Preparation of TaO₂ thin films using NbO₂ template layers by a pulsed laser deposition technique

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Abstract

TaO₂ thin films were prepared using rutile-type NbO₂ template layers on Al₂O₃(0001) substrates by a pulsed laser deposition technique. The structural and electronic properties of the films were characterized by performing four-circle X-ray diffraction (XRD) and X-ray photoemission spectroscopy (XPS) measurements. Four-circle XRD measurements revealed the formation and epitaxial growth of (100)-oriented tetragonal TaO₂ on the NbO₂ template layers. On the other hand, XPS measurements showed two kinds of valence states, namely Ta⁴⁺ and Ta⁵⁺ in the surface region of the film. The results from the XRD and XPS measurements suggest that the film is composed of epitaxially grown TaO₂ with an amorphous Ta₂O₅ surface layer. It is found from control experiments that the NbO₂ template layers play an important role in inducing the crystallization of the TaO₂ films and promoting the formation of Ta⁴⁺ in the films deposited thereon. The results indicate the effectiveness of the NbO₂ template layers for the formation of TaO₂ thin films. Our work presents a promising method for the preparation of TaO₂ thin films and provides a starting point for further research on TaO₂.

Keywords: TaO₂; Thin film; NbO₂ template layer; Epitaxy; XPS

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1. Introduction

TaO₂ has a rutile-type structure with a tetragonal form [1-4]. This compound attracts attention in connection with VO₂ and NbO₂, which show a metal-insulator transition at 67 and 807 °C, respectively [5-7]. Despite the interest, there are few experimental reports on TaO₂ to date. This is mostly because TaO₂ is a metastable compound in a Ta-O binary system [1], and their production as a single phase is difficult.

Several preparation methods have been presented, including oxidation of Ta powder with Zn oxide and oxidation of Ta carbides under steam [2], reduction of Ta₂O₅ with magnesium [8] or with carbon in vacuum [1], and reduction of Ta₂O₅ by shock-loading to 50 - 60 GPa [4]. In these approaches, TaO₂ is obtained in the form of powder and film, but it is not isolated in a pure form. The product usually contains other Ta oxides such as Ta₆O, Ta₂O, and Ta₂O₅. Multiphase products hinder the study of the physical properties of TaO₂. Therefore, one of the main issues in studying this compound is to find a way to stabilize only TaO₂ among Ta-O metastable and stable compounds.

The results of these previous studies suggest that control of the valence of the Ta ion is not sufficient to stabilize TaO₂ and an additional approach is required. One of the most effective ways to obtain a metastable compound is to stabilize the crystal structure of the compound in the form of a film by using a template substrate. For example, a metastable α -Ga₂O₃ with a corundum structure is obtained as a thin film grown on a corundum Al₂O₃ substrate [9]. For rutile-type TaO₂, it is expected that this metastable compound might be stabilized as a thin film grown on a rutile-type substrate.

From the perspective of lattice matching with TaO₂, NbO₂ is a promising substrate. NbO₂ shows a metal-to-insulator transition near 807 °C accompanied by a structural change [7]. In a high-temperature metallic phase, it has a normal rutile-type tetragonal form. In the low-temperature insulating phase, NbO₂ has a distorted rutile-type tetragonal form with Nb-Nb dimers, which lie across the shared edges linking the distorted NbO₆ octahedra along

the c direction. Lattice parameters a and c are represented as $a = 2\sqrt{2}a_r$ and $c = 2c_r$, respectively, where a_r and c_r correspond to the lattice parameters of the subcell with a normal rutile-type tetragonal symmetry. The crystal structure of NbO_2 in the low-temperature phase is depicted in Figure 1. Table 1 shows the lattice parameters a and c for TaO_2 [4] and NbO_2 [10] in the low-temperature phase, and the subcell parameters a_r and c_r for NbO_2 , together with the lattice mismatch between TaO_2 and NbO_2 subcells. The lattice mismatch is 1.9 and 3.1 % for the a - and c -axes, respectively. These values are smaller than the lattice mismatch between TaO_2 and other rutile-type metal dioxides [11], suggesting that NbO_2 is a suitable substrate in terms of lattice matching with TaO_2 . In addition, we have prepared NbO_2 thin films grown epitaxially on $\text{Al}_2\text{O}_3(0001)$ substrates using a pulsed laser deposition (PLD) technique. NbO_2 thin films can be used as a template layer for the growth of TaO_2 films. Hence, it is of interest to prepare TaO_2 thin films using NbO_2 template layers by a PLD method.

