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Chemical Etching of Fission Tracks in Polyfluoro Plastics

Abstract. A method has been developed for the chemical etching of fission tracks in polyfluoro plastics. The formation of fine holes several tens of nanometers in diameter in polyvinylidene fluoride films, bombarded by fission fragments in oxygen and etched in 5-normal sodium hydroxide solution at 85°C, was confirmed by electron microscopy.

The technique of chemical etching of charged particle tracks in plastic materials has been extended to polyfluoro plastics. We have obtained porous polyvinylidene fluoride films with fine holes several tens of nanometers in diameter by the chemical etching of fission tracks.

Plastics used widely in studies and applications of the chemical etching of tracks include polycarbonate, polyethylene terephthalate, and cellulose esters. We are interested in the chemical etching of tracks in substances having high chemical resistivity such as polyfluoro plastics since, from the viewpoint of scientific and technological applications, a membrane filter made by the etching of tracks in a chemically resistive substance will be extremely useful.

We have studied the chemical etching of tracks in polyvinylidene fluoride, because this film is the least porous and most impervious to gases of commercially available polyfluoro plastics, and is suitable for an examination of the growth of very fine holes. Polyvinylidene fluoride is a polymer known to have characteristics for radiation exposure intermediate between those of cross-linked polymers and degradation polymers. Makuuchi *et al.* and Seguchi *et al.* (1) studied the effects of γ - and β -rays on polyvinylidene fluoride and found that exposure to radiation in vacuum results in both cross-linking and chain scission with almost the same G value (the number of molecules changed per absorption of 100 ev of radiation energy) whereas exposure in air favors chain scission with

a resultant decrease in the mean molecular weight. These investigators also measured the concentration of free radicals remaining after exposure of the polymer to radiation and found the lifetime of free radicals to be much longer than 24 hours. Accordingly, for the enhancement of the chemical etching of tracks in polyvinylidene fluoride, it appears that it would be effective to irradiate in oxygen or some other gas that reacts with active species formed in the cylindrical zone around the charged particle trajectories

and to form chemical species of reduced molecular weight. On the basis of these considerations, we have bombarded fission fragments in oxygen and found a method for enlarging fission tracks in polyvinylidene fluoride films.

Polyvinylidene fluoride films 9 μm thick (Kureha Chemical Industries Co. Ltd.) were irradiated by fission fragments obtained from the thermal neutron fission of ^{235}U in reactor JRR-4 of the Japan Atomic Energy Research Institute. A natural uranium layer 100 nm thick deposited on an aluminum foil was used as a source of fission fragments. A collimator was disposed between the film and the fission source to obtain aligned tracks. The film, the fission source, and the collimator were contained in a quartz tube filled with oxygen and irradiated at a thermal neutron flux of $1.7 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$ for 10 minutes. The thickness of the film and of the uranium layer and the oxygen pressure were selected so as to satisfy the condition that all fission fragments entering the film have sufficient energy to penetrate the film. After cooling the film for several days to allow for the decay of fission products, we took the film out of the quartz tube and etched it in sodium hydroxide solution.

Figure 1a is a surface electron micrograph of a film irradiated in oxygen (pressure, 250 torr) and etched for 29 hours in 5N sodium hydroxide at 85°C. The electron micrograph was taken with a field emission scanning electron microscope (Japan Electron Optics Laboratory Co. Ltd., type JSM-F7). Holes about 50 nm

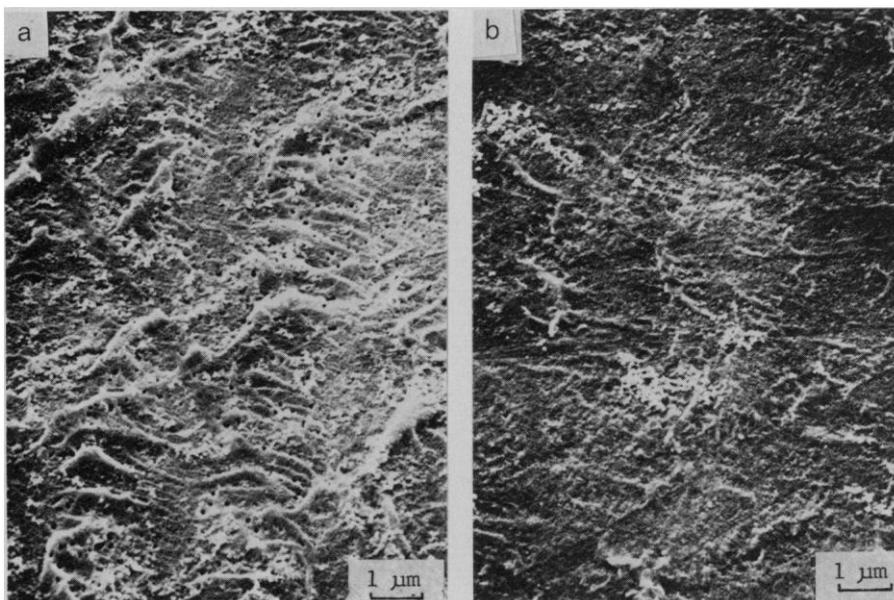


Fig. 1. Tracks of fission fragments in polyvinylidene fluoride film. Scanning electron micrographs of films irradiated in oxygen at a pressure of 250 torr (a) and in vacuum (b). Both were etched for 29 hours in 5N sodium hydroxide at 85°C. A gold-palladium alloy a few nanometers thick was deposited on the film.

in diameter are clearly seen. The hole density is $7 \times 10^8 \text{ cm}^{-2}$. The surface of this film is considerably rougher than that of polycarbonate or polyethylene terephthalate. There are protuberances like mountain chains. The roughness is a characteristic of the original film and remains unaltered after irradiation and chemical etching. We do not believe that the roughness has any effect on the etching of fission tracks. Figure 1b is an electron micrograph of another film irradiated in vacuum and etched under the same conditions as in Fig. 1a. In this case there is almost no indication of chemical etching. A detailed examination, however, shows the existence of obscure dark spots, which are etched tracks in their earlier stage of enlargement.

