Sree Sevugan Annamalai College
Devakottai-630 303
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Sivaganga District
Tamil Nadu

Major Research Project-Final Report

Title

Synthesis and characterization of Novel Dilute Magnetic Semiconducting nanostructures for spintronics applications

Principal Investigator

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ENCLOSURE – I

Major Research Project Final Report

Synthesis and Characterization of Novel Dilute Magnetic Semiconducting Nanostructures for Spintronics Applicatons

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Brief Summary

Synthesis of Nanostructures is of immense interest in leading research laboratories. Many costly equipments were needed and they could be synthesized at higher cost for advanced applications. The advent of chemical routes enabled even rural educational institutes to establish simple techniques and deal with most advanced materials at lowcost. This Project endeavoured to synthesis many advanced materials both as thin film and bulk form. The PI and his team developed low cost indigenous set up to grow advanced materials like ZnO, CdO, Cu_2O, CuO, ZrO_2 using low cost methods like Chemical Bath Deposition(CBD), Aqueus Chemical Growth(ACG) and Successive Ionic Layers by Adsorption Reaction(SILAR). They have also used chemical Precipitation Technique and Reflex method to grow the nanostructures in Powder form.Multi layers of these materials were also grown and devices are being fabricated. They have used the facilities available at Alagappa University, CECRI, IGCAR, IIT Chennai, IISC, Kalasalingam University, etc for Characterization. In their own laboratory they have developed a **JIG** for electrical Characterization and purchased Hall effect equipments for probing the magnetic properties. The photovoltaic properties were also estimated by modifying the

purchased equipments. A Gas Sensor has also been developed for estimating the sensitivity of few nanostructures.

The following systems were grown

Metal Chalcogenides Grown used in Spintronics:

ZnO, CdO, CuO, Cu_2O, ZnS, CdS, ZrO_2 Pristine and Doped with Zr, Sr, Pr, Eu, Fe, Ni, Co as thin films and nano Powders.

Multi Layer Grown: Cu_2O/ZnO: CuO/ZnO, CdS/ZnO, CdO/ZnO, ZnS/ZnO

Techniques Used: *Low cost systems like SILAR, CBD, Chemical Precipitation method, Reflex Method*

Devices Fabrication Envisaged: *PV solar cell, Gas Sensors*

The Characterizations studies:

The effects of reaction time on the structural, morphological and the optical properties of the deposited thin films were studied. The samples were subjected to several characterization studies including X-ray Diffraction (**XRD**), Scanning Electron Microscope (**SEM**), **UV/VIS Spectroscopy**, Energy Dispersive Spectroscopy (**EDS**). The thin films exhibits polycrystalline nature with few XRD peaks. It was observed that an increase in the reaction time changed the structural properties of the thin films and nano structures. The intensities of the XRD peaks revealed many valuable structural formation. The SEM of the samples of few systems revealed that the films are solid crystals and are relatively packed as the reaction time increased. The EDS shows that the film phase consisted of respective metallic and non metallic species. High absorbance in the ultraviolet region was observed in systems like metal oxides which also increases with increase in reaction time, the band gap variations with increase in reaction time and other parameters were extensively studied. The results revealed that increase in the reaction time has significant effect on the structural, morphological and optical properties of the deposited metal oxide films. Some studies related to certain structures and their composition using Fourier Transform Infra Red Spectroscopy (**FTIR**), Raman Spectroscopy(**RS**), Photoluminescence(**PL**), Transmission Electron Microscopy**(TEM),** Vibration Segment Magnetometer (**VSM)**, Xray Photoemission Spectroscopy (XPS), Auger Electron Spectroscopy (AES) have been performed and the results are interesting.

Typical interesting findings include the revelations on the influence of the thickness on the structural, optical and photovoltaic properties of few special systems have been studied. For eg. **Cu_2O/ZnO** structure prepared by combination of methods.The results are promising and the feasibility of developing advanced functional materials based devices grown chemically at lowcost have been envisaged for Future Spintronics Applications.

