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Use of Polythiophene as a Temperature Sensor

¹D. S. KELKAR, ^{*1}A. B. CHOURASIA, ²V. BALASUBRMANIAN

¹ Department of Physics, Institute of Science, Civil Lines, Nagpur – 440 001, India

² Department of Physics, Siddharth College, Mumbai - 400 001, India

*Tel.: +91 9881251338, fax +91 253 2574682

*E-mail: abchourasiansk@rediffmail.com

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Abstract: The polythiophene was chemically synthesized using 2,5-dibromothiophene by debromination with magnesium, catalyzed by nickel chloride. The synthesized polymer was undoped using liquid ammonia and then doped again using 5 % aqueous FeCl₃ for 2.5 and 5 hour duration. Characterization of undoped as well as doped samples using elemental analysis has been carried out. Elemental analysis shows that concentration of Fe⁺ ions increases as the duration of doping increases. All samples were pressed into pellets of about 1cm in diameter and were coated, on both sides, by aluminum using vacuum deposition technique. I – V measurements of undoped and FeCl₃ doped samples, after coating have been carried out using two probe method. I – V measurements were carried out by applying +ve potential on one side from 0 V to 1V in steps of 0.1V and then from 1 V to 10 V in steps of 1 V. The measurements were again carried out after interchanging the polarity of the applied voltage. I – V measurements were also carried out at room temperature as well as at various temperatures in the range from 301 K to 331 K in steps of 5K. These characteristics are just similar to the characteristics of conventional p – n junction diode. The effect of doping is to reduce the knee voltage. I – V characteristics of undoped polythiophene after interchanging the polarity (like reverse bias condition in p–n junction diode) at various temperature are plotted. From the graphs it is observed that the magnitude of current increases as temperature is increased. A straight line graph of temperature versus current for an applied voltage of 3 V indicates that undoped polythiophene can be used as temperature sensor in the temperature range from 301 K to 331 K.

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Keywords: Polythiophene, Conducting polymer, p-n junction diode, Temperature sensor.

1. Introduction

During the past 20 years, a lot of interest has been focused on unsaturated π - conjugated polymers; primarily due to its ability to be doped so as to obtain an electrical conductivity in the semiconducting to metal range. The use of semiconducting conjugated polymers as a material in electronic and microelectronic devices is a new and rapidly growing research field. As a result research on applications of semiconducting polymers in device fabrication has received a considerable attention in recent years.

Several groups have used poly (3-octylthiophene) [1], poly (3 - hexylthiophene) [2 - 4] and polythiophene [5] to fabricate Schottky diode, poly (3 - hexylthiophene) [6] to fabricate tunnel diode and field effect transistor [7].

It has also been reported by J. M. Maud [8] that a thin film of polyoctylthiophene as well as sexithiophene, an oligomer containing six thiophene rings, when deposited by aluminum form a complex (aluminum sulfide) with sulphur of thiophene. Hence it was thought interesting to study I - V characteristics of polythiophene pellet after coating it with aluminum on both sides.

In the present work polythiophene was chemically synthesized, undoped and re-doped with FeCl_3 for 2.5 hr. and 5 hr. duration. I - V measurements of all samples, after coating the pellets by aluminum on both sides, were carried out. Performance of undoped polythiophene sample as a temperature sensor has also been tested.

2. Experimental Method

2.1. Sample Preparation

The polythiophene was chemically prepared from 2,5- dibromothiophene (Aldrich) by debromination with magnesium, catalyzed by nickel chloride [9].

For synthesis 2,5- dibromothiophene is treated with magnesium (Mg) in dry tetrahydrofuran (THF) in the presence of nickel chloride. The Mg reacts with either bromide to form either 2-bromo-5-magnesiobromothiophene or 2-magnesiobromo-5-bromothiophene which is self coupled with the nickel catalyst to form a thiophene dimer carrying an MgBr at one end and a Br at the other. This condensation is propagated and eventually polythiophene is formed as show in Fig. 1.

