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Surface chemical behavior of Ni ion irradiated Kapton-H

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This research work is devoted to the study of surface chemical behavior of Ni irradiated Kapton-H. The surface chemical behaviour is studied by etching process. The etching was done for three hours at each time interval of 30 mins and at two temperatures 40 degree and 50 degree Celsius. The parameters studied are thickness of polymeric sample with etching at the above mentioned two temperatures. These studies are conducted for pristine sample as well as Ni irradiated polymeric samples temperatures. The results clearly show that etch rate increases in case of Ni irradiated samples and with temperature increase. These studies are useful for industrial optoelectronic applications of Kapton-H.

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1. Introduction

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. Poly(4-4' oxydiphenylene pyromellitimide), chemical name of kapton-h , is available in thin film form in standard thickness of 7.5, 12.5, 25, 50, 75 and 125 □m. it is a linear polymer comprising of heterocyclic rings linked together by one or more covalent bonds. Kapton-H film exihibits marvelous electrical, dielectric, physical and mechanical properties retainable over a wide range of frequency and temperature, extending from 4 to 600k. 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.

In the recent past emphasis has been laid on the study of irradiation of macromolecules. Much of this interest is due to the novel properties of polymers, which have resulted from ion-beam irradiation. For example, it has been known for some time that the electrical conductivity of ion irradiated polymers increases by many orders of magnitude when irradiated with only a few times 10^{13} ions/mm^2 as mentioned by Venkatesan (1985) and Brown (1986)[1, 2]. Recently, extremely large mechanical hardness values have been discovered when certain polymers were irradiated with fast heavy ions as studied by Lee et al(1991) and Rao et al (1992)[3, 4]. Lewis et. al [5] developed a theoretical model to calculate the time or fluence dependence of G-values for H, production, G(H,), from the ion irradiation of various polymers. The surface morphology development on materials under energetic particle bombardment has been of paramount importance to the sputtering community for several years. Extensive studies have been undertaken on the formation of conical or pyramidal structures on bombarded metal surfaces to reveal different aspects of interactions of energetic particles with surfaces of materials as mentioned by Grove (1852); Wehner (1955); Behrisch (1964); Kaminsky (1965); Carter and Colligon (1968); Sigmund (1973); McCracken (1975); Tolk et al (1977); Behrisch (1982); Winograd (1982); Navinsek (1976); Harrison (1983); Auciello and Kelly (1984); [6-18]. Despite the vast amount of accumulated experimental material, no established theory exists to explain all details of the experimental findings. Even a less satisfactory situation exists for understanding of the particle interaction phenomena on molecular solids, such as polymers and biological materials. The need for a better understanding of the energetic particle-polymer interaction is stimulated by a rapid increase in the number of particle beam applications. Particle beams are used today for thin polymer film deposition as mentioned by Robertson. Resist exposure in ion lithography as mentioned by Seliger et al (1979); Adesida et al (1982) and Adesida (1983) [19-21]. Pattern delineation of microelectronic structures by ion milling was studied by Gloerson (1975); Carter et al (1979) and Braun et al (1983) [22-24]. Ion beam micromachining of polymers has also found important applications in bioengineering as mentioned by Geis et al (1981) and Banks (1984) [25-26]. Some studies dealing with different aspects of particle beam interaction with polymers have been published. Only a small number of experimental studies have been focused on Polyimides and in particular Kapton-H are very promising materials for many industrial and aerospace applications due to their thermal stability and high radiation resistivity. Michael & Stulik (1987) [27] reported that the inner structure and bonding interactions within the polymer are the major factors responsible for unique features of the surface morphology development. Using a series of particle bombardment-gold coating-SEM investigation-gold layer stripping cycles, they observed that the Kapton-H is extremely resistive to particle bombardment. Under high fluence particle bombardment, the surface morphology development proceeds from uniform rows of submicron protrusions to flat-top columns which later disintegrate into long thin fiber like structures. The average sputtering yield of Kapton-H is about 30 amu/atom (i.e., 0.08 [-$C_{22}H_{10}N_2O_5$-] monomer units/atom). This value is very low when compared to other polymer materials. Irradiation of polymers with energetic heavy ions leads to cleavage of chemical bonds and to creation of various, chemically reactive degradation products as studied by Venkatesan et al (1987) and Chapiro (1988)[28, 29]. Part of the volatile degradation products may escape the specimen. This process leads to gradual dehydrogenation and deoxidation of irradiated material and to the production of excessive free volume as mentione by Hnatowicz et al (2001)[30] which is expected to facilitate inward penetration of dopants which eventually may be captured on defects, created by the ion irradiation. On the other hand, at a higher density of radiation defects a new intermolecular bond can be created leading to well known cross-linking and in turn to the creation of impermeable, compacted regions in the irradiated material representing diffusion barriers as studied by Hnatowicz et al (1996) [31]. The penetration and incorporation of inorganic agents in polymers and radiation degraded polymers is of interest for fundamental reasons as well as for some practical consequences related to aging of pristine and radiation damaged polymers. The doping of polymers with inorganic agents changes their electrical properties and it is considered as a promising technique for creation of new, polymer based electronic and optoelectronic components. The doping with lithium containing agents (e.g. LiCl) in combination with Neutron Depth