

## Recent advances in Sensors applications using AZO and GZO as Plasmonic material in IR and NIR frequency region

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### **Abstract:**

Transparent conducting oxides become the promising alternative material to the conventional metals in the application of plasmonic materials in recent advances in Sensors in NIR and telecommunication frequency region. The optical and electric properties of TCOs have been explored for the study of plasmonic and MM devices as substitute to metals. Heavily doped Zinc oxides have the optical and electrical properties suitable for this application in the optoelectronic Sensors in the optical range based on surface Plasmon resonance. Aluminium doped Zinc oxide and Gallium doped Zinc oxide have the promising application in the field of Surface Plasmon resonance is mostly depending on the thickness of the TCO material and the angle of incidence of the incident exciting electromagnetic light. This study aims to report the study of Aluminium doped ZnO (AZO) and Gallium doped ZnO (GZO) for the propagation of surface Plasmon polariton wave with several thickness and angle of incidence, supported by MATLAB simulations and their application in the recent advances in optoelectronic Sensors.

**Keywords:** AZO, GZO, optoelectronic Sensors, Surface Plasmon Resonance

### **I. Introduction:**

As alternatives to conventional metals, new plasmonic materials offer many advantages in the rapidly growing fields of optoelectronic devices and solar cells [Rech, 1999; Zeman, 2000; Ferlauto, 2002]. These advantages include low intrinsic loss, semiconductor-based design and compatibility with standard nanofabrication processes, tunability, and others. Transparent conducting oxides such as Al: ZnO, Ga:ZnO and indium-tin-oxide (ITO) enable many high-performance metamaterial devices operating in the near-IR region. In recent plasmonic applications in NIR-IR region, Al doped Zinc oxides and Ga doped zinc oxides (ZnO:Ga) become alternatives to conventional metals and indium tin oxide (ITO). Transparent conducting oxides [Brewer, 2004] thin films are greatly used in plasmonic devices as they have good conductivity, high optical transmittance over the visible wavelength region, excellent adhesion to substrates, chemical stability, and photochemical properties. Among all the metal oxides, several studies have been reported on the use of ITO [Franzen, 2009; Franzen, 2008; Brewer, 2002; Losego, 2009; Rhodes, 2006; Rhodes, 2008]. Along with ITO, ZnO: Al and ZnO:Ga are important substitute to metals in recent developments of optoelectronic devices. AZO and GZO 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.

ZnO is a wide band gap semiconductor having negative permittivity in the frequency range and under certain circumstances they can be used as low loss plasmonic materials [Kim, 1997; Hamberg, 1986; Hoffman, 2007; Schuller, 2007]. In the telecommunication wavelength AZO and GZO have lower loss. Intrinsic ZnO is an n type wide band gap semiconductor. Its electrical and optical properties are changed dramatically with the introduction of group III elements such as Al, Sn, Ga into intrinsic ZnO. In this paper the variation of Resonance spectra with the variation of thickness of the metal oxide thin film (AZO and GZO) and the angle of incidence at which the exciting beam incident on the Kretschmann Configuration is presented and the application of AZO and GZO in biosensors are described in details considering the FWHM of the Reflectance Spectra.

## II. Conventional SPR Structure (Kretschmann configuration) for excitation of Surface Plasmons:

The coupling between the conduction electrons of the materials with the interacting electromagnetic waves is described by the classical Drude theory according to which the complex electrical permittivity is described by

$$\varepsilon = \varepsilon' + i\varepsilon'' = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad (1)$$

where,  $\varepsilon_{\infty}$  is the high frequency dielectric constant,  $\gamma$  is damping coefficient of free electrons and  $\omega_p$  is plasma frequency. So, for low loss, material should have small  $\gamma$  value.

Plasma frequency is defined as

$$\omega_p^2 = \frac{ne^2}{\varepsilon_0 m^*} \quad (2)$$

Here  $n$  is the charge carrier density,  $e$  is the charge of the electron,  $m^*$  is the effective mass and  $\varepsilon_0$  is the permittivity of the vacuum. So materials can exhibit metallic properties with high value of carrier density and can be used in plasmonic application.

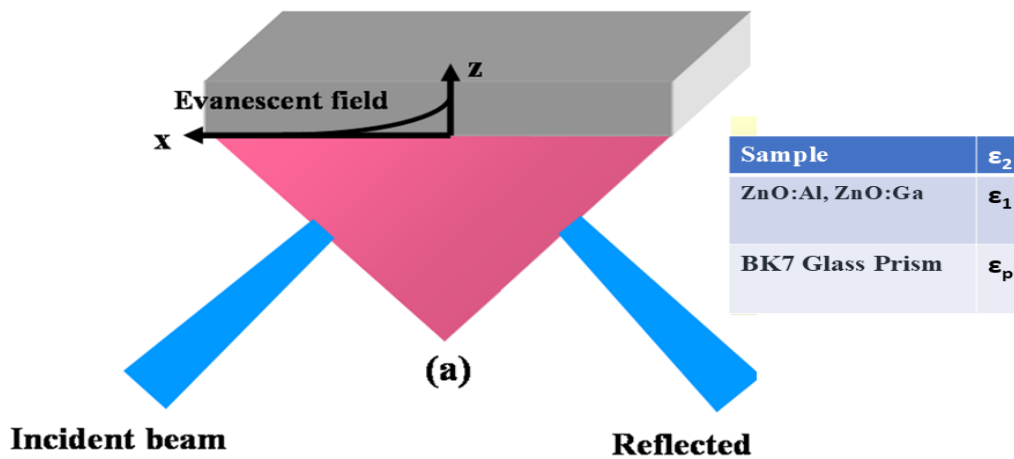
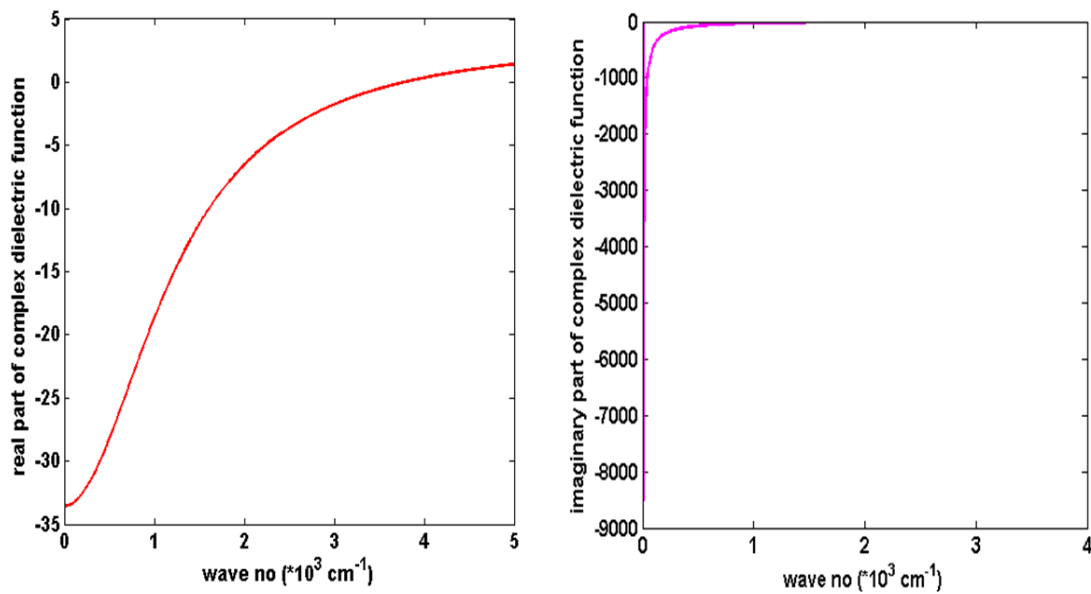


