Colloidal Quantum Dots Nanocomposites Based Resistive Switching for Low-Power Resistive Random Access Memory

A Thesis submitted by

Jayanta Bera

in partial fulfillment of the requirements for the award of the degree of

Doctor of Philosophy



Indian Institute of Technology Jodhpur
Department of Physics

December 2022

Declaration

I hereby declare that the work presented in this thesis titled *Colloidal Quantum Dots Nanocomposites Based Resistive Switching for Low-Power Resistive Random Access Memory* submitted to the Indian Institute of Technology, Jodhpur in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work carried out under the supervision of Dr. Satyajit Sahu. The contents of this thesis in full or in parts, have not been submitted to, and will not be submitted by me to any other Institute or University in India or abroad for the award of any degree or diploma.



Jayanta Bera
P17PH001

Certificate

This is to certify that the thesis titled *Colloidal Quantum Dots Nanocomposites Based Resistive Switching for Low-Power Resistive Random Access Memory,* submitted by Jayanta Bera (P17PH001) to the Indian Institute of Technology, Jodhpur for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work done by him under my supervision. To the best of my knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.



Satyajit Sahu
Ph.D. Thesis Supervisor

Acknowledgements

At first, I express my gratitude to my Ph.D. thesis supervisor, *Dr. Satyajit Sahu*, for mentoring and introducing me to the area of technical writing and its nuances. In the process, I have learnt many technical and non-technical aspects of professional work. I am grateful to him for his help and support in performing experimental and theoretical research work as well as for constantly reminding me to be perfect in the little things that I do each day. Beside research works, he has always motivated and supported me from his energy level and upfront work style. He will always remain a source of inspiration for me.

Also, I am indebted to the members of the doctoral committee, *Dr. Mahesh Kumar, Dr. Ambesh Dixit* and *Dr. Durgamadhab Mishra*, for their enthusiastic and continued guidance during the research work.

I would like to thank *Dr. Satyajit Sahu, Dr. Ambesh Dixit, Dr. Ritu Gupta and Dr. Neha Sardana* for their classes during course work period, which helped me to overcome the tough times during the doctoral program. I would like to thank our research collaborators*, Dr. Arup Kumar Rath, Dr. Ashish Sharma, Dr. Uday Shankar and Dr. Anasuya Bandyopadhyay* for helping me to acquire some of the characterizations data of the materials. I would like to thank the Director of IIT Jodhpur for all supports towards the research culture.

I would like to thank my seniors *Dr. Giriraj Vyas* and *Dr. Parveen Dagar*, who always treated me like their younger brother and discussed several aspects of technical and non-technical findings. They also helped me in gaining various laboratory skills.

Lab mates, colleagues and friends have been an integral part of a long, enjoyable learning and continuous journey of the PhD scholar life. I would like to thank my research group members *Atanu Betal, Dibyajyoti Saikia, Anupam Chetia* and *Chayan Das* along with whom I enjoyed the company and skill transferred on various research problems. My stay at the Institute was a wonderful experience because of my friends and juniors, *Amit kumar Shringi, Vivek Thapa, Abhijeet Kale, Chandra prakash, Ramavatar, Kiran, Rakesh Rosan Pradhan, Arun Jangir, Vishal khandelwal, and Nilesh Dalla* for all the liveliness they infused into the non-academic part of the days at IIT Jodhpur.

I acknowledge and thank my family, especially my mother *Uma Bera*, for the patience and love with which they ushered on me, and for bearing with me even when I was not spending less time with them. I pay respects to my *parents* for all their love, sacrifices and blessings.

