Chapter 5: Application
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Application

5.1 Introduction

There are three fundamental passive circuit elements, used for building circuits, namely, resistors, capacitors and inductors. The behaviour of these elements is described by the relationships between the variables: current, voltage, charge and magnetic flux. In the year 1971, Leon Chua [26], suggested that a fourth circuit element must be added to the list to complete the logic of circuit theory (figure 5.1). The hypothetical element was called ‘memristor’ by him. Its behaviour is described by the relationship between flux ($\phi$) and charge ($q$),

$$d\phi = Mdq$$  \hspace{1cm} (5.1)

where, $M$ is the ‘memristance’ of the memristor. Resistors and memristors are considered to be the subsets of a more general class, memristive systems. Also, $R$, $C$, $L$ and $M$ can be the functions of independent variable in their defining equations, yielding

![Figure 5.1 The four fundamental circuit elements [D.B. Strukov, G.S. Snider, D.R. Stewart and R.S. Williams, Nature. 453, 80 (2008)]](image-url)
nonlinear elements. For example, a charge-controlled memristor is defined by a single-valued function $M(q)$. The basic mathematical definition of a current-controlled memristor for circuit analysis is the differential form,

$$v = R(w)i$$

(5.2)

and,

$$\frac{dw}{dt} = i$$

(5.3)

where, $w$ is the state variable of the device and $R$ is the generalized resistance that depends upon the internal state of the device. In this case the state variable is just the charge. Chua and Kang [127] has described memristive systems by following relations,

$$v = R(w,i)i$$

(5.4)

$$\frac{dw}{dt} = f(w,i)$$

(5.5)

where, $w$ can be a set of state variables and $R$ and $f$ can in general be explicit functions of time. So, in memristive systems, flux is not uniquely defined by charge. From equation 5.4, it is deduced that no current flows through the memristive system when the voltage drop across it is zero. Strukov et al. [27], in the year 2008, presented a physical model of a two-terminal electrical device that behaves like a perfect memristor for a certain restricted range of $w$ and as a memristive system for another range of $w$. Memristance dependent hysteresis loops are obtained from their model. The loops also depend upon the boundary conditions on the state variable $w$. Results obtained from their model explains earlier reported [36-37] current-voltage anomalies like, switching and hysteretic conductance, multiple conductance states and apparent negative differential resistance, especially in thin films and two-terminal nanoscale devices.

The electrical device presented by Strukov et al. [27] consists of a thin semiconductor film of thickness $D$ sandwiched in between two metal contacts (figure 5.2a). The film
consists of two regions of variable resistances, $R_{ON}$ (having high dopant concentration) and $R_{OFF}$ (having low dopant concentration) connected in series.

The boundary between the two regions shifts, on applying external voltage, due to the drift of dopants. Considering the case of simple ohmic electronic conduction and linear ionic drift in a uniform field with average ion mobility $\mu_v$, following relations were obtained to get the expression for memristance,

$$v(t) = \left( R_{ON} \frac{w(t)}{D} + R_{OFF} \left( 1 - \frac{w(t)}{D} \right) \right) i(t)$$  \hspace{1cm} (5.6)

and,

$$\frac{dw(t)}{dt} = \mu_v \frac{R_{ON}}{D} i(t)$$  \hspace{1cm} (5.7)

or,

$$w(t) = \mu_v \frac{R_{ON}}{D} q(t)$$  \hspace{1cm} (5.8)

From equations 5.6 and 5.8, they obtained the memristance as (for $R_{ON} << R_{OFF}$),

$$M(q) = R_{OFF} \left( 1 - \frac{\mu_v R_{ON}}{D^2} q(t) \right)$$  \hspace{1cm} (5.9)

The second term in the right hand side of above equation is the crucial term. It increases with increase in mobility of the dopant and with decrease in $D$. As it is inversely proportional to the square of the film thickness, it increases enormously for nanometre scale dimensions. It is around 1,000,000 times in nanometre scale as compared to that in micrometer scale. Thus, memristance becomes more important for the electrical characteristics of the devices having the critical dimension in nanometre scale.

