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Study of surface chemical behavior of oxygen ion irradiated Kapton-H

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The surface chemical etching behavior of pristine and oxygen irradiated Kapton-H was studied at different time intervals and at different temperatures (at 40°C & 50°C for different time intervals in the steps of 15 minutes). The surface chemical behavior is studied by the etching process. The parameter studied is the thickness of polymeric sample with etching at the above mentioned two temperatures. These studies are conducted for pristine sample as well as oxygen irradiated polymeric samples. The results clearly shows that etch rate increases in case of Oxygen irradiated samples as well as it shows increase at higher temperature. These studies are very useful for industrial optoelectronic applications of Kapton-H, as desired application can be made available if we know the etching parameters.

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1. Introduction

Polymers are a large class of materials consisting of many small molecules (called *monomers)* that can be linked together to form long chains, thus they are known as *macromolecules* [1-3]. The passage of heavily ionizing nuclear particles through most insulating solids creates narrow paths of intense damage on an atomic scale. These damaged tracks may be revealed and made visible in an ordinary optical microscope by treatment with a properly chosen chemical reagent that rapidly and preferentially attacks the damaged material. It less rapidly removes the surrounding undamaged matrix in such a manner to enlarge the etched holes that mark and characterize the sites of the original, individual, damaged regions. This simple technique of observing particles has been used in wide variety of technical fields that range from nuclear science and engineering to cosmic ray astrophysics and from geology, archaeology, and sub oceanic geophysics to lunar sites and meteoritics. When a charged particle passes through a polymeric material, it losses its energy mainly through four processes: electronic stopping (ionization and excitation), nuclear stopping (displacements), radiative losses (bremsstrahlung and Cherenkov) and phonon & plasmon decay. Fleischer et al. [4], suggested that due to irradiation, a burst of ionization takes place along the path of a charged particle to create an electro statically unstable array of adjacent ions which eject one another from their normal sites into interstitial position. Due to this primary ionization an array of interstitial ions and vacant lattice sites is produced by the coulomb energy of the ions that give rise to space charge polarization of the sample [5-11]. This radiation induced polarization is useful in studying surface chemical etching behavior of polymers. We can also say that a fast charged particle will eject electrons from atoms that were close to its path, leading to the polarization of sample induced by irradiation. After this, elastic relaxation diminishes the acute local stress by spreading the strain more widely. So it creates a long range chain that makes possible the direct observation of unetched tracks in crystals by transmission electron microscopy. The electronic stopping process results from the interaction of incident ion with target electrons. The primary products produced during this process are electrons, ions, atoms in excited states, free radicals and molecules. The energy of the incident ions is distributed by the excited molecule among its neighbors as phonons and excitons. These are the processes of ionization and excitation respectively. In addition the chemical bonds may also break (chain scission), when the excited energy is localized in a particular chemical bond. Such radiolysis scission frequently causes the loss of side groups, such as hydrogen. This reaction produces unsaturated bonds in polymer chain or cross-linking when the cleavage of C-H bonds occurs on adjacent molecules. The electronic processes involve electrostatic forces between the incident particle and the electrons surrounding the target nuclei leading to the stripping of these electrons from their orbits or to raising the electrons to less tightly bound states. The nuclear stopping processes involve electrostatic forces between the moving ion and the target nuclei resulting in the ejection of target atoms from lattice sites or out of the molecular chains. This chain scission leads to the formation of large molecular species such as hydrocarbons. When scission occurs at pendent atoms or side groups, unsaturation or cross linking may occur. In radiative losses, a charged particle while passing close to the field of a nucleus gives rise to the emission of electromagnetic radiation known as bremsstrahlung. Bremsstrahlung is an important means of energy loss only for light particles such as electrons. At a given energy of the incident particle the energy loss through bremsstrahlung emission is proportional to (Z_1/m_l) Z_2, where Z_1, m_l are the charge and mass of the incident particle and Z_2 is the charge on the target nucleus. In addition, at velocities greater than the phase velocity of light in the stopping medium, the moving charge causes polarization of atoms near to the particle trajectory and a coherent wave front of radiation is formed known as Cherenkov radiation. For non- relativistic incident particles, radiative losses are negligible. The phonon or plasmon decay mainly constitutes thermal energy losses by atoms and electrons. These do not have any significant impact on materials properties. Among these processes, the first two produce most significant effects in changing material properties. Both electronic and nuclear processes contribute to cross-linking and scission in varying degree. Experimental evidences indicate that electronic processes are responsible mainly for the formation of unsaturated bonds and cross linking while the nuclear processes are the main cause of chain scission. Among many other processes that may occur during irradiation, cross-linking, unsaturated bond formation and chain scission are considered to be the most important processes for modifying the polymeric materials. At the energies, typically more than 1Mev/amu the velocity of the ions or the charged particle is comparable or higher than the Bohr electron velocity. The ions with such high energies are referred to as swift heavy ions (SHI). Nuclear energy losses dominate at lower energies whereas the electronic energy losses dominate at higher energies. The other important change in polymeric properties due to irradiation comes from the compositional modification, loss of gaseous molecules such as hydrogen oxygen and nitrogen alters the chemical composition of polymers drastically. Injected ion species may be trapped at certain preferred sites in the matrix, and can form precipitates by self- clustering or by reacting with host elements, or assist in cross-linking by forming chemical bonds with the polymer chains.

