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Sputtering of Oxygen on Nb Surface by Hydrogen Ions

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Abstract

The rate of oxygen removal from an oxygen-doped Nb membrane by hydrogen ion sputtering was examined by measuring the change in the sticking coefficient of H_2, α. First, the temperature dependence of α was measured at various oxygen concentrations to investigate correlation between bulk oxygen concentration and α. Then the oxygen concentration in the membrane was adjusted to 1.5 at%, and the surface of the membrane was irradiated by hydrogen ions of 600 eV at 1113 K. The change in α with sputtering time was measured, and the reduction in bulk oxygen concentration was estimated from the extent of

change in α. The oxygen concentration decreased with increasing sputtering time by continuous surface segregation of oxygen and sputtering. The sputtering yield of oxygen on the Nb membrane surface was evaluated to range from 0.012 to 0.036.

1. Introduction

Metallic membranes covered by adlayers of non-metallic impurities such as oxygen and sulfur have enormous permeability for atoms and ions of hydrogen isotopes [1]. Hence, such membranes can be applied for particle control in fusion devices [2-5]. The high permeability is due to the suppression of reemission of hydrogen isotopes from incident surfaces by the non-metallic impurities. Therefore, reduction in the impurity coverage by sputtering degrades the permeation capabilities. In other words, compensation for removed impurities is necessary to sustain the performance of membranes under sputtering.

The present authors have reported that oxygen doping in the bulk of a Nb membrane is effective to sustain the permeation capability under sputtering due to continuous surface segregation of oxygen [6-9]. Prolonged sputtering, however, led to the degradation of permeability owing to the reduction in the oxygen concentration in the membrane [9]. This observation indicates that periodic oxygen doping is required as a maintenance work to keep the good permeability. A longer intervening period between oxygen doping treatments is better for the application viewpoint. Namely, the interval should be enough longer than that of discharge time. Otherwise, the permeation membranes could not be used for particle control. One of the key factors determining the intervening period between oxygen doping treatments is the sputtering yield of oxygen on membrane surfaces.

The purpose of the present study is to develop an experimental technique to evaluate the sputtering yields of impurity elements segregated to the surface of membrane materials. First, a Nb membrane was loaded with oxygen to various bulk concentrations, and the correlation between bulk oxygen concentration and the sticking coefficient of H_2, α, was examined by

permeation experiments on account that α could provide a measure of non-destructive evaluation of the bulk oxygen concentration. Then, the bulk oxygen concentration was adjusted to 1.5 %, and sputtering was carried out by hydrogen plasma at 1113 K. The sputtering was periodically interrupted, and α was measured to evaluate the reduction in bulk oxygen concentration with sputtering time. The sputtering yield was estimated from the number of incident hydrogen ions and that of removed oxygen atoms. The value of sputtering yield thus obtained was compared with results of computer simulation with EDDY (computer simulation of Erosion and Deposition based on DYnamic model) code.

2. Experimental

The details of the permeation apparatus used in the present study are reported elsewhere [10], and only a brief description is given here. The permeation apparatus consists of two ultra-high vacuum chambers, i. e. upstream and downstream chambers, separated by a tubular specimen membrane. Both the upstream and downstream chambers are evacuated by turbo-molecular pumps (TMPs) and sputter-ion pumps (IPs) and equipped with analysis instruments such as pressure gauges and mass spectrometers. The upstream chamber comprises the main discharge chamber and auxiliary chamber, and Ta filaments are installed in the former chamber as electron sources for discharge. The latter is equipped with the above-mentioned analysis instruments. The discharge is carried out by applying a voltage between the filaments serving as cathode and the chamber wall serving as anode. The kinetic energy of incident ions onto the membrane surface was controlled by a bias voltage between the chamber wall and the specimen membrane. The specimen membrane in tubular form is heated ohmically, and the temperature of the membrane is measured with a thermocouple inserted in the membrane.

