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Abstract

To explain the previously observed changes in the bulk etching property of CR-39 induced by gamma or high-energy electron irradiation, both a mass balance equation for the radicals, the active sites by irradiation, and a diffusion equation for the dissolved oxygen were applied to calculate the damage distribution in depth. The depth distribution of the damage in gamma-irradiated CR-39 was interpreted as a result of the exhaust of the dissolved oxygen in the deeper layer. The present calculations and the previous experiments imply that latent tracks in CR-39 are also produced through the local oxidation process along the ion path.

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1. Introduction

In order to understand the formation mechanism of the latent tracks in poly-diethylene-glycol bis (allylcarbonate), that etched nuclear track detector with high sensitivity and usually called CR-39, lots of studies have been made on the effect of high dose gamma-ray irradiation on the bulk etch rate in alkaline solutions [1-10]. In these works the examined ranges of the absorbed dose were controlled to be comparable to the local energy deposition in the center of ion tracks [11].

The present authors have also studied the effects of gamma and electron beam irradiation on CR-39 [12-16]. The bulk etch rate was usually determined from both the etching duration and the radius of etched track of high-LET particles like fission fragments which indicates the thickness of layer removed [17]. This is an effective method as far as the etched track is cylindrical in side view and the bulk etch rate is constant. Recently, we have found the "Bottle-like structure" in the etched tracks of fission fragment in the gamma-irradiated CR-39 [15]. The etched track had double stages in radius, larger near the surface and smaller in the deeper region along the common axis of the trajectory, as shown in Fig. 1. The both parts were connected by a thin transition layer, so that the etched track looked like an upper part of a wine bottle. The parts near the surface with lager radius corresponded to the "body" of the bottle and the other part in the deep with smaller radius was equivalent to the "bottle neck". Such a unique etched track was possible when the bulk etch rate increased only in the surface region where the "body" was formed. On the other hand, the "neck" was formed in the deeper layer. The etching rate in this region was found the same as that for CR-39 irradiated in vacuum, fully out-gassed. This implies that the concentration of dissolved oxygen in the deeper layer reached zero during the irradiation. Therefore the damaged region near the surface was inferred to relate to the oxygen fed from the surroundings. We have assessed the dose rate dependence of the thickness of the damaged region [16]. The thickness decreased with increasing the dose rate. At higher dose rates, the oxygen supplied on the surface should be soon consumed in forming the damage and it will become more difficult for the oxygen to diffuse toward deeper layers. Consequently, we should construct a new model for the damage formation under gamma-irradiation that is able to express the depth distribution of the damage.

A similar depth dependent damage distribution has been reported and analyzed for various polymers [18-20]. It is known as radiation-induced oxidative degradation. Referring to these radiochemical studies, we have calculated the dependence of the

damage concentration upon the depth based on two equations; one is the mass balance equation for radicals or active sites produced by irradiation, and the other is the diffusion equation for the dissolved oxygen. The experimentally obtained dose rate dependence of the thickness of the damaged region in CR-39 was reconstructed well by the present calculations.

2. Model of damage formation

The radiation-induced damages related to the increase in the bulk etch rate should be caused by the breaks of the main chain of CR-39 polymer. In this study, the damage was assumed to be formed through the reaction between radiation induced free radicals and the oxygen dissolved. At first, the production rate of the radicals, or the active sites in the polymer, was hypothesized to be proportional to the dose rate, I. Secondly, the radical has some probability to vanish through a natural decay. This assumption is based on the track registration study on the well out-gassed CR-39 [21]. Finally, the rate of the damage formation was postulated to be in proportion to the concentration of the radical, *[P•]*, and the oxygen concentration, *C*. Therefore, the following mass balance equation was derived for the concentration of radicals:

$$\frac{d[P\bullet]}{dt} = \Phi I - k_1[P\bullet] - k_2[P\bullet]C, \qquad (1)$$

where Φ is the specific rate constant for the radical formation, k_1 and k_2 are the rate constant for radical decay and oxidation or fix of the radical, respectively. Under a steady-state condition, it becomes as follows:

$$[P\bullet] = \frac{\Phi I}{k_1 + k_2 C}. \qquad (2)$$

Since the damage density is proportional to *[P•]C* and the irradiation duration, *t*, an uniform damage distribution in depth would be expected in the region where the oxygen exists, provided that k_1 is much less than k_2C. The observation of the bottle-like etched track indicated that the damage distribution should be uniform in the damaged region near the surface [15, 16]. So it is possible to reconstruct the damage distribution using this model. If the cross-linking is dominant, the second term on the right hand side in Eq. (1) is replaced by the square of *[P•]* multiplied by a constant, and such a uniform distribution could not be expected.

On the other hand, the following equation was obtained from the mass balance of the dissolved oxygen,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - k_2[P\bullet]C , \qquad (3)$$

where D is the diffusion coefficient of oxygen in the CR-39 film and x is the depth.

For the boundary conditions on the oxygen concentration at the surface, two different cases were examined. The first was "the constant condition" that means the concentration in the surface is constant during the irradiation. The second was "the surface resistance condition", in which the rate of transfer of diffusing oxygen through a unit area of the surface is proportional to the difference between the actual concentration in the surface, C_s, at any time and the equilibrium concentration, C_o. The equilibrium concentration corresponds to the partial pressure of oxygen in the atmosphere. This means that the second boundary condition can be written as

$$-D\frac{\partial C}{\partial x}\bigg|_{surface} = K_3\left(C_o - C_s\right), \qquad (4)$$

where K_3 is a constant of the proportionality.

Consequently, the damage density, C_d, at the irradiation time of t, is obtainable using the following relation as:

$$C_d\left(x,t\right) = \int_0^t K_2[P\bullet]C\left(x,t'\right)dt' . \qquad (5)$$

If the radical and oxygen concentrations reach steady state in early stage of the irradiation, this can be replaced by simple multiplication.

There are many parameters required in the present model. From the residual gas analysis, the diffusion coefficient and the equilibrium concentration of dissolved oxygen in CR-39 have been determined as $D=1.0\times10^{-8}$ cm^2/s and $C_o=9.4\times10^{-9}$ mole/cm^3, respectively [22]. Based on the reported G-value for the scission in CR-39 [23], the specific rate constant of the radical formation was given as $\Phi=1.6\times10^{-9}$ mole/Gy/cm^3. A lifetime of the radical has been obtained equal to about 40 min, so we assumed the rate constant for radical decay to be equal to $K_1=1/2400$ s^{-1} [21]. About the other parameters of the rate constant for oxidation, K_2, and the proportional constant for the surface resistant condition, K_3, we have made lots of calculations to find appropriate values for reconstruction of the observed depth-dependence and the dose rate dependence of the bulk etch rate.

3. Results and discussion

Calculations were performed for a one-dimensional system with a thickness of

100 μm. The following assumptions have been made in solving the equations numerically: (1) the concentration of radicals was postulated to reach the steady-state condition quickly, and (2) the change of the diffusion coefficient due to irradiation was ignored. The fundamentals and the details of the present numerical calculation were similar to those reported earlier [24].

3.1 Depth dependence

The distribution of dissolved oxygen in depth was calculated with a rate constant for oxidation of K_2=4.5x10^5 cm^3/mole/s and under the boundary condition of constant concentration on the surface, C_o. In Fig. 2, the calculated results in steady state are shown at dose rates of 0.01, 0.05, 0.1, 0.5, 1.0 and 10.0 Gy/s, plotting the relative concentration of the oxygen against the depth from the center of CR-39 sheet. The oxygen is found to be fully consumed around the center in each calculation. The widths of the oxygen-free regions increase with the dose rate. In other words, the thickness of the region, where the oxygen could be supplied, decreases with increasing dose rate. In every calculation, the steady states were attained within a several minutes. This is in agreement with the experimental results that a fractional gamma irradiation hardly affects the total dose dependence of the bulk etch rate [12, 13].

