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UV-VIS Spectral Evaluation of CR-39 Detector Exposed with Diagnostic Dosage

(Penilaian Spektrum UV-Vis Pengesan CR-39 Terdedah dengan Dos Diagnosis)

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ABSTRACT

The effects of the X-ray irradiation and chemical etching on the physical and optical properties of CR-39 plastic detectors were investigated for different doses of X-ray. CR-39 detectors were etched in the solution of the 3 M of NaOH after irradiation for revelations of the track. The tracks formed on CR-39 either by irradiated X-ray or due to the effect of environment. The changes in the thickness after exposed have significant decrease in 60 kVp and started to increase in the range of 70 kVp up to 100 kVp due to the formation of oxidation layer on surface by free radicals. The optical band gaps before etching and after etching were determined by using Ultraviolet-visible (UV-Vis) spectroscopy. The optical band gap is attributed to the indirect transition due to its amorphous nature which is significantly decline trend energy in increase of the energy fluence of radiation. The Urbach's energy, is defined as the width of the tail localized states in the forbidden band gap which change increment trend as increase in dose delivered due to the distortion structure of the CR-39 in terms of the electron charges in valences electron hence attributes to the induced modification of angle bond between the neighboring atoms.

Keywords: CR-39; optical band gap; X-ray irradiation

ABSTRAK

Kesan sinar-X pada beberapa pengesan plastik CR-39 dan punaran kimia telah dikaji dalam dos sinar-X yang berbeza dalam aspek perubahan sifat fizikal dan sifat optik. CR-39 terpunar dalam cecair NaOH 3 M selepas sinaran untuk pendedahan runut terbentuk pada CR-39 sama ada oleh sinaran-X atau kerana kesan alam sekitar. Perubahan ketebalan pendedahan mempunyai peningkatan penurunan yang bererti pada 60 kVp dan memulakan peningkatan dalam julat 70 kVp sehingga 100 kVp kesan daripada pembentukan lapisan pengoksidaan di permukaan oleh radikal bebas. Jurang jalur optik sebelum dan selepas punaran telah ditentukan dengan menggunakan spektrofotometer Ultralembayung-nampak (UV-Vis) yang dikatakan oleh peralihan secara tidak langsung disebabkan sifat amorfus yang ketara menolak trend tenaga di dalam peningkatan fluensi tenaga radiasi. Tenaga Urbach, ditakrifkan sebagai hujung lebar keadaan setempat dalam jurang jalur yang terlarang menukar trend kenaikan sebagai peningkatan dalam dos dihantar disebabkan oleh struktur herotan CR-39 dalam jangka caj elektron dalam elektron valen dan mengakibatkan pengubahsuaian teraruh sudut ikatan di antara atom jiran.

Kata kunci: CR-39; jurang jalur optik; sinar-X

INTRODUCTION

CR-39 plastic detector known as Pollyallyl digycol carbonate (PADC) in forms of transparent, colorless, inflexible plastics, is one of the solid state nuclear track detector (SSNTD) which contains element of component C₁₂H₁₈O₂. Different studies on CR-39 polymer have shown the effect of irradiation to various modification in the physical and chemical properties such as optical, electrical and mechanical on the polymeric materials, which depends on the irradiation fluence and energy of radiation used (Abdul-Kader et al. 2010; Gruhn et al. 1980; Hamilton & Clifton 1981; Vijay Kumar et al. 2009). According to Rupali Rohatgi (2009) and Yamauchi (2003), the bulk etch rate was usually determined from both etching duration and the radius of the etched track of

high-LET particles like fission fragments which indicates that the thickness of layer was removed. On the other hand, due to its susceptibility of etch solution, CR-39 tends to be ionized and may produce more degradation in damaged region that would enhanced of the track form after irradiation. There are number of researches done focusing on the effect of polymer due to high dose radiation which related to the track registration and optical absorption of CR-39 (El-Shahawy et al. 1997; Sharma et al. 2007; Sinha et al. 2001). The range of diagnostic dosage used is capable to induced damage on the polymeric material; therefore a proper study was carried out to look upon such changes of physical and optical properties in term of tracks, thickness and optical absorption.

