Structural analyses and reverse Monte Carlo modeling of niobium oxide amorphous film prepared by sputtering method

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Structural analyses of niobium oxide (NbO_x) amorphous film prepared with a sputtering method have been performed by using synchrotron X-ray radiation at SPring-8. The composition was determined as $\text{Nb}_2\text{O}_5 \cdot 0.8\text{H}_2\text{O}$ from the measurements of Rutherford back scattering, X-ray fluorescence, X-ray absorption near edge structure, and thermal desorption spectroscopy. Structural information was obtained by extended X-ray absorption fine structure and high energy X-ray diffraction measurements. It was supposed from the experimental data that NbO_x consisted of distorted NbO_n polyhedra connected by corner- and edge-sharing. Structural models were constructed with reverse Monte Carlo (RMC) simulations. In the RMC models, the structural characteristics were successfully reproduced, and H atoms were, however, randomly distributed. Then, bond valence sum (BVS) constraint was introduced to the RMC simulation. As the results, narrower distribution in BVS was achieved for all the constituent atoms, and distinct OH bonds were effectively generated in the RMC model.

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1. Introduction

Among the renewable energies, such as wind,¹⁾ terrestrial heat,²⁾ water³⁾ and biomass,⁴⁾ solar energy⁵⁾ is unlimited and most suitable for power generation. Si-based solar cells have been developed and widely used so far.^{6–8)} However, their conversion efficiency is not so high, and furthermore, there is a concern about insufficient supply of Si feedstock and soaring prices of crystalline silicon because demand for silicon for photovoltaic industry is increasing every year.^{9,10)} Hence, new solar power generation devices have been explored.^{11–15)} Photo-electrochemical cell (PEC) is one of the candidates among various photoelectric transducers.^{16,17)} In PEC, electricity is generated due to photo irradiation, where hydrogen is also produced by water electrolysis. TiO_2 has been extensively studied as a PEC material,^{18–20)} and recently, dye sensitized solar cells^{21–23)} have been developed to achieve lower cost and production energy.

In the authors' group, PEC based on niobium oxide, NbO_x has been developed, where NbO_x was sputter-deposited on an Al-coated glass substrate.²⁴⁾ In the PECs with a $\text{NbO}_x/\text{Al}/\text{glass}/\text{KNO}_3\text{aq.}/\text{Al}/\text{glass}$ structure, faint but stable electricity generation has been successfully observed during light irradiation. The maximum power density was obtained, when the NbO_x deposits were not in continuous film structure but in a discrete nano-island structure. It was concluded that the PEC reactions proceeded in the immediate vicinity of the boundary among the nano-islands of niobium oxide, substrate metal, and electrolyte solution. However, actual mechanisms of power generation have

not been solved completely, because NbO_x deposits are amorphous²⁴⁾ and hence their atomic structures have been unknown. If the atomic structures of NbO_x deposits are clarified, their electronic structures will be also elucidated, and it is consequently expected that the power generation mechanism is revealed. It is also helpful to improve the efficiency of PECs.

Thus, the authors' group has investigated electronic and atomistic structures of NbO_x deposits based on optical absorption and photoelectron spectrometries,²⁵⁾ in which density functional theory (DFT) calculations have been performed to interpret the experimental spectra based on the structure. In the DFT calculations, Nb_2O_5 crystals of B-, R-, and M-phases were chosen. The experimental XPS and UPS valence band spectra were broad, and no characteristic sharp peaks were observed. Among the investigated crystals, M-phase Nb_2O_5 showed better reproducibility, and it was supposed that broad distribution of Nb–O bond length was responsible for the broad feature in the photoelectron spectra of NbO_x deposits.

Then, in the present study, detailed structural analyses of amorphous NbO_x deposits have been performed, where structural information was obtained by high energy X-ray diffraction (HEXRD) and X-ray absorption fine structure (XAFS) with synchrotron radiation. Structural models were constructed with a reverse Monte Carlo (RMC) simulation to reproduce the experimental information.

