UV-Vis spectroscopic and chemical etching studies of CR-39 (PADC) exposed to ultraviolet radiation

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UV-Vis spectroscopic and chemical etching studies of CR-39 detector exposed separately to UV radiation of wavelengths 365 nm, and 254 nm at different exposure times were investigated. For CR-39 detector exposed to ultraviolet radiation of wavelength 365 nm, there was no significant changes either in the bulk etching rate V_B or UV-Vis spectra. UV-Vis spectra of CR-39 detector exposed to ultraviolet of wavelength 254 nm) showed a blue and red shift. The direct and indirect band gaps of CR-39 polymer were determined. It was found that the indirect and direct band gap decrease with the increase of the exposure time. The width of the tail of localized states in the band energy gap ΔE was obtained using Urbach's formula. The Urbach's energy ΔE increases by the increase of exposure time. Applying the proposed formula to determine the bulk etch rate of CR-39 exposed to short-wavelength ultraviolet leads to the modification of bulk etch rate by a factor ranging from 18% to 86% after 0.5 hour of etching time. The dependence of CR-39 response on the incident angle was investigated. It is found that the response is decreasing by the increase of incident angle and therefore it should be considered when using CR-39 as UV dosimeter.

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1. Introduction

Poly allyl diglycol carbonate, commercially known as CR-39 detector, is being used for charged particles identification and for radiation dosimetry as well [1, 2]. Many papers are reported the irradiation CR-39 detector with low linear energy transfer (LLET) radiations, such as infrared (IR), ultraviolet wave, gamma rays, and X-rays. LLET radiations induce changes in the initial structure by cross linking, free radical formation, irreversible bond cleavages, etc. These changes give rise to fragmentation of molecules and formation of saturated and unsaturated groups. All these processes introduce the so-called defects inside CR-39 detector, which are responsible for changes in the physical and chemical properties of CR-39 detector [3-6]. Importance of optical properties of CR-39 in case of mixed radiations justifies the need for studying the effects of irradiation on the optical properties of CR-39 such as the absorption and band gaps. The effect of LLET radiations on the physical and chemical properties of CR-39 polymer, such as on the absorption and band gap by using UV-Vis spectrophotometer are reported [7-10]. However, these changes have been applied to use CR-39 UV dosimeter.

One of the important chemical parameters of CR-39 is the bulk etch rate, which is increasing by the increase of Ultraviolet radiation dose just in the exposed surface. This results from the established fact that ultraviolet radiation of short wavelength is completely absorbed in a thin layer of the exposed surface [4, 11-15]. As a consequence, CR-39 detector exposed to ultraviolet radiation is not etched isotropically. In other words, the UV exposed surface is etched faster than the unexposed surface. As mentioned above CR-39 detector is used as UV dosimeter, however, nobody considered the effect of ultraviolet incident angle on the response of CR-39 detector. It is already established fact that electromagnetic waves subjected to reflection, which depends on the incident angle. As a consequence, such issue should be considered when using CR-39 as UV dosimeter to get the actual response of CR-39 to ultraviolet wave.

This work is undertaken to investigate effect of UV radiation on the optical properties and chemical etching of CR-39 detector. Deduction and application of a new formula to measure the actual bulk etch rate of CR-39 exposed to short ultraviolet radiation will be discussed. The induced optical band gaps modification of UV-irradiated CR-39 will be investigated at different exposure times. Finally, the response of CR-39 detector exposed to UV radiation at different incident angles is reported.

2. Effect of ultraviolet of short wavelength on the bulk etch rate of CR-39 detector

Two methods are applied to determine the bulk etch rate; these are: Mass decrement and thickness decrement

