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Microscopic model for chemical etchability along radiation damage paths in solids

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Abstract It would be very interesting to develop a picture about removal of atoms from the radiation damaged paths or latent nuclear tracks and undamaged bulk material in track detectors. Here, theory of chemical etching is described briefly and a new model for chemical etching along radiation damaged paths in solids is developed based on basic scientific facts and valid assumptions. Dependence of chemical etching on radiation damage intensity and etching conditions is discussed. A new parameter for etching along radiation damaged paths is introduced, which is useful for investigation of relationship between chemical etchability and radiation damage in a solid. Results and discussion presented here are also useful for further development of nuclear waste immobilization.

Key words Radiation damage, Chemical etchability, Fission fragments, Nuclear track detection technique, Nuclear waste immobilization, Nanofabrication

CLC numbers TL815^{+}.7, O77

1 Introduction

Chemical etching of latent tracks, damaged cylindrical zones created by moving charged particles in solids, is an important procedure in track detection technique. Comparison of removal of atoms in these damaged zones and in the bulk material may provide useful information about track formation. It is also helpful in understanding radiation damage to materials, which has applications in nuclear waste immobilization[1] and ions implantation in semiconductors[2] etc. A number of researchers have studied track formation mechanism [3-6] and other involved processes, e.g., annealing [7-9] and etching[10-12] of nuclear tracks. Nuclear track etching involves a number of parameters, of which etching temperature, concentration of the etchant and relative chemical reactivity of damaged and bulk material are significant. In track detection technique, a suitable etchant and proper etching conditions are essentially needed. They can influence the interpretation of the experimental data about a nuclear reaction, cosmic ray measurement or radiation dosimetry.

It is always useful to develop a mathematical relationship between parameters involved in a process like chemical etching of latent tracks for analysis and interpretation of experimental data. Here an attempt is made to develop a model for chemical etching of latent tracks starting with the atomic scale picture of the etching process. The mathematical relationship developed for etching at atomic scale is then transformed into a relationship of observable etching parameters. Justification for the assumptions used in doing so is given. In the next section, theory of etching is described very briefly followed by a section containing the mathematical derivation of a model for chemical etching of latent tracks. Experimental data are analyzed using the proposed model. Discussion about significance and application of model and conclusions are given in the last section.

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2 A model for chemical track etching phenomenon

2.1 Physical picture

The parallel processes occurring during chemical etching are diffusion of etching molecules to the etching front in the narrow track and transportation or diffusion of etch products out of narrow channels. Especially, at the start of track formation, the etchant flow into a nanometer sized track channel is complicated. It might be one of the reasons for etch induction time which is the delay in the first appearance of track at micrometer scale. Temperature of the etchant has a strong impact on diffusion of etching molecules and transportation of etch products. Fig. 1 shows a schematic of the typical situation of chemical etching of a latent nuclear track in a solid, which is a well-defined type of radiation damage, utilizing the etching schemes by Ditlov[13] and Schulz *et al*.[14].

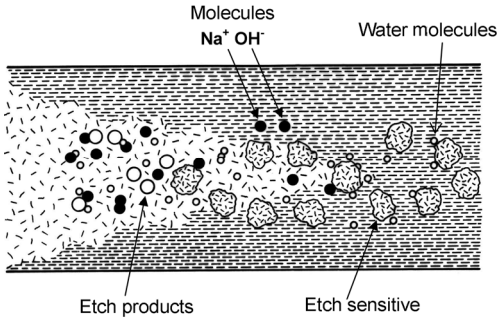

Fig.1 Pictorial representation of etching process of an ion induced damage in a dielectric solid. This picture is a further development of chemical etching schemes by Ditlov[13] and Schulz *et al*[14].

