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Damage evaluation Change of hydrogen concentration after ion beam irradiation on polyimide films with 100-400 degree C annealing

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Irradiation damage in the several thickness polyimide films induced by 2.0MeV He ions has been evaluated by Rutherford backscattering (RBS) and Elastic recoil detection (ERDA) methods. ~~Under the room temperature condition,~~ For the samples without annealing, gradual decrease of hydrogen content has been observed as the increase of ion dose. After 5 min. annealing at 100 °C, large amount of hydrogen atoms disappeared suddenly. ~~Then~~ A small and continuous depletion of hydrogen content was also observed ~~for the annealed film~~ after ion beam irradiation. After 5 min. annealing at 300 °C, ~~slight recover of~~ hydrogen depletion concentration has recovered for the 100 °C annealed film ~~was observed in the case of no ion beam irradiation~~. Initial depletion rate of hydrogen for annealing and change of hydrogen content for the successive ion beam irradiation was found to be dependent on the film thickness.

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1. Introduction

It is said that irradiation of polymers with energetic ions leads to cleavage of chemical bonds along the ion trajectory and subsequently to creation of various degradation products [1]. It can often be observed that the hydrogen yield in a series of ERDA spectra from these polymers decreases with increasing primary ion dose[2-7]. In our previous work, it is demonstrated that hydrogen atoms lost in the surface region[7]. This time, I show the results of ion beam irradiation effect on Kapton-H (PMDA-ODA polyimide) films under the high temperature annealing. Though the Kapton, a popular polyimide, is able to operate in the temperature range as low as -269°C and as high as 400°C[8], even for the 5 minute annealing with 100°C, a large amount of hydrogen depletion in the film was observed from ERDA analysis. I have also investigated the relationship between the film thickness and the extent of hydrogen depletion for the non-annealed and annealed samples. As far as I know, this is the first report of quantitative analysis of hydrogen depletion for the polyimide films under the condition of high temperature annealing.

2. Experimental

The experiments were performed in a high-vacuum chamber coupled to a Tandatron accelerator which produces He^+ ion beams collimated to a 1mm diameter over the range of 0.6-5.1MeV. The chamber contains two SSDs for energy analysis of scattered ions and recoiled particles. The scattering angle for the incident beams to SSD is fixed at 168.8° for RBS analysis and the recoil angle for the incident beams to SSD is fixed at 20° for ERDA analysis.

[Other relevant experimental parameters are solid angles of SSDs \$\Omega=2.00\text{msr}\$ for RBS and \$\Omega=2.75\text{msr}\$ for ERDA, and both SSD resolutions of 15keV.](#) A 6.0 μm Al foil was placed in

front of one SSD to eliminate the He contribution from the hydrogen signal. The incident angle was set to 80° from surface normal, allowing the simultaneous analyses of ERDA and RBS. The shape of beam spot on the sample was ellipse and size was about $1.0 \times 6.0 \text{ mm}^2$. The incident beam energy of He^+ is fixed to 2.0 MeV, to be used as the production of ion beam damage during measurement of ERDA and

-RBS in the range of ion dose of $1\mu\text{C}$ - $20\mu\text{C}$. A $1\mu\text{C}$ ion dose was estimated to 3.45×10^{13} ions/ cm^2 irradiation from the geometric arrangement, resulting in the accumulate ion dose of up to 6.9×10^{14} ions/ cm^2 . The standard Kapton films with 0.2mm, 0.5mm, 0.7mm thick were obtained from Toray-Du Pont Co., Japan[8]. The samples were cut about $1.0 \times 4.0 \text{ cm}^2$ to attach the sample holder and heated using underlying Nickel-Chromium sheet to supply the direct current and its temperature was measured by Chromel-Almel thermocouples attached on the sample. The experiments were repeated to shift the beam position up to down and left to right. There was no critical change of the results for lateral and vertical movement of samples. The computer simulation code I used to estimate the compositional depth profiling of H, O, N, and C from the raw ERDA and RBS spectra is RUMP. In this program, I have adjusted the hydrogen recoil cross section using the table derived by Tirira et. al.[9]