2. Experiment

NbO_x specimens with the thickness of 100 nm with a continuous structure were deposited on various substrates by an RF magnetron reactive sputtering method, where a metallic Nb was sputtered under a 0.39 Pa of an $\text{Ar}:\text{O}_2 = 1:1$ mixture with an RF power of 200 W (more detailed conditions are given in else-

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where²⁴⁾). An oxygen-free graphite sheet (PERMA-FOIL[®]) was used as a substrate for the measurements of Rutherford back scattering (RBS) and X-ray fluorescence (XRF) to determine the composition. A quartz glass was used to estimate the density from X-ray reflectivity (XRR), gas desorption from thermal desorption spectroscopy (TDS), and local structure around Nb atom from XAFS measurement with a fluorescence method. For these measurements, NbO_x specimens of 100 nm thickness were used. As for XAFS measurement, NbO_x film with 5 nm thickness was also prepared to investigate the dependency of film thickness, and reagents of Nb, NbO, Nb₂O₃, NbO₂, and Nb₂O₅ (Kojundo Chemical Lab. Co., Ltd.) were also used for comparison. For HEXRD measurement, NbO_x films of 200 nm were deposited on polymer films (Kapton[®]) with 50 μ m thickness with small X-ray absorption. Nine sheets of the polymer films with NbO_x deposits were stacked to obtain larger scattering intensity from the NbO_x deposits. The measurements of XRR, XAFS and HEXRD were performed in the beam lines of BL46XU, BL01B1 and BL04B2 at SPring-8, respectively. RMC simulation was carried out to obtain structural model reproducing the experimental data.

3. Results and discussion

3.1 Composition and density

As mentioned, NbO_x deposits were prepared with an RF sputtering method. Hence, the deviation from the stoichiometric composition of Nb₂O₅ was expected in the NbO_x deposits. Then, compositional analyses were performed to obtain accurate composition. From RBS measurement, the composition of NbO_x deposits was estimated as O/Nb = 2.9, which was higher than the case of Nb₂O₅ with the Nb valence of +5. Then, it was also evaluated by XRF using a reference sample (Nb₂O₅, Micromatter Co.), and after a thorough analysis,^{26),27)} the same value of O/Nb = 2.9 was obtained. It was supposed that the excess oxygen was present in chemically-adsorbed water or hydroxyl group. Then, TDS measurement was carried out to investigate the desorbed species during heating, from which desorption of water was confirmed at the temperature between 100–400°C. From these results, the composition of NbO_x deposits was finally determined as Nb₂O₅·0.8H₂O. According to the composition, XRR spectrum was analyzed to obtain the density of c.a. 4.5 g/cm³.

3.2 Local structure around Nb from XAFS analyses

Figure 1 shows the results of Nb K-edge XAFS measurements, where difference in the XAFS spectra is quite small between the NbO_x deposits with different thicknesses. The similarity in the XAFS spectra suggests that the local atomic and electronic structures around Nb are not altered even when the thickness changes—from 5 to 100 nm. In Fig. 1(a) of X-ray absorption near edge structure (XANES), the absorption edge shifts to higher energy side with increasing the valence number of niobium. The absorption edge of NbO_x deposits is close to that of Nb₂O₅ (T-Nb_{8.4}O₂₁) crystal, suggesting that Nb atoms in NbO_x deposits have a valence of +5. In Fig. 1(a), a pre-edge peak at ~18990 eV is confirmed in NbO_x deposits. The pre-edge peak is generally described by tetrahedral NbO₄ tetrahedra²⁸⁾ and distorted NbO₆ octahedra.²⁹⁾ The pre-edge peak is also observed in the Nb₂O₅ crystal, which consists of NbO₅, NbO₆, and NbO₇ polyhedra.³⁰⁾ The NbO_x deposits have larger pre-edge peak in intensity than the Nb₂O₅ crystal, which suggests larger distortion of NbO_n polyhedra in the NbO_x deposits. From the X-ray absorption curves [Fig. 1(b)], extended X-ray absorption fine structure (EXAFS) spectra were obtained [Fig. 1(c)]. EXAFS spectra at

Fig. 1. Experimental results of XAFS measurements. (a) XANES spectra, (b) Absorption coefficients, $\mu(E)$ at a photon energy, E , (c) EXAFS spectra, $k^3\chi(k)$ (normalized absorption, $\chi(k)$ at a photoelectron wave-vector, k), and (d) magnitudes of Fourier transform of $k^3\chi(k)$ ($k = 2\text{--}7 \text{ \AA}^{-1}$) for NbO_x deposits with different thicknesses.

$k = 2\text{--}7 \text{ \AA}^{-1}$ [Fig. 1(c)] were Fourier-transformed to obtain radial distribution. In the Fourier transform [Fig. 1(d)], peaks are observed at radius, $r = 1.4$ and $3.0 \text{ \AA}$, which are attributed to the nearest Nb–O and Nb–Nb pairs, respectively. The second peak is small as compared with the first peak, suggesting the structural disorder in the connection between NbO_n polyhedra.

