富山大学水素同位体科学研究センター研究報告 21: 27-37, 2001.

論 文

He予照射タングステンにイオン注入したトリチウムの熱的挙動

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Thermal Behavior of Tritium Implanted in Tungsten Pre-Irradiated with He

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(Received March 31, 2002; Accepted December 20, 2002)

ABSTRACT

Thermal behavior of tritium implanted in tungsten pre-irradiated with a given fluence of helium was examined by β-ray-induced X-ray spectrometry (BIXS) under a condition of isochronal heating. To estimate changes in tritium distribution caused by the heating, Ar(Kα) and W(Mα) X-rays were mainly utilized as probes of tritium detection. The intensity of the former X-rays linearly decreased with increase in heating temperature, while that of the latter X-rays was almost constant up to 600 K and dramatically decreased above this temperature, indicating existence of strong trap sites. Such thermal behavior on X-ray intensity coincides with the understanding of thermal desortption spectra of deuterium. It was thought, therefore, that strong trap sites of tritium were due to the effects of bubbles generated by the helium pre-irradiation, and the trapping energy of tritium was estimated to be about 1.2 eV. Moreover, change in depth profiles of tritium with heating was evaluated by analyzing the observed X-ray spectra by means of computer simulation, and changes in the concentration of tritium retained in surface layers were examined.

1. Introduction

Tungsten is one of promising candidates for divertor materials of the International Thermo-nuclear Experimental Reactor (ITER), because it has advantageous features such as a high melting point, a low vapor pressure and a low sputtering erosion yield. From this viewpoint, a number of studies have been reported for irradiation effects of hydrogen, deuterium, helium and those mixtures on retention and trapping of hydrogen isotopes in tungsten. Recent activities in evaluation of high-Z materials focusing on tungsten and its alloy were reviewed in detail by Yoshida [1]. In addition, for example, Iwakiri et al. [2] have reported about the effects of helium pre-irradiation on the trapping of deuterium implanted into tungsten by using a technique of thermal desorption spectrometry. However, few reports on thermal behavior of tritium for tungsten still appear.

The β-ray-induced X-ray spectrometry (BIXS), which has been recently proposed by Matsuyama et al. [3], is of high potentiality for the measurements of tritium retained in surface layers and/or bulk of a material. In the present measuring technique, "surface layers" means the penetration depth of β-rays in a material, and "the bulk" means a far deeper region than the penetration depth. In comparison with other tritium measuring techniques, BIXS has some advantageous points: e.g., nondestructive and quantitative measurements are possible and tritium amounts in surface layers and bulk of a material can be independently measured.

As an example of practical application of this technique, the present method was employed to estimate diffusion behavior of tritium at room temperature in a tungsten plate [4]. The tungsten plate implanted tritium ions was measured for a long duration at room temperature in the argon atmosphere. Characteristic X-rays of W(Lα) and W(Mα) as well as Ar(Kα) X-rays were observed, and it was seen that intensities of those X-rays clearly changed with time even at room temperature because of the diffusion of tritium from surface layers into the bulk of tungsten. However, when a tungsten plate was irradiated with a given amount of helium ions at room temperature prior to the implantation of tritium, changes in the X-ray intensities with time were negligibly small, indicating that most of the implanted tritium ions are strongly trapped in surface layers of tungsten.

From this view point, in this study, thermal behavior of tritium implanted in tungsten pre-irradiated with helium was examined under condition of isochronal heating by using the BIXS. Changes in the X-ray spectra with heating are shown and effects of helium pre-irradiation for tritium retention will be discussed.

2. Experimental

2. 1. Materials

Polycrystalline tungsten plate fabricated by the powder metallurgy was used as a sample. The purity and the size of a tungsten plate were 99.95% and 10x10x0.02 mm^3, respectively. A given amount of helium ions was irradiated the tungsten plate at room temperature before tritium implantation. Energy and fluence of helium ions were 8 keV and $5x10^{21}$ ions/m^2, respectively. Shape of the implantation spot was ellipse of 5x3.5 mm. It is reported that helium irradiated under the present conditions distributes from a near surface to 80 nm [2].

