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Thermal conductivity tensor of NbO₂

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Abstract

Among several transition metal oxides showing metal to insulator transition, NbO₂ has attracted attention as the active material of memory devices due to its high thermal stability. Although clarification of thermal conductivity (κ) is essentially important for optimizing the NbO₂ device performance, it has not been reported thus far probably due to the anisotropic crystal structure. Here we show the thermal conductivity tensor of NbO₂ crystal. We measured the thermal conductivities of (110)-, (001)-, and (111)-oriented NbO₂ films and found <111>-direction shows $\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$ higher thermal conductivity compared with the other directions ($\sim 3 \text{ W m}^{-1} \text{ K}^{-1}$). Using the measured κ -values, we successfully determined thermal conductivity tensor components κ_{11} , κ_{13} , and κ_{33} . The diagonal components of the thermal conductivity tensor were $\sim 2.5 \text{ W m}^{-1} \text{ K}^{-1}$

while the nonzero off-diagonal component was $\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$. We believe that the present results are of great value in optimizing the performance of NbO₂ based devices.

Introduction

Transition metal oxides exhibiting metal-to-insulator transitions (MIT) are considered to be promising candidates for next generation non-volatile resistive random-access memory (RRAM) applications¹⁻⁴. As memory devices are constantly exposed to read/reset pulses, they are always exposed to high heat accumulation rates, and thermal stability is one of the key issues in the materials selection⁵. For this reason, NbO₂ is gaining interest in the RRAM community⁶⁻¹⁰ since it has high MIT temperature ($\sim 1080 \text{ K}$)¹¹⁻¹² and therefore high thermal stability. The approaches vary from local joule heating¹³⁻¹⁴ to utilizing electroforming current to change its oxidation states¹⁵⁻¹⁶. In all cases, understanding the thermal conductivity of NbO₂ is essential for the device optimization. However, it has been largely overlooked compared to the electrical properties because there is a lack of studies in literature on the thermal conductivity characterization of NbO₂.

One of the difficulties in measuring the thermal conductivity of NbO₂ comes from its anisotropic crystal structure. **Figure 1** schematically represents the unit cell of NbO₂ crystal at room temperature. The crystal structure of NbO₂ is tetragonal and belongs to the space group of $I4_1/a$ with the lattice parameters of $a = 1.37 \text{ nm}$ and $c = 0.599 \text{ nm}$ ¹². In NbO₂, the NbO₆ octahedrons are connected at their edges (side lines) along [001] direction whereas they are connected at their corners (end points) in the other directions. Very recently, Kim *et al.*¹⁷ reported that epitaxial NbO₂ films grown on $\alpha\text{-Al}_2\text{O}_3$ substrates exhibit anisotropic electron transport: the carrier effective mass (m^*) in $[11\bar{2}]$ direction is $0.05 m_0$

whereas that in $[1\bar{1}0]$ and $[001]$ directions are much heavier ($[1\bar{1}0]$: $\sim 1 m_0$, $[001]$: $\sim 0.8 m_0$). The electron transportation in semiconducting oxides is strongly affected by the electron-phonon collisions, which is related to the vibrational properties of the lattice. In addition, the elasticity tensor of NbO_2 shows anisotropy along its major axes and nonzero off-diagonal terms¹⁸⁻¹⁹. All physical properties of NbO_2 suggest that its thermal conductivity would be anisotropic.

In this study, we measured the thermal conductivities along $[110]$ -, $[001]$ -, and $[111]$ -directions using the (110) -, (001) -, and (111) -oriented NbO_2 films and found $[111]$ -direction shows $\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$ higher thermal conductivity compared with the other directions. In order to clarify the heat conduction in NbO_2 crystal, we extracted the full thermal conductivity tensor ($\hat{\kappa}$) from the observed thermal conductivities. $\hat{\kappa}$ has 6 independent terms. In case of NbO_2 , this can be reduced to 3 independent terms because of its 4-fold symmetry in the ab -plane. In a matrix representation, it looks as follows:

$$\hat{\kappa}_{\text{NbO}_2} = \begin{pmatrix} \kappa_{11} & \kappa_{12} & \kappa_{13} \\ \kappa_{12} & \kappa_{22} & \kappa_{23} \\ \kappa_{13} & \kappa_{23} & \kappa_{33} \end{pmatrix} \rightarrow \begin{pmatrix} \kappa_{11} & 0 & \kappa_{13} \\ 0 & \kappa_{11} & \kappa_{13} \\ \kappa_{13} & \kappa_{13} & \kappa_{33} \end{pmatrix} \quad \dots \quad (1)$$

where the subscripts 1, 2, and 3 refer to a -, b -, and c -axis of NbO_2 , respectively. Using the thermal conductivities in three different directions of $[110]$, $[001]$, and $[111]$, we successfully determined $\hat{\kappa}_{\text{NbO}_2}$. The components of $\hat{\kappa}_{\text{NbO}_2}$ were converted to the total thermal conductivity (κ_{tot}) using tensor coordinate transformations (**Supplementary**), and the resulting system of non-linear equations were solved to obtain all components of $\hat{\kappa}_{\text{NbO}_2}$ (Eq. 1). We believe the present results are significantly important for understanding the heat accumulations in NbO_2 based devices, which are critical for enhancing their performance.

Materials and methods

Using RF magnetron sputtering, NbO₂ films with three different crystallographic orientations were grown on (0001) α -Al₂O₃, (10 $\bar{1}$ 0) α -Al₂O₃ and (1 $\bar{1}$ 02) α -Al₂O₃ substrates (Crystal Bank at Pusan National University), respectively. The films were grown at 650 °C under 2.5–5 mTorr of Ar/H partial pressure. The details of our NbO₂ film growth condition are described elsewhere¹⁷. The film thicknesses (*t*) and crystallographic orientations were analyzed by X-ray diffraction (HRXRD, Cu K α ₁ radiation, ATX-G, Rigaku Co.). The total thermal conductivity (κ_{tot}) of the resultant NbO₂ films were measured in the out-of-plane direction with time-domain thermo-reflectance (TDTR, pump beam wavelength: 775 nm, probe beam wavelength: 1550 nm, pulse duration: 1 ps, pulse frequency: 20 MHz method, PicoTR, PicoTherm Co.) at room temperature. Metallic Mo films (~100 nm), which were used as the transducer, were deposited on the top surface of the NbO₂ films by d.c. magnetron sputtering method at room temperature.

Results and discussion

Figure 2 shows the out-of-plane XRD patterns [**Fig. 2(a)**] and the rocking curves (OXRCs) [**Fig. 2(b)**] of the resultant NbO₂ films. Only intense diffraction peaks of 110 (top), 001 (middle), and 111 (bottom) NbO₂ are seen together with the α -Al₂O₃ diffraction peaks in **Fig. 2(a)**, indicating that highly oriented single phase NbO₂ films were grown on the α -Al₂O₃ substrates. Full-width at half maximum (FWHM) of the OXRCs of 440 NbO₂ (top) and 222 NbO₂ (bottom) are ~0.02 °, which corresponds to the resolution of our X-ray diffractometer, indicating strong 110 and 111 orientation of the films while that of 004 NbO₂ (middle) is a bit broader (0.76 °). From these results, the out-of-plane orientation of the

resultant films were clarified as [(110) NbO₂ || (0001) α -Al₂O₃], [(001) NbO₂ || (10 $\bar{1}$ 0) α -Al₂O₃] and [(111) NbO₂ || (1 $\bar{1}$ 02) α -Al₂O₃]. From the X-ray reflection measurements (data not shown), the film thickness of the (110)-, (001)-, and (111)-oriented films were clarified 68, 52, and 72 nm, respectively, which were sufficiently thick for the films to behave like bulk materials (≥ 30 nm, **Supplementary Table S1**)²⁰.

