Alternative method to determine the bulk etch rate of LR-115 detectors

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The measurements using the LR 115 solid-state nuclear track detector (SSNTD) depend critically on the removed thickness of the active layer during etching. In this work, LR 115 detectors exposed to alpha particles were etched under no stirring in a 2.5 N NaOH solution at a temperature of 60±1°C and different etching times (from 0.5 to 2.5 hours). The thickness of the removed layer was determined by a variant of the gravimetric method, so that the bulk etch rate could be deduced from mass change measurements of detectors. The bulk etch rate was found to be 3.63 ± 0.09 μm.h^{-1}, which agrees with most of the reported values. Comparisons of our results with the obtained by the optical density method are in correspondence. We propose here a fast, simple, and nondestructive method to determine the active-layer thickness of the LR 115 SSNTD with good accuracy for routine measurements

Keywords: LR-115 detector; bulk etch rate; gravimetric method; optical density method.

Cuando se emplea el detector de trazas nucleares LR 115 las mediciones dependen críticamente del espesor removido de la capa activa durante el revelado. En este trabajo se revelaron detectores LR 115, expuestos a partículas alfa, sin agitación en una solución 2.5 N de NaOH a temperatura de 60±1°C y durante diferentes tiempos de revelado (desde 0.5 hasta 2.5 horas). El espesor de la capa removida se determinó por una variante del método gravimétrico, de modo que la tasa de revelado masivo se pudiera deducir a partir de mediciones del cambio de masa de los detectores. La tasa de revelado masivo obtenida fue de 3.63 ± 0.09 μm.h^{-1}, la cual está de acuerdo con la mayoría de los valores reportados. Las comparaciones de nuestros resultados con los obtenidos por el método de densidad óptica están en correspondencia. Proponemos aquí un método rápido, simple y no destructivo para determinar el espesor de la capa activa del detector LR 115 con buena exactitud para mediciones rutinarias.

Descriptores: Detector LR-115; tasa de revelado masivo; método gravimétrico; método de densidad óptica.

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1. Introduction

Cellulose nitrate films (commercially available as LR 115 films from DOSIRAD, France) have been commonly used as SSNTDs in which visible tracks can be formed after ion irradiation and suitable chemical etching [1,2]. Ion-track growth in SSNTDs has been suggested to base on two parameters, V_t and V_b [3], where $V_t$is the track etch rate and V_b is the bulk etch rate. V_b is one of the most important parameters that control the formation and development of tracks and with V_t, is needed to simulate track growth and to calculate the track parameters [4,5]. It has been shown that V_b depends on many factors like the purity of the basic substances, the molecular structures of polymers, conditions of polymerization, environmental conditions during the irradiation and finally on etching conditions [6]. Yip *et al.* [7] showed that the bulk etch rate of this SSNTD was affected by the amount of stirring. Measurements with LR 115 detectors depend critically on the thickness of the removed layer during etching. Therefore, actual monitoring of the active-layer thickness is necessary when using this detector.

1.1. Indirect determination of V_b

Based on the detector mass difference (before and after etching) and the known density of the detector, it is possible to determine the thickness of the removed layer and in turn V_b. It is the so called "gravimetric" method [8]. However, this method is limited by the accuracy of mass measurements. Yip *et al.* [9] proposed a method to measure the thickness of the active layer of LR 115 SSNTDs based on the absorption of fluorescence X-ray photons by the active layer. Nevertheless, there is a risk that X-ray radiation affects the track and bulk etching velocities. For example, Clark and Stephenson [10] and Fowler *et al.* [11] have shown X-ray degradation of cellulose nitrates. Ng *et al.* [12] proposed another spectroscopic method by using Fourier transform infrared (FTIR) spectroscopy. Yu and Ng [13] proposed a method based on a color commercial document scanner to determine the active layer thickness of the LR 115 SSNTD.

1.2. Direct measurements of V_b

Measurements of V_b with the micrometer are based on the determination of the thickness of the removed layer during etching. The problem that arises here is the impossibility to apply the same pressure on the detector in two separate measurements. Nikezic and Janicijevic [14] used a surface profilometer to measure V_b in LR 115 detectors. The masking method together with surface profilometery measurements was introduced by Yasuda *et al.* [15]. These methods are destructive, so they can only be used after etching has been completed. Furthermore, for active-layer thickness smaller

than about 5 μm, the surface profilometry data became significantly more scattered [16]. Some a priori non-destructive methods were subsequently proposed for measurements before completion of etching. For example, Yip *et al.* [17] used X-ray fluorescence, while Ng *et al.* [18] used Fourier Transform Infrared (FTIR) spectroscopy. Atomic force microscope (AFM) enabled very accurate measurements of the bulk etch rate by the "masking" method [19]. However, care should be taken in the measurements of the track depth and the track profile with the AFM, since the geometrical incompatibility between the tracks and the AFM probe could lead to inaccuracies [20]. All these direct methods require relatively sophisticated equipment which might not be convenient for dedicated use for measurements of SSNTD thickness.

