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Surface conduction behaviour of 100 Mev Si ion irradiated kapton-H polyimide

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The surface conduction behaviour of kapton-H polyimide irradiated with 100 MeV Si^+ ion (Fluences 2.3×10^{11}, 2.3×10^{12} and 1.3×10^{13} ions/cm^2) has been investigated in the temperature range 21 to 150°C. The current-voltage (I-V) characteristics in the low field region i.e., below 10 kV/cm show ohmic behaviour whereas non-linearity occurs in the high field region. The non-linear region is temperature dependent. The nature of I-V characteristics of pristine kapton-H samples doesn't differ much from the irradiated samples suggesting that the surface charge conduction mechanisms are not much affected due to irradiation. The ionic jump distance estimations (3–18 Å) supports to ionic conduction process below 110°C. The Poole-Frenkel and Schottky coefficient estimations show that Poole-Frenkel and Schottky conduction mechanisms are operative at moderate and low temperatures, respectively. The observed change in surface resistivity (ρ) in the irradiated samples has been associated to the increase in delocalized π-electrons and cross-linking.

1. Introduction

The aromatic polyimide poly (4-4′ oxydiphenylene pyromellitimide), commercially known as kapton-H, is well known for its excellent chemical, mechanical and electrical properties over the wide range of temperature [1–3]. The high-energy heavy ion irradiation effects on this polymer have drawn considerable attention in recent times owing to its possible application in the field of microelectronic, spacecraft, nuclear and high voltage accelerator technology etc. [4, 5]. The field induced thermally stimulated current (FITSC) investigations and the other dielectric studies made over irradiated kapton-H polyimide reveals a significant morphological changes viz. decomposition of carbonyl groups, an increase in water absorbtivity and cross linking of imide groups, in this polymer due to high energy heavy ion irradiation [6, 7]. In addition to the dielectric relaxation investigations the other important aspect of irradiation of kapton-H polyimide is its electrical conduction behaviour which largely gets affected. An increase in conductivity of kapton-H polyimide of several order of magnitudes due to irradiation has been reported by many groups [1, 8] but an exact mechanism is yet to be established for this observed change in conductivity. In the present paper, we report a detailed experimental study of the surface conductivity of kapton-H polyimide irradiated by 100 MeV Si ion.

2. Experimental

The investigations reported here were performed on a 25 μm thick kapton-H polyimide film (Du Pont, USA). The kapton-H samples were irradiated with 100 MeV Si ion (fluences 2.3×10^{11}, 2.3×10^{12} and 1.3×10^{13} ions/cm^2) using PELLETRON facility of Nuclear Science Center, New Delhi. Surface conductivity measurements for pristine as well as irradiated samples were carried out employing the four-point probe technique from 21 to 150°C. The four-point probe arrangement comprises of four individually spring-loaded probes coated with Zn at the tips. The probes are collinear and equally spaced. The Zn coating and individual spring ensure good electrical contacts with the sample. The probes were mounted in a teflon bush which ensure a good electrical insulation between the probes. A teflon spacer near the tips is also provided to keep the probes at equal distance. Sample holder with four probes was kept in a temperature-controlled furnace. Current through the specimen was monitored using a Keithley electrometer (model 610C).

3. Results and discussion

The surface conduction behaviour of pristine and irradiated kapton-H samples at different temperatures in the form of log I-V curves have been depicted in Fig. 1a–d. The currents are transient free. The general nature of these curves is similar for both pristine as well as irradiated samples. These curves show an ohmic behaviour in the field region below 10 kV/cm and on the other hand a deviation from the ohmic behaviour above this field is observed and non-linearity increases with increasing field. These results are being consistent with