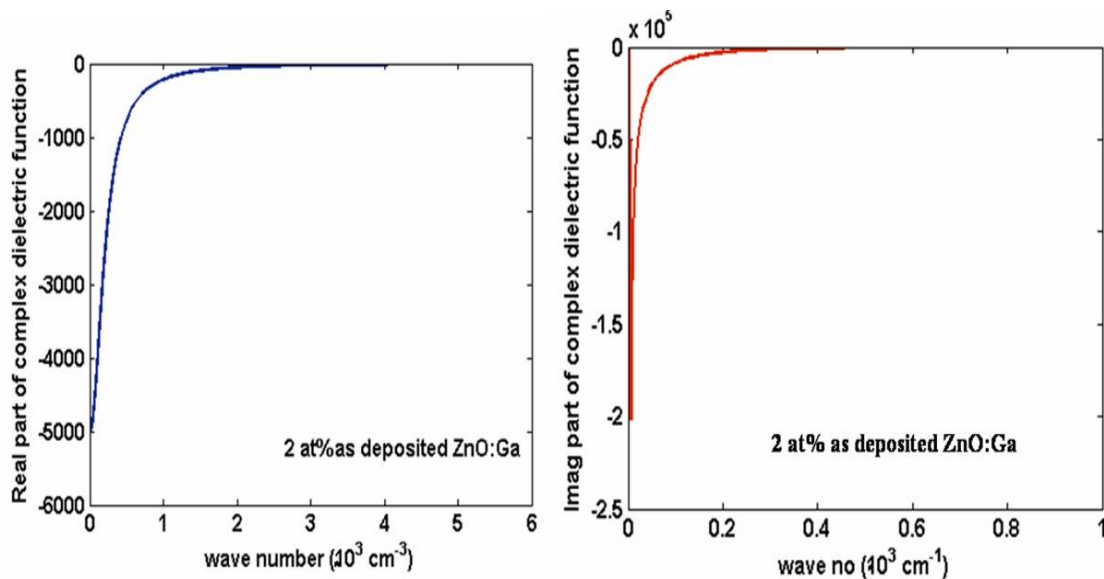
Figure . 1: Kretschmann configuration in three-layer model.

Figure 1 demonstrate the Kretschmann configuration, where the p-polarised electromagnetic radiation propagating through the prism is incident on the metal prism interface and an evanescent wave is generated at the interface. When the ATR condition is achieved then light is totally reflected internally and in the perpendicular direction to the interface of the prism and the metal oxide layer, the evanescent waves decay exponentially.

In this three-phase model, the dielectric constant of prism is  $\varepsilon_p$  and the dielectric constant of the surrounding medium is  $\varepsilon_2$  and  $\theta$  is the angle of incidence at which the in-plane component of the photon wave vector in the BK7 prism coincides with the SPP wave vector at the air- metal oxide interface, the resonant light tunnels through the metal oxide film and results in coupling of light with the Surface Polaritons. At this resonant condition, there is a sharp dip in the reflectance at the detector.



**Figure 2(a):** Variation of real part and imaginary part of complex dielectric function with the wave number of the incident exciting radiation for ZnO: Al layer.



**Figure 2(b):** 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 .

In this configuration, the prism with dielectric constant  $\epsilon_p$  is illuminated by the incident light. The dielectric constant of the prism will be greater than the dielectric constant of the surrounding medium,  $\epsilon_2$  ( $\epsilon_p > \epsilon_2$ ). At a small angle of incidence, a portion of light is reflected at a bottom of the prism and some portion of light is refracted at the interface of prism and metal oxide layer. This optical phenomenon of Reflection and refraction are analysed assuming the plane wave incident light. The critical angle for the total internal reflection is given by the relation

$$\theta_c = \sin^{-1} \sqrt{\frac{\epsilon_2}{\epsilon_p}} \quad (3)$$

For total internal reflection, the metal oxide thin film is illuminated through a prism at an angle of incidence greater than the critical angle. The change of refractive index at the prism- metal oxide interface is used to detect unknown sample. In the optically denser medium, the wave vector of light is higher. At the angle of incidence  $\theta$  at which the in-plane component of the photon wave vector in the BK7 prism coincides with the SPP wave vector at the air- metal oxide interface, the resonant light tunnels through the metal oxide film and results in coupling of light with the Surface Polaritons. At this resonant condition, there at the detector there is a sharp dip in the reflectance.

The intensity of the reflected light reaches its minimum value at a particular angle or wavelength, and it is demonstrated by a sharp dip in the SPR curve. Surface Plasmon Resonance is dependent on energy of incident radiation, thickness of metal or metal oxide film and angle of incidence and described by the three phase Kretschmann (substrate/ overlayer/ ambient) model [Hansen, 1968]. This Kretschmann representation is sensitive for thin film, for larger thicknesses this structure gradually weakens, in agreement with theory. No other collective excitations are observed.

At the interface of Al doped Zinc oxide film and BK7 glass, the Surface Plasmon Polaritons are excited in the near infra-red wavelength (1.45 $\mu\text{m}$  -1.59  $\mu\text{m}$ ) region [Marton, 1977] important optical wavelengths for plasmonic applications such as molecular vibrational spectroscopes and light telecommunications [Rech, 1999; Zeman, 2000].

