CHAPTER 4

STUDIES ON ELECTROCHEMICAL ETCHING (ECE)

4.1 INTRODUCTION

The wide attention which the ECE technique has attracted is primarily because of large scale amplification of latent tracks (about $2 \times 10^4$ for tracks of 200 /um diameter, assuming an original latent track diameter of 100 Å) which the technique affords. This is achieved without compromising on the salient features of the track detectors. The amplification is a useful aid in many nuclear applications where low track densities are encountered as a rule rather than exception. Studies on this technique were initiated in our laboratory to explore its utility for personnel fast neutron dosimetry. Several interesting observations made during these studies are summarised below.

4.2 DESCRIPTION OF ECE CELLS

The first cell used by us for ECE is shown in Fig.4.1. This cell is quite bulky and requires about 200 ml of etchant. This was soon replaced by another cell when it was realised that ECE should be possible on single surface also. This second cell is shown in Fig.4.2. It is quite compact and requires less than 10 ml of etchant. It is normally used for the preparation of electrodeposited radioactive sources but is found useful in ECE studies also.

Fig.4.2 is self-explanatory. Here the exposed side of the
FIG. 4.1. CELL FOR ELECTROCHEMICAL ETCHING.

PART NOS. 1 & 2, PERSPEX
PART NOS. 3, 4, & 5, GLASS & 6, ELECTRODES
SCALE - 1:1, UNIT - mm.
FIG. 4.2 EXPLODED VIEW OF
ELECTROCHEMICAL ETCHING CELL

1) HIGH VOLTAGE ELECTRODE (S.S.)
2) PERSPEX CAP
3) PERSPEX CHIMNEY.
4) SILICONE RUBBER GASKET
5) DETECTOR FILM
6) DISC (S.S.) [PART OF THE
ground electrode]
7) CUP (S.S.) [GROUND ELECTRODE]
8) SCREW FOR MAKING ELECTRICAL
CONNECTION.
film faces the high voltage electrode. If the tracks can appear on both sides, as in the case of recoil atom tracks from neutron irradiation, that side on which the track development is desired will face high voltage electrode. The contact between the film and the ground electrode is improved by introducing a drop of dilute (0.1 N) KOH solution.

The advantages offered by this setup are as follows (Bhagwat and Soman, 1979):

i) The amount of etchant required per cell is about 10 ml or less.

ii) The cell permits ECS at higher temperature also, i.e. upto about 75°C. This is achieved by surrounding the cell with a small heating jacket made for this purpose.

iii) Two or more cells can be connected simultaneously in parallel to the same function generator.

iv) Since only one side of the film is subjected to BCE, the question of background contribution from the other side does not arise. This is a serious drawback in double surface BCE especially when film thicknesses are small.

v) Polycarbonate films with mat finish on one side, i.e. all grades of Makrofol(R), can be conveniently used with this set up as it is possible to avoid BCE on the side with mat finish.

Experiments were also conducted using different shapes of high voltage electrode (part 1, Fig. 4.2) kept at different distances from the films. These variations, however, did not alter the results in any observable way.
4.3 VOLUME OF THE ETCHANT REQUIRED

Since the EGE cell shown in Fig. 4.2 is a miniaturised version of our earlier cell (and that of cells in use in other laboratories) we were tempted to explore the effect of further reduction in etchant volume on the EGE process. Accordingly, experiments were conducted using the cell of Fig. 4.2 and employing progressively smaller volumes of etchant, i.e. 8.0, 4.0, 2.0, 1.0 and 0.5 ml (of 10 N KOH + C₂H₂OH). In all these cases, the fission fragment track sizes were essentially the same. The track sizes were affected when the etchant volume used was 0.25 ml or less (Bhagwat and Soman, 1981a).

In the light of this experience, i.e. the requirement of small etchant volume, a new cell arrangement shown in Fig. 4.3 was tried and found useful. Here, the high voltage electrode also acts as a container for the etchant. The etchant volume required then depends upon the depth of the electrode cup. This new cell not only retains all the advantages of the cell shown in Fig. 4.2, but also makes the film mounting procedure simple and fast. Here one need not worry about the problem of leak tightness of the cell as long as the film is slightly bigger than the electrode faces. This arrangement also avoids completely any kind of mechanical stress on the film. All other cells, which achieve leak tightness through the use of gaskets, subject the film to mechanical stress (Johnson & co-workers, 1978). This cell is extremely useful for brittle film materials like CR-39.
NOTE = HIGH VOLTAGE ELECTRODE ALSO SERVES AS A CONTAINER FOR ETCHANT.

FIG. 4.5. SIMPLIFIED ELECTROCHEMICAL ETCHING SET UP

ALL DIMENSIONS ARE IN 'm m'

NOTE = HIGH VOLTAGE ELECTRODE ALSO SERVES AS A CONTAINER FOR ETCHANT.
4.4 HIGH VOLTAGE FUNCTION GENERATOR (HVFG)

The HVFG used in our experiments is a combination of a function generator (commercially available) and a step up transformer made from a ferrite core; its circuit is shown in Fig. 4.4 (the function generator has been described in Chapter 2). It gives a sinusoidal output from a few volts to 2000 volts (peak to peak) in the frequency range of 0.5 - 10 kHz. Its current capacity is about 3 milliamperes. Unless stated otherwise, sinusoidal waveform alone was used in all our experiments.

4.5 STUDY OF SOLUTION PARAMETERS

In the initial trials on BCE, KOH solution of strength 400 g/liter (i.e. about 7 N) was used arbitrarily. But in the subsequent studies it has been observed, as is explained later, that this concentration of 7 N is ideal for BCE. These studies have been detailed below (Unless stated otherwise, Iexan(R) film was used as a track detector, measurements were made at room temperature and all the chemicals used were of AR/GR quality).

Since alcoholic solutions of KOH (or NaOH) lead to faster development of tracks both in CE and BCE, it was felt desirable to study the role played by alcohol. This implied that the behaviour of KOH solutions be understood first. These behaviours are studied in the light of conductivity and viscosity measurements carried out for these solutions.

4.5.1 Conductivity Measurements

The variation of conductivity of pure KOH solutions with
FIG. 4.4. HIGH VOLTAGE FUNCTION GENERATOR
its normality was studied first. These results are shown in Fig. 4.5 by curve (A). This curve shows that the conductivity is maximum in the range of 6N to 9N. This range should be ideal for EBG experiments if conductivity alone is the criterion.

This was followed by the study of the effect of varying amounts of alcohol on the conductivity of a given KOH solution (7.5 N in this case which also corresponds to the mid-point of the conductivity plateau of curve (A), Fig. 4.5). These results are shown in Fig. 4.6. It is seen clearly that even small amounts of alcohol reduce the conductivity tremendously. The drop in conductivity becomes gradual as the amount of alcohol added increases. Since the role of alcohol is secondary (and that of KOH primary), it was decided that, in all the subsequent work with KOH solutions and alcohol (C\textsubscript{2}H\textsubscript{5}OH) mixtures, the volume ratio of the two components shall be 1:1. The conductivities for such mixtures are shown by Curve (B) in Fig. 4.5.

For this curve (B) the readings are available for KOH solution of normality up to 10 N only, because beyond this point, the equal volumes of the two components do not mix completely at room temperature. Also, the conductivity of mixtures is seen to be very much lower than for pure KOH solutions. This is to be expected in the light of trend seen in Fig. 4.6. However, since it is known that alcoholic solutions give higher track etch rates, it only suggests at this stage that conductivity is not the sole deciding factor.

