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Ga doped ZnO: Alternative Plasmonic material to ITO in IR and NIR frequency range

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1 Introduction

Ga dopped zinc oxides (ZnO:Ga) become alternatives to conventional metals and indium tin oxide (ITO)[1] in recent plasmonic applications in visible-IR region. Metal oxides have good conductivity, high optical transmittance over the visible wavelength region for which they are greatly used in plasmonic devices. Among all the metal oxides, ITO supports SPP resonances in near infra-red (NIR) wavelength region [2-7]. For new plasmonic applications, metal oxide thin films should have lower resistivity and higher optical transmissions over the visible wavelength region. To obtain high transparency and low sheet resistance, the thickness of the film and the type of dopant and its amount conditions must be optimized. Along with ITO, ZnO:Ga is another important substitute to metals in recent developments of optoelectronic devices including solar cells [8-10]. ZnO:Ga thin films possess some extraordinary advantages such as low cost, thermal stability ,tuneable optical properties and can be compatible with standard fabrication and integration procedures.

Due to coherent oscillations of free electrons at metal-dielectric interface, the metallic conductivity of ZnO:Ga plays an important role for the excitement of surface plasmons According to Drude model [11] plasma frequency (ω_p) is defined as $\omega_p=\sqrt{ne^2/\mu\varepsilon_0\ \varepsilon_\infty}$, where ($\varepsilon_0$) is permittivity of free space and (ε_∞) is the high frequency dielectric constant. For high carrier concentration $n\sim10^{21}$ cm^{-3} the plasma frequency of ZnO:Ga exists in the near infrared region.

In the present analysis, three-layer Kretschmann structure (air- metal oxide – prism) is considered. This structure has a potential application in light emitting and waveguide devices [12,13] and in sensing applications.

In plasmonic application, Metals have very large negative permittivity in visible and IR region, but possesses high losses in this region and their optical properties cannot be tuned. Under certain circumstances, wide band gap semiconductors can be used as low loss plasmonic materials [14-17] as they have negative permittivity in the frequency region. Heavily doped wide band gap semiconductors become the potential materials for plasmonic applications [18].

In this paper the resonance spectra of 2 at% Ga dopped ZnO(as-deposited) are studied for incident angle 45^0 to 69^0 of incident radiation and various thick film from 10nm t0 500nm. This paper aims to study surface plasmon excitation in ZnO:Ga film and the optimized conditions of the parameters like the thickness of the thin film and angle of incidence of the exciting beam for surface plasmon resonance.

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2. Classification of different multilayer metallo dielectric coupled nano- plasmonic resonant structures

The polarisation of waves in material is defined by the complex dielectric function of that material. According to classical Drude theory, the complex electrical permittivity or dielectric function is defined as

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

where, ε_{int} is the high frequency dielectric constant, γ is damping coefficient of free electrons and ω_p is plasma frequency.
The damping coefficient of free electrons signifies the optical losses in the material. So for low loss, material should have small γ value. Then plasma frequency can be defined as

$$\omega_p^{\ 2} = \frac{ne^2}{\varepsilon_0 m^*} \tag{2}$$

In equation 2, n is the charge carrier density, e is the charge of the electron, m^* is the effective mass and ε_0 is the permittivity of the vacuum. So with the increase of carrier density i.e doping concentration materials can exhibit metallic properties and can be used in plasmonic application.

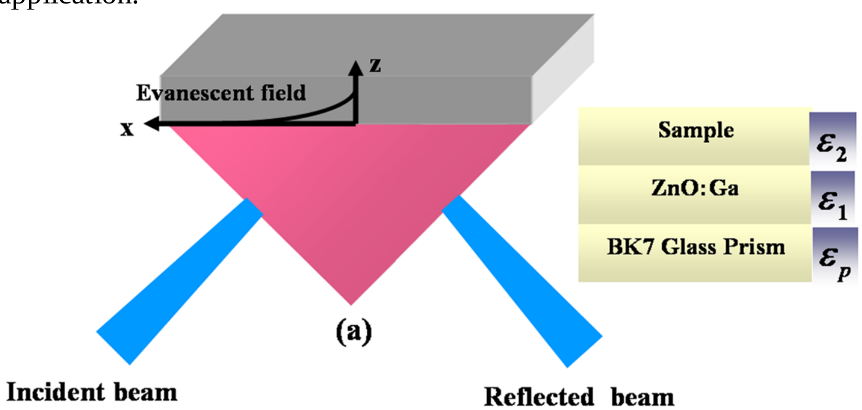

Fig. 1 Krestchmann configuration in three layer model.