Jayanta Bera
P17PH001

List of Figures

Figures	*Title*	*page*
1.1	Classification of semiconductor memory technology	*2*
1.2	Basic structures of (a) DRAM and (b) SRAM	*2*
1.3	Basic structure and operation of a flash memory	*3*
1.4	Current memory hierarchy in terms of storage density, operational speed and cost per bit	*3*
1.5	Basic structure of (a) FERAM, (b) PCM and (c) MRAM	*4*
1.6	Structure of an RRAM device with (a) vertical configuration and (b) lateral configuration	*6*
1.7	(a) Unipolar resistive switching and (b) bipolar resistive switching	*6*
1.8	(a) Migration of active metal ions when a positive bias is applied to the active metal electrode. (b) Formation of the conductive filament by active metals when sufficient voltage to the active metal electrode is applied. This is the SET process where the current is high because of the formation of conductive filament. (c) Rupture of CF when a reverse bias is applied and RESET process occurs at this stage	*7*
1.9	(a) Trapping of electrons in the active layer when the top electrode (TE) is positively biased. The active layer is a composite of nanoparticles and polymer. (b) When voltage is increased further, all the traps are almost occupied by the electrons and they can offer a conductive path across the active layer and the SET process occurs. (c) Application of an opposite polarity bias will extract the electrons from traps and the conductive path will be completely destroyed, which will give rise to the RESET process	*7*
2.1	Schematic illustration of the synthesis procedure of semiconducting MSe (M = Cd, Pb etc.) QDs	*18*
2.2	The photograph of (a) the Schlenk line setup and (b) centrifuge setup	*19*
2.3	Schematic of the synthesis procedure of MS_2 (M = Mo and W) QDs	*20*
2.4	Schematic of the (a) spin coating process and (b) photograph of the spin coater	*21*
2.5	Schematic of the (a) X-ray diffraction in lattice plane, (b) working principle of an X-ray diffractometer and (c) photograph of a commercial X-ray diffractometer	*21*
2.6	Schematic of the generation of (a) X-ray photoelectron, (b) Auger electron [Leng, 2009] and (c) schematic diagram of XPS instrument (Watts 1990).	*22*
2.7	Schematic of the generation of different types of signals by electron-sample interaction	*24*
2.8	(a) Schematic diagram of the working principle of SEM [Inkson, 2016] and (b) photograph of a commercial FESEM	*25*
2.9	(a) Schematic diagram of the working principle of TEM [Inkson, 2016] and (b) photograph of a commercial TEM	*25*
2.10	(a) Schematic diagram of the working principle of AFM [Ali, 2012] and (b) - (c) photographs of a commercial AFM	*27*
2.11	(a) Schematic diagram of the working principle of STM [Debata et al., 2018] and (b) photograph of a commercial Omicron LT STM	*27*
2.12	Schematic diagram of the working principle of absorption spectrometer and (b) – (c) photographs of a commercial UV-VIS spectrometer	*29*
2.13	(a) Schematic diagram of the working principle of fluorescence spectrometer and (b) photograph of a commercial fluorescence spectrometer	*30*
2.14	Photograph of the (a) electrical characterization setup and (b) two probe system with micro positioner (c) substrate heater controller unit and (d) sample stage heater setup	*31*
3.1	Synthesis procedure of colloidal CdSe QDs using the hot injection method. The injection temperature was 225 °C. The CdSe QDs were precipitated using acetone.	*35*
3.2	(a) Device architecture of only CdSe-based device where CdSe is sandwiched between the top aluminum and bottom ITO contacts. (b) The architecture of the device where the active material is a composite of CdSe QDs and PVP sandwiched between the upper Al and lower ITO contacts.	*36*
3.3	(a) Absorption spectra of CdSe quantum dot synthesized at 225 °C. A sharp absorption peak was observed at 523 nm. The inset shows the Tauc plot where the slope to the first peak and the band gap is the value corresponding to the intersection of the tangent (black	*37*

line) and energy axis. (b) XRD pattern of the CdSe sample with peaks corresponding to (111), (220), and (311) planes.

3.4 HR-TEM images of the quantum dots synthesized at 225 °C. (a), (b), and (c) represent the images for quantum dots synthesized at 225 °C. The corresponding scale bar is 50 nm. (d) Particle size distribution of the quantum dots, which fits the Gaussian distribution. (e) EDX spectra of the quantum dots show the presence of Cd and Se elements and the corresponding weight and atomic percentages. *38*

3.5 (a) AFM image of CdSe quantum dot film prepared by dispersing in toluene with a concentration of 5 mg/mL over a glass slide. The scan area is 5 μm × 5 μm with a scale bar of 2 μm. The RMS roughness from the surface is 7.67 nm. The line profile is shown on the right side. (b) AFM image of the CdSe QDs- PVP nanocomposite film over the glass surface. The scan area is 5 μm × 5 μm. The scale bar represents 2 μm. The RMS roughness from the surface is 1.07 nm. The line profile is shown on the right side. *39*