4.5.2 Viscosity Measurements

The next step was the measurement of viscosity of alcoholic
FIG. 4.5 VARIATION OF CONDUCTIVITY OF KOH SOLUTION WITH ITS NORMALITY.
FIG. 4.6 VARIATION OF CONDUCTIVITY OF KOH SOLUTION (7.5 N) WITH INCREASING AMOUNT OF ETHYL ALCOHOL ADDED TO IT.
KOH solutions. These results are shown in Fig. 4. Viscosity curve for pure KOH solutions is also shown for comparison (Hand Book of Phys. and Chem. CRC Press, 1975-76). From this figure it is clear that alcoholic solutions have higher viscosities. The mixing is also associated with slight reduction in volume. The curves for viscosity differ from those for conductivity in one way, in the sense that no saturation is ever reached for them.

We also know from literature that KOH solutions of any given normality give higher etching rates than NaOH solutions of the same normality (Blanford & co-workers, 1970; Dutrannois, 1971; Enge & co-workers, 1974) and that they have lower viscosities too, which lead to higher etching rates, other factors being equal. The higher etching rate of KOH, as compared to that for NaOH, has also been explained to be due to smaller size of the hydrated Potassium ion as compared to that of hydrated Sodium ion (Enge & co-workers, 1974). The size difference contributes to difference in mobility and viscosity.

As viscosity measurements also show an unfavourable trend, i.e. higher viscosities for alcoholic solutions as compared to pure solutions, it is clear that major cause of higher etching rates for alcoholic solutions lies somewhere else. To get the complete picture, therefore, some etching rate measurements - both chemical and electrochemical - were made. These measurements and their interpretations are described below.

4.5.3 Results of Bulk Chemical Etching

Bulk etch rate measurements were made for Lexan(R) film
FIG. 4.7 VARIATION OF VISCOSITY OF KOH SOLUTION WITH ITS NORMALITY.
using the following etchants:

i) 6N KOH, (ii) alcoholic 6N KOH and (iii) alcohol alone, etching temperature being 60°C. For etchants (i) and (ii) the etching rates observed are 146 and 1566 μg.cm⁻².h⁻¹ (corresponding to 1.22 and 13.05 μm.h⁻¹, taking density of Lexan as 1.185 g.cm⁻³) respectively. But for the third etchant, i.e., pure alcohol, no etching effect was observed. On the contrary, it shows weight gain to the extent of 42 μg.cm⁻².h⁻¹ (Bhagwat and Soman, 1981b).

In the light of these results, the role of ethyl alcohol in chemical etching can be interpreted as follows: The presence of ethyl alcohol produces swelling of the polycarbonate foil by penetration which in turn causes relaxation of secondary valence forces between long linear polymer chains and enhances interchain separation (Benton, 1968). This not only increases the susceptibility of separated polymer chains to chemical attack but also enhances penetration of the etchant as a whole. The etch rate enhancement thus obtained is more than an order of magnitude.

In case of etching with pure alcohol, the weight gain was found to have disappeared after some time indicating thereby that the retention of alcohol is not permanent. In case of etching with alcoholic KOH, there was no further loss of weight (for the film) with storage time indicating that alkali action on loosened chains is quick which does not leave any scope for alcohol remaining trapped after etching has ceased.

4.5.4 Track Etch Rate Measurements

A few track-etch rate (i.e., diameter) measurements — both
chemical and electrochemical - were also made at room temperature (24°C) for normally incident fission fragments to understand the role of alcohol. This data which is given in Table 4.1 below is also represented in Fig. 4.8.

Table 4.1

<table>
<thead>
<tr>
<th>Etchant composition</th>
<th>Method of etching</th>
<th>Etch rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>6N KOH</td>
<td>CE</td>
<td>0.162 μm/h</td>
</tr>
<tr>
<td>6N KOH + Alcohol (1:1)</td>
<td>CE</td>
<td>2.74 &quot;</td>
</tr>
<tr>
<td>6N KOH</td>
<td>BCE</td>
<td>22.8 &quot;</td>
</tr>
<tr>
<td>6N KOH + Alcohol (1:1)</td>
<td>BCE</td>
<td>32.5 &quot;</td>
</tr>
</tbody>
</table>

It helps us to clearly identify the role of alcohol in the two processes, i.e. CE and BCE. Thus, while the presence of alcohol leads to a track etch rate enhancement by a factor of about 16.9 in CE, it enhances the rate in BCE only by a factor of about 1.4. This reduced enhancement of track etch rate in BCE is due to lower conductivity and higher viscosity of alcoholic solution. The role of all the three factors, i.e. presence of alcohol, conductivity and viscosity is thus obvious.

There is one more factor, i.e. track shape which further helps us to identify the contribution of viscosity and conductivity
FIG. 4.8 COMPARISON OF VARIOUS ETCHING RATES FOR LEXAN (≈ 280 μm) FOR FISSION TRACKS.
4.5.5 Saturation Effects in Track Etch Rate Curves

Fig. 4.9 is a plot of maximum average diameters of EC etched fission tracks in Lexan versus the normality of KOH solutions. The lower curve denotes the diameter growth rate. These curves clearly show a maximum (i.e. a saturation effect) around 7N. Similar saturation effect had been reported earlier (Sohrabi, 1975) but no explanation was offered for the same. Our investigations have enabled us to explain it.

Variation of bulk etch rate and track etch rate (i.e. diameter measurements) with concentration of etchant show no saturation effect in CE for Lexan as is evident from Fig. 4.10. Similar results have been reported in literature also (Becker, 1973) and the same trends are obtained when alcoholic KOH solutions are used. The curves in Fig. 4.10 are identical in shape too. This is because both these measurements represent a surface phenomenon, which offers no scope for the manifestation of the effects of any property of the etching solution, except representing their overall etching ability. Chemical etch rates were therefore measured for KOH solutions based on track lengths. This data is represented in Fig. 4.11. It shows the existence of saturation in track etch rates around 12N. The appearance of saturation in Figs. 4.11 and 4.9 can now be explained as follows:

In CE, the rate at which the etchant penetrates the track region decreases as its viscosity (i.e. concentration) increases. However, the etching ability of the solution increases with concentration.
FIG. 4.9 EFFECT OF NORMALITY OF KOH SOLUTIONS ON TRACK DIAMETERS IN ECE (FOR FISSION TRACKS) ECE AT 2 kVp & 2 kHz FOR 6 Hrs. USING 280 µm LEXAN.
FIG. 4.10. VARIATION OF BULK AND TRACK ETCH RATE (GROWTH) IN CE WITH CONC. OF KOH AT ROOM TEMPERATURE.
FIG. 4.11 VARIATION OF CHEMICAL TRACK ETCH RATE (TRACK LENGTH) WITH CONCENTRATION OF KOH SOLUTION AT ROOM TEMPERATURE.
The situation at the solid-liquid interface 'inside' the track region is therefore very typical. At this interface, the etchant concentration drops due to attack on the polymer and the high viscosity of the etchant does not permit its quick replacement by fresh solution from the bulk. As a result there is a drop in the track etch rate at very high concentrations, i.e. beyond 12N. Alternatively, the drop in track etch rate is the result of slow penetration of the etchant in the track region due to very high viscosity. The narrow channel characteristics of the track thus give rise to a situation where the effect of viscosity of the etchant becomes evident. The presence of etch products in the track channel may also enhance the viscosity of the etchant and contribute to lowering of etching rates.

