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ASSESSMENT OF THE NATURE OF DEPOLARIZATION CURRENT IN THERMALLY TREATED KAPTON POLYIMIDE

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Abstract

Pyrolysis of normally insulating aromatic polyimide is known to impart electrical conductivity to the polymer due to the formation of carbonized regions in an insulating matrix with a concomitant change in the polymer's structural arrangement. The wholly pyrolyzed polyimide is potentially useful for specific applications in certain types of semiconductor devices because of the polyimide's insulator/conductor transition which creates a barrier type conduction. Pyrolysis, however, degrades the required mechanical integrity of the polyimide for construction of such devices. In order to evaluate the fundamental aspects of barrier conduction by high voltage electron transfer from metal contact that can still produce measurable current in thermally treated non-pyrolyzed polyimide, the nature of depolarization in Kapton was assessed by the thermally stimulated depolarization current (TSDC) technique. The results show that thermal treatment of polyimide without pyrolysis and therefore without loss of mechanical integrity offers a viable means of steady electron conduction for semiconductor operation.

Keywords: barrier conduction, depolarization curves, detrapping energy, pyrolyzed polyimide, TSDC

Introduction

The best known polyimide, DuPont Kapton^R, has found a wide range of applications because of its high-temperature stability as well as its excellent mechanical and electrical properties [1]. The polymer is thermally stable at least up to 400°C in air and is electrically insulating under ambient conditions. When pyrolyzed under vacuum or in inert atmosphere, Kapton undergoes structural changes and becomes conducting, but it still contains insulating regions evidenced by an anomalous low frequency dielectric dispersion at the threshold between the insulating and conducting states [2]. The mechanism of conduction is thought be of the hopping or tunneling type [3–5]. Continuity of conduction is preserved under high voltage by voltage-induced interfacial polarization due to charge crowding between the conducting and insulating phases (Maxwell-Wagner effect [6, 7]). The functional mode of operation of metal/insula-

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tor/semiconductor (MIS) devices makes use of controlled conduction through the polymer insulator by electron transfer from the metal conductor. Similar applications have been considered for other semiconductor devices. For example, pyrolyzed polyimide has been suggested as a gate material for transistors [8] because of the polyimide's insulator/conductor transition. The drawback here is the loss of mechanical strength of the polyimide on pyrolysis. The need has risen for studying the fundamental aspects of barrier conduction that produces measurable current in thermally treated non-pyrolyzed polyimide. The method ideally suited for this is the measurement of thermally stimulated depolarization current (TSDC) from high voltage electron transfer to the polymer from metal contact and calculation of detrapping energy for current discharge with each thermal step. The aim is to assess the nature of depolarization resulting from changes in conduction in Kapton polyimide thermally treated at various below-pyrolysis temperatures prior to polarization.

Theoretical

The TSDC technique [9] is based on a polymer's ability to interact with a voltage field in an increasing thermal environment that causes dipolar and space-charge polarization in the polymer, generally under lower voltage than electron transfer polarization which requires high voltage. The current associated with these polarizations can be discharged by thermal stimulation. The overall process can be expressed in terms of time-dependent discharge current, $i(t)$:$i(t)=-\alpha(T)P(t)$, as the product of temperature-dependent relaxation frequency, $\alpha(T)$, and the time-dependent polarization, $P(t)$. At the lower end of the temperature spectrum, dipole orientation is mainly responsible for the charging process and at higher temperatures, polarization occurs due to injection of electrons from the electrodes to the polymer [10]. The controlling factors for the latter are (i) a high strength voltage field (ii) the dielectric nature of the polymer and (iii) the relative work function of the polymer and the electrodes. The electrons thus injected become trapped at the surface and below-surface levels in the polymer and act as charge carriers. These charge carriers are trapped at deeper levels first before being trapped at the surface. Current discharge follows a reverse order [11] i.e. from the surface first and then from the depth of the polymer structure because of the difference in the potential energy of trap sites. The shape and position of the depolarization peaks are influenced by this energy difference.

