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FTIR AND PHOTO LUMINESCENCE STUDIES OF SILAR DEPOSITED ZNO/MO DOPED ZNO THIN FILMS

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Abstract:

Zinc oxide (ZnO) and Molybdenum doped Zinc Oxide (Mo doped ZnO) thin films were deposited on glass substrates from zinc acetate with NaOH and zinc acetate with molybdenum (v) chloride as cationic precursor following SILAR (Successive ion layer adsorption and reaction) technique respectively. Characterization techniques of Photo Luminescence (PL) and Fourier Transform Infrared spectroscopy (FTIR) were utilized for detailed optical and compositional studies of the coated films. The characteristic stretching vibration mode of ZnO was observed in the absorption band in FTIR spectrum. Photoluminescence spectra revealed that the emission peak intensity increased by Mo doping.

Key Words: ZnO, Mo Doped ZnO, Thin Films, Silar & Optical Properties

1. Introduction:

Zinc oxide (ZnO) is one of transparent conducting oxide (TCO) materials which attracts much interest because of typical properties such as high chemical and mechanical stability, high optical transparency in the visible and near infrared region, low toxicity, a wide direct band gap (3.37 eV at room temperature), abundance in nature, good electrical properties, a large exciting binding energy of 60meV, large piezoelectric constants, strong luminescence, strong sensitivity of surface conductivity [1]. Due to these properties, ZnO is a promising material for electronic and optoelectronic device application such as solar cells, photo-catalysis, surface acoustic devices, piezoelectric transducers, gas sensors, liquid crystal displays, heat mirrors, etc.[2,3]. Several groups are working on ZnO using various film growth techniques such as magnetic sputtering [4],chemical vapour deposition [5], thermal vacuum evaporation [6], Dip coating [7], pulsed laser deposition [8],chemical reaction method[9] and spray pyrolysis method [10,11] and Successive Ionic Layer Adsorption and Reaction(SILAR) deposition method[12,13]. Among these methods SILAR method only having more advantages like, large-scale deposition in glass and metal substrates, commercial-grade production in non-vacuum conditions at low temperatures and low cost [14]. In the present work the pure ZnO thin films were deposited by SILAR method for various dipping cycles (25, 50 and 75) and the Mo doped ZnO thin films were deposited for various molar ratios of Mo and Zn (1:10, 1:15 and 1:20) at 50 dipping cycle, effect of dipping cycles and effect of Mo doping on optical properties of undoped and Mo doped ZnO thin films were studied respectively in detail.

2. Experimental Procedure:

All the chemicals used in the present work were of analytical grade and all the solutions were prepared in Millipore water. To prepare the undoped ZnO thin films with various dipping cycles, the glass substrates (6 cm x 1.25 cm x 1mm) were cleaned thoroughly using soap solution to remove visible impurities, boiling in chromic acid for 45 min and rinsed with double distilled water, after that the glass substrates were subsequently cleaned with acetone. Zinc acetate ($(CH_3COO)_2Zn.2H_2O$) with NaOH used as source of cationic precursor solution and sodium thiosulfate ($Na_2S_2O_3.5H_2O$) used as the source of anionic precursor solution. pH value of the cationic precursor solution can be increased by adding NaOH, which provides to grow smooth films with good adherence and also it helps in nucleation and growth of grains. The cleaned glass substrate was first immersed into 0. 1 mol Zinc acetate and 0.1 mol NaOH solution (pH 10) for 15s followed by the substrate was sufficiently rinsed with double-distilled hot water bath (70 ^{0}C) for 10 s to remove superfluous Zn ions that interacted rather weakly with the substrate. The substrate was then immersed into a 0.1 mol sodium thiosulfate solution (pH 6) for 15 s and rinsed with double-distilled hot water bath (70 ^{0}C) for 10 s. The above deposition cycles were repeated and carried out for 25, 50 and 75 times separately to get the three desired films. To prepare the Mo doped ZnO thin films, cationic precursor (0.1M) zinc acetate (50ml) and (0.01M) molybdenum (v) chloride were taken in a beaker and the anionic precursor (0.1M) Sodium thio sulphate (50ml) was taken in a separate beaker. For the deposition of Mo doped ZnS thin film, well cleaned glass substrate was dipped into the cationic precursor for 15 sec for adsorption of Zn^{2+} and Mo^{6+} ions on the surface of the glass substrate, and then the substrate was dipped into the de-ionized water for 10 sec to avoid precipitation and also to remove the loosely bounded cations. The substrate was then immersed into the anionic precursor bath for 15 sec for reaction of S^{2-} ions with Zn^{2+} and Mo^{6+} ions on the surface of the glass substrate. The procedure was carried out at around 75 °C temperature. Successive dipping cycles repeated up to 50 cycles, to get the well adherent and homogeneous Mo doped ZnO thin films [12]. Then the same procedures were repeated for 0.0066 and 0.005 mol of molybdenum (v) chloride. Mo was doped with Zn in the following molarity ratio Zn10: Mo01, Zn15: Mo01 and Zn20: Mo01 and the corresponding mol percentages are 10, 6.6 and 5 respectively. The prepared

