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CONDUCTION MECHANISMS IN ORGANIC-BASED RECTIFYING DIODE

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ABSTRACT

The temperature dependent current–voltage characteristics of Ag/ZnPc/p-Si Schottky barrier (SB) diode are investigated in the temperature range of 300–450 K, and in the bias range of ± 1 V. By fitting the experimental data to space-charge limited conduction, bulk-limited Poole–Frenkel emission and thermo-ionic emission theory, it was observed that these models can not be applied to evaluate junction parameters for the investigated SB diode. Preliminary results indicated that the charge transport proceeds by different mechanism for low and high values of the applied voltage under forward and reverse bias conditions. It was found that the charge transport is governed by hopping processes for low values of the forward bias. However, for higher values of the forward bias, the charge transport controlled by the bulk limited procesess. The same voltage dependence was also observed for reverse bias conditions.

Keywords: Schottky diode, transport mechanism, phthalocyanine

1. INTRODUCTION

Organic macrocycles exhibit a number of unique properties such as excellent stabilities. Among these conjugated compounds, phthalocyanines (Pcs) and its derivatives have received much attention in the fabrication of a wide range of electronic and optoelectronic devices such as Schottky diodes (SBDs), organic field effect transistors and gas sensors [1–5]. The production of SBDs with improved fundamental parameters is one of the essential prerequisites for high technology devices. The choice of the interlayer material may be crucial for the development of a SB diode with the desired electronic properties. With that regard, phthalocyanines have been considered to be one of the most stable organic semiconductor for various electronic and optoelectronic applications [6]. Sharma et al. [7] reported earlier on the charge conduction process and photoelectrical properties of Schottky barrier device based on sulphonated nickel phthalocyanine. A MIS type Schottky barrier diode using lead phthalocyanine and copper hexadecachlorophthalocyanines thin film as interlayer were obtained and calculated the theoretical Schottky coefficient and the barrier height by Pakhomov et al. [8]. Authours concluded in their work that rectifying behavior of device strongly depends on the conduction type in Pc layer. The photo voltaic and electrical properties of cobalt phthalocyanine film on silicon substrate were studied in the dark and under illumination by El-Nahass et al. [9]. It was observed at low forward bias that in Al/CoPc/p-Si junction charge transport take places via thermoionic emission of the electrons. However, little previous work has been performed on charge transport behavior and dielectric loss spectra, most of this being confined to commercially available metal phthalocyanines. Unlike some commercially available mono phthalocyanines, the electronic properties and the dependence of the conductivity on the temperature of novel 3,4-dihydroxy-3-cyclobuten-1,2-dione substituted zinc phthalocyanine (ZnPc) as an interlayer material between p-Si and Ag metal have not been widely studied.

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One of the purpose of this work is to study the potentiality of this novel ZnPc film for use in Ag/Insulator/p-Si Schottky barrier diode as insulator layer. The other aim of this work is to investigate the conduction mechanism under dc condition and the frequency response of the dielectric loss in MIS structures of Ag/ZnPc/p-Si as a function of temperature.

2. EXPERIMENTAL

The novel metallo (Zn(II)) phthalocyanine have been synthesized from compound **1**, which can be obtained by the reaction of 4-nitrophthalonitrile with 3,4-dihydroxy-3-cyclobuten-1,2-dione. The detailed synthesis procedure of the Pc molecule, shown in Figure 1, was described in [10]. To fabricate the Schottky barrier diode, first the the p-Si substrate was cleaned by ultrasonic treatment in acetone, propanol and water, and subsequently etched in diluted HF solution, to remove the native SiO_2 layer. A p type (1 0 0) oriented silicon wafers with resistivity in the 10–15 Ω cm range was used as substrate. Then, a low-resistivity ohmic back contact to the p-type Si wafer was established by the thermal evaporation of 300 nm high purity (99.999%) Al followed by annealing at 400 °C for 20 min in nitrogen ambient. Thin film of the novel ZnPc compound on the polished surface of p-Si was prepared by spray pyrolisis processes. The substrate temperature was kept constant at 298 °K during deposition of the Pc compound. Then, the Schottky contacts were formed on Pc layer by vacuum thermal evaporation of Ag at a pressure of approximately 2.0×10^{-6} mbar using an Edwards Auto 500 thermal evaporator system.