3. Results and Discussion

Figure 1 shows the variation of hydrogen compositional content (concentration) for successive dose of high energy He ions as a function of sample annealing temperature. Film thickness of the Kapton used for this experiment was 0.2mm. Ion dose is plotted in unit of μC , where $1\mu\text{C}$ is equivalent to 3.45×10^{13} ions/ cm^2 irradiation. The ordinate shows the absolute relative hydrogen concentration in unit of compositional ratio normalized by carbon-initial hydrogen compositional ratio ($\text{C}:22\text{H}:10$) ~~where carbon concentration is assumed not to decrease under the high energy ion irradiation.~~ Stoichiometric composition of Kapton-H is

$C_{22}H_{10}N_2O_5$, which is also used for the correction of hydrogen recoil cross section for the first time ERDA-RBS simultaneous measurement taken by $1\mu C$ He dose at room temperature[6]. As shown in Fig.1, gradual decrease of hydrogen content from the stoichiometry was observed as the increase of ion dose at room temperature. This result is similar to those already reported papers[2,3,5-7]. However, tremendous depletion of hydrogen concentration was observed after 5 minute annealing as high as $100^\circ C$, even though no ion beam irradiation was done(Exactly saying, $1\mu C$ ion dose was done to measure the hydrogen concentration, but this ion dose is quite small). The

absolute concentration of hydrogen decreased up to 0.75 from 10.0, though any visible change could not be observed in the film. Film shape remains same, without roughening, shrinking and coloring, after annealing even at $300^\circ C$ in vacuum. From the result of RBS, no decrease of other elements of oxygen, nitrogen and carbon was observed, indicating predominant desorption of hydrogen element alone (without the form of H_2O). Easy idea of H_2O desorption due to annealing is also denied in the point of recovery of hydrogen concentration over $300^\circ C$ annealing in the 0.5mm and 0.7mm thick Kapton films. In the case of $200^\circ C$ annealing for 5 minute, hydrogen concentration decreased more up to 0.33%. ~~For the ion beam irradiation up to $20\mu C$ Then,~~ hydrogen concentration changed nearly equal or a little bit decrease monotonously for $100^\circ C$ annealed and $200^\circ C$ annealed films for ion beam irradiation shown in Fig.1. For the Kapton films, the effect of heating up is predominant for hydrogen desorption compared with ion beam irradiation. It is noted that after $300^\circ C$ annealing, no hydrogen could be detected within our ERDA detection sensitivity for the 0.2mm thick Kapton film. Figure 2 shows the raw ERDA hydrogen spectra taken at the $1\mu C$ ion dose for the 0.2mm thick Kapton films without annealing, with $100^\circ C$ annealing and with $200^\circ C$ annealing. For the case of annealing, quite small hydrogen signals were observed compared with the spectrum for no annealing. From Fig.2, it has been found out that the hydrogen depletion ex-

tended to whole observable thickness (about $0.3\mu\text{m}$). It is not yet clear why such a tremendous depletion of hydrogen content takes place.

Figure 3 shows the variation of hydrogen concentration for successive dose of He ions as a function of annealing temperature. Film thickness of the Kapton was 0.5mm. In the case of irradiation to the 0.5mm thick Kapton film at room temperature, gradual decrease of hydrogen concentration against the ion dose has been observed. This agrees well with the case of ion beam irradiation to the 0.2mm thick Kapton film. After 150°C annealing for 5 minute, hydrogen content decreased up to [1.010%](#), which shows same tendency with the 0.2mm thick Kapton film case. After 200°C annealing for 5 minute, hydrogen concentration is less than the case of 150°C annealing. The effect of ion beam dose on these two annealed films modifies hydrogen concentration slightly, and no fluctuation of hydrogen concentration against the ion beam irradiation was observed. However, after 300°C annealing for 5 minute, hydrogen content recovered a little for the 200°C annealed film. Moreover, fluctuation of hydrogen concentration against the ion beam irradiation was clearly observed shown in Fig. 3. For the case of 0.2mm thick Kapton film, as hydrogen atoms could not be detected after 5 minute annealing at 300°C , the result of 300°C annealing for 0.5mm thick Kapton film is in clear contrast with the result for 0.2mm thick Kapton film.