films were dried at room temperature for 2 hours and then annealed in air at 450 ^{0}C for 3 hours. FTIR analyses were obtained on Spectrum 100 FTIR (Perkin-Elmer). Photoluminescence (PL) spectra were recorded using Cary Eclipse fluorescence spectrometer with a Xe lamp (15 W) as an excitation source. The films thicknesses were measured using a surface profiler (model: KLA-Tencor).

3. Results and Discussion:

3.1 Fourier Transform Infrared Spectroscopy (FTIR): Figure 3.1 show the compositional analysis of ZnO thin films prepared at different deposition cycles (25, 50 and 75), were carried out by the FTIR measurement at room temperature in the acquired range of 4000–400 cm^{-1}. In the spectrum, the presence of the ZnO nanoparticles is confirmed by the peaks at 475 cm^{-1} for 25 deposition cycles, 490 cm^{-1} and 538 cm^{-1} for 50 deposition cycles, and 490 cm^{-1} for 75 deposition cycles. Presence of sulphur is not found in the film by FTIR studies, because during annealing in air at 450^{o}C for 3 hours, sulphur atoms present in the films were replaced by the oxygen atoms by oxidation process [12].

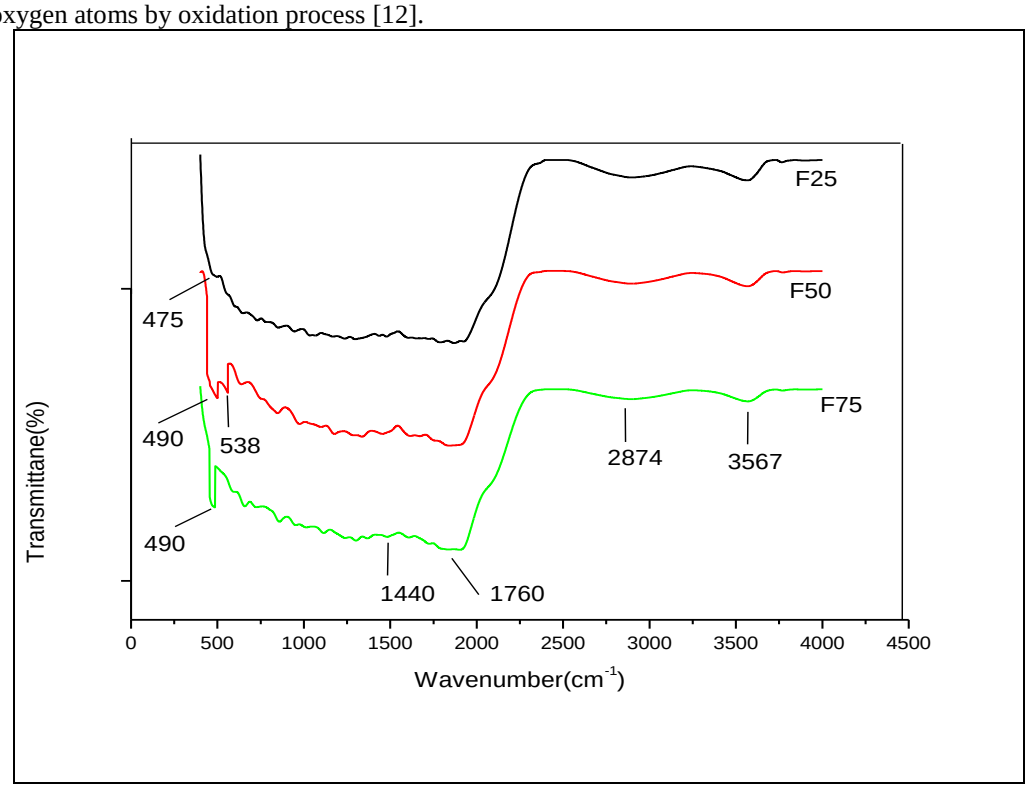

Figure 3.1: FTIR spectrum and their peaks of F25, F50 and F75

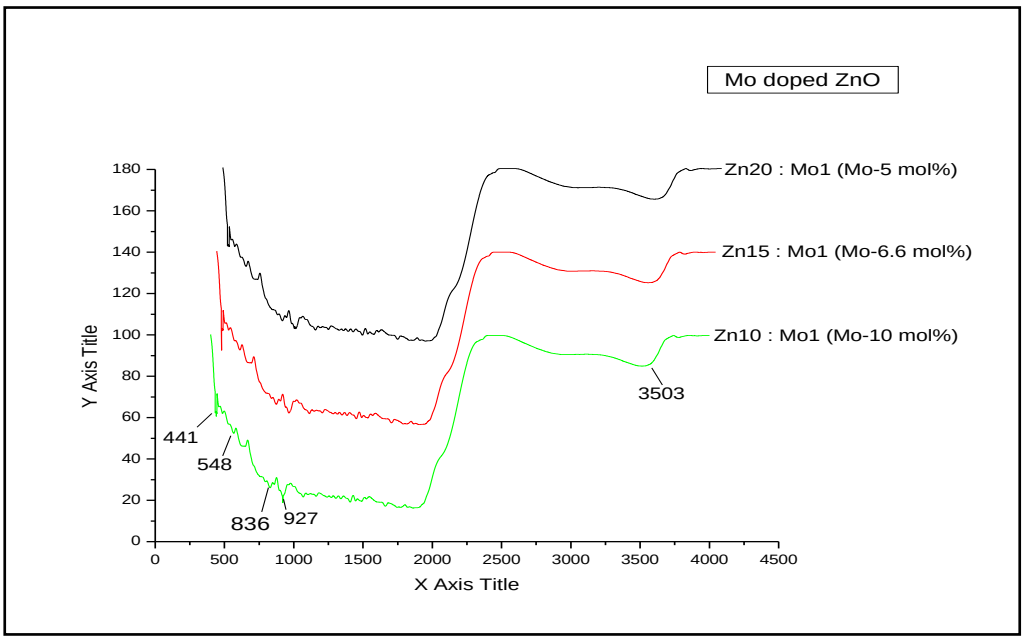

Figure 3.2: FTIR spectrums of Mo-doped ZnO thin films

It is believed that the micro structural changes may be the reason for the splitting of the peaks at 475 cm^{-1} and 538 cm^{-1}in 50 deposition cycles. Of these peaks, 538 cm^{-1} can be attributed to the bending vibration, 475 cm^{-1} and 490 cm^{-1} can be attributed to the stretching vibration of ZnO [15]. The band at 1440 cm^{-1} is due to weakly bound of C-O stretching frequency [16] and 1760 cm^{-1} are due to the