MATERIALS AND METHODS

IRRADIATION WITH X-RAY AND ETCHING PROCESS

CR-39 in form of square shape type of TASTRAK (Track Analysis System Ltd, UK) was obtained from Physics Department at Bristol University in UK. X-ray irradiations of monoenergetic beam (using Toshiba KX0-50S X-ray machine) were made within 3 mAs in parameter of cm and 100 cm SSD which exposed up to 110 kVp. CR-39 then chemically etched with 3 M NaOH solution for 24 h at 70°C. All the samples were placed in dry area at room temperature with the presence of silica gel to avoid contamination and dust.

OPTICAL PROPERTIES AND PHYSICAL PROPERTIES

After the samples preparation, the next step was measuring the thickness using vernier calipers (absolute Digimatic, Mitutoyo). Tracks registration of CR-39 was recorded before and after etching under optical microscope (Meji MT) with a magnification of 10×. UV-1800 (Shimadzu) was used to analyze the optical properties in term of absorbance sample in range of 190 up to 800 nm with double beam photometric system, using air as reference. The spectrophotometer was warm up for 15 min before measurement was recorded in order to obtain stable measurement over a large wavelength region as much as possible.

RESULTS AND DISCUSSION

PHYSICAL PROPERTIES

Based on Figure 1, the variation in the thickness of CR-39 in early pristine up to 50 kVp were steady or no changes in trend were seen before irradiated and before etching.

This may due to energy of photon not enough to be absorb by the molecules that can induced their modification in term of oxidation. Whereas, in the range of 50 to 60 kVp there have abruptly decrease in thickness which may due to the distortion of the polymer structure such bond angle of the molecule CR-39 when induced to higher fluence of radiation. However, in the range of 70 to 110 kVp, the oxidation occurred as the thickness of CR-39 shows slight increment when exposed to higher energy of photon in the presence of the surrounding oxygen thus forms the oxidation layer on the surface of CR-39 (Rana 2002). Apparently, the thickness of CR-39 shown decreasing trend due to the chemical etching itself that would be able to remove the oxidation layer in order to acquire its purities. Additionally, the etched solution can also cause more degradation on the surface of the medium at damaged region than undamaged region and would enhanced the track produce after irradiate (Hepburn & Windle 1980). Apart from that, the tracks were more visible on the surface using optical microscope after soaking in the etching solution (NaOH) due to removal of the surface layer of CR-39 (Figure 2).

OPTICAL PROPERTIES

The concept of absorption edge could obtained some values about the structural, energy gap and induced transitions of molecules due to optical absorption of photon imparted on molecules in vary energies which result in the changes of electronic energy and vibrational energy. Optical absorption coefficient is as following (Halimah et al. 2005):

$$\alpha(\omega) = 2.303 \, A/d,\tag{1}$$

where A is an absorbance and d is thickness in cm of sample. As can be seen in Figure 3, optical absorption spectra of irradiated CR-39, before and after etching were

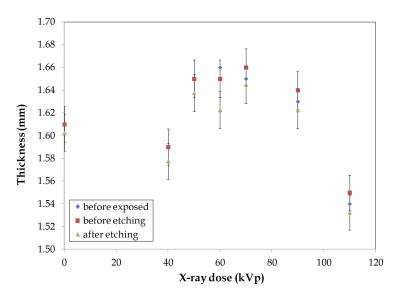


FIGURE 1. Variation thickness of the CR-39

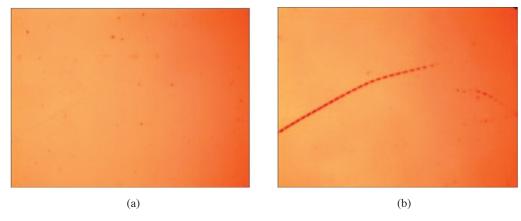


FIGURE 2. Illustration of the track registration of the irradiated CR-39 (a) before etching and (b) after etching