Tritium used for an ion implantation was diluted with deuterium, and the concentration of tritium was about 0.8%. The purity of deuterium was 99.6% and that of argon used for X-ray measurements was 99.999%.

2. 2. Implantation device of tritium ions

The polycrystalline tungsten plate was irradiated with tritium ions by using the specially designed tritium implantation device. Main components of the tritium implantation device consisted of a tritium storage-supply-recovery part, an implantation part equipped with a conventional ion gun, a high vacuum system and a sample transfer system. The detailed construction and specifications of the tritium implantation device is described elsewhere [5].

Figure 1 shows the detailed drawing of a sample holder used for tritium implantation. The sample was sandwiched between a thin molybdenum plate attached with an almel-chromel thermocouple and a shielding plate having four holes of 6 mmϕ in diameter. The molybdenum plate was used to ensure uniform thermal transmission from a heater, which was made of W-Re alloy, and

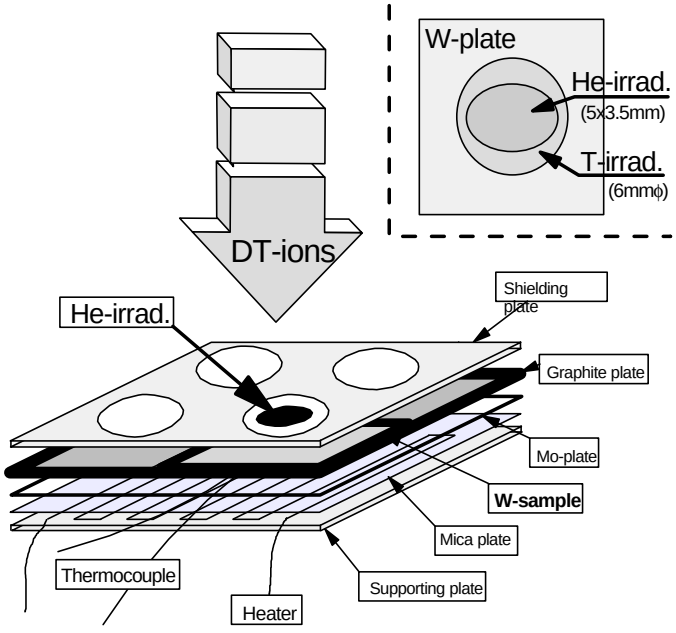

Fig. 1. A bird's-eye view of the sample holder used for tritium implantation.

the heater was fixed with a thin mica foil beneath the molybdenum plate. To estimate the tritium fluence, a thin graphite plate was also placed on the molybdenum plate as a standard material. This is due to a reason that a quantitative measuring technique by BIXS has been already established for graphite sample [6]. To measure ion current during the implantation of tritium, the sample holder was electrically disconnected from the ground level using an insulating material. In addition, the sample was biased +18 V to prevent secondary electron emission due to the ion implantation in order to the measurements of a net ion current.

2. 3. Measuring device of b-ray-induced X-rays

High pure Ge detector, which was purchased from CANBERRA, was used to measure X-rays induced by β-rays. Since major energy distribution of the X-rays is considerably lower than 18.6 keV of the maximum energy of β-rays, a window of the X-ray detector was made of a specially designed beryllium plate (8 μm) to gain effective penetration efficiency of low energy photons. In addition, to lower background level due to natural radioactivity, both detector and sample were sandwiched with two lead bricks of 5 cm in thickness.