Applying the Drude model in the Kretschmann configuration it can be shown that the allowed frequency range of the Surface Plasmon is  $0 < \omega < \frac{\omega_p}{\sqrt{\epsilon_1 + \epsilon_2}}$

In this study three phase layer Kretschmann Configuration is used to detect Surface plasmons in metal oxide thin film. If the field reflectance at metal oxide layer- prism interface is  $r_{p1}$  and the field reflectance at air- metal oxide interface is  $r_{12}$  then this field reflectance can be determined from the following equations

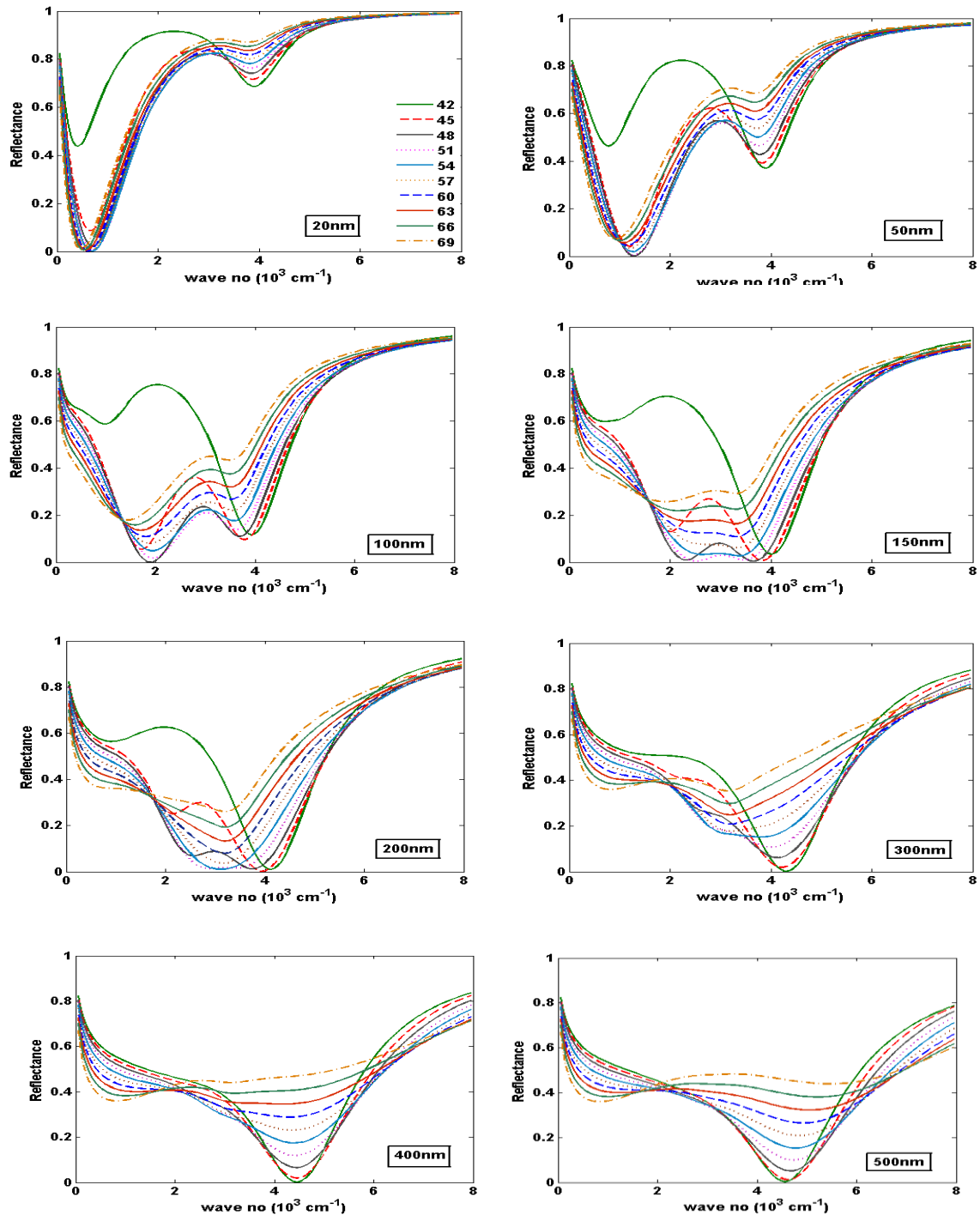
$$r_{p1} = \frac{\frac{\cos\theta \sqrt{\epsilon_1 - n_p^2 \sin^2 \theta}}{n_p} - \frac{\epsilon_1}{\epsilon_1}}{\frac{\cos\theta \sqrt{\epsilon_1 - n_p^2 \sin^2 \theta}}{n_p} + \frac{\epsilon_1}{\epsilon_1}} \quad (4)$$

$$r_{12} = \frac{\frac{\sqrt{\epsilon_1 - n_p^2 \sin^2 \theta}}{\epsilon_1} - \frac{\sqrt{\epsilon_2 - n_p^2 \sin^2 \theta}}{\epsilon_2}}{\frac{\sqrt{\epsilon_1 - n_p^2 \sin^2 \theta}}{\epsilon_1} + \frac{\sqrt{\epsilon_2 - n_p^2 \sin^2 \theta}}{\epsilon_2}} \quad (5)$$

### III. Results and Discussions:

#### a. SPR Reflectance Profile for AZO

The SPP resonance curves are shown in Figure 3 for ZnO: Al as a function of frequency and for incident angle from 42 $^\circ$  to 69 $^\circ$  with 3 $^\circ$  increments in the 1.55-micron wavelength window. Figure 3 consists of nine traces with variation of thickness of trans-conducting film under consideration.