ENCLOSURE – II

PUBLICATIONS

Published in International Journals:

ENCLOSURE – III

Major Research Project Final Report

EXECUTIVE SUMMARY

Synthesis and Characterization of Novel Dilute Magnetic Semiconducting Nanostructures for Spintronics Applicatons

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Executive Summary

Dilute Magnetic Semiconducting oxide thin film and bulk nanostructures have gained renewed interests for highly efficient thin film photovoltaic, spintronics, gas sensors, etc.,. The low cost chemical bath deposition techniques if used to synthesize nanocrystalline thin films onto various substrates like Si, sapphire ITO, polymer and glass substrates it will add to the advancement of Spintronics based device developments. The physical properties of the films that are estimated and compared under normal and annealed conditions add a great deal to this field of research. The objective of this project were to use few low cost techniques like Chemical Bath Deposition,

Solution growth, SILAR and Aqueous Chemical Growth technique for growing valuable and advanced materials both in thin film and bulk nanostructures and were met successfully and the conditions to synthesize advanced materials were arrived successfully were explored for growing desired nanostructures of high quality. The synthesized structures were subjected to characterization employing sophisticated instrumentation facilities available in our country and abroad. The project involved extensive travel, discussions and subsequent analysis that paved way for collaborations. The project added a new dimension to the PI's rural college making it estabilish a nice research laboratory. Few Instruments like SILAR system, Gas analyzer and Four probe resistivity Jigs have been developed indigenously at low cost. The Project enabled collaborations with many laboratories both Inland and abroad.

Aim of the study

The objective of this project was to develop low cost synthesis strategy to prepare nano crystalline metal oxide systems both in powder and thin film forms like Fe: ZnO, CoFeZnO, MgCdO, ZnMgO nano structures and to characterize them using advanced instruments like XRD, SEM, EDAX, Synchrotron radiation, AFM etc.. The studies are to be complimented with theoretical calculations. To use these structures in optoelectronic devices in novel spintronic devices and compare their performances. These studies were essential to understand the basic growth mechanism and to enhance the performance of the devices fabricated with these structures in such applications. Data indicating the preservation of the non-magnetic character of the host materials provide startling new insight in the science of DMS materials. The study is worthwhile and is a need of the hour

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For eg. **Cu_2O/ZnO** structure prepared by SILAR method as described below.

Over Cu_2O layer ZnO thin films were grown by SILAR technique using a solution comprising 0.1 M zinc sulphate, 0.2 M sodium hydroxide of pH value of 9 ± 0.2 at room temperature followed by a dip in water bath of temperature around 90 °C. Before deposition, the glass substrates were cleaned by chromic acid followed by cleaning with acetone. The cleaned substrate was immersed in the chemical bath for a set time followed by immersed in hot water for the same time for hydrogenation. This process of solution dip (step 1) followed by hot water dip (step 2) was repeated for known number of times. The alternative dipping of the substrate in sodium zincate and water baths resulted in the deposition of ZnO on the substrate. The complex layer formed on the substrate during the dipping in sodium zincate bath is changed to ZnO due to dipping in hot water as shown by the following reaction.

$$ZnSO_4 + 2NaOH \longrightarrow Na_2ZnO_2 + H_2SO_4$$

$$Na_2ZnO_2 + H2O \longrightarrow ZnO + 2NaOH$$

For the preparation of Cu_2O layer the copper sulphate pentahydrate ($CuSO_4$, 5H2O), sodium thiosulphate ($Na_2S_2O_3,5H_2O$), and sodium hydroxide (NaOH) were used in an aqueous medium. A 1 M NaOH solution was prepared in a beaker and heated to 70 °C. Separately a solution of copper thiosulfate was prepared by adding 1M $Na_2S_2O_3$ in 1M $CuSO_4$ in the volumetric ratio (5:1) with constant stirring for 10 min. In the first step, the substrate was immersed in the hot NaOH solution for 15 s, and then it was transferred into the copper ion complex solution for 15 s.

For Cu_2O to have different thickness, the reaction period was varied from 10 to 20s with an interval of 5s, After each immersion into anionic and cationic precursors, the substrate were rinsed in a beaker containing double distilled water for 10 sec, so that the unabsorbed ions were removed from the substrate. This immersion cycle was repeated for 50 timesThe results are Photocurrent– voltage measurements were performed using a Keithley 4200 semiconductor parameter analyzer in our collaborating laboratory and the optical illumination was done using a 200 W halogen lamp. The I-V studies were conducted. Preliminary studies were estimated in a set up designed in this project. The results are promising and further studies are under progress. The studies lead to many publications enclosed here with and typical interesting results are presented here.