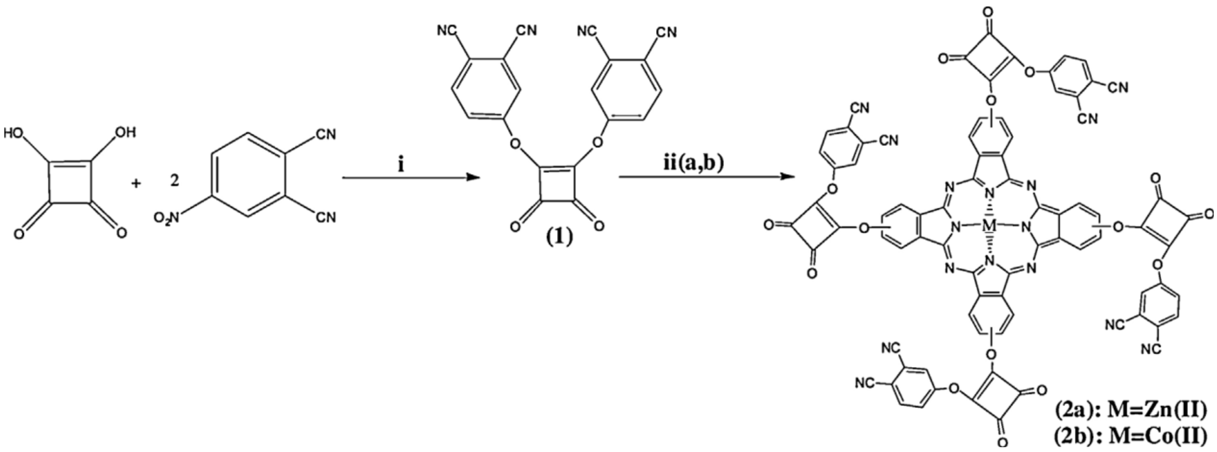

Figure1. Summarization of the synthesis route for ZnPc

The current-voltage (I-V) and impedance spectroscopy measurements were performed on this device. I-V measurements were carried out by using a Keithley 617 electrometer and data for I-V measurements are recorded using a computer and a GPIB data transfer card. Impedance measurements were carried out with a HP 4292 impedance analyzer in the frequency range 20 Hz to 2 10^6 Hz, and in the temperature range from 300 K to 450 K.

3. RESULTS AND DISCUSSION

3.1. Charge Transport Under Dc Condition

Ideality factor, barrier height and series resistance are the main parameters used to characterize a SB diode. Generally, measured I-V characteristics is used to extract these parameters. Figure 2 shows the current–voltage characteristics of a Schottky diode obtained on Ag/ZnPc/p-Si structure at various temperatures. It is clear from the Figure 2 that while the current increases exponentially with applied voltage in the forward bias, in the case of reverse bias conditions the current increases rather slowly with voltage for all temperatures investigated. This observation reveals that devices exhibit rectifying behavior. It was found that the rectification ratio for the device, which is defined as the ratio of the forward current to the reverse current at a certain applied voltage, decreased with incresing temperature.