presence of C=O stretching vibration[17].The bands at 3567cm^{-1} is correspond to O–H mode of vibration [18]. FT-IR spectrums of Mo-doped ZnO with various molar ratios are as shown in Fig. 3.2. A distinct characteristic transmission peak around 3503 cm^{-1} is assigned to the stretching vibration and bending vibration of surface hydroxyl groups on ZnO. The peak at 441 cm^{-1} is attributed to the stretching vibration of ZnO bonds. The presence of MoO_3 depicted with peak at around 548 cm^{-1}, 836 cm^{-1}. The absorption bands at 927 cm^{-1} indicating stretching mode of Mo=O. The presence of additional absorption bands from 404 cm^{-1} to 1110 cm^{-1} compared to ZnO nanoparticles indicates the presence of Molybdenum and its oxides. The M-O frequencies observed for nanoparticles of metal oxides are in accordance with the literature values [19].

3.2 Photo Luminescence (PL) Spectroscopy: Photoluminescence is a contact less non destructive method which is widely used to study luminescence properties of thin films. PL spectra of ZnO thin films with various dipping cycles are represented in Figure 4.10. Spectra represent characteristic intensity peaks in the UV and visible region. From spectra it is clear that pure ZnO particles exhibit emission peaks at 361 nm and 391 nm in the UV Region and broad blue emission peaks around 410 nm, 442 nm, 490 nm and emission peaks near 521 nm corresponding to green luminescence in visible region. Figure 4.10 clearly shows that the intensity peaks are increases when dipping cycle increases from 25 to 50. Further, the intensity peaks are decreases when dipping cycle increases from 50 to 75. Among the three different thin films, 50 dipping cycle only exhibit the good photo luminescence property.