2. 4. Experimental procedures

After the helium-irradiated sample was installed in the implantation device, it was evacuated for about one week at room temperature and then degassed at 673 K in vacuum. After the residual pressure reached below 10^{-5} Pa, the sample was cooled down in vacuum to implant tritium ions. Tritium implantation was carried out under the following conditions: the implantation temperature was set at room temperature. In addition, acceleration energy and implantation time of tritium ions were kept at 1 keV and 15 min, respectively. During the implantation, the total pressure in the implantation device was kept constant at 4 Pa.

After the tritium implantation, the implantation device was evacuated for a week to lower the release of tritium from the walls of the implantation device when taking out the sample. Just before taking out the sample, the implantation device was finally decontaminated by using a conventional tritium removal system to ensure safety. After this decontamination, the sample was transferred from the implantation device to the front of an X-ray detector, and the measurement of an X-ray spectrum was started. During the X-ray measurements, both the sample and the X-ray detector were placed in an argon atmosphere and the distance between them was kept at 5 mm. The flow rate of Ar was controlled at 40 cm^3/min.

To examine retention behavior of tritium at elevated temperatures, the sample implanted tritium was isochronally heated for 30 min at the temperature range from 373 to 973 K by using another conventional vacuum device. An X-ray spectrum was measured at room temperature after vacuum heating at a given temperature. Most X-ray spectra were measured for 12 hours, and those used for analysis of depth profile were measured for above 60 hours.

3. Results and discussion

3.1. Attenuation of b-rays and characteristic X-rays in tungsten

Three characteristic X-ray peaks were observed for the tungsten sample implanted tritium as shown later: one is the characteristic X-rays (Ar(Kα)) of argon, and the others (W(Lα) and W(Mα)) are those of tungsten. The former X-rays can be induced by tritium atoms distributed within the average escape depth of the β-rays. The depth in tungsten was estimated to be 50 nm or smaller. In this paper, this depth is denoted below as "surface layers". On the other hand, the latter X-rays can be mainly induced by β-rays emitted in bulk of tungsten. Energies of characteristic X-rays for W(Lα) and W(Mα) peaks are 8.40 and 1.77 keV, respectively. Intensity of the W(Mα) X-rays will give the information about tritium concentration in shallow layers in comparison with the W(Lα) X-rays. Attenuation curves of β-rays and W(Mα) X-rays in tungsten are shown in Fig. 2. It is clear from the figure that an intensity of the W(Mα) X-rays gives information with respect to tritium concentration within a range from the surface to about 1 μm. This range is denoted below as "sub-surface layers". Although information for tritium distribution in a far deeper region than the sub-surface layers can be obtained from W(Lα) X-ray intensity, it was not favorable for the present study because of a considerably weak intensity. Namely, tritium behavior in the surface and/or sub-surface layers of tungsten can be evaluated by tracking changes

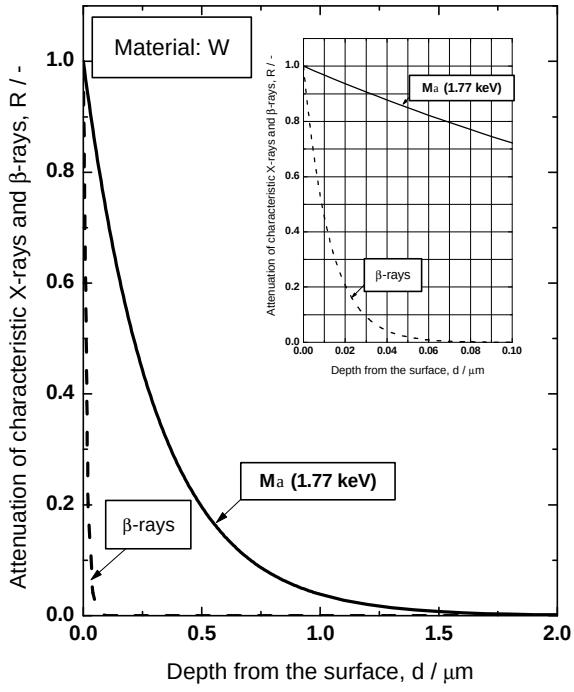

Fig. 2. Attenuation curves for β-rays and W(Mα) in tungsten.