Experimental

2 mil (0.00508 cm) thick Kapton V polyimide samples (work function 4.36 eV) were heat treated at 200, 435 and 525°C in nitrogen atmosphere for 65 min. Only the sample heated at 525°C developed some dark patchy areas indicating a certain degree of carbonization in the sample. An untreated specimen along with the heat treated specimens were polarized individually in a pair of silver electrodes (work function 4.28 eV, total surface area 9.97 cm^2) at a heating rate of 0.083 $K\ s^{-1}$ in air and a volt-

age field of 500 KV cm^{-1}. The choice of electrodes assures maximum electron transfer from the electrodes to the polymer. The voltage was applied at 100°C and the test specimen was annealed under this voltage for 2 h at 200°C. The voltage was maintained over the entire cooling period back to ambient temperature when the voltage was removed. The instrumentation and experimental setup were the same as described before [12]. Current discharge was obtained by heating the sample at 0.083 K s^{-1} up to 295°C.

Results and discussions

Figure 1 shows the depolarization curve for the untreated sample which exhibits a wide distribution of relaxation times. Figures 2–4 are the depolarization curves obtained for the 200, 435 and 525°C treated samples. The rudimentary β- and α-peaks around 95 and 195°C respectively for the untreated sample are due to dipole and

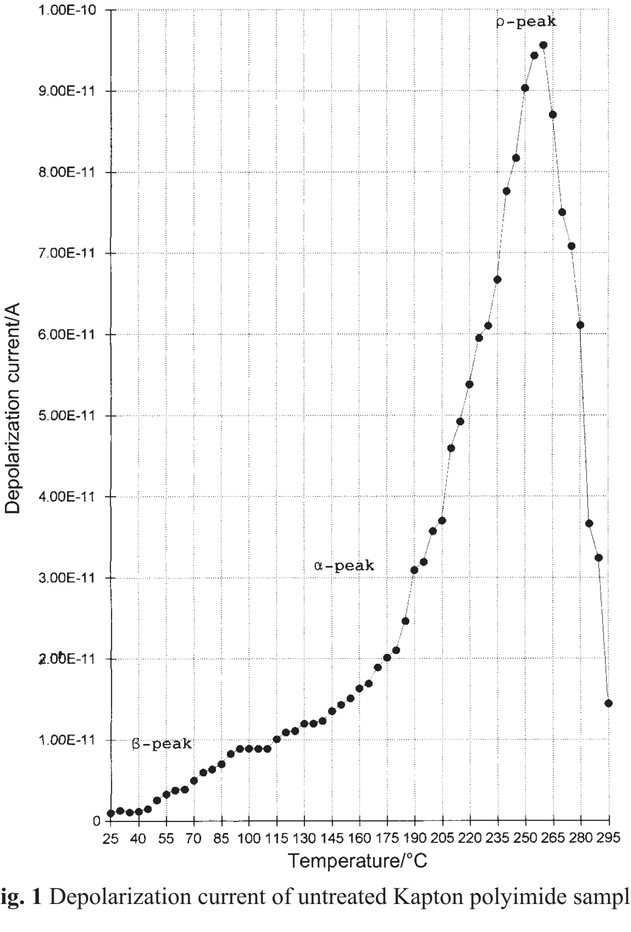

Fig. 1 Depolarization current of untreated Kapton polyimide sample

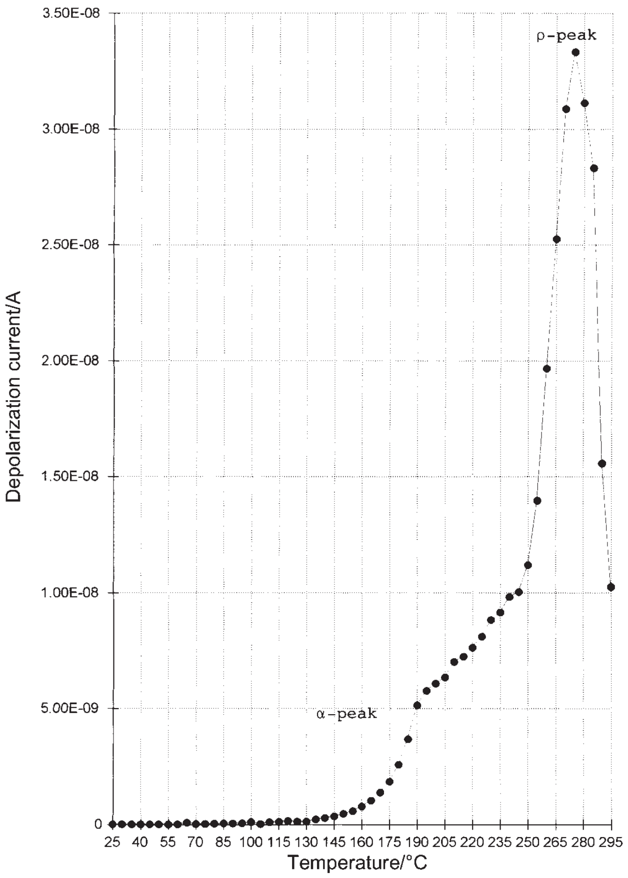

Fig. 2 Depolarization current of Kapton heat treated at 200°C

space-charge orientation. High voltage polarization is known to be unfavorable for their formation. The transitions are swamped by the very large ρ-peak due to the injected electrons. It is evident that significant changes occur in the heat treated samples. Notable among these are the absence of the β-peak and the diminution