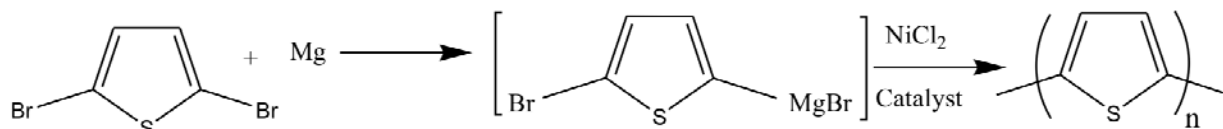


Fig. 1. Chemical Synthesis of polythiophene.

The synthesized polymer was undoped using liquid ammonia and then doped again using 5 % aqueous FeCl_3 . Polythiophene powder was immersed in aqueous FeCl_3 for different (2.5 hr., 5 hr.) durations with constant stirring to obtain uniform doping. The duration of immersion of polythiophene decides the concentration of dopant. Thus polythiophene was doped with different dopant (FeCl_3) concentration. All the samples were pressed into pellets of about 1cm in diameter and of various thicknesses. All the pellets were coated, on both sides, by aluminum using vacuum deposition technique.

2.2. Characterization

Elemental analysis of C, H, S elements was carried out by Thermo finnigan, Italy FLASH EA 1112 series and the analysis for Fe was done by Jobin Yvon, France JY Ultima–2 model.

2.3. I – V Measurements

I – V characteristic measurements were studied using two probe method. The sample was sandwiched between two electrodes as shown in Fig. 2.

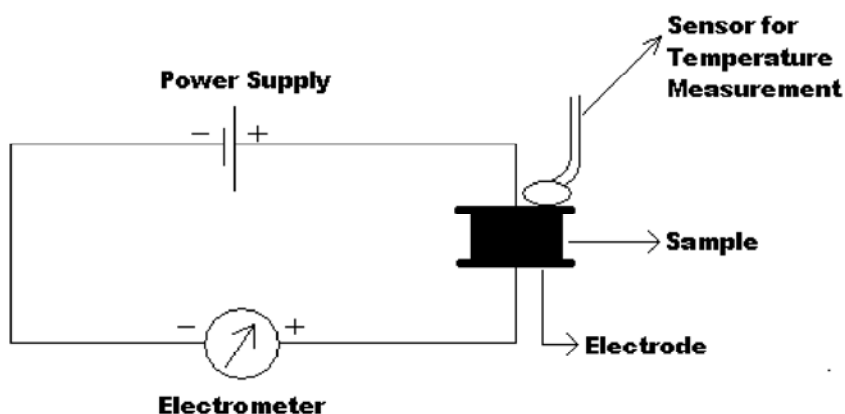


Fig. 2. I-V measurement setup.

The potential was applied using Aplab power supply (model no. L3201). The applied potential across the pellet was measured using Escort digital multimeter (EDM168A). Current measurements were carried out using Keithley electrometer (model no. 6514). For measurement and control of temperature Sonit relay (SE – 2120- RTD) along with temperature sensor PT100 was used. I – V measurements were carried out by applying +ve potential on one side from 0 V to 1V in steps of 0.1V and then from 1 V to 10 V in steps of 1 V. The measurements were again carried out after interchanging the polarity of the applied voltage. I – V measurements were also carried out at room temperature as well as at various temperatures in the range from 301K to 331 K in steps of 5K.

3. Results and Discussion

Elemental analysis: The various elements obtained through analysis are tabulated in Table 1.

Table 1. Percentage of C, H, S and Fe elements.

Sample	C %	H %	S %	Fe ($\mu\text{g/gm}$)
Undoped PT	51.16	2.41	43.03	3.70
2.5 Hr. FeCl ₃ doped PT	50.81	2.39	28.08	537.4
5 Hr. FeCl ₃ doped PT	51.28	2.44	26.28	2348.3

From the Table 1, it is observed that, as the duration of doping increases, Fe contents are increasing while S contents are decreasing.

I–V characteristics of all samples are obtained as shown in Fig. 3. These characteristics are just similar to the characteristics of conventional p – n junction diode which is shown in Fig. 4. The forward knee voltages observed from Fig. 3 for undoped polythiophene, 2.5 hr. and 5 hr. FeCl₃ doped polythiophene are 4.2 V, 3.4 V and 2.5 V respectively.