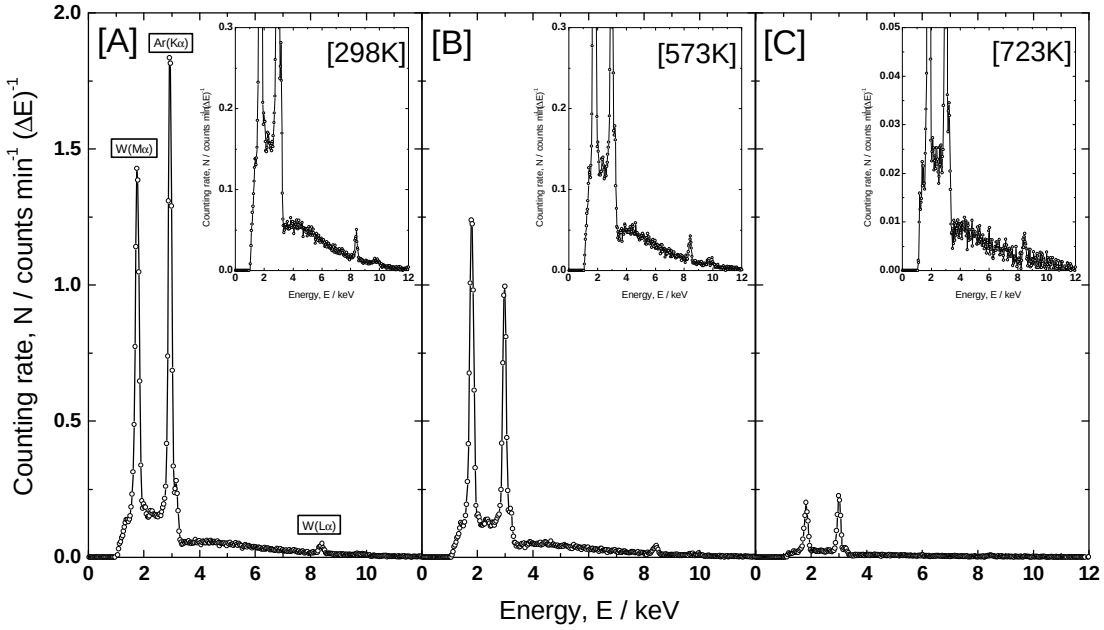

Fig. 3. Example of the X-ray spectra observed after heating at 573 and 723 K for 30 minutes in vacuum.

in each X-ray intensity of Ar(Kα) and W(Mα).

3.2. Changes in the intensity and shape of an X-ray spectrum with heating in vacuum

Figure 3 shows the X-ray spectra observed after heating at 573 and 723 K for 30 minutes in vacuum. Intensities of the characteristic and bremsstrahlung X-rays decreased with increase in heating temperature. However, the shape of bremsstrahlung X-rays little changed as seen from the inset in each spectrum, indicating that the depth profile of tritium in the bulk is very similar to each other. These indicate that a part of the implanted tritium was released from the tungsten, but not diffused into the bulk.

The changes in intensities of Ar(Kα) and W(Mα) X-rays with a heating temperature are