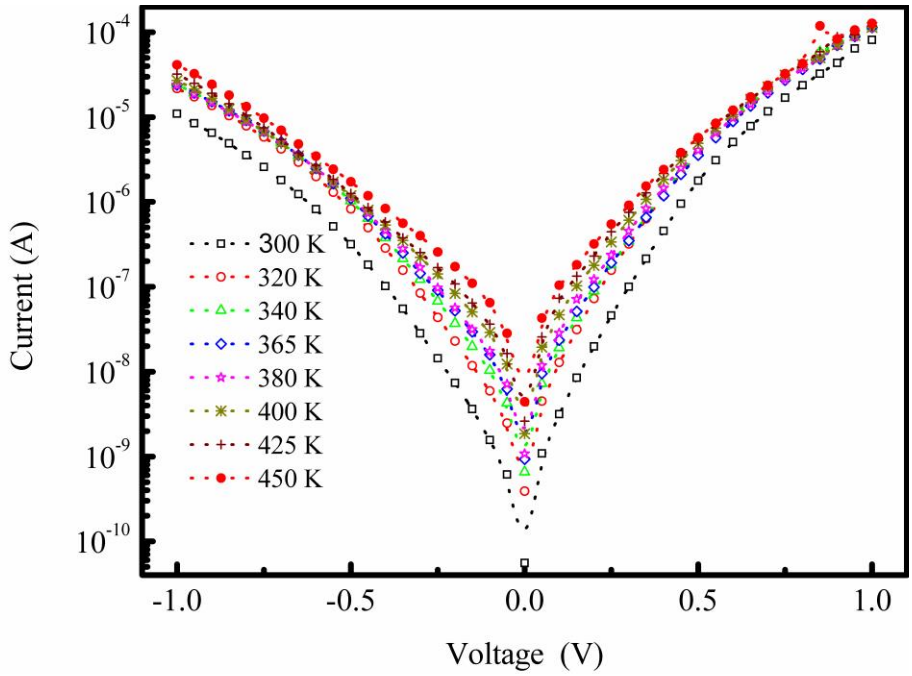

Figure 2. I-V characteristics of the Ag/ZnPc/p-Si structure at indicated temperatures

Various theoretical models such as, space-charge limited conduction (SCLC), thermionic emission and bulk-limited Poole–Frenkel emission theory have been proposed in order to explain the observed non-linear current-voltage characteristics. SCLC in a device can occur if at least one contact is able to inject more carriers than the material has in thermal equilibrium. The SCLC obeys the Mott-Gurney equation.

The forward bias log (I)–log (V) curves of Ag/ZnPc/p-Si devices at different temperatures ranged from 300 to 450 K are depicted in Figure 3. The results show that for the same applied voltage, current increases with increasing temperature, indicating a negative coefficient of resistivity. Based on the nature of the I dependence on V different conduction mechanisms operating in the device can be identified.

The basic assumption of the SCLC model predicts that if the plot of ln (I) *vs.* ln (V) is linear the conduction mechanism dominated by the charge limited conduction mechanism [11]. As can be seen from Figure 3 the dependence of the ln (I) on ln(V) is not consistent with the predictions of SCLC model. Therefore, it can be concluded that the SCLC model can not be applied to evaluate junction parameters for the investigated SB diode. According to the related literature an alternative explanation for the observed non linear I–V characteristics can be given bulk-limited Poole–Frenkel emission theory. If the dominant charge transport mechanism is bulk-limited Poole–Frenkel emission, the plot of ln (I/V) vs. $V^{1/2}$ should be straight line. The variation of the ln (I/V) with the square root of the applied voltage ($V^{1/2}$) for both forward and reverse bias conditions are shown in Figure 4 (a) and (b), respectively. A close investigation of the Figure 4 (a) and (b) indicate that bulk-limited Poole–Frenkel emission theory is also not suitable to model the observed I-V characteristics.