of the α-peak resulting from increased conductivity i.e. increased mobility of charge carriers. The ρ-peak onset is also found to shift to higher temperature with increasing pre-treatment temperature. It is known that the ρ-peak maximum is not a linear function of the strength of the applied voltage. However, increased conductivity is characterized by initial rapid depletion of current originating from internal charging prior to the onset of externally charged ρ-peak for all thermally treated samples.

Arrhenius activation energy values determined from the initial rise of the depolarization curves [13] were found to increase linearly with increasing pre-treatment temperature, as shown in Fig. 5. The shift to higher temperature for the ρ-peak onset is thus due to the progressively higher activation energy requirement for structural rearrangement and to preactivation of electron transport from the electrodes to the polymer. The latter is known to be a high activation energy process. Evidence of structural rearrangement has been found in pyrolyzed Kapton [2].

A relationship has been developed in this study for the energy gap between the polarized state and depolarization, corresponding to the energy of detrapping (ξ), which can be expressed in terms of relaxation times: $\xi=KTI_n(\tau_2/\tau_1)$ since successive relaxation times vary with temperature according to: $\tau_2=\tau_{1\ \mathrm{exp}}(\xi)/KT)$, where K – Boltzmann constant, T – absolute temperature, τ_1 – relaxation time at a given temperature and τ_2 – relaxation time at the next incremental temperature.

The polyimide structure contains many interactive sites that can exert binding forces on charged species which normally makes the polymer a poor conductor. Thermal treatment prior to polarization regulates the randomized stray charges inherent in the polymer and diminishes these interactive forces, thus increasing conductivity.