Fig 1 describes the simple three-layer configuration where prism is surrounded by air medium for generation of surface plasmon polariton (SPP).

3. Computational procedure for reflectivity calculation

To measure the total reflectance R, in Kretschmann configuration depicted in Fig 1, the field reflectance at the boundaries of metal oxide-air and prism- metal oxide film should be considered. 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:

$$r_{p1} = \frac{\cos\theta / n_p - \left(\sqrt{\varepsilon_1 - n_p^{\ 2}\sin^2\theta}\right) / \varepsilon_1}{\cos\theta / n_p + \left(\sqrt{\varepsilon_1 - n_p^{\ 2}\sin^2\theta}\right) / \varepsilon_1} \tag{3}$$

$$r_{12} = \frac{\left(\sqrt{\varepsilon_2 - n_p{}^2 \sin^2\theta}\right)\Big/\varepsilon_2 - \left(\sqrt{\varepsilon_2 - n_p{}^2 \sin^2\theta}\right)\Big/\varepsilon_2}{\left(\sqrt{\varepsilon_2 - n_p{}^2 \sin^2\theta}\right)\Big/\varepsilon_2 + \left(\sqrt{\varepsilon_2 - n_p{}^2 \sin^2\theta}\right)\Big/\varepsilon_2} \quad (4)$$

where ε_1 is the dielectric constant of Ga doped zinc oxide layer and ε_2 is the dielectric constant of air.

In this three-layer model, according to Airy equation, the field reflectance r_{p12} is defined as,

$$r_{p12} = \frac{r_{p1} + r_{12} e^{2ik_{z1}d_1}}{1 + r_{p1} r_{12} e^{2ik_{z1}d_1}} \quad (5)$$

where, in the phase term, k_{z1} is the z component of the wave vector in medium 1 i.e. in CMO layer and d_1 is the thickness of the film.
Then the reflectance is

$$R = \left| r_{p12} \right|^2 \quad (6)$$

4. Simulation of resonance curves for different nanoplasmonic structures

Gallium doped zinc oxides are often opaque and transparent depending upon the angle of incidence and thickness of the film. ZnO:Ga have optimized constraints to give resonance to excitations by external light and also to dual peak resonance.

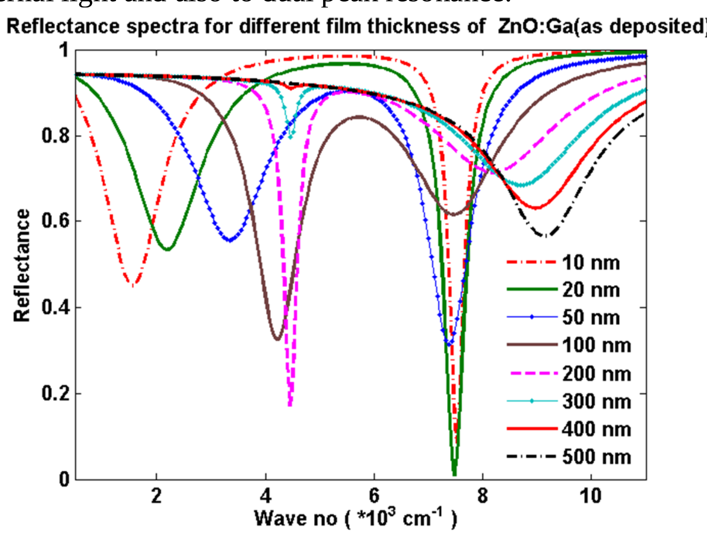

Fig. 2 Reflectance as a function of wave number with the variation of thickness of the ZnO:Ga thin film

The coupling of incident optical radiation with the oscillations of conduction electrons i.e. surface plasmons is demonstrated for ZnO:Ga film in kretschmann configuration for different thick film layer in Fig. 2 . From this variation of reflection spectra it can be noticed that annealed ZnO:Ga supports SPP resonance more sharply with minimum reflection for different thick films. The increment of the thickness of the ZnO:Ga film effects the reflectance of the light detected from the kretschmann configuration. The thickness of the film layer (below 50nm) has more probability of exciting electrons with the incident exciting beam than thick film layer of Zinc Oxide layer when incident beam is to fall on the configuration in 45^0. 20nm thickness of ZnO:Ga film has been chosen as optimized thickness as it provides minimum reflectance value in two type of investigations.