3.3 Short and medium range structures from HEXRD analyses

Figure 2 shows the results of HEXRD measurements. Figure 2(a) indicates the HEXRD patterns of the stacked sheets of polymer substrates with NbO_x deposits (Curve A) and the sheets of polymer substrates without NbO_x deposits (Curve B). Scattering intensity curve of NbO_x deposits (Curve C) was obtained by subtracting Curve B from Curve A. In Curve C, peaks are clearly confirmed at the diffraction angle $2\theta = \sim 4$ and $\sim 7^\circ$, which correspond to the peaks at ~ 2 and $\sim 4 \text{ \AA}^{-1}$ of structure factor, $S(Q)$ in Fig. 2(b). The $S(Q)$ curve at higher Q (reciprocal lattice vector) region is noisy, because the subtracted scattering intensities at higher 2θ region are small, and the S/N ratio of $S(Q)$ is also small at higher Q region [Fig. 2(b)]. Total correlation function, $T(r)$ given in Fig. 2(c) was obtained by the Fourier transform of $S(Q)$ at the Q region of $0.5\text{--}15 \text{ \AA}^{-1}$. In $T(r)$,

Fig. 2. Experimental results of HEXRD measurements. (a) Scattering intensity curves of stacked sheets of polymer substrates with NbO_x deposits (Curve A), sheets of polymer substrates without NbO_x deposits (Curve B), and NbO_x deposits obtained by subtraction (Curve C), (b) structure factor, $S(Q)$ and (c) total correlation function, $T(r)$.

however, clear peaks are confirmed at $\sim 2\text{ \AA}$ attributed to the nearest Nb–O pairs and $\sim 4\text{ \AA}$ ascribed by Nb–Nb pairs in the neighboring NbO_n polyhedra. In the longer radial distance, $r > 4.5\text{ \AA}$, the amplitude of fine structure decreases suddenly, which probably results from the structural disorder in the NbO_n polyhedral arrangement. Such the medium range structural disorder is also supposed from the Fourier transform of EXFAS spectra [Fig. 1(d)].

Differential correlation functions, $D(r)$ of some niobium oxide crystals were calculated from their structural parameters given in the literatures.^{30)–38)} Figure 3 shows the calculated $D(r)$, where experimental $D(r)$ of NbO_x deposit is also shown for comparison.

In $D(r)$ curves, a large peak is commonly confirmed at $\sim 3.9\text{ \AA}$, and another peak is seen at $\sim 3.4\text{ \AA}$ except for $\text{B-Nb}_2\text{O}_5$ and HNbO_3 . These peaks are due to Nb–Nb pairs in corner- and edge-sharing NbO_n polyhedra, respectively. $\text{B-Nb}_2\text{O}_5$ consists of corner- and edge-sharing NbO_6 units with comparatively higher symmetry,³¹⁾ which results in large and symmetric Nb–Nb peak at $\sim 3.7\text{ \AA}$. HNbO_3 which consists of only corner-sharing NbO_6 octahedra³⁸⁾ has the closest composition to the amorphous NbO_x ($\text{H}_{0.8}\text{Nb}_{2.9}$). However, the $3.4\text{ \AA}$ peak is recognized in $D(r)$ of NbO_x , indicating the presence of edge-sharing NbO_n units in NbO_x and dissimilarity to HNbO_3 in the connection form of NbO_n units. The dissimilarity to HNbO_3 is also confirmed in the peak of Nb–O pairs at $\sim 2.0\text{ \AA}$. In HNbO_3 , the peak is symmetric, and in NbO_x , tailing to the longer side is recognized. Such the tailing of the Nb–O peak is also seen in $\text{N-Nb}_2\text{O}_5$ and $\text{H-Nb}_2\text{O}_5$, where these crystals^{34),35)} are constituted by distorted NbO_6 octahedra. In the previous spectroscopic study,²⁵⁾ DFT calculations

Fig. 3. Differential correlation functions, $D(r)$ calculated from niobium oxide crystals and NbO_x film.

suggested the structural similarity to $\text{M-Nb}_2\text{O}_5$, and in $D(r)$, however, it is hard to say that $\text{M-Nb}_2\text{O}_5$ shows the best agreement with NbO_x . XANES spectra [Fig. 1(a)] suggests the structural similarity between the amorphous NbO_x film and $\text{T-Nb}_{8.4}\text{O}_{21}$ crystal, and in $D(r)$ curves, however, $\text{T-Nb}_{8.4}\text{O}_{21}$ crystal does not show the closest resemblance to NbO_x . Presence of a large variety of Nb_2O_5 -related polymorphs makes the structural analysis of NbO_x so difficult. In any case, it is consequently considered from XAFS and HEXRD analyses that amorphous NbO_x consists of distorted NbO_n polyhedra connected by corner- and edge-sharing.