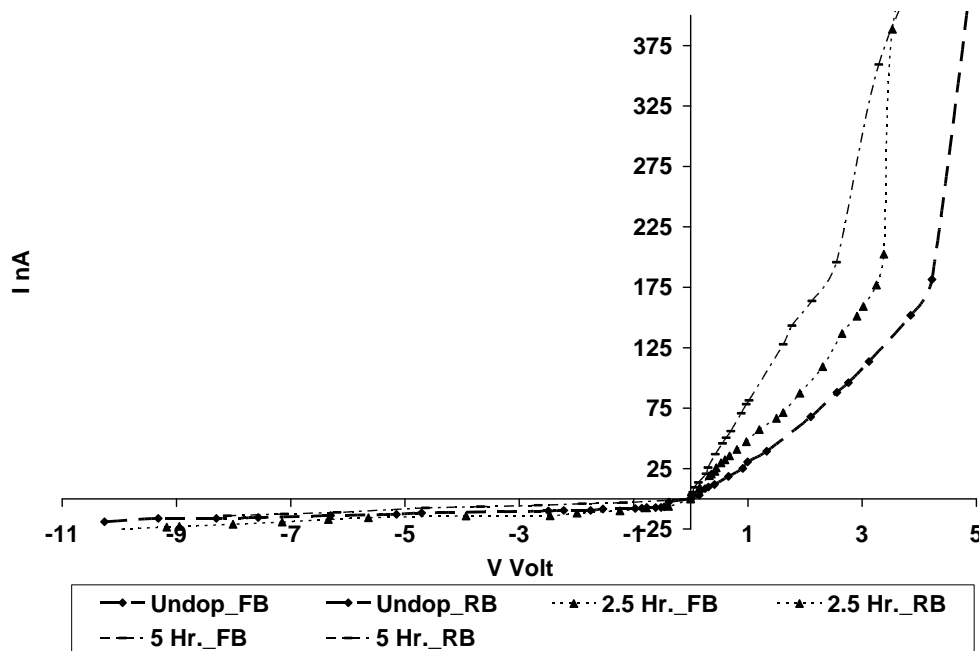


Fig. 3. I-V plots of undoped , 2.5 hr. and 5 hr. FeCl₃ doped polythiophene.

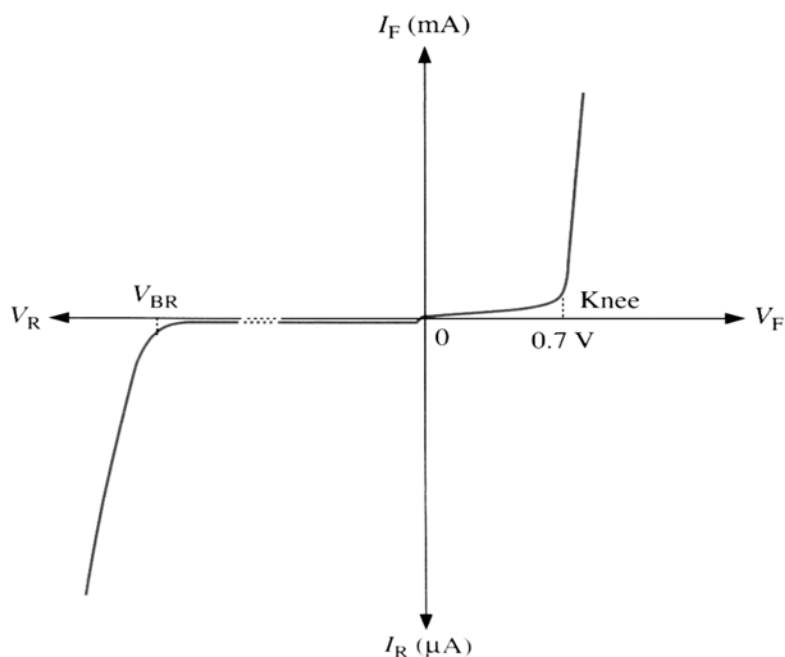


Fig. 4. Typical characteristics of conventional p-n junction diode for silicon (Si).

I – V characteristics of undoped polythiophene before and after interchanging the polarity of applied voltages at 301 K, 316 K, 331 K are obtained as shown in Fig. 5. These characteristics are similar to the conventional p-n junction diode at different temperatures as shown in Fig. 6.