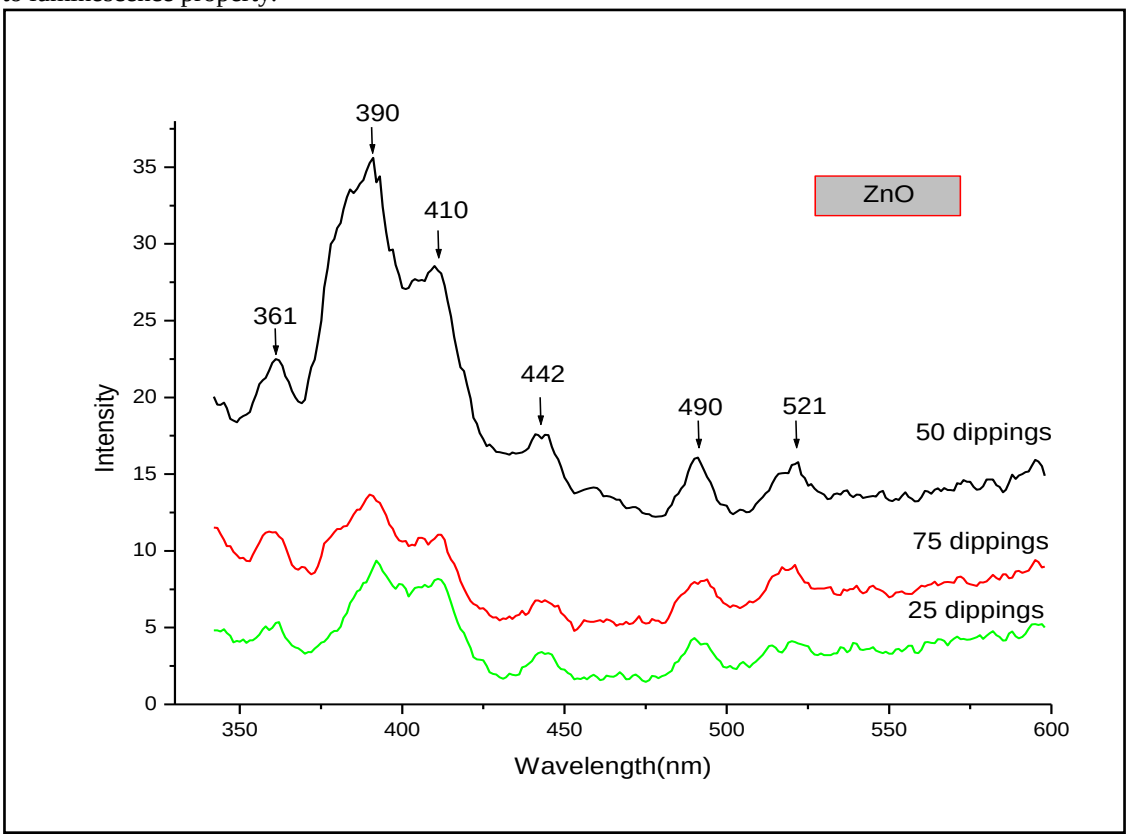

Figure 3.3: PL spectra of ZnO thin films with various dipping cycles

Figure 3.4 gives the comparison of photoluminescence spectra of Mo doped ZnO films prepared with different starting solution molarities. The emission peaks were noticed at 361 nm and 392 nm in the UV Region and broad blue emission peaks around 413 nm, 443 nm, 492 nm and emission peaks near 522 nm corresponding to green luminescence in visible region. With the increase of solution molarity in the ZnO crystal lattice, the intensity of the all peaks was gradually increased, which confirms that optical behaviour of Mo-doped ZnO layers was increasing with solution molarity. It is believed that, wavelength of peaks (392nm, 413nm, 443nm, 492nm and 522nm) of Mo doped ZnO thin films were shifted due to incorporation of Mo with the ZnO.