Typical Results and discussion for Multilayer

Structural characteristics

Fig. 1 shows the XRD spectra of SILAR coated ZnO and Cu_2O films on glass substrate. It can be seen from the XRD data, that the deposited ZnO films samples are polycrystalline exhibiting single-phase ZnO hexagonal wurtzite structure (P63mc space group, JCPDS, 36–1451), whose c-axis is preferentially oriented normal to the glass substrate [17]. X-ray diffraction patterns of three Cu_2O films prepared at 10, 15 and 20s are also shown in Fig. 1. The dominant peak appeared at 36.2° corresponds to (111) plane of cubic Cu_2O [18]. We can see from the diffraction patterns that the peak intensity increases as the number of reaction time increases and this is due to the increase of Cu_2O film thickness for the increased reaction time.

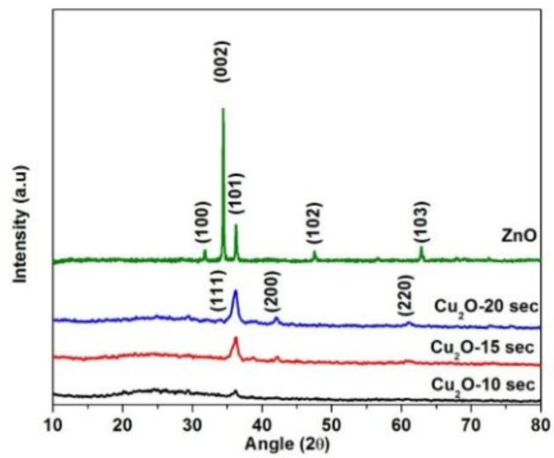


Fig. 1. X-ray diffraction pattern of Cu_2O and ZnO thin films onto glass substrate.

Morphological characteristics

The surface morphology of SILAR coated Cu_2O and ZnO films are shown Fig. 2(a)-(d). It is found that the sample morphology of the film was found to depend on the reaction time. Fig. 2(a)-(c) show the Cu_2O film deposited with different reaction time, they also show morphology of nanorod distributing uniformly on the whole area of the substrate. It has shown large number of grains with well defined particle edges. Fig. 2 (d) shows the ZnO nanorod film, which clearly shows the rod shaped morphology of the films with uniform coverage of the surface. There is no void between the grains, indicating full coverage of the surface, it is also essential for good devices, otherwise the defects and/or residues of coating chemicals could be trapped inside them and thus deteriorate the device performance.