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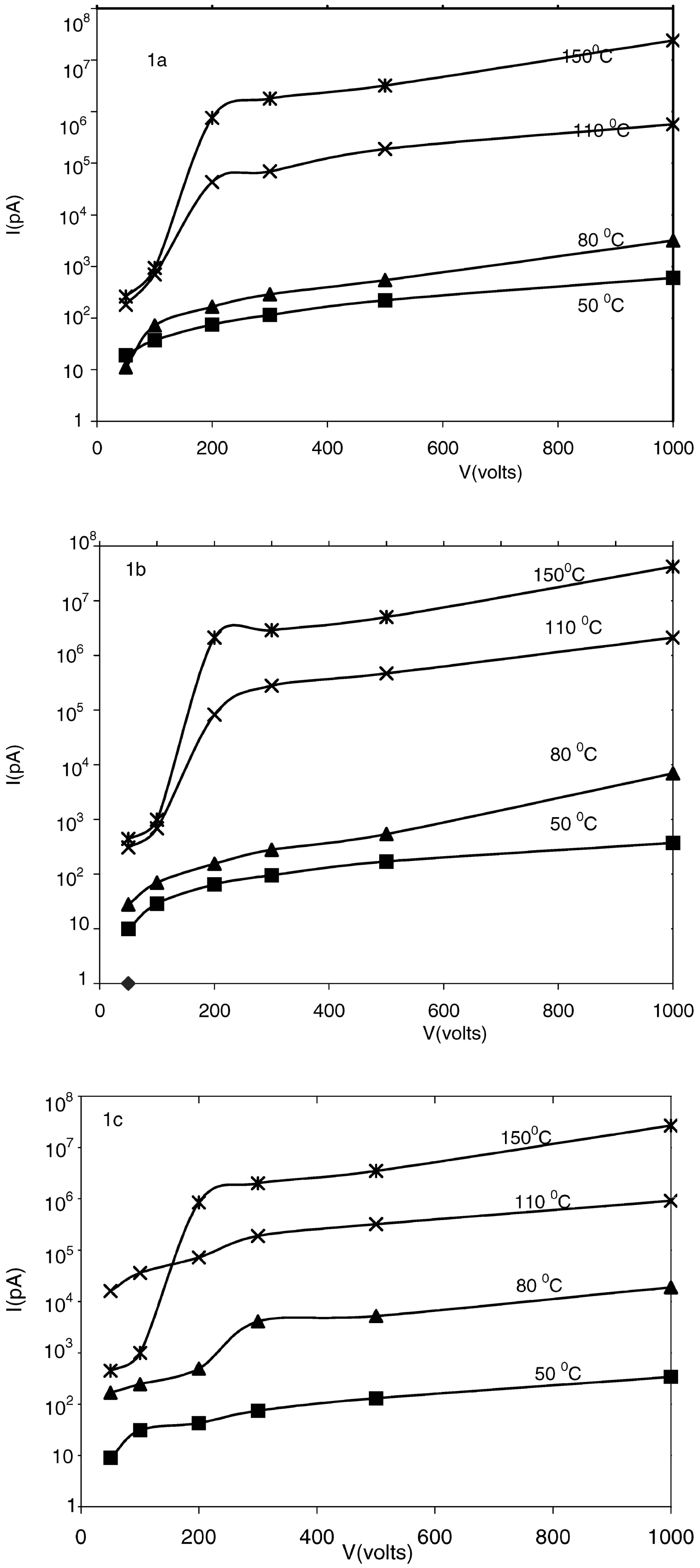

Figure 1 Surface conduction behaviour (log$I$-V plots) at various temperatures for (a) Pristine, (b) 2.3×10^{11} ions/cm^2, (c) 2.3×10^{12} ions/cm^2, and (d) 1.3×10^{13} ions/cm^2 irradiated kapton-H samples. (*Continued*)