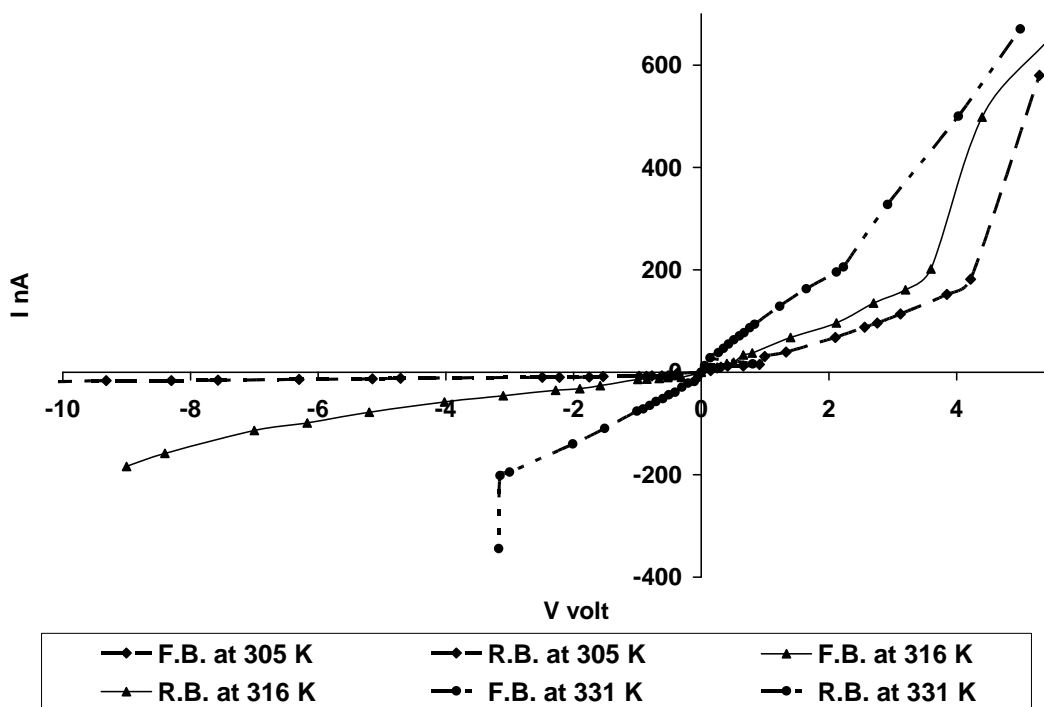


Fig. 5. I-V plots of undoped polythiophene at 305 K, 316 K and 331 K.

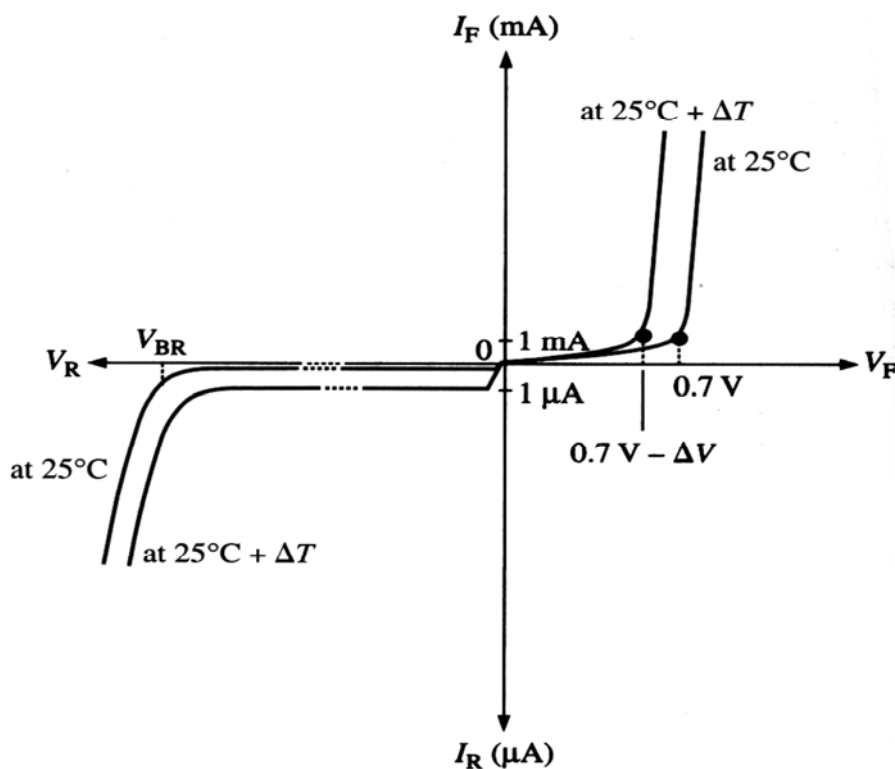


Fig. 6. Typical characteristics of conventional p-n junction diode for silicon at different temperatures.