The above situation which can be considered as a shape or geometry factor gets further magnified in ECE due to voluminous nature of the ECE track. The ECE track is connected to the surface through a small channel or orifice (Griffith & co-workers, 1977) as shown in Fig. 4.12. We were unable to take nice photographs of this type showing the depth-wise profile of an ECE track. However, we were able to photograph nicely the small orifice on the mouth of the ECE track. These photographs are depicted in Fig. 4.13. During ECE therefore it can be visualised as though a small reservoir (i.e. ECE track) is connected to a big reservoir (bulk of the etchant) through a small opening or the orifice. At high viscosities the small orifice does not permit rapid mixing of solutions in the two compartments and the drop in concentration of the etchant in the track volume is not adequately compensated. Alternatively, the track
FIG. 4.12 VERTICAL SHAPE OF A NEUTRON INDUCED RECOIL ATOM TRACK-EC ETCHED. (MICROPHOTOGRAPH FROM A SLICED SAMPLE. Ref: (GRIFFITH AND OTHERS, 1977))
FIG. 4.13. MICRO PHOTOGRAPHS OF ECE TRACKS SHOWING THE ORIFICE (OR THE MOUTH) OF THE VOLUMINOUS TRACK AS SEEN UNDER (a) TRANSMITED AND (b) REFLECTED LIGHT.
FIG. 4.13. MICROPHOTOGRAPHS OF ECE TRACKS SHOWING THE ORIFICE (OR THE MOUTH) OF THE VOLUMINOUS TRACK AS SEEN UNDER (a) TRANSMITED AND (b) REFLECTED LIGHT.
etch rate drops due to slow penetration of the etchant, in the track volume, at very high viscosity. This gives rise to the observed effect, i.e. drop in EC etch rate at higher concentration/viscosity.

The presence of etch products may also contribute to lowering of etching rates, as stated earlier.

If viscosity were the only parameter of importance in ECE, the peak EC etch rate should have occurred around 12N, as observed in case of CE and shown in Fig. 4.11. But the peak etch rate in ECE corresponds to a concentration of 7N. This shifting of peak towards lower concentration is due to conductivity saturation (or peak conductivity) for the etchant occurring at a lower concentration. Thus, for pure KOH solution as etchant in ECE, a concentration of about 7N is ideal. However, a concentration of 6N has been used very often, as it permits easy comparison with published results.

Similar comments should apply to ECE with alcoholic KOH solutions also. Fig. 4.14 shows the effect of variation of concentration of KOH solution in alcoholic KOH on the maximum average diameters of EC etched fission tracks in Lexan. This curve differs from Fig. 4.9 (which refers to ECE with pure KOH solution) in two ways:

1) Here the EC etch rates continue to increase up to 10N with slight saturation appearing after 9N. The trend of the curve could not be followed beyond 10N for the reason stated earlier. Assuming that the saturation occurs at 10N, it is clear that there is a rightward shift of the peak from 7N to 10N when we switch over from pure KOH solutions to alcoholic KOH solutions.
FIG. 4.14. EFFECT OF NORMALITY OF KOH SOLUTION USED IN THE MIXTURE OF C₂H₅OH + KOH SOLUTION (EQUAL VOL.) ON TRACK DIAMETERS (FOR FISSION TRACKS) IN ECE
ii) The second point is somewhat hypothetical. Had there been a clear peak in Fig. 4.14, it would have been broader than that observed in Fig. 4.9. Justification for this statement comes from the fact that conductivity and viscosity changes for alcoholic solutions are gradual when compared with those for pure solutions (See Figs. 4.5 and 4.7).

4.5.6 Some Additional Results

It was also expected that the variation of bulk etch rates with concentration of KOH during BCE should follow the same trend as for chemical bulk etch rates. This was found to be so, because both of these measurements represent a surface phenomenon.

Similarly, while studying the effect of alcohol on chemical etch rate (bulk and diameter growth rate), it is noticed that the presence of alcohol leads to larger enhancements at higher KOH concentration, e.g. bulk etch rate for 10N KOH + C2H5OH mixture at room temperature (24°C) is higher by a factor of about 28 as compared to that of pure 10N KOH solution. This factor is only about 17 for KOH concentration of 6N. The increases are lower when track etch rates based on track length are considered - being about 5 and 7 for KOH concentrations of 6N and 10N respectively. This is expected in view of the effect of track shape when track lengths are considered.

4.5.7 Effect of Temperature on Etch Rates

When we compare the curve in Fig. 4.9 with the work reported in literature for higher temperature, i.e. 70°C (Somogyi, 1977b), we find that no peak indicating saturation appears in the latter case. We also know that high temperatures reduce viscosity and increase
conductivity. This has probably pushed the peak beyond 10^N, the concentration up to which results have been reported. The effect of high temperature is thus obvious.

4.6 STUDY OF ELECTRICAL PARAMETERS

4.6.1 Effect of Frequency, Voltage and Time of ECE

The effect of frequency was studied on both track density and track sizes for fast neutron induced recoil particle tracks. The effect on track density is shown in Figs. 4.15 and 4.16 for pure KOH solution (Shagwat and Soman, 1991) and alcoholic KOH solution respectively. It is clearly seen that track density increases as the frequency of applied voltage decreases. The same trend was noticed for control films also, though the increase was less rapid. It is thus obvious that the net track density increases with decreasing frequency. The sensitivity (tracks/neutron) also increases correspondingly. These figures also show that background track density is large whenever alcoholic KOH is employed as etchant.

The above curves could not be studied further towards lower frequencies because of limitations of equipment output. However, it is clear that the curve's cannot be expected to rise indefinitely as they must drop at some stage so as to pass through origin at zero frequency (this is a physical constraint). Thus, it appears that the peak lies somewhere between zero and 0.25 kHz. This peak position is different from that reported by Schrabi (1975) which is in the region of 1.5 to 2.0 kHz.
Fig. 4.15. Effect of frequency on number of recoil atom tracks (Am-Be neutrons) at const. $V_p$; $V_p = 1500$
etchant: pure KOH soln. (6 N)
film: Lexan ($\approx 280 \mu m$)
Time of EC: 6 h.

Note: The dashed line passing through origin indicates the expected trend for the irradiated film.
FIG. 4.16. EFFECT OF VARIATION OF FREQUENCY ON TRACK DENSITY FOR RECOIL ATOM TRACKS

\( V_p : 2000 \), ETCHANT : IONKOH + \( \text{C}_2\text{H}_5\text{OH} \),

FILM : LEXAN (≈ 280 \( \mu \text{m} \)), TIME OF ECE : 3 h,

Am-Be NEUTRON SOURCE.

NOTE: THE DASHED LINES SHOW THE TREND THAT COULD BE EXPECTED BELOW 0.25 kHz.
There is no immediate explanation for this difference in positions of peaks except that it may be the result of different overall circuit which also includes cell design, type of film material, its crystallinity etc. Recently it has been reported (Ramli, Lovick and Durrani, 1981, to be published) that the potential dividers, used to measure the output voltages of amplifiers, show a dependence on frequency and on the load impedance of the oscilloscope. This only confirms the lack of complete understanding of the relevant parameters at present. One point, however, may be mentioned: it may be possible at a later date, to shift the peak position, by changing the circuit parameters, to a point where other advantages such as largest track diameters or minimum background are also attainable.

From Fig. 4.15 and 4.16 it is also evident that the net track densities are very large when alcoholic solutions are used in place of pure KOH solutions, i.e. alcoholic solutions lead to sensitivity enhancement of the film. This is due to alcoholic solutions having a lower detection threshold which leads to development of those tracks as well which could not be developed by pure KOH solution. This is not difficult to understand when we consider the fact that with alcoholic solutions background tracks also increase in number. The increase in (or production of) background tracks has been explained (Somogyi & co-workers 1979) by the fact that the presence of electrolyte and electric field produce new conductive zones, originally non-existent and then develop them into EC etched tracks. It is thus clear that if the alcoholic solutions have the ability to produce background tracks in control films, they certainly have the ability
to develop those tracks which could not be developed by pure KOH solution.