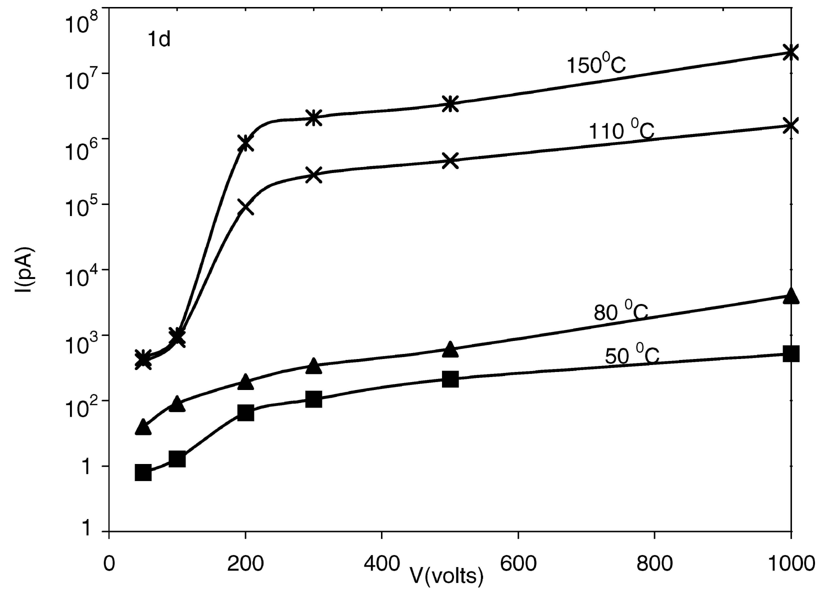

Figure 1 (*Continued*).

TABLE I Ionic jump distance 'a' obtained from the log I-E curves for pristine and irradiated kapton-H samples with different fluences

	$a \pm 0.5$ Å			
	Fluence			
T (°C)	Pristine	2.3×10^{11} ions/cm^2	2.3×10^{12} ions/cm^2	1.3×10^{13} ions/cm^2
21	4.5	3.9	3.0	5.1
50	4.4	4.4	4.4	5.6
80	7.2	8.0	7.2	6.6
110	11.8	13.7	13.1	12.9
150	18.9	19.2	18.1	18.1

those observed by Sacher *et al.* and Sawa *et al.* [9, 10]. However in their case the non linearity occurs at much higher field (above 100 kV/cm), which may not be surprising as their conduction experiments were performed on two side metallized samples where as in the present case the measurements have been made only on the surface. In polymers the charge transport mechanism, in addition to the ohmic conduction, is also governed by other mechanisms viz. ionic hopping, tunneling, Schottky and Poole-Frenkel etc. [9–11]. In kapton-H polyimide the non-linear I-V characteristics can be examined in the light of above mentioned charge transport mechanisms. The current I for the ionic hopping conduction is given by

$$I = 2.S.q.m.a.\nu.\ \exp(-U/kT)\ \sinh(qEa/2kT) \tag{1}$$

where q is the charge of ion, m is the ionic concentration, a is the ionic jump distance, U is the barrier height, k is the Boltzmann constant, ν is the frequency of attempt for an electron/ion to escape from the trap, T is the absolute temperature and S is the effective electrode area.

In the high electric field region ($qEa \gg 2kT$), Equation 1 can be reduced to

$$I = I_0\ \exp(qEa/2kT) \tag{2}$$

where $I_0 = 2.S.q.m.a.\nu.\ \exp(-U/kT)$.

The slope of the straight-line log I versus E (where $qEa \gg 2kT$) gives the ionic jump distance 'a'. The jump distance 'a' estimated for pristine and irradiated samples, from the slope of these curves are given in Table I. The 'a' values don't much differ in pristine and irradiated samples. The ionic jump distance for pristine kapton-H polyimide has also been reported by Sawa *et al.* [10] and Hanscomb *et al.* [12]. While the Hanscomb data, for 'a' (measured in temperature range 150–250°C) are almost independent of temperature, a moderate dependence of 'a' on temperature (measured in temperature range 70–180°C) have been observed by Sawa *et al.* Our own earlier findings also show a strong dependence of 'a' on temperature [13]. The temperature variation of 'a' in some other organic polymers has also been reported but no one has offered the exact mechanism for this. The major difference between the present data and the all other earlier reported data [10–13] is the magnitude of 'a'. The average 'a' values reported for kapton-H polyimide by Sessler [11], Hanscomb [12], Sawa [10] and the authors [13] lie between 70–75, 50–60, 80–115 and 43–225 Å respectively. Such high value of 'a' seems to militate against ionic hopping as an operating conduction mechanism. Interestingly in the present study the 'a' values particularly below 80°C are within the range of few Å, implying the possibility of surface conduction due to ionic hopping.

