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Sol-Gel Dip Coated Pure and Fe-Doped Nanostructured ZnO Thin Films.

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ABSTRACT

Pure and Fe-doped zinc oxide thin films were coated on glass substrates using sol-gel dip technique. Zinc acetate dihydrate and ferrous chloride anhydrous were used as the host and dopant precursor salts respectively. X-ray diffraction patterns confirmed the hexagonal wurtzite structure with polycrystalline nature of the films. Morphological studies revealed the tightly packed spherical shaped grains for both the pure and Fe-doped films. The optical characteristics were observed using UV- Vis spectrophotometer in the wave length range of 300-800 nm. The Fe-doped ZnO film showed a greater absorption in the visible region compared to that of pure ZnO film. The decrease in band gap and electrical resistance with Fe-doping were observed for the Fe-doped ZnO thin film.

Keywords: Sol-gel; ZnO; Doping; Thin films.

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INTRODUCTION

One of the most prominent metal oxide materials namely zinc oxide (ZnO) has been exploited to the core by the scientific community due to its functional and catalytic nature. Being an n-type semiconducting material with larger band gap (3.37 eV) and exciton binding energy (~60 meV)[1–3], it attracts scientists across various fundamental and applied fields of science due to its resourcefulness. It has been identified as one of the versatile and predominant candidates for the electronic, optoelectronic, sensing, solar cell and laser applications[4–6]. Moreover, the field of “nano” has surprisingly brought out the low dimensional features of this flexible material to a newer dimension. The different nanostructures of ZnO and their uniqueness indeed captured a reasonable map of the literature on the metal oxide materials. The presence of intrinsic defects like oxygen vacancies and zinc interstitials in the ZnO nano scale has furthered its applications in the area of magnetic devices[7].

Structural, morphological, optical and electrical properties of the thin film form of this “Queen of Metal Oxides” can be varied by modulating the different synthesis parameters of both the physical and chemical deposition techniques. Further, tuning of its transport properties by impurity doping has reached newer heights in the recent past. Doping ZnO has helped to modulate the band gap and hence all its related electronic and optical properties in turn resulted in the development of modern optoelectronic devices. In the past, metal oxides like TiO₂[8], MoO₃[9], CuO[10] were doped with ZnO but in recent times, doping transition metals (TM) like Mn, Fe, Ni and Co in ZnO has gained significant technological advantages in fabricating spintronic and optoelectronic devices[11–13]. Among these transition metals, Fe doping in ZnO has strongly influenced the magnetic behavior of ZnO and particularly Fe-doping facilitates the manipulation of its charge and spin degrees of freedom[11]. In particular, the partially filled d states of Fe atom has a strong influence on exhibiting the magnetic behavior of ZnO. The electronic state interaction or exchange between Fe dopants and host ZnO, directly influence its band gap by raising and lowering the valence and conduction band edges respectively[14,15]. Chen *et al.* reported the influence of Fe-dopants on the structural and photoluminescence characteristics of ZnO thin films[16]. Similarly, the effect of synthesis conditions and Fe-doping on the various characteristic features of ZnO thin films were investigated by Zhan *et al.*[12].

Since deposition parameters of various thin film coating techniques like spray pyrolysis, citrate decomposition, hydrothermal, RF sputtering, pulsed laser deposition, etc., play a crucial role in fine-tuning the physical and chemical properties of ZnO, sol-gel dip technique has been considered in this work to deposit Fe-doped ZnO thin film. Compared to other techniques sol-gel dip coating has many advantages such as simple deposition conditions, cost effectiveness and control over the structural and morphological properties of thin films [1,17]. Hence in this work, a major focus is given to investigate the structural, morphological, optical, electrical properties of Fe-doped ZnO thin films employing sol-gel dip coating technique.

