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Gallium doped ZnO -a promising plasmonic material in Sensors in IR and NIR frequency range

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Abstract
This study aims to report the recent advances in the field of Sensors using Gallium doped ZnO as plasmonic material in IR and NIR frequency range with the help of MATLAB simulations. Here comparative study of resonance spectra of both annealed and as- deposited ZnO:Ga (GZO) with several thickness and angle of incidence are investigated. The films are highly transparent in visible –NIR ranges and gives better sensitivity to plasmonic resonance condition for below 100nm thickness.

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Introduction

Ga doped Zinc Oxides (GZO) become alternative to conventional metals and indium tin oxide (ITO) [1] in recent Plasmonic applications in optoelectronic devices including solar cells [2-4] and in the field of sensors. In earlier stage of Plasmonics, a considerable number of studies have been made on the use of Indium tin oxides [5-10] as plasmonic material in optoelectronic devices. But the high price of indium necessitates the searching of alternatives. For new plasmonic applications, metal oxide thin films should have lower resistivity and higher optical transmission over the visible wavelength region. ZnO:Ga thin films possess some extraordinary advantages such as low cost, thermal stability, and comparatively low deposition temperature with greater stability under hydrogen plasma bombardment. It can exhibit tunable optical properties and can be compatible with standard fabrication and integration procedures.

For the excitement of Surface Plasmons, the metallic conductivity of ZnO:Ga plays an important role due to its coherent oscillations of free electrons at metal-dielectric interface. For high carrier concentration $n \sim 10^{21}$ cm^{-3} the plasma frequency of ZnO:Ga exists in the near infrared region. In the present analysis, three-layer Kretschmann structure (air- metal – prism) is considered. This structure has a potential application in light emitting diodes and waveguide devices [11, 12] and also in sensing applications.

To be plasmonic the materials should have negative permittivity. Trans conducting oxides like indium tin oxide (ITO), aluminum doped zinc oxide (AZO) and gallium doped zinc oxide (GZO) are the metallic substitute and promising plasmonic materials in near IR region. For photonics and nanophononics applications in the telecommunication wavelength AZO and GZO have lower loss.

The free electron density in the Ga:ZnO increases due to the doping of Ga into ZnO, resulting in the decrease of resistivity [13]. The electrical resistivity of Ga-doped ZnO films is lower than that of pure ZnO films. Annealing treatment has a significant effect on the optical and electrical properties of Ga dopped ZnO. After annealing treatment to a certain temperature, the carrier density in Ga dopped Zinc oxide decreases causing an increment in resistivity. The optical band gap of ZnO:Ga (~60 MeV) thin film which is grown on sapphire substrates by laser ablation [14] is higher as compared with that of annealed ZnO:Ga (<60 MeV). After doping Ga into pure ZnO film, a significant variation of refractive index is also noticed due to decrease of film density or an increment in energy band gap.

In this work, the resonance spectra of 2 at% Ga doped ZnO (as-deposited) and after heat treatment are studied for incident angle 45^0 to 69^0 of incident radiation and for various films with thickness varying from 10nm to 500nm. Despite good potential of Ga doped ZnO thin films prepared by electron beam evaporation technique, less attention has been paid to the study of annealing temperature effect on the nature of resonance spectra before and after heat treatment. The study confirms Surface Plasmon excitation in ZnO:Ga film and the comparative analysis based on Surface Plasmon Resonance spectra of ZnO:Ga film in its 2 at % as-deposited state and after annealing in air.

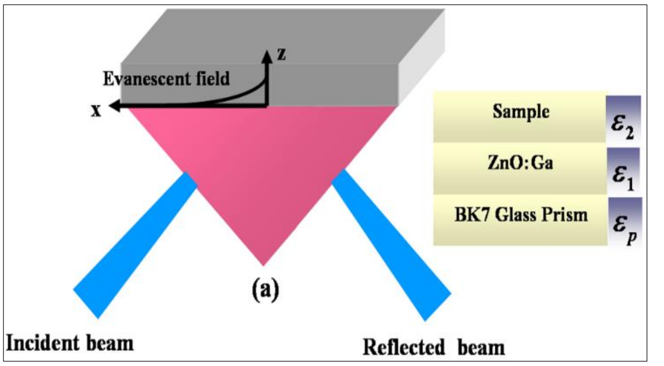


Fig 1: Kretschmann configuration in three-layer model.

