Temperature and frequency dependent dielectric constant/loss studies in 50 MeV $\text{Si}^+$ ion irradiated kapton-H film

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The kapton-H polyimide film samples (25 μm thickness) have been irradiated with 50 MeV $\text{Si}^+$ ion beam with fluences $2.3 \times 10^{13}$ and $1.38 \times 10^{13}$ ions/cm$^2$. The dielectric constant/loss for irradiated samples have been measured in the temperature range 30-250 °C for different frequencies 120 Hz, 1 kHz, 10 kHz and 100 kHz. An increase in the low temperature (30-70 °C) low frequency $\varepsilon'$ has been ascribed to the increase in water absorption capacity ($\gamma$-relaxation) due to high energy ion irradiation. Dielectric loss maximum around 50°C is in conformity with this relaxation. The dielectric constant in temperature range 70-180 °C is mainly governed by dipolar relaxation and space charge relaxation due to shallow energy traps. The $\varepsilon'$ value for low flux sample is observed to be more than that for high flux sample. It is suggested that though the space charge relaxation tends to increase $\varepsilon'$, a major loss in carbonyl groups due to high energy ion irradiation results in a decrease of $\varepsilon'$. In high temperature region (180-250 °C) the interfacial polarization due to creation of new phases by irradiation increases the $\varepsilon'$ value. The maximum in $\varepsilon''$-T curve at 250 °C confirms the presence of this relaxation. However, in this temperature region increase in crystallinity of kapton-H results in a decrease of $\varepsilon'$. The dominance of any one determines the nature of $\varepsilon''$-T curve.

1 Introduction

The high-energy ion-irradiation effects in kapton-H polyimide have been investigated by many groups with different aspects. Particularly the electrical conduction behaviour and change in its optical properties due to high energy ion irradiation have been of much interest owing to its possible application as conducting polymer and in the development of optical devices. However the high-energy heavy ion-irradiation effects on dielectric behaviour have not been reported much. This study may play an important role in determining the configurational changes in polyimide due to irradiation. Quamara et al. have recently reported the effect of high energy $\text{Li}^+$, $\text{O}^+$ and $\text{U}^{238}$ ions on relaxation behaviour of kapton-H polyimide using thermally stimulated discharge current (TSDC) technique. The appearance of new shallow/deep energy traps, decomposition of carbonyl groups and cross-linking are some of the consequences of high energy heavy ion-irradiation which have been discussed in these reported communications. Though the TSDC technique is now commonly used for characterizing the various relaxation processes, only dipolar relaxation can be studied in detail using this technique. For a dipolar relaxation the efficiency will be 100% but it is usually not true for space charge and interfacial relaxations. Further limitation for TSDC technique arises from its low frequency (10$^{-3}$ to 10$^{-1}$ Hz) character due to which a complete dielectric spectrum cannot be obtained. A bridge method, which allows the study of dielectric behaviour at different frequency ranges, will overcome the shortcomings of TSDC technique. At the same time a sound footing to the findings of TSDC may be provided by dielectric constant/loss measurements. In this study we are mainly concerned with a detailed elucidation of the temperature dependent dielectric constant/loss behaviour of kapton-H polyimide by high-energy $\text{Si}^+$ ions.

2 Experimental Details

Kapton-H polyimide, whose chemical name is poly(4-4'-oxydiiphenylene-pyromellitimide), was procured from Dupont in film form. It maintained its physical, chemical, electrical and mechanical properties over a wide range of temperature and frequency. It has the rigid chain structure, as shown below, and has no glass transition temperature up to 500 °C.
The samples (thickness 25 µm) were irradiated with 50 MeV Si\(^{18}\) ion with fluences \(2.3 \times 10^{13}\) and \(1.38 \times 10^{13}\) ions/cm\(^2\) at Nuclear Science Center (PELLETRON facility), New Delhi. The 50 MeV Si\(^{18}\) beam was obtained by reducing the original energy of 100 MeV beam, by passing it through a kapton-H film of certain thickness calculated using TRIM. Samples with 0.5 cm diameter were metallized on both sides by vacuum evaporation of aluminium for electrical contacts. The samples were fitted in a dielectric cell and kept in a specially prepared temperature controlled furnace. This furnace was shielded against stray pick-ups. The dielectric constant/loss measurements were made in the temperature range of room temperature to 250 °C using a precession LCZ meter (Keithley 3321) at frequencies 120 Hz, 1 kHz, 10 kHz and 100 kHz.