It would be useful to devise methods to measure the thickness of the removed layer of the LR 115 detector in a fast and non-destructive way. After such a measurement, if the thickness of a detector has not reached the desired value, further etching can still be carried out. In the present work, an attempt will be made to develop a variant of the gravimetric method to determine the active-layer thickness of LR 115 SSNTD with accuracy in a fast, simple and non-destructive way.

2. Materials and methods

The LR 115 detectors were purchased from DOSIRAD, France (LR 115 film, Type 2, non-strippable, 12 μm red cellulose nitrate on a 100 μm clear polyester base). In the present experiments, the detectors were cut with a size of $1\times$ 1 cm^2. They were etched separately in a 25 N NaOH solution at 60°C using a water bath controlled with a thermostat (standard etching conditions). The temperature was kept constant with an accuracy of $\pm$1°C. At selected time intervals, *i.e.*, 60, 90, 120 and 180 min for etching under no stirring, the detectors were taken out from the etchant and immediately rinsed with distillated water during 30 min and in a 1:1 solution of distilled water and ethyl alcohol during 2 min. These last two operations were conducted under stirring.

For comparisons of the dependences of the removed layer with the etching time, and so the obtained bulk etch rates, we use a low-cost color commercial scanner to generate images of the detectors that were used to determine the active-layer thickness of LR 115 SSNTD according to the method proposed by Yu and Ng [13]. The color commercial scanner, included in the HP OfficeJet 7313 All-in One Series, was employed for scanning the LR 115 detectors. It offers to 19200 ppp optical resolution and a bit depth of true 48-bit color. However, for the investigation described in this paper, the resolution of 600$\times$600 pixels per sq. inch was used. TIFF (Tagged Image File Format) images were generated. The ImageJ 1.29X (Image Processing and Analysis in Java) software (http://rsb.info.nih.gov/ij/) was then employed to perform an RGB split of the scanned image of the detector. We used the image of the detector in 8-bit grayscale at the red (R) color. The reduction in the light passing through the LR 115 detector was expressed by the optical density (OD), calculated from the average gray value for the R band (R value) in the selected area and the R value in areas without the presence of a detector.

3. Results and discussions

3.1. Alternative variant of the gravimetric method

Consider $M_i = m_{ci} + m_p$ the initial total detector mass before the etching process, where m_{ci} is the initial mass of the cellulose nitrate layer and $m_p$the mass of the polyester base. After etching the detector mass will be $M_f = m_{cf} + m_p$, where m_{cf} is the final mass of the cellulose nitrate layer. Both equations can be rewritten as:

$$M_i = A(\rho_p z_p + \rho_c z_{ci}) \tag{1}$$

and

$$M_f = A(\rho_p z_p + \rho_c z_{cf}) \tag{2}$$

where ρ_p and ρ_c are the polyester base and cellulose nitrate film densities, respectively, z_p is the thickness of the polyester base, while $z_{ci}$and z_{cf} are the initial and final thickness of the cellulose nitrate layer, respectively. It was assumed that the areas of the involved materials and the thickness of the polyester base are not modified by the etching process.

The relationship between the Eqs. (1) and (2) is:

$$\frac{M_i}{M_f} = \frac{\rho_p z_p + \rho_c z_{ci}}{\rho_p z_p + \rho_c z_{cf}} \tag{3}$$

From Eq. (3) and considering the removed layer of cellulose nitrate in time Δt as $\Delta z = z_{ci} - z_{cf}$, the following expression can be obtained:

$$\Delta z = z_{ci} - z_{cf} = \Big(z_{ci} + \frac{\rho_p}{\rho_c} z_p\Big)\Big(1 - \frac{M_f}{M_i}\Big) \tag{4}$$

According to the manufacturer z_p=100 μm, z_{ci}=12 μm, ρ_p=1.395 g/cm^3 and ρ_c = 1.44 g/cm^3, so that Eq. (4), expressed in μm units, can be rewritten as:

$$\Delta z = 96,875\Big(1 - \frac{M_f}{M_i}\Big) \tag{5}$$

3.2. Estimation of bulk etch rate (V_B)

To evaluate the effect of the etchant on the polyester base of the LR-115 detector, before etching the red cellulose nitrate layers of three 1cm$\times$1cm LR-115 sheets were removed by a razor and the colorless polyester bases were weighted. After that they were introduced in the etching solution at 60°C for several hours and weighted again. The obtained results demonstrate that the effect can be neglected since the mass differences are less than the uncertainty in the measurements with the analytical microbalance.