Figure 3 summarizes the thermo-reflectance signals from the NbO₂ films grown on α -Al₂O₃ substrates at room temperature. Sharp increase and decay curves before ~ 2 ns are due to the Mo transducer. The decay of (111)-oriented NbO₂ film is slightly faster than (110)- and (001)-oriented NbO₂ films, clearly indicating that κ_{tot} in the (111) direction is higher than that in the (110) and (001) directions. We analyzed the thermo-reflectance decay curves with the software package provided by the manufacturer and obtained the κ_{tot} of 3.0 W m⁻¹ K⁻¹ for (110), 2.9 W m⁻¹ K⁻¹ for (001), and 4.0 W m⁻¹ K⁻¹ for (111), respectively.

Acoustic longitudinal phonons usually dominate the lattice thermal conductivity²¹⁻²³. While the presence of soft phonons in the phonon dispersion relations makes it challenging to obtain detailed phonon transport characteristics of NbO₂²⁴, the speed of acoustic longitudinal phonons can be estimated with its elastic stiffness constants¹⁸⁻¹⁹. According to our calculations, the speed of elastic longitudinal waves along [111], [110], and [001] are 8476 m s⁻¹, 7978 m s⁻¹, and 8109 m s⁻¹, respectively (**Supplementary**). Therefore, the high thermal conductivity observed from the (111) oriented film is attributed to the speed of acoustic longitudinal phonons. We would like to note that the

observed thermal conductivities are not proportional to the calculated acoustic longitudinal phonon speeds, and the calculation results only explain why (111) film shows the highest thermal conductivity. To fully explain the observed thermal conductivities, it is necessary to understand the coupling of soft phonons, which are mainly populated near P point (Brillouin Zone edge along [111]). Since these phonons are shear waves along [111] with large displacement fields⁷, one possibility is anisotropic soft phonon scattering effect. In this scenario, soft phonon scattering would reduce the thermal transport properties along [001] and [110] films whereas its effect on the [111] longitudinal waves will be relatively small since their displacement fields ([111] longitudinal and transverse) are perpendicular. At elevated temperatures, as phonon softening will be compensated by an increase in the phonon population, the soft phonon effect will be enhanced, and the anisotropy will likely increase.

The observed thermal conductivity κ_{tot} is sum of the lattice thermal conductivity (κ_{lat}) and the electron thermal conductivity (κ_{ele}). In order to estimate the maximum contribution of carrier electrons (κ_{ele}) to the observed κ_{tot} , we measured the in-plane electrical resistivity (ρ) of the NbO₂ films by the d.c. four-probe method in van der Pauw electrode configuration at room temperature (**Table I**). The ρ values of (110)-, (001)-, and (111)-oriented films were 51, 2, and 51 Ω cm, respectively. Using these ρ values, we estimated κ_{ele} assuming the Wiedemann-Franz law ($\kappa_{\text{ele}} = L \cdot \sigma \cdot T$, where L is the Lorenz number of a free electron gas ($2.45 \times 10^{-8} \text{ W } \Omega^{-1} \text{ K}^{-2}$)²⁵, σ is the electrical conductivity ($=\rho^{-1}$), and T is the absolute temperature). While the Wiedemann-Franz law is often not suitable for describing mobile electrons in oxides²⁶, it does offer reasonable estimations for the upper bound for κ_{ele} . Note that the κ_{ele} values are negligibly small ($< 4 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-1}$) as compared with κ_{tot} . Therefore, we concluded that the heat transportation in NbO₂ crystal is mostly dominated by lattice vibrations ($\equiv$ phonons, κ_{lat}).