represented, respectively. From these spectral changes, it can be seen that there is a little peak of fluctuations (smooth spectra) as compared with Figure 3(b) due to the removal of impurities on the surfaces of CR-39. Besides that, it can be seen in Figure 3(b) that at the wavelength range of 300-400 nm are significant changes at spectra due to the formation of new chemical groups in chemical reaction between CR-39 polymer and NaOH solution (Khan et al. 2005; Siegel et al. 2008). The values of optical band gap energy in polymers were obtained using extrapolating linear portion by plotting for indirect band gap as a function of photon energy as shown in Figure 4. The graph plotted by the formulas that has been simplified by Davis and Mott 1970 from (1) in more general form (Tauc 1974).

$$\alpha(\omega) = \frac{\left(\hbar\omega - \mathbf{E}_{opt}\right)^n}{\hbar\omega},\tag{2}$$

where, E_{opt} is the optical band gap energy and n is constant to be related as electronic transition whether direct or indirect during the absorption process in the K-space, in

which the dependence on (2) is too small to be sure as the exact value of the exponent n (Zaki 2008).

As can be seen in Figure 4(c) both indirect band gaps shows slightly decrement trend as there are increment in terms of X-ray exposure besides its amorphous nature of CR-39 (Vijay Kumar et al. 2009). The decrease of optical band gap of irradiation would produces faults in CR-39 polymer such free radical and oxidation which increase the electronic disorder and induce the creation of a permitted state in forbidden band (El-Badry et al. 2008; Halimah et al. 2005).

The optical activation energy, also known as Urbach's energy is the width of the tail of localized states in the forbidden band gap using the following formula:

$$\alpha(\omega) = B \exp\left(\frac{\hbar\omega}{\Delta E}\right),$$
 (3)

where B is constant, ΔE is a measure of band tailing. The Urbach's energy was calculated by taking the reciprocal of the slopes linear portion of the lower photon energy

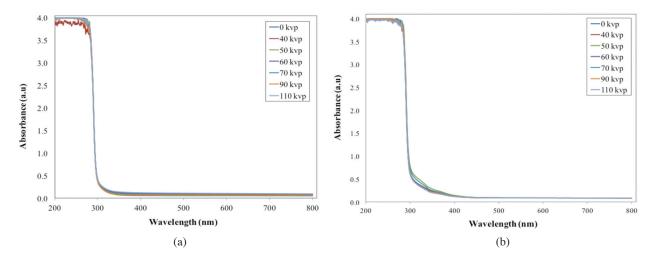


FIGURE 3. Optical absorption spectra of irradiated CR-39 (a) before etching and (b) after etching

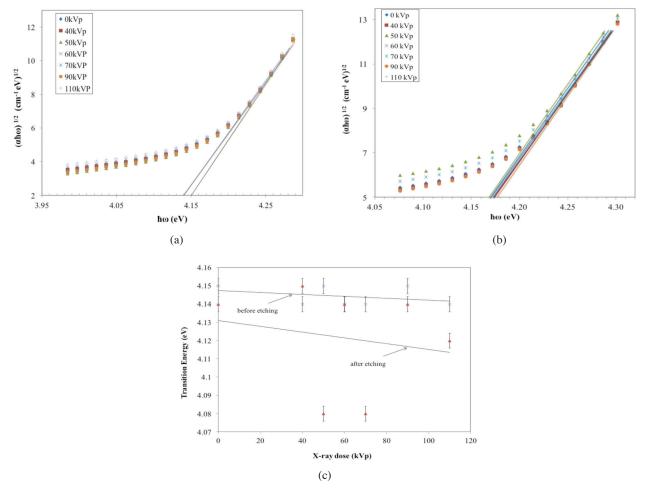


FIGURE 4. Plot of against photon energy for indirect band gap (a) before etching, (b) after etching and (c) variation of the allowed transitions on energy photon for before etching and after etching