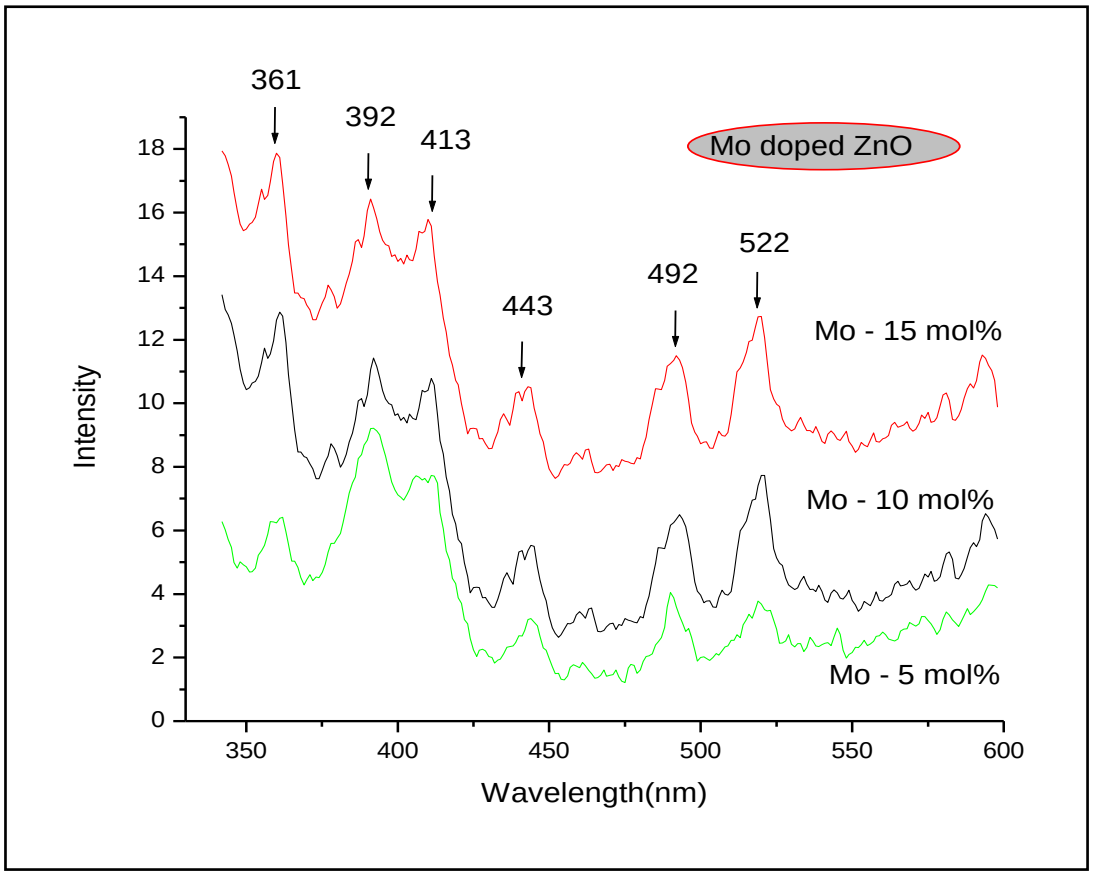

Figure 3.4: PL spectra of Mo doped ZnO thin films with various doping concentration

Figure 3.5 shows the variation of thickness with deposition cycles of undoped ZnO thin films. It reveals that, thickness of the film increases with dipping cycles (25 & 50 dipping cycles). For further increase in dipping cycles thickness of the film reduces in 75 dipping cycles. These results shows, during the deposition, formation of the film were saturated in 50 dippings after that there is no improvement in film growth and some amount of ions were removed from the substrate. Fig 3.6 shows the variation of thickness with the Mo doping concentration of Mo doped ZnO thin film. Thickness of the film increases with the Mo doping concentration, which may be due to the formation of stress by the smaller radius of Mo^{6+} ions (0.41Å) compared with Zn^{2+} ions (0.60Å).