The ρ of (110) and (111) oriented NbO₂ films are within agreements with our previous studies ¹⁷. However, the ρ of (001) film was noticeably lower than that of the other two films. This implies the presence of oxygen vacancies ²⁷, which may be attributed to the large lattice mismatch (1.75 % and 10.6 %) between the (10 $\bar{1}$ 0) α -Al₂O₃ substrate and (001) NbO₂ ^{12, 28}. As oxygen vacancies can affect the thermal conductivity ²⁹⁻³⁰, their effects must be quantified to avoid mischaracterizing $\hat{\kappa}_{NbO_2}$. To examine the effect of oxygen vacancies on κ_{tot} of our NbO₂ films, we slightly adjusted the sputter deposition condition to fabricate oxygen deficient NbO_{2-x} films and measured their thermal conductivities (**Supplementary Table S1**). The ρ values of NbO_{2-x} films were orders of magnitude lower than the ρ values in **Table I**, but κ_{tot} values remained almost unchanged. These results confirm that the effect oxygen deficiency on the κ_{tot} of our NbO₂ films is negligibly small.

Here we show the thermal conductivity tensor, $\hat{\kappa}_{NbO_2}$. Equation (1) describes $\hat{\kappa}_{NbO_2}$ when the c -axis of the film is perpendicular to its top surface. Since the orientations of the NbO₂ films are not identical, $\hat{\kappa}_{NbO_2}$ needs to be transformed accordingly to properly interpret κ_{tot} observed from differently oriented films. The following matrices represent $\hat{\kappa}_{NbO_2}$ of (110) and (111) oriented films in a Cartesian coordinate when $\hat{z}$ -axis is perpendicular to the substrate (**See Supplementary information**):

$$\hat{\kappa}_{NbO_2,(110)} = \begin{pmatrix} \kappa_{33} & 0 & \sqrt{2}\kappa_{13} \\ 0 & \kappa_{11} & 0 \\ \sqrt{2}\kappa_{13} & 0 & \kappa_{11} \end{pmatrix} \quad \dots \quad (2a)$$

$$\hat{\kappa}_{NbO_2,(111)} = \begin{pmatrix} \frac{1}{3}(\kappa_{11} - 4\kappa_{13} + 2\kappa_{33}) & 0 & \frac{\sqrt{2}}{3}(\kappa_{11} - \kappa_{13} - \kappa_{33}) \\ 0 & \kappa_{11} & 0 \\ \frac{\sqrt{2}}{3}(\kappa_{11} - \kappa_{13} - \kappa_{33}) & 0 & \frac{1}{3}(2\kappa_{11} + 4\kappa_{13} + \kappa_{33}) \end{pmatrix} \quad \dots \quad (2b)$$

where $\hat{\kappa}_{NbO_2,(hkl)}$ represents the thermal conductivity tensor of the (hkl) -oriented NbO₂ film. The heat flux $\vec{j}$ in the film induced by the temperature gradient $\vec{\nabla}T$ across the film can be written as:

$$\vec{j} = -\hat{\kappa}_{NbO_2,(hkl)}\vec{\nabla}T \quad \dots \quad (3)$$

During TDTR measurements, the pump laser creates a temperature difference across the film, and the resulting signal reflects the total heat flux leaving the top surface. Therefore, $\vec{\nabla}T = (0, 0, \nabla T)$ and $\kappa_{tot} = |\vec{j}|/\nabla T$. This yields 3 different coupled non-linear equations **(See Supplementary information)**:

$$\kappa_{tot[001]} = \sqrt{k_{33}^2 + 2k_{13}^2} = 2.9 \text{ W m}^{-1} \text{ K}^{-1} \quad \dots \quad (4a)$$

$$\kappa_{tot[110]} = \sqrt{k_{11}^2 + 2k_{13}^2} = 3.0 \text{ W m}^{-1} \text{ K}^{-1} \quad \dots \quad (4b)$$

$$\kappa_{tot[111]} = \frac{1}{3}\sqrt{2(k_{11} - k_{13} - k_{33})^2 + (2k_{11} + 4k_{13} + k_{33})^2} = 4.0 \text{ W m}^{-1} \text{ K}^{-1} \quad \dots \quad (4c)$$