In this model, the state variable $w$ (bounded between 0 and $D$) depends on charge $q$ that passes through the device until its value approaches $D$, called ‘hard switching’. Till the system remains in the memristor regime, any symmetrical alternating-current voltage bias results in double-loop current-voltage hysteresis that collapses to a straight line for
high frequencies (figure 5.2b). Multiple continuous states will also be obtained if there is any sort of asymmetry in the applied bias (figure 5.2c).

Equation 5.9 is valid for values of $w$ in the interval 0 to $D$. But in case of any hard switching, imposed by various boundary conditions, the device satisfies the equation for memristive systems (equations 5.4 and 5.5). For example, the case when $w$ reaches either of the boundaries and remains constant until the voltage reverses polarity satisfies the memristive system equations. According to Strukov et al., different current-voltage curves are possible for memristive devices. Three of them are shown in figures 5.3a, b and c. In case of figure 5.3a, the upper boundary is reached but the derivative of the voltage is negative, which produces a dynamical negative differential resistance. It differs from the static negative differential resistance on the way it is dependent on the device history. The dynamical differential resistance is the result of the charge dependent change in the device resistance and depends strongly on the frequency of the sinusoidal driving voltage. In case of figure 3b, the boundary is reached much faster on

Figure 5.2 Model developed by Strukov et al. [D.B. Strukov, G.S. Snider, D.R. Stewart and R.S.Williams, Nature. 453, 80 (2008)]
doubling the magnitude of the applied voltage, the switching is a monotonic function of the current. In both these cases there is a threshold voltage for switching from the 'off' state to the 'on' state and the switching is dynamical. This means that any positive voltage $v$ applied to the device in off state will switch it to the on state after time $\sim D^2 R_{OFF}/(2\mu v + R_{ON})$. But, even a small negative voltage will switch it back to the off state, and there is no current-hysteresis loop in the negative voltage sweep (figure 5.3a, b). Figure 3c, shows the case when there is nonlinear ionic transport, generally caused in nanoscale devices, where a small voltage produces high electric fields. Specifically, the figure illustrates the case when right-hand side of equation 5.7 is multiplied by a function $w(1-w)/D^2$, which corresponds to non-linear drift when $w$ is close to 0 or $D$. Here, the switching requires a significantly larger amount of charge in order for $w$ to reach either boundary. So, the switching is essentially binary because the on and off states can be held much longer if the voltage does not exceed a specific threshold. Nonlinearity is also expected when there is tunnelling through the interfaces or in case of high-field electron hopping. In all the above cases, qualitatively different current-voltage hysteresis shapes are due to the specific dependence of $w/D$ on the electric field near the boundaries. Figure 5.3d shows the experimental result for the device having metal/oxide/ metal cross-point device within which the critical 5nm thick oxide film initially contained one layer of insulating TiO$_2$ and one layer of oxygen-poor TiO$_{2-x}$ [128-129]. According to them, oxygen vacancies act as mobile +2-charged dopants, which drift on applying electric field. The hysteresis behaviour observed in many thin-films, two-terminal devices is now explained as memristive behaviour. As the active region of the electronic devices shrink to the nanoscale region, even low applied voltage
causes high electric field, thereby causing the charged move, which in turn changes the device resistance.

Bipolar switching, defined by equations 5.6 and 5.7, has been experimentally observed in various material systems such as organic films [28-32], chalcogenides [32-35], and metal oxides [32,36-38], notably TiO$_2$ [32,39-41] and various perovskites [32,42-46]. Typical hysteresis have also been reported by some workers [31,38,44-46]. Many of these hysteretic I-V curves show the memristive behaviour. Also the current-voltage resembling to that of figure 5.3a and b, have been reported by many workers [31,38,44-46]. Important applications of memristor include ultradense, semi-non-volatile memories and learning networks that require a synapse-like function [27].

