Multifunctional polymer nanocomposite thin films for tunable optoelectronics and flexible memory device applications

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Chapter 7

Summary and future scope

The study in Chapter 3 & 4 demonstrates biomimetic self-assembly of anisotropic semiconducting nanoclusters composed of ZnO Quantum Dots and its hybrid nanocomposites with optically transparent Polymethyl methacrylate matrix. The self-assembly obeyed non-classical crystallization mechanism where organic ligand conjugated nanocrystals grew into lattice aligned nanoclusters. Diethanolamine molecules incorporated themselves during the mesoscopic crystal growth and were part of the final crystal structure which is counterintuitive to the bulk ion by ion crystal growth. The oriented attachment (OA) process resulted in precisely aligned quantum dots possessing preferential orientation along <100> plane. Golic et al. [170] synthesized self-assembled ZnO nanostructures by sol gel method without surface modification and did not observe any preferred lattice alignment thus establishing the significant role of DEA in Oriented Attachment mechanism achieved in our work. Owing to the unique structure and surface engineering, the colloids exhibited excellent long-term physico-chemical stability as evident from the DLS and Zeta potential studies. The final nanoclusters, even though 40-50 nm in size, retained the quantum characteristics of individual quantum dots and displayed size-dependent, tunable optical properties such as the wavelength of PL emission, blue shift of absorption shoulder and band gap energy which is a unique observation, characteristic of mesocrystal morphology and cannot be obtained in bulk nanostructures. Eita et al. [135] prepared spin-coated ZnO/PMMA thin films but did not observe quantum confinement effects in the band structure and obtained an E_g value of 3.34 eV while the nanoclusters in our work displayed strong confinement with a blue-shift in band-gap energy to 3.54 eV. Surface morphology of mesocrystals implied a porous microstructure with highly enhanced effective surface area compared to bulk nanoparticles of similar size range. A large number of surface defects were induced in the nanoclusters owing to the unique crystallization mechanism which was experimentally confirmed by the sharp green PL emission peak with a narrow bandwidth. Diethanolamine moiety played a significant role in (a) Crystal growth and alignment, (b) Colloidal stability by altering the surface potential and (c) Promoting strong interfacial interactions between chemically opposite polar ZnO and non-polar PMMA phase. Such strong chemical bonding was absent in unmodified ZnO/PMMA nanocomposites prepared by Singh et al. [187] and Chen et al. [116] which also led to agglomeration of nanostructures in the matrix as observed in the electron microscopy images.

Topographical and morphological surface studies by AFM and FE-SEM techniques confirmed the homogenous dispersion of nanofillers in the polymer matrix without any agglomeration which is necessary to prevent loss of transparency in the resulting hybrids. Surface roughness measurements gave extremely low roughness values, 0.179 nm and 2.905 nm for pristine PMMA and PMMA/ZnO nanocomposite thin films respectively. Eita et al. [135] obtained RMS roughness of nanocomposites ranging from 3.6 nm to 8.4 nm while Chen et al. [116] measured a RMS value 6.6 nm and avg. value 5.1 nm. A highly uniform, smooth morphology achieved in our work was attributed to several factors: (a) Surface plasma treatment of Si substrates, (b) High rpm spin-coating and (c) Excellent surface and interfacial properties bestowed by diethanolamine mediated chemical interactions between the organic and inorganic phase. XPS binding energy curves quantitatively studied the surface and interfacial chemistry of nanocomposite films. C1s spectra observed a shift in O-C=O peak attributed to hydrogen bonding between the carboxyl group and DEA-capped ZnO surface and an additional peak was observed in N1s spectra at 401.1 eV which could be attributed to the covalent bond (N-C=O) between PMMA chains and DEA molecules. The existence of chemical interactions at the interface provide evidence of the nanocomposite surface's excellent stability, which could efficiently enhance the performance and durability of thin film-based devices and coatings.

The amalgamation of functionalities imparted by unique ZnO nanoclusters and PMMA matrix results in truly multifunctional hybrid nanomaterials with superior surface and interfacial properties, enhanced surface area/absorption cross-section, tunable optical properties, excellent long-term colloidal stability and broad range UV absorption capabilities. The surface defect engineered nanoclusters with porous morphology combined with the ease of processing, hydrophobicity and flexibility of polymer could find application in high performance gas sensors, UV shielding surface coatings, flexible and tunable organic LED’s and photocatalytic degradation of organic pollutants in water [197] which would also benefit from the immobility of nanostructures. Inexpensive, non-toxic raw materials, cost-effective low temperature synthesis and facile method with high repeatability would further enhance the scalability of these biomimetic mesocrystal based nanocomposites from research to industrial scale.