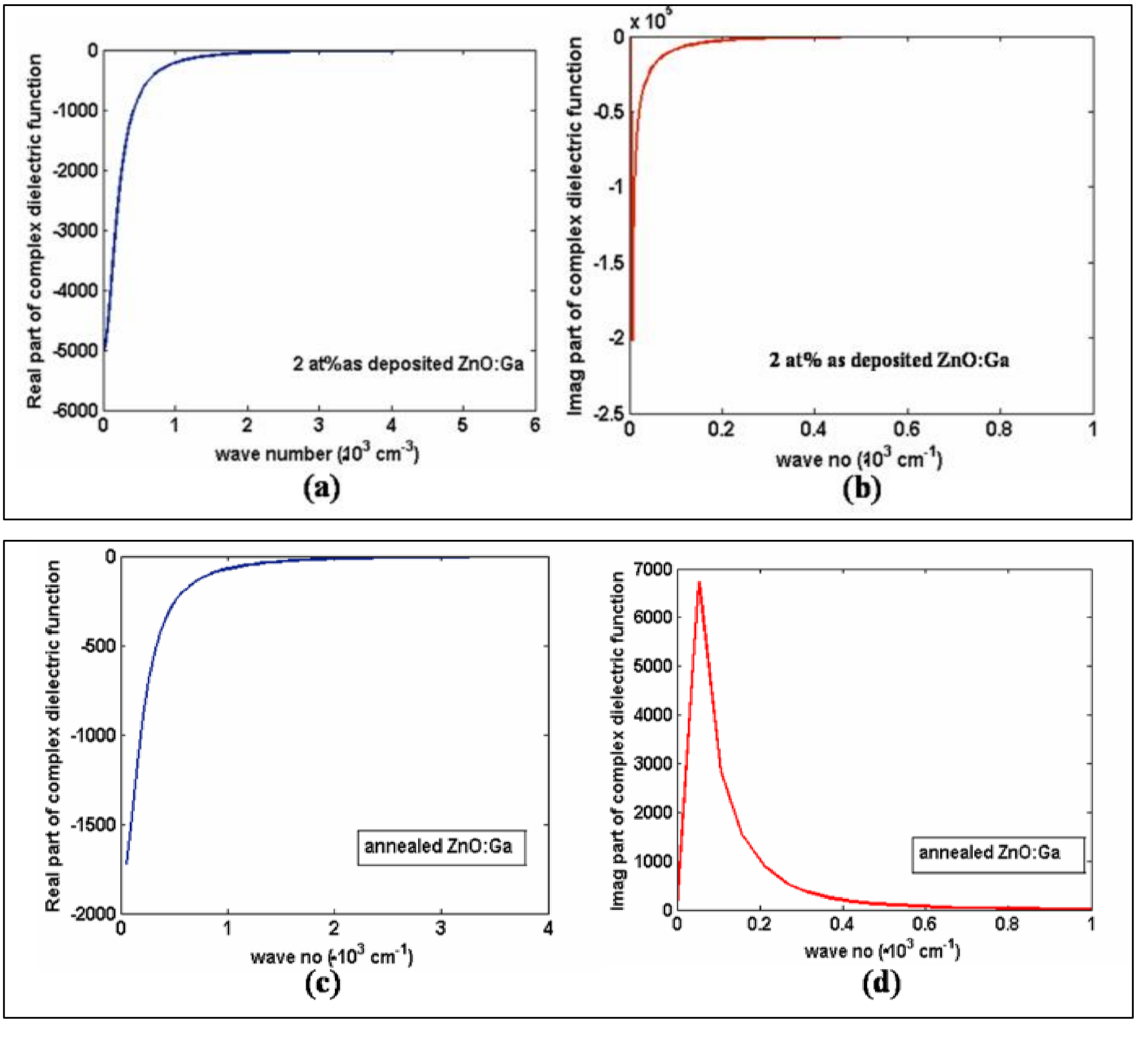


Fig 2: Variation of real part and imaginary part of complex dielectric function with the wave number of the incident exciting radiation for 2 at % as-deposited ZnO:Ga (a, b) respectively. The same for annealed ZnO:Ga are in (c, d) respectively