Polyimides constitute an important class of materials because of their many desirable characteristics viz. excellent mechanical properties, low dielectric constant , low relative permittivity, high breakdown voltage, low dielectric loss over a wide range of frequency, good polarization, good processing capability, wear resistance, radiation resistance, inertness to solvents, good adhesion properties, low thermal expansion, good hydrolytic stability and long term stability. Because of these traits, polyimides have found applications in a host of technologies as inter-metal dielectric, high temperature adhesive, photoresist etc. the applications of polyimides range from aerospace to microelectronics besides optoelectronics and composites. The oxydianiline (ODA) - pyromellitic dianhydride (PMDA) polyimide, with a commercial name kapton-h, attracted the attention of researchers over other polyimides because, ether structure of ODA would enhance possibilities for a moulding resin. Therefore kapton-h polyimide, which is superior to other polyimides, has been used in the present investigations. The kapton-H polyimide (chemical name: poly 4-4′ Oxydiphenylene Pyromellitimde, PMDA-ODA) used in the present study was procured from DuPont(USA) in film form. Solid state nuclear track detectors (SSNTDs) when used for detection and identification of ionizing particles need to be calibrated using known ions. Whatever may be the mechanism for production of latent tracks the basis for identification lie in the data acquisition on the various etched-track parameters viz., track length *L*, residual range *R*, track etch rate $V_{T,}$ etch rate ratio, etch-pit diameter and growth profile besides REL, (d*E/dx)* and primarly ionization data. Many methods such as ***L-R*** plots, track profiling, V_T vs *R*, V_T vs (Z^*/β), mean etch rate ratio vs mean total energy etc. are available [4, 12-14]. Almost all of these methods require rigorous geometrical measurements on the track parameters and hence are time consuming. Ruddy et al [14] and Grabez et al [15] using the concept of etch-induction time (T_{ind} the time interval which elapses between the start of the etching and the first appearance of a microscopically observable track in the given detector) suggested a correlation between T_{ind} and characteristics like Z and β of the incoming ion. However this concept does not appear to be justified as it means that an etched track of size 0.3μm (which is invisible through an optical microscope) would be ignored and hence the measured value of T_{ind} would be larger than the actual value when the track-size grows 10 dimensions comparable with the mean wavelength of the light used. One can, therefore conclude that this concept cannot be used for sub-microscopic track events. Again the observations on etch induction time measurements made by Schwenck et al [16] on Fe-ion (500 MeV/n) tracks in Daicel cellulose nitrate suggested that there existed a 1-2 μm thick surface crust in which track etching does not take place, leading to a delay between the start of the track etching and the immersion of the detector in the etchant. All the methods used for identification of particles using solid state nuclear track detectors are based upon the acquisition of data on the various etched track geometrical parameters, as well as REL and (d*E/dx)* values. Chakarvarty et al [17] has attempted to explore the possibility of making use of breakthrough time information obtained during electrolytically controlled etching of nuclear track filter foils of Cellulose Nitrate (CN), (Daicel and Kodak) and Cellulose Acetate (CA), (Daicel) for