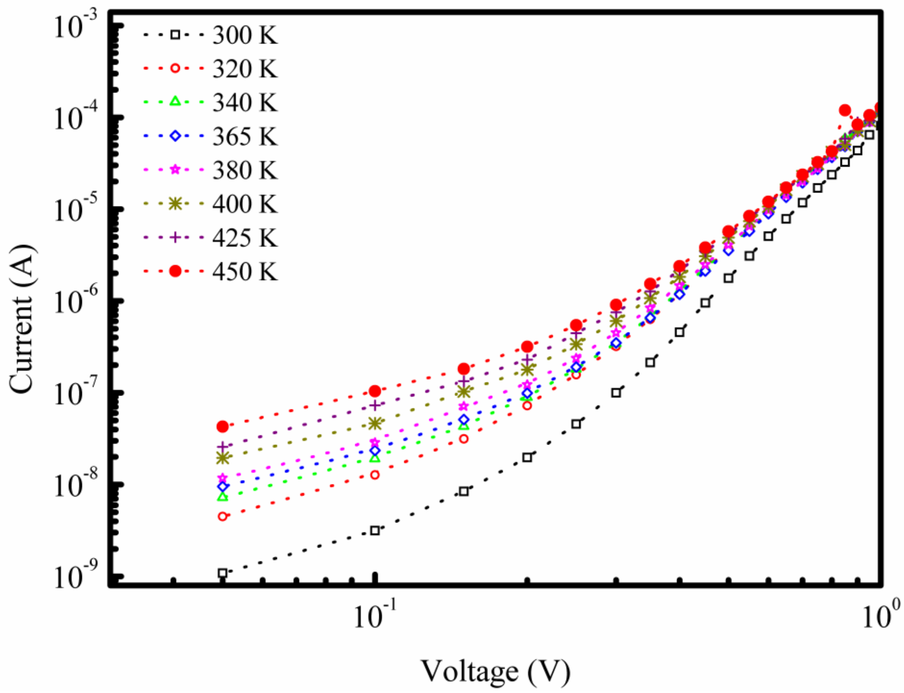

Figure 3. Log–log plots showing current–voltage characteristics of Ag/ZnPc/p-Si structure at indicated temperatures

Thermionic-emission theory, which is widely used to fit the experimental data, suggests a voltage dependence of the current as in Eq. (1) [12].

$$I = AA^{*}T^{2}\exp\left(\frac{q\Phi_B}{kT}\right)\left(\exp\left(\frac{qV}{nkT}\right)-1\right) \qquad (1)$$

where A, A^*, T, q, Φ_B, k, V, and n are diode area, Richardson constant for p-type Si ($A^* = 32$ cm^{-2} K^{-2}) [13], temperature in Kelvin, electron charge, effective SB height, Boltzmann's constant, applied voltage and the ideality factor, respectively. The value of the ideality factor of the Ag/ZnPc/p-Si structure was determined from slope of the straight-line region of the semi-log forward bias ln I–V characteristics through the relation [13]:

$$n = \frac{q}{kT}\frac{dV}{d(\ln I)} \qquad (2)$$

It was observed that the obtained n values by this way are higher than unity. A nearly temperature indpendent ideality factor was observed. The barrier height of the diode was also determined using the saturation current value, which is obtained from Figure 2 and was found to be 0.79 eV at room temperature.

In the light of the thermionic-emission theory (Eq. (1)), it can be say that if the transport of the charge carriers proceeds by thermionic-emission the ln (I) vs.V plots should give a straight line. The plots of the ln (I) vs.V (not shown here but it can be seen from the Figure 2) graphs indicaded that the thermionic-emission theory can not be applied our experimental data.

In order to gain insight into the charge transport mechanism in Ag/ZnPc/p-Si structure, the measured I-V characteristics analyzed for low and high values of the applied voltage. The I-V caracteristics of the device was analyzed according to the hopping model for low applied voltage. On the other hand, high voltage I-V characteristics was analyzed by using bulk limited conduction mechanism. In hopping model, the electron transfer occurs over the barrier, following the dependence on driving force predicted by Marcus theory [14]. Because this process involves a series of hopping sites, this thermally activated mechanism does not exhibit the exponential distance dependence found in coherent tunneling, but it varies in proportion to the inverse of the thicknesess of the interlayer. In the case of hopping conduction, the ln (I) vs. V plots should give a straight line with a constnat slope. Figure 5 shows, for lower values of the applied voltage, the variation of the ln (I) with applied voltage V at indicated temperatures. From this observation it became clear that the charge transport in Ag/ZnPz/p-Si structure is governed by the hopping of the charge carriers. As mentioned above, for higher values of the applied bias the ln (I) vs. V plots deviates considerably from linearity.