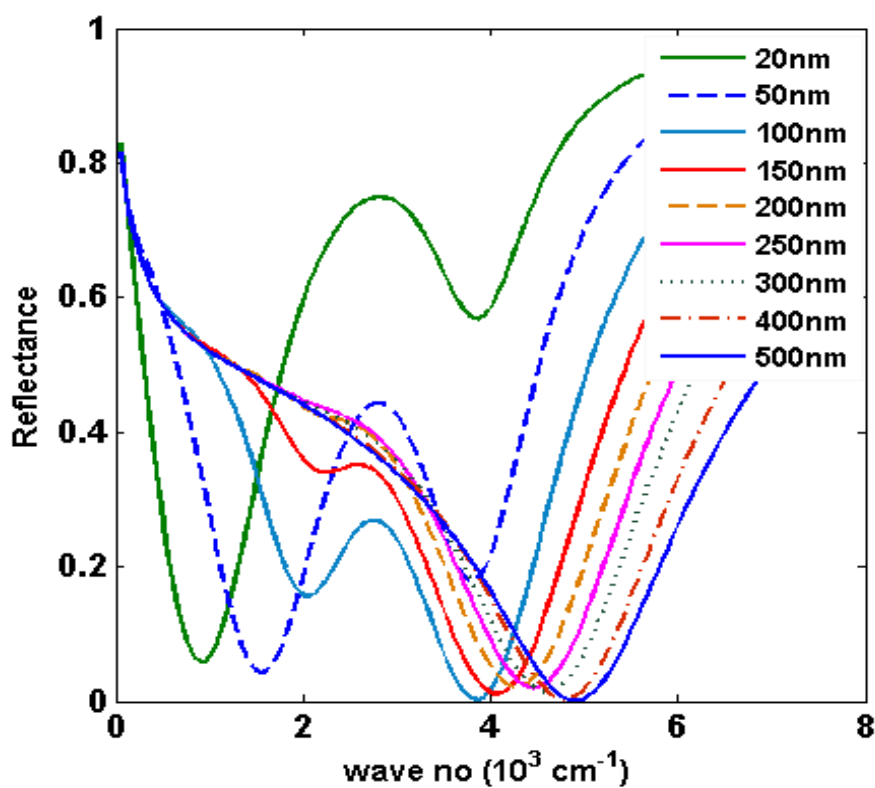


**Figure 3:** Reflectance vs. wave number curves for different thicknesses of ZnO: Al film from 20 nm to 500 nm, with  $\theta$  varying from  $42^\circ$  to  $69^\circ$  in steps of  $3^\circ$ .

Here, from the theoretical data we have found that the angle of incidence at which resonance occurs is  $42^\circ$  for ZnO: Al. With every increment of  $\theta$  the SBPP resonant frequency does not alter though the reflectivity increases to some extent which means absorbance of the incident light decreases as evident from the resulting change of profile (from red line to pink line). With increased thickness, for 100 nm

ZnO: Al, at resonant frequency, reflectivity dip (in between  $2000\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ ) almost approaches zero and incident light is efficiently coupled to plasmons.

With further increase of the film thickness, the SBPP resonance appears to behave differently. The resonant frequency shifts to higher energies for lower incident angle ( $3820\text{ cm}^{-1}$  for  $42^\circ$ ) and to lower energies for higher incident angle ( $1698\text{ cm}^{-1}$  for  $48^\circ$ ) and beyond that resonant energy is found to be almost independent of  $\theta$ , which corresponds to SPP resonance. From the reflectance vs wave no curves for different thickness panels, it can be observed that SPP coupling is optimum for 150 nm thickness. If the thickness of the Al doped Zinc oxide coating is 500 nm thick, then it is noticed that only lower angles can support SPP excitation although not much efficient, and for  $\theta$  above  $48^\circ$ , practically there is no coupling between plasmons and incident radiation. Figure 3 shows the reflectance profile for a particular angle of incidence  $42^\circ$  with different thicknesses of ZnO: Al film indicated in the legend. Here also, dual resonance dips are noticed with varying reflectance minima values for thickness below 100 nm.



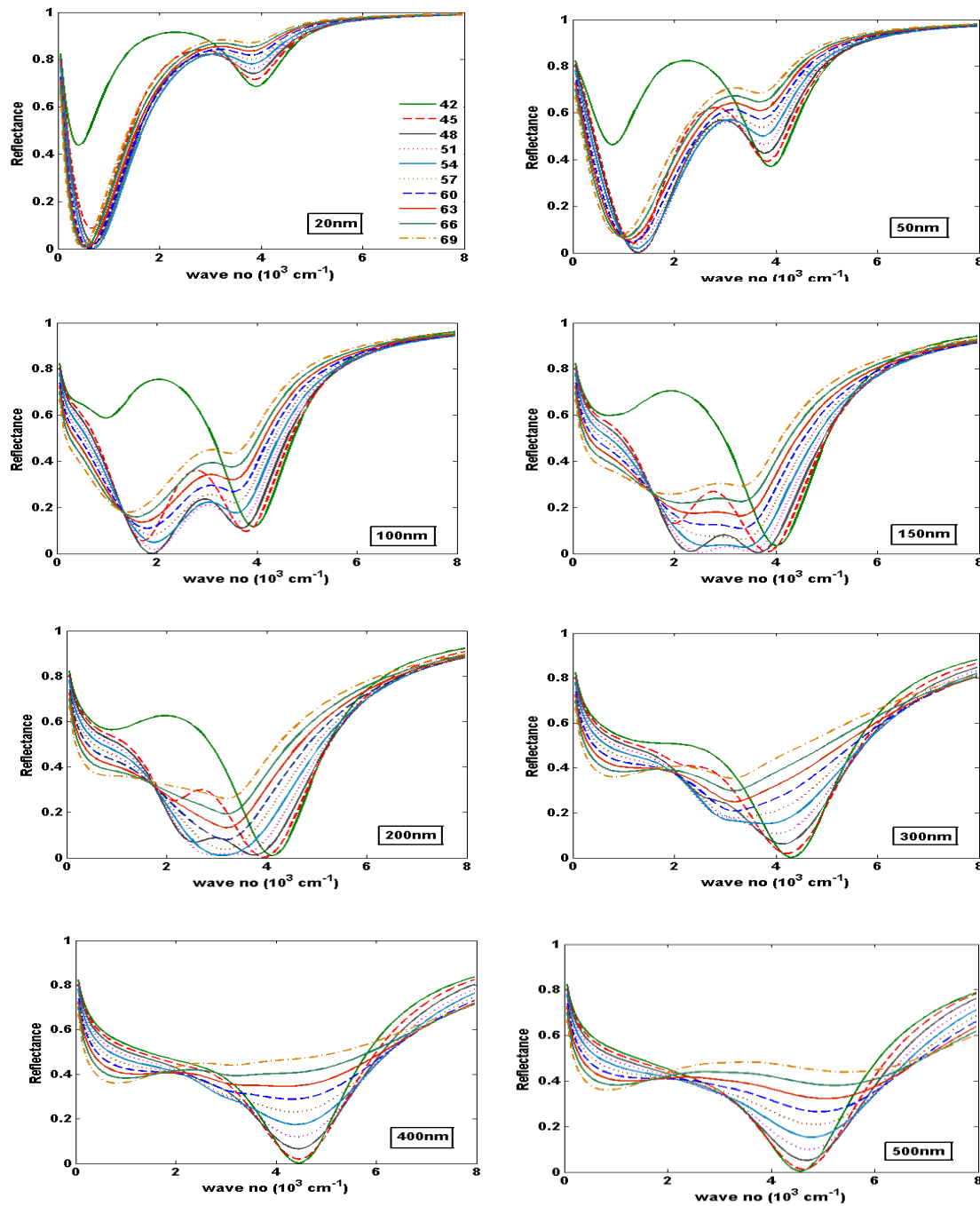
**Figure 4:** Thickness variation of Reflectance with wave number for different thicknesses of ZnO: Al film from 20 nm to 500 nm in  $1.55\ \mu\text{m}$  range

So, Figure 4 shows the variation of reflectance profile with wave no for different thicknesses of ZnO: Al. Here this type of resonance is called Fano resonance or asymmetric type of dual dips. In our simulation, we have noticed that for  $\theta > 51^\circ$ , the reflectance profile does not correspond to SPP excitation of interest. For 30 nm ZnO: Al film, dual dips having minima at  $954\text{ cm}^{-1}$  and  $3873\text{ cm}^{-1}$  corresponding to angle  $51^\circ$  and  $43^\circ$  respectively. The reflectance profile is deeper for lower incident angle for second dip. Again, for 500 nm thickness, resonance curve become symmetric type with a single reflecting dip occurring at  $4651\text{ cm}^{-1}$  (0.58 eV).