The specimen used was the membrane of polycrystalline Nb of 0.1 mm thickness. Before the measurement of sputtering yield, the correlation between bulk oxygen

concentration and the sticking coefficient of H_2, α, was examined by permeation experiments at various oxygen concentrations under symmetric membrane condition, i. e. the recombination coefficients of H_2 on the upstream and downstream surfaces are equal to each other. Under such condition, α can be evaluated from the permeation flux ϕ_p by the following relation: $\alpha = 2\phi_p / \phi_{H2}$, where ϕ_{H2} is incident flux of H_2 on the upstream surface. The details of permeation experiments are described elsewhere [11].

First, oxygen was removed from the membrane at around 1000 K by sputtering with hydrogen ions at H_2 pressures from 0.3 to 0.6 Pa and bias voltages from 300 to 600 V. The ion current density was kept at 2 mA•cm^{-2}; this ion current density corresponds to the ion flux of 1×10^{16} cm^{-2}•s^{-1}. The sticking coefficient α which was 2.1×10^{-4} at 970 K before sputtering reached the maximum value, 2.6×10^{-3}, after sputtering for 320 min. Such increase in α was ascribed to oxygen removal form the surface and bulk of membrane caused by continuous surface segregation of oxygen and sputtering as described in Section 3. The value of α after sputtering indicates that the oxygen concentration was about 0.03 at%. This oxygen concentration is considered to be determined by a balance between the rates of oxygen removal by sputtering and deposition by oxygen-containing impurity species in the plasma. Then, oxygen was introduced into the membrane step by step up to 1.5 at%, and the temperature dependence of α was measured at each step of oxygen doping. The method of oxygen introduction is given in a previous paper [12].

After the introduction of oxygen up to 1.5 at%, the membrane was sputtered by hydrogen plasma at 1113 K. The discharge was periodically interrupted, and the change in the bulk oxygen concentration was examined by measuring α. During the sputtering, the bias voltage and ion current density were adjusted to 600 eV and 1.1 mA•cm^{-2}; this ion current density corresponds to the ion flux of 7×10^{15} cm^{-2}•s^{-1}.

The surface concentration of oxygen was examined by Auger electron spectroscopy in the Department of Advanced Energy Engineering Science, Kyushu University. Sheet type

specimens containing 1 and 2 at% of oxygen were prepared, and Auger spectra were measured at 1113 K, i. e. the same temperature as the above-mentioned sputtering experiments. The energy of primary electron beam was adjusted to 3 keV. The pressure of residual gas during the measurements was less than 1×10^{-7} Pa.

3. Results and discussion

Figure 1 shows the temperature dependence of α after sputtering for given periods of time along with that observed for specimens of various oxygen concentrations. The open symbols indicate the values of α before sputtering. It is evident that α has strong dependence on the bulk oxygen concentration C_{OX}; it decreased radically with increasing C_{OX}. Hence, it was concluded that non-destructive evaluation of bulk oxygen concentration is possible by measuring α. This result is consistent with the observation in the previous study [12] that the
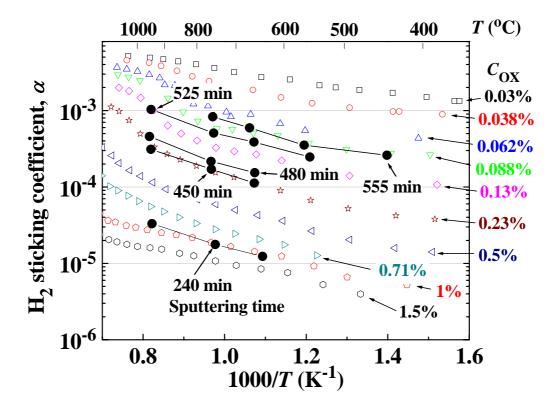

Fig.1   Change in α with bulk oxygen concentration and sputtering time.