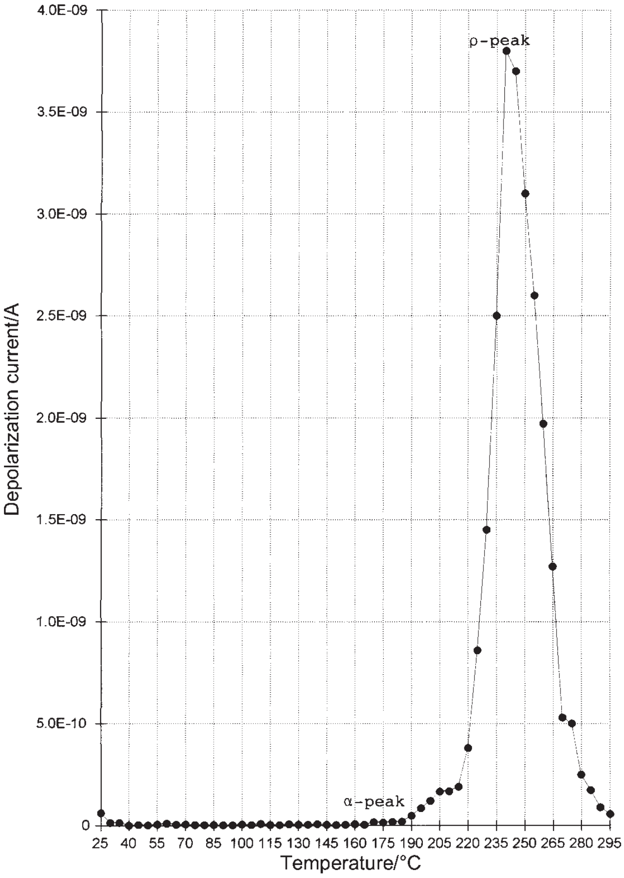

Fig. 3 Depolarization current of Kapton heat treated at 435°C

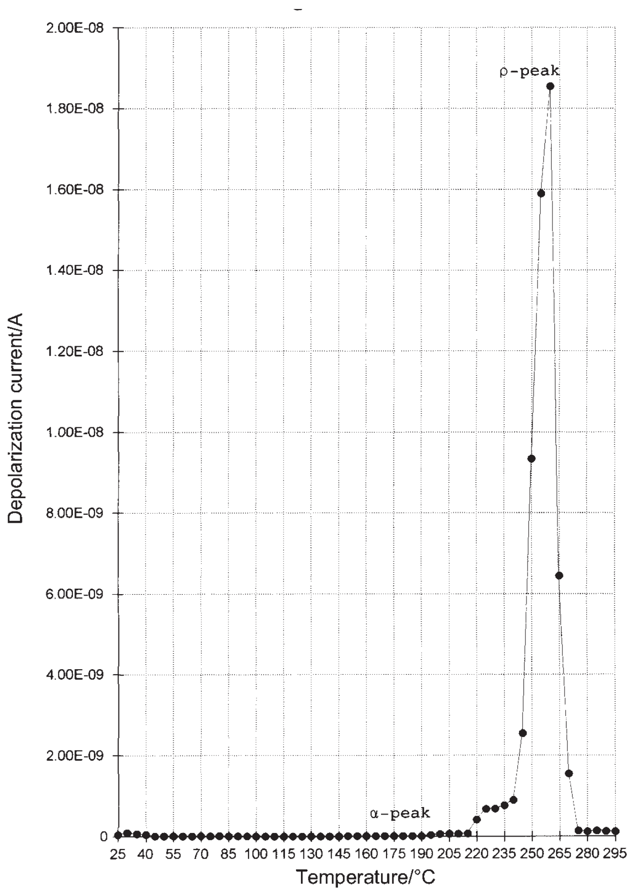

Fig. 4 Depolarization current of Kapton heat treated at 525°C

Plots of detrapping energy (ξ) *vs.* depolarization temperature for all samples are shown in Fig. 6. The successive detrapping energy is seen to change rapidly with temperature for the untreated sample whereas the changes are non-variant for the heat treated samples. It is also evident that at the lower pre-treatment temperatures of 200 and 435°C there is no difference in the level of detrapping energy but at the near-pyrolysis temperature of 525°C, the level of detrapping energy is significantly higher. Although depolarization originates from different trap levels, thermal treatment and structural rearrangement remove the energy differences between the trap sites. However, a threshold in energy level exists well below the pyrolysis temperature and increasingly symmetrical depolarization current can be obtained with increasing pre-treatment temperatures below pyrolysis. These results clearly indicate that thermal treatment of polyimide without pyrolysis and without loss of mechanical integrity offers a viable means of steady electron conduction for semiconductor operation.

