

H AND D RETENTION IN WNO_x FILMS

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Abstract

W is the main wall material in the international fusion device and seeding of N containing gas is under consideration for plasma edge cooling and H isotope removal from the wall. In this environment with residual oxygen gas, it is highly anticipated that WNO_x layers are formed on W. Thus, knowledge of H-isotope retention in WNO_x layers is important for understanding of H-isotope recycling. Using WNO_x ($x=0.4\pm0.2$) films prepared on C-plane-cut-sapphire ($\text{C-Al}_2\text{O}_3$) substrate, we have investigated H and D retention, and depth profile of H and D, using $\text{D}({}^3\text{He}, \alpha)\text{H}$ nuclear reaction analysis (NRA), $\text{H}({}^{15}\text{N}, \gamma)\text{O}$ -NRA and elastic recoil detection (ERD). In as-deposited films, we find a high density ($0.4\times10^{22}\text{ cm}^{-3}$) of H by ${}^{15}\text{N}$ -NRA. After low energy D-plasma exposure ($\sim10^{18}\text{ cm}^{-2}$), we also find a large amount of D-retention ($\sim10^{17}\text{ cm}^{-2}$) by ${}^3\text{He}$ -NRA, as well as high density D by ERD, and that high density of H remains in the film. These results cannot be understood by a simple H-D replacement.

Keywords: WNO_x , H and D retention, Ion beam analysis

1. INTRODUCTION

W is the main wall material in the international fusion device and there are many issues of plasma-surface (wall) interactions as described in [1]. One of the issues is cooling of the plasma edge, reducing thermal load on the wall and for this purpose, N_2 seeding is considered [2, 3]. Furthermore, discharge of N_2 containing gas is concerned for removal of H isotopes in the wall, referring to the results of C wall [4, 5]. During N-plasma exposure or N ion implantation, formation of tungsten nitride on W has been observed [6, 7] and negligible diffusion of D in tungsten nitride has been reported [8]. It is highly anticipated in the presence of residual oxygen gas that tungsten oxynitride layers are formed on W. Thus, knowledge of H-isotope retention in WNO_x layers is important for understanding of H-isotope recycling.

In this study, WNO_x films are prepared on $\text{C-Al}_2\text{O}_3$ substrate. Rutherford backscattering spectroscopy (RBS) of He^+ ions leads to the composition, $x=0.4$ considering sample variation and the film thickness of $\sim50\text{ nm}$. X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation shows a strong peak at the diffraction angle (2θ) $\approx37^\circ$ and a weak peak at $\approx77^\circ$. These peaks are assigned as hexagonal-WN, referring to JCPDS card data and no peaks are observed other than WN and $\text{C-Al}_2\text{O}_3$ ($2\theta=41.7^\circ$) [9]. Films are exposed to H or D plasma generated by discharge at low voltage. We have investigated H and D retention, and depth profile of H and D, using $\text{D}({}^3\text{He}, \alpha)\text{H}$ -NRA, $\text{H}({}^{15}\text{N}, \gamma)\text{O}$ -NRA and ERD. We find a large amount of H and D retention. Based on these results, H-D replacement is discussed.

2. EXPERIMENTAL

2.1 Sample preparation and characterization of as-deposited film

WNO_x films are prepared on $\text{C-Al}_2\text{O}_3$ substrate ($\sim0.5\times1\text{ cm}^2$ in size and 0.3 mm in thickness) at substrate temperature of 425°C by using the method described in [10], i.e., a reactive radio-frequency (RF)-magnetron-sputtering deposition method with W target (99.95 % purity) and 8 Pa of N_2 gas. Substrates are subjected to ultrasonic rinse in ethanol prior to film deposition. RBS of 1.8 MeV He^+ ions are

employed to evaluate the film composition and thickness. Stopping powers required for RBS analysis are calculated using the TRIM code [11]. N_2 gas pressure described above is chosen so that the N composition is close to unity (N_2 gas variation from 1 to 20 Pa results in the composition N/W from 1.25 to 1.1). Crystalline structure and quality of films are examined by XRD. The substrate temperature is optimized so that the XRD intensity is maximized.