Another point of importance in connection with large background track densities resulting from the use of alcoholic KOH solutions is the fact that the reliability of measurement of low doses is affected. Hence for Personnel Neutron Dosimetry, it may be preferable to use pure KOH solutions as etchants in spite of their lower sensitivity. The low background track densities prevailing in the latter cases make the dose measurements reliable.

The effect of frequency on the size of recoil atom tracks is shown in Fig. 4.17 for alcoholic solutions. It is seen that maximum track diameters are obtained around 1.5 kHz and they decrease at both lower and higher frequencies. With pure KOH solutions, a similar peak position could not be ascertained. This is mainly due to the fact that very few tracks were obtainable above 1.0 kHz for the irradiations carried out. It is further observed that below 0.5 kHz the tracks become very small in size and with alcoholic solutions, the contrast also diminishes.

The effect of voltage, at a given frequency on track density was also considered. This data is shown in Fig. 4.18. It is seen that there is substantial improvement in net track density with increasing voltage. The curves could not be extended beyond 2000 Vp (70 kVp.cm⁻¹) due to limitations on equipment output. But from the shape of the curve for irradiated film it appears that saturation should be reached at somewhat higher voltages, say around 2500 Vp (90 kVp.cm⁻¹). Similar saturation has been reported by Sohrabi earlier (1975).
FIG. 4.7. VARIATION OF TRACK DIAMETER WITH FREQUENCY FOR RECOIL ATOM TRACKS
(Am-Be NEUTRONS)
ETCHANT: 10 N KOH + C₂H₅OH,
Vₚ: 2000, TIME: 3 h,
FILM: LEXAN (≈ 280 μm)
FIG. 4.18. EFFECT OF VARIATION OF VOLTAGE ON TRACK DENSITY AT CONST. FREQ. (1 kHz). ETCHANT: 10 N KOH + C₂H₅OH
TIME OF ECE: 3 Hrs. FILM: LEXAN (≈ 280 μm) (FOR RECOIL ATOM TRACKS).
Thus, when we take an overall view of the effect of frequency on density and track sizes, it is seen that:

i) frequency range of 0.25 - 0.5 kHz appears ideal when pure KOH solutions are used.

ii) with alcoholic solutions, the frequency range of 0.5 to 1.5 kHz is considered suitable, exact value depending upon the level of background tracks acceptable.

iii) high voltages up to 2000 Vp give better results; i.e. a combination of high voltage and low frequency is desired for best results.

The effect of time of ECE was also considered. When we compare the number of tracks obtained at 90 and 180 minutes of ECE (for recoil atom tracks using alcoholic KOH solution at 1.0 kHz and 2 kVp), it is seen that there is no significant gain in net number of tracks, although background increases tremendously. Thus, it can be concluded that with alcoholic solutions, the time of ECE should be kept minimum consistent with track size requirement, though longer etching times produce bigger tracks which are easy to count. With pure KOH solutions, however, there is a significant gain in net number of tracks with increasing time of ECE. This is because, growth in background track-density is negligible. Practical considerations, however, limit the time of ECE to not more than 12 hours.

4.6.2 Comments on Results from Literature

i) Recent results (Al-Najjar, Bull & Durrani, 1979) suggest that in CR-39 plastic, ECE track spots of alphas, neutron induced recoils and protons are found to develop best at 15 kVp.cm⁻¹ and 40 kHz. This
frequency is very much higher than the value of 2 kHz reported earlier (Sohrabi, 1975) for neutron induced recoil particle tracks in Lexan. This suggests that the hypothesis of Sohrabi, i.e. "etchant ions become immobile with increasing frequency and hence the growth of ECE spots is affected" is not fully justified. The nature of plastic should also influence the frequency where optimum results can be obtained.

ii) The minimum field strength required to initiate treeing for fission fragments, 1 and 3 MeV alpha particles has been reported (Somogyi, 1977a) to be 3, 12 and 15 kVp.cm\(^{-1}\) (for Makrofol E at 70°C and frequency of 2 kHz using ESW solution). It has also been suggested that this difference may be due to different curvatures, at the tips of the tracks, which depends on particle parameters.

While it is understandable that fission fragments and alpha particles have tips of different kind (i.e., with different curvatures), the same cannot be said to hold good for alpha particles of different energies, i.e. 1 and 3 MeV. These alpha particles will have identical tips and the differences probably arise because of the position of the Bragg maximum. For 1 MeV alpha particles, this maximum lies on the surface of the detector while for 3 MeV alpha particles it lies deep in the detector, thus requiring higher field strength for initiation of treeing.

4.6.3 Comparison Between Recoil Tracks and Fission Tracks

The effect of frequency on track density and diameter growth of normally incident fission fragments (from a \(^{252}\)Cf source) was also
studied. These results are shown in Figs. 4.19 and 4.20 respectively. From Fig. 4.19, it is clear that frequency has no effect on track density almost up to 4.5 kHz. Beyond this point, of course, the track density begins to fall off rapidly. Here the etching time was restricted to 90 minutes only. During this time there was a growth of background tracks also. But they were small in size compared to fission fragment tracks and hence could be easily distinguished and discarded. The fission fragment tracks on the contrary were quite bold in appearance and fell in narrow range of sizes (the curve in Fig. 4.19 does not include background tracks). From Fig. 4.20, it is also clear that the track diameters are maximum and fairly constant in the frequency range of 1 to 4 kHz and values drop beyond this range on either side.

The above curves differ appreciably from corresponding curves for recoil atom tracks (See Figs. 4.15 to 4.17). The differences are probably due to distinct differences in the two types of tracks which are listed below:

i) fission fragment tracks are intensely ionising and have a narrow range of initial energy values (in terms of energy/amu). Here the fission fragments were only normally incident.

ii) recoil atom tracks have a spectrum of energies from almost zero to a certain maximum which depends upon neutron energy and the mass of the recoiling atom. The energy/amu at the maximum is also very much lower (for neutrons encountered in a reactor environment) for carbon and oxygen recoils as compared to that for fission fragments. Further, the recoil particle tracks lie in 2\(\pi\) geometry (when neutron energy is not too high), although the neutrons are normally incident during irradiation.
FIG. 4.13. EFFECT OF FREQUENCY ON TRACK DENSITY FOR FISSION TRACKS (PERPENDICULAR IRRADIATION) AT CONSTANT Vp = 2000,
ECE FOR 30 min., ETCHANT = ION KOH + C2H5OH,
FILM: LEXAN (~ 280 µm)
FIG. 4.20. EFFECT OF FREQUENCY ON DIAMETER GROWTH OF f.f. TRACKS (NORMAL INCIDENCE)

$V_p : 1500, \ 6N \ KOH \ (PURE), \ TIME \ OF \ ECE : \ 6 \ h, \ \ \ FILM : LEXAN \ (280 \ \mu m)$
From the above observations, it appears that lower frequencies are better suited for tracks having angular and energy distribution similar to those of recoil particle tracks encountered here.

4.6.4 Leakage Current (LC) Measurements

A possible role for LC in track development process has been mentioned in literature (Sohrabi, 1975, Johnson & co-workers, 1978). In order to investigate this role, LC measurements were carried out for a number of films of different type: Lexan, Makrofol, CTF, CN (made in our laboratory) and polyester film (made by M/s Garware Plastics, India). For each film the current was measured as a function of frequency in the range of 0.2 to 10.0 MHz and at a constant voltage of 1000 Vp. Measurements were also repeated for the same films after gamma irradiation to doses in the range of 50 to 100 megarads (500-1000 kGy).

The general pattern of these curves, shown in Fig. 4.21, is identical for all the films - both unirradiated and irradiated, the latter ones showing slightly higher values (Bhagwat and Soman, 1981c). These curves thus show very broad peaks which have a maximum in the vicinity of 3 to 4 MHz.