Profiling technique (NDP) have been shown to be an effective tool for non-destructive examination of the surface layers of polymers to the depths of several μm asmentioned by Fink et al (1996); Hnatowicz et al (1997) and Vac´ık et al (1998)[32-34]. Cervena et al (2002) [35] conducted studies on Polyimide–Kapton (PI) foils, 50 μm thick were irradiated with 100 keV He^+, Ne^+, Ar^+, $Kr^+$and Xe^+ ions to the fluencies from 1×10^{12} to 1×10^{16} cm^{-2} and subsequently doped from 5 M/1 water solution of LiCl for 1 and 25 h at room temperature. They concluded that the dopant uptake is a complicated function of the ion mass, ion fluence and the doping time. The depth profiles of the dopant in the PI samples irradiated to the fluences below 1×10^{13} cm^{-2} are similar to that from unirradiated PI. At higher fluences an anomalous profile component appears, the width of which correlates well with the ion projected range. Lee et al (1996) [36]. Kapton, a popular polyimide, is able to operate in the temperature range of as low as -269 ^{0}C and as high as 400 ^{0}C Du Pont Product Bulletin (1998)[37]. When a highly energetic charged ion strikes a polymer target, it loses most of its energy in exciting electrons and or ionizing atoms. Target ionization causes bond cleavages; the formed free radicals are expected to come to rest and may react in a molecular site of a different type from their original site as mentioned by Picq et al (1998) [38]. These radicals are responsible for most of the chemical transformations observed in the polymer films. The very high value of energy transferred induces an unusual density of electron-hole pairs close to the ion path and consequently the polymer modifications differ from those observed with low ionizing projectiles as studied by Balanzat et al (1995); Balanzat et al (1996) and Steckenreiter et al (1997)[39–41]. Virk (2002) [42] reported the physical and chemical response of 70 MeV carbon ion irradiated Kapton-H polymer. The UV-visible spectra revealed a decrease in absorption initially with fluence, but for the higher fluences it showed a recovery characteristic. A decrease in band-gap energy of 0.07 eV was observed. The FTIR analysis indicated the high resistance to radiation induced degradation of polymer. The diffraction pattern of Kapton-H indicates that this polymer is semi-crystalline. In case of irradiated one, there was an average increase of crystallite size by 20%, but diffuse pattern indicates that there was a decrease in crystallinity, which may be attributed to the formation of complex structure induced by the cross-linking of the polymeric chains. A lot of work has been done on polymer solids irradiated by swift heavy ions in the electronic slowing down regime where high-density electronic excitations and ionizations are generated in the material inside the primary track core as mentioned by Balanzat et al (1996); Balanzat et al (1996); [43, 44]. It is recognized that first steps of polymer degradation under ion beams involve bond scission or cross-linking, and rearrangements of the damaged macro-molecules that lead to emission of some gaseous species Venkatesan et al (1987); Davenas et al (1993) [45, 46]. In the case of swift heavy ion irradiations, chemical modifications of some polymers were carefully studied with the evolution of the FTIR spectra as a function of the absorbed dose by varying the mass, fluence (Φt) and electronic stopping power S_e =(-dE/dx)$_e$ of the ions as studied by Venkatesan et al (1987); Davenas et al (1993); Balanzat et al (1996); Balanzat et al (1996) and Steckenreiter et al (1999) [43, 47]. In particular, the formation of C≡C (acetylene) and C≡N (alkyne, cyanate) triple bonds was evidenced in the damaged polymers as mentioned by Steckenreiter et al (1999) [47]. In the last steps of degradation, it is generally believed that a carbonaceous material is formed with a variable sp^2/sp^3 ratio, where sp^2 bonding seems to be favoured by the electronic excitations as studied by Davenas et al (1993) [45]. Constantini et al. (2002) [48] extensively studied the damage of polyimide (Kapton-H) thin films by heavy ion irradiations in the 1MeV/amu energy range. They observed that the irradiation-induced insulator–conductor transition proceeds through four stages on the basis of the progressive formation of a 3D graphite-like structure when track overlaps increase. With visible micro-Raman spectra the spectral features of the pristine polymer progressively disappear during stages I and II, and only two broad peaks at around 1360 and 1580 cm^{-1}, corresponding respectively to the well-known D and G bands of disordered graphitic materials, remain in stages III and IV regardless of the ion. High-energy irradiation of polymers causes the modification in physico-chemical properties due to irradiation in the development of new sensor devices or generating conducting properties in polymers as mentioned by Lee et al (1996); Garg and Quamara (2001)[49, 50] on one hand and morphological changes occurring that affects the performance of polymers in a radioactive environment as mentioned by Rutledge et al (1990); Ektessabi and Hakamata (2000) [51, 52] on the other hand. Quamra et al (2004) [53] reported the effect of high-energy ion irradiation on dielectric relaxation. The TSDC spectrum of the irradiated samples reveal that the β-peak (appearing at nearly 80 ^{0}C) associated with dipolar relaxation has been largely affected due to irradiation. At higher fluence, β-peak almost vanished. The peak appearing at approximately 180 ^{0}C (α-peak) was due to space charge relaxation. They reported the increase in peak magnitude in samples irradiated with higher fluence. This is attributed to the creation of new energy traps by irradiation. The ion irradiation resulted in a large increase in low temperature dielectric constant (30–70 ^{0}C) ascribed to the increase in water absorption capacity. The dielectric constant in temperature range 70–180 ^{0}C is mainly governed by dipolar relaxation and space charge relaxation. It has been suggested that though the space charge relaxation tends to increase ε` a major loss in carbonyl groups due to high-energy ion irradiation results in a decrease in ε`. In high temperature region (180–250 ^{0}C) the dominance of interfacial polarization increases the ε` value. The loss peaks appearing at approximately 50, 180 and 250 ^{0}C are representative of the various relaxation processes.