Simulation of resonance curves for different state of Ga doped ZnO

The collective oscillations of free charges in as-deposited ZnO:Ga and also in its annealed state result in excitation of Surface Plasmon Resonance under some optimised selection of the angle of incidence. Both types of Gallium doped zinc oxides are often opaque and transparent and depending upon the angle of incidence and thickness of the film, they have optimized constraints to show resonance to excitations by external light and also give dual peak resonance.

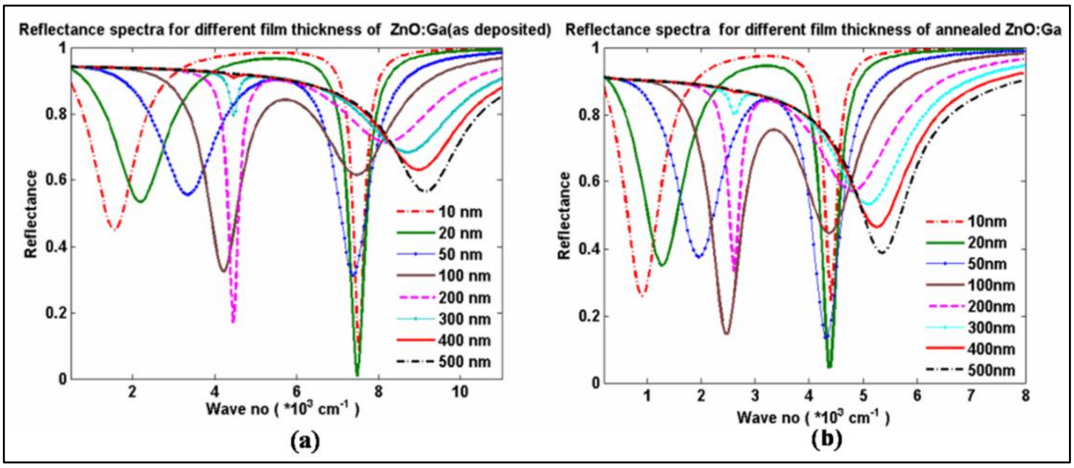


Fig 3: Reflectance as a function of wave number with the variation of thickness of the (a) pre annealing and (b) post annealing state of ZnO:Ga layer

The thickness of the film layer (below 50nm) has more probability of exciting electrons with the incident exciting beam than thick film layer considering the incident beam to fall on the configuration at 45^0. Though in the following figures it is noticed that 20nm thickness of ZnO:Ga film for both pre-annealing state and post-annealing state supports Surface Plasmon Resonance as it provides minimum reflectance value in two type of investigations.