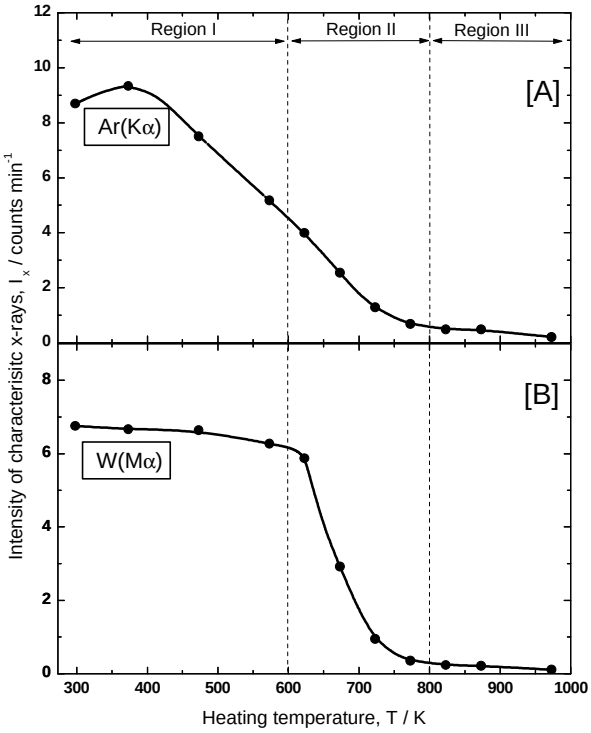

Fig. 4. Changes in intensities of Ar(Kα) and W(Mα) X-rays by heating.

illustrated in Fig. 4. It is clear that change in the Ar(Kα) intensity with a temperature was quite different from that in the (Mα) intensity, indicating that the thermal behavior of tritium trapped in the surface and sub-surface layers is different. For convenience sake, changes in the X-ray intensity were divided into three regions, basing on the change in the W(Mα) X-ray intensity: namely, Region I is the range from room temperature to 600K, Region II is 600 to 800 K, and Region III is above 800 K. The intensity of Ar(Kα) X-rays slightly increased at 373 K, but it decreased linearly with increase in heating temperature up to 773 K and above that temperature a slow decrease appeared. If only tritium retained in the surface layers are released by heating, it seems that the desorption rate of tritium will increase with a heating temperature and the intensity of Ar(Kα) X-rays will drastically decrease as a function of temperature. However, the X-ray intensity corresponding to the amount of tritium resided in the surface layers did not decrease in such a manner. Namely, it is suggested that tritium in the surface layers could be continuously supplied from the bulk. This may be a reason why the linear decrease of tritium in surface layers was observed. On the other hand, the intensity of W(Mα) X-rays decreased very slightly up to 600 K, and most of tritium in sub-surface layers disappeared in the Region II. From both intensity changes in Ar(Kα) and W(Mα) X-rays, it can be understood that at least there are two or more kinds of the trapping sites for the implanted tritium.

A technique of thermal desorption spectrometry (TDS) is frequently used to estimate thermal behavior of hydrogen isotopes implanted into materials. Figure 5 [B] and [C] show the deuterium desorption spectra obtained by TDS for tungsten samples with and without helium pre-irradiation. The deuterium fluence for those samples was $1x10^{21}$ ions/m^2. Detailed experimental

