® International Journal of Research Available at https://edupediapublications.org/journals
e-ISSN: 2348-6848
p-ISSN: 2348-795X
Volume 05 Issue 12
April 2018

INVESTIGATIONS ON SYNTHESIS AND CHARACTERIZATION OF Mn DOPED ZnO THINFILMS AND COBALT DOPED TiO2 THIN FILMS

Mr.G.Sankar[a],Dr.R.Mahendran[b], Dr.P.Anbarasu[c] ,Dr.T.Sivakumar[d]

[a]Assistant Professor, Dept of Electronics, Rathnavel Subramaniam College of Arts and Science, Sulur, Coimbatore, IN
[b]Assistant Professor, Dept of Electronics, Government Arts College, Kulithalai, INDIA
[c]Associate Professor & Head, Dept of Electronics, Government Arts College, Kulithalai, INDIA
[d]Head, Dept of Electronics, Rathnavel Subramaniam College of Arts and Science, Sulur, Coimbatore, INDIA

b
a d

Keywords: SEM Analysis, EDAX Analysis AFM studies, Optical properties, Magnetic Studies (VSM), Structural Properties (XRD).

ABSTRACT: In this paper, Titanium dioxide (TiO_2) is considered as the most desired photocatalyst material due to its superior properties such as high chemical stability without dissolving in acid and alkali, band gap of 3.2eV, rendering it transparent to visible light and low cost. Semiconductor thin films exhibits high electrical conductivity and optical transparency which are most wanted properties in solar cells, flat panel displays ,gas sensors optical waveguides and magneto optic applications. MZO thin films were prepared by sol-gel spin coating method on glass substrates. Zinc acetate dihydrate, 2-Methoxyethanol and Mono-Ethanolamine (MEA) were used as the starting material, solvent and stabilizer respectively. The concentration of Zn acetate was 1.0 M, the molar ratio of MEA to zinc acetate dihydrate was kept as 1: 1 and the molar ratio of dopant Manganese Acetate Tetra hydrate in the solution was 5 wt%. The solution was stirred at 70°C for 1 h. The precursor solution was dropped onto glass substrate which was rotated at 3000 rpm for 30 s. After each coating the films were dried at 300°C for 10 minutes in a furnace . The coating-to-drying process was repeated for 7 times. Finally, the films were annealed at 300°C, 450°C and 500°C for 1 h.

INTRODUCTION

ZnO doped with Mn has also been considered as an ideal material for short wavelength magneto-optical applications due to its wide band gap and the thermal solubility of Mn in ZnO.There are number of reports on the growth of $Mg_xZn_{1-x}O$ thin films using various techniques, the spin coating technique has several distinct advantages, e.g. process simplicity, cost effectiveness and easy thickness monitoring over a very large area.

In this present work, sol-gel spin coating technique was used to prepare Mn doped ZnO thin films and the prepared samples were annealed at different temperatures of 300 C, 450 C and 500 C. The structural, optical and magnetic properties of the prepared samples were analyzed. Most of the reported work mainly correlates with the ferromagnetic properties of Mn-doped ZnO nanostructures and its origin.

TiO2 THIN FILMS:

Nanomaterials are expected to be at the heart of the next technological revolution in solid-state electronics, to emerge as new structural materials, for degradation of pollutants, to serve as systems for controlled drug delivery and to have a considerable impact in particularly all domains of science. The unique functional properties of nanomaterials, such as chemical, optical, magnetic, mechanical, optoelectronic properties have been drastically influencing the direction of development of today's science and technology. Nanomaterials refer to materials with at least one dimension less than 100nm.

EXPRIMENTAL METHOD

The MZO thin films were prepared by sol-gel spin coating method on glass substrates. Zinc acetate dihydrate, 2-Methoxyethanol and Mono-Ethanolamine (MEA) were used as the starting material, solvent and stabilizer respectively. The concentration of Zn acetate was 1.0 M, the molar ratio of MEA to zinc acetate dihydrate was kept as 1: 1 and the molar ratio of dopant Manganese Acetate Tetra hydrate in the solution was 5 wt%. The solution was stirred at 70^oC for 1 h. The precursor solution was dropped onto glass substrate which was rotated at 3000 rpm for 30 s. After each coating the films were dried at 300^oC for 10 minutes in a furnace . The coating-to-drying process was repeated for 7 times. Finally, the films were annealed at 300^oC, 450^oC and 500^oC for 1 h.