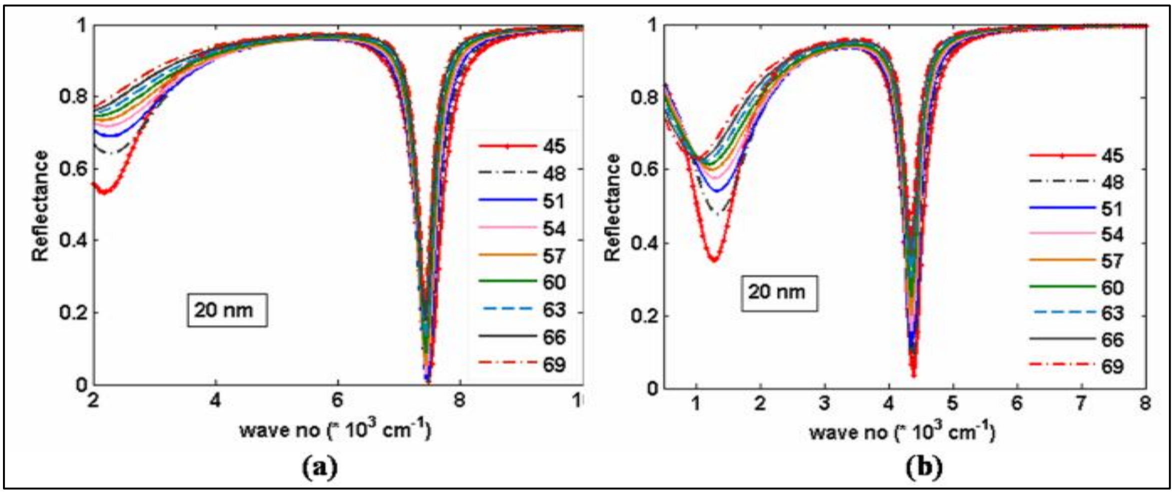


Fig 4: Reflectance spectra of Gallium dopped Zinc oxide (a) as deposited (b) post annealing state as a function of wave number for different incident angles in the range $45^0 – 69^0$, with steps of 3^0.

The variation of reflection spectra with the incident angle of the exciting beam for 20 nm ZnO:Ga film both for its pre-annealed and post-annealed state respectively are described in Figure.4 (a). 20nm 2 at% as deposited GZO film gives resonance at 7480 cm^{-1} when the exciting radiation is incident at 45^0 which is its plasmon frequency and 20 nm ZnO:Ga after heat treatment responses to exciting radiation at 4403 cm^{-1} as shown in Figure.4 (b). For comparison of performance between the two states, pre annealing and post annealing, the zinc oxides the thickness for minimum reflectance is taken as 20nm.

To understand the thickness dependency of the resonance phenomenon, more detailed study has been done. The variation of the reflectance curves for the metal oxide layer for different angle of incidence and different thickness is depicted in Figure.5. The reflectance minimum is sensitive to angle of incidence of the exciting radiation, excitation frequency and thickness of the metal oxide thin film. In Figure.5(a), SPR occurs at 7480 cm^{-1} for 20 nm Ga dopped as-deposited ZnO when exciting radiation incident at 45^0 with 0.73% reflectance minimum. After annealing 20 nm ZnO:Ga give response to exciting radiation at 4403 cm^{-1} with 3.4% reflectance of light at 45^0 incident angle as shown in Figure.5(b). Further increasing of angle of incidence, results in resonance occurrence at 7427 cm^{-1} with approx 77% transmission of light through 50 nm Ga dopped ZnO layer of 2 at % as deposited (Figure.5(a)). The thickness of the metal oxide layer is further increased from 100 nm to 500nm. It is found that in Figure. 5(b) that 100 nm as-deposited film gives resonance at 69^0 with 2.77% reflection of the exciting beam. At 45^0 incident angle for both state of ZnO:Ga (pre-annealing state and also its post annealing state) shows dual peak resonance. But for higher thickness, dual peak resonance is not noticed. Minimum reflectance value for 150 nm as deposited ZnO:Ga film gets shifted from 4403 cm^{-1} with 2.3% reflectance to 6419 cm^{-1} with 0.233% reflectance when the angle of incidence changes from 45^0 to 69^0 respectively as shown in Figure.5(c). Figure.5(d). SPR is prominent for film thickness upto 200 nm and a bove 200 nm thick film (Figure.5(e-h)) resonance does not occur.