3.4 RMC structural modeling

In RMC structural simulation, 1175 atoms (Nb = 250, O = 725, and H = 200) were put in a simulation box with a side length of $23.42\text{ \AA}$. The RMC constraints used were as follows: $S(Q)$ at $Q = 1.5\text{--}10\text{ \AA}^{-1}$, $k^3\chi(k)$ at $k = 4.3\text{--}6.5\text{ \AA}^{-1}$, minimum inter-atomic distances of Nb–Nb = 2.90 , Nb–O = 1.50 , Nb–H = 1.50 , O–O = 1.60 , O–H = 0.80 , and H–H = $1.50\text{ \AA}$. In the simulation of $k^3\chi(k)$, single-scattering of Nb–Nb, Nb–O, and Nb–H pairs was assumed, because the second peak in Fourier transform of $k^3\chi(k)$ [Fig. 1(d)] was small, suggesting little contribution of multiple-scattering to EXAFS in amorphous NbO_x .

As mentioned, hydrogen atoms are present in NbO_x deposits, and it is quite difficult to reproduce their position even though using HEXRD and EXAFS. It is supposed that bond valence sum (BVS) constraint is suitable to avoid chemically-unstable or highly-distorted coordination structures around atoms because BVS depends on bond length and coordination number.^{39),40)} Then, in the present study, BVS constraint of Nb = $+5$, O = -2 , and H = $+1$ was also introduced to RMC simulation. In the RMC simulation, an RMC code, RMCprofile⁴¹⁾ was chosen to apply the constraints of HEXRD, EXAFS, and BVS.

Figure 4 shows the RMC model obtained by using the BVS constraint in addition to HEXRD and EXAFS constraints. It is

Fig. 4. RMC model of the amorphous niobium oxide, $\text{Nb}_2\text{O}_5 \cdot 0.8\text{H}_2\text{O}$ optimized with BVS constraint. Green: niobium, red: oxygen, and pink: hydrogen. Nb–O and O–H bonds are drawn for the respective pairs within 2.8 and 1.5 Å.

Fig. 5. (a) Structure factors, $S(Q)$ and (b) EXAFS spectra, $k^3\chi(k)$ obtained from experiments and RMC models.

difficult to find apparent differences in the arrangement of Nb and O atoms from the model without BVS constraint. In the model shown in Fig. 4, small numbers of H_2O molecules are found, which are mostly present as a ligand of Nb atoms and rarely separate from NbO_n polyhedra. As shown in Fig. 5, the experimental $S(Q)$ and $k^3\chi(k)$ spectra are successfully reproduced by the RMC simulations regardless of BVS constraint. As for BVS shown in Fig. 6, however, large difference is confirmed between the results with and without BVS constraint. As for Nb and O atoms, distribution of BVS becomes narrower when applying BVS constraint. Average BVS increases commonly with BVS constraint. The changes in average BVS of Nb and O atom are comparatively small compared with that of H atom. Average BVS of H atom is quite small without BVS constraint.

Figure 7 shows partial pair distribution functions, $g(r)$ of RMC models. Significant change in $g(r)$ is not observed except for O–H. As shown in Fig. 6, BVS distribution of Nb and O atoms become narrower with BVS constraint, and it is hence expected that the first $g(r)$ peak for Nb–O becomes narrower with BVS constraint, and the change in $g(r)$ is, however, quite small after applying BVS constraint, which is also the case in $S(Q)$ and $k^3\chi(k)$ spectra as shown in Fig. 5, suggesting that BVS is more sensitive to the local structure than $g(r)$, $S(Q)$ and $k^3\chi(k)$ spectra. In the $g(r)$ of Nb–Nb pair, two peaks are successfully reproduced at 3–4 Å, which correspond to the peaks observed in $T(r)$

Fig. 6. Distribution of bond valence sum, BVS of the elements in RMC models.

Fig. 7. Partial pair distribution functions $g(r)$ in RMC models (solid lines: with BVS constraint, broken lines: without BVS constraint).