In Fig. 3, the damage density at the absorbed dose of 100 kGy is shown as a function of the distance from the center, corresponding to the oxygen distributions given in Fig. 2. The curves have semi-plateau near the surface as expected from the previous consideration based on the Eq. (2). The oxygen concentration decreases in the deeper region as shown in Fig. 2. On the other hand, the concentration of the radical will increase with the depth and reach the maximum where no oxygen exists. So, the semi-plateau is the result of both effects. Such calculated damage distribution was in concordance with the observed results that the bulk etch rate was almost constant in the damaged region where the "body" was formed [15, 16]. The thickness of the damaged region was determined as the width of the region where the damage density was not zero. The results are presented in Fig. 4, plotting as the curve against the dose rate, together with the fitting curves that experimentally obtained as broken one [16]. This indicates that the calculated thickness is in agreement with the experimental one.

3.2 Dose rate effect

To reconstruct the dose rate effect on the bulk etch rate, we must take into

account the feed of oxygen into CR-39 sheet from the atmosphere. As the first approximation, the surface resistance condition was applied. The depth distributions of the oxygen and the damage density were calculated with a proportional its constant of $K_3 = 0.11$ cm/s. In Fig. 5, the relative oxygen concentration at several dose rates is shown against the distance from the center. The concentration in the surface decreases with increasing dose rate. The corresponding damage density at the absorbed dose of 100 kGy is shown in Fig. 6. In general, the damage density decreases with the dose rate. The density at the surface varies significantly with the dose rates in the range between 0.1 and 1 Gy/s. This is concordant with the qualitative observations [13].

The used values for K_2 and K_3 in the present calculation had been selected arbitrarily to reconstruct the dose rate dependence of the thickness of the damaged region and the bulk etch rate. So the reliability of these values is dependent on that of other parameters of Φ, and C_o. It is necessary to obtain more reliable values for Φ and C_o for the purpose of improving the present model in accuracy.

4. Conclusion

Mass balance equations for the radicals and the dissolved oxygen have been applied to explain the observed damage distribution in gamma-irradiated CR-39 nuclear track detector. The damage was assumed to be formed through the reaction between the radicals and the oxygen. The production rate of the radical was postulated to be proportional to the dose rate, and the oxygen was hypothesized to be provided from the surrounding air and consumed in the damage formation. The depth distribution of the damage in the gamma-irradiated CR-39 was interpreted as a result of the exhaust of the dissolved oxygen in the deeper layer. The damage was formed only near the surface region where the oxygen was supplied during the irradiation from air. The dose rate effect on the bulk etch rate was also explained by introducing the surface resistant boundary condition for the feed of the oxygen from air.

A similar reaction between the radical and the oxygen is expected to occur also in the latent track formation process. The attained parameters for the present work may be useful to develop a new track formation model in CR-39, in which the temporal and spatial dependence for the track was included. The previous experiments and the present calculations on the etching property of gamma-irradiated CR-39 might imply that the latent track in CR-39 was also produced through the local radiation induced oxidation process along the ion path.

References

[1] R. Akber, K. Nadeem, C.A. Majid, A. Hussain, N. Zaman and H.A. Khan, Nucl. Instrum. Meth. 173 (1980) 217.

[2] P.F. Green, A.G. Ramli, S.A.R. Ai-Najjar, F. Abu-Jarad and S.A. Durrani, Nucl. Instrum. Meth. 203 (1982) 551.

[3] M. Zamani and Stef. Charalambous, Int. J. Appl. Radiat. Isot. 36 (1985) 525.

[4] T. Portwood and D.L. Henshaw, Nuclear Tracks, 12 (1986) 105.