[9,16-17]. The bulk etch rate based on the mass decrement method is determined by using the relation [18]:

$$V = \frac{\Delta m}{2 t_e A \rho}, \quad (1)$$

where Δm is the mass difference before and after the chemical etching time of t_e measured in hours. A is the total area of detector's surfaces, and ρ is the density of CR-39. The bulk etching rate is measured by the direct thickness decrement and determined by using the relation [3]:

$$V_B = \frac{d_1 - d_2}{t_e}, \quad (2)$$

where d_1 and d_2 are CR-39 thickness before and after chemical etching time of t_e, respectively. Kodaira et al. [19] have established a new and precise method, known as the optical method to measure the bulk etching rate. It, more or less, depends on the measurement of the thickness difference with a high accuracy (±0.2 μm) using an optical displacement sensor. However, the methods mentioned above assumed that the bulk etch rates over all surfaces of CR-39 detector are isotropic. However, it is not true for CR-39 detector exposed to ultraviolet wave, which is stopped completely in few microns of exposed surface [20]. Therefore both methods, practically, average the bulk etch rate over the all surfaces of CR-39 detector.

Let V_{buv} is the measured bulk etch rate of CR-39 detector exposed to ultraviolet radiation of short wavelength, and V_B is the bulk etching rate for un-exposed CR-39 detector surface. V_{buv} expresses simply the average value of the bulk etch rates for the exposed-and non-exposed surface of CR-39. As a consequence, the measured bulk etching is written in the following form:

$$V_{buv} = \frac{V_{buv-net} + V_B}{2}. \quad (3)$$

The net bulk etching rate $V_{buv\text{-}net}$ for the exposed CR-39 detector' surface to short ultraviolet wave is determined by:

$$V_{buv-net} = 2V_{buv} - V_B. \quad (4)$$

2. Experimental procedure

CR-39 plastic detector sheet, TASTRAK type (Track Analysis System Ltd., UK), of thickness 1500 μm were cut in pieces of 4 cm^2. UV lamp (Raytech model LS-7CB) of power 4 watt delivers wavelengths of 365-and 254 nm. CR-39 samples are divided into three sets. The first set was exposed to ultraviolet radiation of wavelength 365 nm meanwhile the second set was exposed to ultraviolet radiation of wavelength 254 nm for different durations. The third set was exposed for 72 hour to ultraviolet radiation of wavelength 254 nm at different incident angles of 0°, 15°, and 60°. During the irradiation process, the temperature was maintained constant at 23 °C to ensure that no thermal effect will be produced by UV lamp. CR-39 detector are etched in an aqueous solution 6.25N NaOH at (70±0.5)° C. The bulk etch rate, V_B, was measured using the weight decrement method. The optical absorption spectra were measured using an UV-Vis spectrophotometer (Model Spectro dual split beam, UVS-2700). All samples were scanned in the wavelengths ranging from 190-to-700 nm in a step of 0.5 nm, keeping air as a reference.

3. Results and discussion

CR-39 detector is colorless, upon exposure to ultraviolet radiation of wavelength 254 nm, CR-39 detector was become yellowish, which increasing by the increase of the exposure time. This may be attributed dissolution of atmospheric oxygen during the irradiation process in air, which is in turn enhances the color centers in CR-39 detector. It may be arising from the trapped free radicals or charge species in the detector material [20]. For ultraviolet radiation of wavelength of 365 nm there was no color change even after 80 hours exposure time.

The optical absorption coefficient,α of the CR-39 reflects the detector ability to stop and detect the incident radiation. In principle, the higher the stopping power, the higher the detection efficiency. The optical absorption coefficient of CR-39 (α) depends on the ultraviolet wavelength, it is calculated from the UV-Vis spectra by using the equation:

$$\alpha(h\nu) = 2.303 \frac{Abs(h\nu)}{d}, \quad (5)$$

where d is thickness in cm and Abs is defined by Abs = log (I_O/I) where I_O and I are the intensity of incident and transmitted beams, respectively. An important feature of Eq. 5 is the huge optical absorption coefficient fluctuation for different wavelengths. For instance, the maximum optical absorption coefficient amounts to 54 cm^{-1} in the wavelength interval of 215-242 nm, meanwhile in the UV-A (315-400) nm it amounts to 1cm^{-1}. This fact opens a question about the suitability of CR-39 to be used as a unique personal dosimeter over the ultraviolet wavelengths' broadband [12-13-16-17].