From these reflectance profiles it is showed that the optimised angle of incidence for 100 nm Al doped ZnO is  $48^\circ$  and for 200 nm AZO it is  $43^\circ$ . At this angle of incidence, the exciting radiation coupled with the Surface Plasmons and the reflectance detected at the detector is minimum.

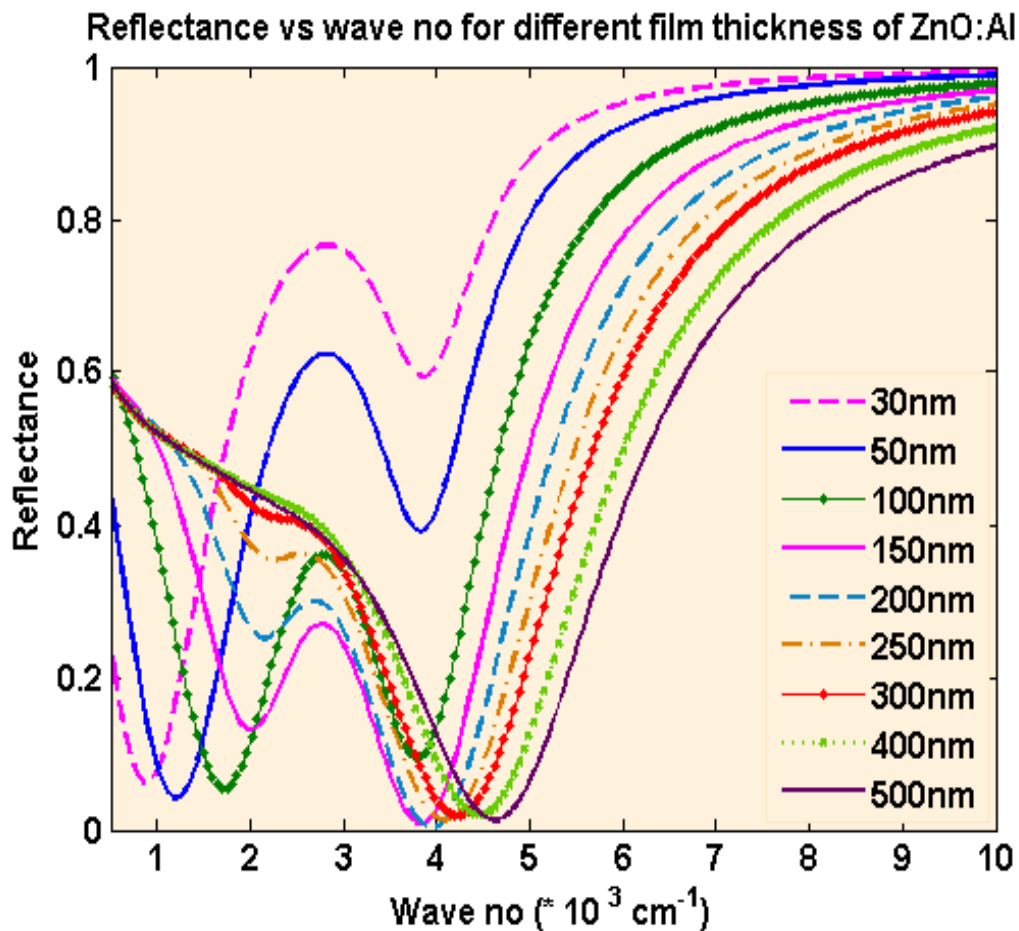
**b. Analysis for conventional SPR structure in 2.5  $\mu\text{m}$  range:**

Figure 5 shows the variable nature of Reflectance with the angle of incidence of the exciting radiation. Here Al doped ZnO support the SPP excitation in the mid infra-red (2.5 micron) wavelength range.



**Figure 5:** Reflectance vs. wave number curves for different thicknesses of ZnO: Al film from 20 nm to 500 nm, with  $\theta$  varying from  $42^\circ$  (red dotted line) to  $69^\circ$  (pink solid line) in steps of  $3^\circ$

Figure 5 is the two-dimensional variation of Reflectivity with frequency for different thicknesses from 30 nm (pink line) to 500 nm (violet line) when exciting radiation incident at an angle  $45^\circ$  to the metal oxide layer. Minimum reflectivity position for ZnO: Al is lower or in other words, corresponds to higher absorbance of incident light. Above 200 nm thickness, ZnO: Al gives almost 100% absorption.



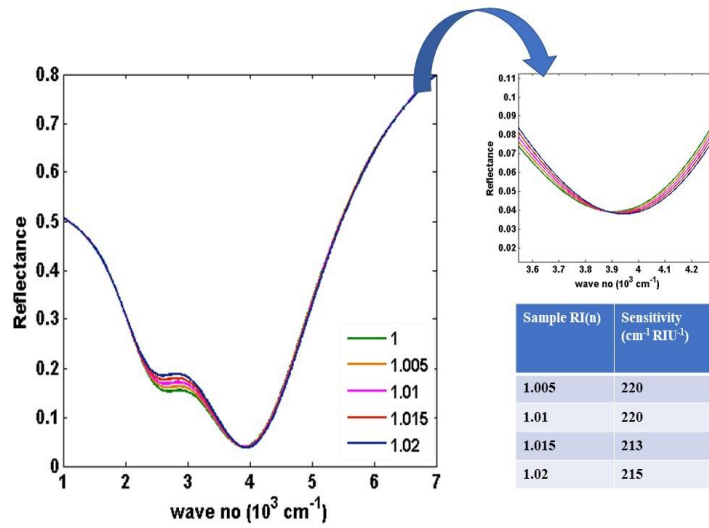
**Figure 6:** Variation of Reflectance profile with different increasing thickness of ZnO: Al (from 30 nm to 500 nm) at  $45^\circ$  incident angle.