MATERIALS AND METHODS

Film deposition

Pure and Fe-doped nanostructured ZnO thin films were coated on glass substrates using sol-gel dip coating (HOLMARC, HO-TH-02) technique. Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, (Sigma Aldrich, 99% purity)] and ferrous chloride anhydrous [FeCl_2 , (MERCK, 99% purity)] were used as the precursor salts. Ethanol and monoethanol amine were used as solvent and stabilizer respectively. The sol was prepared by dissolving 0.05 M of zinc acetate dihydrate and ferrous chloride anhydrous in a mixture of 25 ml of ethanol and 0.05 M of MEA. The molar ratio of the dopant atoms in the precursor solution was considered as 0 and 2 at%. The solution was stirred at room temperature for 15 min to produce clear solution. Flow chart representing the deposition of undoped and Fe-doped ZnO films is shown in Fig.1. Glass substrates (Blue Star, Mumbai) were ultrasonically (Supersonic, Mumbai) cleaned with acetone and deionized water for 15 min. Films were coated by dipping them at the speed of 9000 $\mu\text{m}/\text{sec}$ and retrieving them by 1000 $\mu\text{m}/\text{sec}$ speed. The time of interval between each dipping and drying was maintained at 1 min in order to avoid “peeling off” as a layer and also to enhance the adhesive nature of the films. All the coating conditions were auto controlled by the processor. Films were deposited on glass substrates by preheating the substrate at 348 K before each dipping cycle. The dip coating and preheating were repeated 5 times. The pure and Fe-doped ZnO films were subsequently annealed at 723 K for 3 hrs.

Characterization techniques

Structural characteristics of the films were studied using X-ray diffractometer (X'PERT PANalytical, Netherland) with Cu $K\alpha$ source ($\lambda = 1.5408 \text{ \AA}$) in the 2θ range of 10 to 80°. Surface morphology of the films was examined using Field Emission Scanning Electron Microscope (FE-SEM) (JSM-6701F, JEOL, Japan). Optical properties were studied using UV-Vis spectrophotometer (Perkin Elmer, Lambda 25, USA) in the wavelength range of 300 to 800 nm. The electrical conductivity was measured using two probe electrometer (6517A, Keithley Inc., USA).

RESULTS AND DISCUSSION

Structural studies

The structural features of the undoped and Fe-doped ZnO thin films were characterized using X-ray diffractometer (Fig. 2). Both the pure and Fe-doped films were found to be polycrystalline in nature with hexagonal wurtzite structure. The diffraction peaks corresponding to (100) (002) (101) planes were observed. There was no specific diffraction patterns were observed for any secondary phases such as FeO, Fe_2O_3 , Fe_3O_4 and $\text{Zn}_2\text{Fe}_4\text{O}$. This has confirmed that the Fe atoms were perfectly replaced the Zn atoms. The crystallite size was calculated using Debye Scherrer (Eq. 1) formula and was found to be 15 and 27 nm for the pure and Fe-doped films respectively.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where, 'D' is the crystallite size, ' λ ' is the wavelength of the X-ray used (1.5406 Å for Cu K α), ' θ ' is the Bragg's angle and ' β ' is the full width at half maximum. It can be seen from the XRD patterns that the FWHM was high for undoped sample, whereas for Fe-doped ZnO film the FWHM was decreased. This decrease in FWHM confirmed the increase in crystallite size for Fe-doped ZnO film[18].

Morphological studies

Scanning electron micrographs of the pure and Fe-doped ZnO thin films are shown in Fig. 3, which showed the formation of films with a tightly packed spherical shaped grains. The surface morphology of pure film showed a uniform distribution of smaller grains throughout the substrate, whereas the micrograph of Fe-doped films showed an unevenly arranged larger grains with voids. This increase in grain size was also revealed by the XRD data.

Optical studies

The optical absorbance spectra of the annealed pure and Fe-doped ZnO thin films are shown in Fig. 4. Fe-doped ZnO thin film showed a higher absorption of photons in the visible region and low absorption in the region below 350 nm. This increase in absorption between 350-400 nm might be due to the radiative direct transition of electrons. A sharp absorption edge rise at 390 nm for the pure sample corresponds to the characteristic spectrum of pure ZnO. For Fe-doped sample the absorption region was found to be extended from UV to UV-Visible region. This has confirmed the incorporation of Fe-dopants into ZnO lattice as well as the formation of new donor impurity level below the conduction band of ZnO[19]. Optical band gap values of the films were calculated using Tauc's plot by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portions of the absorption edge to find the intercept with energy axis. Fig. 5 shows the band gap variation of the pure and Fe-doped ZnO thin films. The band gap energy value was found to be decreased for the Fe-doped film. This decrease in band gap might be due to the sp-d spin exchange interaction between host and dopant ions, which in-turn influenced the valence and conduction band edges resulted in a reduced band gap[14,15,20].