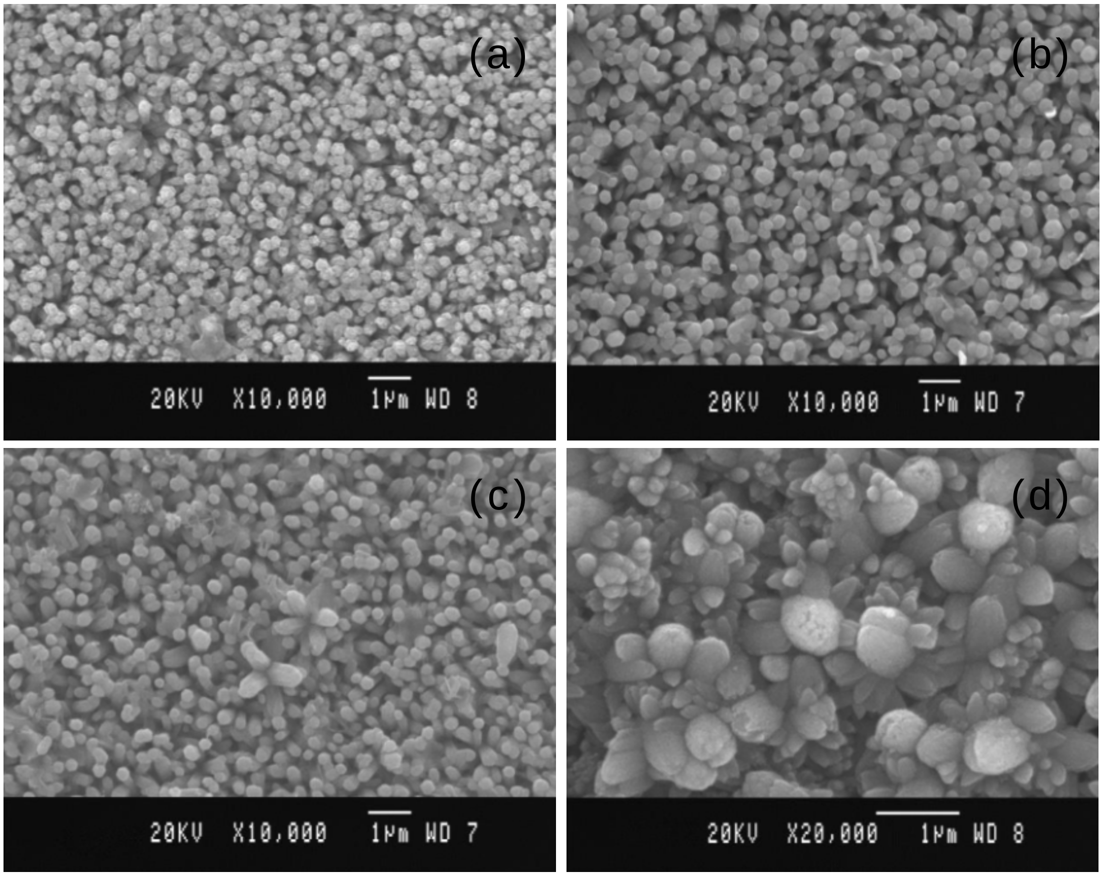


Fig. 2. Scanning electron microscopy image of as-deposited Cu_2O thin film a) 10s, b) 15s and c) 20s and d) ZnO thin film.

Optical characteristics

Optical absorption of Cu_2O films of various thicknesses was obtained as the function of light wavelength and it is shown in the Fig.3. It is clear from the absorption spectrum that the optical absorption edge is observed at around 750–900 nm. The difference in the absorption edge of the three samples is due to the improvement of crystallinity of the films prepared using 10, 15 and 20sec reaction time (samples T1, T2 and T3). It is attributed to the increase of crystallite size and decrease of crystal imperfections due to the increase of reaction time. The optical band gap energies of samples T1, T2 and T3 estimated by extrapolating the linear portion of plot of $(\alpha hv)^2$ *vs. hv (fig 4)* to the energy axis are 2.12, 2.08 and 1.82 eV, respectively. These values are in good agreement with the reported values. Fig. 5 shows the transmittance spectrum of ZnO thin film. It has shown a 78% transmittance, thus making ZnO as a good candidate, as a transparent window in solar cells. The determined energy gap for ZnO thin film is found to be 3.37 eV (fig. 6).

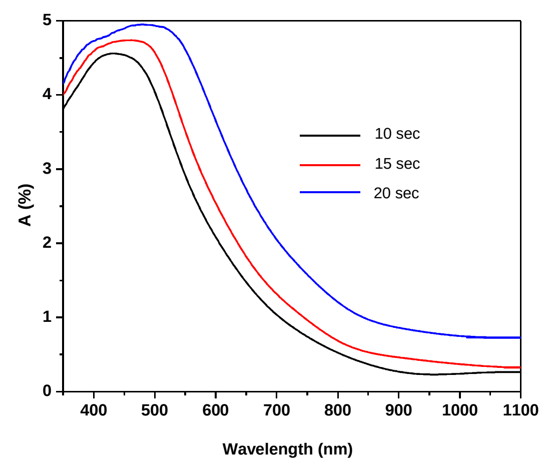


Fig. 3. Optical absorption spectra of Cu_2O film

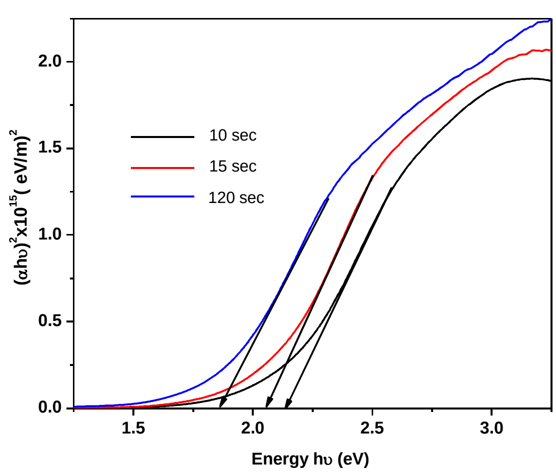


Fig. 4. Plot of $(\alpha h\nu)^2$ (eV^2 cm^{-2}) vs. photon energy (eV) of Cu_2O film