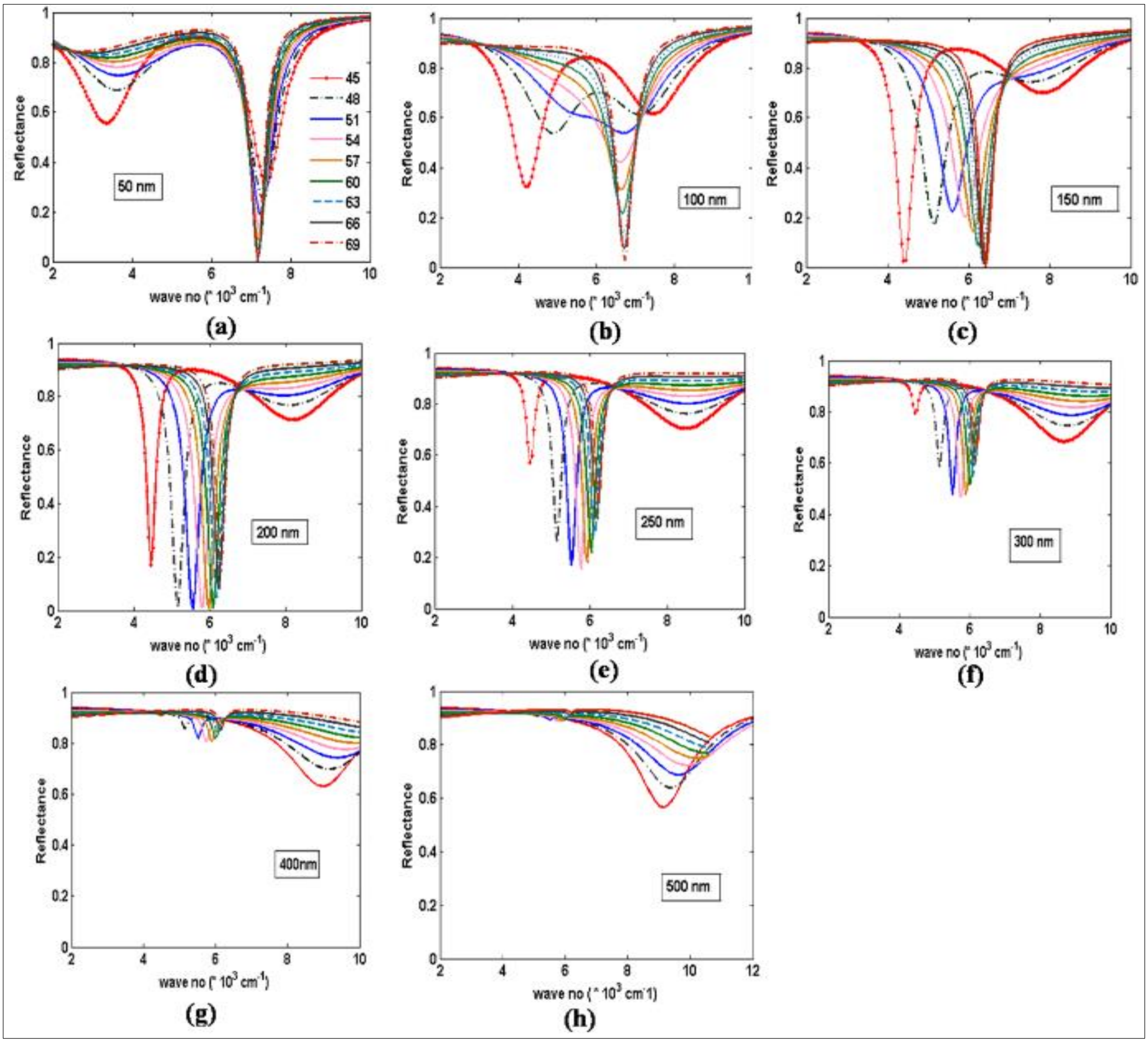
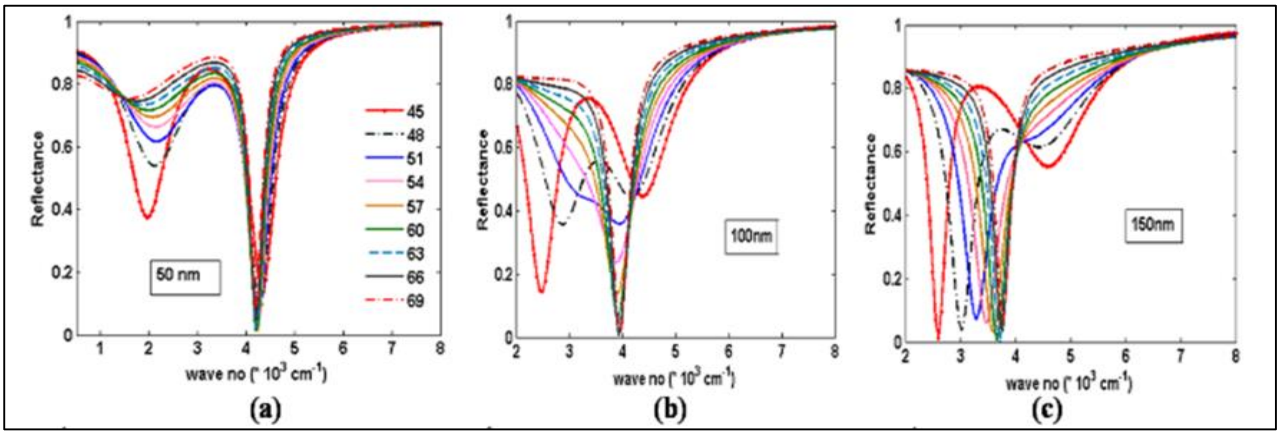