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surface recombination coefficient of deuterium decreased with increasing bulk oxygen concentration. The mechanism underlying the correlation between α and C_{OX} will be discussed in a separate paper.

As mentioned in the previous section, the sputtering was started at $C_{OX} = 1.5$ at%. The sticking coefficient α increased with sputtering time as shown by the filled circles in Fig. 1. Such increase in α can be ascribed to the removal of oxygen not only from the surface but also from the bulk caused by continuous surface segregation of oxygen and sputtering. This is because no significant change in α was observed between respective runs of the sputtering experiments; α should decrease in the intervals of sputtering owing to the resegregation of oxygen if only surface concentration of oxygen was reduced and C_{OX} kept the initial value.

The change in C_{OX} with sputtering time t_S is shown in Fig. 2. The bulk oxygen concentration decreased with increasing t_S. This plot is roughly approximated by a single straight line, indicating that the sputtering yield and oxygen surface coverage kept almost
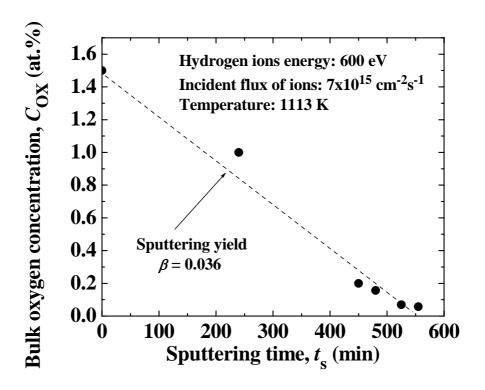

Fig. 2   Change in bulk oxygen concentration with sputtering time.

constant value in the range of C_{OX} from 1.5 to 0.058 at %. The sputtering yield of oxygen β can be evaluated from the slope of the plot by the following equation:

$$-dC_{OX} / dt_s = \beta \bullet \phi_{in} \bullet N / f \bullet h \tag{1}$$

where ϕ_{in} is the incident flux of ions, f the factor to convert the bulk oxygen concentration from at% to atoms$\bullet$cm^{-3}, h the thickness of membrane, and N the number of protons contained in incident ions, i. e. $N = 1$ for H$^+$, 2 for H$_2^+$ and 3 for H$_3^+$. By assuming $N = 1$, β was evaluated to be 0.036. The abundance ratio of H$^+$, H$_2^+$ and H$_3^+$ in the plasma, however, was not measured because operation of mass spectrometer during discharge was difficult due to its geometrical configuration. Hence, the value of β can range from 0.012 (for each proton in H$_3^+$) to 0.036 (for H$^+$). Another factor bringing uncertainty in β is the emission of secondary electron by ion bombardment. Namely, the secondary electron emission leads to the overestimation of incident ion flux. Ion beam experiments independently carried out in Bonch-Bruyevich University indicated that the emission yield of secondary electron was 0.2-0.3 for 20 keV H$_3^+$ (0.07-0.1 for each proton). Therefore, the error induced by secondary electron emission is considered to be about 10 %.

Figure 3 shows a typical example of Auger electron spectra obtained at 1113 K for Nb specimen containing 1 at% of oxygen. Only peaks of Nb and oxygen were observed, and no other impurity was detected. The peak-to-peak height ratio of Nb (167 eV) and oxygen (512 eV) was measured at several different points randomly-selected on the specimen surface. It ranged from 0.29 to 0.36, and the average value was 0.33. By assuming that oxygen was present only at the top layer, the oxygen coverage θ_{OX} was evaluated from the average value of peak-to-peak height ratio by taking account of the escape depth of Auger electrons from Nb. Namely, θ_{OX} was determined by the following equation:

$$\theta_{OX} \cong [O]/[Nb] = \frac{I(O)}{I(Nb)} \frac{S_{Nb}}{S_O} \frac{1}{\int_0^\infty \exp(\frac{-x}{\lambda \cos \delta}) dx}, \tag{2}$$