3.1. Effect of UV on the bulk etch rate of CR-39 detector

For irradiated CR-39 detector with ultraviolet radiation of wavelength 365 nm, there was no significant change in bulk etching rate. This implies, however, that for long-wavelength ultraviolet could not be observed using the change in bulk rate and/or from UV-Vis spectrum. According to Eq. 5, the optical absorption coefficient at wavelength amounts to 80 m^{-1}, which means CR-39

detector is practically transparent at this wavelength. For short-wavelength ultraviolet of 254 nm, the bulk etch rate increases by the increase of the exposure time and finally getting saturated and V_B becomes constant and doesn't show significant changes whatever the exposure time, as demonstrated in Fig. 1. Tse et al. [4] have attributed this saturation effect in the bulk etch rate to intermolecular cross-linkings caused by free radical created by scission at CR-39 detector surfaces. This layer, however, acts as protective layer which increased the hardness of CR-39 detector. The bulk etching rates were measured for CR-39 detector exposed to short-ultraviolet ultraviolet of 254 nm for different durations.

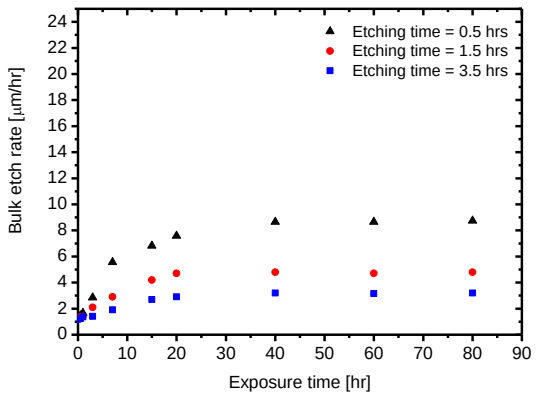

Fig. 1. Bulk etch rate, according to Eq.1 of CR-39 detector exposed to ultraviolet radiation of wavelength 254.

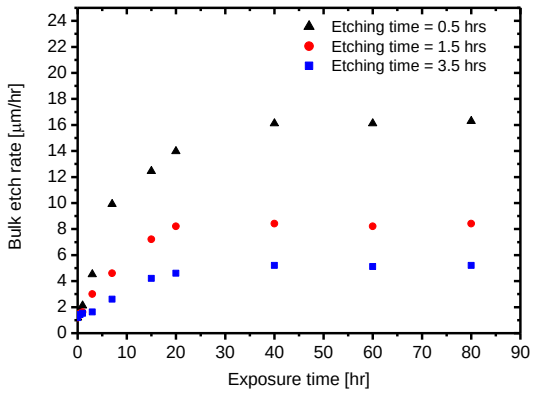

Fig. 2. Recalculation of the bulk etch rate in Fig. 1 according to Eq. 4 of CR-39 detector exposed to for ultraviolet of wavelength 254 nm.

Recalculation the bulk etching rate according to Eq. 4, leads to the increase of bulk etch rate by a factor 86% as shown in Fig. 2 for exposure time of 80 hour. Considering this fact will produce huge variation in the response function, critical angle, and removal thickness of CR-39 detector. These parameters are utilized to characterize tracks within CR-39 detector. All of these parameters will significantly change due to the bulk etch rate modification. For example, the bulk etch rates of UV exposed CR-39 in Ref.[3] have been underestimated approximately by a factor ranging from 18% to 88% for an etching time of 0.5 hour.

3.1. Effect of ultraviolet on the optical properties of CR-39

Fig. 3 shows UV-Vis spectra of un-exposed and exposed CR-39 detector to long-wavelength ultraviolet of 365 nm, no significant chemical degradation is observed even for the prolong exposure time until 80 hours. Based on the fact that, long-wavelength ultraviolet (365 nm) has transmission through CR-39 detector approximately more than 90%. These results ensure that, it is not possible to use CR-39 detector as personal dosimeter for long-wavelength ultraviolet wave, which is in a good agreement with the results reported by Tse et al. [4].