Equations (4a–4c) have two different sets of solutions: $(k_{11}, k_{13}, k_{33}) = (2.60, 1.06, 2.48) \text{ W m}^{-1} \text{ K}^{-1}$ and $(1.60, 1.79, 1.41) \text{ W m}^{-1} \text{ K}^{-1}$. In this case, elasticity can be used to choose a more appropriate solution since propagation of elastic waves can be reasonable estimations for the propagation of phonons. According to previous studies, the terms in the elasticity of NbO₂ representing compression/tension are always greater than the terms representing shear¹⁹. This suggests the latter solution needs to be discarded since its off-diagonal term is greater than the two diagonal terms, which is highly unlikely. Therefore, if *a*-, *b*-, and *c*-axes of the NbO₂ unit cell are used as the Cartesian axes, $\hat{\kappa}_{NbO_2}$ is expressed by the following matrix:

$$\hat{\kappa}_{NbO_2} = \begin{pmatrix} 2.60 & 0 & 1.06 \\ 0 & 2.60 & 1.06 \\ 1.06 & 1.06 & 2.48 \end{pmatrix} \text{ W m}^{-1} \text{ K}^{-1} (@ 300\text{K}) \quad \dots \quad (4)$$

Using the $\hat{\kappa}_{NbO_2}$, one can calculate the heat flux in NbO₂ along any directions, which is useful for understanding the heat flux in NbO₂ based devices.

Conclusion

In summary, we successfully clarified the full thermal conductivity tensor of NbO₂ for the first time using the thermal conductivity values of (001)-, (110)-, and (111)-oriented NbO₂ films grown on α -Al₂O₃ substrates. Using the (110)-, (001)-, and (111)-oriented NbO₂ films, we measured the thermal conductivity of [110]-, [001]-, and [111]-directions and found [111]-direction shows $\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$ higher thermal conductivity compared with the other directions ($\sim 3 \text{ W m}^{-1} \text{ K}^{-1}$). The diagonal components of the thermal conductivity tensor were $\sim 2.5 \text{ W m}^{-1} \text{ K}^{-1}$ while the nonzero off-diagonal component was $\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$. These results will be essential for understanding the flow of heat in NbO₂ based devices, which is critical for their design and efficiency optimization.

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Table I | Anisotropic thermal conductivity of the NbO₂ films at room temperature. Total thermal conductivity (κ_{tot}) in the out-of-plane direction, in-plane resistivity (ρ), and electron thermal conductivity (κ_{ele}) assumed with Wiedemann-Franz law of the (110)-, (001)-, and (111)-oriented NbO₂ films are listed. (111)-oriented film shows higher κ_{tot} compared with (110)- and (001)-oriented films. Note that the κ_{ele} values are negligibly small compared to κ_{tot} .

Orientations	t (nm)	κ_{tot}	ρ	κ_{ele}
		(out-of-plane, $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	(in-plane, $\Omega\cdot\text{cm}$)	($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)
(110)	68	3.0	51	1.4×10^{-5}
(001)	52	2.9	2	3.7×10^{-4}
(111)	72	4.0	51	1.4×10^{-5}