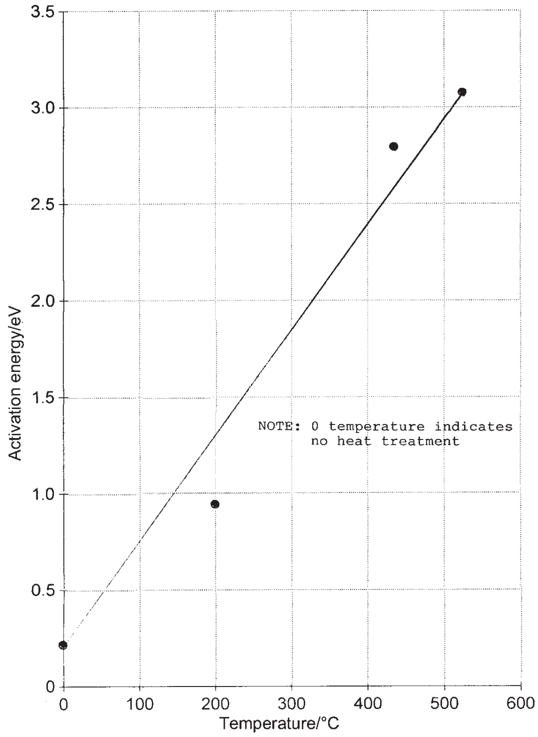

Fig. 5 Comparison of activation energies for untreated and treated samples

Conclusions

Pyrolyzed polyimide is known to be capable of electrical barrier conduction due to formation of conducting regions in an otherwise insulating matrix. This property is useful in the operation of certain types of semiconductor devices. However, the structural transformation produced by pyrolysis also result in loss of the required mechanical integrity of the polymer. The nature of the conduction current in Kapton^R polyimide heat treated at various below-pyrolysis temperatures was assessed, using high voltage electronic polarization of the polymer in contact with silver electrodes and subsequent thermal discharge. The discharge current originating from electron transfer polarization showed the effects of increased conduction and preactivation for the heat treated samples in terms of increasing peak symmetry and shift to increasingly higher onset temperature respectively with increase in pre-treatment temperature. Heat treatment was found to remove the differences in detrapping energy from different trap sites but also increased the level of detrapping energy for the sample treated at near-pyrolysis temperature. These results clearly indicate that thermal treatment of polyimide without pyrolysis and without loss of mechanical integrity offers a viable means of steady electron conduction for semiconductor operation.

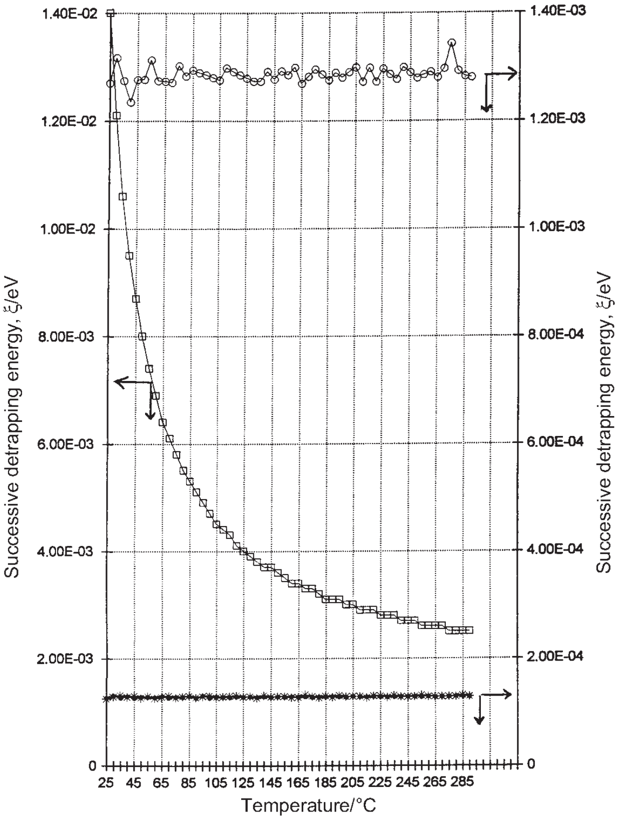

Fig. 6 Successive detrapping energy *vs.* depolarization temperature for Kapton samples heat treated at various temperatures prior to polarization

The consequence of voltage pile-up leading localized increase in current density as a result of barrier conduction in Kapton jacketing of airplane wiring causing possible fire, as recently reported from accident investigations, could be an area of future experimental study.

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