Figure 7 shows the sensitivity responses of Al doped Zinc oxides in IR and NIR optical regions. These are the reflectance curves with the incident light wave number for different samples whose refractive indices are mentioned in the legend of the curves shown in (a) and (b). The shift in the wave number due to change in the refractive index of the sample is very small. In this study, the sensitivity is calculated as the change in the wave number at resonance due to change of the refractive index of the sample.

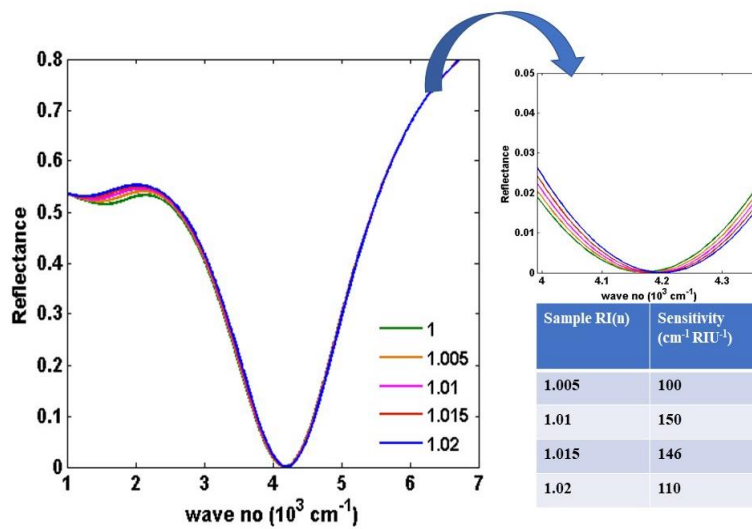
We have theoretically studied sensing of different gaseous samples using the proposed structure taking air as reference. We investigated the sensitivity of 150 nm thick ZnO: Al in the 1.55-micron frequency range and 250 nm thick ZnO: Al film in 2.5-micron frequency range. The dip shift on the reflection spectrum is used to detect the sample in terms of refractive index. Zoomed insets of the corresponding dips are used in order to calculate sensitivity. Figure 7 shows that resonance wave number shifts to higher value when sample refractive index increases. This implies that measurements with ZnO: Al thin film layer is sensitive in both and can be used as sensing materials in case of sensors. One of the prospective approaches to further improving the sensing technique involves both detection accuracy and sensitivity.



**c. Sensor performance of AZO and related sensitivity issues:**



(a)

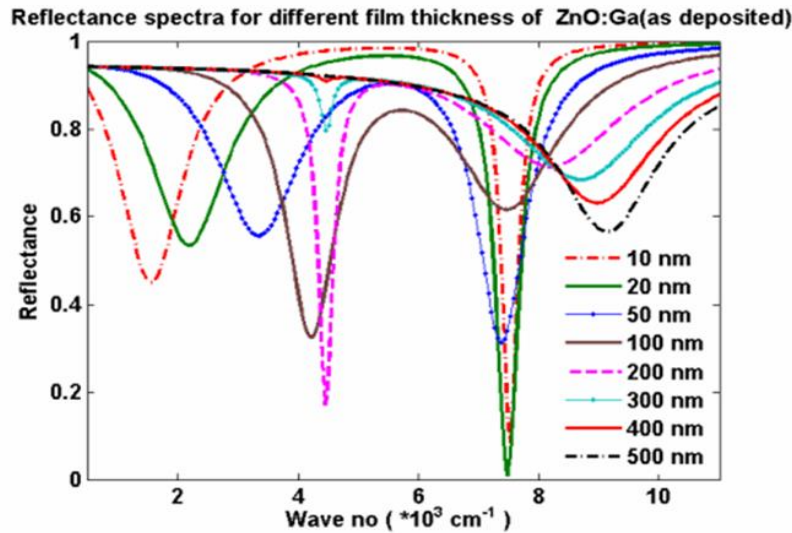


(b)

**Figure 7:** Sensing of gaseous samples using ZnO: Al film in (a) 1.55 micron (b) 2.5-micron incident frequency range

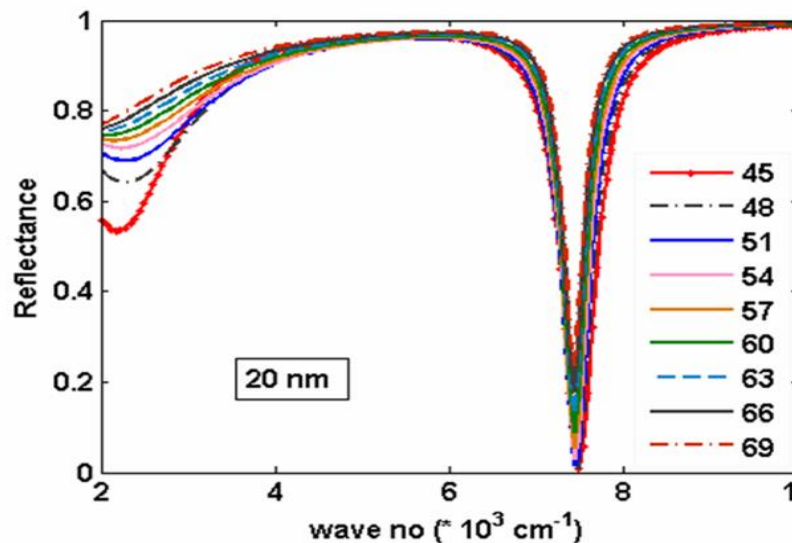
**d. Surface Plasmon Reflectance Profile for GZO:**

The coupling of incident optical radiation with the oscillations of conduction electrons i.e. Surface Plasmons is demonstrated in Figure 8 for ZnO:Ga film in Kretschmann configuration for different thickness of the film. The increment of the thickness of the ZnO:Ga film effects the reflectance of the light detected from the Kretschmann configuration as can be visualized from Figure 8.