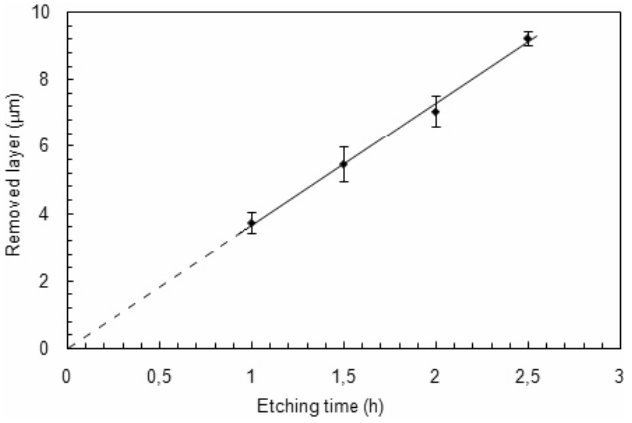

FIGURE 1. Relationship between the thicknesses of the removed active layer of the LR 115 detector calculated by Eq. (5) and the etching time. The line corresponds to the best linear fit of the experimental data. The bar errors correspond to the obtained standard deviation for ten detectors by each treatment.

TABLE I. Removed layer values for different etching times using the method proposed here and the optical density method.

	Removed layer (μm) by:		
Etching time (h)	Proposed method	Optical density	Difference (%)
1.0	3.72	3.58	3.76
1.5	5.46	5.24	4.06
2.0	7.05	7.19	2.02
2.5	9.22	8.91	3.42

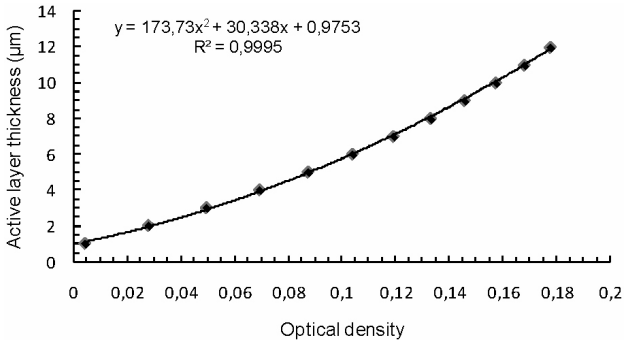

FIGURE 2. Relationship between the active-layer thickness for the LR 115 SSNTD measured by surface profilometry and the corresponding optical density. The solid line is the best-fit second order polynomial curve to the experimental data.

The thickness of the removed layer was calculated by the Eq. (5). The mean value for the removed-layer thickness is obtained by taking the average of the measurements for 10 different detectors for each etching time. The average bulk etch rate can be determined knowing the amount of removed layer (Δz) for different etching times (Δt). If the dependence between both variables is lineal, then the bulk etch rate is given by the slope of the straight line that better fit the experimental results.

The relationship between the thickness of removed active layer and the etching time is shown in Fig. 1. By fitting the linear relationship y = Ax to the experimental data, where y (μm) is the thickness of the active layer and x(hours) is the etching duration, we have A=3.63$\pm$0.09 with R^2=0996. The obtained results show not only linearity of the dependence of V_B with the etching time, but also no removed layer for zero etching time (see extrapolation). For etching times between 1.0 and 2.5 hours a constant bulk etch rate of 3.63$\pm$ 0.09 μm/h was attained; this value agrees with the obtained by other authors using different sophisticated methods as profilometry, R-X, AFM, densitometry, etc.

The calculated bulk etch rate is different from the value of 3.27 $\pm$ 0.08 μm.h^{-1}obtained by Nikezic and Janicijevic [14], but is very close to the calculated by Yip *et al.* [21] (both with the same etching conditions as in our experiments), where the thickness of the active layer of the LR 115 detectors were measured by the surface profile method (3.61 $\pm$ 0.14 μm.h^{-1}). In the first case, the difference may be due to the different convection present in the etchants. A second observation is that the initial thickness of the active layer might not be exactly 12 μm, as usually taken for granted.

According to our results, under the standard etching conditions the removed layer for 2 h of etching is 7.26 μm, and the remaining thickness of the sensitive layer is 12-7.26=4.74 μm. Now that V_b has been determined, this can be combined with the track etch rate V_t to give the V function, which is required for calculating track parameters [22]

3.3. Experimental verification

For the images obtained in our color commercial document scanner, ρ was found to be very close to the value obtained by Yu and Ng [13], so that for calibration we use their results of optical densities vs. active-layer thickness measured by surface profilometry. As can be seen in Fig. 2, a second order polynomial equation fit well the data.

Using the calibration equation showed in the graph, the removed layer during the different etching times was calculated by this method. Table I shows that the differences between the removed layer values obtained by the use of the method proposed here and by the optical density method are less than 5%, so that the accuracy of the proposed method can be considered satisfactory.

4. Conclusions

The method of detector mass measurement before and after etching proposed here has been developed and used to measure the thickness of the active layer of the LR 115 detectors. The bulk etch rate under no stirring is 3.63$\pm$ 0.09 μmh^1 for the standard etching conditions. The calculated bulk etch rate is in correspondence with the reported in many papers. The differences of the removed layer thicknesses obtained by

the proposed method and by the optical density method are less than 5%. In this way, we have successfully established a simple, fast and non-destructive a priori technique based on detector mass measurements to determine the removed-layer thickness of etched LR 115 SSNTDs.

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