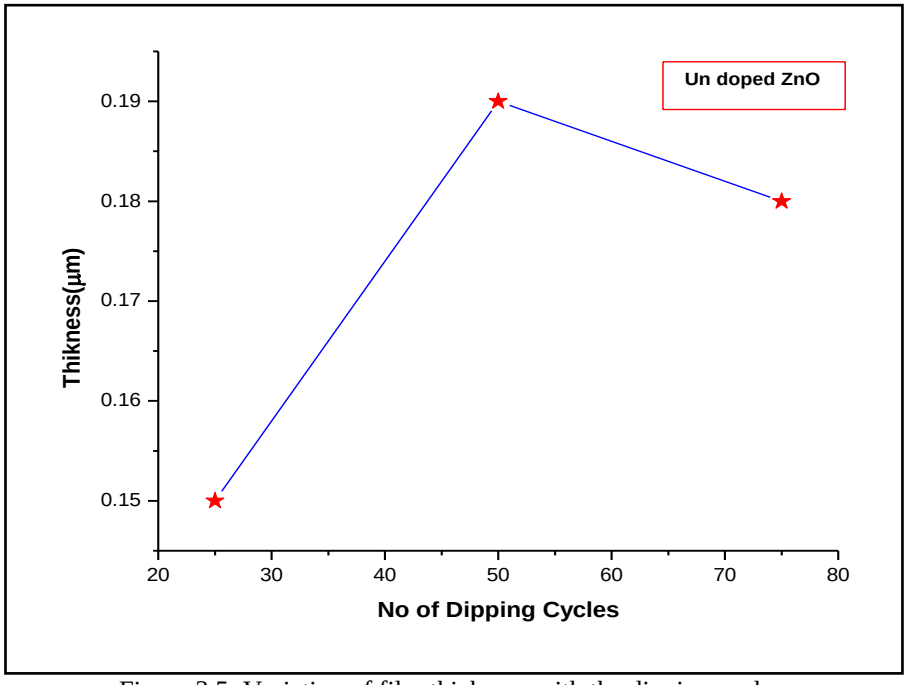

Figure 3.5: Variation of film thickness with the dipping cycles.

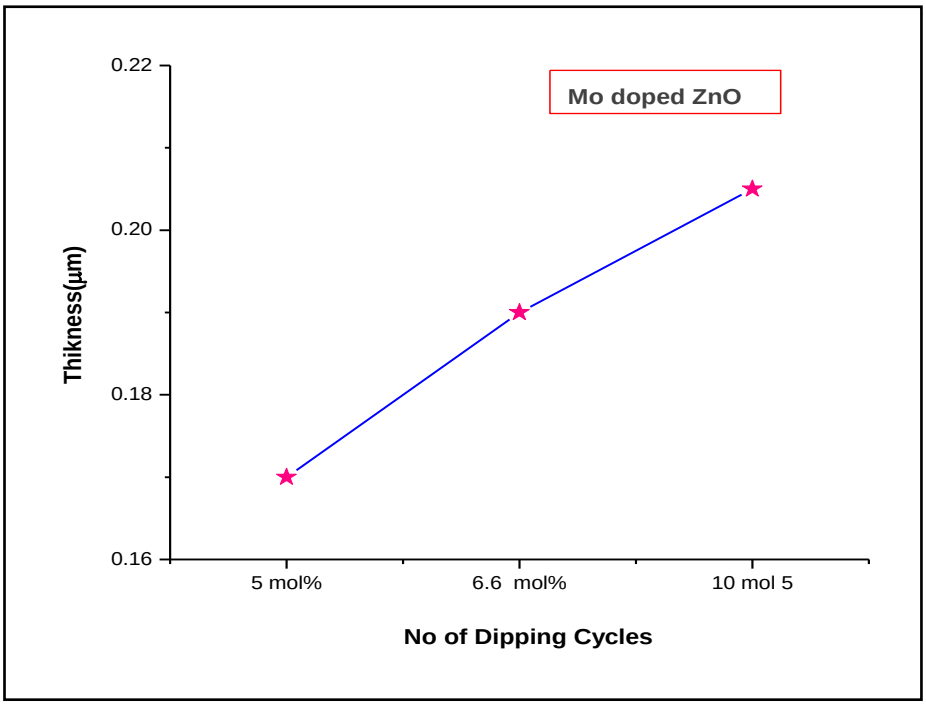

Figure 3.6: Variation of film thickness with the various Mo mol%.

4. Conclusions:

Pure ZnO and Mo doped ZnO thin films are deposited on glass substrates by SILAR deposition method. The effect of dipping cycles and Mo doping on optical properties of ZnO films and Mo doped ZnO films were studied respectively. The FTIR analysis confirms the formation of ZnO and Mo doped ZnO. PL studies of pure ZnO thin film reveals that, the emission peaks of thin film increase with increasing the dipping cycles(50), for further increase in dipping cycles(75) the emission peaks are decreased, it reveals that in 50 dipping cycles only pure ZnO thin film shows good optical property. PL studies of Mo doped ZnO shows that, the emission peaks increase with the Mo mol %. This is in good agreement with the optical data observed in the study, which confirms that optical behaviour of Mo-doped ZnO layers was increasing with solution molarity.

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