3 Results and Discussion

The dielectric relaxation behaviour of kapton-H polypimide is usually governed by absorbed water (\(\gamma\)-relaxation), its dipolar (\(\beta\)-relaxation) and crystalline nature\(^{11-14}\). The variation of dielectric constant \((\varepsilon')\) and dielectric loss \((\varepsilon'')\) with temperature at different frequencies for pristine (called as KP) as well as irradiated (called as KI) samples have been illustrated in Figs 1(a)-(d) and Figs 2(a)-(c). The variation of \(\varepsilon'\) with temperature at different frequencies for pristine and Si-ion irradiated kapton-H samples have been illustrated in Figs 1(a)-(d) and Figs 2(a)-(c). The variation of \(\varepsilon''\) with temperature at frequency 1 kHz for (a) pristine and Si-ion irradiated kapton-H samples with a fluence of (b) \(2.3 \times 10^{13}\) ions/cm\(^2\); (b) Variation of dielectric constant with temperature at frequency 1 kHz for (a) pristine and Si-ion irradiated kapton-H samples with a fluence of (b) \(2.3 \times 10^{13}\) ions/cm\(^2\) and (c) \(1.38 \times 10^{13}\) ions/cm\(^2\).

3.1 Temperature region 1 (30-70 °C)

Low frequency dielectric behaviour - The low frequency [120 Hz and 1 kHz, Figs 1(a) and 1(b)] dielectric constant of irradiated sample in this region is higher than the pristine sample. Interestingly the high flux KI samples \((1.38 \times 10^{13}\) ions/cm\(^2\)) show \(\varepsilon'\) value nearly 90% more as compared to KP samples, which falls very rapidly with increasing temperature in this region. This temperature region mainly belongs to \(\gamma\)-relaxation (absorbed water). The water dependent relaxation behaviour, studied by many groups\(^{14-17}\), in kapton-H polypimide is quite complex and presumably results from several different competitive mechanisms involving various physical states of the absorbed water. Vanderschueren and Linkerns\(^{14}\) have shown that the low temperature relaxations are significantly affected by the presence of water. Shrinet et al.\(^{15}\) have shown an increase in water absorption capacity in kapton-H due to irradiation. The four carbonyl groups and the
oxygen of the ether linkage are the most probable sites where the water molecules can be bound\(^4\). At low frequency, with increasing water content an increase in \(\varepsilon'\) has been observed. This enhances the \(\gamma\)-relaxation causing an increase in \(\varepsilon'\) in KI samples. Rapid fall in \(\varepsilon'\) with temperature in this region is due to the confinement of \(\gamma\)-relaxation to a very short temperature region. The significance of \(\gamma\)-relaxation in KI samples is also observed in the form of maximum in dielectric loss \(\varepsilon''\)-T curve (Figs 2(b) and (c)) around 50 °C. The same is not present in pristine sample [Fig. 2(a)].

**High frequency dielectric behaviour** - In this temperature region the high frequency \(\varepsilon'\) for higher flux is less than \(\varepsilon'\) for lower flux [Figs 1(c) and (d)]. This is mainly due to reduced contribution of \(\gamma\)-relaxation at higher frequency and this reduction will be more in case of sample irradiated with higher flux. Further, to some extent the dipolar relaxation (\(\beta\)-relaxation) in this temperature region also contributes to \(\varepsilon'\). The loss in \(\beta\)-relaxation is more in high flux sample, as discussed later, will result in an overall decrease of \(\varepsilon'\) of high flux KI sample more than that of the low flux sample. A broad peak \(\varepsilon''\)-T curve at higher frequency around 50 °C indicates the presence of \(\beta\)-relaxation along with \(\gamma\)-relaxation with distributive relaxation times. We observe that the \(\varepsilon''\) values for higher flux sample are nearly 10 times more than the loss values for lower flux sample. This is in conformity with the fact that the water component increases with flux resulting in an increase in the dielectric loss.