The identical shape of LC curves for all the plastics also suggests that the nature of species acting as current carriers is probably the same though the plastics differ widely in composition and properties. The fact that irradiated films also show similar shapes indicated that the species produced because of radiation damage have similar current carrying properties.
FIG. 4.21. VARIATION OF LEAKAGE CURRENT WITH FREQUENCY FOR LEXAN = 130 μm THICK, VOLTAGE = 1000 Vp
If we consider the net LG, i.e., difference between irradiated and unirradiated films, it is observed that this difference has a maximum, though not sharp, in the region of 0.5 to 0.7 kHz for all the films. It is expected that this maximum should manifest itself in some way during the ECE process.

When we see the effect of frequency on EC etched tracks in a film like Lexan (e.g., for fission fragments) which responds nicely to ECE, it is difficult to notice any effect which can be assigned to this maximum. Consequently, a film which responds poorly to ECE in general was also examined to see if the effect of this maximum could show itself up. Accordingly, in CTA film, it was observed that the best results that could be obtained corresponded to this peak region. Tracks in Lexan and CTA can be seen in Figs. 4.29 and 4.33. This only suggests that the maximum in the net LC curve (or the frequency corresponding to it) has only a minor role to play, which manifests itself when other factors for track growth are not very favourable.

It was further observed that at any given frequency, the LC increased linearly with voltage. Thus, once a frequency is chosen, higher voltages will give faster track development (and faster growth of track density also for tracks similar to neutron induced recoils). No saturation of current was noticed within the range of voltages available from our equipment (i.e., up to 2000 Vp).

4.6.5 Effect of Film Thickness

Most of the plastic films used as SSNTD are commercial products and are not uniform in thickness over large areas. A thickness
variation of $\pm 10\%$ is very common in them. That the variation in thickness has an influence on sensitivity of neutron induced recoil atom tracks has been demonstrated and reported in literature (Sohrabi, 1975). It was therefore the purpose of these experiments to look for a parameter which controls ECE best irrespective of thickness variations.

Accordingly Lexan films of two different thicknesses, i.e. 400$\mu$m and 240$\mu$m were chosen. They were then exposed to normally incident fission fragments and subjected to ECE at a constant frequency of 1.0 kHz and one of the following conditions:

i) same total voltage across the film

ii) same total IC through the film

iii) same $V_p/\mu$m of the film thickness

iv) same $LC/\mu$m of film thickness.

The basis for comparison of the results was track diameters as all the normally incident fission fragments grow into BC etched tracks under the specified experimental conditions. The results are shown in Table 4.2. From these experiments it is seen that when total IC is kept constant, tracks of very nearly the same size are obtained (Bhagwat and Soman, 1981c). The parameter that can be considered next best is constant $V_p/\mu$m. Thus IC is an important parameter (in addition to frequency) in ECE. This should be expected, as IC is an internal parameter for the film and should therefore serve as a measure for any radiation induced changes occurring in the film. Thus IC should also form an integral part of any optimisation process.
Table 4.2

Effect of film thickness on diameter growth

<table>
<thead>
<tr>
<th>Sl. No. of film</th>
<th>Film thickness</th>
<th>Parameter kept constant</th>
<th>Max. average track diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 &amp; 8</td>
<td>405 μm</td>
<td>Total Vp = 2025</td>
<td>98.4 μm</td>
</tr>
<tr>
<td>11 &amp; 12</td>
<td>236 μm</td>
<td></td>
<td>118.35 μm</td>
</tr>
<tr>
<td>1 &amp; 2</td>
<td>403 μm</td>
<td>Total LC = 180 μA</td>
<td>90.04 μm</td>
</tr>
<tr>
<td>5 &amp; 6</td>
<td>239 μm</td>
<td></td>
<td>95.27 μm</td>
</tr>
<tr>
<td>7 &amp; 8</td>
<td>405 μm</td>
<td>5 Vp/μm</td>
<td>98.4 μm</td>
</tr>
<tr>
<td>9 &amp; 10</td>
<td>248 μm</td>
<td></td>
<td>89.28 μm</td>
</tr>
<tr>
<td>1 &amp; 8</td>
<td>403 μm</td>
<td>0.446 μA/μm</td>
<td>90.04 μm</td>
</tr>
<tr>
<td>3 &amp; 4</td>
<td>247 μm</td>
<td></td>
<td>71.7 μm</td>
</tr>
</tbody>
</table>

* ECE for 90 min, using 10N KOH + O$_2$H$_2$OH

When we consider the reported decrease in sensitivity of Lexan film with increasing thickness at constant Vp, for fast neutron induced recoil particle tracks (Sohrabi, 1975), we find that this is probably due to decrease in IC with increasing film thickness. From Fig. 4.22 which depicts the variation of IC with film thickness at constant Vp for Lexan, it is clear that decreasing IC does not match with decreasing sensitivity (sensitivity curve from Sohrabi's thesis is reproduced for convenience). It is therefore felt that there are
FIG. 4.22 VARIATION OF LC WITH THICKNESS AT CONSTANT $V_p = 2000$ (SENSITIVITY CURVE FROM FIG. 15 OF SOHRABI'S Ph.D. THESIS IS ALSO REPRODUCED HERE FOR COMPARISON)
other factors also which combine with LC in reducing the film sensitivity. More effort will be needed, in future, to understand the phenomenon completely.

4.7 MISCELLANEOUS STUDIES

4.7.1 Electric Field at the Tip of (ECE) Track

Fig. 4.23 shows the track diameter growth of an ECE track (fast neutron induced recoil atom track) with the time of ECE. It is clear from this figure that the etching rate increases initially with time and then becomes constant (Bhagwat and Soman, 1981b). For recoil tracks as well as fission fragment tracks encountered in routine dosimetry work, we are dealing with damage density regions at low energy end of the curves for damage density versus energy/amu of charged particles. This region is depicted in Fig. 4.24, for Mylar (the shape of curves for Lexan would be similar) for various charged particles (North Cliffe and Schilling, 1969-70). It is clear that the damage density falls off as the particle (producing track) slows down. The shapes of chemically etched tracks corresponding to this region are shown in Fig. 4.25 (Fleischer & co-workers, 1975). This figure clearly establishes the point that as the chemical etching proceeds:

1) the ratio of major axis to minor axis of the track decreases,

or ii) the tip radius 'r' increases,

or iii) the distance 'd' of the track from the other surface of the detector decreases.

Now let us look at the following equations (1) and (2) (Eichhorn, 1977) which give electrical stress at the tip of the track
FIG. 4.23 VARIATION OF TRACK DIAMETER WITH ETCHING TIME (ECE AT -2 kVp, 2 kHz WITH 10 N KOH + C2H5OH FOR RECOIL ATOM TRACKS) FILM = LEXAN (130 µm)
FIG. 4.24. VARIATION OF ELECTRONIC STOPPING POWER (OR DAMAGE DENSITY) VERSUS ENERGY/α μu FOR VARIOUS CHARGED PARTICLES IN MYLAR (POLYETHYLENE TERPHTHALATE, C10H8O4).
$r_1 < r_2 < r_3 < r_4$

$d_1 > d_2 > d_3 > d_4$

**FIG. 4.25.** PROFILE OF A CHEMICALLY ETCHED TRACK WITH ETCHING TIME, WHERE DAMAGE DENSITY DECREASES WITH DEPTH.
in terms of average field applied to the insulator.

\[ \frac{E_{\text{max}}}{E_{\text{av}}} = 2n^3/m \ln \frac{m+n}{m-n} - 2n \quad \ldots \ldots (1) \]

by Bateman

where \( E_{\text{max}} \) = electrical field at the tip of the track

\( E_{\text{av}} \) = average electrical field applied to the insulator

\( m \) = ratio of major axis to minor axis = \( \frac{c}{a} \)

\( n = \sqrt{\frac{2}{m-1}} \)

and \[ \frac{E_{\text{max}}}{E_{\text{av}}} = 2 \frac{d}{r} \ln \left(1 + \frac{4d}{r}\right) \quad \ldots \ldots (2) \]

by Mason

where \( E_{\text{max}} \) and the \( E_{\text{av}} \) are the same as in eqn. (1)

\( r \) = radius of the tip (of the track)

\( d \) = distance of the tip from the opposite surface of the film.