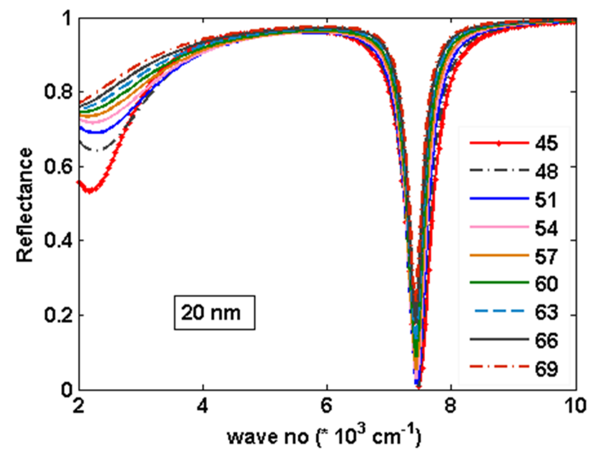

Fig. 3 Reflectance spectra of Gallium dopped Zinc oxide as a function of wave number for different incident angles in the range 45^0 – 69^0, with steps of 3^0.

Fig. 3 depict the variation of reflection spectra with the incident angle of the exciting beam for 20 nm ZnO:Ga film .20nm 2 at% as deposited ZnO:Ga film gives resonance at 7480 cm^{-1} when the exciting radiation incident at 45^0 which is its plasmon frequency.

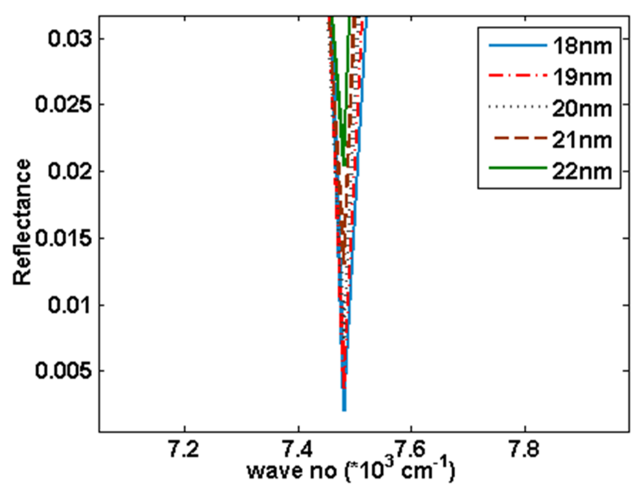

Fig. 4 Zoomed portion of minimum reflectance position for 20 nm as optimized thickness

For the finding of actual optimized thickness for which the reflectance nature gets minimum value Fig. 4 is drawn. Though reflectance gets minimum value for 18nm for 2 at % as deposited Zinc oxide, for which maximum coupling of the incident radiation with the surface plasmon is happened.

In order to understand the thickness dependency of the resonance phenomenon, more details 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 is depicted in Fig. 5. The reflectance minimum is sensitive to angle of incidence of the exciting radiation, excitation frequency and thickness of the metal oxide thin film. We have selected the 20nm as the optimized thickness for Ga:ZnO as shown in Fig 5. In Fig 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. Further increasing of angle of incidence, results in resonance occurrence at 7427 cm^{-1} with approx 77% transmission of light through 50 nm Ga doped ZnO layer of 2 at % as deposited (Fig 5(a)). The thickness of the metal oxide layer is further increases from 100 nm to 500nm. It is found that in Fig 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, Reflectance profile for ZnO:Ga shows dual peak resonance. But at higher thickness dual peak resonance cannot be noticed. Resonance wave no with minimum reflectance value for 150 nm as deposited ZnO:Ga film 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 Fig.5(c). Fig.5(d) suggests that SPR is prominent for film thickness upto 200 nm. Above 200 nm thick film (Fig. 5(e-h)) resonance doesn't occur.