Composition and crystalline structure of as-deposited films are determined from RBS, XRD, atomic force microscopy (AFM) and Energy-dispersive X-ray (EDX) [10]. Composition is obtained to be $WN_{1.1\pm0.1}O_x$ and $x=0.4\pm0.2$ (considering sample variation) from RBS (RBS accuracy is estimated to be 10 % for N composition). O and C are observed by EDX, and C impurities (evaluated to be $\leq 10^{16} \text{ cm}^{-2}$ by RBS) are most likely located near surface of films. XRD shows a strong peak at $\sim 37^\circ$ and a weak peak at 77° . No peaks are observed other than WN and $C-Al_2O_3$ ($2\theta=41.7^\circ$), i.e., peaks of W ($2\theta=40, 58^\circ$), WO_3 ($2\theta=23, \sim 48^\circ$) are not observed [9]. Non-circular shape of grains is observed by AFM, indicating non-cubic crystalline structure. From these results and JCPDS data, crystalline structure is identified as hexagonal WN. It also appears that the ratio of XRD intensity at $\sim 77^\circ$ over that of (100) diffraction at $\sim 37^\circ$ varies from 4-9 % depending on samples and thus the diffraction at $\sim 77^\circ$ is assigned as (102) diffraction, since the ratio is expected to be a constant, if (200) diffraction is responsible for the diffraction at $\sim 77^\circ$ and it is assumed that a small fraction of grains has (102) growth orientation. Hereafter $WNO_{0.4}$ is employed for ion beam analysis. The film density necessary for RBS and calculation of range parameters of D (H) is evaluated to be $5.2 \times 10^{22} \text{ W cm}^{-3}$ (17.64 g cm^{-3}), using a- and c-lattice-parameters of 0.28117 and 0.2815 nm, respectively, which are determined from the diffraction angles of 36.88° (100) and 77.4° (102), respectively, averaging more than ten samples. These lattice parameters appear to be smaller by 2.8 % and 0.4 %, respectively than the values in the literature [9]. Using the film thickness determined from RBS, the deposition rate is obtained to be $\sim 0.8 \text{ nm/min}$ for the deposition time of 10 - 180 min.

2.2 H and D exposure

Exposure to D- or H-plasma is performed at room temperature, using a similar method [12]. WNO_x films are placed on one of the stainless-steel-disk-electrodes (2 cm in diameter) covered with W sheet in a glass-tube (the base pressure is $\sim 3 \text{ Pa}$) and exposed to glow-discharge plasma at AC (60 Hz)-voltage of 1.5 kV between the electrodes (separation of $\sim 3 \text{ cm}$) in 67 Pa of D_2 - or H_2 - gas. The temperature rise during exposure is $\sim 20^\circ \text{C}$. In this discharge condition, fractions of D_3^+ (or H_3^+) and D_2^+ (or H_2^+) are 60 % and 40 %, respectively. A fraction of D^+ (or H^+) is negligibly small (a few %) [13]. The maximum energy of D (H) corresponding to D_3^+ (or H_3^+) and D_2^+ (or H_2^+) are 0.707 and 1.06 keV, respectively, assuming that D_3^+ (or H_3^+) and D_2^+ (or H_2^+) are split into three and two D (H) upon incidence on the sample surface. The corresponding projected range calculated using TRIM [11] are 3.8 nm (0.707 keV D), 5.3 nm (1.06 keV D), 3.6 nm (0.707 keV H) and 5.1 nm (1.06 keV H), respectively.