A comparison of Fig. 1, a and b, indicates the effectiveness of oxygen for enhancing the preferential etching rate. The reaction of oxygen with active species formed by the passage of fission fragments must be occurring during bombardment of fission fragments as well as during the cooling time after irradiation.

The hole density can be calculated from the irradiating condition by the use of the formula

$$\rho = 2N\sigma\phi tA/S$$

where ρ is the hole density, N is the number of ^{235}U atoms, σ is the fission cross section of ^{235}U for thermal neutron, ϕ is the thermal neutron flux, t is the irradiation time, A is the fraction of fission fragments that enters into the film, and S is the irradiation area. The value of A , determined by the geometry of the collimator, is 1/70 in the present experiments. The calculation gives $\rho = 3.0 \times 10^8 \text{ cm}^{-2}$, which is comparable with the observed density in Fig. 1a.

We also took transmission electron micrographs with a high-voltage electron microscope (Japan Electron Optics Laboratory Co. Ltd., 1000 kv) in order to see the growth of etched tracks across the film. A specimen 9 μm thick was directly observed. Several circular spots glittered intensely, and many somewhat opaque patterns of various lengths were recognized. When the specimen was tilted several degrees, the spots changed to opaque patterns whose lengths increased with the angle of inclination. At the same time some of the opaque patterns became shorter in length and changed to spots. We believe that the spots that glitter are due to the passage of the electron beam through the holes, which are oriented exactly parallel to the beam direction. The opaque patterns are the images

of the holes inclined to the electron beam. We also determined that the etched tracks penetrated the film by detecting the passage of gases and aqueous solutions through the film.

The chemical etching of the charged particle tracks has been studied in various dielectric materials, and etching methods are now widely used in the detection of charged particles as well as in many technological applications (2). Monnin (3) has examined the chemical etching in polyethylene, polyvinyl chloride, polyvinyl-polyvinylidene chloride copolymer, and several other plastics, but polyfluoro plastics were not included. Bopp (4) attempted the chemical etching of α -particle tracks in polytetrafluoroethylene, polychlorotrifluoroethylene, and polyvinylidene fluoride under severe etching conditions (concentrated sulfuric acid at 300°C and 50 percent sodium hydroxide solution at 155°C) but could not find etch pits in any of the polyfluoro plastics. Maybury and Libby (5) revealed fission tracks in polytetrafluoroethylene by graft copolymerization of acrylic acid and by the fixation of dye so that its fluorescence could be observed under ultraviolet light. Chemical etching was not used.

The rate at which the track width in polyvinylidene fluoride enlarges, obtained by dividing the hole diameter by the etching time in Fig. 1a, is 1.7 nm/hour. The value is smaller by almost

three orders of magnitude than the corresponding rate in polycarbonate or polyethylene terephthalate. It seems unlikely that polyvinylidene fluoride will develop holes several micrometers in diameter by practical experimental procedures, sufficient to permit them to be seen under an optical microscope. A slow etching rate is anticipated for all polyfluoro plastics. Probably polyfluoro plastics are suitable for the formation of a membrane filter with fine holes a few hundred nanometers or less in diameter.

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A Fluorite Isotype of SnO_2 and a New Modification of TiO_2 : Implications for the Earth's Lower Mantle

Abstract. *The existence of a cubic fluorite-type SnO_2 and a hexagonal TiO_2 (which may be related to the fluorite structure) have been demonstrated by an in situ x-ray diffraction study in which a diamond-anvil pressure cell was used after the samples had been heated by a continuous yttrium-aluminum-garnet laser. At room temperature, the lattice parameter for SnO_2 (fluorite) is $a = 4.925 \pm 0.005$ angstroms and those for TiO_2 (fluorite-related) are $a = 9.22 \pm 0.01$ angstroms and $c = 5.685 \pm 0.006$ angstroms at about 250 kilobars. The volume change associated with the transition from rutile to fluorite (or related structure) is about -8 percent for SnO_2 and -10.5 percent for TiO_2 at transition. Upon release of pressure, both the fluorite-type SnO_2 and the TiO_2 reverted to the $\alpha\text{-PbO}_2$ structure at room temperature. The hypothesis that the earth's lower mantle is composed of oxide phases might be feasible if it were possible for SiO_2 to possess the fluorite structure or its related forms at high pressure, as shown for SnO_2 and TiO_2 in this study. The oxide hypothesis proposed here differs from that postulated by Birch in that the primary coordination of silicon is 6 for Birch's hypothesis and 8 for the hypothesis presented here.*

Because of the stoichiometric similarity between SiO_2 and TiO_2 , Thompson predicted in 1952 that SiO_2 might crystallize in the rutile (TiO_2) structure at high pressure; this idea was partly the basis of Birch's hypothesis that the earth's lower

mantle consisted predominantly of oxide phases (1). Stishov and Popova (2) later synthesized the rutile form of SiO_2 , which was subsequently named stishovite (3). Further phase transformation of stishovite to the fluorite structure has