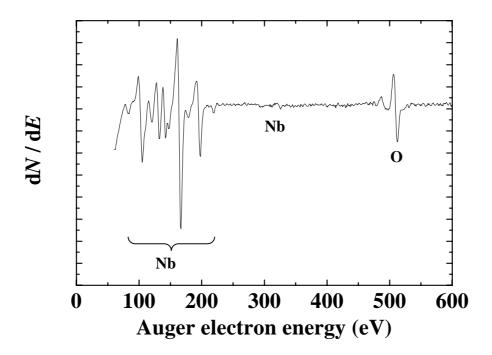where $I(O) / I(Nb)$ is the peak-to-peak height ratio, S_{Nb} and S_O are the atomic sensitivity

Fig. 3   Typical example of Auger spectra obtained at 1113 K for the specimen containing 1 at% of oxygen.

factors of Nb (1.3284) and oxygen (1.2571) at 3 keV of primary electron beam energy [13], x is the depth from the surface, λ the mean escape depth of Auger electrons from Nb (167 eV) in Nb, and δ the angle between detector and normal direction to the specimen surface. The escape depth λ was evaluated by the equation proposed by Seah and Dench [14]. The value of θ_{OX} thus evaluated was close to unity. The oxygen coverage on the specimen containing 2 at% of oxygen was also estimated to be   1. Hence, it was concluded that θ_{OX} on the surface of specimen used for the sputtering experiments, C_{OX} in which was 1.5 at%, was also close to unity. It is appropriate to consider that θ_{OX} kept the value close to unity even under sputtering, because no significant reduction in plasma-driven permeation rate was observed during the discharge. Namely, the above-mentioned sputtering yield, 0.012-0.036, corresponds to the value at θ_{OX} 1. It appears that the rate of oxygen diffusion was high enough in comparison with that of sputtering under the present conditions.

The sputtering yield obtained experimentally was compared with the results of calculation with EDDY code. The physical sputtering yield can be evaluated with this code by

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taking account of both elastic and inelastic collisions. The details of this code are described elsewhere [15]. In the calculation, the oxygen concentration on the surface was adjusted to 50 at% as mentioned above and that in bulk to 1 at%. The binding energy of oxygen on the surface was adjusted to 7.2 eV as a summation of the heat of adsorption of O_2 molecule on the surface of group 5 metals (4.6 eV for $1/2O_2$) [16] and the dissociation energy of O_2 (2.6 eV for $1/2O_2$) [17]. The dominant incident ion is assumed to be H^+. The calculation was carried out with various incident energies from 200 to 600 eV to simulate the incidence of 600 eV H^+, H_2^+ and H_3^+ ions and incident angles from 0° to 89° against the normal direction to the surface. The sputtering yield was more sensitive to the incident angle than the incident energy, and it ranged from 0.0038 to 0.0058 at 0° and 0.036 to 0.050 at 89°. The values of sputtering yield obtained experimentally, 0.012-0.036, fall in this range. Therefore, it is appropriate to consider that both the experiments and calculations are reliable, and physical sputtering is the dominant process of oxygen removal from the membrane surface under the present conditions. The characterization of incident ions, i. e. incident angle distribution and the abundance ratio of H^+, H_2^+ and H_3^+ ions, is necessary for more detailed discussion.

4. Conclusions

(1) The sticking coefficient of H_2, α, on Nb surface sensitively decreased with increasing bulk oxygen concentration and could be used as a reliable measure for non-destructive evaluation of bulk oxygen concentration.

(2) The surface oxygen coverage was close to unity at 1113 K and 1-2 at% of bulk concentration.

(3) The sputtering yield of oxygen on Nb surface by hydrogen ions was estimated to be 0.012-0.036 under the bias voltage of 600 eV.