[5] M. Zamani, D. Samponidis and Stef. Charalambous, Nuclear Tracks, 12 (1986) 125.

[6] J. Chavat and F. Spurny, Nucl. Tracks Radiat. Meas. 14 (1988) 451.

[7] S. L. Sharma, T. Pal, V.V. Rao and W. Enge, Nucl. Tracks Radiat. Meas. 18 (1991) 385.

[8] R. Shweikani and S.A. Durrani and T. Tsuruta, Nucl. Tracks Radiat. Meas. 22 (1993) 153.

[9] S. Sinha, S. Ghosh, A. Srivastava, V.G. Degaonkar and K.K. Dwivedi, Radiat. Meas. 28 (1997) 145.

[10] Fazal-ur-Rehman, F. Abu-Jarad, M.I. Al-Jarallah and M. Farhat, Radiat. Meas. 34 (2001) 617.

[11] M.P.R. Waligorski, R.N. Hamm and R. Katz, Nucl. Tracks Radiat. Meas. 11 (1986) 309.

[12] K. Oda, K. Yoshida, T. Yamauchi, T. Ikeda, Y. Honda and S. Tagawa, Radiat. Meas. 28 (1997) 85.

[13] T. Yamauchi, T. Taniguchi, K. Oda, T. Ikeda, Y. Honda and S. Tagawa, Radiat. Meas. 31 (1999) 121.

[14] T. Yamauchi, H. Ichijo and K. Oda, Gamma-ray and ions irradiation effects on the optical property of CR-39 detector and their latent track size, Proc. The First International Symposium on Supercritical Water-cooled Reactors, Tokyo 6-9 November 2000. (2000) 274.

[15] T. Yamauchi, H. Ichijo and K. Oda, Radiat. Meas. 33 (2001) 189.

[16] T. Yamauchi, H. Ichijo and K. Oda, Radiat. Meas. 34 (2001) 85.

[17] R. Henke, K. Ogura and E.V. Benton, Nuclear Tracks, 12 (1986) 307.

[18] T. Seguchi, S. Hashimoto, K. Arakawa, N. Hayakawa, W. Kawakami and I. Kuriyama, Radiat. Phys. Chem. 17 (1981) 195.

[19] T. Seguchi, K. Arakawa, N. Hayakawa, Y. Watanabe and I. Kuriyama, Radiat.

Phys. Chem. 19 (1982) 321.

[20] R. Clough Encyclopedia of Polymer Science and Engineering 2nd edition, Vol. 13, John Wiley&Sins, New York (1988) 667.

[21] T. Yamauchi, K. Oda, and H. Miyake, Nucl. Tracks Radiat. Meas. 20 (1992) 615.

[22] H. Miyake, T. Yamauchi and K. Oda, Ionizing Radiation 16 (1990) 59. (in Japanese)

[23] D. O'Sullivan, P.B. Price, K. Kinoshita and C.G. Willson, SOLID STATE NUCLEAR TRACK DETECTORS, Edit. P.H. Fowler and V.M. Clapham, Pergamon Press (1982) 81.

[24] T. Seguchi, S. Hashimoto, W. Kawakami and I. Kuriyama, Japan atomic Energy Reserch Institute Report, JAERI-M 7315 (1977)

Figure Captions

Fig. 1.   Bottle-like etched track and corresponding depth distribution of the damage.

Fig. 2.   Concentration of the dissolved oxygen in steady states calculated under a constant boundary condition at the surface.

Fig. 3.   Depth distribution of the damage density in steady states calculated under a constant boundary condition at the surface. The total dose is 100 kGy.

Fig. 4.   Dose rate dependence of the thickness of the damaged region.

Fig. 5.   Concentration of the dissolved oxygen in steady states calculated under a surface resistant condition at the surface.