**Figure 8:** Reflectance as a function of wave number with the variation of thickness of ZnO:Ga layer.

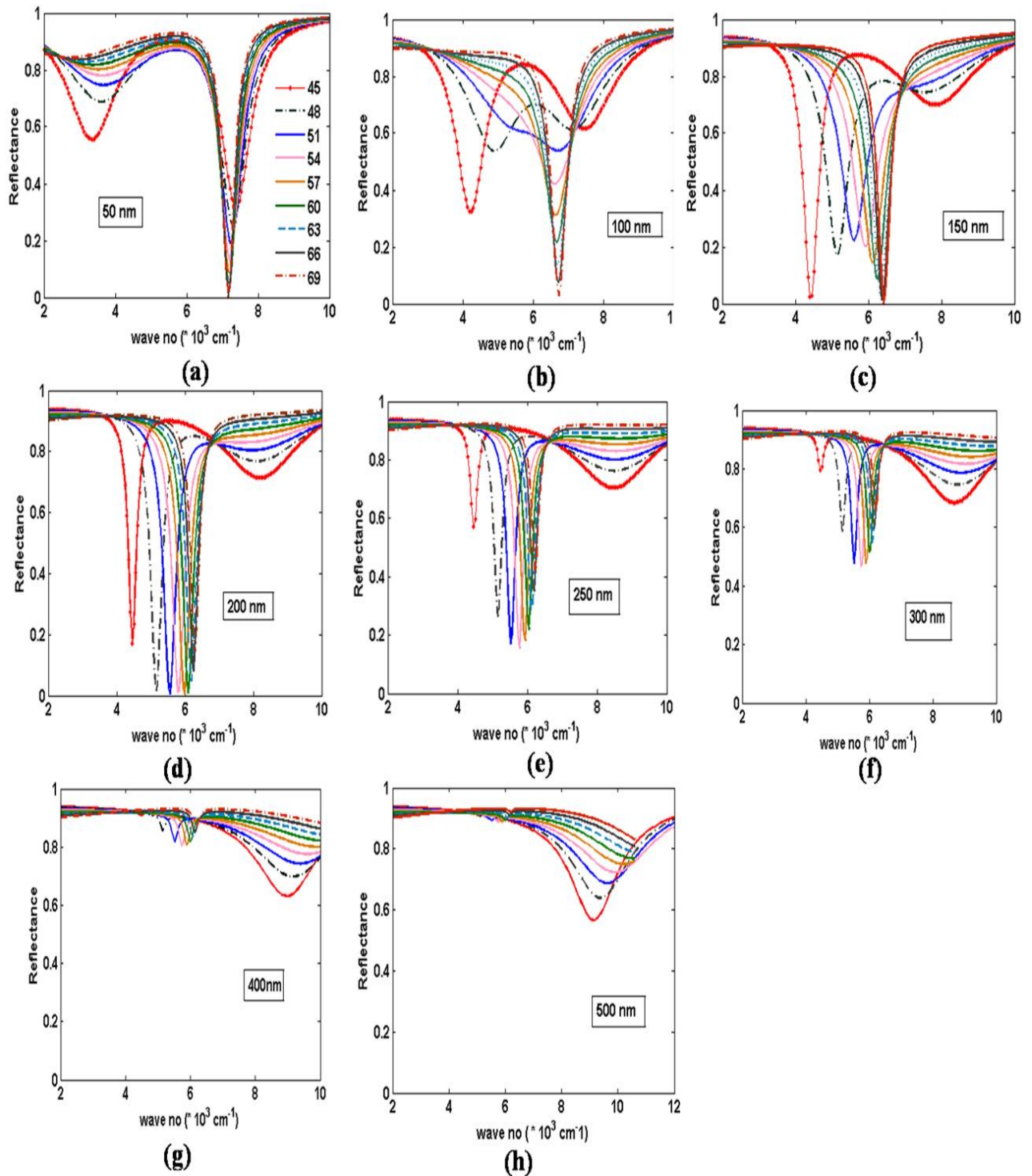
The thickness of the film layer (below 50 nm) has more probability of exciting electrons with the incident exciting beam than thick film layer considering the incident beam to fall on the configuration at  $45^\circ$ . Though in the following Figure s it is noticed that 20 nm thickness of ZnO:Ga film supports Surface Plasmon Resonance as it provides minimum reflectance value in two type of investigations.



**Figure 9:** Reflectance spectra of Gallium doped Zinc oxide as a function of wave number for different incident angles in the range  $45^\circ - 69^\circ$ , with steps of  $3^\circ$ .

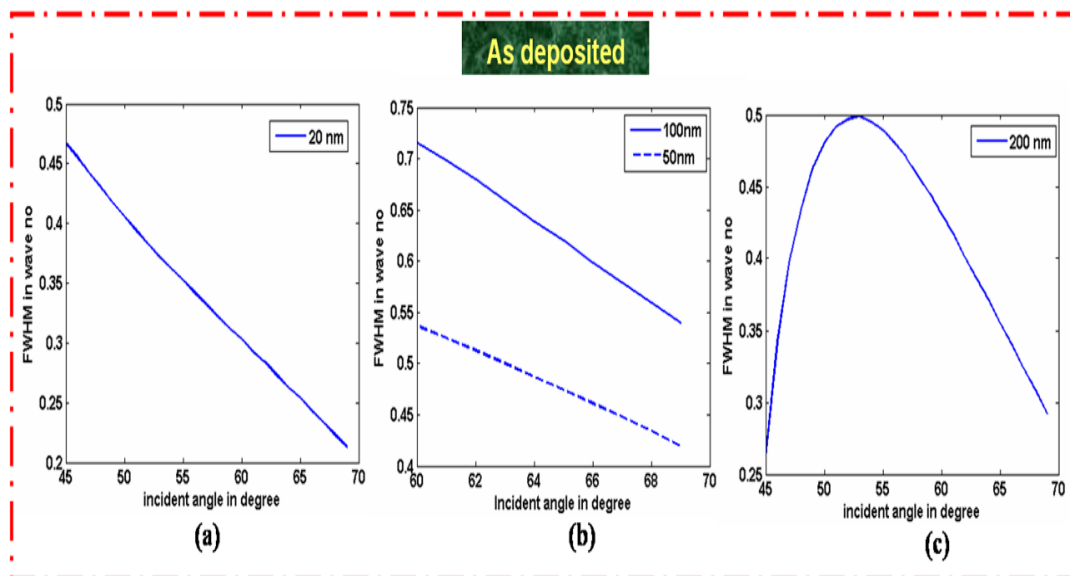
Figure 9 depict the variation of reflection spectra with the incident angle of the exciting beam for 20 nm ZnO:Ga film . 20 nm 2 at% as deposited ZnO:Ga film gives resonance at  $7480\text{ cm}^{-1}$  when the exciting radiation is incident at  $45^\circ$  which is its plasmon frequency.