Maximization of preferential track etching for a particle track with the component of deposited energy density used to cause disorder $\varepsilon_{\rm dis}=\varepsilon-\varepsilon_{\rm esc}$, determining the ratio of track to bulk etching cross section $\sigma_{\rm e}^{\rm T}/\sigma_{\rm e}^{\rm B}$ for a given detector material, along the track is possible by the optimisation of (a) the etchant selection, which determines the activation energy of etching $E_{\rm e}^{\rm a}$, (b) concentration of the etchant, the measure of concentration of etching molecules/atoms $c_{\rm e}$ in the etchant, (c) the temperature of the etchant, the measure of attempt frequency *v*, and (d) introduction of proper magnitude of stirring or turbulence in the etchant, rotation or oscillation frequency q of the etchant. The function of stirring is to remove etch products out of growing tracks and to keep concentration and temperature of the etchant uniform. The stirring or pumping (say, millilitre per sec scale) of the etching solution from and to etching bath shall introduce steady oscillatory or rotational flow within the etching bath.

2.2 Mathematical model

The ratio of track etch cross section to bulk etch cross section is given by

$$\sigma_{\rm e}^{\rm t}/\sigma_{\rm e}^{\rm b}=g(\varepsilon_{\rm dis},\bar{\varepsilon}_{\rm bind}^{\rm b}) \tag{1}$$

where $\bar{\varepsilon}_{\rm bind}^{\rm b}$ is the average binding energy of atoms in the bulk detector material. The bulk and track etch cross sections are defined as

$$\frac{N_{\rm e}^{\rm b}}{N_{\rm o}^{\rm b}}=\sigma_{\rm e}^{\rm b}C_{\rm e}d_{\rm e}^{\rm b}\nu_{\rm b}\tau\ {\rm e}^{-\frac{E_{\rm b}}{kT}} \tag{2}$$

and

$$\frac{N_{\rm e}^{\rm t}}{N_{\rm o}^{\rm t}}=\sigma_{\rm e}^{\rm t}C_{\rm e}d_{\rm e}^{\rm t}\nu_{\rm t}\tau\ e^{-\frac{E_{\rm t}}{kT}} \tag{3}$$

where $N_{\rm o}^{\rm b}$ and $N_{\rm o}^{\rm t}$ are numbers of atoms in bulk of volume $d_{\rm e}^{\rm b}a$ and track volume $d_{\rm e}^{\rm t}a$ materials, whereas a is the area of the latent damaged trail of radiation; $N_{\rm e}^{\rm b}$ and $N_{\rm e}^{\rm t}$ are numbers of atoms removed in etching time interval τ per unit volume of etching front with thickness equal to the depth ($d_{\rm e}^{\rm b}$ or $d_{\rm e}^{\rm t}$ for bulk and track etching, respectively) at which the attempt frequency $\nu_{\rm t}$ or $\nu_{\rm b}$ has a non-zero value.

$$\frac{N_{\rm e}^{\rm t}}{N_{\rm o}^{\rm t}}/\frac{N_{\rm e}^{\rm b}}{N_{\rm o}^{\rm b}}=\sigma_{\rm e}^{\rm t}d_{\rm e}^{\rm t}\nu_{\rm t}{\rm e}^{-\frac{E_{\rm t}}{kT}}/\sigma_{\rm e}^{\rm b}d_{\rm e}^{\rm b}\nu_{\rm b}{\rm e}^{-\frac{E_{\rm b}}{kT}} \tag{4}$$

$$\begin{aligned}\sigma_{\rm e}^{\rm t}/\sigma_{\rm e}^{\rm b}&=\frac{d_{\rm e}^{\rm b}\nu_{\rm b}}{d_{\rm e}^{\rm t}\nu_{\rm t}}[\frac{N_{\rm e}^{\rm t}}{N_{\rm o}^{\rm t}}/\frac{N_{\rm e}^{\rm b}}{N_{\rm o}^{\rm b}}]{\rm e}^{\frac{E_{\rm t}-E_{\rm b}}{kT}}\\&=(\frac{d_{\rm e}^{\rm b}\nu_{\rm b}}{d_{\rm e}^{\rm t}\nu_{\rm t}})(\frac{N_{\rm e}^{\rm t}}{N_{\rm o}^{\rm t}})(\frac{N_{\rm o}^{\rm b}}{N_{\rm e}^{\rm b}}){\rm e}^{\frac{E_{\rm t}-E_{\rm b}}{kT}}\end{aligned} \tag{5}$$