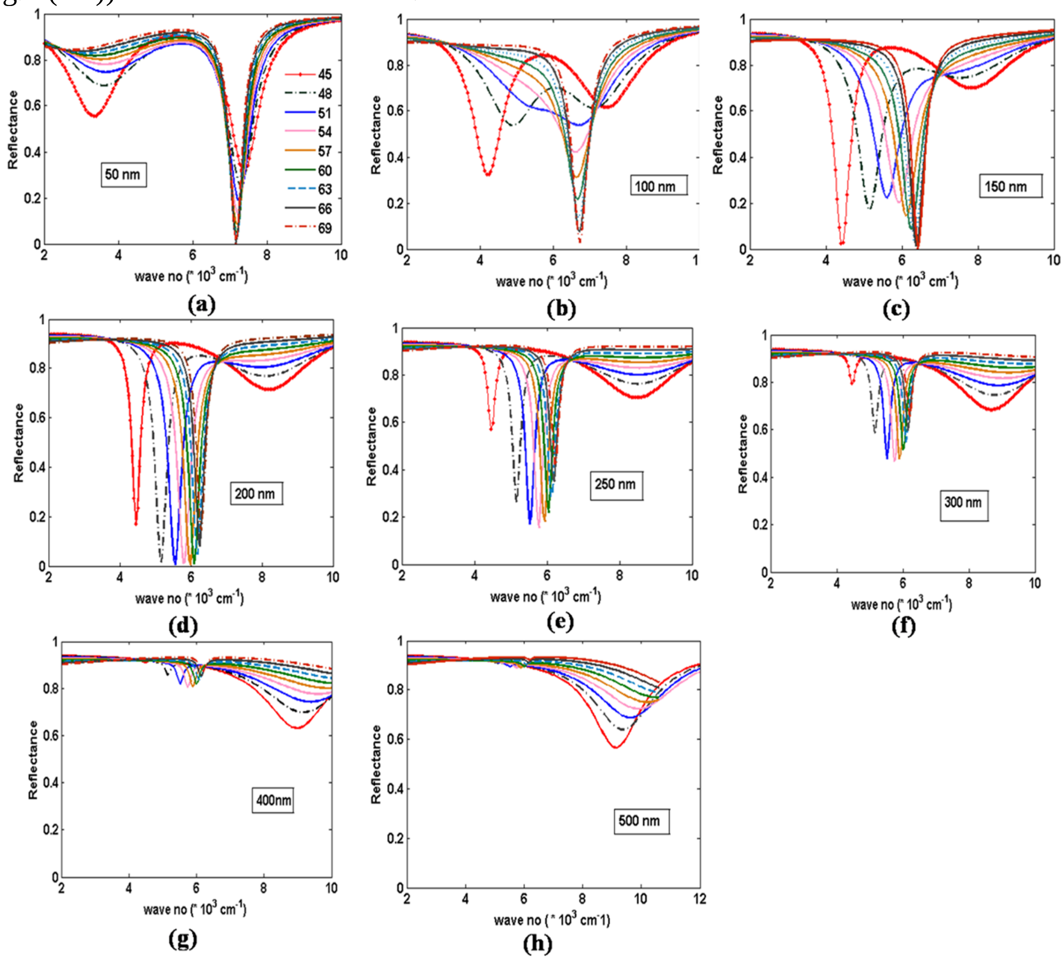

Fig. 5 Reflectance spectra of 2 at% as deposited ZnO:Ga as a function of wave number of the incident beam and the incident angle for different thick layers.

In case of selection of film thickness full width half maximum (FWHM) has to be considered. FWHM has been plotted in angular interrogation in Fig. 6. It can be seen that upto 100 nm FWHM decreases linearly (Fig. 6) with incident angle but 200 nm thick ZnO:Ga show different look .From these values it can be concluded that Ga doped Zinc oxide can response to the plasmonic excitation. For instance, for 50nm thickness, FWHM for as deposited at 69^0 is 419 cm^{-1}. For 200 nm thickness pre annealed ZnO:Ga, FWHM increases to 499 cm^{-1} in the region of incident angle from 45^0 to 53^0 and then decreases to its minimum value resulting sharp peak in resonance curve. Detection accuracy is defined as the inverse of the FWHM. Therefore, small FWHM provides high detection accuracy of the system.

