Chapter 5

SUMMARY

* A work of art is never completed, Only abandoned.  
  -Paul Valery

5.1 INTRODUCTION

The futuristic electronics is getting smaller yet powerful. The scaling down of transistor has been the driving force behind the availability of high speed gadgets supported by large memories. The continuous scaling down is leading electronics into the realm of biology where organic molecules offer to act as nanoelectronic devices. DNA, carbon nanotubes, proteins etc are possible candidates that are very small in size and their functionality can be tuned to customize their electronic performance. This will be trendsetting change in integrated circuit technology that will evolve a new class of devices that will be classified as molecular electron devices. The need of hour is to model robust methods for fabrication processes that can be used to replicate the achievements of lithographic processes. Attaining control over the properties of metal-molecule or molecule-molecule interfaces would further help in creating molecular integrated circuits. This achievement would pave a path towards interfacing biological systems with ultra-dense molecular integrated circuitry. In this dissertation, the four bases of DNA Adenine, Thymine, Guanine and Cytosine have been studied individually with an intention to investigate their electronic properties. An effort has been made to explore the electrical characteristics of these DNA bases so as to exploit them in modeling DNA based molecular devices. This final chapter summarises the major contributions of this thesis and discusses future scope of the work for extension of this work. A summary of these results is presented in the next section. The discussions on the area of research and future research directions are suggested in sections 5.3 and 5.4.
5.2 SUMMARY OF MAJOR CONTRIBUTIONS

DNA strands have been the focus of study by scientists for use in nanoelectronics. Various experimental and theoretical projects have been carried out to investigate the conductivity profile of these molecules. In this thesis the four DNA bases Adenine, Thymine, Guanine and Cytosine that have been isolated from the backbone, are the subject of theoretical study. Various observations and interpretations of the results obtained constitute the major contributions of this work. These are listed here to provide a comprehensive summary of the observations and results of the study.

- The values of energy levels of DNA bases were calculated to observe the equilibrium energy level pattern of the four DNA bases. Well separated energy levels were observed in the four bases. The discrete energy levels make the molecules suitable for single electron effects which are an integral ingredient of nanoelectronics. The HLGs describe the hardness of a molecule in context to the conductivity properties. The HLGs of the four DNA bases Adenine, Thymine, Guanine and Cytosine were calculated to verify the room temperature stability of the molecules. The large values of HLGs (Adenine- 12.76 eV, Cytosine- 12.78 eV, Guanine- 12.62 eV and Thymine- 13.68 eV) render the four molecules suitable for room temperature electronics. From the HOMO and LUMO energy levels that the order for charging or triggering for molecules A, C, G and T inserted individually between gold terminals for electron transport is A (0.65eV) < C (0.87eV) < G (0.95eV) < T (1.11eV). For hole transport the threshold potentials with same terminals are G (11.67eV) < C (11.92eV), A (12.11eV) < T (12.57eV). These are also much higher than the thermal energy (~K_B T =0.026eV) and suggest room temperature utilisation.

- The well separated discrete energy levels motivated the study of presence of single electron effects in the DNA bases. So the equilibrium energy levels were redrawn after adding and removing electrons one at a time. The energy values for the molecular orbitals were calculated for the
anionic (-1), double anionic (-2), Cationic (+1), bi cationic (+2) states of the four molecules. Remarkable energy shifting is observed in the molecules. It is seen that energy reorientation displays a typical pattern. The energy levels of a molecular orbitals are elevated on addition of electrons onto the molecule and the energy levels are lowered on removal of electrons. The inter-orbital energy difference varies and the HLGs are also affected. The shifting of energy gap after application of unit positive and unit negative charge implies formation of a quantum well and quantum barrier in the molecular structures. Also the energy gap shifting from n to n+1 level implies conductivity peak in the conductivity characteristics of the DNA bases.

- If the sum of thermal energy $k_B T$ and the energy from voltage supplied is not enough to overcome the barrier, the current is blocked representing the coulomb blockade. As the zero bias charging energy for all the bases are much larger than the thermal energies at room temperature, it satisfies the condition for coulomb blockade. As observed in the previous result, the energy level of the molecular orbitals can be tuned by adding or removing charge from the DNA bases. This suggests the use of DNA bases in three terminal molecular single electron devices.

- Theoretical investigations were carried to observe the pattern of current flow through four DNA bases when a sweep of voltage is applied. Choosing the bias voltage (0-0.5V) less than charging energies, all the bases have been characterized for the Current flow through them. The molecule Guanine and Adenine displayed linear curves with resistance of $1.04 \times 10^6 \ \Omega$ and $4.3 \times 10^6 \ \Omega$ while Thymine had comparatively very small resistance of $3.1 \times 10^2 \ \Omega$ when a voltage sweep of 0 - 0.5 V is applied. The fourth DNA base Cytosine exhibited a typical characteristic in which the large resistance of the molecule ($6.2 \times 10^6 \ \Omega$) for the potential 0-0.4V suddenly reduces to $17.8 \Omega$ representing single electron transfer at 0.4V. All the bases exhibit tunneling and the amount of current varies from nA for purines (A & G) to µA for pyrimidines (C & T). These
characteristics are the function of polarity of the bias and the orientation of the molecule between the electrodes as all these bases are Asymmetric. From the current-voltage plots obtained it is observed that magnitude of resistance is much larger than Quantum resistance \((\hbar/e^2=26k\Omega)\) which satisfy the criteria for single electron tunneling.