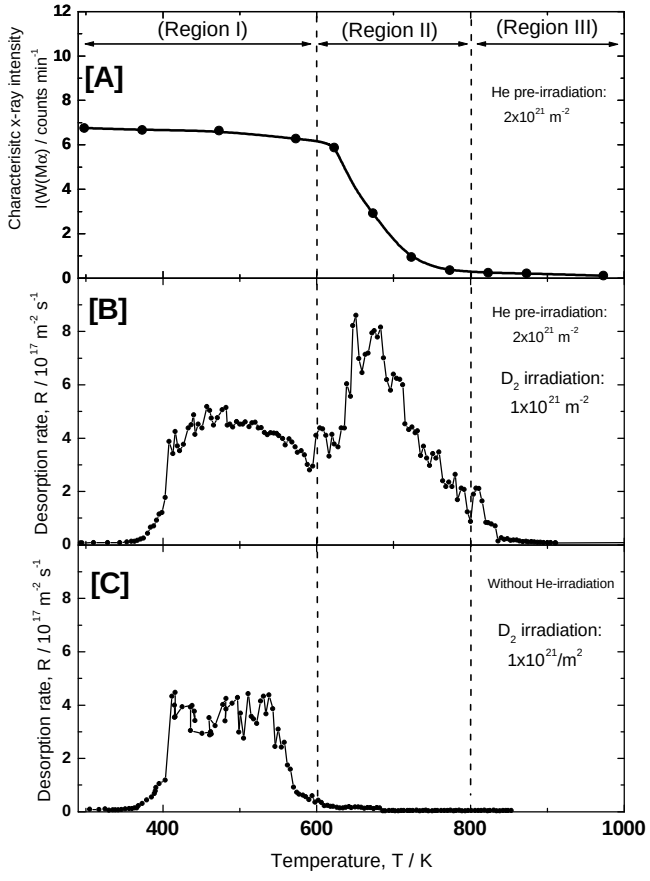

Fig. 5. Comparison of the change in W(Mα) intensity with thermal desorption spectra of deuterium.

conditions for TDS were described elsewhere [2]. To compare with the change in W(Mα) X-ray intensity, Fig. 4 [B] is also shown in Fig. 5 [A]. The desorption spectrum of deuterium for no helium pre-irradiation sample formed a broad peak in the Region I, but the pre-irradiation of helium newly produced the desorption peak in the Region II in addition to the Region I. However, when the dose of deuterium in this sample was lowered to a fluence of $5x10^{20}$ ions/m^2, only a single desorption peak appeared in the Region II. These suggest that the decrease of W(Mα) X-ray intensity in the Region II is due to the desorption of tritium trapped at the sites induced newly by helium pre-irradiation. It is clear, therefore, that the pre-irradiation of helium plays an important role for formation of new trapping sites of hydrogen isotopes.

According to the observation of a helium pre-irradiation sample by a transmission electron microscope, production of a large number of small helium bubbles were observed under the present helium pre-irradiation conditions. In addition, it is known that the helium bubbles formed in tungsten are almost stable if a heating temperature is below *ca*. 1000 K. This was confirmed by the result that no annealing effect was observed for intensity and shape of an X-ray spectrum though the second tritium implantation was carried out under the same implantation conditions after heating at 973 K in the first experiment. Namely, it can be seen that the present decreasing behavior of a W(Mα) X-ray intensity will be strongly related to the effects of helium bubbles on the formation of new trapping sites.

To estimate apparent activation energy of the reduction rate of tritium in sub-surface layers, the reduction rate of the W(Mα) X-ray intensity was plotted against the reciprocal temperature as shown in Fig. 6. I was assumed that the reduction rate obeys the second law kinetics with respect to a tritium amount in sub-surface layers. In this figure, I(T1) and I(T2) describe the W(Mα) X-ray intensity at respective heating temperatures. The apparent activation energy was estimated to be 1.21 eV from the slope of a line. It is reported by Franzen et al. [7] that the trap energy of ion-induced trap sites was 1.25 eV for single crystal tungsten irradiated with deuterium. Further examinations are

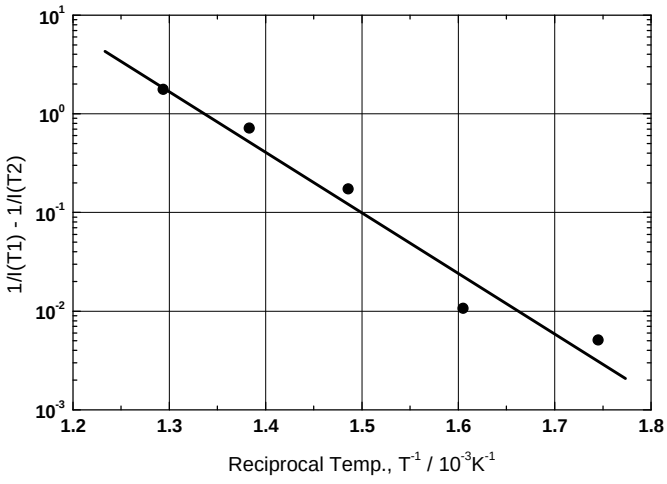

Fig. 6. Reduction rate of the W(Mα) X-ray intensity as a function of heating temperature.

required to clarify the desorption mechanism and kinetic data of tritium retained in irradiation-induced trap sites.