Electrical studies

The electrical conductivity behaviour of the pure and Fe-doped ZnO thin films are depicted in Fig. 6. The electrical conductivity of Fe-doped ZnO thin film was found to be increased with reference to the pure film. This might be due to the increase in crystallite size and also increase in donor concentration of the Fe-doped ZnO thin film [17,21].

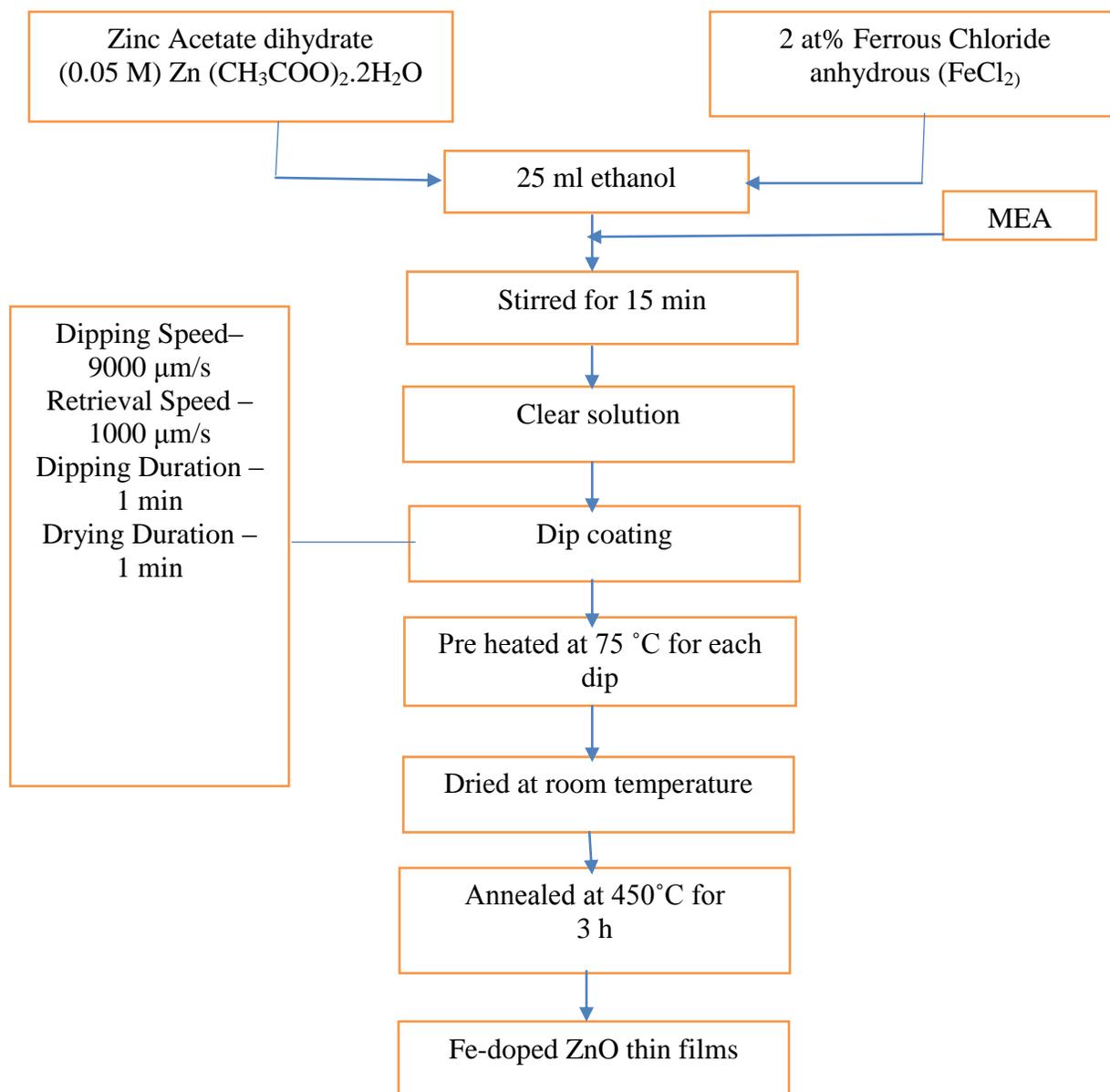


Figure 1: Flow chart representation of the deposition process.

In this investigation, pure and Fe-doped ZnO thin films were successfully deposited on glass substrates using sol-gel dip coating. The influence