2.3 H and D detection

Three methods are employed to detect D and H; $D(^3\text{He}, \alpha)p$ -NRA, $H(^{15}\text{N}, \gamma)\text{O}$ -NRA and ERD. ^3He -NRA is a less time consuming method. The amount of D retained in the films is analyzed by detecting α particles from $D(^3\text{He}, \alpha)p$ with a solid state detector (SSD), using 0.7 MeV $^3\text{He}^+$ ions at normal incidence angle and detection angle of 150° . The NRA cross section is taken to be 34.3 mb/sr [14]. The probing depth is estimated to be $0.5 \mu\text{m}$, based on the calculated path length [11] where the ^3He beam of 0.7 MeV slowed down to 0.25 MeV, i.e., the NRA cross section is reduced to one-fifth of the maximum value. The probing depth is much larger than the film thickness of $\sim 50 \text{ nm}$ used in this study. As will be mentioned later, the depth resolution is poor and only integrated amount of D is meaningful. To analyze H and D concentration, $H(^{15}\text{N}, \gamma)\text{O}$ -NRA and ERD are useful as described below.

H concentration is analyzed by $H(^{15}\text{N}, \gamma)\text{O}$, using ^{15}N beam at normal incidence with a BGO scintillating detector. ZrH_2 sample is employed for reference. ^{15}N beam of 6-7 MeV is obtained utilizing a Tandem accelerator at Japan Atomic Energy Agency, Tokai. To obtain both D and H concentration, ERD is performed with a SSD, using 1.5 MeV He^+ at incident angle of 12° and detecting angle of 10° measured from the sample surface (recoil angle of 22°). A film of $6 \mu\text{m}$ Al is placed in front of the SSD to stop scattered He. RBS at scattering angle of 150° is also measured at the same time of ERD measurement

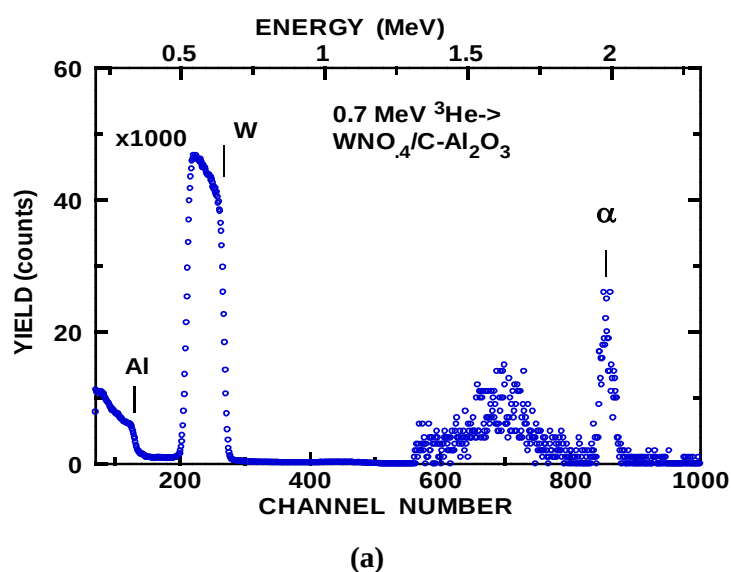
for obtaining the number of incident He ions. ZrH₂ and ZrD₂ samples are employed for reference ($N_{Zr}=4.29 \times 10^{22} \text{ cm}^{-3}$).