In this paper, we report the results of the preparation of TaO_2 thin films using NbO_2 template layers on $\text{Al}_2\text{O}_3(0001)$ substrates by a PLD method. The structural and electronic properties of the films were characterized by performing four-circle X-ray diffraction (XRD) and X-ray photoemission spectroscopy (XPS) measurements. The effectiveness of the NbO_2 template layers for the formation of TaO_2 thin films was also examined by XRD and XPS measurements.

2. Experimental

TaO_2 thin films were fabricated using NbO_2 template layers on $\text{Al}_2\text{O}_3(0001)$ substrates by a PLD method with a KrF excimer laser ($\lambda = 248$ nm). Nb_2O_5 (99.9 %, Rare Metallic) and Ta_2O_5 (99.99 %, Rare Metallic) bulk pellets were used as target materials. KrF excimer conditions were a pulse duration of 50 ns and a laser fluence of 60 mJcm^{-2} . The distance between the target and substrate was 3.5 cm. For the preparation of the NbO_2 template layer, the pressure in the growth chamber was maintained at about 10^{-6} Pa, providing a reducing

atmosphere. During deposition, the substrate temperature was maintained at 550 °C. Deposition times of 30 min with a repetition rate of 1 Hz and 15 – 60 min with a repetition rate of 3 Hz (4,500 – 12,600 shots) were used. After deposition, the target material was changed to Ta₂O₅, while pressure and substrate temperature were unchanged. For the TaO₂ thin films, the deposition was carried out under the same reducing conditions as in the case of the NbO₂ template layer. Deposition times of 30 min with a repetition rate of 1 Hz and 90 min with a repetition rate of 3 Hz (17,000 shots) were used. When the deposition was completed, the heater was turned off and the films were cooled down to 25 °C under the same pressure. Surface morphologies of the films were observed by an atomic force microscope (AFM, SPA400 + SPI3800N, Seiko Instruments). Dynamic force microscope was employed as an operating mode. An aluminum-coated Si cantilever with a resonance frequency of 133 kHz, force constant of 15 N/m and Q factor of approximately 350 was used. Calibration of AFM was done using a grid pattern with a 3 μm pitch in both the x and y directions and a 100 μm height in the z direction (STS3-1000P, VLSI). The root-mean-square noise was 0.03 nm. The prepared films were examined by four-circle XRD analysis using Cu Kα radiation (Rigaku RINT-2000/PC). The scattering geometry used in the X-ray diffractometer is a focusing geometry. The graphite monochromator and scintillation detector were used. The widths of the divergence and scatter slit were 1/2 °, and that of the receiving slit was 0.3 mm. The thickness of the NbO₂ template layer was 8 - 12 nm, which was determined from the Scherrer's equation. The thickness of the TaO₂ thin films was estimated to be 28 nm from a plot of laser pulse number vs. thickness of TaO₂ thin films made using the Scherrer's equation. XPS measurements were carried out on the beamline BL-5, at the Hiroshima Synchrotron Radiation Center in Hiroshima University with non-monochromatic Mg Kα X-ray source ($h\nu = 1253.6$ eV). For XPS samples, very thin amorphous NbO_x (2-3 nm) films were coated at 25 °C in the PLD chamber to prevent the oxidation of the film surface. Ta 4f core-level spectra were measured under an ultrahigh vacuum of $\sim 10^{-7}$ Pa using a VSW hemispherical analyzer.