The etchability is proportional to cross section ration given in above equation. So,

$$S = V_t / V_b \propto \sigma_e^t / \sigma_e^b \quad (6)$$

$$S = K(\frac{d_e^b v_b}{d_e^t v_t})(\frac{N_e^t}{N_o^t})(\frac{N_o^b}{N_e^b})e^{\frac{E_t - E_b}{kT}} \quad (7)$$

where V_t and V_b are, respectively, track and bulk etch rates, K is constant of proportionality. Parameters d_e^b or d_e^t are very important and depend on chemical reaction kinetics and porosity of the latent tracks.

$$V_t = K(\frac{d_e^b v_b}{d_e^t v_t})(\frac{N_e^t}{N_o^t})(\frac{N_o^b}{N_e^b})e^{\frac{E_t - E_b}{kT}} V_b \quad (8)$$

For various radiations and the same target and etching conditions, V_b will be constant.

The term "reduced etch rate" was defined for the purpose of analysis and comparison between different track data sets as it has weaker dependence on etching conditions compared with track etch rate. Now, it is realized that reduced etch rate is not quite independent of etching conditions. Eq. (7) shows that dependence of reduced etch rate on temperature is considerable due to direct dependence of term $\exp[(E_t–E_b)/kT]$ on temperature, whereas ratio of bulk to track attempt frequencies v_b/v_t might also depend upon temperature. It is clear from Eq. (7) that there is no direct dependence of S on concentration of the etchant. The track etch rate in Eq. (8) strongly depends on temperature and concentration of the etchant.

A new parameter S_T called here as "temperature normalized reduced etch rate" is defined as

$$S_T = S\, e^{-\frac{E_b - E_t}{kT}} \quad (9)$$

Using this definition, Eq. (7) may be written as,

$$S_T = K(\frac{d_e^b v_b}{d_e^t v_t})(\frac{N_e^t}{N_o^t})(\frac{N_o^b}{N_e^b}) \quad (10)$$

If average values of activation energies of bulk and track etching are known for a range of ions, the S_T will be a very suitable parameter for analysis of a track data set and comparison of different data sets.

3 Experimental method and results

CR-39 detectors from Pershore Mouldings (UK) were irradiated with fission fragments of ^{252}Cf using 2π geometry placing detector samples directly on ^{252}Cf source holder, as shown in Fig. 2a. The irradiated detectors were etched in NaOH solution of concentration 1~7 mol·L^{-1} at temperatures 50~80°C for 45 min after which track length measurements were made. Another set of CR-39 detectors was irradiated with fission fragments and etched for 3 h under similar conditions. Variation in set values of etching temperature was not more than ±1°C. Fig. 2b shows the etching procedure of irradiated CR-39 detectors. Details are given in our previous paper presenting initial results[15].

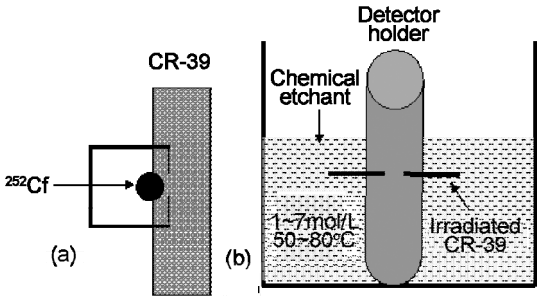

Fig.2 Diagram showing (a) exposure geometry and (b) etching procedure of fission fragment irradiated CR-39 detectors.

After chemical etching, lengths and diameters of fission fragment tracks in CR-39 detectors were measured using a Leitz DAILUX 22EB optical microscope. Track lengths were corrected for bulk etch rate. Track length measurements yielded fission fragment track etch rates whereas bulk etch rates were measured using track diameter variation method. Average diameter value of 25 most circular fission fragment tracks (selected out of 125 measurements) was used for determination of bulk etch rate under different etching conditions. Details are given elsewhere[16].

Fig. 3 shows the temperature dependence of traditionally used reduced etch rate S and that of newly introduced parameter $S_T = S \exp[(E_t–E_b)/kT]$ in the proposed model in Section 2, which is temperature normalised reduced etch rate, over a wide range of etchant concentration (1~7 mol·L^{-1} NaOH water solution). Experimental results in this figure clearly demonstrate that the dependence of S_T on temperature is much weaker than that of S. For analysis and comparison of nuclear track etching results from

different etching conditions, and possibly from different laboratories for the same detector, the new parameter S_T will provide more reliable and conclusive picture of physical processes involved.

