論文内容の要旨

論文題目

Synthesis and Functionalization of Oxynitride Semiconductor Anatase TaON

（酸窒化物半導体アナターゼ型TaONの合成と機能化）

氏名　鈴木　温

Introduction

Anatase tantalum oxynitride (δ-TaON), being one of the metastable polymorphs of TaON, is a oxynitride semiconductor with d^0 electron configuration and has the same crystal structure as anatase TiO_2, which is an oxide semiconductor applied to electric devices such a photoelectrode and a transparent electrode because of high photocatalytic efficiency and high Hall mobility (μ_H ~20 $cm^2V^{-1}s^{-1}$) [1]. This leads to an expectation that δ-TaON can be also applied to the electric devices with interesting electric and optical properties. However, δ-TaON has been synthesized only in polycrystalline fine powder form by ammonolysis, and doping of 5-15 % Mg or Sc is needed to stabilize the metastable structure [2]. As a result, the grain boundaries and doped impurities prevented the characterizations of intrinsic properties of δ-TaON. Indeed, physical properties of δ-TaON have never been reported except optical ones and even those optical properties showed large variation.

To overcome these problems, I synthesized undoped δ-TaON in epitaxial thin film form on the lattice matched single crystal substrates by using nitrogen plasma assisted pulsed laser deposition (NPA-PLD). Investigation of intrinsic optical and electric transport properties of these films was carried out. Considering the practical applications of δ- TaON, δ-TaON further needs modification of its properties and development of synthetic process: controlling optical and transport properties, and low-cost and large-area fabrication. Thus, I also investigated these issues.

High-Mobility Electron Conduction in Oxynitride: Anatase TaON

δ-TaON epitaxial thin films were fabricated by NPA-PLD on $(LaAlO_3)_{0.3}$-$(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) (100) substrate, which is expected to show good lattice-matching with δ-TaON. A Ta_2O_5 target was ablated by a KrF excimer laser. Substrates temperature (T_S) was varied from 650 to 800°C as a growth parameter. The deposition was conducted under N_2 gas activated into radicals by a radio-frequency wave plasma source.

Figure 1 compares θ-2θ XRD patterns of the TaON films grown at various T_S examined by X-ray diffraction

(XRD). The films fabricated at 750 and 800°C showed a clear 004 peak of δ-TaON at $2\theta \sim 35°$ without any impurity peaks. Furthermore, the pole figure of the δ-TaON 101 peak ensured 001-oriented epitaxial growth of δ-TaON. Therefore, I concluded that (001)-oriented δ-TaON thin films were epitaxially grown on LSAT substrate at T_S = 750 and 800°C. The chemical composition of the δ-TaON thin film fabricated at 750°C evaluated by SEM-energy dispersive x-ray spectroscopy was almost stoichiometric, $TaO_{0.94\pm0.09}N_{1.04\pm0.1}$.

Figure 2 shows optical extinction coefficient (k) and refractive index (n) of the δ-TaON film grown at 750°C determined by spectroscopic ellipsometry. k increases around 2.3 eV and the E_g of δ-TaON was determined to be 2.37 eV from a Tauc plot under an assumption that δ-TaON is an indirect band gap semiconductor. n indicates about 3.3 in visible light region.

Transport properties were characterized based on the van der Pauw method. Temperature dependence of resistivity (ρ) of the δ-TaON films fabricated at 750°C and 800°C are shown in Fig. 3a. The film fabricated at 750°C exhibits $\rho \sim 10^2$ Ωcm at 300 K. Meanwhile, ρ(300 K) of the film fabricated at 800°C is four orders lower ($\sim 10^{-2}$ Ωcm) than that of the film fabricated at 750°C. Hall measurements revealed that carrier type of the δ-TaON film was electron (n-type semiconductor). From the T_S dependence of ρ and the type of carriers (n-type), it is suggested that the carriers originate from anion vacancy introduced at high growth temperature as usually seen in oxide or nitride semiconductors. In fact, ρ was substantially reduced by the annealing, and the ρ–T curve of the annealed film was comparable to that of the anatase TaON film grown at T_S = 800 °C, supporting the above hypothesis about the carrier source. Figures 3b and 3c show carrier density (n_e) and Hall mobility (μ_H) of the δ-TaON fabricated at 800°C, respectively. n_e was almost constant irrespective of temperature, indicating that the δ-TaON film was a degenerated semiconductor. Remarkably, μ_H at 300 K was ~17 $cm^2V^{-1}s^{-1}$, which is comparably high as that of anatase TiO_2 [1].