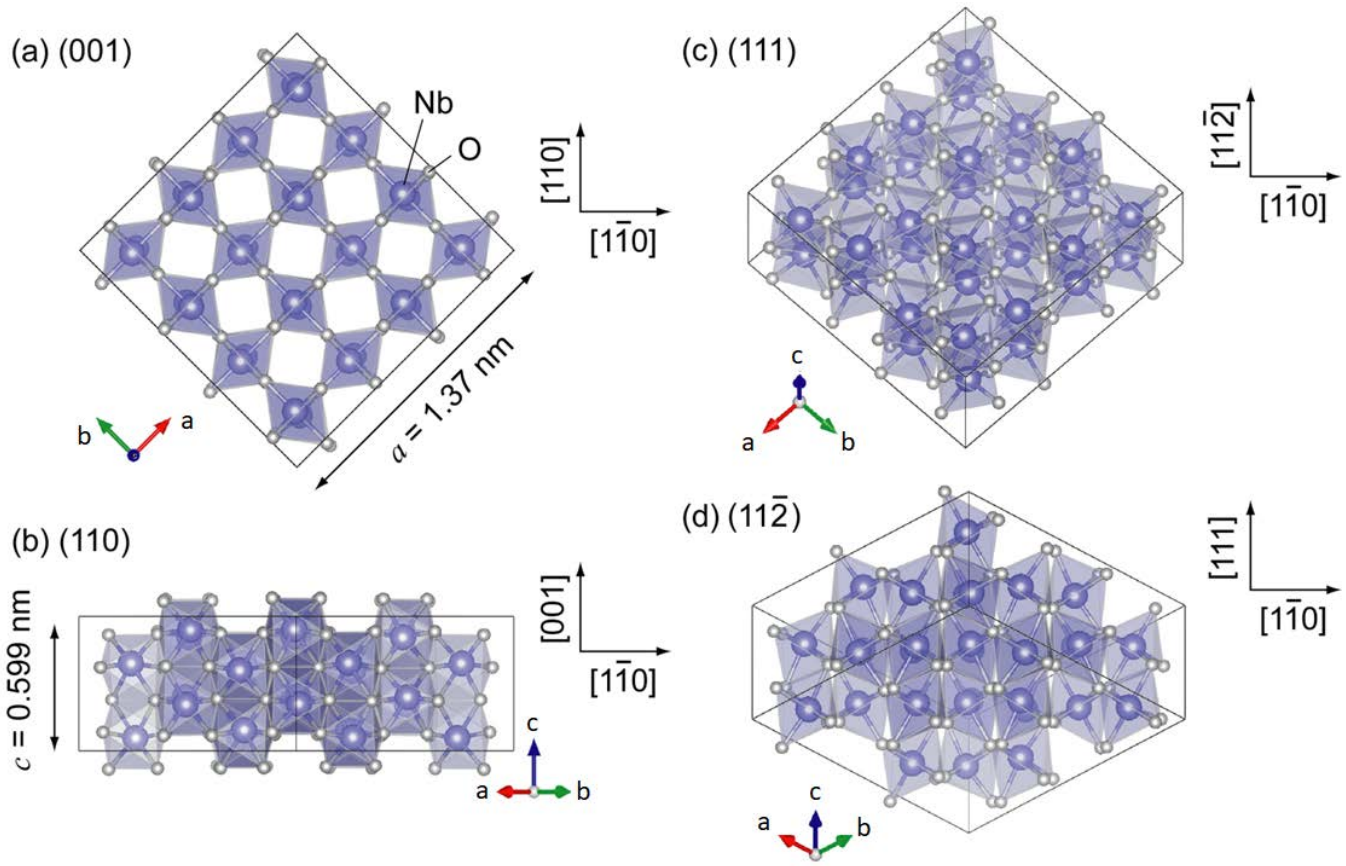


Figure 1 | Schematic crystal structure of NbO_2 at room temperature. Projection along the normal to (a) (001), (b) (110), (c) (111), and (d) $[11\bar{2}]$. The space group is $I4_1/a$ and the lattice parameters are $a = 1.37 \text{ nm}$ and $c = 0.599 \text{ nm}$ ¹². Note that the NbO_6 octahedrons are connected at their edges (side lines) in [001] direction whereas they are connected at their corners (end points) in other directions.