regions as shown in Figure 5. It can be seen that the values of variation Urbach's energy shows slight increment trend as there is increasing fluence of radiation. Mott and Davies have reported that values of ΔE for a range of amorphous semiconductors are very close, which is 0.4087 and 0.6532 eV. As the width of the tail of localized states increase, CR-39 polymer tends to be more extension of the localized between band gap as the increase amount of energy delivered due to the electronic disorder in valences electron during the interaction of energy photon. These changes of irregularities were probably due to the structural arrangement, which slightly attributes to the modification of angle bond between neighbor atom. Whereas values of ΔE after etching shows decrement trend with increasing fluence of radiation, probably due to the decrease in the concentration of weak bonds in valence band tail and suggests weak bond to dangling bond conversion decrease the width of valence band tail (Costea et al. 2007). Besides, it is obviously seen that the value of ΔE is slightly higher before etching as shown in Figure 4. It was probably due to the temperature dependence during etching process that would give effect towards Urbach energy that the weak excitation, which is phonon coupling will result in

a horizontal displacement of the Urbach tail towards low energy as the temperature increase (Klafter & Jortneer 1977). In the same way, width of the tail of localized states in the forbidden band gap tends to be more localized that is shows for the recovery of irregularity in the band gap of CR-39 (Surinder & Sangeeta 2004).

CONCLUSION

A detail study was performed to identify significant changes in terms of physical and optical response of the irradiated CR-39 with the diagnostic dosage after chemically etching. The results showed a decreasing trend in the thickness when CR-39 was exposed to some effluence of X-ray. On the other hand, there was an increase in the thickness as soon as higher energy effluence of radiation were used due to the formation of oxidation layer. Meanwhile, the chemical etching will produce a significant decrease in terms of thickness and presence of track registration by removing the impurities on the surface layer of CR-39. The values of the optical band gap and Urbach's energy were determined using optical absorption spectra. It was concluded that values of the indirect band gap before and

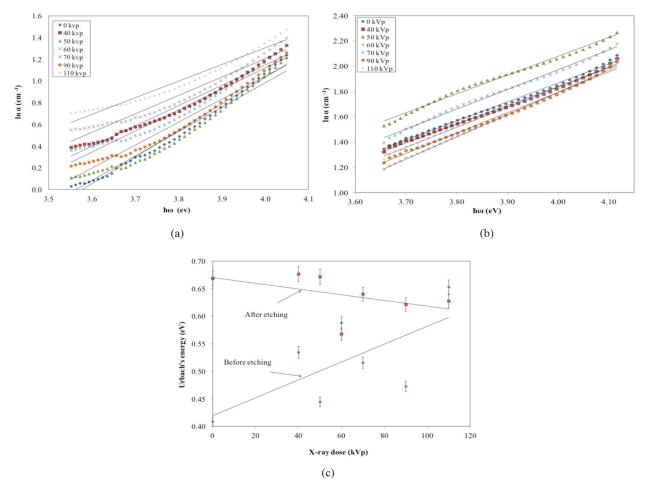


FIGURE 5. The dependence of the natural logarithm of on a photon energy in range wavelength 200-800nm (a) before etching, (b) after etching and (c) variation Urbach's energy with different kVp

after etching was slightly decrease as the X-ray effluence increase due to changes in irregularities of energy band gap. In contrast, Urbach's energy before etching is higher as the dose of X-ray delivered increased due to the localization of the atom whereas after etching, there was decrement in trend due to concentration of weak bond in valence band tail.

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REFERENCES

Abdul-Kader, A.M., El-Badry, B.A., Zaki, M.F., Hegazy, T.M. & Hashem, H.M. 2010. Ion beam modification of surface properties of CR-39. *Philosophical Magazine* 90: 2543-2555.

Costea, S., Kherani, N. P., Zukotynski, S., 2007. Metastable defect creation in tritiated hydrogenated amorphous silicon and the Staebler-Wronski effect. *Journal of Material Science: Materials in Electronics* 18(1 Supplement): 175-182.