(4) The results of computer simulation with EDDY (computer simulation of Erosion and Deposition based on DYnamic model) code was in reasonable agreement with the

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experimentally-obtained sputtering yield.

Acknowledgements

References

[1] For examples, A. I. Livshits, Vacuum, **29** (1979) 103; A. I. Livshits, M. E. Notkin, Y. M. Pustovoit and A. A. Samartsev, Vacuum, **29** (1979) 113; F. Waelbroeck, "Influence of Bulk and Surface Phenomena on the Hydrogen Permeation through Metals", Forschungszentrum Jülich report, Jül-1966, 1984; A. I. Livshits, M. E. Notkin and A. A. Sammartsev, J. Nucl. Mater., **170** (1990) 79.

[2] A. I. Livshits, N. Ohyabu, M. Bacal, Y. Nakamura, A. Busnyuk, M. Notkin, V. Alimov, A. Samartsev, H. Suzuki and F. Sube, J. Nucl. Mater., **266-269** (1999) 1267.

[3] Y. Nakamura, S. Sengoku, Y. Nakahara, N. Suzuki, H. Suzuki, N. Ohyabu, A. Busnyuk, M. Notkin and A. Livshits, J. Nucl. Mater., **278** (2000) 312.

[4] Y. Nakamura, N. Ohyabu, H. Suzuki, Y. Nakahara, A. Livshits, M. Notkin, V. Alimov and A. Busnyuk, Fusion Eng. Des., **49-50** (2000) 899.

[5] A. I. Livshits, Y. Hatano and K. Watanabe, Fusion Sci. Technol., **41** (2002) 882.

[6] Y. Nakamura, A. Busnyuk, H. Suzuki, Y. Nakahara, N. Ohyabu and A. Livshits, J. Appl. Phys., **89** (2001) 760.

[7] A. Busnyuk, Y. Nakamura, Y. Nakahara, H. Suzuki, N. Ohyabu and A. Livshits, J. Nucl. Mater., **290-293** (2001) 57-60.

[8] M. E. Notkin, A. I. Livshits, A. M. Bruneteau and M. Bacal., Nucl. Intstrum. Meth. Phys. Res. B, **179** (2001) 373.

[9] A. I. Livshits, M. E. Notkin, N. Ohyabu, Y. Nakamura, I. P. Grigoriadi and A. A. Samartsev, Phys. Scr., **T108** (2004) 23.

[10] Y. Hatano, M. Nomura, K. Watanabe, A. I. Livshits, A. O. Busnyuk, Y. Nakamura and N. Ohyabu, Ann. Rep. Hydrogen Isotope Res. Ctr. Toyama Univ., **21** (2001) 13.

[11] Y. Hatano, A. Livshits, A. Busnyuk, M. Nomura, K. Hashizume, M. Sugisaki, Y. Nakamura, N. Ohyabu and K. Watanabe, Phys. Scr., **T108** (2004) 14.

[12] R. Hayakawa, A. Busnyuk, Y. Hatano, A. Livshits and K. Watanabe, Phys. Scr., **T103** (2003) 113.

[13] K. D. Childs, B. A. Carlson, L. A. LaVanier, J. F. Moulder, D. F. Paul, W. F. Stickle and D. G. Watson, "Handbook of Auger Electron Spectroscopy", 3 rd edition (edited by C. L. Hedberg), Physical Electronics, Eden Prairie, MN, 1995, p. 404.

[14] M. P. Seah and W. A. Dench, Surf. Interf. Anal., **1** (1979) 2.

[15] K. Ohya et al., J. Nucl. Mater., **290-293** (2001) 303.

[16] G. A. Somorjai, "Chemistry in Two Dimensions: Surfaces", Cornell University Press, Itacha, NY, 1981, p. 293.

[17] for example, K. Takayanagi, "Denshi•Genshi•Bunshi no Shototsu", Baifu-kan, Tokyo, 1972, p. 139. (in Japanese)