- The detailed study of Adenine and Guanine molecules displays some significant observations and results. The current-voltage characteristic of the two molecules resembles that of a tunneling diode in both the positive and negative bias regime. The curves are marked by presence of peaks displaying resonance. They show that resonant tunneling occurs whenever fermi level is aligned to an occupied or unoccupied molecular orbital. The DNA base Adenine exhibits more resonant peaks for negative bias while it is true for positive bias in case DNA base Guanine. This is due to the unique energy levels of the molecular orbitals of the two molecules. Both the molecules have large peak to valley current ratios that ensures useful application of the two molecules as resonant tunneling diodes.

- There is a sudden rise in the value of current in the current-voltage plot for cytosine, displaying single electron characteristics in the molecule. Detailed probing of the characteristics of the molecule was done by coupling the third terminal ‘gate’ to the two probe structure of the gold-cytosine-gold assembly. Application of gate potential results in enhancing the current values as compared to no gate values resulting in overall shifting of the characteristics. Coulomb oscillations are also observed in the current due gate voltage. The increase in value of current on application of gate potential confirmed the single electron effects in the molecule. Hence the three terminal assembly can be considered characteristically as a single electron transistor. The suppression of current around zero source voltage with zero gate potential is called coulomb blockade. The detailed probing of gated current-voltage characteristics has shown that switching behavior which can be exploited to use the cytosine based transistor as a molecular switch. This switch is used to assemble the
circuits acting as AND gate and OR gate. The cytosine based transistor can be used as a memory as you can control the ON/OFF pattern by applying adequate bias.

5.3 DISCUSSION

Molecules are the building blocks of matter and materialistic systems. They support the various mechanisms and phenomena that govern the organic and inorganic systems that form this universe. The unending zest of humans to have voice, video and data in his palm backed by ample memory and speed is motivating the scientists to exploit the molecular conduction phenomena in electronics. Molecular electronics intends to use molecular structures whose function involves discrete molecules, which are distinguished from organic thin film transistors that use bulk materials and bulk-effect electron transport. It provides a bottom-up way to produce sub-nanometer sized functional devices.

DNA the essence of life is being studied to perform same role in electronics too. The DNA molecules virtue their self-assembly and self-recognition properties are strong contenders for use in molecular electronics.

The discrete spacing of the energy levels of the molecular orbitals and adequate HLGs make DNA bases particularly suitable for DNA based nanoelectronics. The molecules are particularly suitable for molecular single electronics virtue their small size and energy shifting pattern. It is inferred that four DNA bases G, A, C & T can be used in molecular electronics for various applications at room temperature. Guanine & Adenine can be used as high resistance linear devices. Thymine can be used in power electronics devices, due to the large current flowing through them. DNA base Cytosine exhibits the typical graph which renders it for suitable for use in digital circuits. The DNA base Cytosine can be used in applications such as digital switches and logic gates. The distinct electronic properties of four DNA bases combined with their self assembly and selectivity properties can be explored for next generation electronic devices.
In this work the DNA bases A and G are proposed to be used as Resonant Tunneling Diodes. These molecular RTDs exhibit excellent PVRs that mean that these devices shall be highly suitable for digital applications. The DNA base C is proposed to be utilized as a three terminal device: Single Electron Transistor. The two basic logic gates AND and OR are conceptually suggested using DNA based SET. The various results and their utilization in the proposed applications recommend use of DNA based electron devices in futuristic molecular digital electronics. They promise high speed integrating circuits boasting of large device densities.

5.4 FUTURE SCOPE OF THE WORK

During the course of this work, several avenues for continuation of this work become evident. There are various problems and issues that are still open for study in future. In this work the alligator clips have not been used for interfacing metal with molecule. Choice and comparative study of alligator clips like sulphur forms an essential future extension of this work. DNA bases are asymmetric in nature. So the current-voltage characteristics might vary if we change the orientation of molecules between the two metal terminals. Obtaining the characteristics for different orientations of the bases forms an interesting extension of work. Use of various materials like platinum and CNTs for terminals is also another interesting aspect of the study. The right exploitation of smart self-assembly capabilities of DNA to realize a complex organic structure is an open issue as yet.

Last but not the least is due on need for progress in the investigation tools. Development of advanced synthesis procedures for the structural modifications and due optimization of these procedures forms an essential aspect. Concerning direct conductivity measurements, techniques for deposition of the molecules onto inorganic substrates and between electrodes must be optimized. Moreover, the experimental settings and contacts must be controlled to a high degree of accuracy in order to attain an uncontroversial interpretation and high reproducibility of the data. On the theoretical side, a
significant breakthrough might be the combination of mesoscopic theories for the study of quantum conductance and first-principle electronic structure calculations, suitable for applications to the complex molecules and device configurations of interest. Given this background, it can be believed that there is still plenty of room to shed light onto the appealing issue of charge mobility in DNA, for both the scientific interest in conduction through one-dimensional polymers and the nanotechnological applications. The interesting and highly interdisciplinary nature of such a research manifesto necessarily implies hybridization of the traditional subjects like solid-state physics, chemistry and biological physics to evolve new generation of electronic circuits.