# Palladium Doping Effects on Structural and Optical Characteristics of ZnO Thin Films Prepared via SILAR

**Svetlana Ivanova***

*Senior Researcher, Department of Physics, Novosibirsk State University, 630090 Novosibirsk, Russia

## ABSTRACT

Pd-doped ZnO (Pd : ZnO) thin films prepared from sodium zincate bath. SILAR technique used for preparation of the films. X-ray diffraction reveals the polycrystalline nature of the films. X-ray line broadening analysis gives the particle size of the films. It shows decreasing trend with increasing palladium impurification. The particle size for pure ZnO is 43.8 nm and 31·9 nm for 20% Pd:ZnO. Strain broadening was neglectedin the evaluation process. By palladium doping the preferred c-axis orientation is lost and degree of polycrystallinity of the films increases. The bandgap of the films increases with Pd dopant. The fundamental absorption edge is 3·34 eV for pure ZnO and 3·79 eV for 20% Pd:ZnO.

**KEYWORDS**: Bandgap, Pd:ZnO thin film, SILAR, X-ray broadening .

## I. INTRODUCTION

Zinc oxide has many unique properties such as chemical stability, biocompatibility, high catalytic activity in different gas environment, piezoelectricity, optical transparency and nonlinearity[1] in high voltage and current situation etc. It has many applications, such as heat mirrors, solar cells, electrodes, light emitter device, sensor, photothermal conversion systems, transducer [1-3] etc. Its physical properties[4] can be varied by doping. Different physical and chemical processes has successfully used to prepare pure and doped ZnO thin films. Different dopants doped with thin films of ZnO such as Al, Ni, Mn, Pd, Cu, Fe, Cd etc[5-10] . By doping the physical properties of the undoped thin films can be changed. Palladium-doped ZnO has application in optoelectronics, different gas sensors and also for the creation of ZnO based devices[11]. But the physical properties of Pd doped ZnO thin films has very limited information until recent times. The tetragonal structure and a narrow direct bandgap of 2·13±0.03 eV of palladium oxide rather than the ZnO, a wide bandgap of 3·2 eV[12-13] can be able to modify the physical properties of ZnO upon mixing with PdO. Different amounts of Pd incorporation[14-19] successfully has done in recent research works. Palladium substituted the zinc ion has been reported by complicated physical processes and chemical processes such as pulsed laser deposition (PLD)[15,] sol–gel[11,16,18] ,spin coating[17] and spray pyrolysis[10] have been employed to deposit Pd-doped ZnO films. Chemical techniques are relatively simpler and cost effective. A modified chemical dipping process has taken into account to prepare Pd doped ZnO thin films in this research work. In this method, a glass slide is placed vertically into beakers . The beakers contain aqueous solutions or distilled water. The chemical reaction take place at the surface of the slide. The slides can be dipped into beakers containing various reactants for a specific length of time. The time depends on the nature and speed of the reaction. The number of dipping is varied upto any number. It is restricted only by the deposition process problems and the separation of thin film from the substrate interface. At first the process was developed by Call et al (1980)[19] and Ristov et al (1987)[20]. Nicolau et al (1990)[21] gave the name successive ion layer adsorption and reaction. SILAR deposition technique is simple and economical process for depositing thin film. But the process is seldom used and studied than the other processes. The apparatus need for this technique are low cost and the process is very much simple.

Chatterjee et al 1999[22] and Mitra and Khan 2006[23] reported the preparation of ZnO thin films and Mondal et al 2008[24] reported the Al doped ZnO thin films by SILAR. Now we are trying to prepare Pd doped ZnO thin films by this technique.

## II. MATERIALS AND METHODS

ZnO and Pd-doped ZnO thin films were deposited by a modified chemical dipping technique name SILAR, which is Successive ion layer adsorption and reaction. 0·1M sodium zincate ($Na_2ZnO_2$) solution and hot water bath were taken into two beaker. At first sodium hydroxide (NaOH pellets, Merck, mol. wt 40·00) added in zinc sulphate (ZnSO4·7H2O, Merck, mol. wt 287·54) solution. By which sodium zincate solution was prepared. The pH of this solution was 13·60. A systronics pH meter , Model No.335 was used for pH measurement. Secondly Palladium chloride ($PdCl_2\,H_2O$, GR grade, Loba Chemie) was added in sodium zincate bath for preparation of Pd-doped ZnO thin films. In Chatterjee et al 1999; Mitra and Khan 2006; Mondal et al 2008 preparation of pure ZnO thin films by this method has been reported. In short glass slide of microscopic range was cleaned in three