3.3. Simulation of the observed X-ray spectra and determination of a tritium depth profile

As shown in Fig. 4, the different decreasing behavior in characteristic X-ray intensities of Ar(Kα) and W(Mα) X-rays appeared during a isochronal heating, indicating that the thermal behavior of tritium retained in the surface layers is different from that of tritium trapped in sub-surface layers. Namely, it is of an important item to estimate the changes in a depth profile of tritium in tungsten with heating. A tritium depth profile can be estimated by computational simulation of an observed X-ray spectrum as reported so far [4]. Parameter in the computational simulation is only a tritium depth profile in the materials. The detailed analysis procedures are described elsewhere [8]. An example of comparison of the observed spectrum with the simulated one is shown in Fig. 7. It was seen that both spectra agreed well, indicating that the observed X-ray spectrum can be numerically reproduced well by assuming a given depth profile of tritium. The tritium depth profiles determined by such computational simulation are shown in Fig. 8.

It can be seen from Fig. 8 that about a

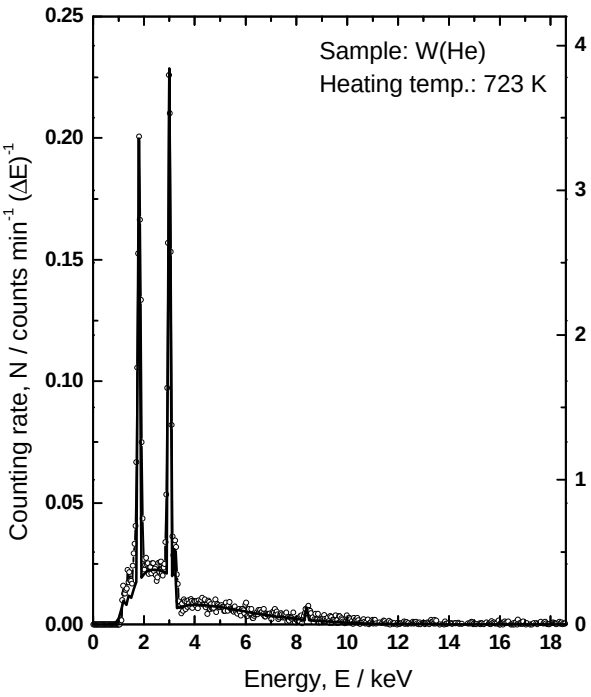

Fig. 7. An example of comparison of the observed spectrum with the simulation one. The open circles and the solid line show the observed and the simulated spectrum, respectively.

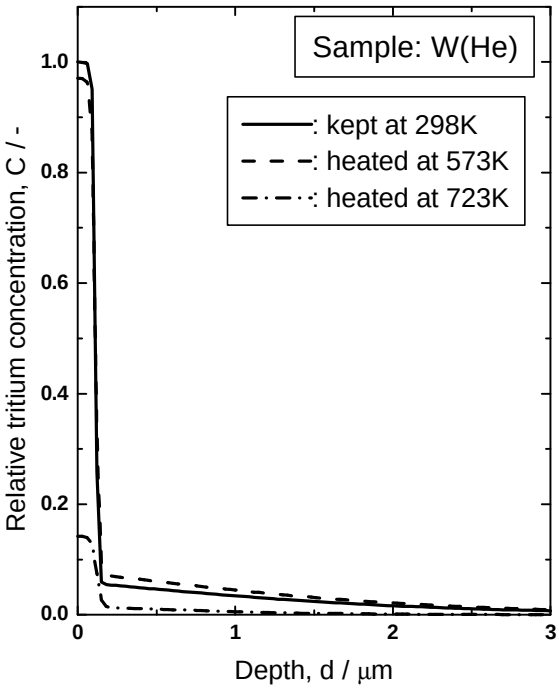

Fig. 8. Tritium depth profiles determined at given temperatures by computational simulation.