Figure 4 shows the variation of hydrogen concentration for successive dose of He ions as a function of annealing temperature. Film thickness of the Kapton was 0.7mm. In the case of irradiation to the 0.7mm thick Kapton film at room temperature, gradual decrease of hydrogen concentration against the ion dose has also been observed, showing same tendency with the 0.2mm thick Kapton film and the 0.5mm thick Kapton film. After 170°C annealing for 5 minute, hydrogen content decreased up to [1.515%](#), which also shows same tendency with the 0.2mm thick Kapton case and 0.5mm thick Kapton case. After 300°C annealing for 5 minute, hydrogen content recovered for the 170°C annealed film. The tendency is nearly same as the

case of irradiation to the 0.5mm thick Kapton film. However, the extent of hydrogen concentration after 300°C annealing to the 0.7mm thick Kapton film is ~~3.232%~~, twice greater than the case for 300°C annealing to the 0.5mm thick Kapton film, indicating much more recovery at the same temperature. Then, after 390°C annealing for 5 minute, hydrogen content decreased again up to 1.5. In this film, fluctuation of hydrogen concentration against the ion dose was observed severely for the annealed films at 300°C and at 390°C. For detailed discussions, I summarize the characteristics of the variation of hydrogen concentration for successive change of ion beam dose under the high temperature annealing for 0.2mm, 0.5mm and 0.7mm thick Kapton films. Common characteristics and difference for each sample is as follows.

- If the hydrogen concentration once decreases and tends to recover over 300°C, minimum hydrogen concentration will appear for 150°C-200°C annealing.
- The 0.2mm thick Kapton film is too thin to recover the hydrogen concentration for over 300°C annealing.
- When hydrogen concentration starts to recover over 200°C, unstable state for hydrogen concentration for the ion beam irradiation is observed.
- As thick film thickness of Kapton such as 0.7mm thick is, as high annealing temperature around 400°C where hydrogen is missing and as high hydrogen concentration when recovering.

I show the model of the annealing effect and irradiation effect on the Kapton films with different film thicknesses in Figure. 5. This is only my hypotheses. One hypothesis is shown upper side in Fig. 5. I call it for “Simple interpretation”. As the difference is only film thickness for each experiment, over 300°C annealing hydrogen atoms go toward surface area from at least 0.2mm deeper area by diffusion for thick films. In this model, the problem is the possibility of desorption of hydrogen locating in the 0.2mm deeper area for only 100°C annealing. The dis-

tance of 0.2mm seems to be huge. Second one is shown lower side in Fig. 5. In this model, desorption area of hydrogen is quite shallower than 0.2mm depth. The difference is hydrogen diffusion coefficient. At high temperature, hydrogen diffusion coefficient changes to be larger for thick films than it of thin films. Though it is not so realistic, if the hypothesis is correct, the reason where hydrogen appears in the surface region after 300°C annealing for thick Kapton films can be explainable. [I did not take into account the change of density with hydrogen loss or possible thermal gradients due to the poor thermal conductivity. As the experimental results are few, I cannot say any comment. I also don't know whether hydrogen loss is homogeneous or not laterally in this system.](#) Anyway, further experiment and discussion must be needed in this system. It is noted that we show the hydrogen concentration as an average value from topmost surface to 0.3μm depth. For the case of 0.2mm thick Kapton film (at all annealing temperature), and 0.5mm thick Kapton film and 0.7mm thick Kapton film for less than 200°C annealing, depth profile was uniform. However, depth profile of hydrogen for thick Kapton films after high temperature annealing is not rather than flat. Just inside the film close to the surface (about 0.1μm deeper from the surface), hydrogen concentration is less than its of surface area's. This might be also the key to solve the phenomena.

4. Conclusion

Irradiation damage in the several thickness polyimide films induced by 2.0MeV He ions has been evaluated by Rutherford backscattering (RBS) and Elastic recoil detection (ERDA) methods. Under the room temperature condition, gradual decrease of hydrogen content has been observed as the increase of ion dose. After 5 minute annealing at 100 °C, large amount of hydrogen atoms disappeared suddenly. A small and continuous depletion of hydrogen content was also observed for the annealed film after ion beam irradiation. After 5 minute annealing at 300 °C, slight recover of hydrogen depletion for the 100 °C annealed film was observed for the 0.5mm thick and 0.7mm thick Kapton films. Initial depletion rate of hydro-

gen for annealing and change of hydrogen content for the successive ion beam irradiation was found to be dependent on the film thickness.