### 3.2 Temperature region 2 (70-180 °C)

**Low frequency dielectric behaviour** - In this region the dielectric constant for high flux KI sample is less than that of KP sample, whereas KI sample with lesser flux shows higher \(\varepsilon'\) value than KP sample. Our TSDC results show that this region mainly belongs to dipolar relaxation and to some extent space charge effects due to shallow energy traps\(^7\). The dipolar nature (\(\beta\)-relaxation) in kapton-H mainly arises from the presence of carbonyl groups and the ether linkage\(^6\). The number of carbonyl groups contributing to \(\beta\)-relaxation turns out to be approximately \(7.5 \times 10^6\) for a thickness of 25 \(\mu\)m in 1 cm\(^2\) based on the estimation made by Shire et al\(^8\). The energy required to dissociate a carbonyl group is 6.63 eV (Ref. 20). Considering that nearly 20 MeV out of 50 MeV energy is utilized for demerization of carbonyl group, number of carbonyl groups decomposed with a fluence of \(1.38 \times 10^{13}\) and \(2.3 \times 10^{12}\) ions/cm\(^2\) is of the order of \(2.76 \times 10^9\) and \(4.6 \times 10^8\) respectively. Even if we consider that a fraction of this energy is utilized for actual decomposition, an effective number of carbonyl groups would be dissociated resulting in a significant decrease in the \(\varepsilon'\) in KI samples. Now, on the other hand, appearance of space charge relaxation (secondary relaxation) owing to the creation of shallow traps should result in an increase in \(\varepsilon'\). The new shallow energy traps...
arise due to the formation of free radicals by high-energy ion irradiation in the following way:

Since both the mechanisms (appearance of secondary relaxation and loss in β-relaxation) are operative in this temperature region an increase or decrease will be governed by the dominance of the respective mechanism. The presence of secondary relaxation is revealed in the form of maximum around 150 and 200 °C in lower and higher flux samples respectively in ε″-T curve (Fig 2b,c). These peaks can be compared with the ε″ peaks in pristine sample, which appears around 100 and 180 °C. Thus a shift in the peak position towards higher temperature is occurring due to irradiation. This is also confirmed through the TSDC behaviour of high energy KI samples where we observe maximum around 150 °C (Fig. 3). The TSDC peak in this region has been attributed to the existence of shallow energy traps.

High frequency dielectric behaviour - According to Kirkwood model\(^n\), if the molecular configuration and the intra and inter molecular interactions are not changed in the working temperature range, the dielectric constant is determined by the $1/T$ factor i.e. with increasing temperature dielectric constant should decrease. However, for polar polymers ε' should increase with increasing temperature. The dielectric constant at 100 kHz in the KP samples is observed to be almost temperature independent in this region [Fig 1(d)], indicating that the factors responsible for the decrease and increase are balancing each other. This balance between the two will be disturbed as a result of irradiation and the decrease or the increase in ε' will be governed by the mechanism dominating at that moment. An initial increase in ε' from 80-120 °C in the lower flux sample shows that the dipolar relaxation is not completely destroyed. Interestingly the ε" in this region is observed to be almost independent of temperature in contrast to the pristine sample.