half of tritium ions injected in tungsten at room temperature was trapped within 0.1 μm from the surface and the others diffused into a depth of a few μm: two kinds of tritium distributions were suggested from the computational simulation. It is thought that one of reasons for appearance of such profiles is due to the difference of areas between helium and tritium ion irradiation. Because the tritium irradiation area was about two times greater than that of the helium pre-irradiation area as shown in Fig. 1. , The former distribution, therefore, shows effects of the helium pre-irradiation, and the latter distribution is due to the diffusion of tritium into the helium-unirradiated area. For heating at 573 K, only a little decrease in the tritium amount in sub-surface layers appeared, while for heating at 723 K gave rise to a significant decrease without diffusion of tritium into the bulk. This agrees well changes in a W(Mα) X-ray intensity as shown in Fig. 3.

Table 1 Temperature dependence of tritium amounts retained in the surface and sub-surface layers of tungsten determined from simulation analyses of the observed X-ray spectra. An unit of cpm describes the counts/min, and the numerical values in parentheses are relative amounts of tritium.

		298K	573K	723K
Surface layers	Obs.	8.69 cpm (1.00)	5.17 cpm (0.59)	1.29 cpm (0.15)
	Simula.	8.1 (1.00)	4.3 (0.53)	1.1 (0.14)
Sub-surface layers	Obs.	6.75 cpm (1.00)	6.27 cpm (0.93)	0.94 cpm (0.14)
	Simula.	88.8 (1.00)	86.2 (0.97)	12.6 (0.15)
(Surface) / (Total)		0.083	0.048	0.078

Tritium amounts in the surface and sub-surface layers are summarized in Table 1, which were calculated from the observed spectra shown in Fig. 3 and the depth profiles shown in Fig. 8. In this table, the observed values describe intensities of Ar(Kα) and W(Mα) X-rays, while the simulation shows the values calculated from area of a depth profile. The numerical values in parentheses represent relative tritium amount in each temperature. Changes in the relative tritium amounts evaluated from the observed X-ray intensity were almost the same as those from the simulation, indicating that the tritium depth profiles illustrated in Fig. 8 correspond well to practical ones. In addition, it was seen that the amount of tritium in surface layers was below 10% in all the remaining tritium.

4. Conclusions

Thermal behavior of tritium implanted in a tungsten sample which was irradiated in

advance with energetic helium ions was examined by utilizing the β-ray-induced X-ray spectrometry (BIXS). Ar(Kα) and W(Mα) X-rays were mainly utilized as probes of tritium detection: the former X-ray intensity gives information about tritium amount in surface layers, whereas the latter one gives information about the amount and distribution of tritium in sub-surface layers, taking into account of attenuation of X-rays in tungsten.

Quite different behavior appeared in changes of both X-ray intensities with heating. Intensity of the Ar(Kα) X-rays linearly decreased with a heating temperature, while that of W(Mα) X-rays was almost constant up to 600 K and above this temperature drastically decreased. Namely, it was suggested that there are two and more kinds of trapping sites. In addition, changes in the latter X-ray intensity by heating agreed quite well with appearance of the second desorption peak in the thermal desorption spectrum of deuterium. It was suggested that creation of the strong trap sites are due to the effects of He-bubbles formed by the helium pre-irradiation, and the trapping energy of those sites was estimated to be about 1.21 eV. Change in depth profiles of tritium with heating was evaluated by analyzing the observed X-ray spectra by means of computer simulation. From the simulation analyses, it was seen that the strong trap sites distributed up to a region of 0.1 μm beneath the surface and that about half of the implanted tritium ions were trapped in this region.

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