of Fe-doping on the structural, morphological, optical and electrical properties of ZnO were observed and correlated. The deposited films showed polycrystalline nature with a preferential orientation along (002) plane. Morphological studies revealed the formation of films with tightly packed spherical shaped grain morphology. Optical studies revealed the enhanced absorption of photons by the Fe-doped ZnO thin film. The optical band gap energy and electrical resistance of the ZnO film was found to be decreased upon Fe-doping.

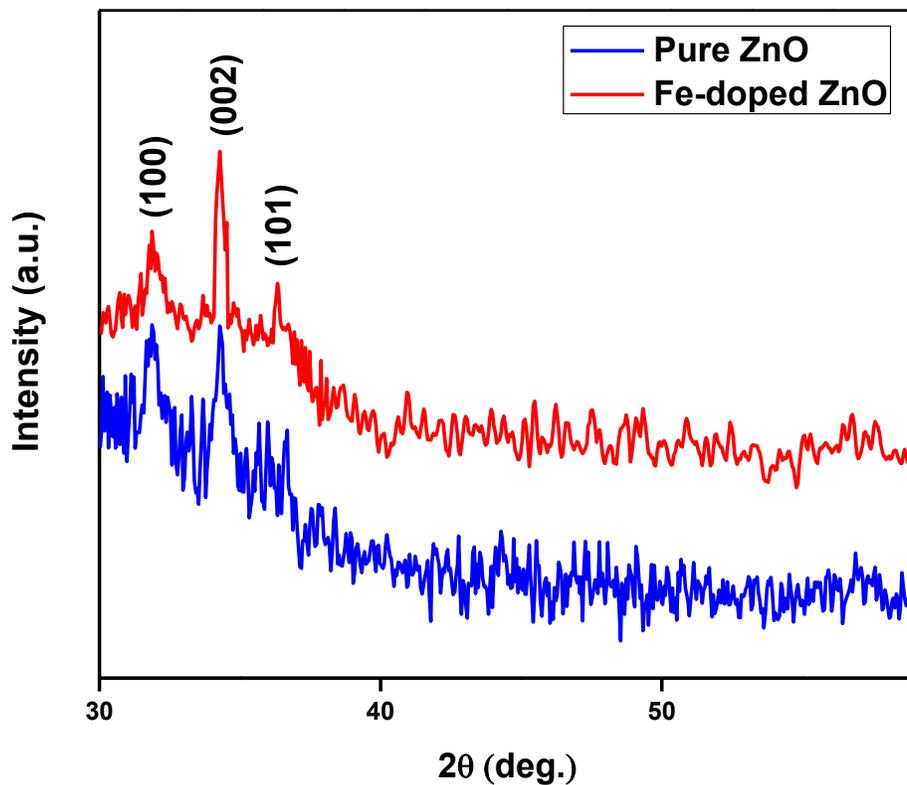
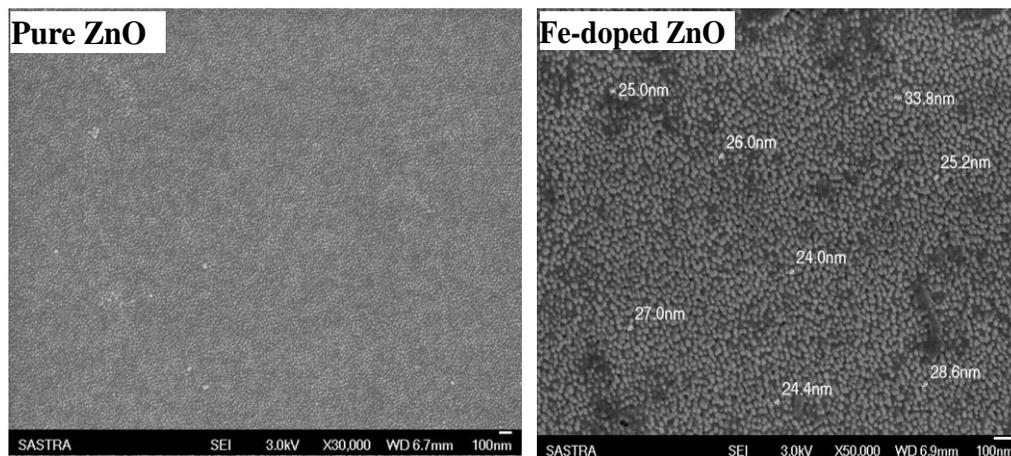