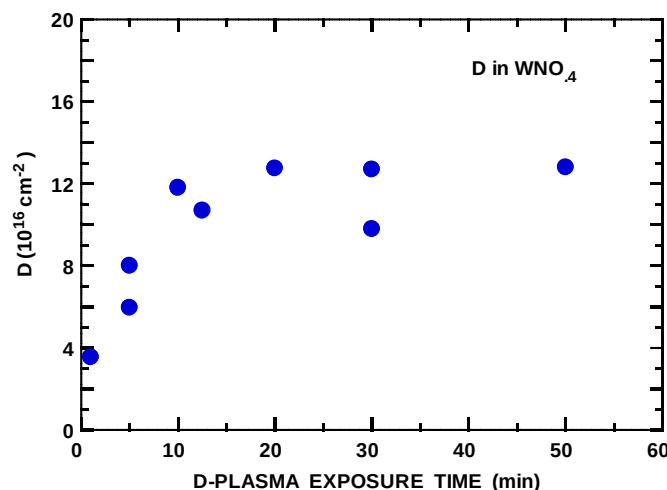
3. RESULTS AND DISCUSSION

3.1 D retention

Fig. 1(a) shows a typical spectrum of α -particles around 1.98 MeV from $D(^3\text{He}, \alpha)p$ nuclear reaction and RBS spectrum of W with its edge at 0.66 MeV. A broad peak seen ~ 1.7 MeV is due to protons from the nuclear reaction, noticing that the partial energy of protons (emitting energy of 12.74 MeV) is deposited in the depletion layer of the SSD (the maximum depletion layer is $\sim 100 \mu\text{m}$), which is detected through amplifier and multi-channel analyzer, and that the depletion layer and thus the energy of peak depend on the applied bias voltage of SSD. Width of α -particle spectrum is obtained to be $\sim 40 \text{ keV}$, which is larger by a factor of 2 than the width obtained by 1.5 MeV He^+ RBS of thin film of Au (a few nm) on Si. The depth resolution corresponding to 40 keV is estimated to be $0.7 \mu\text{m}$. This is larger by a factor of 10 than the film thickness and the discrepancy could be due to poor accuracy of the estimated stopping power factor (conversion factor from the observed energy to depth, so-called stopping power factor, of -59 eV/nm , given by $dE_\alpha/dE_1 \cdot S_1/\cos(\theta_1) + S_2/\cos(\theta_2)$), which is very sensitive to the NRA geometry and the energy spread originated from a finite solid angle of SSD. Here, E_α and E_1 are the energies of α -particles and the incident ^3He , S_1 and S_2 stopping powers of α -particles and incident ^3He , and θ_1 and θ_2 incident angle (0°) and detection angle (30°) measured from the normal to the sample. Thus, total counts of particles or the integrated amount of D is concerned.

From total yield of α and W yield near edge, the areal density of D (integrated D concentration over the film thickness) is evaluated and the areal density vs exposure time is shown in Fig. 1(b). It is seen that D areal density saturates at $13 \times 10^{16} \text{ cm}^{-2}$ around exposure time of 20 min. It is also found that D of $3 \times 10^{16} \text{ cm}^{-2}$ and W of $3.5 \times 10^{15} \text{ cm}^{-2}$ (0.56 nm) are detected for D-exposure to C-Al₂O₃ substrate for 20 min. Thus the correct saturation-value is $10 \times 10^{16} \text{ cm}^{-2}$. Furthermore, film thickness used for D-retention ranges from 35 to 80 nm and it appears that D retention is independent of film thickness, indicating that D's are distributed within the minimum thickness. As mentioned earlier, the projected ranges of H and D are nearly the same and H's are found to be uniformly distributed within 20 nm by $\text{H}(^{15}\text{N}, \gamma)\text{O-NRA}$ and calculated range profile as described later. D concentration is estimated to be $\sim 5 \times 10^{22} \text{ cm}^{-3}$, meaning that D/W in WNO_x is nearly unity.





(b)

Fig. 1 (a) NRA spectrum of α -particles (1.98 MeV) and protons (~ 1.7 MeV) for WNO_x film on C- Al_2O_3 obtained by using 0.7 MeV $^3\text{He}^+$. RBS is seen below 0.7 MeV with the W edge at 0.66 MeV. Yields below channel number of 550 are to be multiplied by 10^3 . Film thickness of this film is 67 nm. (b) D areal density (estimated error of 10 %) as a function of exposure time of D-plasma (applied voltage of 1.5 kV in 67 Pa of D_2 gas).