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Figure Captions

- Fig. 1 Variation of hydrogen concentration for successive dose of He ion beam for the 0.2mm thick Kapton films. The ordinate represents absolute hydrogen compositional ratio. The annealing conditions are (a) no annealing, (b) 5 minute annealing at 100°C and (c) 5 minute annealing at 200°C.
- Fig. 2 ERDA hydrogen spectra taken at the 1 μ C ion dose for the 0.2mm thick Kapton films without annealing, with 100°C annealing and with 200°C annealing. Depth distribution of hydrogen concentration is found to be nearly constant within the observable thickness(about 0.3 μ m).
- Fig. 3 Variation of hydrogen concentration for successive dose of He ion beam for the 0.5mm thick Kapton. The annealing conditions are (a) no annealing, (b) 5 minute annealing at 150°C, (c) 5 minute annealing at 200°C and (d) 5 minute annealing at 300°C.
- Fig. 4 Variation of hydrogen concentration for successive dose of He ion beam for the 0.7mm thick Kapton. The annealing conditions are (a) no annealing, (b) 5 minute annealing at 170°C, (c) 5 minute annealing at 300°C and (d) 5 minute annealing at 390°C.
- Fig. 5 A model of the annealing effect and irradiation effect on the Kapton films with different film thicknesses of 0.2mm, 0.5mm and 0.7mm thick.