Figure 5.3 Simulations for voltage-driven memristive device [D.B. Strukov, G.S. Snider, D.R. Stewart and R.S.Williams, Nature. 453, 80 (2008)]

5.2 Present work

Inspired by the encouraging theoretical predictions by Strukov et al. [27], an electrochemical device (figure 5.6) is fabricated, as detailed below, to investigate the switching and memristive properties of the fabricated nanoparticles.

Two very thin wires of copper/silver are used as electrodes. The wires are fixed over a glass slide. The ends of the wires are kept very close to each other (~ 0.1 cm) and a single tiny drop of the prepared sample is put over it to make a contact. The slide is then
dried and connected to the circuit shown in figure 5.4. DC voltage is then applied and the current is recorded. Experimental set-up given in figure 5.5 is used to check the charge storing property of the sample. A small resistor is connected in parallel to the input voltage to discharge the accumulated charge in the sample, while a capacitor is connected in parallel to stabilize the input voltage. After each measurement, the power supply is turned off and the device was allowed to get discharged for 20 minutes through the resistor. The characteristics of the device are found to be repeatable after proper discharging.

![Figure 5.4 Experimental set-up to record the I-V characteristic](image)

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![Figure 5.5 Experimental set-up to check the charge storing property of the device](image)

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5.2.1 Current-voltage characteristics

Observed current-voltage curves for the semiconductor/PVOH nanocomposites are presented below:

(a) ZnS samples

The current-voltage characteristic of sample S₆ is shown in figure 5.7. The characteristic is studied for increasing and decreasing voltage in the forward as well as reverse direction. The current conduction in the nanocrystals embedded in polymer matrix is governed through tunnelling. Initially the current is very low as a certain minimum voltage is required for the tunnelling to start. This minimum voltage depends upon the properties and thickness of the matrix in between the nanocrystals. This voltage is found to be different for different samples having different width of matrix in between the nanocrystals. In figure 5.7 the value is around 1V after which the current rises almost linearly with voltage. Then as we start decreasing the voltage towards zero, the current also starts decreasing, but does not retrace its earlier path showing ‘hysteresis’. We know that in case of memristor, the value of the current flowing through the material does not, in the second half of the cycle retraces the path it took in the first. Because of
this ‘hysteresis’ effect, the memristor acts as a nonlinear resistor, the resistance of which depends on the history of the voltage across it—its name, a contraction of ‘memory resistor’ reflects just that property [130]. For memristor, any symmetrical alternating current voltage bias results in double-loop current-voltage hysteresis that collapses to a straight line for high frequencies (figure 5.2b). If there is any sort of asymmetry in the applied bias, multiple continuous states will be obtained (figure 5.2c). Thus for dc voltages, the current-voltage characteristics may be expected to exhibit hysteresis and for successive observations (repeated immediately), multiple loops may be expected. Such multiple hysteresis loops are observed in figures 5.8, 5.10 and 5.11. Also we checked the repeatability of the samples. For this, we recorded the current-voltage curve of ZnS samples, after discharging them through a resistance (figure 5.5). The curves thus obtained for sample S6, are shown in figure 5.8, which confirms repeatability [131]. Along with the hysteresis, we have also obtained binary switching property (sample S1, figure 5.12) which is similar to (figure 5.3c) that modelled by Strukov et al. In this curve the current starts decreasing after attaining its maximum value and the saturation region is very narrow. The curve clearly shows the switching property. Figure 5.13 shows the current-voltage behaviour of sample S2, which seems to resemble the behaviour of a voltage regulator for increasing voltage in the reverse direction.

The effect of doping on the current-voltage behaviour has also been studied. Figures 5.14 and 5.15 show the current-voltage curves for Cu and Fe doped samples of S6, respectively. Comparison of these figures with figure 5.7 reveals that doping reduces the asymmetry as well as memristive property.
The current-voltage curves show that the conductivity of the samples is low compared to similar experiments done earlier [98]. This may be because of less tunnelling current in the present experiment due to larger dimension of non-conducting matrix compared to the earlier experiment and due to the absence of excitation from laser source. Conductivity can also be improved by the use of conducting polymer for matrix.
Figure 5.9 I-V curves recorded before and after discharging sample S₆ for 20 minutes.