discriminating heavy energetic ions viz., ^{208}Pb (17.1 MeV/n), ^{238}U (13.64 MeV/n, 16.34 MeV/n) and ^{132}Xe (14 MeV/n). They found that the breakthrough time in a given detector and under given etch conditions depends upon (d *E/dx)* and also is function of (Z^*/β) of the particle. The method was non microscopic and useful only for charged particles of range of thickness of detector foil. Zhu *et al* [20] have reported the bulk-etch rate value for Kapton as 0.88 μm/h with 10% NaOCl at 70°C, Vater *et al* [21] have reported the bulk-etch rate value for Kapton as 1.3 µm /h with 13% NaOCl as the etchant at 70°C. It has not been mentioned whether the etching was carried out under no-light or light-exposed conditions. Chakarvarty & Mahna [22] have reported bulk-etch rate value to be about 1.6 times the reported values of Vater *et al.* [21] under no-light exposure and with stirring conditions with a NaOCl solution with an even lower amount of Cl (4%). At 30°C it was found that average bulk-etch rates for Kapton under light exposure are reduced to *ca* 50% of the value obtained under no-light conditions. In the case of Thermalimide, the corresponding values of V_b have an insignificant difference up to the first 60 hrs duration of etching. The etching tends to become slower for longer (> 60 hrs) etch-times. At higher temperatures (50°C, 60°C and 70°C), Thermalimide is found to have relatively higher bulk-etch rates under no-light and no-stirring conditions. With NaOCl + ethanol (1:1) mixture at 60°C, the etching is faster, and there is an enhancement in the rates by factors of *ca* 5 and 4 in the case of Kapton and Thermalimide, respectively. They extended the study to other temperatures also. Under no-light conditions, etching of Kapton using 4% NaOCl with stirring, the V_b values increase by a factor of *ca* 2 at etch temperatures of 30°C -70°C. Thus, they concluded that this etchant (NaOCl + ethanol) may be used even without stirring for obtaining faster etching. However, they observed that long-duration etching with an ethanol mixture caused a loss in mechanical strength and optical transparency, and produced brittleness. Quamara [21] has reported the polarization induced surface chemical etching behaviour of kapton-H polyimide using NaOCl as etchant at 55°C. The poling has been done at 80°C, 120 °C and 150°C using a dc field of 1000V following the usual method. He has also investigated the etching behaviour for the samples given similar heat-treatment but without applying any field. It was observed that the bulk etch rate increases in heat-treated samples. The induced polarization results in a decrease in the etching rate. The imide and the carbonyl groups both appear to be responsible for etching process. Loss of absorbed water due to heat treatment and increase in inter molecular forces due to polarization mainly governs the etching behaviour of polarized Kapton-H. Garg & Quamra [22] applied FTIR spectroscopy technique for the analysis of high energy heavy ion irradiated kapton-H polyimide. The kapton-H samples were irradiated with 75 MeV oxygen, 80 MeV nickel and 50 MeV lithium ions. A very broad peak in 2500-3500 cm^{-1} is due to the presence of absorbed water in irradiated samples. The reduction in the intensity of 1702 cm^{-1} peak in irradiated samples as compared to pristine samples is associated to the demerization of carbonyl groups. The increase in the intensity of this peak with increase in fluence was due to the increase in cross linked structure causing the reduction in demerization of carbonyl groups. The FTIR spectrum was independent of the nature of ion.