3.6 (a) *I–V* characteristic curve for the CdSe+PVP composites device scanned between −2 and 2 V in successive loops. The threshold where the current jumps from the low current to the high current state is shown by an upward arrow in the first quadrant and is called the SET condition, whereas the threshold where the current jumps from the high conducting state to the low conducting state is shown by the upward arrow in the third quadrant and is called the RESET condition. The inset shows the I_{ON}/I_{OFF} of the CdSe+PVP composites device with the highest I_{ON}/I_{OFF} of 10^5. The lower inset shows the *I–V* characteristic of the only CdSe-based device without PVP (b) The low and high conducting states of the CdSe+PVP composites device in the forward bias plotted with both the axis in log scale are fitted. In the high conducting state, the current varies linearly, whereas the low conducting state current has multiple slopes. *39*

3.7 (a) Random-access memory (RAM) study was performed by writing at 3 V and erasing at −3 V and then reading the states at 0.5 V. The write, erase and read voltages were applied for 6 s each. (b) Read-only memory study of the device with the average on (grey) and off (yellow) state currents. (c) The response speed of the device was tested by applying a square wave pulse of 4 V_{p-p}. (d) Endurance of the device was tested by observing the stability of the on and off state currents for more than 1000 *I–V* cycles. *41*

3.8 (a) Schematic of the distribution of energy levels of PVP and CdSe quantum dots along with the corresponding work functions of the metal contacts. (b) Alignment of energy levels with applied moderate forward bias. (c) Alignment of energy levels with very high positive voltage. (d) Alignment of energy levels with moderate negative voltage. (e) Alignment of energy levels with high negative voltage. *42*

4.1 Schematic of synthesis and cleaning procedure of CdSe QDs by the hot-injection method. The inset shows the TEM image of synthesized QDs. *47*

4.2 The illustrative representation of Al/CdSe-PVP/Al resistive memory device along with the electrical characterization set-up. *48*

4.3 (a) XRD spectra of CdSe QDs. The peaks at 25°, 42.50°, and 49.70° correspond to (111), (220), and (311) planes. (b) and (c) XPS spectra of CdSe where the $Cd3d_{5/2}$ and $Cd3d_{3/2}$ states have a binding energy of 406 eV and 413 eV, respectively and Se3d has a binding energy of 55.58 eV. (d) Absorption spectra (shown by red curve) and PL spectra (shown by green curve) of synthesized CdSe QDs. A sharp peak at 538 nm in absorption spectra and a sharp emission peak at 552 nm indicates the synthesis of high-quality monodispersed QDs. The Tauc plot has been shown in the inset. *50*

4.4 (a) Photographs of as prepared CdSe QDs dispersed in toluene under ambient light and UV light. Strong green emission can be seen when the red color CdSe QDs solution was illuminated by UV light. (b) PL emission spectra and (c) integrated PL intensity Vs absorbance graph of CdSe QDs with four different concentrations in toluene. (d) PL emission spectra and (e) integrated PL intensity Vs absorbance graph of fluorescein dye with four different concentrations in DI water. *51*

4.5 (a) STM image and (b) STS spectra of CdSe QDs. *51*

4.6 (a) AFM image with line profile of CdSe QDs film deposited on a glass substrate. (b) The AFM image with line profile of CdSe QDs blended in PVP matrix deposited film on a glass substrate. *52*

4.7 (a) TEM image of the synthesized QDs with a scale bar of 100 nm (b) enlarged view with a scale bar of 50 nm. (c) EDAX spectra for elemental mapping of CdSe QDs in TEM. A slightly larger atomic percentage of Cd indicates that the surface of synthesized CdSe QDs is Cd *53*

rich. (d) Size distribution curve fitted by Gaussian function indicating Gaussian distribution. The average size of the QDs has been found to be 3.56 nm from the curve. (e) Cross-sectional view of the Al\CdSe-PVP\Al device taken by FESEM. Four distinct layers of top Al, CdSe-PVP, bottom Al and glass were clearly visible. Al, CdSe-PVP and glass are marked with white, red and blue colors, respectively, for illustration purposes only and the scale bar is 500 nm.