3.3 Temperature region 3 (180-250 °C)

Low frequency dielectric behaviour - In the high temperature region, the low frequency ε' can be discussed mainly on three lines i.e. molecular movement of the interfacial polarization, large segmental group and the change in crystallinity. Interfacial polarization arises from the trapping/detrapping of charge carriers, under the influence of field, at the defect sites or at the interface of different phases in dielectric with different dielectric constant and conductivity\(^2\). Interfacial polarization being an important and dominating factor in multi-phase system is expected to play an important role in determining the low frequency ε' at high temperature. This relaxation should increase ε' with increasing temperature. The higher ε' in KI sample as compared to KP samples is due to the dominance of interfacial polarization and this increase in ε' will be enhanced by the space charge relaxation due to the movement of large segmental groups. In KI samples radiation induced damages result in a production of large number of defect sites as well as the creation of new phases with distributive relaxation time\(^1\). Damage to the configurational order due to irradiation has been discussed by Marletta et al\(^1\). The peak around 200 °C in the TSDC spectrum (Fig. 3) of KI sample also confirms the existence of interfacial polarization. However
the role played by the variation in the crystalline nature is to decrease the $\varepsilon'$ with increasing temperature. An increase in crystallinity in kapton-H polyimide with increasing temperature has been reported by Sacher. As the crystallinity increases fewer amorphous dipoles per unit volume are available to enter into the relaxation processes and the original relaxation in the amorphous phase is suppressed because its cooperative motion is obstructed by the appearance of crystalline phase. So in the high temperature region also we have two mechanisms which govern the $\varepsilon'$ in opposite mode. Space charge and the interfacial polarization try to increase the $\varepsilon'$ whereas as increase in crystallinity tries to decrease the $\varepsilon'$ with increasing temperature.

In pristine kapton-H sample the interfacial polarization does not dominate much and the decrease in $\varepsilon'$ [Fig. 1(a)] is due to increase in the crystallinity owing to the annealing like effect. A rise in $\varepsilon'$ at very high temperature (around 250 °C) is due to space charge relaxation. Since the high flux irradiated samples will be richer in interfacial polarization, an increasing trend in $\varepsilon'$ with temperature should be obvious. The presence of interfacial polarization is also evident from the dielectric loss peak [Fig 2(c), 1kHz frequency] around 240 °C which is not present in pristine sample [Fig 2(a)]. The dielectric loss data for 120 Hz could not be obtained due to instability and 1 KHz data are being treated for interfacial polarization at very high temperature.

High frequency dielectric behaviour - The high frequency $\varepsilon'$ values in this temperature region are to be determined by some secondary dipolar and space charge relaxations. The $\varepsilon''$-$T$ curves follow the same trend as in region 2. High temperature peak in $\varepsilon''$-$T$ curve [Fig. 2(b)] around 250 °C, which is nearly 30 °C above loss peak in pristine sample, confirms the presence of secondary relaxations responsible at high temperature. This is also supported by the TSDC peak around 250 °C (Fig. 3).

4 Conclusion

In kapton-H polyimide all the main relaxations i.e. $\gamma$, $\beta$ and $\alpha$-relaxations associated with absorbed water, dipolar and interfacial polarization respectively are affected due to ion irradiation. The nature of variation in dielectric constant/loss with temperature has been divided into three regions: (i) From 30-70 °C, an increase in $\varepsilon'$ of irradiated sample due to increase in $\gamma$-relaxation, resulting from increase in water absorption capacity by ion irradiation, (ii) From 70-180 °C $\varepsilon''$-$T$ curve is governed by dipolar ($\beta$-relaxation) and space charge relaxations due to shallow traps. A decrease in $\varepsilon'$ is due to a significant loss in carbonyl group in irradiated samples, whereas the formation of free radicals and space charges tend to increase the $\varepsilon'$, and (iii) Temperature region from 180-250 °C mainly pertains to interfacial polarization. The high energy ion irradiation results in the creation of new phases. This is responsible for increased interfacial polarization, causing an increase in $\varepsilon'$. On the other hand increase in crystallinity tends to decrease the $\varepsilon'$ and the balance between the two determines the ultimate variation.

Maximums in the $\varepsilon''$-$T$ curve around 50, 200 and 250 °C confirm the presence of various relaxations in the different temperature regions.

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