2. Experimental details

The Kapton-H samples was irradiated with an ion viz Ni using PELLETRON facility at Nuclear Science Center, New Delhi. The energy and the fluence associated with this ion are listed in the Table 1.

Table 1. The ion beam, energy and fluence used in the present investigations.

Ions	Energy (MeV)	Fluence (ions/cm^2)
Ni	80	$2.7x10^{12}$

Kapton-H polyimide samples whose chemical name is poly (4-4'-oxydiphenylene pyromellitimide) were procured from Dupont in thin film form. This polymer is known for its marvelous physical, chemical, mechanical and electrical properties over a wide range of frequency and temperatures. The test pieces were cut from the as received polyimide film of different thicknesses. The samples were irradiated using 80 MeV Ni ion beam of fluence 2.7 x 10^{12} ions/cm^2 at PELLETRON facility, Nuclear Science Center, New Delhi. The pristine and the irradiated samples were simultaneously etched in interruption mode in 2N NaOH (40°C, 50°C). After each etching cycle the samples were washed in distilled water and then dried. All the measurements for a particular sample were taken on a pre marked area. Etch rate was determined by monitoring the foil thickness using dial gauge. Table-2 shows the details of thickness removed.

Table 2. Cummulative thickness removed (in µm) in 2N NaOH with time at 40^O C and 50°C.

Time (min)	40^{0}C		50^{0}C	
	Pristine	Irradiated	Pristine	Irradiated
30	0	3	6	10
60	3	5	10	12
90	6	7	18	19
120	9	10	21	23
150	11	12	23	25
180	12	15	24	26
210	15	16	--	--
240	16	17	--	--
270	18	19	--	--
300	20	22	--	--

3. Results and discussion

3.1 Effect of irradiation

The etching process in irradiated samples has two effects. There should be an increase in etch rate due to the ease in the chemical reaction due to breaking of some linkages. There should be a decrease in the etch rate due to the increase in the crystallinity of the sample. The net change in the etch rate will be the algebraic some of the both the cases and an increase or decrease in the etch rate will be governed by the predominance of one case. Fig. 1 and Fig. 2 shows the effect of irradiation on the etching behavior of Kapton-H at 40^0 and 50^0 Celsius.