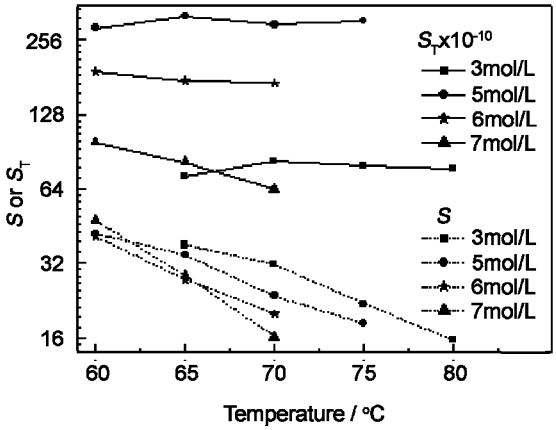

Fig.3 Dependence of S_T on temperature is very weak compared with that of *S*.

4 Discussion and conclusion

Along the radiation damaged paths, atomic binding energy and density[17] in the target material is lowered, resulting in preferential etching along radiation damaged paths (nuclear tracks). Intensity of preferential etching depends on intensity of radiation damage and etching conditions. For reliable analysis of relationship between chemical etchability and intensity of radiation damage in the target material, an experiment results based etching parameter P is essentially required, showing ideally no dependence on etching conditions, as given below:

$$P(T,C) = P \tag{11}$$

where T and C are etchant temperature and concentration. Following this motivation, a new parameter S_T for nuclear track etching is discovered, which shows very weak dependence on etching temperature. So, use of S_T over S will be very useful for enhancing chemical etchability of radiation damaged paths or nuclear tracks. Definition of new parameter S_T includes activation energies of track and bulk etching, which will help understanding these important etching energetics related parameters during analysis of experimental data based on this new parameter. The microscopic model describing chemical etchability of latent tracks developed here is supported by experimental results and will be helpful in understanding radiation damage and possibly micro and nanofabrication of channels using single ions[18].

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References

1 Farnan I, Cho H, Weber W J. Nature, 2007, **445**: 190-193.
2 Grambole D, Herrmann F, Heera V, *et al*. Nucl Instr Meth B, 2007, **260**: 276-280.
3 Westphal A J, Price P B, Weaver B A, *et al*. Nature, 1998, **396**: 50-52.
4 Fleischer R L, Price P B, Symes E M, *et al*. Science, 1964, **143**: 349-351.
5 Dartyge E, Daraud J P, Langevin Y, *et al*. Phys Rev B, 1981, **23**: 5213-5229.
6 Tombrello T A, Wie C R, Itoh N, *et al*. Phys Lett A, 1984, **100**: 42-44.
7 Price P B, Gerbier G, Park H S, *et al*. Nucl Instr Meth B, 1987, **28**: 53-55.
8 Rana M A, Qureshi I E, Khan E U, *et al*. Nucl Instr Meth B, 2000, **170**: 149-155.
9 Rana M A, Qureshi I E, Manzoor S, *et al*. Nucl Instr Meth B, 2001, **179**: 249-254.
10 Somogi G. Nucl Instr Meth, 1980, **173**: 21-42.
11 Pandey A K, Kalsi P C, Iyer R H. Nucl Instr Meth B, 1998, **134**: 393-399.
12 Fink D, Ghosh S, Klett R, *et al*. Nucl Instr Meth B, 1998, **146**: 486-490.
13 Ditlov V. Radiat Meas, 2005, **40**: 240-248.
14 Schulz A, Danziger M, Trofimov V V, *et al*. Radiat Meas, 1997, **28**: 27-30.
15 Rana M A, Qureshi I E. Nucl Instr Meth B, 2002, **198**:129-134.
16 Rana M A. Chin Phys Lett, 2007, **24**: 3107-3110.
17 Rana M A. Nucl Sci Tech, 2007, **18**: 349-353.
18 Yousef H, Lindeberg M, Hjort K. Nucl Instr Meth B, 2008, **266**: 1659-1665.