Figure 2: X-ray diffraction patterns of the undoped and Fe-doped ZnO thin films.

Figure 3: FE-SEM images of the undoped and Fe-doped ZnO thin films.



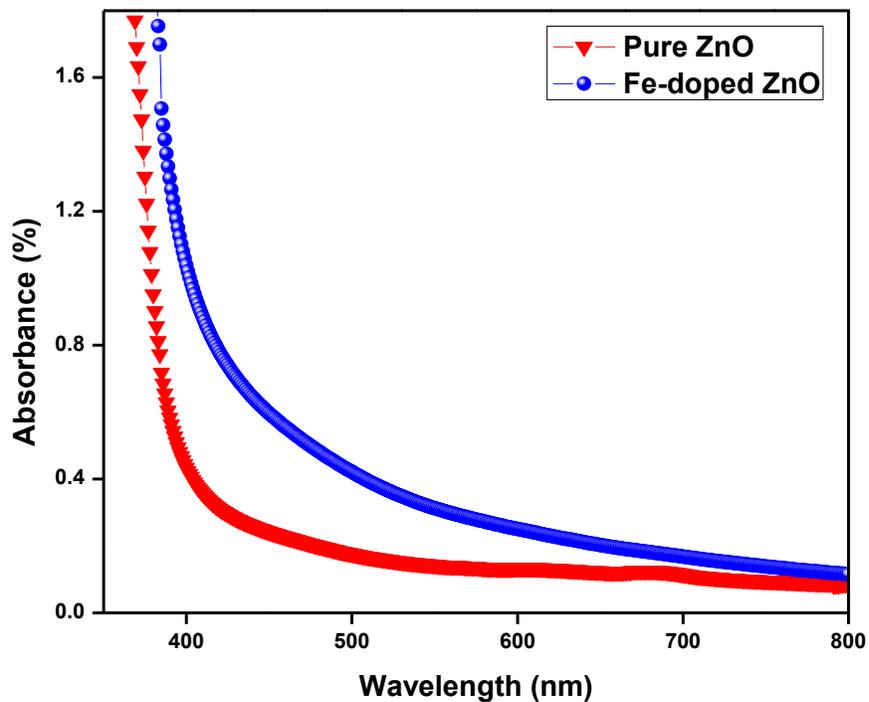


Figure 4: Absorbance spectra of the undoped and Fe-doped ZnO thin films.