4.8 (a) Full energy range UPS spectra and magnified (b) low energy onset region (c) high energy secondary cut-off region in UPS spectra of CdSe QDs. (d) Full energy range UPS spectra and magnified (e) low energy onset region (f) high energy secondary cut-off region in UPS spectra of PVP. 54

4.9 (a) I-V characteristics of the fabricated Al\CdSe-PVP\Al device in linear scale within a voltage range of -0.8V to +0.8V. The green arrow indicates the SET process and the red arrow indicates the RESET process. The I-V characteristic in a semi-log scale has been shown in the inset. (b) I-V characteristics in semi-log scale for 1st, 50th, 100th and 150th switching cycles. (c) The variation of SET and RESET voltage with a number of switching cycles. (d) The variation of I_{ON}/I_{OFF} with applied voltage for 1st, 50th, 100th and 150th switching cycles. 55

4.10 (a) The device's endurance test is performed by recording the current in the on and off states at +0.4 V for 150 switching cycles. (b) The retention characteristic of the device at +0.4 V. The device retains its on and off states with an on-off ratio > 10^4 for more than 35,000 s. (c) RAM characteristic of the device. A sequence of pulses "erase (-1V) → read (+0.4 V) → write (+1V) → read (+0.4 V)" with a pulse width of 6 s each was applied. An enlarged view of one cycle has been shown on the right-hand side where E, R and W represent erase, read and write, respectively. (d) Response time of the device by applying a square wave pulse with a pulse width of 50 µs in the device and the output signal was recorded. 57

4.11 The I-V characteristics of Al/PVP/Al device with a voltage range of (a) -0.8 V to +0.8 V and (b) -3V to +3V. The Al/PVP/Al device does not show any resistive switching. 57

4.12 (a) log (I) vs log (V) curve for the positive half cycle. This curve has four distinct regions indicated by A, B, C and D. In the OFF state, $\log(I) \propto V^{1/2}$ indicates conduction due to thermally excited carriers and $I \propto V^2$ suggests the SCLC mechanism. In the ON state, $I \propto V$ indicates ohmic conduction. (b) $\log(I)$ vs $V^{1/2}$ plot in the voltage range 0 V to 0.44 V in the OFF state. In this region $\log(I) \propto V^{1/2}$. 58

4.13 The energy band diagram at (a) zero bias where the HOMO and LUMO energy levels of CdSe QDs are shown by green block and red block, respectively. (b) low positive bias where conduction takes place due to few thermally excited hot electrons and (c) high positive bias where all the trapping centers are almost occupied by electrons and conduction is due to the SCLC process. As all the trapping centers are almost filled by electrons and if the voltage is further increased, they can generate a local or internal field to form a conductive filament or pathway, which leads to the SET process of the device. (d) Energy band diagram at a high negative voltage where de-trapping of the electrons from trapping centers completely destroys the conductive pathways and the RESET process occurs. 60

5.1 Schematic illustration of the synthesis procedure of MoS_2 QDs. 64

5.2 Schematic representation of the device structure. 65

5.3 (a) XRD pattern of MoS_2 QDs. XPS spectra with curve fitting of (b) Absorption spectra of MoS_2 QDs and the inset shows Tauc plot to determine the band gap. (c) Mo 3d and (d) S 2p states of as-synthesized MoS_2 QDs. (e) AFM image of MoS_2 QDs with line profile. 66

5.4 TEM image of MoS_2 QDs (a) with 20 nm scale bar (b) magnified image with 10 nm scale bar (c) statistical size distribution curve with Gaussian fitting as measured from TEM image. Mean diameter of 4.43 nm has been obtained from the size distribution curve (d) HRTEM image of a single QD with clearly visible lattice fringes. The lattice spacing of 0.256 nm and 0.228 nm correspond to (100) and (110) planes which were confirmed from the (e) SAED pattern. (f) FESEM image of a cross-sectional view of the fabricated device. The Top Al layer, an active layer of MoS_2-PVP and the bottom ITO layer is clearly visible from the FESEM image. 67

5.5 (a) Full energy range UPS spectra and magnified (b) low energy onset region (c) high energy secondary cut-off region in UPS spectra of MoS_2 QDs. (d) Full energy range UPS 68

spectra and magnified (e) low energy onset region (f) high energy secondary cut-off region in UPS spectra of PVP.