If we now consider the role of chemical etching alone, during ECE, we find that chemical etching changes 'c/a' or 'd' or 'r' in such a way as to reduce the electrical stress at the tip of the track. Hence EC etch rate should drop as ECE proceeds. But this will be contrary to the observations as shown in Fig. 4.23. It is therefore suggested that the role of electric field is so strong that it does not permit the retardation effects of chemical etching to show up. Alternatively it may also be argued that during ECE the track tip is continuously advancing and changes in 'c/a' or 'd' or 'r' due to chemical etching do not keep pace with advancing track tip, with the result that the
conditions at the tip are always conducive to further growth (Bhagwat and Soman, 1981b).

Our studies are partial because they take into account the lateral growth of the track. Unfortunately we were not equipped to carry out measurements on vertical growth. However, we strongly feel that our explanation should find justification for the latter case also.

The equation (2) also suggests that for a given track, the thicker detector film would give higher value of \( \frac{E_{\text{max}}}{E_{\text{av}}} \). But the large thickness of the detector film leads to smaller value of field strength for a given applied voltage. Thus the higher film thickness has both an advantage and a disadvantage. It appears, however, that the disadvantage is more prominent as lower sensitivities have been reported (Sohrabi, 1975) for thicker films and our observation has also been similar.

The importance of sharp tips becomes evident when we consider that no ECE is possible for chemically etched tracks for which the tips have become rounded. It is also felt that the inability of alcohol to enhance the EC etch rates by the same factor as for CE, may be due to the fact that the alcoholic KOH solution reduces slightly the sharpness of the track tip owing to its high CE rate. This in turn will reduce the electrical stress \( \left( \frac{E_{\text{max}}}{E_{\text{av}}} \right) \) at the track tip.

### 4.7.2 Comparison of Diameter Growth Rate Curves in CE and ECE

When we compare Fig. 4.23 with Fig. 4.26 which represents the diameter growth of a fission fragment track with time during
FIG. 4.26. VARIATION OF HOLE DIAMETER IN 10 \( \mu m \) THICK MAKROFOL WITH ETCHING TIME IN 6N NaOH AT 60 °C (IRRADIATION OF FILM WITH PERPENDICULARLY INCIDENT FISSION FRAGMENTS)
conventional chemical etching, we find that the two figures differ from each other in the initial regions in one important way. The straight line portion in Fig. 4.26 when extrapolated gives a positive intercept on the Y-axis while Fig. 4.23 gives a negative intercept. In conventional chemical etching the etch rate in the beginning is very high which falls off gradually as the etching proceeds to a constant value (equal to the bulk etch rate), i.e. the region with high track etch rate leaves its imprint on the track diameter versus time curve. For BCE curve, the growth rate looks slow initially. It then increases gradually to a high constant value. The general growth rate in BCE is thus so high that it wipes out the imprint of initial high chemical etch rate from the BCE curve. The unique feature of the BCE process is that such high etch rates can be sustained over long periods of time. The role of electric stress is thus very much obvious.

4.7.3 Effect of Polarisation

We know that the power (energy) transferred to an insulating material, when subjected to an alternating field is a function, not only of the potential across the material and its frequency but also of the physical characteristics of the material. It is therefore suggested that the properties of the material also influence the energy transferred.

One of the important effects of the electric field on the insulating material is to displace the bound charges in it slightly relative to one another. Each molecule then acquires an electric dipole moment parallel to and in the same direction as the electric field.
This effect is known as dielectric polarisation.

There are four distinct mechanisms which contribute to the process of polarisation: (i) electronic, (ii) atomic (ionic), (iii) dipolar and (iv) interfacial. Each of these processes is characterised by a relaxation time 'T' which is the time taken by the particular polarisation to respond to the applied electric field. The polarisation times for the above four processes are - (i) $10^{-16}$ sec, (ii) $10^{-12} - 10^{-13}$ sec, (iii) $10^{-5} - 10^{-10}$ sec and (iv) $1 - 10^{-3}$ sec respectively. For any polarisation to make its full contribution to total polarisation, the period of oscillation $t (= 1/f)$ of the field (where 'f' is the frequency) should be much greater than the corresponding relaxation time 'T', so that the polarisation is able to establish itself completely before the field is reversed (Birks, 1960).

In most of the studies on BCE, one is dealing with dielectric materials which are homogeneous in nature. The interfacial polarisation should then be of no consequence as it applies only to inhomogeneous dielectrics. Even if dielectrics under investigation have inhomogeneities of any kind, it may be remembered that interfacial polarisation will be extremely slow in establishing itself ($1 - 10^{-3}$ sec), as mentioned above. Very often it is so slow that it takes place at frequencies which are very much lower than 1 Hz (Harrop, 1972). We also know from the experimental results that the frequencies in the range of 0.5 to 50 kHz make a tremendous difference in the results of BCE. Since this frequency range will affect only the dipolar polarisation, it may be considered that this type of polarisation alone plays an important part
in the process of BCE as far as the track recording material is concerned (Bhagwat & co-workers, 1983). By implication it means that the role of electronic and atomic (ionic) polarisations is small.

4.7.4 Retention of Individual Track Identify in BCE

Fig. 4.27 (a) and (b) are typical microphotographs of fission and recoil atom tracks respectively in Lexan (Etchant 7N KOH). From these photographs, it is evident that BCE leads to formation of circular spots as long as they do not occur very close to each other. When two or more tracks are situated close together, their circular growth is inhibited in the direction of other track(s), and no overlapping occurs. Tracks with such inhibited growth are indicated by arrows in the photographs. This phenomenon may be due to (Bhagwat and Soman, 1979) repulsion between identical polarities at the tips of tracks and its manifestation in the form of

1) depletion of current carriers in the region lying in between
and 2) reduction of lateral field gradients along those directions. These repulsive forces are so strong that they affect the growth of the tracks but no overlapping takes place even at high track densities. This is depicted in Fig. 4.28 which is again a microphotograph of recoil particle tracks.

4.7.5 Structure of BCE Tracks

Our studies on BCE have embraced the following film materials:
Polycarbonate (Lexan and Makrofol), Polyethylene terephthalate (Chromar), Polyester (type ER of M/s Garware Plastics and Polyester Private Limited, India), Cellulose triacetate, Cellulose nitrate (CA.80.15) and CR-39.
FIG. 4.27. MICROPHOTOGRAPHS OF EC ETCHED (a) FISSION TRACKS (b) FAST NEUTRON INDUCED RECOIL ATOM TRACKS IN LEXAN (≈ 280 μm)

(a) 500 μm

(b) 200 μm
FIG. 4.28. MICROPHOTOGRAPH OF EC ETCHED RECOIL ATOM TRACKS INDICATING THE ABSENCE OF OVERLAPPING EVENTS AT HIGH TRACK DENSITIES.
Some of the observations made by us with these films (for fission fragments) are listed below:

(1) While the tracks in Lexan, Makrofol and Chronar show a good contrast, the star like appearance is presented only by Lexan and Makrofol. From literature it is known that Lexan is an extruded product while Makrofol N is prepared by a casting process; their behaviour in ECE is however, the same. The tracks in Chronar show no veins at all and their shapes are also irregular. These three types of tracks are shown in Fig. 4.29.