The total energy resolution was about 1.1 eV. The binding energy of the films was corrected using the peak position of Ta 4f core-level spectra, which were measured with synchrotron radiation and whose Fermi level position was determined by measuring the molybdenum spectra. Before measurements, the films were annealed at 120 °C under ultrahigh vacuum ($\sim 10^{-6}$ Pa) for 10 min to obtain a clean surface.

3. Results and discussion

3.1. Characterization of NbO₂ template layers

Figure 2 shows an AFM image of the NbO₂ template layer (film thickness of 12 nm). A smooth surface was observed. Figure 3 shows the X-ray diffraction (XRD) pattern of the NbO₂ thin film. The NbO₂ (440) and (880) peaks are observed at $2\theta = 37.34^\circ$ and 79.62° , respectively. No other peaks beside those from NbO₂ and Al₂O₃ substrate were detected, indicating that the film is an (110)-oriented single phase. Figure 4 shows the X-ray ϕ scan taken on NbO₂ (400) reflection (tilt angle $\psi = 45^\circ$). Since NbO₂ has a tetragonal structure, the X-ray ϕ scan of the NbO₂ thin film is expected to show a two-fold symmetry (*i.e.* two (400) reflection peaks separated by 180°). However, six peaks separated by 60° were observed. The number of peaks is three times higher than expected. This is because of the three-fold symmetry of the Al₂O₃(0001) substrate. The result indicates that the NbO₂ template layer has an in-plane 3-variant structure separated by 120° from each other, as shown in Figure 5. This result is reasonable evidence of the epitaxial growth of the NbO₂ template layer on the Al₂O₃(0001) substrate.

3.2. Preparation of TaO₂ thin films using NbO₂ template layers

Figure 6(a) shows the XRD patterns for the NbO₂ template layer in a low-temperature phase formed on an Al₂O₃(0001) substrate (denoted as NbO₂/Al₂O₃ hereafter), and a TaO₂ thin

film prepared using the NbO₂ template layer on Al₂O₃(0001) substrate (denoted as TaO₂/NbO₂/Al₂O₃ hereafter). The film thickness of the NbO₂ template layer was 8 nm. For TaO₂/NbO₂/Al₂O₃, two distinct peaks are observed aside from those of the Al₂O₃(0001) substrate. Moreover, the positions of these peaks are close to those of the NbO₂ template layer, with no other peak being detected. A simple XRD pattern suggests the formation of the TaO₂ film with a certain orientation. To identify the phase of the film, the peaks were examined in more detail.

Figures 6(b) and 6(c) show enlarged XRD patterns around the peaks at lower and higher 2θ angles, respectively, for TaO₂/NbO₂/Al₂O₃. The peak for NbO₂/Al₂O₃ is also shown in the same figure for comparison. At the lower 2θ angle, the intense peak is observed at $2\theta = 37.62^\circ$. The peak position is higher than that of NbO₂. According to the literature [4], this peak position is similar to that of the (200) diffraction peak in bulk TaO₂. The same is observed for the higher 2θ angle. The peak is observed at $2\theta = 80.39^\circ$, with a shoulder at the lower angle. The shoulder corresponds to the (880) diffraction peak of the NbO₂ template layer. The observed peak position is close to that of the (400) diffraction peak in bulk TaO₂. Hence, the results of the XRD measurements suggest the formation of the (100)-oriented TaO₂ film.

In order to examine the formation and epitaxy of the (100)-oriented TaO₂ thin film, four-circle XRD measurements were performed. Using this technique, asymmetric X-ray diffraction peaks can be observed in epitaxial thin films. In the experiment, the (110)-oriented TaO₂ was chosen as an asymmetric plane. This plane has a d -spacing of 0.3359 nm in the bulk [4], which is unique to Ta-O binary compounds and found only in TaO₂. Thus, the (110) diffraction peak is a good indicator of the TaO₂ epitaxial thin film formation. The a -axis length was determined from the peaks in Figure 6(b) to be 0.478 nm. If the film is (100)-oriented TaO₂ with a rutile-type tetragonal symmetry, then we should observe a (110) diffraction peak at $2\theta = 26.36^\circ$ with tilt angle $\psi = 45^\circ$, where the tilt angle is the angle