Figure. 5. Reflectance spectra of 2 at% ZnO:Ga for pre annealing state as a function of wave number of the incident beam and the incident angle for different thick layers

Similar study has been done for post annealed ZnO:Ga for the same thicknesses as shown in Figure.6. It is to be noted that 100 nm layer provides resonance at 3926 cm^{-1} at 66^0 incident angle whereas 150 nm thickness corresponds to 3714 cm^{-1} wave number with incident angle at 63^0 as shown in Figure.6(b, c) respectively. Coupling of the incident light to the SPs is more prominent for thin film ~below 200nm of ZnO:Ga.



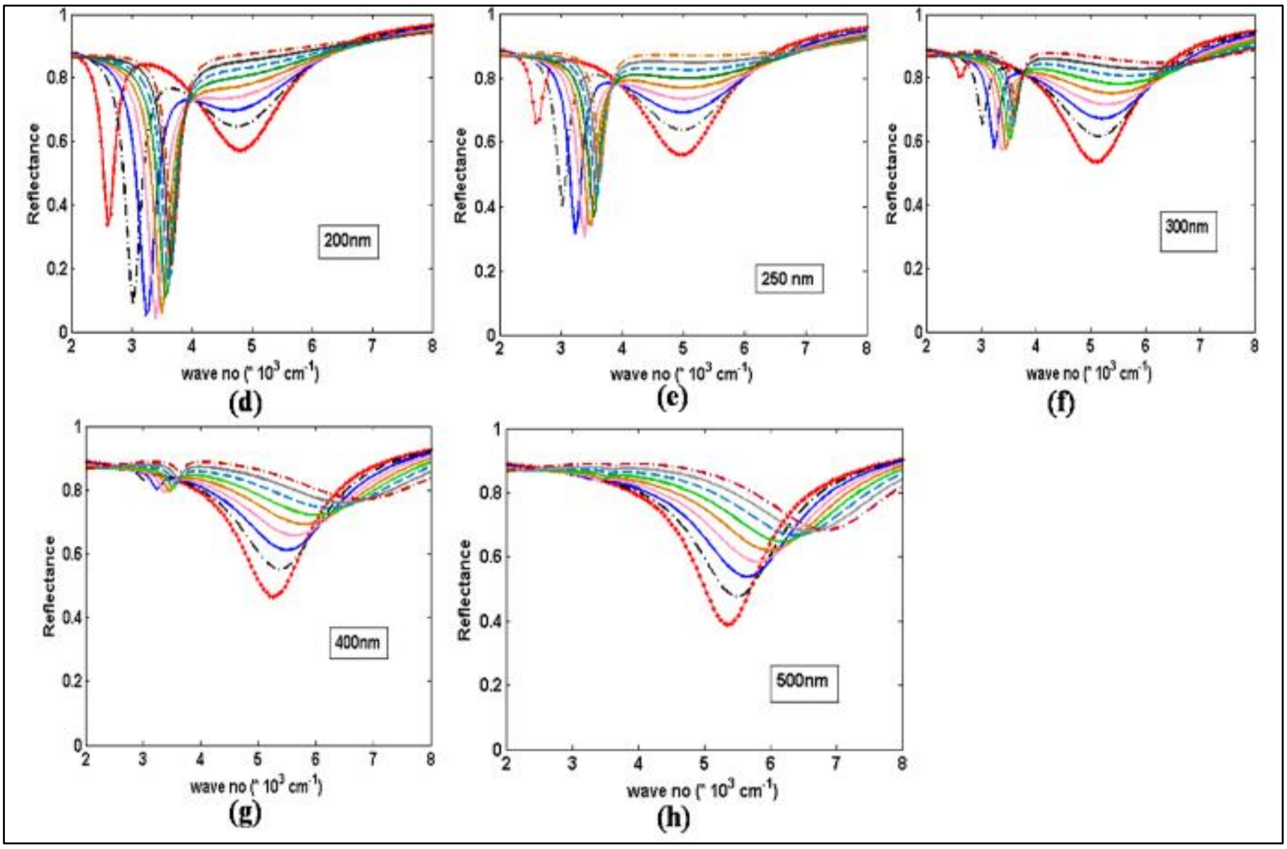
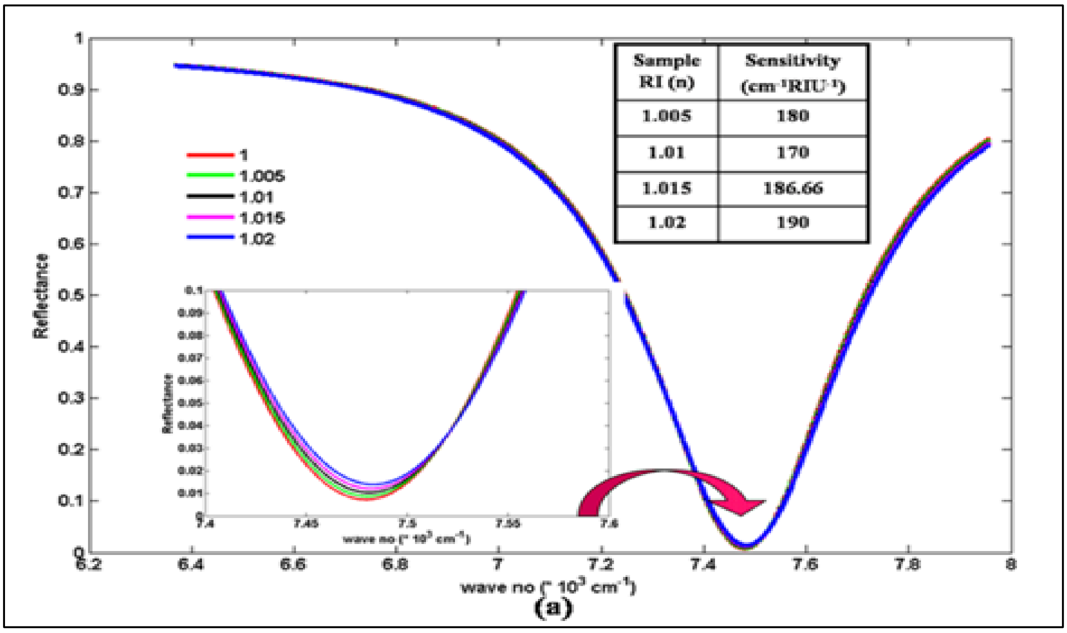


Fig 6: Reflectance spectra of 2 at% ZnO:Ga for post-annealing state as a function of wave number of the incident beam and the incident angle for different thick layers