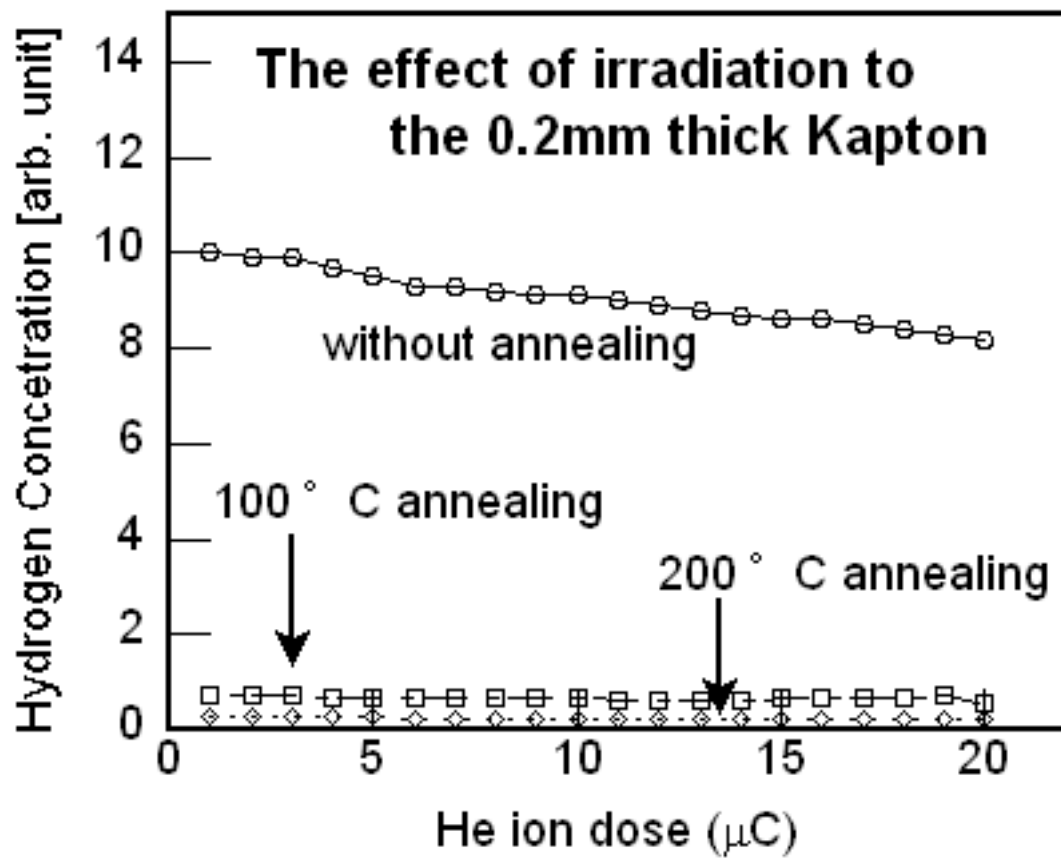


Fig. 1 M.Watamori

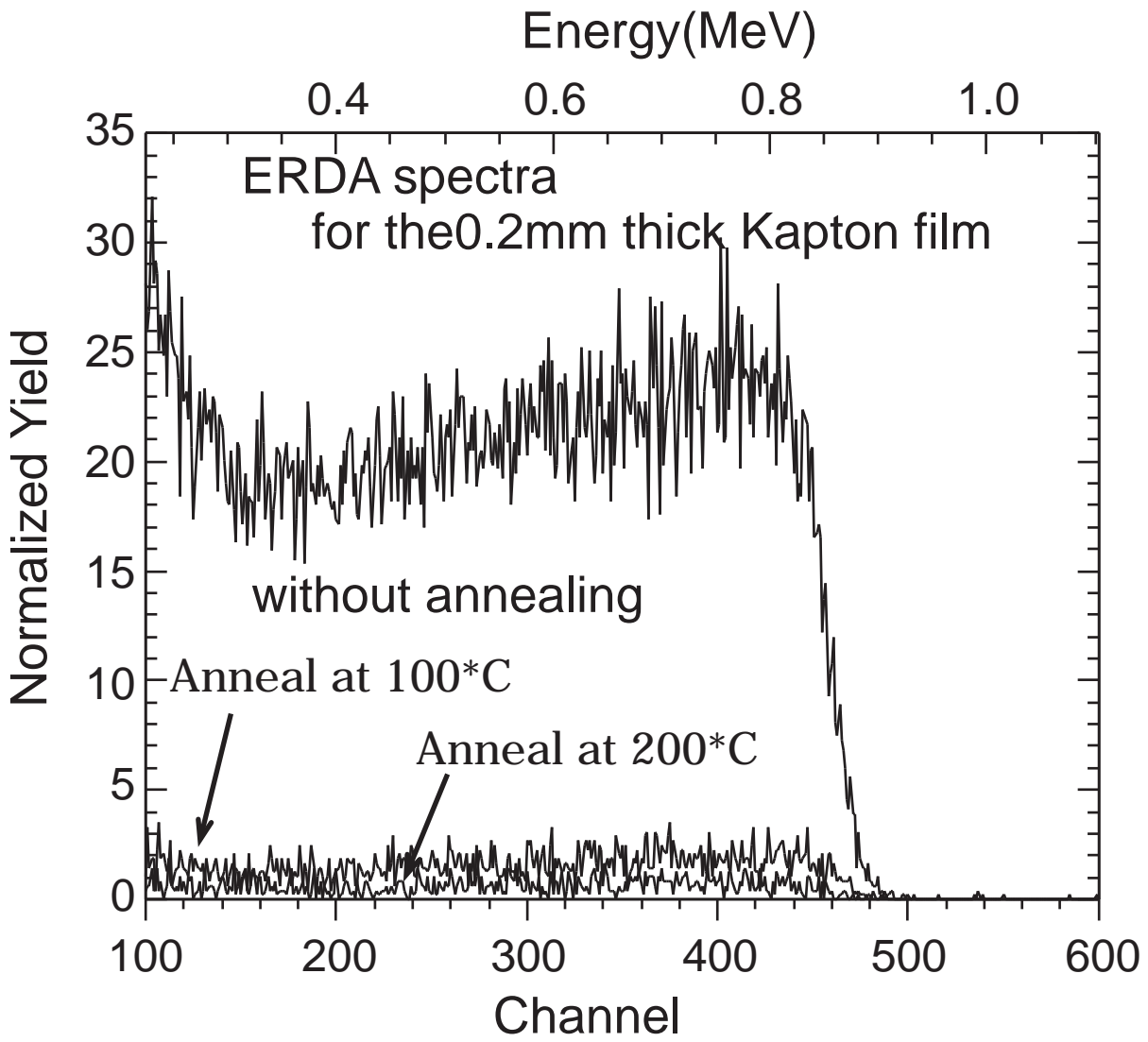


Fig. 2 M.Watamori

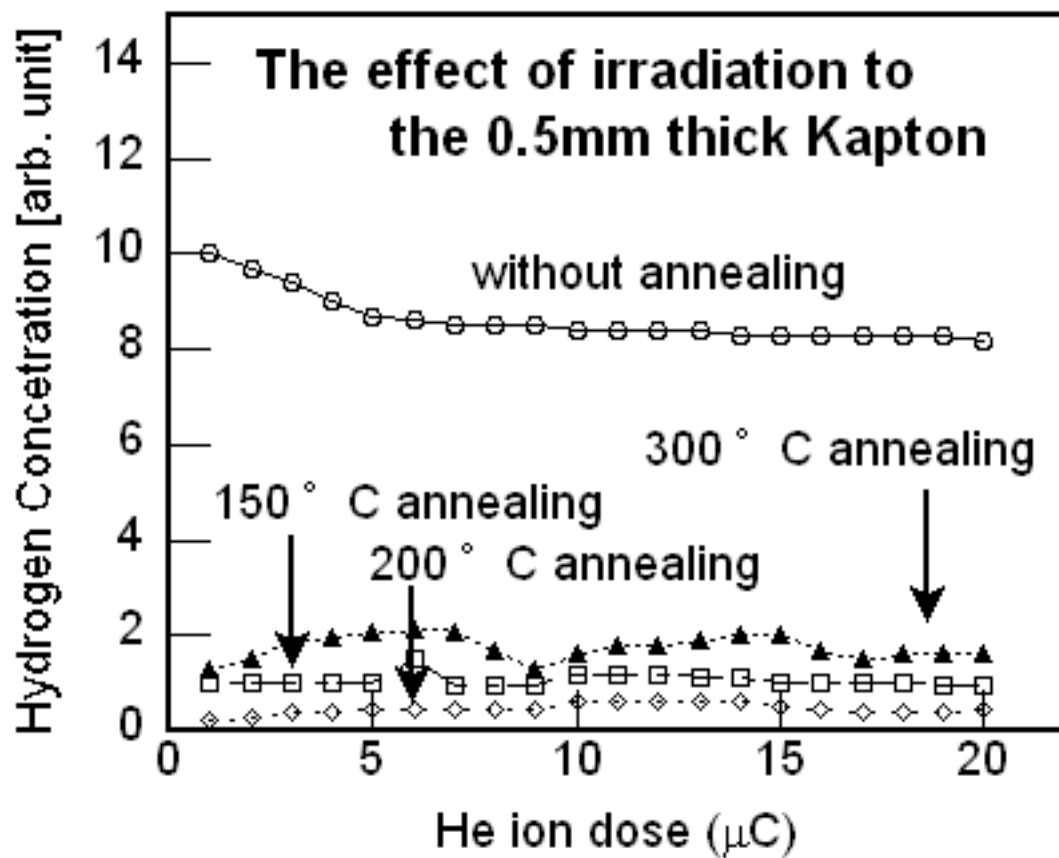