between the reflection plane and substrate surface plane. From Figure 7, a peak at $2\theta = 26.32^\circ$ is clearly observed. This peak position is in good agreement with our expected result. Note that the NbO₂ template layer also has a (400) reflection at around $2\theta = 26^\circ$, as shown in Figure 7, but the peak is distinguishable in both intensity and position from the peak at $2\theta = 26.32^\circ$. These results strongly indicate the formation and epitaxy of a rutile-type tetragonal TaO₂ thin film with (100)-orientation.

One may consider the possibility that the diffraction peaks from TaO₂/NbO₂/Al₂O₃ shown in Figures 6(a) and 6(b) originate from the thermodynamically stable Ta₂O₅. This possibility is unlikely because the stable Ta₂O₅ does not have the d -value corresponding to $2\theta = 37.62^\circ$. In order to further exclude this possibility, we performed an experiment where the film was heated, examining the change in the corresponding XRD pattern. At higher temperature, the film should be composed of stable Ta₂O₅. If the as-prepared film was regarded as stable Ta₂O₅, then their XRD pattern should remain unchanged before and after heating. In the experiment, the film was heated at 800 °C for 30 min in air. After heating, the film became colorless while the as-prepared film was black. The results from the XRD measurement are shown in Figure 8. After heating, the peak at $2\theta = 37.62^\circ$ tended to disappear and a new peak appeared at $2\theta = 36.64^\circ$. This new peak was assigned to the (111) reflection of Ta₂O₅ [12]. This clearly indicates that the diffraction peak at $2\theta = 37.62^\circ$ is not originated from Ta₂O₅, and thus, the above-mentioned possibility can be ruled out. The obtained result supports the formation of the TaO₂ thin film with (100)-orientation.

3.3. Epitaxy of TaO₂ thin films

The epitaxial growth of the tetragonal TaO₂ thin film was also studied using X-ray ϕ scans. Figure 9 shows the ϕ scan of the (110) reflection ($\psi = 45^\circ$) for the (100)-oriented TaO₂ thin film. X-ray ϕ scans of the (400) reflection ($\psi = 45^\circ$) for the (110)-oriented NbO₂

template layer and $(10\bar{1}2)$ reflection ($\psi = 57.6^\circ$) for the $\text{Al}_2\text{O}_3(0001)$ substrate are also shown. The TaO_2 thin film is expected to have a two-fold symmetry (two (110) reflection peaks separated by 180°) in the case of a tetragonal structure. During the measurement, six peaks separated by 60° were observed. The number of peaks is three times higher than expected. This is because of the three-fold symmetry of the $\text{Al}_2\text{O}_3(0001)$ substrate. The film consists of three domains separated by 120° from each other. This result is reasonable evidence of the epitaxial growth of the tetragonal TaO_2 thin film. X-ray pole figure was also recorded. Figure 10 shows the X-ray pole figure plot for the $\{110\}$ configuration with X-ray diffraction from (100) -oriented TaO_2 films in the tilt angle range ψ from 0 to 75° . Six poles at $\psi = 45^\circ$ with 60° intervals were seen and no other distinct pole was observed. This result supports the epitaxial growth of tetragonal $\text{TaO}_2(100)$ thin film.

When comparing the two ϕ scans for the TaO_2 film and NbO_2 template layer, we find that all six peaks have the same position. This indicates that the TaO_2 thin film is well aligned with the plane of the NbO_2 template layer. The epitaxial correlation between the TaO_2 thin film and NbO_2 template layer is $(100)[001]\text{TaO}_2// (110)[001]\text{NbO}_2$ and $(100)[010]\text{TaO}_2// (110)[\bar{1}\bar{1}0]\text{NbO}_2$. This can be represented using a normal rutile-type subcell of NbO_2 to $(100)[001]\text{TaO}_2// (100)[001]\text{NbO}_2(\text{subcell})$ and $(100)[010]\text{TaO}_2// (100)[010]\text{NbO}_2(\text{subcell})$. The obtained epitaxial correlation suggests that the tetragonal TaO_2 thin film is stabilized by the NbO_2 template layer with a rutile-type tetragonal structure.