(2) The tracks in all the three films mentioned in (1) appear faintly black immediately after ECE. The track contrast, however, improves after a few hours or on the next day when they look dark black. This improvement is due to the fact that water present in the track cavities immediately after ECE gradually evaporates filling the cavity with air. The index of refraction of plastic relative to air being more than that relative to water, the resultant improvement is not difficult to understand.

(3) The ECE tracks have a circular opening on the surface of the film which can be often seen under the biological microscope (i.e. transmission type). This opening becomes very clear when the films are examined under a metallurgical microscope (i.e. reflection type) with an aluminised Mylar kept below the film. These tracks are already shown in Fig. 4.13.

(4) ECE tracks in Lexan tend to be circular as long as KOH concentration does not exceed 7N. Beyond this concentration, as well as
FIG. 4.29. MICROPHOTOGRAPHS OF EC ETCHED FISSION TRACKS IN
(a) LEXAN (b) MAKROFOL AND (c) CHRONAR.
with alcoholic KOH solutions, tracks of irregular shape are observed.

(5) ECE tracks in Lexan show at times rings of small pits on the surface of the film around the track hole. These are shown in Fig. 4.30. The reason for this pitting is not yet clear except that it is observed when strong alcoholic etchants are employed.

(6) The surface features of ECE tracks in Lexan were also examined under the scanning electron microscope. It reveals the existence of a big surface pit at each track hole as shown in Fig. 4.31. This pit itself has a pitted structure as seen in the photograph. Fig. 4.31 also shows SEM photographs of EC etched fission track in CTA and CN. The track opening (or mouth) of track in CTA is surrounded by a large pit, while that in CN appears to be surrounded by a large bulge. The photograph of track in CTA produces an optical illusion, i.e. when the photograph is rotated through 180°, the pit starts appearing as a bulge. This is true, to a lesser extent, for the photograph from Lexan film also.

Points (1), (5) and (6) reveal the effects of electric stress on the film and the track cavity but the exact mechanisms of the track production and why they differ from one material to another, are not clear.

(7) The tracks in the Garware polyester film (type ER) were somewhat elongated (i.e. elliptical in shape) in one direction as shown in Fig. 4.32. This observation has also been reported for Melinex-O (PET) (Sorogyi, 1977a, 1977b). This may be due to some axial orientation produced in the film during the manufacturing process. In the absence
FIG. 4.30. MICROPHOTOGRAPH OF RINGS OF SMALL PITS, ON THE SURFACE OF LEXAN FILM, AROUND THE TRACK-HOLE.
FIG. 4. SCANNING ELECTRON MICROSCOPE PHOTOGRAPHS SHOWING THE SURFACE FEATURES OF EC ETCHED FISSION FRAGMENT TRACKS.

FIG. 4. SCANNING ELECTRON MICROSCOPE PHOTOGRAPHS SHOWING THE SURFACE FEATURES OF EC ETCHED FISSION FRAGMENT TRACKS.
FIG. 4.32. MICROPHOTOGRAPH OF EC ETCHED FISSION TRACKS IN GARWARE POLYESTER FILM (TYPE-ER) SHOWING ELONGATION OF TRACKS IN ONE DIRECTION.
of any actual manufacturing details, we were unable to confirm this point. If no orientation is purposely introduced during manufacture and the elongation is still seen, it could be a consequence of anisotropic orientation of polymer molecules themselves.

(8) ECE tracks were also seen in CN (CA.80.15) and CTA. They are hazy and lack the contrast of tracks in Lexan. The reasons for their appearance of this kind are cited in the introductory chapter. These tracks are shown in Fig. 4.33.

4.7.6 Effect of Polymer Type

Table 4.3 lists a number of properties of seven different film materials, e.g. CA, CTA, CAB, PC, PET, PE and PTFE, for which data was available in literature (British Plastics Year Book, 1972; Modern Plastics Encyclopedia, 1979–80). Of these, the effects of first four properties, i.e. tensile strength, dielectric strength, volume resistivity and water absorptivity were discussed by Johnson & co-workers (1977) for the first four materials, i.e. CA, CTA, CAB, and PC. Some of the values given in our table are different from those given by Johnson. As stated above, our values refer to films since we are dealing with films only (The form of material has not been specified by Johnson in her Table). We have added three more materials to the list, i.e. PET, PE and PTFE. Further, a few more properties like dielectric constant, dissipation factor and the dielectric loss factor were considered for all the materials.

The picture now appears to have changed a little. Based on tensile strength, dielectric constant and volume resistivity, PET appears
FIG. 4.33. MICROPHOTOGRAPHS OF EC ETCHED FISSION TRACKS IN CN AND CTA.
Table 4.3

Properties of plastic films

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile strength (p.s.i.)</th>
<th>Dielectric strength volts/mil</th>
<th>Volume resistivity ohm.cm</th>
<th>Water absorption in % for 24 h</th>
<th>Dielectric constant for 1 mil thickness at 1.0 kHz</th>
<th>Dissipation factor for 1 mil thickness at 1.0 kHz</th>
<th>Dielectric loss factor at 1 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA</td>
<td>7000-16,400</td>
<td>1700-3200</td>
<td>$10^10$ - $10^{15}$</td>
<td>3.1-5</td>
<td>3.6</td>
<td>0.013</td>
<td>0.0468</td>
</tr>
<tr>
<td>CTA</td>
<td>9000-16,000</td>
<td>2250-3100</td>
<td>$10^{13}$ - $10^{15}$</td>
<td>2.4-5</td>
<td>3.2-4.5</td>
<td>0.016</td>
<td>0.0512</td>
</tr>
<tr>
<td>CAB</td>
<td>5000-9000</td>
<td>2250-3700</td>
<td>$10^{11}$ - $10^{15}$</td>
<td>1-2</td>
<td>2.9</td>
<td>0.013</td>
<td>0.0377</td>
</tr>
<tr>
<td>PC</td>
<td>5400-8800</td>
<td>6300(1 mil) 2000(5 mil)</td>
<td>$10^{16}$</td>
<td>0.35</td>
<td>2.99</td>
<td>0.0015</td>
<td>0.004485</td>
</tr>
<tr>
<td>PBT</td>
<td>20,000-35,000</td>
<td>7500(1 mil) 3400(5 mil)</td>
<td>$10^{18}$</td>
<td>&lt;0.8</td>
<td>3.2</td>
<td>0.005</td>
<td>0.0160</td>
</tr>
<tr>
<td>PE</td>
<td>1500-4000 (low density)</td>
<td>5000(1 mil) 3000(5 mil)</td>
<td>$10^{16}$</td>
<td>&lt;0.01</td>
<td>2.2</td>
<td>0.0003</td>
<td>0.00066</td>
</tr>
<tr>
<td>PTFE</td>
<td>1500-4500</td>
<td>1200(1 mil) 1000(5 mil)</td>
<td>$10^{18}$</td>
<td>Nil</td>
<td>2.0-2.1</td>
<td>0.0002</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

References: Modern Plastics Encyclopedia (1979-80); British Plastics Year Book (1972).
to be superior to all other materials (only the water absorption is somewhat higher than that for PC) but the track formation in it is not as good as in PC. Thus, while the importance of these properties cannot be underestimated, they do not tell the full story.

When we consider the additional three properties mentioned above, for all the materials, a little more light is shed on the topic (here we confine our discussion to the values of these properties measured at 1 kHz only because that is the point about which most of the experimental values have been determined). At 1 kHz the difference between the highest and the lowest values of dielectric constants for these materials is less than a factor of two, i.e. they are about the same. This property therefore does not bring out the differences significantly. But when we consider the values of dissipation factor or dielectric loss factor, tremendous differences are observed.