The detailed study of surface chemical etching behaviour of Kapton- H polyimide with various etchants is required in the field of electronics where the subtraction of material is done through chemical etching process. The removal of material from polyimide using laser and oxygen plasma etching process is faster than the chemical etching process but this is applicable only where etching is required at very small area. The development of micro-pore nuclear track filters is the area which requires a precise etching. This is done through the process of high-energy heavy ion interaction polymeric materials. Therefore a detailed investigation of surface chemical etching behaviour of an engineering polymer like Kapton-H in pristine and irradiated form with different etching temperature would be an important aspect in the field of nuclear track filters and has not been reported much. The present work deals with the study of surface chemical etching behaviour of pristine as well as oxygen ion irradiated Kapton-H polyimide using NaOH as etchants at two different temperatures.

2. Experimental details

Pristine Kapton-H (4-4'-oxydiphenylene pyromellitimide) were procured from Dupont (U.S.A.) in the form of thin film of thickness 30 µm. The samples were irradiated using 75 MeV/nucleon O^+ ion beam of fluence 1.875 x 10^{12} ions/cm^2 at PELLETRON facility, Nuclear Science Centre, New Delhi in collaboration with Department of Applied Physics, NIT, Kurukshetra. The pristine and the irradiated samples were simultaneously etched with 4N NaOH at 40°C & 50°C for different time intervals in the steps of 15 minutes. After each etching interval the samples were washed thoroughly in distilled water and then dried in open air. The etchant was changed periodically so that concentration of etchant remained the same during the experiment. The thickness measurements for a particular sample were taken before & after etching on a specified area. Etch rate was determined by measuring the foil thickness using dial gauge having least count of 1 µm.

3. Results and discussion

The surface chemical etching behavior of pristine and irradiated Kapton-H was studied by measuring the half layer thickness (one-half of the total etched-out thickness on both sides of the sample, as measured by the dial gauge before and after etching), removed. The measured values of half layer thickness removed (in µm) in pristine and O^+ irradiated samples at different time intervals and at temperature 40^0 C and 50^0 C are listed in Table 1. The comparison of average bulk etch rate (μm/h) for pristine & O$^+$ irradiated Kapton-H (15 μm thickness) at 40^0 C and 50^0 C is given in Table 2. The Effect of temperature on average bulk etch rate (μm/h) for pristine and O$^+$ irradiated Kapton-H is given in Table 3.

Table 1. Half layer thickness removed (in μm) in 4N NaOH with time at 40^0 C and 50^0 C.

TIME (min)	Half layer thickness removed (μm)			
	40^0C		50^0C	
	Pristine	O$^+$ Irradiated	Pristine	O$^+$ Irradiated
15	0.5	1.0	1.0	1.5
30	1.0	1.5	4.0	5.0
45	1.5	2.0	5.5	6.0
60	2.0	4.0	8.0	9.5
75	3.0	5.0	9.5	11.0
90	5.0	6.0	--	--
105	6.0	7.0	--	--
120	6.5	7.5	--	--
135	7.0	8.0	--	--
150	8.0	9.0	--	--

Table 2. Comparison of average bulk etching rate (μm/h) for pristine and irradiated Kapton-H.

Etching temperature	Sample	Average bulk etching rate(μm/h)
40^0 C	Pristine	3.2
	O$^+$ Irradiated	3.6
50^0 C	Pristine	8.3
	O$^+$ Irradiated	9.6

Table 3. Effect of temperature on average bulk etch rate (μm/h) for pristine & O$^+$ irradiated Kapton-H.