3.4. X-ray photoemission spectroscopy

The formation of the TaO_2 film was examined by XPS. The Ta $4f$ core-level spectra were measured to check the valence states of Ta ions in the film. Figure 11 shows the Ta $4f$ core-level spectrum of the film. The spectrum shows the peak structure at a binding energy of

~ 27 eV and a shoulder around 25 eV. The obtained spectral shape suggests that there are at least two kinds of valence states of Ta ions in the film. To determine the valence states of Ta ions, a fit of the spectrum was performed. For the fitting procedure, the difference in binding energy between Ta $4f_{7/2}$ and Ta $4f_{5/2}$ was set at 1.9 eV [13], and the peak width was identical for all of the peaks. As shown in Figure 11, a good fitting of the experimental spectrum was achieved with two components. One component at a lower binding energy (around 25 eV) originates from the Ta⁴⁺ valence state [14,15], thus supporting the formation of TaO₂ in the film. The other component at around 27 eV was attributed to the Ta⁵⁺ valence state [14,15]. This indicates the presence of not only TaO₂ but also Ta₂O₅ in the film. The amount of Ta⁴⁺ and Ta⁵⁺ states was estimated from the peak areas to be 14 and 86 %, respectively. The fitting parameters for the two components are presented in Table 2.

The results from the XPS measurements do not seem to be consistent with those from the XRD measurements, where only the epitaxial grown TaO₂ was observed. A possible interpretation for this inconsistency is that an amorphous Ta₂O₅ layer is formed at the surface of the film, and the amount of Ta₂O₅ decreases on going toward the innermost portion of the film. During the XPS measurements of such a film, the Ta₂O₅ should be predominantly observed because XPS is a surface sensitive measurement (mean free path of photoelectrons was several nanometers for our experiments), while TaO₂ should barely be detected. On the other hand, during XRD measurements, the amorphous Ta₂O₅ is not observed due to poor crystallinity and only the crystalline TaO₂ is detected. According to the literature, the thickness of the amorphous Ta₂O₅ can be estimated [16], and it was determined to be about 3 nm. Here, the amorphous Ta₂O₅ is assumed to form a layer over the TaO₂ film, and a value of 1.6 nm is used as the mean free path of the photoelectrons for both TaO₂ and Ta₂O₅ [16]. The estimated thickness is small compared with the total thickness of the film (28 nm), supporting the presence of Ta₂O₅ on the surface of the film. The results of XPS and XRD measurements suggest that the film is composed of TaO₂ with an amorphous Ta₂O₅ layer at the surface. In

order to check the formation of the Ta₂O₅ amorphous surface layer, we recorded the X-ray pole figure at $2\theta = 28.29^\circ$ corresponding to the strongest reflection, (1110) peak of Ta₂O₅. No pole was observed. This supports the formation of an amorphous Ta₂O₅ surface layer.

It would be interesting to know whether the Ta₂O₅ layer would be detectable after time. We performed XRD measurements of the films after XPS measurements. The XRD patterns did not change, and no diffraction peaks from Ta₂O₅ layer were detected. The result supports that the Ta₂O₅ surface layer is not crystalline but amorphous. The schematic illustration of TaO₂/NbO₂/Al₂O₃(0001) is shown in Figure 12.

The amorphous Ta₂O₅ is produced probably due to the oxidation of TaO₂. The surface oxidation occurs when the film is exposed to air during the transport from our laboratory to the synchrotron facility (about 1 day). For our film, Ta₂O₅ was formed even though a thin NbO_x layer was coated to prevent the surface oxidation. The surface of the TaO₂ film might be unstable and may easily take up oxygen from the air to form stable Ta₂O₅. In order to clarify the origin of the amorphous Ta₂O₅, further study will be necessary.