The fit of the present results to other charge transport processes mainly Schottky and Poole-Frenkel type of conduction mechanisms can also be examined. The current density for these processes are expressed respectively as

$$I = AT^2\ \exp[(\beta_s E^{1/2} - \phi)/kT] \tag{3}$$

and

$$I = BE^{1/2}\ \exp[(\beta_f E^{1/2} - \phi)/kT] \qquad (4)$$

where A and B are constant, E is the applied electric field, ϕ is the effective work function, β_s and β_f are the Schottky and Poole-Frenkel coefficients respectively given as

$$\beta_s = (e^3/4\pi K\varepsilon_0)^{1/2} \quad \text{and} \qquad (5)$$
$$\beta_f = 2\beta_s$$

where e is the electronic charge, ε_0 is the vacuum permittivity and K is the high frequency dielectric constant.

The Schottky mechanism involves the field assisted thermionic emission of charges from electrodes into the samples (resulting in a field dependent lowering of potential barrier) where as in the Poole-Frenkel effect, the current is considered to be due to field assisted thermal excitation of electrons from traps into conduction band. To study these mechanisms the data is replotted in form of log $I - E^{1/2}$, known as Schottky plots. The slope of these curves will give the experimental values of β (β_{exp}). The theoretical values of β (β_{th}) have been obtained by using Equation 5. The value of K for pristine and irradiated samples has been measured using precision LCR meter. Table II represents the β_{th} and β_{exp} values for pristine and irradiated kapton-H samples at different temperature. In the low temperature region i.e., below 80°C, the β_{exp} values are nearly equal to β_{th} values for the pristine as well as irradiated samples. This suggests that there is a definite possibility of Schottky type of conduction in the low temperature region. At 110°C, β_{exp} values are approximately twice the β_{th} values suggesting the occurrence of a Poole-Frenkel type conduction mechanism at moderate temperature. At 150°C there is a large deviation between the β_{exp} and β_{th} values discarding any possibility of Schottky or Poole-Frenkel type mechanism at higher temperatures. Many other groups [10–12] have also made a similar observation for pristine kapton-H. Though in the present case the high temperature surface conduction behaviour (for pristine as well as irradiated samples) is not associated with Schottky or Poole-Frenkel type mechanism, the same is not the case in irradiated two side metallized kapton-H samples. Our earlier studies [13] shows that the Poole-Frenkel may be the possible mechanism in irradiated kapton-H samples at higher temperatures. However this is not surprising considering the fact that the Poole-Frenkel mechanism which involves the detrapping of charge carriers would be prominent when the conduction measurements are carried out between two sided metallized system as compared to surface measurement. The identical nature of Schottky coefficients for pristine and irradiated samples shows that the neither Schottky nor Poole-Frenkel mechanisms are much affected by high-energy ion irradiation.

TABLE II The value of β_{exp} (±0.05) and β_{th} for the pristine and irradiated kapton-H samples

Fluence (ions/cm^2)	β(Jm$^{1/2}$V$^{-1/2}$) $\times 10^{-24}$	T (°C) 21	50	80	110	150
Pristine	β_{th}	3.45	3.03	5.01	8.56	13.13
	β_{exp}	3.58	3.66	3.78	3.80	3.72
2.3 x 10^{11}	β_{th}	2.70	3.03	5.16	5.60	13.65
	β_{exp}	3.50	3.73	3.83	3.83	3.85
2.3 x 10^{12}	β_{th}	3.15	2.98	4.96	4.28	13.25
	β_{exp}	3.6	3.69	3.74	3.83	3.87
1.3 x 10^{13}	β_{th}	3.52	3.83	4.33	9.14	12.95
	β_{exp}	3.72	3.87	3.97	4.03	4.38