Absorption in visible light and high μ_H are necessary for high efficiency photoelectrode. δ-TaON is expected to show high efficiency because δ-TaON meets the both requests. Another unique property of δ-TaON is its high n value comparing with conventional oxide-based transparent electrode such as Sn:In_2O_3 (n ~2.0) and Nb:TiO_2 (n ~2.6). Development of a transparent electrode with high n is desirable because transparent conducting materials with wide lineup of n values are favorable to achieve refractive index matching, which is important for reducing reflection loss of incident light at the interface between transparent electrode and active layer. Thus, I concluded that δ-TaON is promising as a photoelectrode and a transparent electrode.

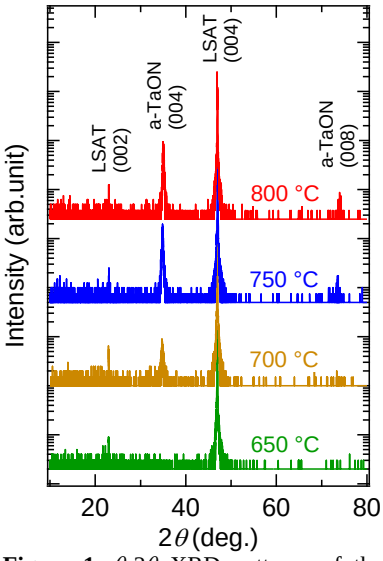

Figure 1. θ-2θ XRD patterns of the TaON films grown on LSAT substrates at various T_S. "a-TaON" represents anatase TaON.

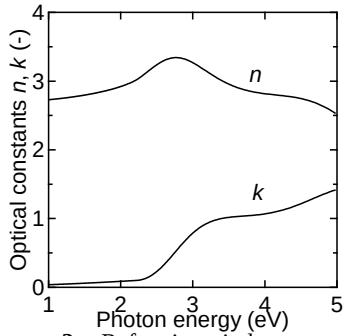

Figure 2. Refractive index n and extinction coefficient k of the anatase TaON thin film grown at T_S = 750 °C.

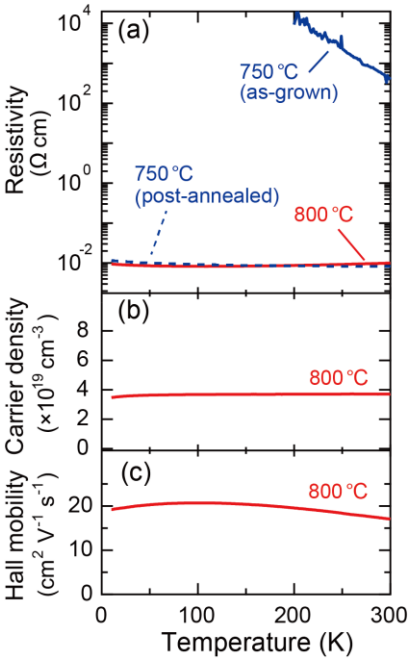

Figure 3. (a) Resistivity of anatase TaON epitaxial thin films plotted as functions of temperature. The dashed lines represent the data of the film grown at 750 °C and successively annealed at 800 °C under base pressure in the growth chamber. The resistivity of the film grown at 750 °C (as-grown) was measured by a two-probe method due to the high resistance. (b) Carrier density, and (c) Hall mobility of the films grown at 800 °C plotted as functions of temperature.

Figure 1-3 were reprinted from A. Suzuki *et al.*, Chem. Mater. **26**, 976 (2014) "Copyright 2013, American Chemical Society"

Tuning of optical properties in solid-solution of anatase $(TiO_2)_x(TaON)_{1-x}$

As mentioned above, tuning optical properties is important for the applications of δ-TaON. In case of conventional compound semiconductors, solid-solution of materials with the same crystal structure and different optical properties is an established way for this purpose. Here I synthesized solid-solution of δ-TaON and anatase TiO_2 ($(TiO_2)_x(TaON)_{1-x}$: TTON) thin films with various chemical composition x and demonstrated the tunability of their optical properties.