Etching temperature	Sample	Average bulk etch rate(μm/h)
40^0 C	Pristine	3.2
50^0 C		8.3
40^0 C	O$^+$ Irradiated	3.6
50^0 C		9.6

The variation of half layer thickness removed of (A) pristine and (B) 75 MeV/nucleon O$^+$ ions (fluence 1.875 x 10^{12} ions/ cm^2) irradiated Kapton-H (15 μm thickness) samples at 40^0 C is shown in Fig. 1. The variation of half layer thickness removed of (A) pristine and (B) 75 MeV/nucleon O$^+$ ions (fluence 1.875 x 10^{12} ions/ cm^2) irradiated Kapton-H (15 μm thickness) samples at 50^0 C is shown in Fig. 2.

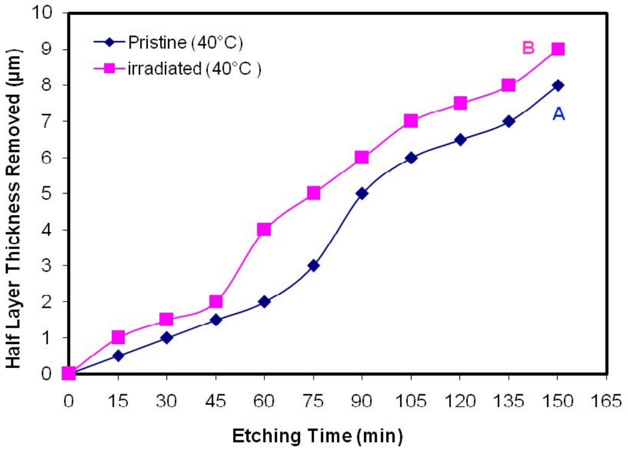

Fig. 1. Variation of half layer thickness removed of (A) pristine and (B) 75MeV/nucleon O$^+$ ions (fluence 1.875 x 10^{12} ions/ cm^2) irradiated Kapton-H (15 μm thickness) samples with 4N NaOH at 40^0 C.

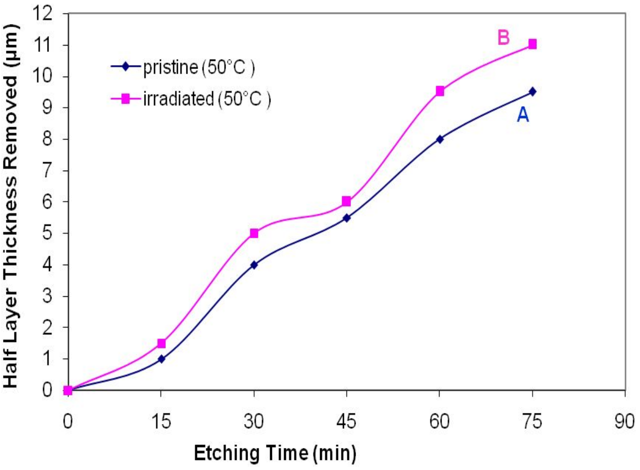

Fig. 2. Variation of half layer thickness removed of (A) pristine and (B) 75 MeV/nucleon O$^+$ ions (fluence 1.875 x 10^{12} ions/ cm^2) irradiated Kapton-H (15 μm thickness) samples with 4N NaOH at 50^0 C.

The general nature of the etching characteristics of O$^+$ irradiated sample appears almost similar to that of pristine sample as seen from Fig. 1 and Fig. 2. However, a significant change in the half layer thickness removed during different durations of etching has been observed in O$^+$ irradiated sample as shown in Fig. 1 and Fig. 2. In O$^+$ irradiated sample, the etching is fast during the 0-30 min time interval of etching after which it shows a decrease for time interval of 30-45 min. This can be understood on the basis of factors on which the etching process in O$^+$ irradiated samples depends.

The etching process in irradiated samples depends upon:

An increase in average bulk etch rate due to breaking of some linkages leading to an ease in the chemical reaction.

