Structural optical and electronic properties of Fe and Ga doped ZnO thin films grown using pulsed laser deposition technique

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Abstract. Band gap engineering in ZnO thin films have been subject of intensive studies. The thin films of 2 wt % Fe and 2 wt % Ga doped ZnO and undoped ZnO were deposited on glass substrate by pulse laser deposition technique. Structural, optical and electronic structure properties of these thin films were investigated by X-Ray diffraction (XRD), UV-Vis spectroscopy and X-ray absorption spectroscopy (XAS), respectively. XRD studies show that all the thin films are highly oriented along the c-axis and maintain the wurtzite structure. Out of plane lattice parameter in Ga doped is smaller while in Fe doped is larger, compared to undoped ZnO. The band gaps of doped films have been found to increase due to doping of the Ga and Fe ions. XAS studies across O K edges of doped thin films show that the conduction band edge structure probed via oxygen 1s to 2p transitions have modified significantly in Ga doped sample.

1. Introduction
ZnO is a very promising material for semiconductor device applications and for the understanding of semiconductor Physics [1]. ZnO has large direct wide bandgap in the near-UV spectral region. With this property, ZnO is considered as potent applicant in optoelectronics in the blue/UV region, including light-emitting diodes, laser diodes and photodetectors [2]. Band gap engineering plays an important role in the modification of the optical properties of ZnO. Recently, doping has been found an effective method for bandgap regulation [3].
On the other hand, current technological applications of ZnO such as varistors, transparent conductive electrodes for solar cells, piezoelectric devices and gas sensors finds the use of ZnO polycrystalline thin films on glass substrate. So, the effect of doping in ZnO on glass substrate has become a topic of numerous scientific investigations.
Various techniques have been established to deposit the thin films such as sol gel, chemical vapor deposition (CVD), molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), R.F sputtering and PLD techniques [3]. Among all of these PLD technique is considered to be one of the best techniques to grow the thin film because of its excellent stoichiometric transfer of the material from target to substrate. We have successfully grown the pure and doped ZnO (2 wt % Fe (FZO) and 2 wt % Ga (GZO)) on glass substrate using pulsed laser deposition technique. Thin films were characterized by X-ray diffraction (XRD), UV visible and X-ray absorption (XAS) techniques to study the structural, optical and electronic properties of thin films respectively.

2. Experimental details
Pure ZnO and doped ZnO (Zn_{0.98}Ga_{0.02}O, Zn_{0.98}Fe_{0.02}O) thin films were deposited using by pulsed laser deposition technique on the glass substrate. Substrate was ultrasonically cleaned with acetone and methanol prior to deposition. Pure and doped ZnO were used as the target materials. KrF eximer laser (\(\lambda=248\)nm) with the repetition rate of 10 Hz and laser pulse energy of 220 mJ was focussed on highly compressed targets. During deposition, oxygen partial pressure was maintained at 1 mTorr and the substrate temperature was maintained at 450°C. Prior to deposition vacuum base pressure of 1x10^{-6} Torr was achieved. The target to substrate distance was maintained at 5cm. The thickness of thin films as calculated by Stylus profilometer came out to be \(\sim 100\) nm. X-ray diffraction (XRD) measurements were performed by Bruker D8 Advance diffractometer using Cu Ka radiation of wavelength 1.54 Å. The optical band gap energies of the samples were calculated using UV-vis-NIR spectrophotometer from JASCO V-550. Room temperature soft X-ray absorption spectroscopy across O K edge was carried out at the beam line BL-01 (soft X-ray absorption spectroscopy beamline) at Indus-2 Raja Ramana centre for Advanced Technologies Indore. SXAS measurements were performed in total electron yield mode (TEY). Energy resolution during SXAS measurements at oxygen K edge energy was better than \(\sim 250\) meV energy.

3. Results and discussion
Figure 1 shows the XRD patterns of the ZnO, GZO and FZO thin films. The ZnO, FZO and GZO thin films shows a strong reflection from \(0 0 2\) plane corresponding to wurtzite structure of ZnO [4]. XRD patterns confirm the crystalline nature, single phase and highly oriented growth of thin films along the \(c\)-axis. The \(0 0 2\) reflection can be used to calculate the grain size of both pure and doped ZnO thin films using Deby Scherrer formula explained below:

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  

Where \(\lambda = 1.54\) Å is the X-ray wavelength, \(\beta\) is the full width half maximum (FWHM) in radian and \(\theta\) is the Bragg’s angle. The calculated values of grain size are 17, 29 and 8 nm for pure ZnO, GZO and FZO respectively. Ga doping has been found to increase the crystallinity, while Fe doping decreases the crystallinity. With Ga doping \(c\)-lattice parameter decreases slightly, while Fe doping causes increase in \(c\)-lattice parameter as observed from the position of \(0 0 2\) reflection.
Figure 1. X-ray diffraction pattern of pure ZnO and doped ZnO (FZO and GZO) thin films.

Figure 2 (a) represents the optical transmittance spectra of PLD grown pure ZnO, FZO and GZO thin films. The transmittance is measured as a function of wavelength in the range 300–800 nm. The transmittance is more than 90% in the visible range and starts to decrease as the UV visible range (300-400 nm) approaches. The optical band gap energy was calculated with from Tauc plots (shown in Fig 2(b)) with the help of Tauc’s equation [5] read as:

\[
(\alpha h \nu)^2 = A (h \nu - E_g)
\]  

(2)

Band gap energies of pure ZnO, FZO and GZO are calculated as 3.24 eV, 3.27 eV and 3.5 eV, respectively. The band energy for FZO thin film does not change much from the pure ZnO, while there is a significant increase in the band gap of GZO thin film. This blue shift in the band gap can be explained in terms of an increase of the carrier concentration which blocks the lowest states in the conduction band, this phenomenon is called Burstein–Moss shift [5].

Figure 3 shows the O K edge XAS in Fe doped and Ga doped ZnO samples, deposited on glass substrate. Different features of O K-edge XAS spectra are marked as a (530-535 eV), b (~537 eV), c & d (~540-550 eV), and e (~557 eV). The energy region of ~530-539 eV forms the bottom of the conduction band and is attributed to O 2p-Zn 4s/Fe 3d/Ga 4s hybridized states. The features in between 540 to 550 eV can be assigned to O 2p hybridization with Zn 4p/Fe 4sp/ Ga 4p states and features above 550 eV arise due to the hybridization of O 2p with extended Zn orbitals [6]. Ga doping
Figure 3. O K-edge X-ray absorption spectrum of pure and doped ZnO (FZO and GZO) has significantly modified the bottom of conduction band in Ga doped ZnO sample. Additional localized feature (a) observed in Ga doped sample at the conduction band edge may be related to increased band gap/ Burstein–Moss shift.

4. Conclusion
XRD studies show that all the thin films are highly oriented along the c-axis and maintain the wurtzite structure. However, out of plane lattice parameter in Ga doped is smaller while in Fe doped is larger, compared to undoped ZnO. The band gaps of doped films have been found to increase due to doping of the Ga and Fe ions. XAS studies across O K edges of doped thin films show that the conduction band edge structure probed via oxygen 1s to 2p transitions has modified significantly in Ga doped sample.

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