The TTON epitaxial thin films were grown on LSAT (100) single crystal substrates by using NPA-PLD. Oxide ceramic targets with different Ti to Ta ratio, $Ti_xTa_{1-x}O_y$, were used for controlling cation compositions in the films. After the careful optimization of anion compositions by adjusting partial pressure of N_2 and O_2 gas introduced into the chamber, I succeeded in fabricating solid-solution of TTON thin films with composition ratio x = 0.1, 0.3, 0.5, 0.7, and 0.9. All of TTON thin films with various x values showed 004 diffraction of anatase structure without any impurity peaks, which was examined by XRD measurements. Furthermore, both in-plane and out-of-plane lattice parameters of the TTON thin films linearly decreased as x increases in accordance with Vegard's law, clearly indicating complete solid-solution of δ-TaON and anatase TiO_2.

Next, E_g and n of the TTON thin films were determined by spectroscopic ellipsometry. As s result, E_g systematically changed from visible light region (~2.4 eV) to ultraviolet region (> 3.2 eV) as x increased. This implies that TTON could be optimized for wide applications from visible light active photoelectrode and transparent electrode by adjusting x. I also confirmed that refractive index n could be continuously tuned from ~3.3 (TaON) to ~2.7 (TiO_2).

These tendencies of E_g and n can be explained as follows. In most of oxynitrides, valence band top consists of N 2p orbital, which is shallower than O 2p orbital due to smaller electronegativity of nitrogen than oxygen. When x increases, contribution from N 2p orbital decreases and the valence band top is pushed down, resulting in the increased E_g. On the other hand, refractive index n of a solid generally decreases with decreasing bond covalency. Since M-O bonds have smaller covalency than M-N bonds, n of the TTON films decreased with an increase of x.

Carrier doping to anatase TaON

In order to use δ-TaON as transparent electrodes for optoelectronic devices, ρ less than 1×10^{-3} Ωcm is required. On the other hand, the resistivity of reduced δ-TaON is ρ ~1×10^{-2} Ωcm, which is mainly due to the lower carrier density ($n_e < 5\times10^{19}$ cm^{-3}) than those of typical transparent electrode materials ($n_e > 1\times10^{20}$ cm^{-3}). Therefore, carrier doping method must be developed for practical use as a transparent electrode.

I first tried conventional cation substitution, that is, W^{6+} substitution for Ta^{5+} by using W-doped Ta_2O_5 ceramic targets, as in the case of Nb^{5+}- or Ta^{5+}-substitution for Ti^{4+} in TiO_2. However, I found that W did not act as electron donor in δ-TaON, probably because doped electrons were compensated by substitution of N^{3-} for O^{2-} during the film growth. This suggests that carrier doping process after the film growth process (i.e. after O/N ratio is fixed) is effective to avoid the charge compensation.

Based on this idea, I examined Li insertion into interstitial sites of δ-TaON by dipping a crystal in an n-butyllithium solution, as reported in Li-doped anatase TiO_2 [3]. δ-TaON thin films fabricated at 750°C by NPA-PLD were reacted with n-butyllithium in hexane solutions (Sigma-Aldrich) at 60°C for 6 hours under an inert N_2 gas atmosphere. 1.6 M, 1.6×10^{-2} M, and 1.6×10^{-4} M n-butyllithium solutions were used to investigate the effect of n-butyllithium concentration.

After the reaction, crystal structure was examined by XRD. While no impurity phase was observed, 0.10 % expansion of the out-of-plane lattice parameters of δ-TaON was observed after the reaction with 1.6 M n-butyllithium solution. This lattice expansion suggests Li insertion into the anatase lattice. Indeed, secondary ion mass spectrometry confirmed existence of Li inside the film, of which amount was controllable over about four orders of magnitude by changing the concentration of n-butyllithium solution.

Transport properties of the Li-doped δ-TaON were determined by van der Pauw method. As a result, n_e strongly

depends on the concentration of the *n*-butyllithium solution, which indicates that Li introduction into *δ*-TaON generated electron carriers, as expected. I also conducted the Li insertion to *δ*-TaON fabricated at 800°C with lower resistivity than that fabricated at 750°C. The resistivity of the film reacted with 1.6×10^{-2} M *n*-butyllithium solution was decreased down to ρ ~6.7×10^{-4} Ωcm, which is enough low for transparent electrode applications.