Fig. 3 M.Watamori

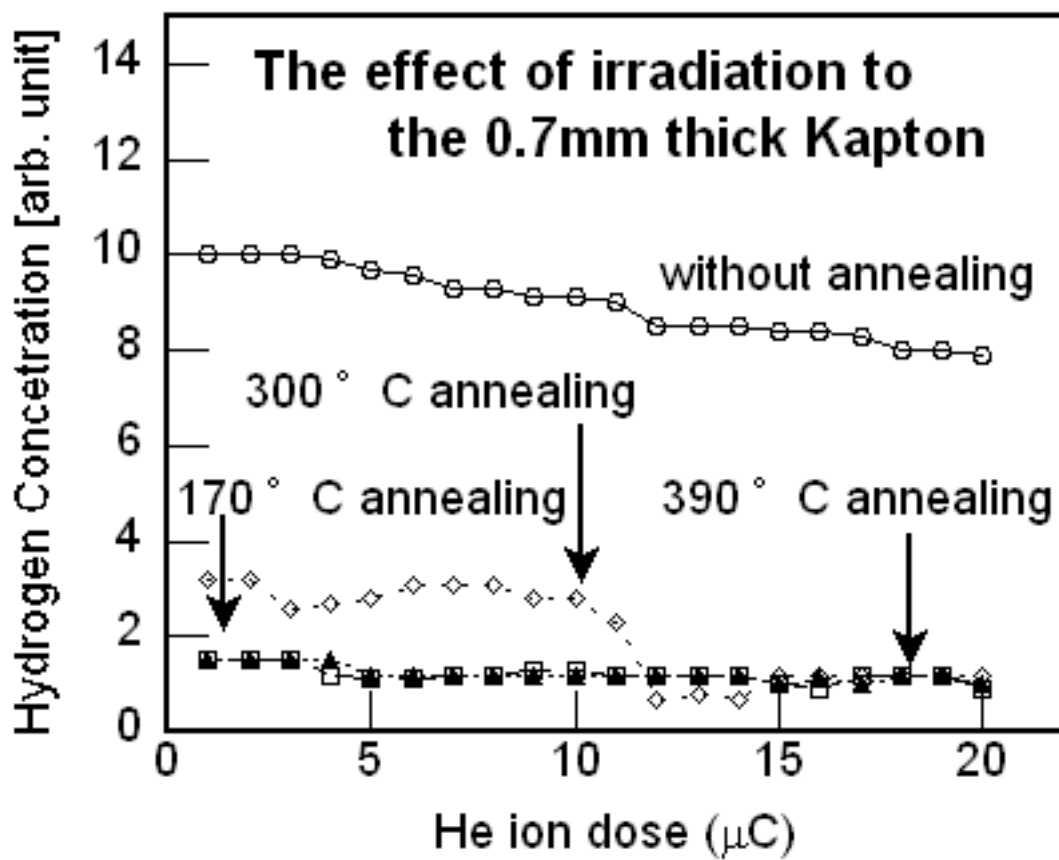
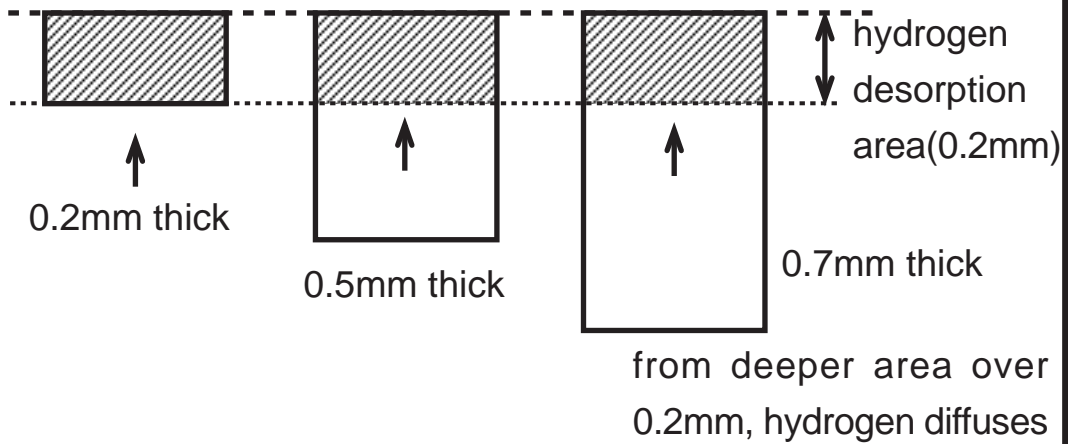
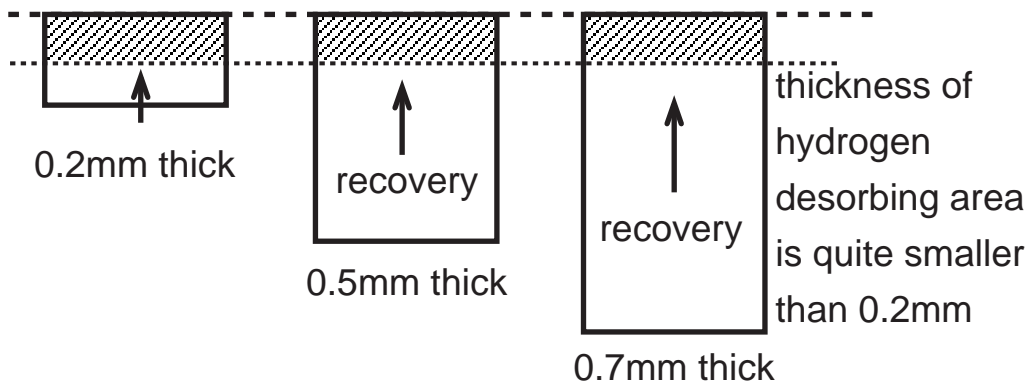


Fig. 4 M.Watamori

A model of Annealing Effect



1) Simple interpretation



2) The effect of film thickness is a change of diffusion coefficient

Fig. 5 M.Watamori