El-Badry, B.A., Zaki, M.F., Hegazy, T.M. & Morsy, A.A. 2008. An optical method for fast neutron dosimetry using CR-39.

Journal of Radiation Effects and Defects in Solids 163: 821-825.

El-Shahawy, M.A. 1997. Spectral changes of CR-39 induced by irradiation and heat treatment. *Journal of Polymer Degradation and Stability* 57: 157-161.

Gruhn, T.A., Li, W.K., Benton, E.V., Cassou, R.M. & Johnson, C.S. 1980. Etching mechanism and behavior of polycarbonates in hydroxide solution: Lexan and CR-39. In *Solid State Nuclear Track Detectors*, edited by Francois, H., Kurtz, N. & Massue, J.P. Proceeding of the 10th International Conference, Lyon, 2-6 July, New York: Elsevier Ltd.

Halimah, M.K., Daud, W.M., Sidek, H.A.A., Zainal, A.T., Zainul,
H. & Juniah, H. 2005. Optical properties of borotelluterite
glasses. *American Journal of Applied Sciences* (Special Issue): 63-66.

Hamilton, E.I. & Clifton, R.J. 1981. CR-39, a new α-particle sensitive polymeric detector applied to investigation of environmental radioactivity. *Journal of Applied Radiation and Isotopes* 32: 313-324.

Hepburn, C. & Windle, A.H. 1980. Review solid state nuclear track detector. *Journal of Materials Science* 15: 279-301.

Khan, E.U., Husaini, S.N., Malik, F.M., Sajid, M., Karim, S. & Qureshi, I.E. 2002. A quick method for maintaining the molarity of NaOH solution during continuos etching of CR-39. *Journal of Radiation Measurements* 35: 41-45.

- Klafter, J. & Jortner, J. 1977. Urbach rule in the optical spectra of crystalline and amorphous organic solids. *Chemical Physics* 26: 421-430.
- Rana, M.A. 2002. Swelling and structure of radiation induced near-surface damage in CR-39 and its chemical etching. *Journal of Radiation Measurement* 47: 50-56.
- Rupali Rohatgi, Deepa Sathian, Jayalaksmi, V., Sarala Nair, Marathe, P.K., Chaurasiya, G. & Kannan, S. 2009. Reduction of background in CR-39 SSNTD using chemical pre-etching methods. *Indian Journal Physics* 83: 845-850.
- Sharma, T., Aggarwal, S., Sharma, A., Kumar, S., Kanjilal, D., Deshpande, S.K. & Goyal, P.S. 2007. Effect of nitrogen ion implantation on the optical and structural characteristics of CR-39 polymer. *Journal of Applied Physics* 102: 063527.
- Siegel, J., Reznickkova, A., Chaloupka, A., Slepicka, P. & Svorcik, V. 2008. Ablation and water etching of plasmatreated polymers. *Radiation Effects & Defects in Solids* 163: 779-788.
- Sinha, D., Phukan, T., Tripathy, S.P., Mishra, R. & Dwivedi, K.K. 2001. Optical and electrical properties of gamma irradiated PADC detector. *Journal of Radiation Measurements* 34: 109-111.
- Surinder, S. & Sangeeta, P. 2004. UV-Vis spectroscopic and etching studies of IR exposed CR-39 plastic track detector. Journal of Nuclear Instruments and Methods in Physics Research B 215: 169-173.
- Tauc, J. 1974. Amorphous and Liquid Semiconductors. London and New York: Plenum Publishing Company Ltd. pp. 159-220.

- Vijay Kumar, Sonkawade, R.G., Dhaliwal, A.S. & Rohit Mehra. 2009. Study of neutron induced modification on optical band gap of CR-39 polymeric detector. *Asian Journal of Chemistry* 21(10): S279-283.
- Yamauchi, T. 2003. Studies on the nuclear tracks in CR-39 plastics. *Journal of Radiation Measurements* 36: 73-81.
- Zaki, M.F. 2008. Gamma-induced modification on optical band gap of CR-39 SSNTD. *Journal of Physics D: Applied Physics* 41: 175404.

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