A decrease in etch rate is due to the increase in the crystallinity of the sample [24-25].

The resultant etch rate will be the algebraic sum of both the factors and an increase/decrease in the etch rate will be given by the predominance of one of the factor. The present study shows an increase in etch rate of the O^+ irradiated samples in 0-30 min time interval of etching, which suggest the dominance of the breaking of imide linkages. However, a decrease in the etch rate in 30-45 min time interval of etching suggests an increase in the crystallinity of the sample.

The average bulk etch rate is different for the pristine and the O^+ irradiated samples and it is found to be more in case of O^+ irradiated Kapton-H as compared to the pristine sample as listed in Table 2. The effect of temperature on variation of half layer thickness removed of pristine Kapton-H (A) at 40^0 C and (B) 50^0 C is shown in Fig. 3. The effect of temperature on variation of half layer thickness removed of 75 MeV/nucleon O^+ ions (fluence 1.875 x 10^{12} ions/ cm^2) irradiated Kapton-H (15 µm thickness) (A) at 40^0 C and (B) 50^0 C is shown in Fig. 4.

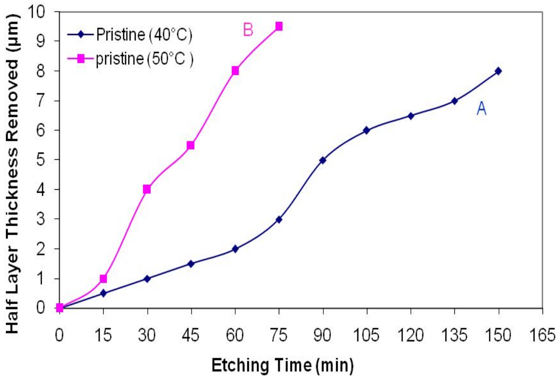

Fig. 3. Effect of temperature on variation of half layer thickness removed of pristine Kapton-H (15 µm thickness) with 4N NaOH (A) at 40^0 C and (B) 50^0 C.

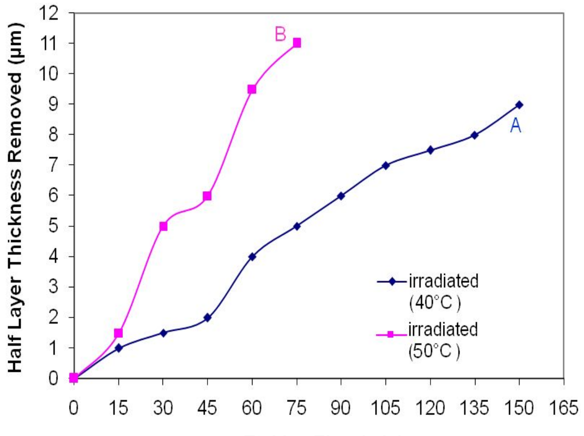

Fig. 4. Effect of temperature on variation of half layer thickness removed of 75 MeV/nucleon O^+ ions (fluence 1.875 x 10^{12} ions/ cm^2) irradiated Kapton-(15 µm thickness) with 4N NaOH (A) at 40^0 C and (B) 50^0 C.

Conclusions

The present study shows an increase in etch rate with increase in the etching temperature as can be seen from Fig. 3 and Fig. 4. The average bulk etch rate increases with rise in etching temperature as listed in Table 3. This increase in average bulk etch rate with rise in temperature can be understood due to the increase in solubility of carboxylate salt during the reaction of NaOH with Kapton-H along with the cleavage of O-carboxyamide bonds at temperature above 40^0 C [25]. The present study concludes that the irradiation of the sample by high energy heavy ions modifies the surface chemical etching behaviour of Kapton-H polyimide. The etching rate is found to increase in case of the O^+ irradiated sample. The etch rate is also found to increase with increase in etching temperature. These results are also supported by our earlier studies on Ni irradiated Kapton-H [26].

