# 論文の内容の要旨

## Buffer Layer-Enhanced Epitaxial Growth of Oxynitride Thin Films for Photoelectrochemical Applications

（光電気化学応用へ向けたバッファ層を用いた酸窒化物薄膜の

エピタキシャル成長）

MOTANEEYACHART Vitchaphol

モタニーヤシャート　ビッチャプール

Photoelectrochemical (PEC) solar light-induced water splitting has received significant attention as a promising process for hydrogen and oxygen production with no greenhouse gas emission. Two fundamental requirements for an electrode material to achieve better photocatalytic efficiency are (1) visible light absorption with suitable band edge potentials for water splitting and (2) low amount of defects to reduce the recombination of photogenerated electrons and holes. Transition metal oxynitrides with $d^0$ electronic configuration have suitable band edge potentials with active in visible light. However, oxynitrides obtained by conventional synthesis method usually show high density of pores and defects on their surface resulting in lower the photocatalytic activity. Therefore, to enhance the efficiency of PEC solar water splitting in oxynitride, it is significant to synthesize thin films with dense and smooth surface and little defects. For this purpose, heteroepitaxial growth of single crystalline films is a promising method. In this study, I am especially focused on the interface between the oxynitride film and the substrate, and tried to improve the crystallinity and chemical stoichiometry of the films by inserting a self-seed layer for low temperature crystallization or inserting a buffer layer for reduction of the density of defects due to lattice mismatch between the film and the substrate.

I started with a simple ternary compound: baddeleyite NbON in order to enhance the photocatalytic activity by reducing the band gap of baddeleyite TaON where is the most widely studied semiconductor for water splitting. $NbO_xN_y$ thin films were deposited by nitrogen plasma assisted pulsed laser deposition (NPA-PLD) on (100) plane of yttria-stabilized zirconia (YSZ) substrates, of which lattice constants are matched with those of (100) plane of baddeleyite NbON. In $NbO_xN_y$ system, it suggests that high $T_S$ (600 ºC) is effective for the crystal growth while low $T_S$ (500 ºC) is necessary for growing films with good stoichiometry. To overcome this dilemma, I introduced a self-seed layer

method, where a thin layer of $NbO_xN_y$ (seed layer) was first grown at 600 ºC on YSZ substrate and then thick main layer was deposited on it at 500 ºC. The baddeleyite $NbO_xN_y$ film was successfully obtained by using this method. Furthermore, the chemical composition of the film was nearly stoichiometric, evaluated as $NbO_{0.89}N$ (nominal charge of Nb was +4.77). AFM images of the film showed small grain-like structure reflecting this multiple domain structure. The baddeleyite NbON thin film exhibited $E_g$ of ~2.3 eV, which is smaller than that of $\beta$-TaON (2.5 eV) as expected. On the other hand, the films showed rather large in-gap absorption. In transport properties, NbON film showed *n*-type semiconducting behavior with high carrier density ($n_e = 1.5\times10^{22}$ $cm^{-3}$) which might attributable not only to the slight reduction of Nb but also to the presence of $NbN_x$ phase as suggested by in-gap optical absorption. The mobility ($\mu_H = 1.6\times10^{-3}$ $cm^2V^{-1}s^{-1}$) is rather small compared with those of conventional oxide semiconductors, which is probably due to carrier scattering by defects and grain boundaries associated with the multiple domain structure.

These results demonstrate the benefit of self-seed layer technique for low temperature epitaxial growth of baddeleyite NbON thin film but still insufficient to avoid the reduction of Nb perfectly.

Because it is difficult to reduce the bandgap of ternary oxynitride with using chemically unstable $Nb^{5+}$, I next focused on the lowest bandgap material in perovskite-type quaternary oxynitride semiconductor with chemically stable $Ta^{5+}$ ions: $BaTaO_2N$. It has few reports on the synthesis of $BaTaO_2N$ epitaxial thin films due to lack of commercially available single crystalline substrate with good lattice matching. Recently, it was reported that $BaSnO_3$, of which lattice constant is matched with that of $BaTaO_2N$ (+0.1% mismatch), with high crystallinity and an atomically flat surface could be fabricated on commercial $SrTiO_3$ (STO) substrates (−5.4% mismatch). Thus, in this study, I fabricated $BaTaO_2N$ epitaxial thin films with improved crystallinity on $SrTiO_3$ substrate by inserting a $BaSnO_3$ buffer layer which is matched in lattice constant. The $BaTaO_2N$ film which directly grew on STO (110) substrate had a single phase of (110) plane with stoichiometry. However the crystallinity of the film was low (FWHM on (110)-oriented peak = ~1.25°). Furthermore, the surface of the film was rather rough, of which root-mean-square (RMS) roughness was ~5 nm. On the other hand, $BaTaO_2N$ thin film fabricated on the $BaSnO_3$ buffer layer indicated much improvement in both crystallinity and surface morphology (FWHM on (110)-oriented peak = 0.3° and the RMS of surface roughness = ~1 nm) which compared to the films directly grew on STO (110) substrate. Both of the films showed clear visible light absorption with absorption edges of ~1.9 eV, being consistent with the previous report. On the other hand, stronger absorption in visible light region with sharper absorption onset was observed in the $BaTaO_2N$ film grew on $BaSnO_3$ buffer layer.

While the crystallinity, the surface morphology, and the optical properties were improved by the $BaSnO_3$ buffer layer, defects in the film were not completely suppressed: Dielectric measurements of the films indicated large dielectric loss tangent even on the $BaSnO_3$ buffer layer, suggesting the existence of anion deficiency. Furthermore, the photoelectrochemical current measured by linear sweep voltammograms in aqueous solution (pH = 13, 0.1M $Na_2SO_4$) under visible light illumination

was very low, although a small increase was observed by inserting the buffer layer.

In summary, I have succeeded in synthesizing epitaxial thin films of narrow band gap oxynitrides, baddeleyite NbON and perovskite $BaTaO_2N$, by inserting a self-seed layer or a buffer layer. These results demonstrated that insertion of a seed/buffer layer with a suitable crystal structure and lattice constants is a promising way to improve anion stoichiometry as well as crystallinity and surface morphology.