The study in Chapter 5 & 6 presents a new high performance and remarkably flexible RRAM device based on polymethyl methacrylate embedded reduced graphene oxide/zinc oxide heterostructures as the switching layer, fabricated on Indium tin oxide coated flexible PET substrate. The multifunctionality bestowed by the polymer embedded heterostructure system renders the device with excellent electrical properties. Hybrid organic-inorganic device architecture exploits the synergistic effects of the hole blocking property of large band-gap PMMA, excellent charge trapping and transport capabilities of reduced graphene oxide, and high electron mobility of ZnO nanostructures. Owing to this multifunctional design, the device exhibits an excellent current ratio of ~10^6 between the HRS and LRS which significantly increases the reliability of the read/write operation. Owing to reduced operating voltages VSET/VRESET -1.7/+1.98, the power consumption of the device is radically decreased thus facilitating its application in low power portable and wearable electronics. Furthermore, the device displays good endurance and retention characteristics, with no significant degradation for more than 50 switching cycles and a high retention time of ~ 10^4 seconds. Double logarithmic I-V plot indicated Ohmic, SCLC and TCLC to be the major conduction mechanisms. Band gap modelling of the hierarchical device architecture successfully explained the switching operation and non-volatile bistable memory characteristics through trap controlled SCLC mechanism and FN tunneling.

For practical applications, mechanical stability is also an extremely critical parameter. Hence, comprehensive flexibility studies were carried out and the device exhibited outstanding electrical performance under various applied mechanical stresses. A highly stable memory operation was achieved even for an extreme bending radius of 6mm. The device showed minimal degradation after more than 1000 bending cycles and a high current ratio, similar to the one in flat configuration, was also achieved for a critical bending radius of 6mm. The proposed device has the potential to be used in a wide range of applications, including flexible electronics, low-power devices, and high-density memory storage. The simple and inexpensive, solution-processed spin coating fabrication process and compatibility with large-scale production make this device a promising candidate for future memory technology.

Concluding Remarks

- Biomimetic self-assembly of lattice-aligned, highly anisotropic semiconducting ZnO nanoclusters high a Zeta potential (~ 46mV) and excellent long-term physico-chemical stability.
- Polymer nanocomposite thin films with radically enhanced interfacial interactions and size-dependent optoelectronic properties for UV shielding and Photocatalytic applications.

- Highly flexible non-volatile resistive memory device based on PMMA embedded r-GO/ZnO NP heterostructure with low operating voltage range (-2V/+2V) and extremely high current ratio of 10^6

- Excellent flexibility performance of the device with a critical bending radius of 6mm and a bending endurance of 1000 cycles.

Future Scope

The results and findings presented in this thesis open several avenues for further research and potential applications. Here are some key areas where future work can be directed:

Enhanced Functionalization of Nanoclusters:

- Surface Engineering: Further exploration of surface functionalization techniques can optimize the physico-chemical properties of ZnO quantum dots and their hybrids, enhancing their performance in various applications.
- Ligand Studies: Investigating different organic ligands besides diethanolamine (DEA) could uncover new pathways for achieving superior colloidal stability and tailored optical properties.

Application-Specific Modifications:

- Gas Sensors: Tailoring the surface properties and defect density of ZnO nanoclusters for specific gas sensing applications, focusing on selectivity and sensitivity improvements.
- UV Protection Coatings: Developing UV protection coatings with enhanced durability and efficiency for various industrial applications, such as automotive and aerospace industries.

Flexible Electronics:

- Flexible Memory Devices: Further optimization of the RRAM device architecture for improved performance metrics, including endurance, retention, and power consumption, under various mechanical stresses.
- Wearable Technology: Exploring the integration of these flexible memory devices into wearable technology, focusing on durability and functionality under real-world conditions.

Theoretical Modelling and Simulation:

- Computational Studies: Conducting detailed theoretical modelling and simulation studies to predict and optimize the properties and performance of the nanocomposites and devices.
- Machine Learning: Leveraging machine learning algorithms to analyze large datasets from experiments and simulations, accelerating the discovery of new materials and processes.

By addressing these future research directions, the potential of ZnO quantum dots and their hybrid nanocomposites with 2D nanomaterials can be further harnessed, leading to innovative applications and technological advancements in the field of optoelectronics and flexible memory devices.