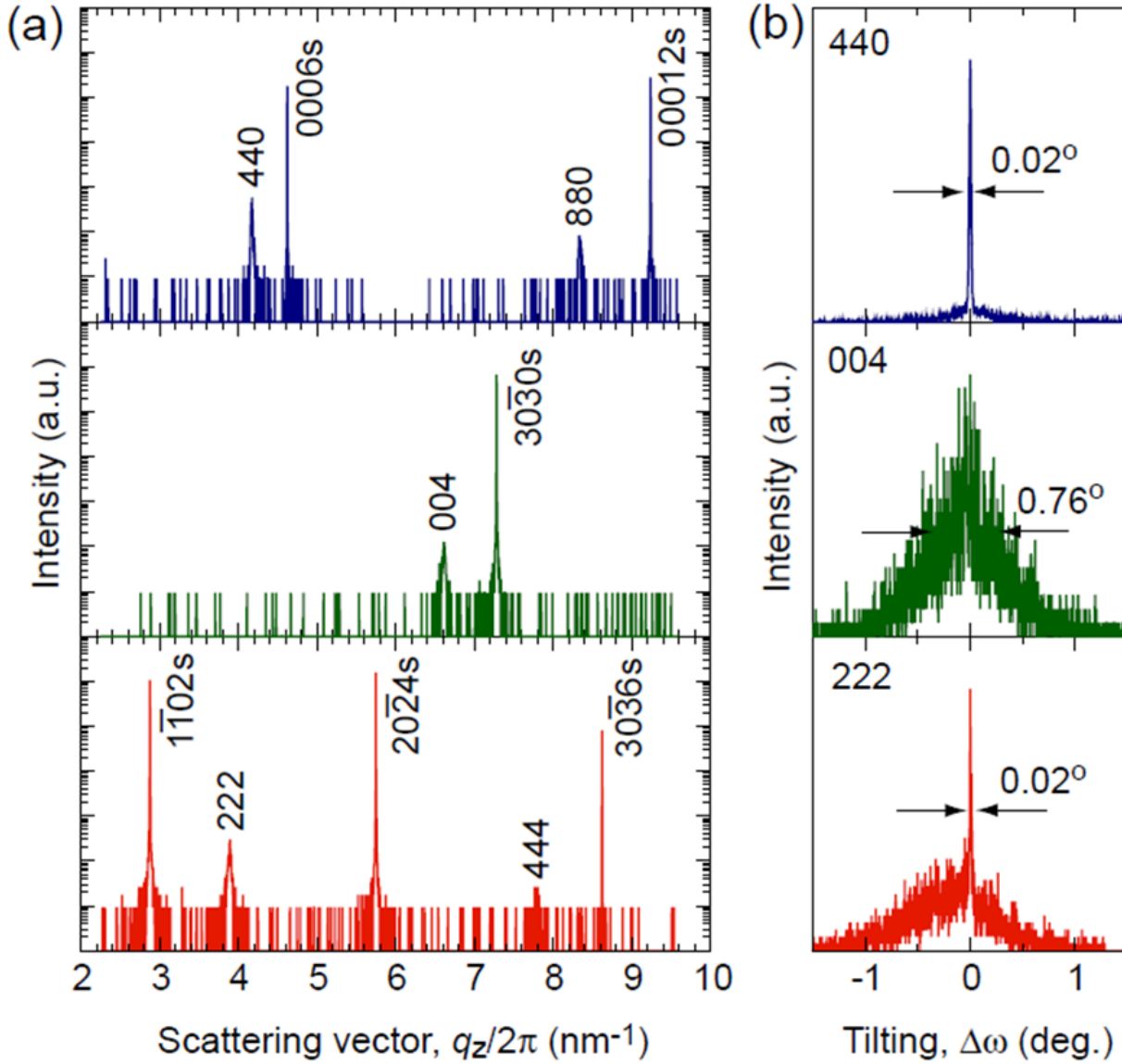


FIG. 2 | Crystallographic orientation of the resultant NbO₂ films. (a) Out-of-plane X-ray Bragg diffraction patterns and (b) corresponding out-of-plane X-ray rocking curves (OXRCs) of the resultant NbO₂ films. Only intense diffraction peaks of 110 (top), 001 (middle), and 111 (bottom) NbO₂ are seen together with the α -Al₂O₃ diffraction peaks in (a), indicating that highly oriented single phase NbO₂ films were grown on the α -Al₂O₃ substrates. FWHM of the OXRCs of 440 NbO₂ (top) and 222 NbO₂ (bottom) are $\sim 0.02^\circ$, which corresponds to the resolution of our X-ray diffractometer, indicating strong 110 and 111 orientation of the films, while that of 004 NbO₂ (middle) is a bit broader (0.76°).