To understand the thickness dependency of the resonance phenomenon, more detailed study has been done. Moreover, the importance of selection of incident angle has been performed. The variation of the reflectance curves for the metal oxide layer for different angle of incidence and different thickness

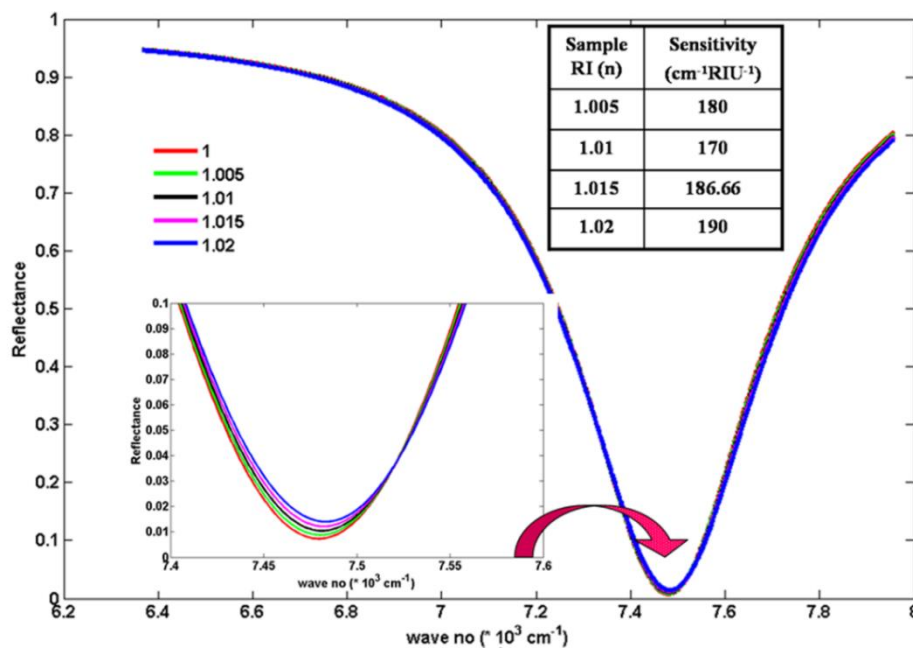


**Figure 10:** Reflectance spectra of 2 at% ZnO:Ga as a function of wave number of the incident beam and the incident angle for different thick layers.

is depicted in Figure F10. 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 9 SPR occurs at  $7480 \text{ cm}^{-1}$  for 20 nm Ga doped as-deposited ZnO when exciting radiation incident at  $45^\circ$  with 0.73% reflectance minimum. Further increasing of angle of incidence, results in resonance occurrence at  $7427 \text{ cm}^{-1}$  with approximately 77% transmission of light through 50 nm Ga doped ZnO layer of 2 at % as



**Figure 11:** FWHM curves for different thicknesses of (a-c) as deposited ZnO:Ga in angular interrogation.



**Figure 12.** Sensing of gaseous samples using as-deposited ZnO:Ga films of thickness 20 nm. The inset in fig is magnified view of the dip of resonances in reflection. Refractive index sensitivities obtained by considering air as reference.

deposited. The thickness of the metal oxide layer is further increased from 100 nm to 500 nm. It is found that in 100 nm as-deposited film gives resonance at 69° with 2.77% reflection of the exciting beam. At 45° incident angle ZnO:Ga shows dual peak resonance. But for higher thickness, dual peak resonance is not noticed. Resonance wave no with minimum reflectance value for 150 nm as deposited ZnO:Ga film gets shifted from 4403 cm<sup>-1</sup> with 2.3% reflectance to 6419 cm<sup>-1</sup> with 0.233% reflectance

when the angle of incidence changes from  $45^{\circ}$  to  $69^{\circ}$  respectively as shown in Figure 10(c). Figure 10 (d) suggests that SPR is prominent for film thickness upto 200 nm. Above 200 nm thick film (Figure 10 (e-h)) resonance does not occur. In case of selection of film thickness full width half maximum (FWHM) has to be considered. FWHM has been plotted in angular interrogation in Figure 11. It can be seen that up to 100 nm FWHM decreases linearly with incident angle, but 200 nm thick ZnO:Ga show different look. Maximum and minimum value which signifies how much the metal oxide films supports the coupling for SPP resonance. for 50 nm thickness, FWHM for as deposited at  $69^{\circ}$  is  $419\text{ cm}^{-1}$ . Detection accuracy is defined as the inverse of the FWHM. Therefore, small FWHM provides high detection accuracy of the system.

Lower FWHM is always preferable as it gives better performance in terms of detection accuracy which is important parameter in sensing.. Moreover, 20 nm thickness is still preferable as it provides lower FWHM of the metal oxide film.

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

At first 20 nm thickness of ZnO: Ga 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 12. shows the reflectance curves for different samples whose refractive indices are mentioned in legend. The shift in resonance is not visible. Corresponding dips are zoomed in order to calculate sensitivity 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. This implies that measurements with as deposited layer is more sensitive compared with that of annealed film.

#### **IV. Conclusions:**

In the mid infrared wavelength window, ZnO: Al thin film resonant frequency shifts from  $3926\text{ cm}^{-1}$  to  $4668\text{ cm}^{-1}$  due to increased thickness. We observed that Al doped ZnO thin film can support SPP resonance in the both IR and NIR optical range and can be a good replacement for ITO. If the exciting p polarised light is of 2.5-micron wavelength, at minimum reflectivity position, the coupling of the SPWs with the exciting light is better in ZnO: Al compared to ITO. Because of this fact, the absorbance profile will be higher for ZnO: Al for thickness greater than 150 nm. In the both IR and NIR optical frequency, ZnO: Al shows good agreement to support SPR effect at an incident angle between  $42^{\circ}$  to  $51^{\circ}$ . The collective oscillations of free charges in as-deposited ZnO:Ga result in excitation of Surface Plasmon Resonance under some optimised selection of the angle of incidence. 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 give dual peak resonance.

In this study, we investigate the variation of reflectance with the wave number of the incident radiation for different thickness of the metal oxide layer. It is observed that the position of minimum reflectivity is sensitive to both angle of incidence of the exciting radiation and also to the thickness of the metal oxide layer. For 20 nm Ga doped as-deposited Zinc oxide, it is noticed that Surface Plasmon Resonance when excited with the incident radiation at  $45^{\circ}$  occurred at  $7480\text{ cm}^{-1}$  and gets shifted to  $7427\text{ cm}^{-1}$  with increased angle of incidence. For the increasing angle of incidence reflected light will be detected less i.e. the transmission of incident light through the metal oxide layer is more feasible. If the metal oxide layer is thicker i.e. for 100 nm thick layer Surface Plasmon Resonance is sharper and more transmission of light is possible for higher angle of incidence. In case of FWHM, for as deposited it is noticed that for thickness below 100 nm, it decreases. Above 100 nm thickness FWHM gets a peak value at  $53^{\circ}$  angle and then decreases to a certain lower value at  $69^{\circ}$  incident angle. But as far as the sensitivity is concerned, it is noticed that 150 nm thick ZnO:Ga is more suitable.

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