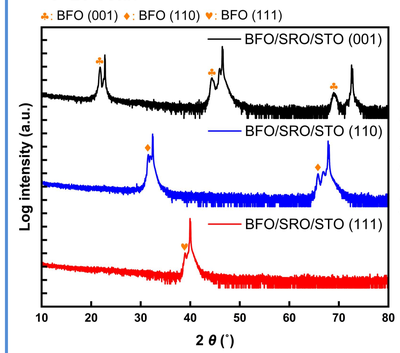
❖ For epitaxial growth, PLD method was conducted

Material characterization (SEM / XRD / Raman)

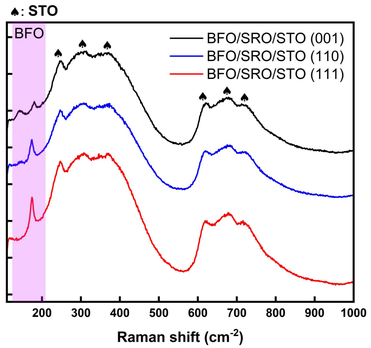
SEM



θ–2θ scan



Raman

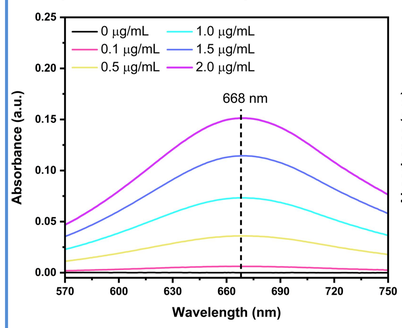


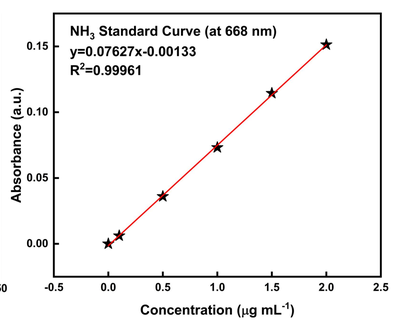
❖ Through SEM analysis, we observed that $BiFeO_3$ thin-films were uniformly deposited on STO substrate.

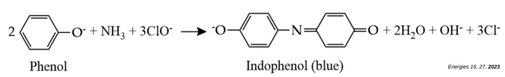
❖ In order to confirm the crystallinity of the prepared sample, XRD and Raman analyzes were performed, and as a result, the characteristics of a single crystal thin film were shown according to the crystal orientation.

Quantitative analysis

Indophenol blue method (UV-vis absorbance / calibration curves)





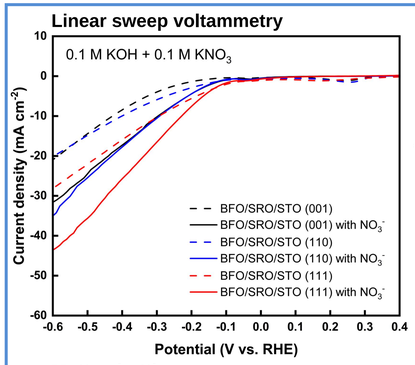


❖ Ammonia produced by the EC NRA reaction was quantitatively analyzed through the indophenol blue method.

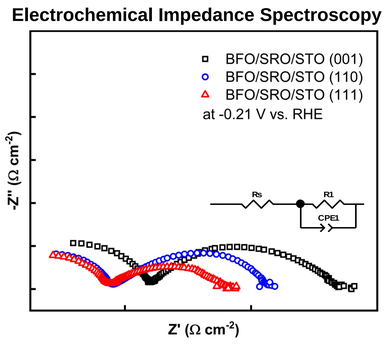
❖ As a result of measuring the calibration curve based on the UV-vis absorbance result, it showed a high accuracy of 99.9%.

Electrochemical analysis

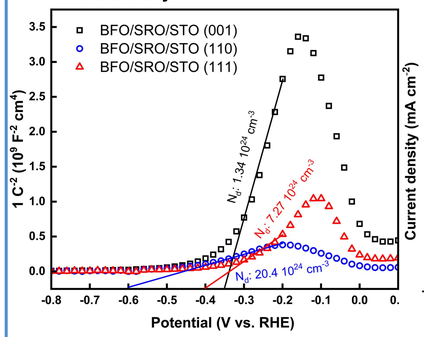
Linear sweep voltammetry



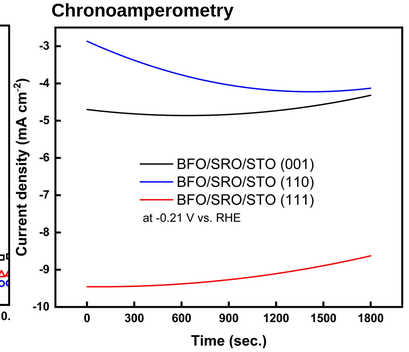
Electrochemical Impedance Spectroscopy



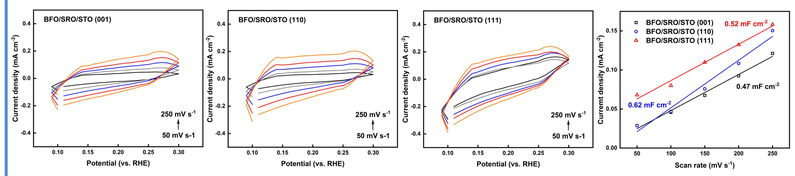
Mott-schottky



Chronoamperometry



Electrochemical active surface area analysis



❖ BFO/SRO/STO (111) shows high current density in the all potential range and low resistance (at -0.21 V vs. RHE).

❖ However, the BFO/SRO/STO (110) sample showed a much higher donor density than the other samples and was found to have the largest active surface area as a result of ECSA analysis.

Conclusion

1. We successfully synthesized epitaxial $BiFeO_3$ films with different crystallographic orientations on STO (001, 110, 111) substrates via PLD system with precisely controlled growth conditions.
2. Through various electrochemical analyzes, the possibility of the $BiFeO_3$ single crystal thin film as an EC NRA catalyst was confirmed, and the difference in activity according to the crystal orientation was confirmed.
3. In the future, we plan to understand the behavior of the catalyst by analyzing the amount of ammonia produced according to the applied potential.

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