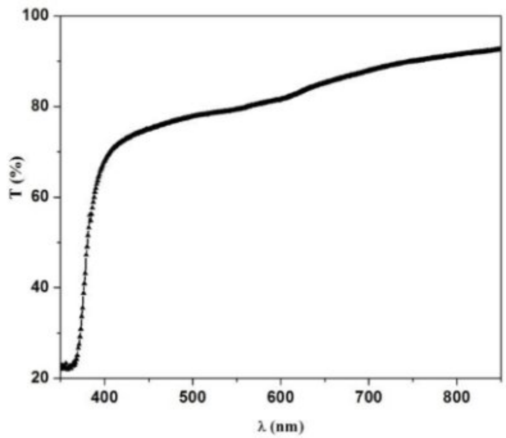


Fig. 5. Optical transmittance spectrum of ZnO film

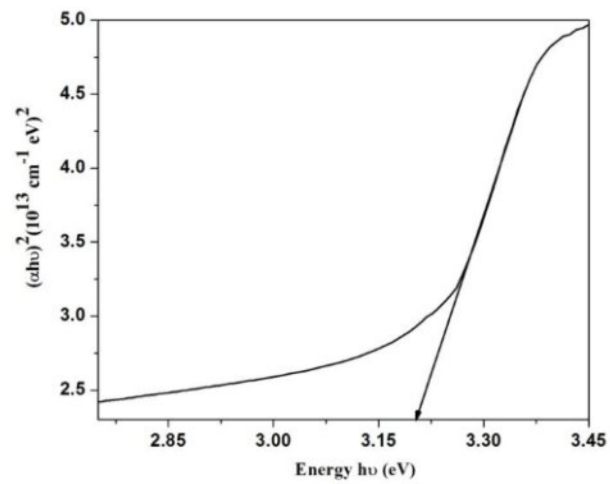
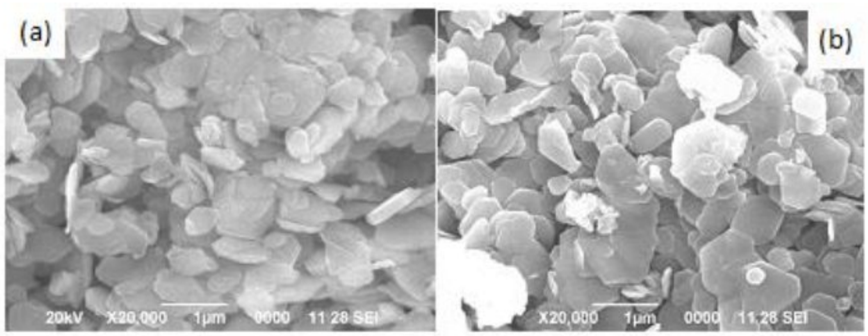
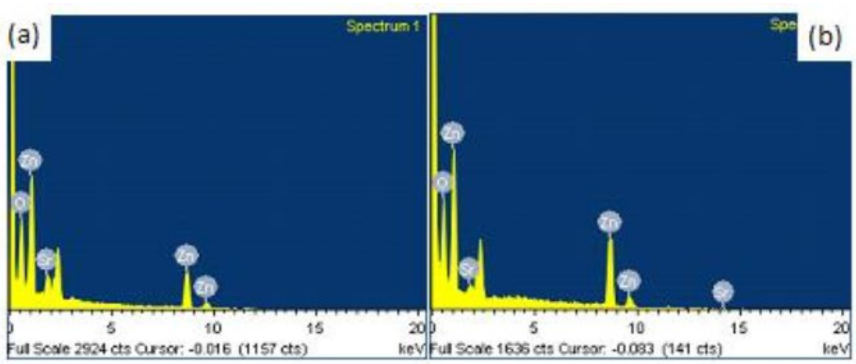


Fig. 6. Plot of $(\alpha h\nu)^2$ ($eV^2\ cm^{-2}$) vs. photon energy (eV) of ZnO film.

Few results of interest like various morphologies obtained for few advanced materials are presented as representative ones. Extensive characterizations studies have been made and are analysed that are partly published and are to be communicated in future.