5.6 (a) I-V characteristic curve of the MoS_2 QDs-PVP device. The inset shows the variation of I_{ON}/I_{OFF} with applied bias. (b) Endurance plot at a read voltage of −0.6 V (c) Retention characteristic of the device at a read voltage of −0.6 V (d) "write-read-erase-read" sequence of the device where the enlarged view of a single complete operation is shown on right hand side. *70*

5.7 I-V characteristic curve of the MoS_2 QDs-PVP device at (a) RT, 40 °C, 50 °C, 60 °C, and 70 °C, (b) 80 °C, 90 °C, 100 °C, 120 °C and 130 °C. (c) Response time of the device by applying a square wave pulse of 2 V (V_{pp}) with a pulse width of 50 µs. (d) The I-V characteristic of pure PVP-based (Al\PVP\ITO) device. The pure PVP-based device does not exhibit significant resistive switching. *71*

5.8 (a) The$\log(I)$ vs $\log(V)$ plot of the device for the positive sweep. (b) The $\log(I)$ vs $V^{1/2}$ plot in the voltage range 0.18 V to 0.53 V in the OFF state and in this region $\log(I) \propto V^{1/2}$. *72*

5.9 The energy band diagram of the device at (a) zero bias (b) small positive bias where electrons are getting trapped by the MoS_2 QDs (c) high positive voltage and SET process, where a conductive channel through the PVP matrix is established as most of the vacant cites, were already filled by injected electrons (d) negative bias where breaking of the conductive channel occurs and conduction is due to the release of the trapped charges from the trapping centers. *73*

A1 The interface of the LabVIEW program "Sweep with Log" to acquire the I-V curves. *79*

A2 The interface of the LabVIEW program "Retention long run" to acquire the retention characteristic of the device. *80*

A3 The interface of the LabVIEW program "Read-Write-Erase" to acquire "Erase-Read-Write-Read" data of the device. *80*

List of Tables

Table	*Title*	*page*
1.1	Comparison of current memory and emerging memory technologies [Endoh et al., 2016; Wolf et al., 2010]	*5*
1.2	List of different conduction mechanism models.	*8*
4.1	Relevant data of CdSe QDs and fluorescein dye for QY measurement.	*51*
4.2	The obtained value of HOMO and LUMO energy of CdSe QDs and PVP from UPS measurements.	*52*
4.3	Comparison of SET (RESET) voltages, $I_{ON/OFF,}$ retention time and power consumption of different CdSe QDs based memristors with our work	*56*

List of Symbols

Symbol	*Description*
A	Absorbance
Al	Aluminium
Ag	Silver
Au	Gold
α	Absorption coefficient
Br	Bromine
Cu	Copper
°	Degree
°C	Degree Celsius
d	Barrier width
d_{hkl}	Inter planer lattice spacing
E_k	Kinetic energy
E_b	Binding energy
ε	Dielectric constant
ε_m	Molar absorptivity
h	Planck's constant
ħ	Reduced Planck's constant
I	Current
I_L	Intensity of light
I_t	Tunneling current
J	Current density
K_B	Boltzmann constant
L	Path length
λ	Wavelength
m	Order of the diffraction
m*	Effective mass
ms	Millisecond
μ	Mobility of the charge carrier
n	Refractive index
ν	Frequency of the incident photon
nm	Nanometer
ns	Nanosecond
Pt	Platinum
Ø	Barrier height
Q	Quantum yield
q	Elementary charge
S	Sulphur
T	Temperature
T_m	Transmittance
θ	Incident angle
V	Voltage
W	Watt