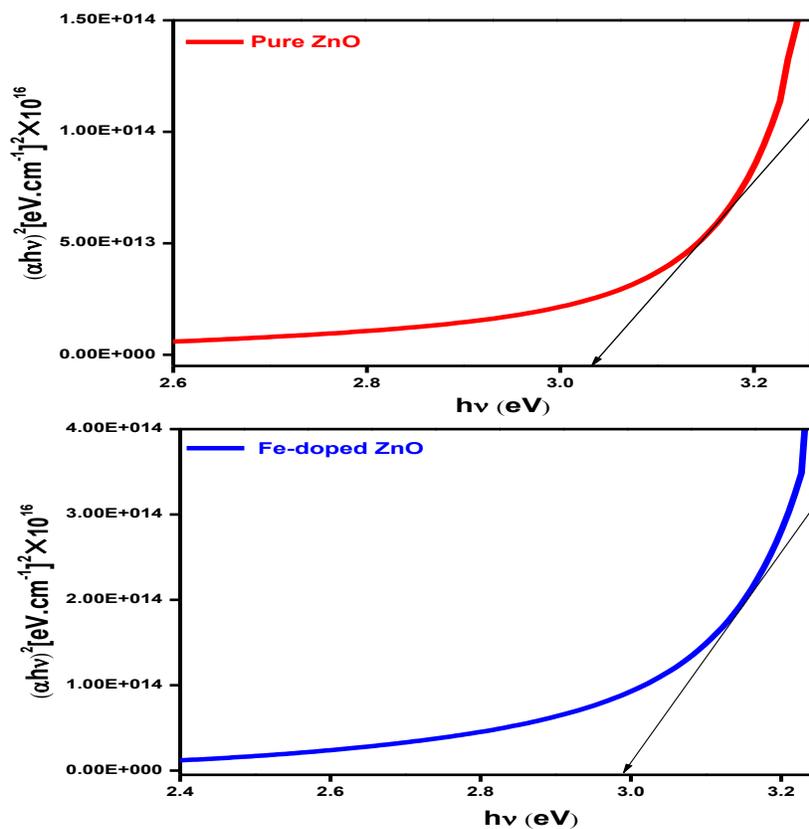


Figure 5: Tauc's plot for the undoped and Fe-doped ZnO thin films.

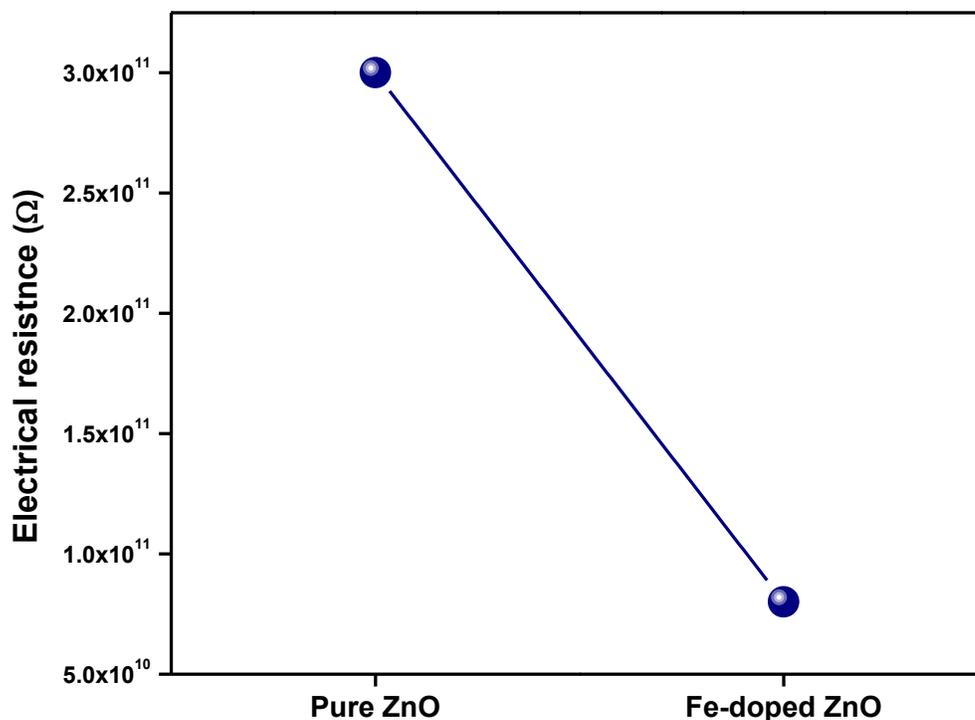


Figure 6: Electrical resistance variation of the undoped and Fe-doped ZnO thin films.

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