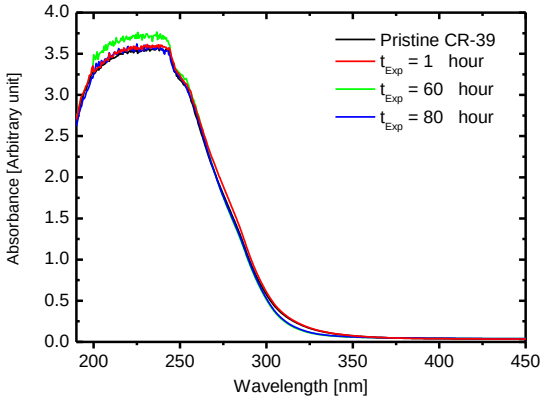

Fig. 3. UV-Vis spectra of pristine CR-39 detector and CR-39 detector exposed to ultraviolet of wavelength 365 nm for different durations.

Ultraviolet radiation of wavelength 254 nm has sufficient energy of 4.88 eV to cleave the bonds in the polymer chains with the production of free radicals, which can initiate further reactions with molecular oxygen. These result in the splitting of the macromolecular chains [6] this stimulates significant change in UV-Vis spectra of CR-39 detector as depicted in Fig. 4. For prolong exposures there are a slightly changes in the UV-Vis spectra showing a saturation effect. There are different shifts are clearly visible on the UV-Vis spectra of CR-39 detector exposed to short-ultraviolet wave; these are: the blue shift in the UV-Vis spectra before the wavelength 275 nm and red shift in the UV-Vis spectra after the same wavelength. Unfortunately, there is no explanation for such effect although the measurements have been measured many times, the effect has been observed in all samples. In Figure 4 the strong absorption bands between 190 and 250 nm are attributed to the C=C bond, this is associated by $\pi \rightarrow \pi^*$ transition, which happens in unsaturated centers in the molecules contain double bonds [4].

The absorption coefficient for non-crystalline material can be expressed as a function of the optical energy gap between the valance-and the conduction band E_g and the photons energy hν via the following equation [21]:

$$\alpha(h\nu) = \frac{C(h\nu - E_g)^n}{h\nu}, \quad (6)$$

where n is the power, which characterizes the transition process in the K-space. It can assume the values 0.5, 1.5, 2, and 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden, respectively [21].

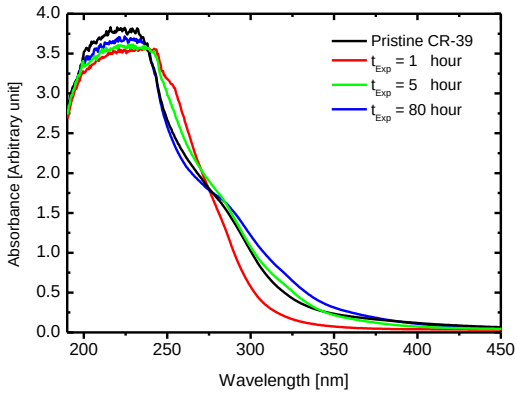

Fig. 4. UV-Vis spectra of pristine CR-39 and CR-39 exposed to ultraviolet of wavelength 254 nm for different durations.

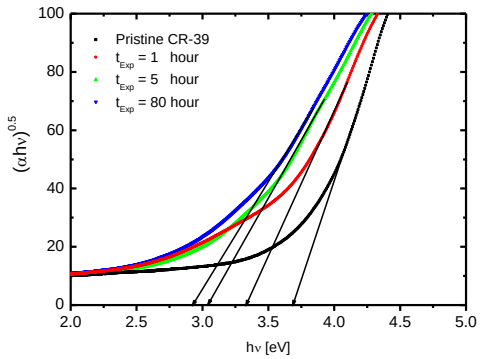

Fig. 5. Plot of $(\alpha h\nu)^{0.5}$ versus photon energy (eV) in CR-39 polymer before and after exposure to ultraviolet radiation of wavelength 254 nm.