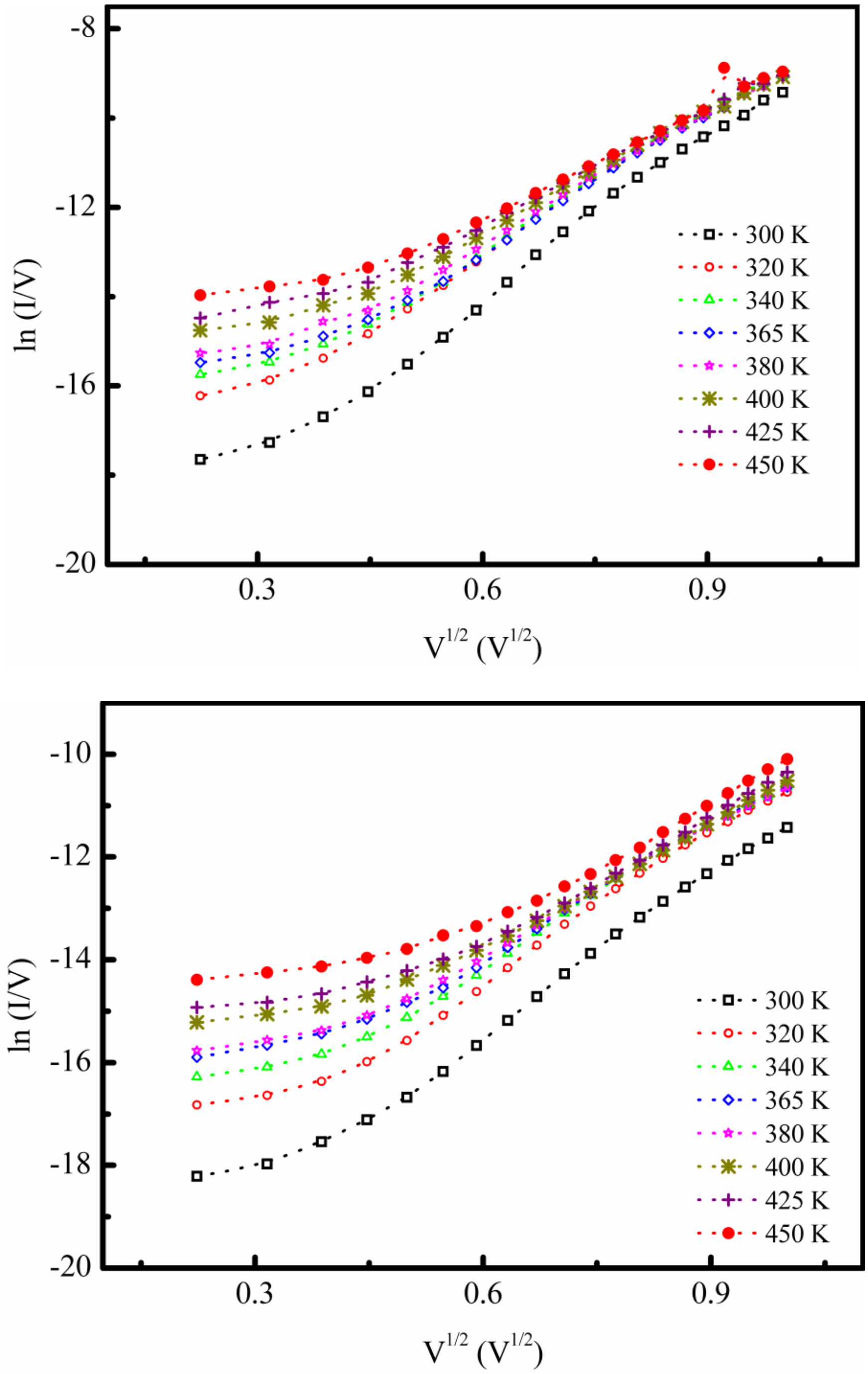

Figure 4. Plots of ln (I/V) vs. $V^{1/2}$ for forward (a) and reverse (b) bias

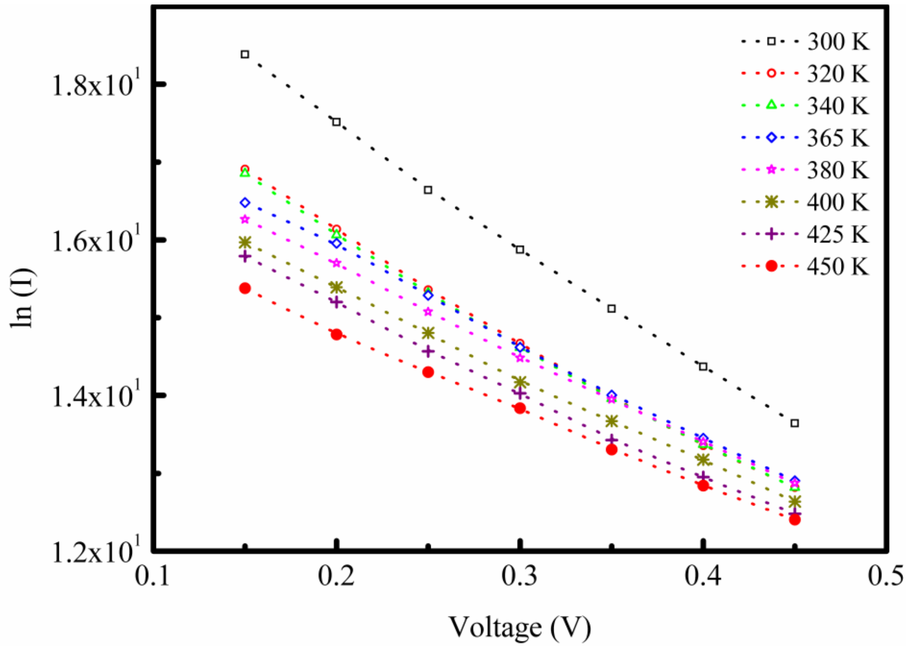

Figure 5. Plots of ln I vs V of Ag/ZnPcp-Si device for low forward bias

Therefore, for higher applied bias voltages, the I-V characteristics was analyzed according to the bulk limited conduction model predictions. Figure 6 compares the high voltage I-V characteristics, which are plotted according to the bulk limited conduction model, of the investigated device at various temperature. As is clear from the Figure 6, a straigt lines with a constant slope was observed for all temperature investigated indicating the applicability of the bulk limited conduction model to evaluate the charge transport mechanism in Ag/ZnPcp-Si structures. The same type of voltage dependence was also observed for the applied voltages in reverse bias conditions.