The temperature dependence of conduction behaviour of kapton-H samples is illustrated in Fig. 2 in the form of log I vs. $1/T$ plots. These plots consist of two straight lines with a break point around 50°C. The activation energy calculated from the slopes of these straight lines in the high temperature region is of the order of 1.5 eV. The slope is almost negligible in the low temperature region and the corresponding low activation of conduction (~0.02 eV) can be associated to the shallow energy trap centers. The change in the slope of

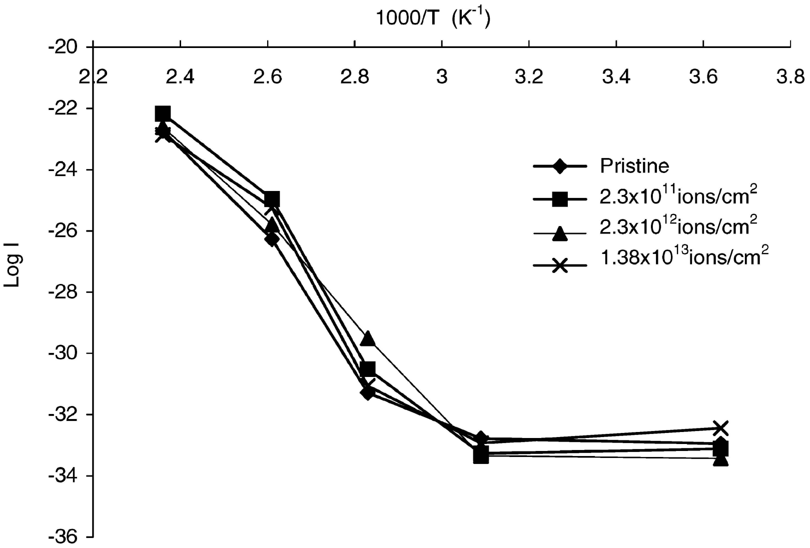

Figure 2 The log I-$1/T$ curves for pristine and irradiated with various fluences kapton-H samples (biasing voltage: 500 V).

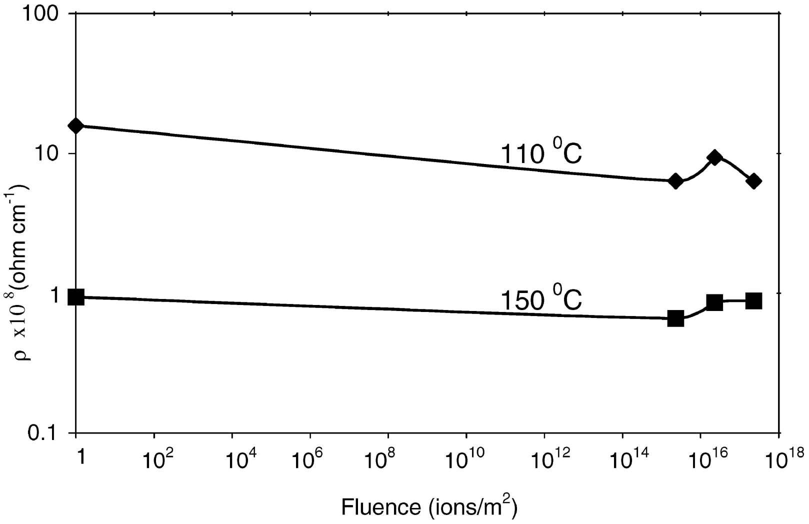

Figure 3 Surface resistivity (ρ) as a function of fluence.

ln$I$ vs. $1/T$ curves indicates the presence of more than one type of trapping levels. Although there is not much difference between the activation energy of pristine and irradiated kapton-H samples but the general trend with increase in fluence is the decrease in activation energy of conduction.