When the pellets are coated with aluminum on both sides, aluminum forms complex (aluminum sulfide) with sulfur atom of the thiophene and transfers negative charge from aluminum to sulfur. It has been reported that during formation of aluminum sulfide (Al_2S_3), aluminum of aluminum sulfide takes central position in tetrahedral structure which is embedded in the hexagonally closed-packed arrangement of the sulfide anions. The aluminum atom shares its single electron and forms a bond with sulfur atoms. With a rise in temperature the above structure starts getting disturbed and the central position of aluminum becomes randomized to give “defect wurtzite” structure. At still higher temperature this structure gets converted into γ - Al_2S_3 form with a structure similar to γ - Al_2O_3 . This indicates that structure of aluminum sulfide can be changed.

In the present case +ve and -ve terminals are connected to pellet i.e. Al_2S_3 . From observations it is quite likely that structure of Al_2S_3 (formed at aluminum /polythiophene interface) after application of either +ve or -ve potential changes and it takes up a form suitable for electron attraction and electron repulsion. Once this structural change has taken place due to +ve and -ve potentials they become permanent and irreversible. The side of aluminum coated fresh pellet when connected to -ve potential for the first time, always behaves as n-type semiconductor and the other side of the pellet behaves like a p-type semiconductor. The polythiophene units between the surface coatings transport the respective charge carriers through them and thus overall the pellet shows behavior similar to p-n junction diode.

The effect of doping is to increase the number of charge carriers. As is evident from the results of elemental analysis (Table 1), as the duration of doping increases, the Fe^+ contents are increasing. Further more from I – V plots (Fig. 3) it is observed that as the duration of doping increases the knee voltage decreases. This is due to the fact that more charge carriers are available due to doping and therefore at lower forward biasing voltage large amount of current flows.

3.1. Temperature Sensor

When the potential is applied to all polythiophene pellets in one direction it shows I – V similar to the I – V of conventional p – n junction diode in forward bias condition and when the potential terminals are interchanged, the behavior is very much similar to that of the conventional p – n junction diode in reverse bias conditions. It was therefore thought to test if undoped polythiophene pellet can be used as a temperature sensor. I – V characteristics of undoped polythiophene after interchanging the polarity (like reverse bias condition in p – n junction diode) at various temperatures is shown in Fig. 7. From the graphs it is observed that the magnitude of current increases as temperature is increased.

The graph of temperature versus current for an applied potential of 3 V is shown in Fig. 8. A straight line graph indicates that current increases in the same proportion as temperature increases and hence can be used as temperature sensor. It has been observed that if the temperature is increased above 331 K, current slightly reduces indicating that the device is useful as a temperature sensor within the range from 301 K to 331 K only. Linearity and repeatability of the sensor within the specified range is a basic requirement of any sensor. This condition is satisfied by undoped polythiophene sample. Repeatedly experiments were carried out to test the repeatability of the sensor and same behavior is observed.