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References

[1] F. W. Billmeyer Jr., Text Book of Polymer Science, John Wiley and sons, 1984.
[2] D. R. Askeland, P. P. Phule, The Science and Engineering of Materials, 4th Ed., Brooks/Cole, 2003.
[3] A. Rudin, The Elements of Polymer Science and Engineering 2nd Ed., Academic Press, 1999.
[4] R. L. Fleischer, P. B. Price, R. M. Walker, Nuclear Tracks in Solids, University of California Press, Berkeley, 1975.
[5] S. A. Durrani, R. K. Bull, Solid State Nuclear Track Detection, Pergamon Press, 1987.
[6] G. M. Sessler (ed.), Electrets, 2nd Enlarged Edition, Springer Verlag, 1987.
[7] R. L. Fleischer, P. B. Price, Science**140**, 1221 (1963).
[8] R. L. Fleischer, P. B. Price, J. Geophys. Res. **69**, 331 (1964).
[9] R. L. Fleischer, H. R. Hart, Jr., in Proceedings Burg Wartenstein Conference on Calibration of Hominoid Evolution, W. W. Bishop, J. A. Miller, S. Cole (eds.), Edinburgh: Scottish Academic Press, 135, 1972.
[10] G. E. Blanford, Jr., R. M. Walker, J. P. Wefel, Rad. Effects **3**, 267 (1970).
[11] R. B. Seymour, Engineering Polymer Sourcebook McGraw-Hill, 1990; E. H. Lee, in: M.K. Ghosh, K. L. Mittal (eds.), Polyimides: Fundamentals and Applications, Marcel Dekker, New York, 471, 1996.
[12] R. A. Dine-Hart, D. B. V. Parker, W. W. Wright, Br Polymer J. **3**, 222 (1971); B. Grabez, R. Beckmann. P. Vater, R. Brandt, Nucl. Instr. and Meth. **211**, 209 (1983) .
[13] B. Grabez, P. Vater, R. Brandt, GSI Scientific Rep.,

GSI (88-1) ISSN 0174-0814, 249, 1988.
[14] F. H. Ruddy, H. B. Knowles, S. C. Luctstead, G. F. Tripard. NucL Instr. and Meth. **147**, 25 (1977).
[15] B. Grabez. P. Vater, R. Brandt, Nucl. Tracks **5**(3), 291 (1981).
[16] P. Schwenck, G. Sermund, W. Enge, Proc. 12th Int. Conf. on SSNTDs. Mexico, 1983.
[17] S. K. Chakarvarti, S. K. Mahna, L. V. Sud, Nuclear Instruments and Methods in Physics Research B **44**, North-Holland, 242 (1989).
[18] T. C. Zhu, P. Vater, R. Brandt, J. Vetter, Microfilters with tiny holes in Kapton. GSI Sci. Rep. 253, 1987.
[19] P. Vater, T. C. Zhu, S. Heise, R. Brandt, J. Vetter, GSI Sci. Rep., 243, 1988.
[20] S. K. Chakarvarti, S. K. Mahna, Nucl. Tracks Radiat. Meas. **20**(4), 589 (1992).
[21] J. K. Quamara, Indian J. of Pure & Applied Physics **36**(11), 661 (1998).
[22] M. Garg, J. K. Quamara, Indian J. of Pure & Applied Physics **45**(7), 563 (2007).
[23] M. Garg, J. K. Quamara, Nucl. Instrum. Meth. B **179**, 83 (2001).
[24] J. K. Quamara, M. Garg, T. Prabhavathi, Thin Solid Films **449**, 242 (2004).
[25] C. E. Diener, J. R. Susko, Polyimide **1**, edited by K. L. Mittal, Plenum Press, New York, 353, 1982.
[26] V. Mehta, S. Kumar, J. K. Sharma, Optoelectron. Adv. Mater. - Rapid Comm. **3**(3), 265 (2009).

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