Stabilization of anatase TaON by using anatase TiO_2 seed layer

The high growth temperature ($T_s \geq$ 750°C) and use of expensive single crystal substrates required for the growth of *δ*-TaON are serious disadvantages towards practical applications. In general, thin film growth can be promoted by introducing a seed layer with the same crystal structure as those of the thin film. Thus, *δ*-TaON can be stabilized by using an anatase TiO_2 seed layer, which has the same crystal structure as *δ*-TaON. This stabilization effect would reduce the film growth temperature. The seed layer might enable the growth of *δ*-TaON even on a glass substrate.

First, to investigate the seed layer effect on growth temperature, *δ*-TaON was fabricated on LSAT substrate with a ~5-nm-thick (001)-oriented anatase TiO_2 seed layer. Figure 4 shows the *θ*-2*θ* XRD patterns of the films grown at various T_s = 550, 600, 650, and 700°C with and without the anatase TiO_2 seed layer. The intensity of the 004 diffraction of *δ*-TaON was obviously enhanced by introducing the seed layer. From the peak intensity of the 004 diffraction of *δ*-TaON, it was estimated that the growth temperature was lowered by 50–100°C by the seed layer.

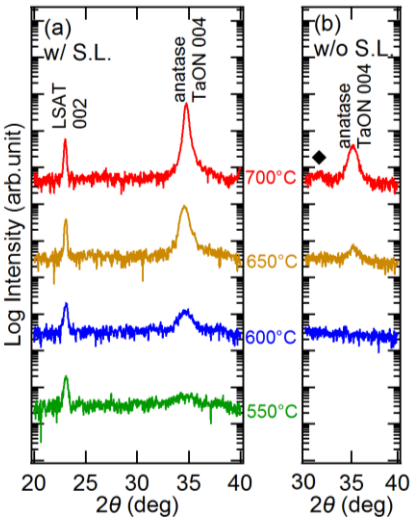

Fig. 4. *θ*-2*θ* XRD patterns of TaON films grown on LSAT substrate (a) with and (b) without anatase TiO_2 seed layer (T_S = 550, 600, 650, and 700°C). The filled diamond represents diffraction from an impurity phase.
Reprint from A. Suzuki *et al.*, Jpn. J. Appl. Phys. **54**, 080303 (2015) "Copyright 2015, The Japan Society of Applied Physics"

Next, *δ*-TaON was grown on fused silica with and without a ~10-nm-thick polycrystalline anatase TiO_2 seed layer, which was formed from amorphous precursor by solid phase crystallization. The TaON thin film directly grown on fused silica substrate has baddeleyite structure. In contrast, by introducing the anatase TiO_2 seed layer, the peaks originated from baddeleyite phase disappeared and a new peak appeared. I analyzed crystal structure and its orientation using a simulation software, and assigned the peak to 112 diffraction from *δ*-TaON of which [112] axis tilted by ~6° from the surface normal. These results proved that the structural matching at the interface between anatase TiO_2 and *δ*-TaON essentially enhanced the growth of the *δ*-TaON thin films.

Summary

I succeeded in synthesizing undoped *δ*-TaON epitaxial thin films by using NPA-PLD. The obtained *δ*-TaON films showed E_g of 2.37 eV and *n*~3.3 in visible light region. Transport measurements revealed that the anatase TaON films fabricated at 800°C can be categorized as a degenerated semiconductor with high μ_H of ~17 $cm^2V^{-1}s^{-1}$. From these results, I concluded that anatase TaON is a promising for photoelectrode and transparent electrode. To widen the range of application of the material, I succeeded in controlling the optical and transport properties of *δ*-TaON. I also established a process to synthesize *δ*-TaON at lower growth temperature and without expensive single crystal substrates. These achievements made a significant progress for practical application of *δ*-TaON.

References

[1] L. Forro *et al.*, J. Appl. Phys, **75**, 633 (2004).
[2] H. Schilling *et al.*, J. Solid State Chem. **179**, 2416 (2006).
[3] T. Ebina *et al.*, J. Power Sources **81**, 393 (1999).