steps. First cleaned by chromic acid, second rinsing by distilled water and last by ultrasonic cleansing. For ultrasonic cleaning the solution was prepared by mixing of equivolume acetone and alcohol. A holder tightly held the cleaned slide for performing deposition. Now the slide alternatively dipped in zincate bath(room temp.) for 2 s and in hot water (kept 96-98.5$^0$C) for 2 s. In this experiment 60 dippings has done. Gravimetry method was used to calculate the thickness of the films, which give ≈ 1.0 μm. Crystalline structure characterization and phase identification was done by X-ray diffractometer of Philips PW 1830 X-ray diffractometer with CuKα radiation (λ = 1·5418 Å). The Miller peaks were indexed and the peak positions were verified by standard JCPDS file. SEM model no. S530,Hitachi, Japan was used for surface morphology investigation and explanation for the formation of crystallite on thin film surface. Shimadzu UV-1800 spectrophotometer was used for absorption spectra. The whole experiment done at room temperature. And hence the bandgap of the films were calculated.

## III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of undoped ZnO and 20% Pd-doped ZnO films. All the pure ZnO and Pd-doped ZnO films were heat treated at 350$^0$C for 2 h before mounted for diffraction pattern. The films were scanned in the range 20$^0$–80$^0$. The diffraction pattern shows 2θ variation with a 0·05 degrees step and a time step of 1s and intensity in the plot is in arbitrary units. Intensity vs 2θ plot of the diffraction pattern shows that the peaks are at 32·1°, 34·35°, 36·02°, 47·55° , 56·25°, 62.78°, and 67.70° for undoped ZnO and 31.19$^0$,34.48$^0$,36.1$^0$,47.40$^0$,56.40$^0$,62.78$^0$ and 67.86$^0$ for 20% Pd-doped ZnO. The XRD pattern of the films shows that all the peaks are in good agreement with the JCPDS data. It reveals the hexagonal ZnO structure. Both the diffraction pattern shows one sharp and six small peaks. These pattern fully agreed the polycryastalline nature of the films with the crystal planes (100),(002),(101),(102),(110),(103) and (112) .The (002) peak appears with a maximum intensity at 34·35◦ for pure ZnO but for 20% Pd:ZnO intensityity of (002) peak decreases and the relative intensity of (101) peak increases for Pd:ZnO films. Thus palladium doping in ZnO films results loss of preferred orientation along c-axis since (101) peak appears with maximum intensity (Mitra and Khan 2006). By evaluating the X-ray diffraction data, the particle size was estimated by Scherrer equation (Klug and Alexander 1974[26]; Gupta et al 2009[27]): $D = k\lambda \beta \cos \theta$ , (1) where D the particle size, k the Scherrer constant, λ is the wavelength of radiation used (1·542 Å for CuKα radiation ), β (FWHM) intensity of the diffraction peak for which the particle size is to be calculated and θ the diffraction angle of the concerned diffraction peak . The value of particle size 37·93 nm. The actual particle size will be a little higher because strain broadening was not taken into account. SEM images of pure and 20% Pd:ZnO films are shown in figure 2(a) and 2(b) respectively. The uniform morphology of pure and Pd-doped ZnO films were established. The porous nature of the Pd-doped films is also established. The direct bandgap is determined using this equation when straight portion of the $(\alpha h\nu)^2$ against hν plot is extrapolated to intersect the energy axis at α = 0. For determination of optical band gap the plot of $(\alpha h\nu)^2$ against hν for undoped and palladium-doped ZnO films are shown in figure 3. Figure 3(a) shows the absorption spectra for pure and 20%Pd doped ZnO. Figure 3(b) shows the spectrum for pure ZnO while figure 3(c) show the spectrum for 20% Pd:ZnO, respectively. The fundamental absorption edge increases with the Pd doping in ZnO films. The value of Eg for undoped ZnO is 3·34 eV. It increases to 3·79 eV for 20%Pd:ZnO. By the large difference in band gap values of ZnO and PdO[25] this change of $E_g$. value may be accounted.