EXPRIMENTAL METHOD - TiO2

Pulsed laser deposition (PLD) is a thin-film deposition method, which uses short and intensive laser pulses to evaporate target material. The ablated particles accelerate from the target and condensed on the substrate. The deposition process occurs in vacuum chamber to minimize the scattering of the particles. In some cases, however, reactive gases are used to vary the stoichiometry of the deposition.

PLD method uses a high power laser as an external energy source to vaporize materials and to deposit thin films. In simply rastering the laser spot over the target surface the laser energy excites electrons and then this energy is responsible for thermal, chemical and even mechanical cause of evaporation, ablation, excitation, plasma formation and exfoliation. Evaporation from target consists of mixture of energetic species including atoms, molecules, electrons, ions, and clusters, micro sized solid particulates and molten globules. The “plume” is highly forward directional and rapidly expands into the vacuum from the target surface to form a nozzle jet with hydro flow characteristics. Then the energetic species undergo thermal and non-thermal interactions with substrate and ultimately lead to film formation and grain growth.

CHARECTERIZATION :

The structural properties of the MZO thin films were analyzed using X-ray diffractometer with Cu-K$_\alpha$ radiation (PANalytical X’Pert Pro). The surface morphology of the samples was investigated by scanning electron microscopy, SEM, (Hitachi S-3400N, Japan).Tthe chemical composition was examined using EDAX attachment (Nortan system six, Thermo electron corporation instrument, Super DRY 11, USA) with the SEM unit. The thickness of the films was determined by Surftest SJ-301 stylus profilometer. AFM surface topography (3D images) of ZnO films deposited on glass substrates were observed. For optical characterization, the optical transmittance and obsorbance spectra of ZnO and MZO thin films were recorded using spectrophotometer (Hitachi-3400 UV-Vis-NIR). Laser Raman spectroscopy was carried out by Renishaw invia Laser Raman spectrometer. The magnetic characterizations of Mn doped ZnO thin films were performed using VSM.

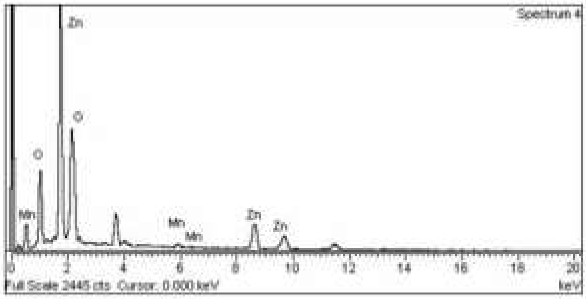
Properties of TiO2

Substochiometric TiO_{2-x} is both a poor insulator and a modest semiconductor. Therefore several attempts have been made either to control the oxygen vacancy concentration or to introduce charge carriers (doping) inside TiO_2 in order to increase or decrease the electrical conductivity, depending on the desired application. During the last 40 years, almost half the atoms of the periodic table have been incorporated into TiO_2. The majority of dopants enhance the *n*-type semiconducting properties of TiO_2.

EDAX Analysis :

The EDAX analysis of MZO shows that the amount of Mn incorporation increased with the increase in Mn concentration and also revealed the dominance of oxygen in all the samples exhibiting oxygen rich stoichiometry of thin films.