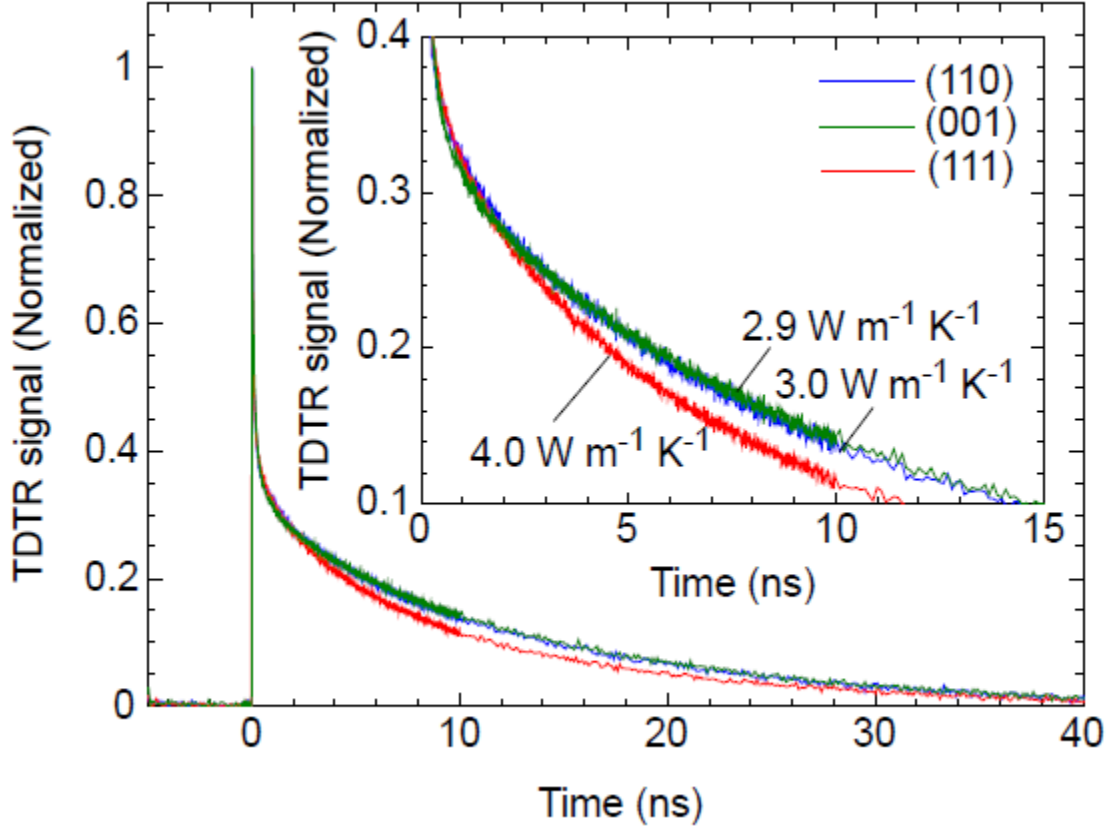


FIG. 3 | Thermo-reflectance signal of the NbO₂ films grown on α -Al₂O₃ substrates at room temperature. Sharp increase and decay curves until ~ 2 ns are due to the Mo transducer. The decay of (111)-oriented NbO₂ film is slightly faster than (110)- and (001)-oriented NbO₂ films, clearly indicating that κ_{tot} in the (111) direction is higher than that in the (110) and (001) directions. Using these thermo-reflectance decay curves, we obtained the κ_{tot} of $3.0 \text{ W m}^{-1} \text{ K}^{-1}$ for (110), $2.9 \text{ W m}^{-1} \text{ K}^{-1}$ for (001), and $4.0 \text{ W m}^{-1} \text{ K}^{-1}$ for (001), respectively.

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