[Fig. 2(c)] and $D(r)$ (Fig. 3). The shorter and longer Nb–Nb pairs result from edge- and corner-sharing NbO_n polyhedra in the RMC models, respectively. In the $g(r)$ of Nb–O pair, tailing of the first peak at 2 Å to longer r in $D(r)$ is also reproduced. As for O–H pair, however, BVS constraint results in a significant difference in $g(r)$, that is, no characteristic O–H peaks are observed from the RMC model without BVS constraint, which results from random distribution of H atoms. On the other hand, a peak is clearly confirmed at ~ 1.0 Å from the RMC model with BVS constraint. The increase in shorter O–H bonds results in the larger increase in BVS of H atoms (Fig. 6). Thus, it is suggested that BVS constraint is effective to improve structural order around atoms with less structural information such as hydrogen. The longest dis-

Fig. 8. Distribution of coordination numbers in RMC models. Average coordination numbers are given in the parentheses.

tances of Nb–O and O–H bonds are estimated as 2.8 and 1.5 Å, respectively, from the first peak edge of longer side in $g(r)$ for Nb–O and O–H pairs, and the distances are used as cut-off distances in bond determination (Figs. 4 and 8).

Figure 8 shows distribution of coordination numbers. NbO_5 , NbO_6 and NbO_7 polyhedra are abundant in RMC models, and by using BVS constraint, slightly broader distribution around Nb is obtained, that is, NbO_6 unit decreases while NbO_5 and NbO_7 units increases in population. However, the change in coordination number distribution against BVS constraint is much smaller than the change in BVS distribution (Fig. 6), which also suggests that BVS is quite sensitive to local structure. In the case of number of O around H shown in Fig. 8(c), significant change is observed as expected from the change in BVS of H (Fig. 6). In the RMC model without BVS constraint, ~50% of H atoms have no neighbors of O atoms within 1.5 Å. In the RMC model with BVS constraint, however, ~80% of H have one O atom as a neighbor, but only a few percent of H atoms are used for H_2O molecules. Among O in OH bonds, 54% was non-bridging oxygen which had one neighboring Nb atom, indicating non-selective bond formation of H atoms with O atoms. Connection form of NbO_n units in the RMC models was also examined; fractions of corner-, edge-, and face-sharing were 73, 25, and 2%, respectively.

By using RMC simulation, a structural model was successfully obtained, where structural characteristics of amorphous NbO_x film were also revealed. Electronic structure of the RMC model should be evaluated to clarify photo-electrochemical properties. The RMC model produced in this study consists of 1175 atoms, and it is too large to perform band calculation. Hence, different theoretical calculation is required for the estimation of electronic structure, and it should be a future task.

4. Conclusion

The structural analyses of amorphous NbO_x deposited by

sputtering method have been performed, where structural information was obtained from XAFS and HEXRD measurements by using synchrotron radiation. From RBS and XRF analyses, O/Nb atomic ratio was estimated as 2.9, and from XANES analysis, however, valence state of Nb atoms was identified as +5. Then, it was supposed that the excess oxygen atoms were present in OH group, and H_2O desorption during heat-treatment was successfully confirmed in TDS measurement. Hence, the composition of NbO_x deposits was finally determined as $\text{Nb}_2\text{O}_5 \cdot 0.8\text{H}_2\text{O}$.

In XANES spectra, a pre-edge peak was found, and its intensity was larger than that of Nb_2O_5 crystal, from which larger distortion of NbO_n polyhedra was suggested in amorphous NbO_x . Such the distortion was also suggested from the asymmetrical Nb–O peak in differential correlation function, $D(r)$. In $D(r)$, the peak due to Nb–Nb pairs was split into two components, which were attributed to the corner- and edge-sharing NbO_n units. In the radial distribution obtained from EXAFS spectra, the second peak due to Nb–Nb pairs with smaller intensity was observed, suggesting the disordered arrangement of the neighboring NbO_n units.

The structural models have been constructed with RMC simulation, in which HEXRD and EXAFS data were successfully reproduced. Structural characteristics found in the above analyses were also reproduced in the RMC model. However, hydrogen atoms were randomly distributed in the structural model. Then, BVS constraint was also introduced to the RMC simulation, and in partial pair distribution function, $g(r)$ of O–H pair, a clear peak appeared at $r \sim 1$ Å. At that time, local structures around Nb and O atoms showed no significant change in $D(r)$, and in BVS, however, drastic change was confirmed in these atoms, that is, BVS distribution became quite narrower. It was consequently suggested that BVS constraint was effective to improve the regularity in local structure around the atoms especially with less structural information, such as H atom in the present case.

In the present study, however, no experimental information for the structural roles of H atoms has been obtained, and it is necessary to examine local structure of H atoms. Furthermore, it is also indispensable to investigate the electronic structure of amorphous NbO_x . Based on the knowledges acquired, power generation mechanism of NbO_x should be clarified, and it should be possible to design NbO_x -based PECs with higher conversion efficiency.

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