® International Journal of Research Available at https://edupediapublications.org/journals
e-ISSN: 2348-6848
p-ISSN: 2348-795X
Volume 05 Issue 12
April 2018



EDAX Analysis of MZO thin film at 450° C

Sol-Gel Method:

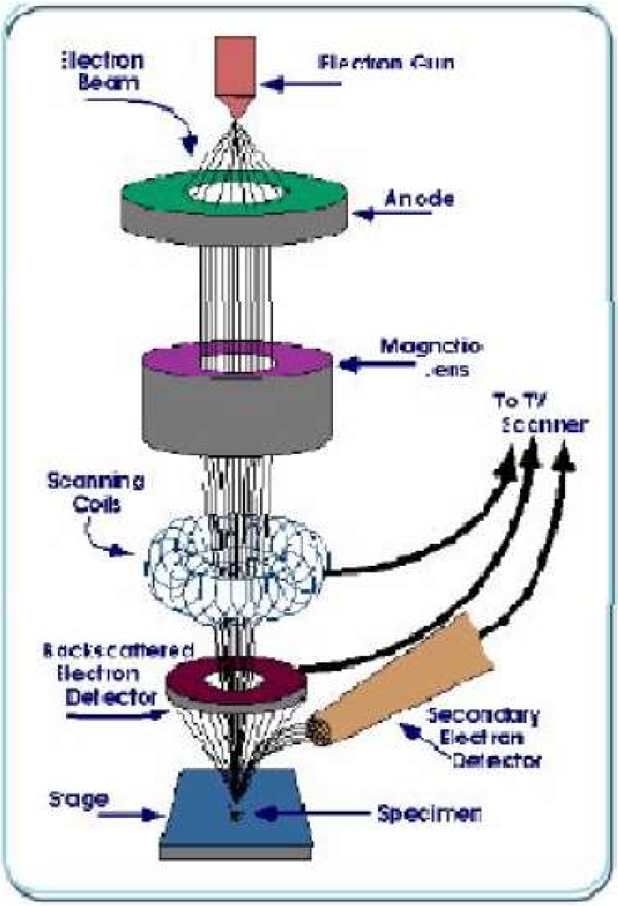
The sol-gel process is a wet chemical technique widely used in the field of material science. In this method, a set of chemical reactions irreversibly convert a homogeneous solution of molecular reactant precursors (sol) into three dimensional network (gel) filling the same volume as the solution. The sol-gel solutions are composed of a metal alkaloid and an alcohol. The metal alkaloid undergoes a hydrolysis reaction followed by condensation polymerization. The alkaloid species react with alcohol and produces oxide network. This oxide network extends as far as the hydrolysis conditions permit. The oxide network (gel) so formed is a three dimensional skeleton with interconnected pores and this can be dried and shrunk to form a rigid solid.

Preparation of Manganese doped zinc oxide thin films:

Pure ZnO and Mn doped ZnO thin films have been deposited on glass substrate.
Films have been prepared using sol-gel spin coating method (programmable spin coater SCU-2008C). Zinc acetate dihydrate, 2-methoxyethanol and monoethanolamine (MEA) were used as the starting material, solvent and stabilizer respectively. The sol was prepared using conventional acetate precursors i.e zinc acetate,Zn $(CH_3COO)_2 2H_2O$ and manganese acetate $Mn(CH_3COO)_2.4H_2O$ taken in stoichiometric amount and dissolved in 2-methoxyethanol.Monoethanolamine was added to the solution and it acted as stabilizer.The molar concentration of sol was maintained at 0.5mol/l.

SCANNING ELECTRON MICROSCOPY:

The scanning electron microscopy is the most widely used instrument for obtaining morphological features of a film is shown in figure3.5. In this, the area to be examined or the micro volumes to be analyzed are irradiated with a fine electron beam produced by the electro gun and focused by electron lenses. The scanning coils deflect this beam and sweep it over the film surface. A cathode ray tube is scanned synchronously by the signal that arises from the interaction of the beam with the film surface element under study. The strength of this signal is thus translated into image contrast. The type of signal produced when the electron beam impinges on the specimen surface includes secondary electrons, auger electron, characteristic X- rays and photons of the various energies. The emanating secondary electrons are used for the z-modulation in corresponding raster on the television or oscilloscope screen. For morphological feature determination, the secondary electron mode is generally preferred since these electrons emanates only from a depth of about 10Å or less from the film surface and hence the picture obtained is a faithful reproduction of the surface features.