The discharge current is obtained to be ~ 1.2 mA, and D_3^+ and D^+ flux is roughly estimated to be 1.8×10^{14} and $1.2 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, assuming that one half of the discharge power is dissipated in ionization and another one half is carried by electrons, and considering further a factor of 2 for two electrodes (~ 0.15 mA of D_3^+ and D_2^+). Then total flux of D is evaluated to be $7.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, taking 60 % of D_3^+ and 40% of D_2^+ (a small fraction of D^+ is discarded) into account as mentioned earlier. The fluence is $9 \times 10^{17} \text{ cm}^{-2}$ for 20 min and thus the retention efficiency (defined as the ratio of D-retention over D-fluence) is $\sim 10\%$. Similar efficiency has been reported [15]. Low retention efficiency implies dynamic retention. It also appears that D-retention remains nearly unchanged when sample is kept in vacuum and that decreases to half after a week when sample is kept in desiccator (in air) at room temperature (slow release) as shown in Fig. 2. Similar results are observed for TiO_2 [16] and Fe_2O_3 [17].

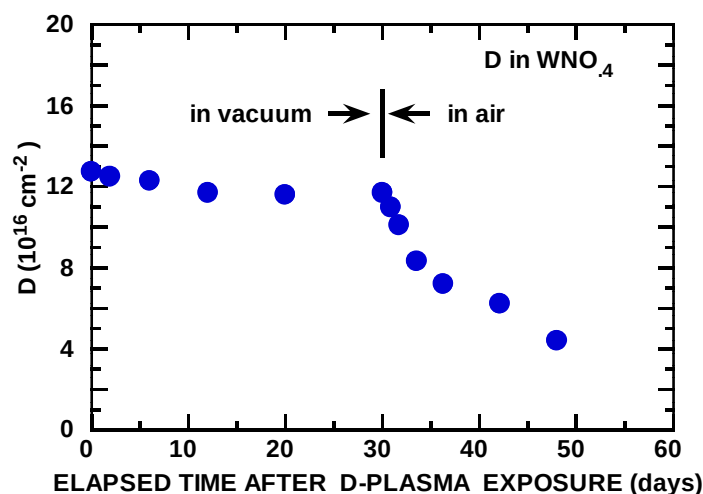


Fig. 2 Amount of D-retention in WNO_x (film thickness of 67 nm) vs elapsed time (days) after D-plasma exposure kept in vacuum and in air afterwards.

3.2 H and D concentration

Spectrum of γ (energy of ~ 4.4 MeV) from ^{15}N -NRA for WNO_x is shown in Fig. 3(a) and background spectrum is also shown for comparison. Background yield is less than $0.1 \text{ counts s}^{-1}$. From total γ -yield (total counts in the region indicated by an arrow in Fig. 3(a)) and reference yields for ZrH_2 , H concentration is evaluated as a function of depth after ^{15}N beam energy is converted to the depth, which is calculated using TRIM code [11]. The natural width of the nuclear reaction is very narrow (1.8 keV at the resonance energy of 6.385 MeV), however the effective width becomes much broader ~ 10 keV, by taking the Doppler broadening due thermal vibration of H into account [18]. Here, one dimensional formula and thermal energy of H (0.025 eV) are employed. H existing in the depth corresponding to the effective width contributes to the NRA yield. Thermal vibration amplitude is assumed to be independent of sample in this study and this point is to be investigated. H concentration is shown in Fig. 4 for WNO_x (H-plasma exposure of 20 min) and as-deposited film. In as-deposited film, H distribution is nearly uniform except for a slightly high concentration around very near surface, and the areal density is evaluated to be $1.9 \times 10^{16} \text{ cm}^{-2}$ (concentration of $0.38 \times 10^{22} \text{ cm}^{-3}$ times film thickness of 50 nm). For the film exposed to H-plasma, H concentration increases near surface within 20 nm and this profile agrees with the calculated range profile shown in Fig. 5 and also consistent with the result of negligible diffusion in WN [8]. However, the H concentration is much lower (a factor of 5) than the value estimated from the D-retention as described earlier. When the reaction width of 10 keV (corrected for the Doppler broadening) is applied, the depth resolution is estimated to be 2 nm (4.74 keV/nm for ^{15}N at 6.4 MeV in WNO_x) and this cannot explain the above discrepancy. The discrepancy could be partly due to sample dependence of thermal vibration amplitude and to be investigated. However this may not be a major factor, because it is unlikely that thermal vibration amplitude differs by more than a factor of 5.