The indirect and direct band gap energies are determined by plotting $(\alpha h\nu)^{0.5}$ as shown in Fig. 5 and $(\alpha h\nu)^2$ against the photon energy (hν) as shown in Fig. 6. By considering the linear section of the fundamental absorption edge of the UV-Vis spectra and find the intercept of the best fit lines on the (hν) axis. The values of the indirect and direct bands are reported in Table 1 with their standard errors. One may observe two important features from Table 1 the first one is the absence of a clear relation between short-wavelength ultraviolet exposure time and both of indirect and direct optical band gap, the second one the indirect band gap is lower than the corresponding values for the direct band gap [20-23].

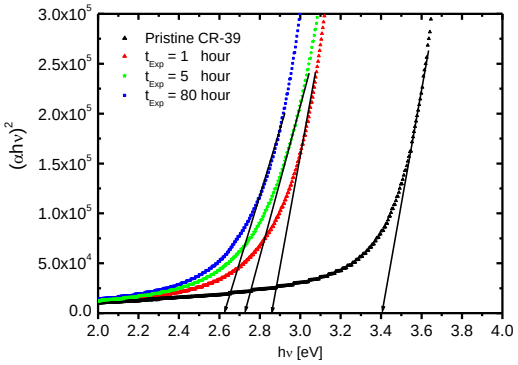

Fig. 6. Plot of $(\alpha h\nu)^2$ versus photon energy (hν) in CR-39 polymer before and after exposure to ultraviolet radiation of wavelength 254 nm.

The irregularities in band gaps level of CR-39 detector are defined in terms of Urbach's energy using the following equation [24]:

$$\alpha(h\nu) = \alpha \circ Exp(\frac{h\nu}{\Delta E}), \quad (7)$$

here, α_o is a constant and α(hν) is the absorption coefficient, ΔE is an energy that is interpreted as the width of the tail of localized states in the forbidden gap. It is considered as thermal vibration in lattice. The Urbach's energies, tabulated in Table 1, are calculated from the inverse of the slop of the linear part of plotting curve of lnα (hν) against hν as depicted in Fig. 7.

Table 1. Indirect, direct band gaps and Urbach's energies of CR-39 detector exposed to ultraviolet radiation of 254 nm.

$T_{exp.}$[h]	Indirect band Gap [eV]	Direct band Gap [eV]	Δ E [eV]
Pristine	3.40±0.06	3.69±0.06	0.29
1	2.85±0.03	3.32±0.03	0.30
3	2.78± 0.03	3.22±0.05	0.42
5	2.72±0.02	3.01±0.05	0.45
20	2.63±0.05	3.11±0.04	0.53
40	2.51±0.04	3.00±0.06	0.52
80	2.62±0.05	2.92±0.06	0.50

The represented results show some disagreement with the results reported by Tse et al. [4], which could be attributed to utilizing of a different CR-39 polymer, which are prepared in different ways (e.g., different initiator, different inhibitors, the polarization process, etc.).

The correlation between physical and chemical properties is studied by the correlation between the chemical etch rate and the band gaps modifications and Urbach's energies of CR-39 exposed to ultraviolet of wavelength 254 nm. The bulk etch rate shows an opposite behavior relative to the change in energy bands, bulk etch rate increases by the increase of exposure time, while band gaps decrease. On the other hand, both of the bulk etch rate and Urbach's energies have the same behavior, they increase by the increase of the exposure time as depicted in Fig. 8.

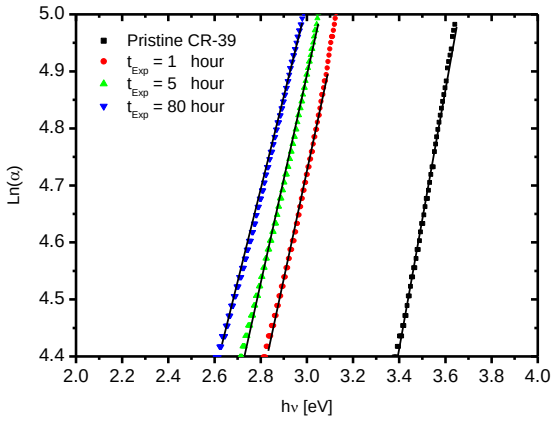

Fig. 7. Dependence of the natural logarithm of α on photon energy (hν) of CR-39 exposed to ultraviolet radiation of wavelength 254 nm for different durations.