One may think that the brief low temperature anneal prior to the XPS measurements can have any effect. We tried to anneal the films at 300 °C for 10 min. After annealing, we performed the XPS measurements. The XPS spectra of the annealed films did not change at all compared with those of the film annealed at 120 °C for 10 min. No remarkable annealing effect is found at present. The annealing temperature of 300 °C might be too low to see the effect of annealing temperature. Higher annealing temperature would be necessary to see the effects of annealing on the XPS spectra.

3.5. Effectiveness of NbO₂ template layers

Control experiments were carried out to study the exact role of the NbO₂ template layer in the formation of the TaO₂ thin film. A TaO₂ film was deposited directly on the Al₂O₃(0001) substrate under the same conditions (denoted as TaO₂/Al₂O₃), and XRD measurements of the

film were performed. As seen in Figure 13, no XRD peaks other than those from $\text{Al}_2\text{O}_3(0001)$ are detected. This result indicates that the film is either amorphous or nanocrystalline, and is difficult to crystallize directly on the $\text{Al}_2\text{O}_3(0001)$. In addition, this result clearly shows that the NbO_2 template layer induces the crystallization of TaO_2 thin film. In order to further investigate the importance of the NbO_2 template layer, XPS measurements were performed and valence states of Ta ions in $\text{TaO}_2/\text{Al}_2\text{O}_3$ were examined.

Figure 14 shows the Ta 4f core-level spectrum of $\text{TaO}_2/\text{Al}_2\text{O}_3$. The spectrum of $\text{TaO}_2/\text{NbO}_2/\text{Al}_2\text{O}_3$ is also shown for comparison. The spectrum of $\text{TaO}_2/\text{Al}_2\text{O}_3$ shows a set of peaks at a binding energy around 27 eV, and a shoulder around 23-25 eV, suggesting the presence of several valence states of Ta ions in the film. When comparing with the spectrum of $\text{TaO}_2/\text{NbO}_2/\text{Al}_2\text{O}_3$, we notice that the shoulder structure shifts to a lower binding energy, while the peak around 27 eV is almost the same in intensity and position. This suggests that the valence states of Ta ions in $\text{TaO}_2/\text{Al}_2\text{O}_3$ are more dispersed than those in $\text{TaO}_2/\text{NbO}_2/\text{Al}_2\text{O}_3$. For an analysis of the valence states of Ta ions in the film, a fit of the spectrum was carried out. As seen in Figure 15, the spectrum can be fitted by using three components. Among them, two of these peaks, those at binding energies of around 25 and 27 eV, are identical to those in Figure 11, indicating the presence of both Ta^{4+} and Ta^{5+} states. The other one at a binding energy of 23.89 eV is attributed to a Ta^{2+} valence state [14,15]. Hence, the analysis of the XPS spectrum reveals the presence of three kinds of valence states, namely Ta^{2+} , Ta^{4+} , and Ta^{5+} in $\text{TaO}_2/\text{Al}_2\text{O}_3$. The amounts of Ta^{2+} , Ta^{4+} , and Ta^{5+} were estimated from the peak areas to be 4.6, 4.5, and 90.9 %, respectively. The fitting parameters of the spectrum are shown in Table 3.

From the fitting results of the XPS spectra for $\text{TaO}_2/\text{Al}_2\text{O}_3$ and $\text{TaO}_2/\text{NbO}_2/\text{Al}_2\text{O}_3$, it is seen that by using the NbO_2 template layer, the values changed from 4.5 to 14 % for Ta^{4+} , from 4.5 to 0 for Ta^{2+} , and from 90.9 to 85.9 % for Ta^{5+} . The amount of Ta^{4+} is enhanced three times, while Ta^{2+} disappears and that of Ta^{5+} is slightly reduced. This indicates that the NbO_2

template layer plays an important role in promoting the formation of Ta^{4+} in the films deposited thereon.