ERD spectrum is shown in Fig. 6 for WNO_x (exposed to D-plasma for 30 min). It is seen that D and H distribute within the film. Maximum H and D concentrations are evaluated to be 2.2 and $3.7 \times 10^{22} \text{ cm}^{-3}$, respectively, using ZrH_2 and ZrD_2 as references. H concentration is larger by a factor of 5 than that before D-plasma exposure (Fig. 4), indicating H uptake during D-plasma exposure and/or underestimation of H concentration by ^{15}N -NRA. D concentration is slightly smaller but comparable with that estimated from ^3He -NRA. These results cannot be explained by a simple replacement of H and D.

Finally, it is found that the XRD intensity of (100) diffraction decreases by $\sim 20\%$ at exposure time of 20 min and decreases further as increasing the time, in contrast to the saturation of D-retention at 20 min. It is also found that the diffraction angle decreases (increase of lattice parameter) by $\sim 0.7\%$ at 20 min exposure. Inclusion of D or H, and irradiation of low energy D or H on lattice disordering is to be investigated.

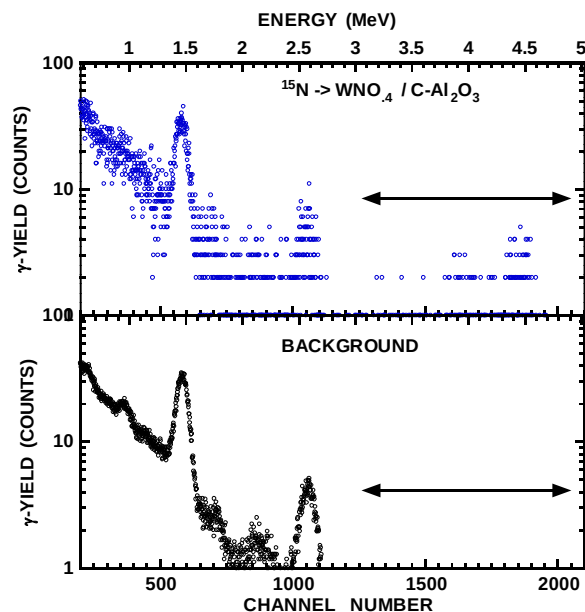


Fig. 3 (a) Spectrum of γ (energy of ~ 4.4 MeV) from $H(^{15}\text{N}, \gamma)\text{O}$ nuclear reaction for WNO_x (H-plasma exposure for 20min). A horizontal arrow indicates the energy region (3 - 4.9 MeV) to obtain total γ yields for evaluation of H concentration. Time of measurement is 100 sec. (b) Background spectrum for equivalent time of measurement is 100 sec.

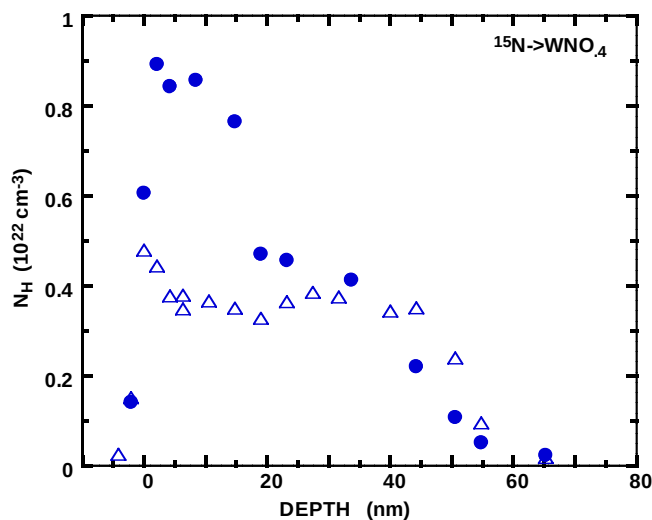


Fig. 4 H concentration obtained by $H(^{15}\text{N}, \gamma)\text{O}$ -NRA for WNO_x (H-plasma exposure for 20min) ($\bullet$) and as deposited film (Δ).