Application of GZO in sensing: Sensor performance and related sensitivity issues

At first 20 nm thickness of GZO has been considered for sensing application. We have studied sensing of different gaseous samples taking air as reference using the proposed structure. The dip shift on the reflection spectrum is used to detect the sample in terms of refractive index. The sensitivity can be calculated as the change in the wave number at resonance due to change of the refractive index of the sample. Figure.7 shows the reflectance curves for different samples whose refractive indices are mentioned in legend. The shift in resonance is not visible for both as deposited and annealed state in Figure. 7(a, b). Corresponding dips are zoomed to calculate sensitivity. Figure. 7(a) shows that resonance wave no shifts to higher value when sample refractive index increases. Similar trend is also visible in case of post-annealed sample. Sensitivity of the annealed state is lower than that of as deposited state for a particular sample as tabulated in Figure. 7. This implies that measurements with as deposited layer is more sensitive compared with that of annealed film.



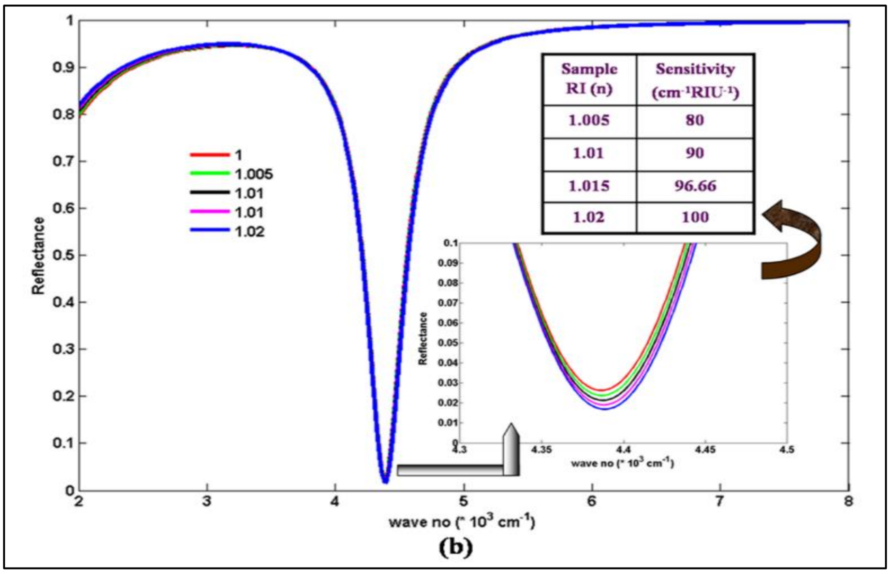


Fig 7: Sensing of gaseous samples using (a) as-deposited and (b) annealed ZnO:Ga films of thickness 20nm. The inset in (a, b) are magnified view of the dip of resonances in reflection. Refractive index sensitivities obtained by considering air as reference.

If the sensitivity application is studied for 150nm Ga dopped ZnO when the electromagnetic radiation is incident on the Kretschmann configuration, using different gaseous samples, then also it can be noticed that Sensitivity of the as deposited state is higher than that of annealed state for a particular sample. This implies again that measurements with as deposited layer is more sensitive compared with that of annealed film for higher thickness of 150nm.
But annealed ZnO:Ga is found to provide higher detection accuracy in comparison to as deposited state. One of the prospective approaches to further improving the sensing technique involves both detection accuracy and sensitivity.

Conclusions

For 20 nm Ga dopped as-deposited Zinc oxide, it is noticed that Surface Plasmon Resonance when excited with the incident radiation at 45^0 occurred at 7480 cm^{-1} and gets shifted to 7427 cm^{-1} with increased angle of incidence. For Ga dopped ZnO after annealing, the Surface Plasmon Resonance occurs at 4403 cm^{-1}.
Both Ga dopped ZnO, before and after heat treatment supports Surface Plasmon excitations for thin film thickness below 200nm. As-deposited film supports SPP resonance at higher frequency than the film after annealing.

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