Fig. 6.   Depth distribution of the damage density in steady states calculated under a surface resistant condition at the surface.
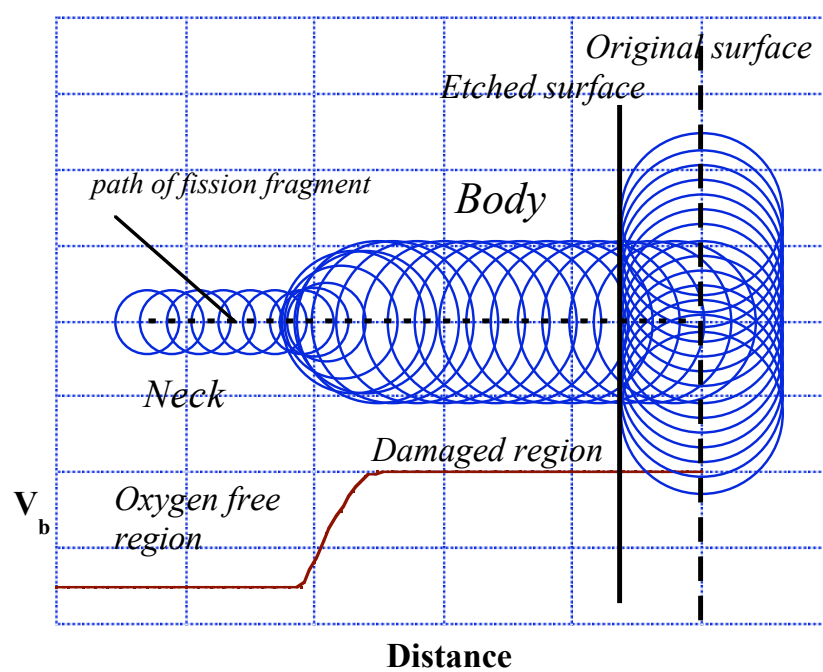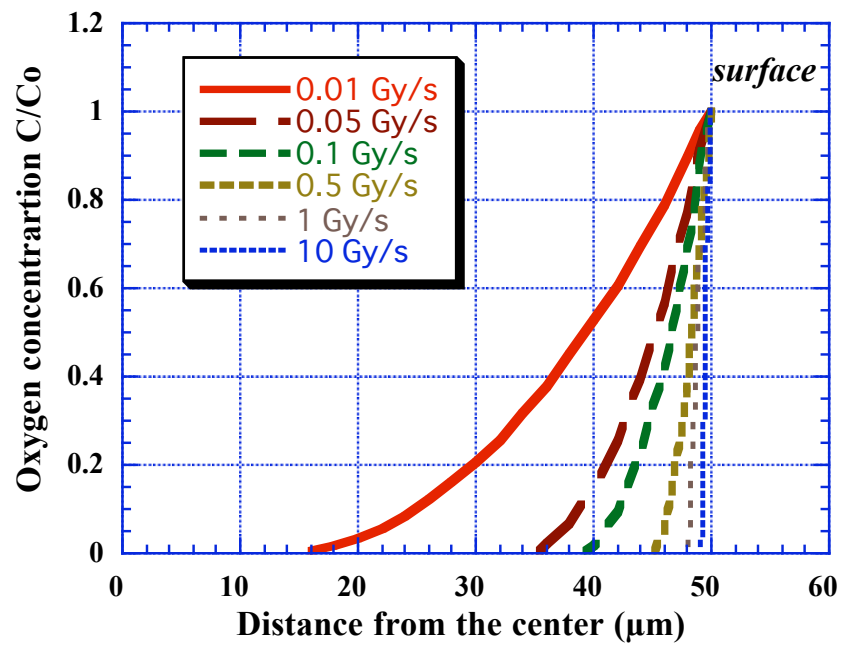