Thus PC, which gives best results for ECE, has a low value of both dissipation factor and the dielectric loss factor. PET, which shows somewhat higher values of these quantities, gives results that are next best, while CA, CTA and CAB which show quite high values of these quantities give very poor results in ECE. It may therefore be inferred that a low value of dissipation factor or dielectric loss factor is very much essential for obtaining good results in ECE.

On this basis, PE and PTFE, which show still lower values of dissipation factor and dielectric loss factor, should give better results than those for PC. But this is not the case. (In PE it can take several days to produce ECE tracks while no results have been
reported for FIFE so far). This anomaly will be understandable when we remember that HD and PTFE are both non-polar materials.

Thus, it should be possible to conclude that good ECE tracks should result in materials with the following properties (Biagwat & co-workers, 1983):

1. good electrical properties, i.e. high values of tensile strength, dielectric strength and volume-resistivity,
2. low water absorptivity,
3. low value of dissipation factor or dielectric loss factor
4. polar nature.

The last criterion, i.e. polar nature of the material is especially important because it has a major role to play in dipolar polarisation. The importance of polarisation and hence the polymer type is thus obvious.

Finally, we see that although some more information has been added to criteria for track registration by ECE, we are still far from being able to quantify them. This area thus still retains its charm and should attract more workers to unmask its secrets.

4.8 SOME NEUTRON DOSIMETRY RESULTS

For counting of fast neutron induced recoil atom tracks developed by ECE, we had a choice of three methods - (i) microscope, (ii) microfiche card reader, and (iii) optical density method. The third method is useful when track densities are equal to or greater
than about 1500 \text{tracks.cm}^{-2} \text{ and their sizes about 200 \mu m in diameter (Bhagwat and Soman, 1979). For other cases, only the first two methods are suitable. In our studies where track densities were invariably below 1000. \text{cm}^{-2}. Microfische card reader was used extensively.}

From earlier investigations it appears that the conditions of ECE for Lexan, for personnel fast neutron dosimetry based on recoil track registration, may be fixed as follows. Voltage = 2000 Vp (about 70 kVp/cm for 280 \mu m thick film); Frequency = 1 kHz (because high output voltages are not consistently obtainable, over long periods at lower frequencies, from our setup); Etchant and its concentration = 6N KOH (without alcohol); time of ECE = 12 hours (at room temp.) Accordingly a number of films were irradiated with Am-Be neutrons and etched under these conditions. Their results are given in Table 4.4.

It is seen that the sensitivity value, in units of (\text{tracks.cm}^{-2}) per \text{Sv}, is 3760 \pm 5.5 \%. No correction for background was made as it was quite low, e.g. for the eight films processed as controls, the background track density was 3.1 \pm 1.8 \text{ tracks.cm}^{-2}.

If \(D_m\) denotes the minimum detection limit of dose \((D)\) for which the fractional error \(E(= \frac{\sigma_D}{D})\) is 0.5, i.e. 50 \%, then \(D_m\) is given by (Thomas, 1971; see Appendix Ch.5):

\[
D_m = \frac{2 (1 + \sqrt{1 + 2B})}{K}
\]

where \(B = \text{background track density}\)

\[
= 3.1 \pm 1.8 \text{ tracks/cm}^2 \text{ in our case}
\]

and \(K = \text{constant of proportionality}\)

\[
= \frac{3760 \text{ tracks/cm}^2}{\text{Sv}} \text{ in our case.}
\]
Table 4.4
Response of Lexan film to (Am-Be) neutrons

<table>
<thead>
<tr>
<th>Film No.</th>
<th>No. of tracks counted</th>
<th>Tracks.cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1011</td>
<td>901 ± 3.1 %</td>
</tr>
<tr>
<td>2</td>
<td>952</td>
<td>848 ± 3.2 %</td>
</tr>
<tr>
<td>3</td>
<td>946</td>
<td>843 ± 3.3 %</td>
</tr>
<tr>
<td>4</td>
<td>880</td>
<td>784 ± 3.37 %</td>
</tr>
<tr>
<td>5</td>
<td>945</td>
<td>842 ± 3.3 %</td>
</tr>
<tr>
<td>6</td>
<td>849</td>
<td>756 ± 3.4 %</td>
</tr>
<tr>
<td>7</td>
<td>907</td>
<td>810 ± 3.3 %</td>
</tr>
<tr>
<td>8</td>
<td>963</td>
<td>858 ± 3.3 %</td>
</tr>
</tbody>
</table>

Grand mean and standard deviation of = 830 ± 45
tracks.cm⁻² = 830 ± 5.5 %

Integral exposure of films = 6.3 x 10⁸ n.cm⁻²

and \( \frac{\text{Tracks.cm}^{-2}}{\text{Sv}} = 3760 ± 5.5 \% \)

(taking 1 n.cm⁻² = 3.51 x 10⁻¹⁰ Sv)

and minimum detection limit \( D_m \) is

\[ D_m = 2 \text{ mSv} \]

\( D_m \) thus works out to 2 mSv (= 200 mrem). It is thus seen that the system is useful for personnel fast neutron dosimetric purposes. The
directional response of the detector can be taken care of by mounting it on a cylindrical backing (Sohrabi and Morgan, 1975). The other parameters such as backscattering, neutron energy dependence etc. will also require consideration before actual application is taken up.

4.9 ECE with Thin Films

In their experiments with thin films, Tommasino and co-workers (1981b) have also stated that the use of Freon can be avoided in the ECE cell because of good non-shorting characteristics achieved when the thin aluminium layer is at positive polarity, i.e. air can also act as an equally good dielectric - the only difference being that the holes in the aluminium layer now have larger diameters.

Encouraged by the above observations, we were inclined to use our new ECE cell (Bhagwat and Soman, 1981a) for the ECE of thin films. Our efforts in this direction were fruitful and the results so obtained (for fission fragments) are briefly described below.

The cell arrangement used in this study is shown in Fig. 4.34. About 12 μm thick aluminised polyester film (aluminium coating on one side only) was used as detector. Irradiations were carried out using a planchet type 252 Cf source. Positive pulses of height 30 volts, obtained directly from a commercially available function generator (described in Chapter 2) were used for this purpose. The etchant used was 6N KOH at room temperature (25°C) and the aluminium layer was at positive polarity.

Excellent results were obtained for an ECE time of 3.5 hours at all the frequencies in the range of 2-10 kHz. Fig. 4.35 shows a
TIP FOR ELECTRICAL CONNECTION

S.S. WEIGHT

ALUMINISED (ONLY ON TOP SIDE) POLYESTER FILM AT POSITIVE POLARITY

S.S. CUP WITH ETCHANT

PERSPEX BLOCK

PERSPEX STAND

GROUND ELECTRODE CONNECTION.

FIG. 4.34 ECE SETUP FOR THIN FILMS.
FIG. 4.35. FISSION TRACK HOLES IN ALUMINISED POLYESTER FILM (AS SEEN ON MICROFISCHER CARD READER) DEVELOPED BY THIN FILM ECE METHOD WHEN Al. LAYER IS ANODE.

FIG. 4.36. EFFECT OF NEGATIVE POLARITY AT THE ALUMINIUM ELECTRODE DURING THIN FILM ECE
photograph of track holes obtained in this way on a microfiche card reader. The effect of aluminium layer being at negative polarity is shown in Fig. 4.36. Here, the cathodic dissolution of aluminium was so rapid that the first few holes consumed the entire layer of aluminium leading to formation of a big hole. The individual track identity was therefore completely lost. The advantage with our cell arrangement is that the appearance and the growth of holes can be seen throughout as the portion of the film where ECE takes place is always visible.

Further studies along these lines are in progress and the details of the work will be reported in due course.