Based on the XRD and XPS results, the different roles of the NbO_2 template layer in the formation of the TaO_2 thin film can be determined: the first is to induce the crystallization of the TaO_2 thin film, while the second is to promote the formation of Ta^{4+} in the film deposited thereon. From these findings, it can be concluded that the presence of the NbO_2 template layer is crucial for the formation of TaO_2 thin films.

It would be challenging to prepare a TaO_2 thin film without any Ta_2O_5 using an NbO_2 template layer. Growing the film under a reducing atmosphere such as hydrogen is a possible way. Finding optimal experimental conditions will lead to the establishment of preparation methods for high-quality TaO_2 thin films. A high-quality TaO_2 film will give an opportunity to study the intrinsic physical properties of TaO_2 . Our work provides a good starting point for further research on TaO_2 .

4. Conclusions

In conclusion, we have prepared TaO_2 thin films using an NbO_2 template layer on $\text{Al}_2\text{O}_3(001)$ substrates. Four-circle XRD measurements revealed the epitaxial formation of TaO_2 thin films. XPS measurements revealed the presence of two kinds of phases, namely TaO_2 and Ta_2O_5 . The results of XRD and XPS measurements suggest that the film is composed of epitaxially grown TaO_2 with an amorphous Ta_2O_5 layer at the surface. Control experiments revealed that the NbO_2 template layer played an important role in both inducing the crystallization of the TaO_2 thin films, and promoting the formation of Ta^{4+} in the films deposited thereon. These results indicate that the presence of NbO_2 template layers is crucial for the formation of TaO_2 thin films.

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Figure captions

Figure 1. Crystal structure of a distorted rutile-type tetragonal NbO₂ in a low-temperature phase projected (upper panel) along a axis and (lower panel) c axis. Solid lines represent the unit cell of the low-temperature phase for NbO₂. Bold line shows the subcell corresponding to a normal rutile-type tetragonal unit cell. The subcell parameters of a_r and c_r are also shown. Crystal structures are illustrated with the program VESTA [17].

Figure 2. AFM image ($2 \times 2 \mu\text{m}$ scale) of an NbO₂ template layer grown on an Al₂O₃(0001) substrate. The film thickness of the NbO₂ template layer was 12 nm.

Figure 3. XRD pattern of an NbO₂ template layer grown on an Al₂O₃(0001) substrate.

*contamination originating from the XRD apparatus used.

Figure 4. XRD ϕ scans of (lower panel) (400) reflection ($\psi = 45^\circ$) for an (110)-oriented NbO₂ template layer and (upper panel) (10 $\bar{1}2$) reflection ($\psi = 57.6^\circ$) for an Al₂O₃(0001) substrate.

The tilt angle ψ is the angle between the reflection plane and substrate surface plane.

Figure 5. Schematic illustration of an in-plane 3-variant structure of the (110)-oriented NbO₂ template layer on an Al₂O₃(0001) substrate.

Figure 6. (a) XRD patterns of a template layer of a distorted rutile-type tetragonal NbO₂ formed on an Al₂O₃(0001) substrate (NbO₂/Al₂O₃) and a TaO₂ thin film prepared using a NbO₂ template layer on an Al₂O₃(0001) substrate (TaO₂/NbO₂/Al₂O₃). The film thickness of the NbO₂ template layer was 8 nm. * : contamination originating from the XRD apparatus used. Several small peaks are visible in the XRD pattern of NbO₂/Al₂O₃. The d -values of the

peaks at around $2\theta = 20^\circ$ and 64° are close to the values of one-third and one-ninth of the c -axis length of the Al_2O_3 substrate, respectively. The d -value of the peak at around $2\theta = 77^\circ$ is close to that of $\text{NbO}_2(624)$. The origin of the peak at around $2\theta = 44^\circ$ is unknown. (b) Enlarged XRD patterns around peaks at lower (b) and higher 2θ angles (c) for $\text{TaO}_2/\text{NbO}_2/\text{Al}_2\text{O}_3$. The peaks marked by ▼ in the NbO_2 template layer correspond to a part of thickness fringes.