Fig. 1.   T. Yamauchi et al.
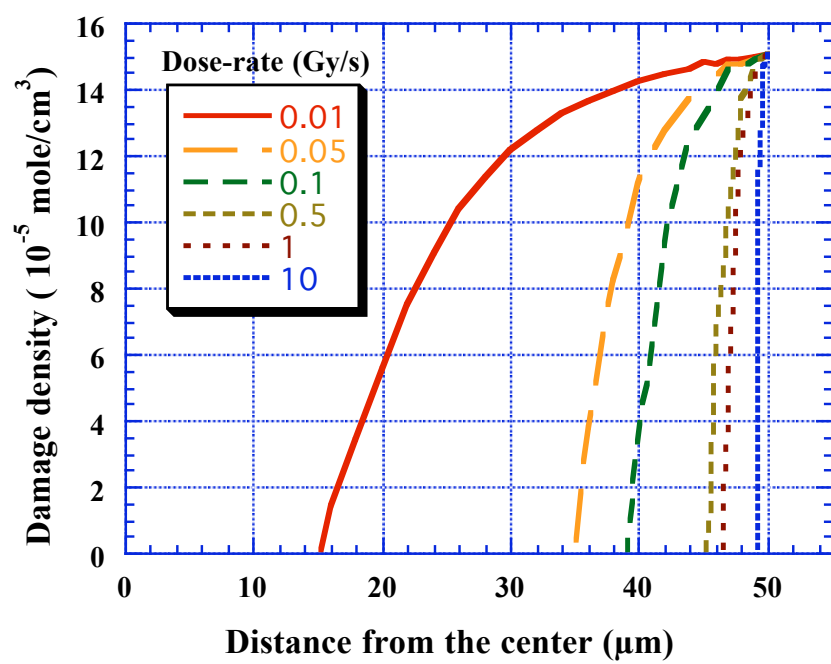
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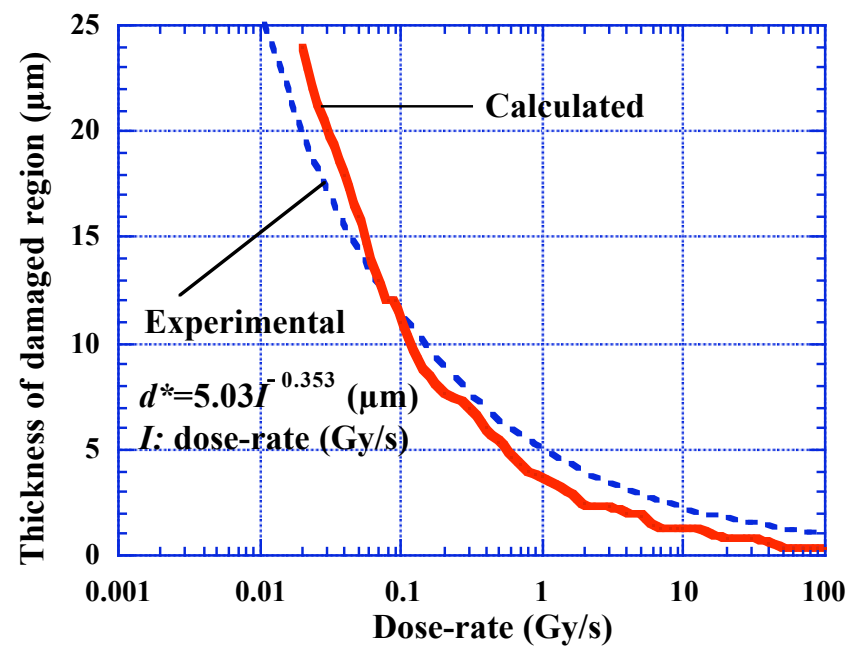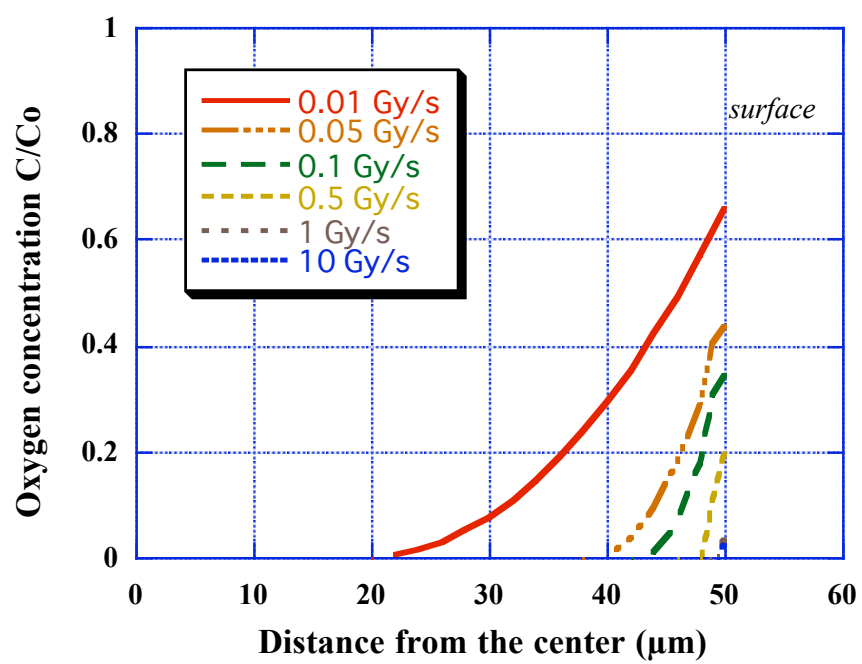
Fig. 3.   T. Yamauchi et al.