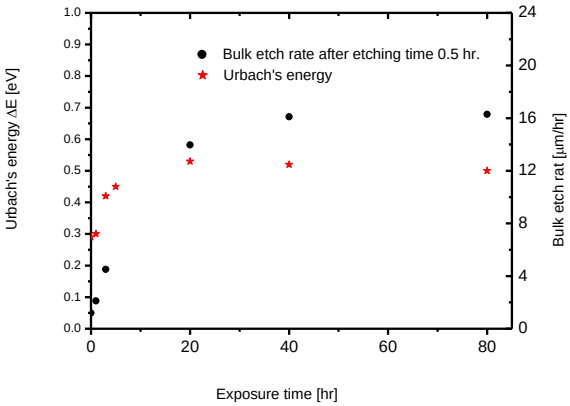

Fig. 8. Urbach's energy and bulk etch rate of CR-39 detector as a function of exposure time of ultraviolet of wavelength 254 nm.

3.2 Effect of UV-irradiation incident angle on CR-39 detector's absorption spectra

Ultraviolet is an electromagnetic wave, which subjected to reflection. Based on this fact, one may expect that CR-39 detector response to ultraviolet depends on UV incident angle. Fig. 9 shows the UV-Vis spectra of unexposed and exposed CR-39 detectors at three incidence angles 0 (perpendicular), 15, and 60° for 72 hours with short-wavelength ultraviolet (254 nm). There is a difference in UV-Vis absorbance spectra of four CR-39 detector samples, for example, the red shift is decreased by increasing the incident angle (the angle between CR-39 detector and UV lamp). The red shift in the UV-Vis spectra is greater for 0° (perpendicular incidence) than for 15°and 60°. Blue shift in the UV-Vis spectra increases slightly by the decrease of the ultraviolet incident angle as well.

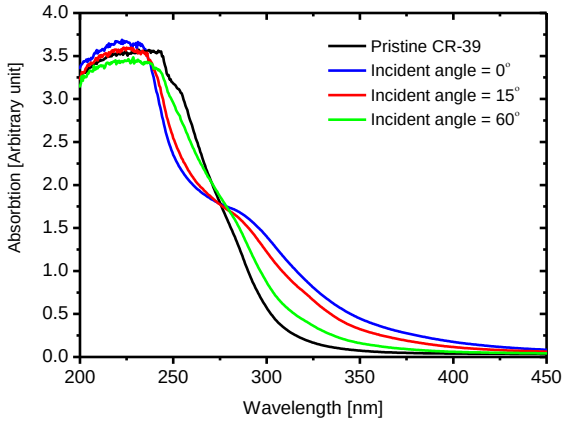

Fig. 9. UV-Vis spectra of, pristine CR-39 and CR-39 exposed to ultraviolet of wavelength 254 nm at different incident angles.

These results introduce new factor which affects the response of CR-39 detector to ultraviolet wave. It should be taken into account when studying the effect of ultraviolet radiation on the tracks characteristics in CR-39 detector. It expected that when this experiment is repeated again using coherent ultraviolet source (which is not available in our Lab.) as reported in [3], it should provide quantitative and accurate results. The significance of the current results is to explain the results obtained by Abu-Jarad et al. [16], where they have attributed the difference in CR-39 detector response between horizontally mounted CR-39 detector (where the angle of incidence depends on the sun position) and when CR-39 detector mounted on the solar tracker (CR-39 is always perpendicular to the incident solar ultraviolet radiation) to the solar ultraviolet radiation to the nature backing material

4. Conclusion

A new proposed formula should be applied to determine the real value of bulk etch rate for CR-39 polymer exposed to ultraviolet radiation. The optical band gaps and Urbach's energy were determined with the aid of the optical absorption spectra. The indirect and direct band gaps decreasing by the increase of the exposure times, meanwhile Urbach's energy increased by the increase of the exposure time to the ultraviolet radiation of wavelength 254 nm. The response of CR-39 detector to ultraviolet wave is affected by the incident angle ultraviolet wave; such effect should be considered when CR-39 is used as an UV dosimeter.

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