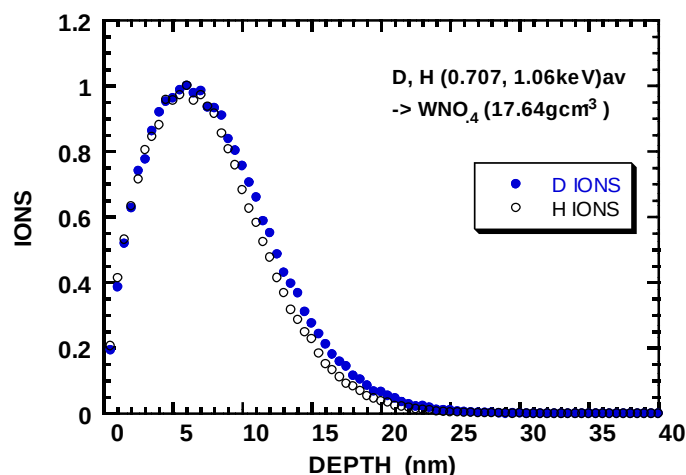


Fig. 5 Calculated range profile of D (●) for 60 % D_3^+ and 40 % D_2^+ with the maximum energy of 2.12 keV and H (Δ) [10] for 60 % H_3^+ and 40 % H_2^+ .

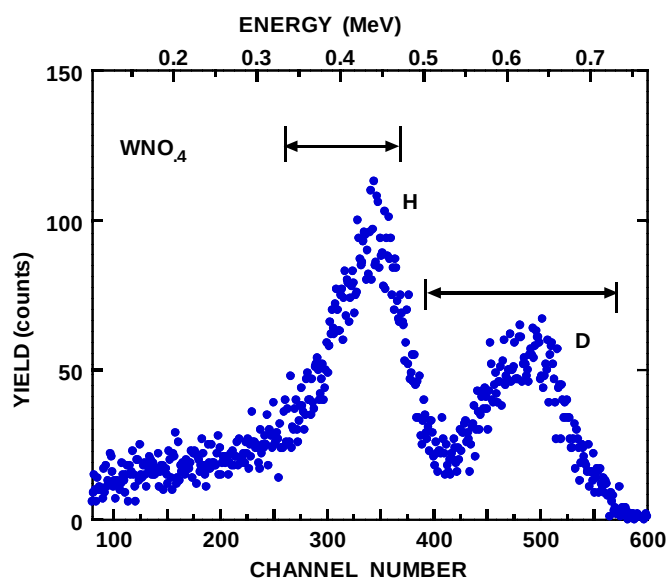


Fig. 6 Elastic recoil yields of H and D obtained by 1.5 MeV He^+ for WNO_x exposed to D-plasma (30 min). Peaks at right and left hand sides represent D and H recoil spectra. Horizontal lines with arrows indicate the surface to the depth corresponding to the film thickness.

4. SUMMARY

We have prepared hexagonal- WNO_4 films on $C-Al_2O_3$ and crystalline structure has been determined from the results of composition analysis (RBS), surface morphology (AFM) as well as XRD. We have investigated H and D retention under low energy H- or D-plasma exposure. It appears that H and D distribute within the film thickness and it is more likely within 20 nm of the calculated range profile. A serious discrepancy of H concentration is found depending on the method.

ACKNOWLEDGEMENT

XRD has been performed at Radio Isotope Center, Nagoya University. The authors thank to Mr. T. Masuda for technical support of usage of accelerators at Nagoya University.

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