SEM photograph: (a) ZnO:Sr (5%) and (b) ZnO:Sr (10%)

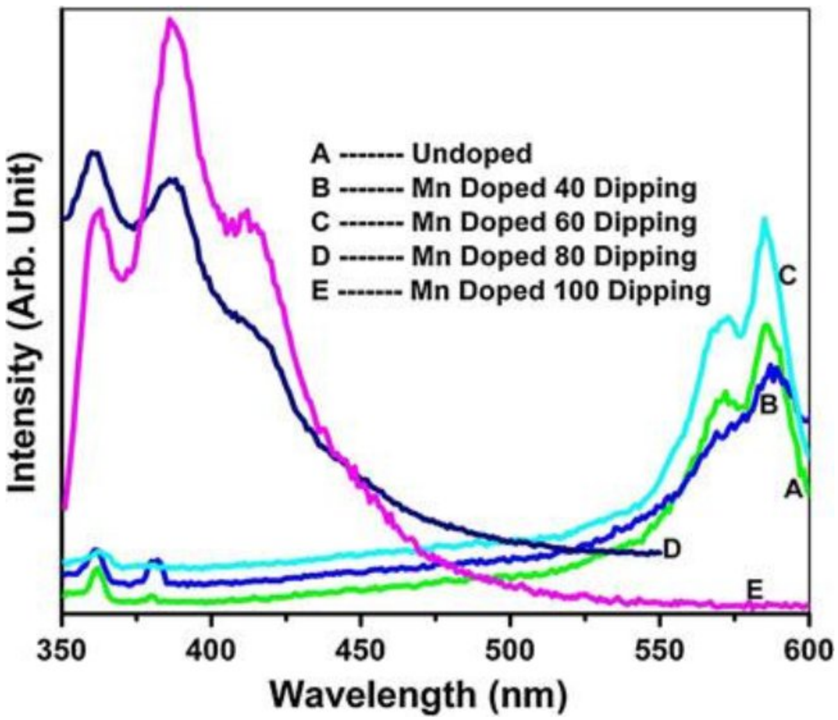


EDX Spectrum (a) ZnO:Sr (5%) and (b) ZnO:Sr (10%)

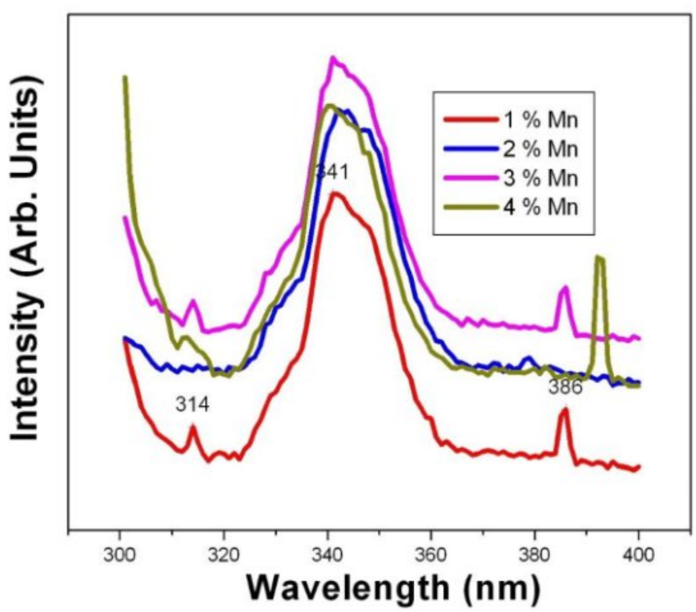
Unit cell parameters	**ZnO:Sr (5%)**	**ZnO:Sr (10%)**
Lattice constant a_0	3.251 Å	3.238 Å
Lattice constant c_0	5.192 Å	5.185 Å
Bond length	1.976 Å	1.971 Å

Second-nearest neighbour distance b'_1	3.214 Å	3.209 Å
Second-nearest neighbour distance b'_2	3.804 Å	3.792 Å
Second-nearest neighbour distance b'_3	3.804 Å	3.792 Å
Bond angle α	108.2602	108.323
Bond angle β	110.655	110.595