Figure 7. (110) reflection of the (100)-oriented TaO_2 thin film. (400) reflection of the (110)-oriented NbO_2 template layer is also shown for comparison.

Figure 8. XRD patterns around peaks at lower 2θ angles for $\text{TaO}_2/\text{NbO}_2/\text{Al}_2\text{O}_3$ before and after heating at 800°C for 30 min in air.

Figure 9. XRD ϕ scans of (upper panel) the (110) reflection for the (100)-oriented TaO_2 thin film, (middle panel) (400) reflection for the (110)-oriented NbO_2 template layer and (lower panel) $(10\bar{1}2)$ reflection for the $\text{Al}_2\text{O}_3(0001)$ substrate.

Figure 10. X-ray pole figure plot for the {110} configuration with X-ray diffraction from (100)-oriented TaO_2 films.

Figure 11. Ta 4f core-level spectrum for $\text{TaO}_2/\text{NbO}_2/\text{Al}_2\text{O}_3$. The solid line through the data is the fit resulting from the sum of the two-labeled components.

Figure 12. Schematic illustration of $\text{TaO}_2(100)/\text{NbO}_2(100)/\text{Al}_2\text{O}_3(0001)$.

Figure 13. XRD pattern of a TaO₂ film deposited directly on an Al₂O₃(0001) substrate (TaO₂/Al₂O₃) (upper panel). XRD pattern of TaO₂/NbO₂/Al₂O₃ (lower panel) is also shown for comparison.

Figure 14. Ta 4*f* core-level spectrum for TaO₂/Al₂O₃ (green line), together with that of TaO₂/NbO₂/Al₂O₃ (red line) for comparison.

Figure 15. Ta 4*f* spectrum for TaO₂/Al₂O₃ (same as Figure 14). The solid line through the data is the fit resulting from the sum of the three-labeled components.

Table 1 Lattice parameters a and c for TaO₂ and a distorted rutile-type tetragonal NbO₂ in a low-temperature phase. Subcell parameters a_r and c_r for NbO₂ and the lattice mismatch between TaO₂ and NbO₂ subcells are also shown.

Lattice parameter/ material	$a / \text{\AA}$	$c / \text{\AA}$
TaO ₂ [4]	4.751	3.087
NbO ₂ [10]	13.696	5.981
	4.842 (a_r) [*]	2.991 (c_r) [*]
Lattice mismatch / %	1.92	3.11

^{*}Relationships between a and a_r , and between c and c_r are represented as $a = 2\sqrt{2}a_r$ and $c = 2c_r$, respectively.

Table 2 Binding energies and the amounts of Ta₂O₅ and TaO₂ in TaO₂/NbO₂/Al₂O₃

TaO _x	Orbital	Binding energy / eV	Amounts of TaO _x / %
Ta ₂ O ₅	Ta 4 <i>f</i> _{5/2}	28.94	85.9
	Ta 4 <i>f</i> _{7/2}	27.04	
TaO ₂	Ta 4 <i>f</i> _{5/2}	26.92	14.1
	Ta 4 <i>f</i> _{7/2}	25.02	

Table 3 Binding energies and the amounts of Ta₂O₅, TaO₂, and TaO in TaO₂/Al₂O₃

TaO _y	Orbital	Binding energy /eV	Amounts of TaO _y / %
Ta ₂ O ₅	Ta 4 <i>f</i> _{5/2}	28.94	90.9
	Ta 4 <i>f</i> _{7/2}	27.04	
TaO ₂	Ta 4 <i>f</i> _{5/2}	26.92	4.5
	Ta 4 <i>f</i> _{7/2}	25.02	
TaO	Ta 4 <i>f</i> _{5/2}	25.79	4.6
	Ta 4 <i>f</i> _{7/2}	23.89

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Figs. 6(a)(b)(c)

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14

Fig. 15