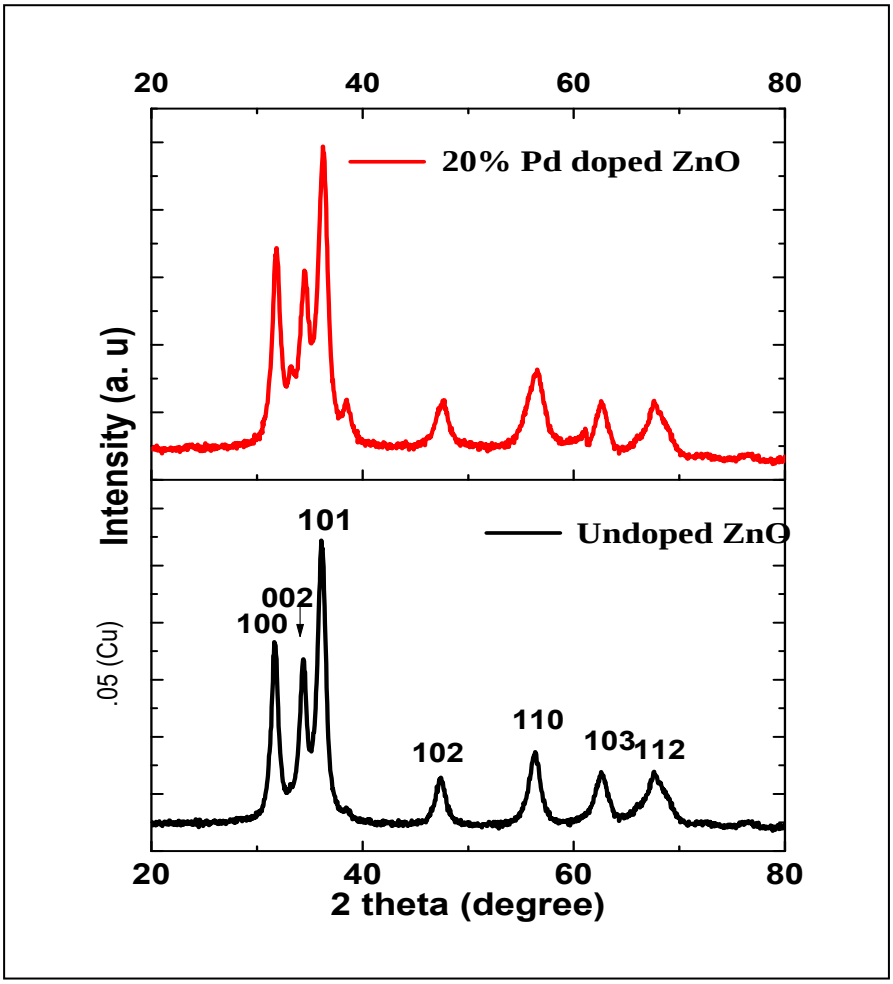


*Fig. 1:XRD pattern of undoped and 20% Pd doped ZnO.*

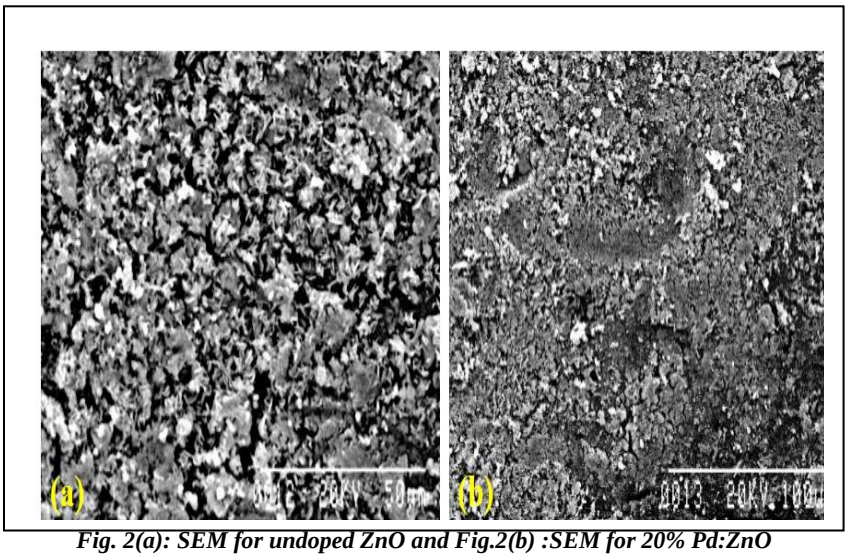


*Fig. 2(a): SEM for undoped ZnO and Fig.2(b) :SEM for 20% Pd:ZnO*

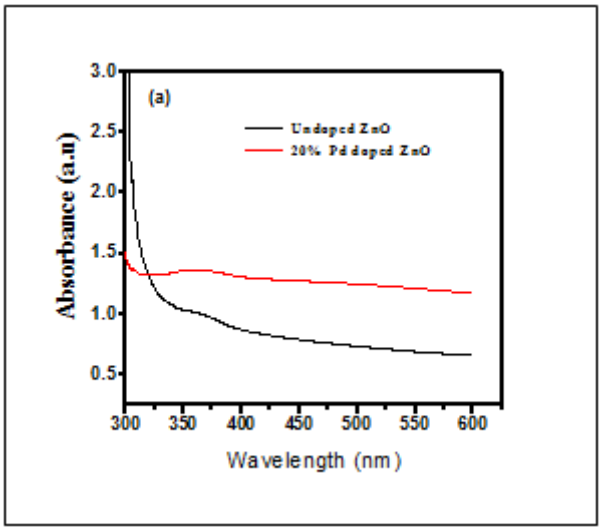


*Fig: 3 (a) absorption Spectra of undoped and 20% Pd doped ZnO*

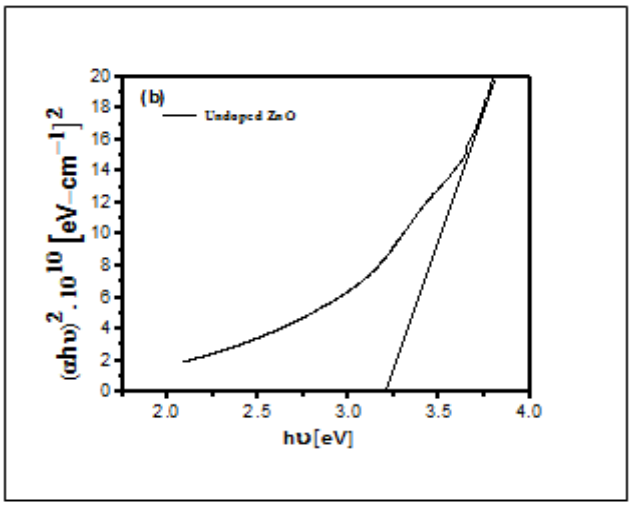


*Fig. 3 (b): $(\alpha hv)^2$ vs Hv plot of undoped ZnO*

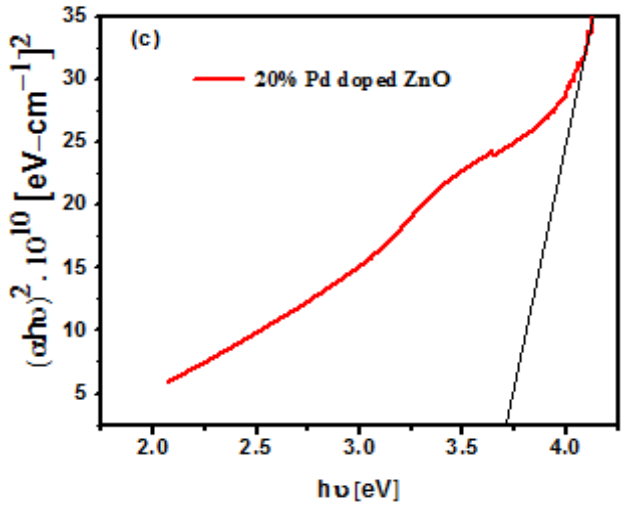


*Fig. 3(c): $(\alpha hv)^2$ vs hv plot of 20%Pd doped ZnO.*

## IV. CONCLUSION

An inexpensive, simple method was used to prepare Pd-doped ZnO thin films successfully. The particle size, structure, bandgap energy and surface morphology of the Pd-doped thin films were investigated which were obtained by SILAR. The polycrystalline thin films showed hexagonal structure by XRD spectra. The particle

size is 37.93nm for pure ZnO and it reduces to 31.9nm for 20% Pd:ZnO. SEM shows the uniform films are porous which has grain size of nano scale. At last optical band gap also measured. The absorption edge increases to 3.79 eV for 20% Pd:ZnO which is 3.34 eV for pure ZnO.

## V. FUTURE SCOPE

Nanoscale porous polycrystalline Pd-doped ZnO thin films would be applicable as sensors. As the band gap energy changes it might have immense application in band gap energy

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