So far our above-mentioned conclusions don't show any significant effect on the nature of charge transport mechanism due to high-energy ion irradiation. However the charge carrier density gets affected, as evident in Fig. 3 (ρ vs. fluence curve). We observe an overall decrease in the resistivity, as compared to pristine kapton-H, in all the samples irradiated at different fluence. However there is a relative increase in the resistivity in samples irradiated with 2.3×10^{12} ions/cm^2 as compared to 2.3×10^{11} and 1.38×10^{13} ions/cm^2. Many groups [1, 14, 15] have discussed high-energy heavy ion irradiation effects in kapton-H polyimide. The high-energy heavy ion irradiation mainly induces chain scission, liberation of small gaseous molecules, production of free radicals and cross-linking etc. The decrease in resistivity is mainly due to an increase in delocalized π-electrons from the unsaturated bonds and an increase of charge mobility enhanced by the chain cross-linking [1]. The authors have reported that the decomposition of carbonyl groups increases shallow/deep energy trap centers density. The effect is more pronounced at high fluence. The increase in trap density would result in the depletion of the charge carriers, which may cause an increase in resistivity at high fluence (Fig. 3). However at very high fluence the factors responsible for decrease in resistivity may again dominate.

4. Conclusions

The surface conduction behaviour of 100 MeV Si$^+$ ion irradiated kapton-H polyimide film has been investigated in the temperature range 21 to 150°C. The following conclusions can be drawn:

1. The nature of I-V characteristics is not much affected due to ion-irradiation.
2. The ionic jump distance estimations confirms the ionic hopping as a charge transport mechanism below 110°C.
3. The Schottky coefficient estimations show that the Poole-Frenkel and Schottky conduction mechanism are operative at moderate and low temperature regions, respectively.
4. Change in the slope of log I vs. $1/T$ curve indicates the presence of more than one type of charge trapping centers.
5. The overall decrease in the resistivity is observed due to irradiation. This decrease in resistivity is mainly attributed to an increase in delocalized π-electrons from the unsaturated bonds and the enhanced chain cross-linking which increases the mobility of charge carriers.

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References

1. EAL H. LEE, in "Polyimide: Fundamentals and Applications," edited by Malay K. Ghosh and K. L. Mittal (Plenum Press, New York, 1996) p. 471.
2. M. I. BESSONOV and N. P. KUZNETSOV, in "Polyimides: Synthesis, Characterization and Applications," edited by K. L. Mittal (Press, New York, 1984) p. 385.
3. J. A. BRYDSON, in "Plastic Materials" (Butterworth Heinmann, 1995) p. 499.
4. W. L. BROWN, *Radiat. Effects* **98** (1986) 115.
5. J. DAVENAS and G. BIOYEUX, *Adv. Mater.* **2** (1990) 521.
6. M. GARG, S. KUMAR and J. K. QUAMARA, *Nucl. Instr. Meth. Phys. Res.* B**179** (2001) 83.
7. *Idem., Indian J. Pure Appl. Phys.* **39** (2001) 455.
8. T. HIOKI, S. NODA, M. SUGIURA, M. KAKENO, K. YAMADA and J. KAWAMOTO, *Appl. Phys. Lett.* **43** (1983) 30.

9. E. SACHER, *IEEE Trans. Electri. Insul.* **EI-14** (1979) 85.
10. G. SAWA, S. NAKAMURA, K. IIDA and M. IEDA, *Jap. J. Appl. Phys.* **19**(3) (1980) 45.
11. G. M. SESSLER, B. HOHN and D. Y. YOON, *J Appl. Phys.* **60**(1) (1986) 318.
12. J. R. HANSCOMB and J. H. CALDERWOOD, *J Phys. D: Appl. Phys.* **6** (1973) 1093.
13. M. GARG and J. K. QUAMARA, *Nucl. Instr. Meth. Phys. Res.* B **179** (2001) 389.
14. G. MARLETTA, S. PIGNATARO and C. OLIVERI, *ibid.* B **39** (1989) 792.
15. K. YOSHIDA and M. IWAKI, *ibid.* B**19/20** (2001) 878.

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