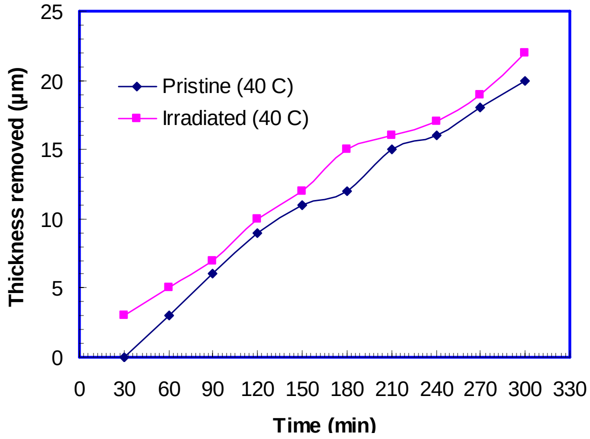

Fig. 1. Effect of irradiation on the etching behaviour of Kapton-H at 40^0C.

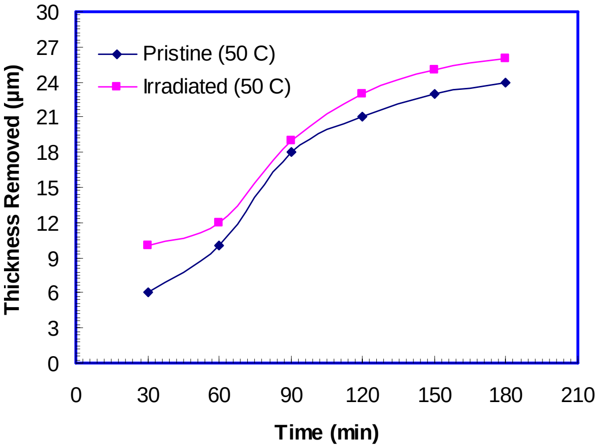

Fig. 2. Effect of irradiation on the etching behaviour of Kapton-H at 50^0C.

3.2 Effect of temperature

The effect of etching temperature on thickness removed (best fit curve) for pristine as well as irradiated Kapton-H samples (thickness: 30μm) was shown in Fig. 3 and Fig. 4, respectively. The increase in average bulk-etching rate with the increase in temperature is due to the increase in solubility of carboxylate salt during the reaction of NaOH with Kapton-H and secondly, O-carboxyamide bonds are cleaved at temperatures above 40°C (Ref. 7).

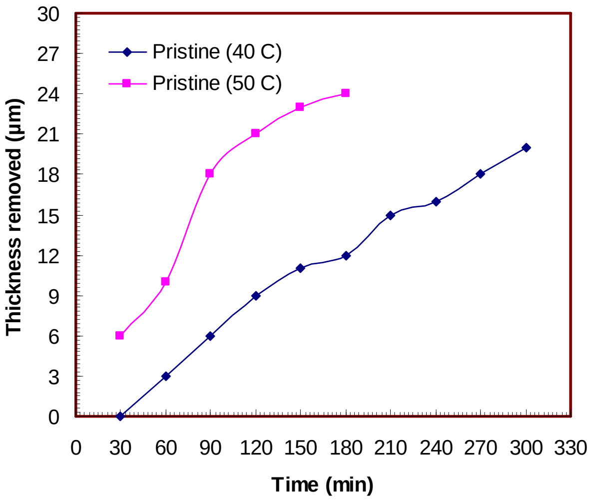

Fig. 3. Effect of temperature on the etching behaviour of Kapton-H in pristine condition.

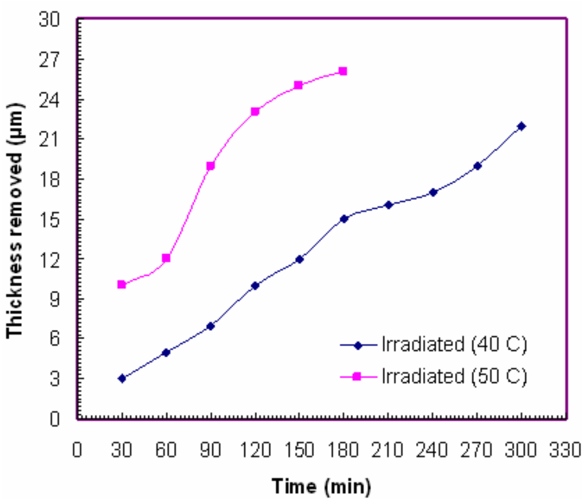

Fig. 4. Effect of temperature on the etching behaviour of Kapton-H after irradiation.

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