AFM Analysis

Basic principles of AFM

Scanning force microscopy is based on the existence of a separation-dependency force between any two bodies. It is the force between the tip and the substrate that is present at close separations. Typically, pyramidal silicon nitride tips are used, which have a radius of curvature on the order of 100A0. These are made by etching process that removes silicon from the substrate, leaving an etched or sharpened tip behind. The force is detected by placing the top on a flexible cantilever that deflects proportionally to the exerted force. The deflection is then measured by some convenient procedure, such as laser deflection or some other device. Actually, the main innovation may be seen as being a copy of the principle behind the record player. AFMs operate by measuring force between a probe and the sample. Normally, the probe is a sharp tip, which is a 3-6 um tall pyramid with 15-40nm end radius. Though the lateral resolution of AFM is low (~30nm) due to the convolution, the vertical resolution can be up to 0.1nm. To acquire the image resolution, AFMs can generally measure the vertical and lateral deflections of the cantilever by using the optical lever. The optical lever operates by reflecting a laser beam off the cantilever. The reflected laser beam strikes a position-sensitive photodetector consisting of four-segment photo-detector. The differences between the segments of photo-detector of signals indicate the position of the laser spot on the detector and thus the angular deflections of the cantilever.

CONCLUSION

The MZO thinfilm, as the annealing temperature increases from 300 to 500°C.From AFM analysis we observed that for thickness greater than 40 nm, the films grow steadily with multi orientations independent of the thickness, there exists only (002) and (100) orientations. The PL spectra reveals that, MZO thin film exhibit the decrease in intensity of the band edge emission peak while the intensity of the deep level emission peak increases in the films coated on glass substrate. The magnetic characterizations of Mn doped ZnO thin films were performed using VSM. The presence of greater amount of oxygen interstitials in the ZnO host matrix will increase the distance between the magnetic ions (Mn^{2+}), reducing the coupling and thus the ferromagnetism. Thus Mn doped ZnO thin films grown under optimal annealing temperatures exhibit enhanced Zn–O bonding, resulting in enhanced ferromagnetic ordering.This is well suited for magneto optic applications.

Nano structured TiO_2 thin films were successfully deposited by PLD technique. KrF Excimer laser operating at 248 nm connected to a ultra high vacuum chamber. The thickness of the deposited TiO_2 thin films was found to be ~100 nm.Co^{2+} ions. Were doped into these films using 30 keV ion accelerator. GIXRD, Micro-Raman, SEM, AFM and UV-Vis were used for evaluation of structural, morphological and optical properties of TiO_2 thin films before and after cobalt doping. The nano-structured nature was confirmed using GIXRD and AFM. The crystallite size of the asdeposited TiO_2 thin films was measured using Scherrer formula and found to be ~40 nm. After co doping the crystallite size was reduced to 8 nm.Significant change in morphology and reduction in band gap (from 3.44eV to 3.1eV) was also observed.

References

[1] A.Fujishima, T.N.Rao, D.A.Tryk, Titanium dioxide photo catalysis, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1–21.

[2] M.KRam O.Yavuz, Lahsangah, and V.Aldissi," CO gas sensing ultrathin nanocomposit conducting polimer", Journal of Sensors and Actuators B. 106 (2005),P.75

[3] Yasumichi Matsumoto, Jun –ichi Kurimoto, Tateki Shimizu, and Ei-ichi sato. Photoelectrochemical Properties of Polycrystaline TiO2 Doped with 3d Transition Metals. J.Electrochem.Soc.:Electrochemical science and technology (1981).

[4] Heo YW, Ivill MP, Ip K, Norton DP, Pearton SJ, Kelly JG, et al. Effects of high-dose Mn implantation into ZnO grown on sapphire. Applied Physics Letters. 2004;84:2292-4.

[5] Pradhan AK, Zhang K, Mohanty S, Dadson JB, Hunter D, Zhang J, et al. High-temperature ferromagnetism in pulsed-laser deposited epitaxial (Zn,Mn)O thin films: Effects of substrate temperature. Applied Physics Letters. 2005;86:152511.