Preface

Miniaturization is a general aim of technology development to produce smaller, faster, reliable and low cost devices with greater functionality using less raw materials with least amount of processing energy. In the present time, modern electronic devices including computers and other commercial gadgets demand fast advancement of data storage technology. The existing conventional memories such as static random access memory (SRAM), dynamic random access memory (DRAM) and FLASH memory serve this purpose to greater extent but still these technologies are facing certain formidable device scaling challenges. Enormous efforts are going on world-wide in both industrial and academic labs to overcome these challenges but these fields yet to improve to the required level.

Recently, various emerging nonvolatile memory (NVM) technologies such as phase change random access memory (PCRAM), magnetic random access memory (MRAM) and resistive random access memory (ReRAM) are being explored as potential alternatives of existing memories for future computing systems. These emerging NVM technologies are well capable of combining the speed of SRAM, the density of DRAM and non-volatility of Flash memory and hence they have become very attractive alternatives and competitive candidates for future as universal memory devices. Today, all these emerging memory technologies are getting mature with a faster rate which has made them a hottest topic of research in scientific community to explore their usage at different level of memory hierarchy. It is anticipated that these technologies will break important ground and move closer to market very rapidly. Therefore, understanding the benefits and limitations of such memory technologies is important to implement them into the memory hierarchies which can open up new opportunities for future memory designs. Though NVMs are getting mature but it is still not feasible for them to directly replace existing NAND Flash
memory because of their limitation of manufacturer. Among all the upcoming new emerging NVM technologies, ReRAM have drawn extensive research interest as a leading candidate due to its versatile features such as simple device structure, high storage density, low operating voltage, long retention and low fabrication cost etc. which makes this module to use it in main memory or on chip cache of memory hierarchy. Therefore, the present research is fully devoted towards this direction.

Since after the discovery of first ReRAM device, the memristor is under development by various research teams including many companies such as Hewlett-Packard, SK Hynix, HRL Laboratories, Unity Semiconductor Corp., Adesto Technology Inc. and Fujitsu etc. The resistive switching effects have been actively explored in large variety of materials, spanning from binary and complex metal oxides, solid electrolytes, polymers, bio-molecules to organic materials including organic/inorganic molecules. It is well realized from these reports that memristive effect becomes stronger as the feature sizes in circuits become smaller. Therefore, the field has achieved considerable importance with the advancement of nanoscience. Till now, wide variety of nanomaterials including metals, semiconductors and metal oxides are reported, however, a better understanding is still strongly required towards this direction. Furthermore, various memory effects, such as volatile resistive switching, non-volatile resistive switching and write once read many times (WORM) have been realized successfully in different device structures fabricated in simple as well as complex crossbar format. It is well observed that the material structure is one of the pivotal factors in tuning the performances of memory devices. Therefore, it is very important parameter to develop new design principles and memory material systems for better development and understanding of these memory devices.

In the present thesis, an attempt is made to design and develop reliable, efficient, bi-stable non-volatile resistive memory devices of low cost using hybrid
nanostructures of various metals, metal oxides and metal compounds such as Ag, Au, Al₂O₃, TiO₂ and Cul. The memristive devices of these nanostructural materials are constructed by forming their suitable heterojunctions in simplest device format of metal-insulator-metal junctions. Preparation of these nanoparticles utilizing facile, greener and environmentally benign routes of synthesis is also one of the major key interest of this work. In order to achieve mentioned requirements of synthesis, two different methods named as chemical and electrochemical have been used successfully. Gold, silver, silver-graphene composites and copper iodide nanoparticles were synthesized chemically whereas Al₂O₃ and TiO₂ nanoparticles were prepared by electrochemical method. A biocompatible thiol containing molecule (L-cysteine) was chosen as a capping agent for the synthesis of nanoparticles whereas sodium borohydride was utilized as a reducing agent for all chemical synthesis. The aqueous colloidal solutions of prepared nanoparticles were used for thin film formation to fabricate memory devices on two different conducting substrates (Al and ITO) which were used as bottom contact to constitute metal-insulator-metal memristive junctions. Different methods such as dip coating and drop casting are utilized to achieve thin films of low thicknesses. Further, soft Hg and evaporated Al contacts were taken as top metal electrodes of memristive devices. Selection of top contact was made based on the better memristive response of the prepared resistive memory devices. A small drop of Hg with diameter of 1.5 mm was taken for all the cases whereas top Al contact was formed by evaporating it under a shadow mask of circular shape having diameter of 1.8 mm using metal evaporator at high vacuum ~10⁻⁵ torr. After the formation of these contacts electrical conductivity measurements were studied using Keithley 2636A source meter in cyclic mode using Labview programming. The various memristive device structures with suitable top contacts are discussed briefly in various chapters of the present thesis. The work is divided into five basic chapters whereas the conclusions of the work are mentioned
in the last chapter of present thesis. The thesis is planned in the following way:

**Chapter One:** First chapter reviews detailed introduction about memristor, historical background and its various types. Chapter also provides a concise discussion on various emerging memory technologies. Different mechanisms involved behind their memristive behaviors are also discussed in the same chapter. Role and importance of nanomaterials in resistive memory device systems is also illustrated here. A brief review on different prospects for resistive memory devices is presented with their relevant literature. At the end of the chapter, the motivation of the present work is discussed.

**Chapter Two:** This chapter provides a brief introduction about nanomaterials. The general chemical synthetic techniques for the synthesis of various nanoparticles are also summarized in detail. A concise discussion on different characterization techniques used for the analysis of prepared nanoparticles is also presented in this chapter. These include mainly optical absorption spectroscopy, fluorescence spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning & transmission electron microscopy (SEM & TEM), energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Finally, the detailed information about electrical charge transport measurements of metal-insulator-metal (MIM) junctions are discussed.

**Chapter Three:** This chapter is purely based on the fabrication of memory devices utilizing aluminum oxide (Al$_2$O$_3$) nanoparticles as a memristive element. The chapter gives the detail about the simple chemical method used for the formation of Al$_2$O$_3$ nanoparticles, its characterization and fabrication of Hg/Al$_2$O$_3$/Al memristive device. Next, the role of three different thiol containing molecules named as 1-Dodecanethiol, 1-Heptanethiol and 3- Mercaptopropionic acid on memristive behavior of prepared Al$_2$O$_3$ memristor is also studied in the same chapter. Further, the effect of contact electrodes (Hg and Al) on Al$_2$O$_3$
memristive device is also investigated here. Procedure for the formation of different memristive devices is given in brief and their cyclic charge transport measurements along with important results and storage mechanisms are discussed.

Chapter Four: This chapter is fully devoted to study the role of metal nanoparticles (Au and Ag) on memristive behavior of Al₂O₃ memristor by forming their thin heterojunction with memristive element. In the beginning of this chapter, a detailed description on chemical synthesis procedures followed to prepare various sized gold nanoparticles and silver nanoparticles is described. Next, the important results obtained from their characterization techniques are presented with their respective synthesis part. Further, procedure to fabricate resistive memory devices based on heterojunctions of these nanoparticles and Al₂O₃ is given. In the end, their characteristic charge transport behavior along with the storage mechanisms involved are discussed concisely.

Chapter Five: This chapter describes the effect of heterojunction formation between wide band gap semiconductor nanoparticles (TiO₂ and CuI) and graphene-silver nanoparticle composites with Al₂O₃ memristive element on memristive behavior of Al₂O₃ memristor. Initially, a brief synthetic procedures followed to prepare these nanoparticles are given. Next, the characterization results of individual nanoparticles are discussed separately. Further, device fabrication and their charge transport measurements are described. In the end, analysis of the obtained charge transport behavior is carried out.

Chapter Six: The conclusion of entire thesis work is given in this chapter. The important results obtained from various resistive memory devices are briefed here. At the end, scopes for further work are given based on the present work.