Figure 5.10 I-V curve obtained for consecutive voltage cycles for sample S₃ (with Cu wire as electrodes).

Figure 5.11 I-V curve obtained for consecutive voltage cycles for sample S₄ (with Cu wire as electrodes).
Figure 5.12 I-V curve of sample $S_1$ with Cu wire as electrodes

Figure 5.13 I-V curve of sample $S_2$ with Cu wire as electrodes

Figure 5.14 I-V curve of Cu doped $S_0$, with copper wires as electrodes
Figure 5.15 I-V curve of Fe doped Sr, with Ag wire as electrodes

(b) ZnO samples

Initial studies on current-voltage characteristics of ZnO nanoparticles embedded in polymer matrix are carried out using figure 5.16. The prepared ZnO sample deposited over a glass slide is used to determine the electrical properties. Two parallel silver lines are drawn over the film, carefully, using silver paint to make electrodes (figure 5.17). The separation between the lines is kept very low (~ 0.1cm). The electrodes are connected to the circuit using copper clips with pressure contacts. Then dc voltage is applied and current is recorded. The characteristic is first checked in atmospheric pressure and then in vacuum. We also tried to check the variation in current after exposing the sample to white light.

The curves recorded for sample O₁, at atmospheric pressure and in vacuum, are shown in figure 5.18. The current-voltage characteristic of the nanocrystalline ZnS/PVOH shows linearity with more resistivity in vacuum compared to that in air. With increase in pressure, the near band edge PL emission feature and the broadband shifts toward higher energy as the ZnO band gap increase [70] and hence, the surface states increase. This explains the decrease in resistivity at atmospheric pressure as compared to that in
vacuum (figure 5.18). We checked the current-voltage response of the sample after exposing it to white light. The response is similar to the one obtained at atmospheric pressure. Thus, white light has no effect on the conduction. However, the importance of the simple experiment is that variation in current with voltage has been achieved which indicates the possibility of getting proper characteristic for switching with improved experimentation. Using highly sensitive CV meter and the set-up given in figure 5.4, switching property is achieved in sample O₃ (figure 5.19).

**Figure 5.16 Experimental set-up for I-V study**

**5.17 Samples with silver lines for current-voltage measurement**
The current-voltage curves of ZnO samples, recorded with the set-up given in figures 5.4 and 5.5, are presented below:

The current-voltage curves observed in case of ZnO samples are similar to that of the ZnS samples, the only difference being the magnitude of current which is less for ZnO samples as compared to that for ZnS samples. The reason may be the presence of larger density of non-conducting polymer between the electrodes as the method adopted to prepare ZnO results in more viscous sample as compared to ZnS. We obtained hysteresis loops (figure 5.20) similar to the case of ZnS samples and the loops described
by Strukov et al. [27]. Multiple loops (figure 5.21) for successive observations and repeatability of characteristics (figure 5.22 and 5.23) are also observed for ZnO samples.

Figure 5.20 I-V curve for sample O₄ with Ag wire as electrodes

Figure 5.21 I-V curves obtained for consecutive voltage cycles for sample O₄

Figure 5.22 I-V curves recorded before and after discharging sample O₄, for 20 minutes
Figure 5.23 I-V curves recorded before and after discharging sample O₅, for 20 minutes

5.3 Conclusion

Both ZnS/PVOH and ZnO/PVOH nanocomposite samples are found to exhibit switching as well as memristive properties. However, the switching property is more prominent in ZnO/PVOH samples compared to ZnS/PVOH samples whereas the memristive property is more prominent in ZnS/PVOH samples compared to ZnO/PVOH samples. Ageing effect is tested and general behaviour is found to be retained. The concept for application of the nanocomposites fabricated as switching as well as memristive device is developed in the present work and with advanced technological facilities for device fabrication suitable devices with these samples can be developed for relevant applications in the field of electronics.