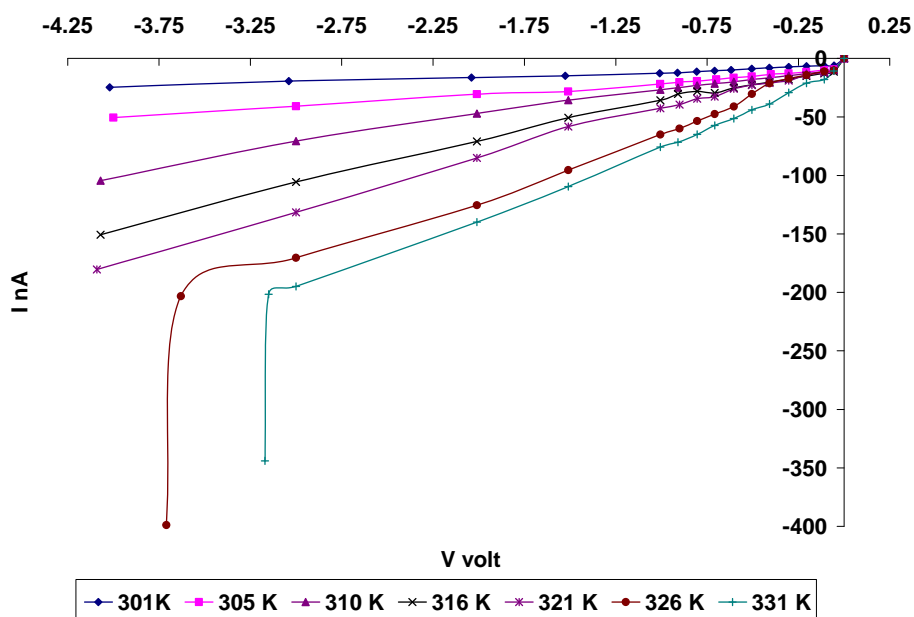


Fig. 7. I-V plots of undoped polythiophene after interchanging the potential terminals in the temperature range from 301 K to 331 K.

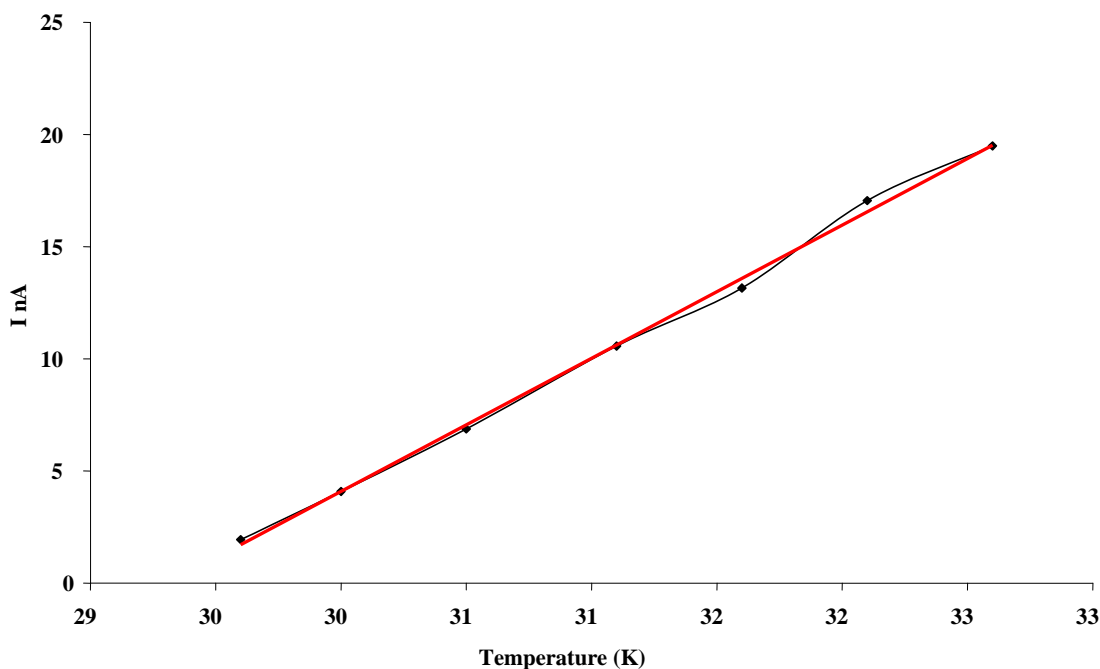


Fig. 8. Graph of temperature versus current for undoped polythiophene at 3 V in the temperature range from 301 K to 331 K.

4. Conclusion

Polythiophene can be doped with FeCl₃. Fe contents increases as the duration of doping increases. Undoped and FeCl₃ doped (for 2.5 and 5 hour durations) pellets after coating by aluminum on both sides behaves like a conventional p – n junction diode. Both side aluminum coated pellet of undoped polythiophene can be used as a temperature sensor within range of 30 K from 301 K to 331 K.

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