The graph shows Thickness of damaged region (µm) versus Dose-rate (Gy/s), with "Calculated" and "Experimental" curves, and the equation:

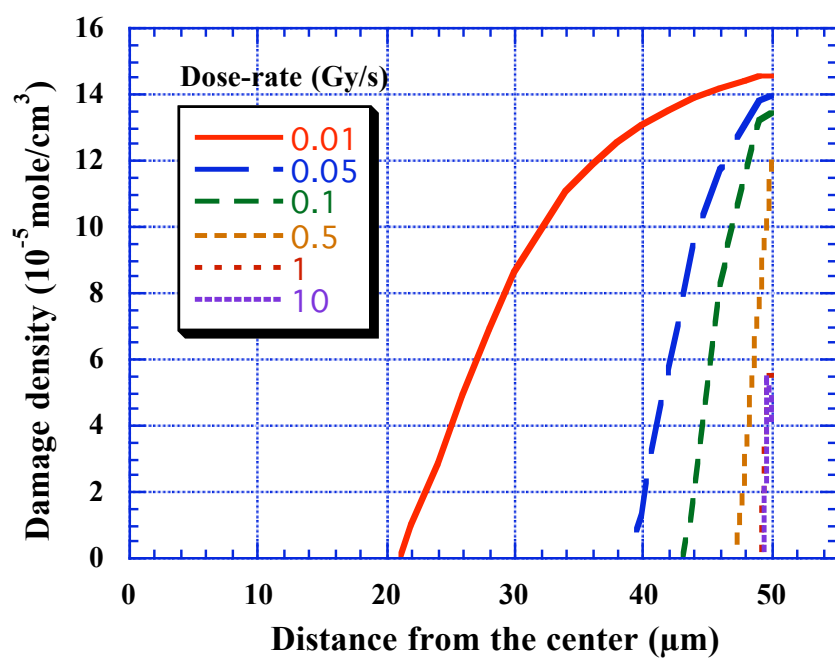$d* = 5.03 I^{-0.353}$ (µm)

I: dose-rate (Gy/s)

Fig. 4.   T. Yamauchi et al.

Fig. 5.   T. Yamauchi et al.

Fig. 6.   T. Yamauchi et al.