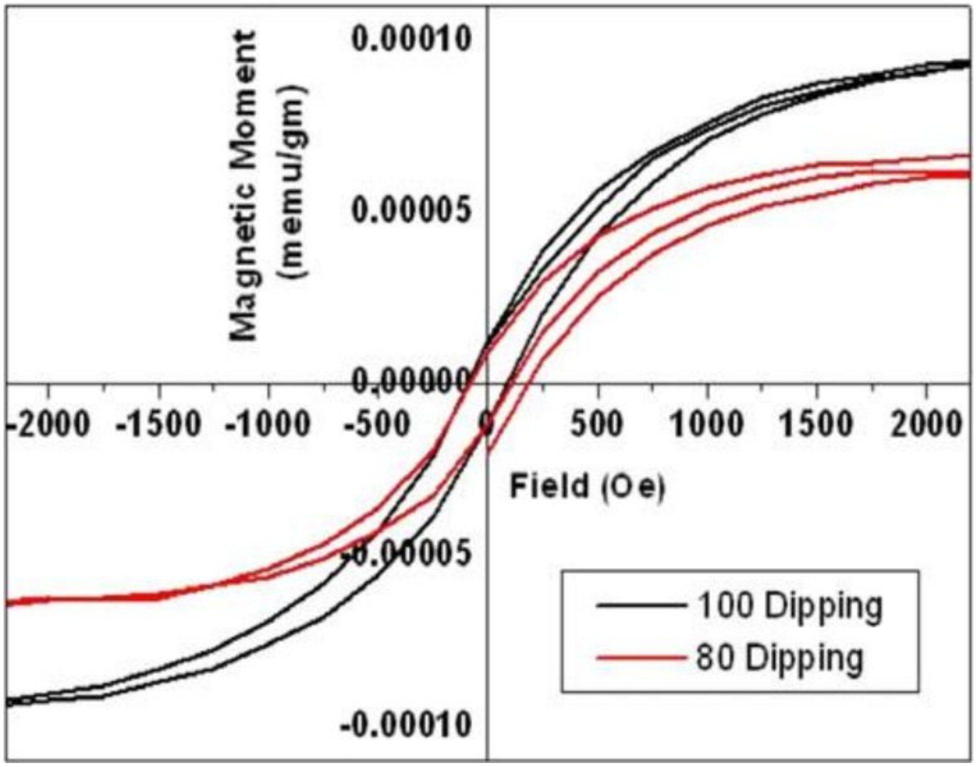
Unit Cell Parameters of Sr:ZnO



A ------- Undoped
B ------- Mn Doped 40 Dipping
C ------- Mn Doped 60 Dipping
D ------- Mn Doped 80 Dipping
E ------- Mn Doped 100 Dipping
Intensity (Arb. Unit)
Wavelength (nm)
350
400
450
500
550
600
A
B
C
D
E



1 % Mn
2 % Mn
3 % Mn
4 % Mn
341
314
386
Intensity (Arb. Units)
Wavelength (nm)
300
320
340
360
380
400



Outcome of this project and Conclusion:

Many advanced materials used in Spinntronics have been grown as nanostructures both in thin film and bulk form using low cost chemical routes. The effect of thickness and bath conditions were studied. The effect of post annealing were also studied. Interesting revelations on the morphology of different valuable systems were obtained. The opportunity to train manpower in this rural part has been enabled by this Major Research Project. Few permanent additions like valuable equipments and chemicals were added to this rural laboratory that motivated install a full fledged PG and research department of Physics in this college. In their own laboratory they have developed a **JIG** for electrical Characterization and purchased Hall effect equipments for probing the magnetic properties. The photovoltaic properties were also estimated by modifying the purchased equipments. A Gas Sensor has also been developed for estimating the sensitivity of few nanostructures. Many collaborations have been established that lead to joint publications in many International journals and presentation in various conferences.

Many Facilities were added:

Special facilities for growth and Characterization, The list includes Microwave heaters, Centrifuge, Furnaces, magnetic stirrers, UV irradiation facility, US cleaner, Ovens, Digital balance, Four Probe resistivity set up at elevated temperatures, Hall effect measurements-2.

Packages Purchased

MAPLE: A software for Analysis of results and advancing the

ORIGIN

The Project Assistant has registered for Ph.D at Alagappa University. Two women faculties with out Ph.D earlier has started doing their research work enthused by the research team. The research laboratory established and supported by UGC partial financed by this Major Research Project supports all PG and Research students in this area. The systems studied under investigation are of latest interst and speculated for future commercial spintronics devces and the results are useful for the R&D of Spintronics.

All this value addition to our college motivated our college for accreditation and the MRP's sanctioned promoted as NAAC 'B" grade rural college with 2.6/4.0. We thank UGC new Delhi for sanction of Major Research Project that made this campus vibrant with research endeavors,

augmenting facilities, upliftment of college and production of many publications. We solicit similar encouragement with future funding for our Institution and faculties.