List of Abbreviations

Abbreviation	*Full form*
8HQ	8-hydroxyquinoline
AFM	Atomic force microscope
AIDCN	2-amino-4,5-imidazoledicarbonitrile
ALD	Atomic layer deposition
Al_2O_x	Aluminum oxide
Alq_3	Tris (8-hydroxyquinoline) aluminum
BE	Bottom electrode
BIP	Imidazole-[4,5-b] phenazine
BRS	Bipolar resistive switching
CdO	Cadmium oxide
CdS	Cadmium Sulfide
CdSe	Cadmium Selenide
CF	Conductive filament
CMOS	Complementary metal oxide semiconductor
CPU	Central processing unit
$CsPbBr_3$	Cesium lead bromide
Cu	Copper
$CuInS_2$	Copper indium sulfide
DDQ	2,3-Dichloro-5,6-dicyano-*p*-benzoquinone
DDT	1-dodecanethiol
DI	Deionized water
DRAM	Dynamic random access memory
EDX	Energy dispersive X-ray
eV	Electron volt
FERAM	Ferroelectric random access memory
FESEM	Field emission scanning electron microscope
FN	Fowler–Nordheim
FTO	Fluorine doped tin oxide
GO	Graphene oxide
hBN	Hexagonal boron nitride
HDD	Hard disk drive
HOMO	Highest occupied molecular orbital
HOPG	Highly oriented pyrolytic graphite
HRS	High resistance state
HRTEM	High resolution transmission electron microscope
In_2O_3	Indium oxide
InP	Indium phosphide
IoT	Internet of things
ITO	Indium tin oxide
LBL	Layer by layer
LED	Light emitting diode
LUMO	Lowest unoccupied molecular orbital
LRS	Low resistance state
$MAPbBr_3$	Methyl ammonium lead bromide
MgO	Magnesium oxide
MIM	Metal-insulator-metal
MMT	5-mercapto-1-methyl tetrazole

MnO_x	Manganese oxide
MoS_2	Molybdenum di sulfide
µW	Micro watt
MRAM	Magnetic random access memory
$(NH_4)_2MoS_4$)	Ammonium tetrathiomolybdate
NiO	Nickel oxide
NP	Nano particle
NPB	N,N′-di(naphthalen1yl)-N,N′-diphenyl-benzidine
NPS	3,3′-dinitro-diphenylsulfone
NVM	Nonvolatile memory
nW	Nano watt
OA	Oleic acid
OAM	Oleyl amine
ODE	1-octadecene
OXD	Oxadiazole
P3HT	Poly(3-hexylthiophene-2,5-diyl)
PAM	Polyazomethine
PANI	Polyaniline
PbS	Lead sulfide
PCM	Phase change memory
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PEG	Poly (ethylene glycol)
pEGDMA	Poly(ethylene glycol dimethacrylate)
PET	Polyethylene terephthalate
PFCz-NH_2	Poly[(9,9-dioctylfluorene)-alt-(4-amino-phenylcarbazole)]
PL	Photoluminescence
PMMA	Polymethyl methacrylate
PMSSQ	Polymethylsil-sesquioxane
PVA	Polyvinyl alcohol
PVK	Poly(9-vinylcarbazole)
PVP	Poly(4-vinyl pyridine)
PVPOH	Poly(4-vinylphenol)
PVPY	Polyvinylpyrrolidone
pW	Pico watt
P3BT	poly(3-butylthiophene)
QD	Quantum dot
RAM	Random access memory
RMS	Root mean square
RS	Resistive switching
RRAM	Resistive random access memory
RT	Room temperature
SAED	Selected area (electron) diffraction
SCLC	Space charge limited current
Se	Selenium
SEM	Scanning electron microscope
SRAM	Static random access memory
SSD	Solid state drive
STM	Scanning tunneling microscope
STS	Scanning tunneling spectroscopy
TaO_x	Tantalum oxide
TE	Top electrode
TEM	Transmission electron microscope

TiO_2	Titanium oxide
TMO	Transition metal oxide
TPA	Triphenylamine
TPAPAM	Arylamine polyazomethine
UPS	Ultraviolet photoelectron spectroscopy
URS	Unipolar resistive switching
USB	Universal serial bus
UV	Ultraviolet
WORM	Write once-read many times memory
WRER	Write-read-erase-read
WS_2	Tungsten di sulfide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZnO	Zinc Oxide
ZnS	Zinc Sulfide
ZnSe	Zinc Selenide
Zn_2TiO_4	Zinc titanate
ZrO_2	Zirconium dioxide