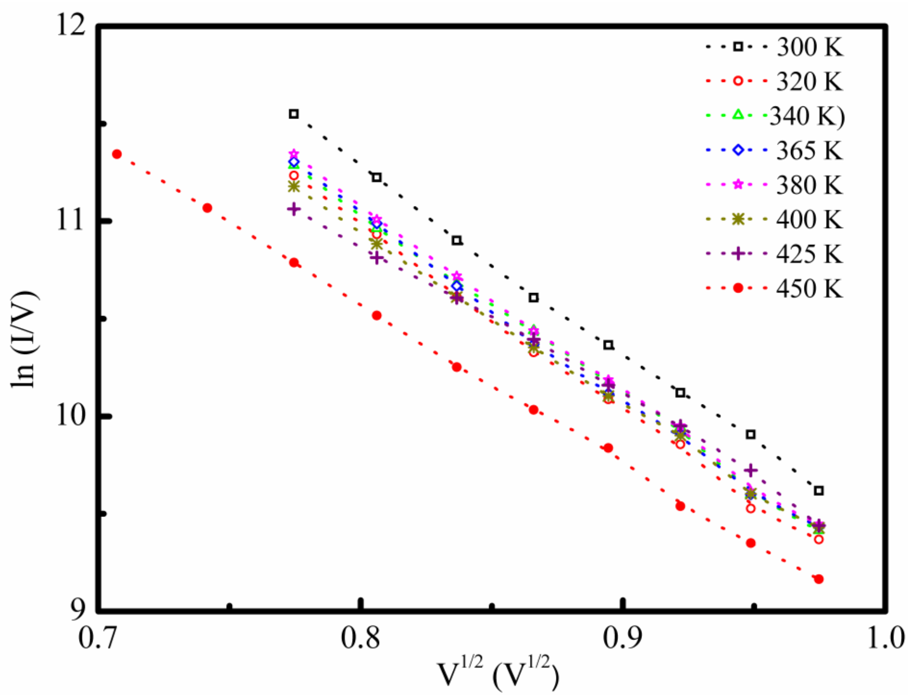

Figure 6. Analysis ingof the high voltage I-V curves according to bulk limited conduction model

4. CONCLUSION

A Schhottky barrier diode in Ag/Pc/p-Si confuguration has been fabricated by coating of ZnPc on the polished surface of a p-Si. It has been observed that this structure showed rectifying behaviour with a rectification ratio of ~ 8 at ±1 V. Deviation from the ideal I–V characteristics was observed and it was attributed to the series resistance and the presence of an interfacial layer. The obtained results indicated that the barrier heights of the SB diode may be tuned by using the thin interlayers of phthalocyanine molecules. It can be concluded that by means of the choice of the organic molecule, the device can be designed to exhibit the desired properties.

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