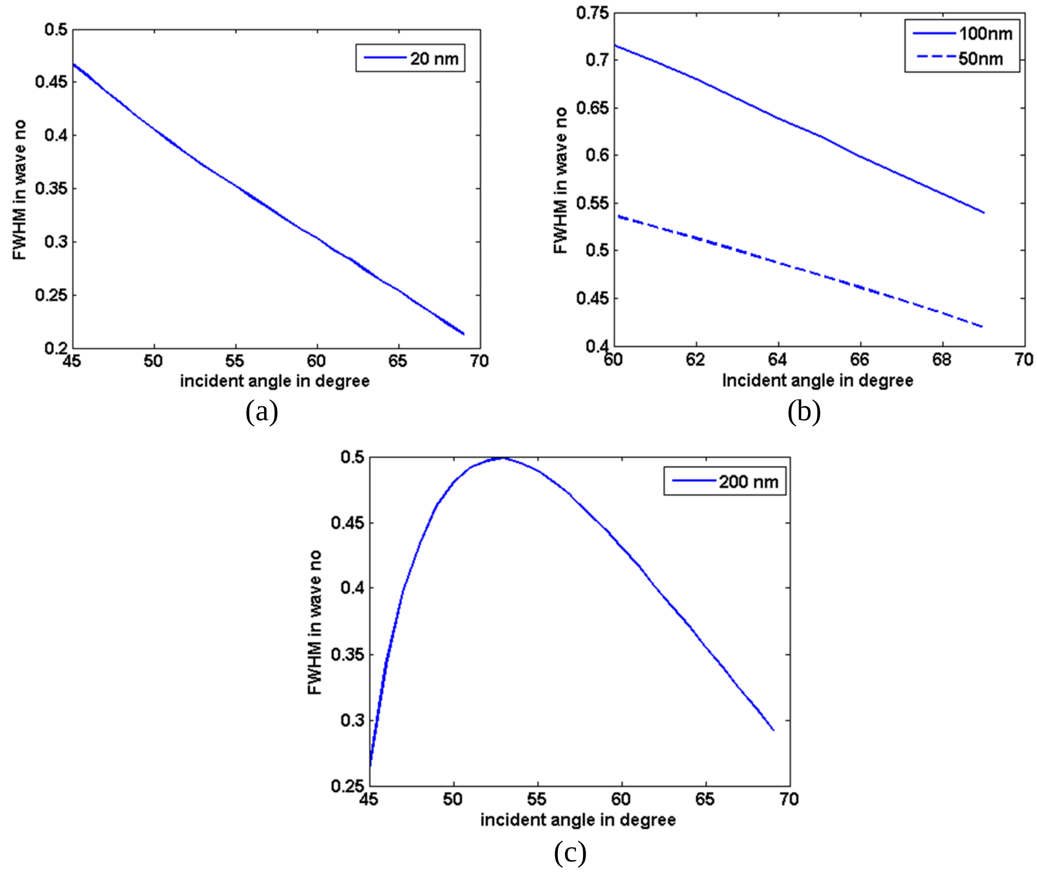

Fig. 7 FWHM curves for different thicknesses of as- deposited ZnO:Ga in angular interrogation.

Lower FWHM is always preferable as it gives better performance in terms of detection accuracy which is important parameter in sensing. The aforesaid feature is noticed in post annealed film for each thickness. Moreover, 20 nm thickness is still preferable as it provides lower FWHM for both states of the metal oxide film.

5. Application in sensing Sensor performance: related sensitivity issues

20 nm thickness of ZnO: Ga has been used 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. Fig. 8 shows the reflectance curves for different samples whose refractive indices are mentioned in legend. The shift in resonance is not visible for as deposited state. Zoomed of the corresponding dips are studied in order to calculate sensitivity. Fig. 8 shows that resonance wave no shifts to higher value when sample refractive index increases.

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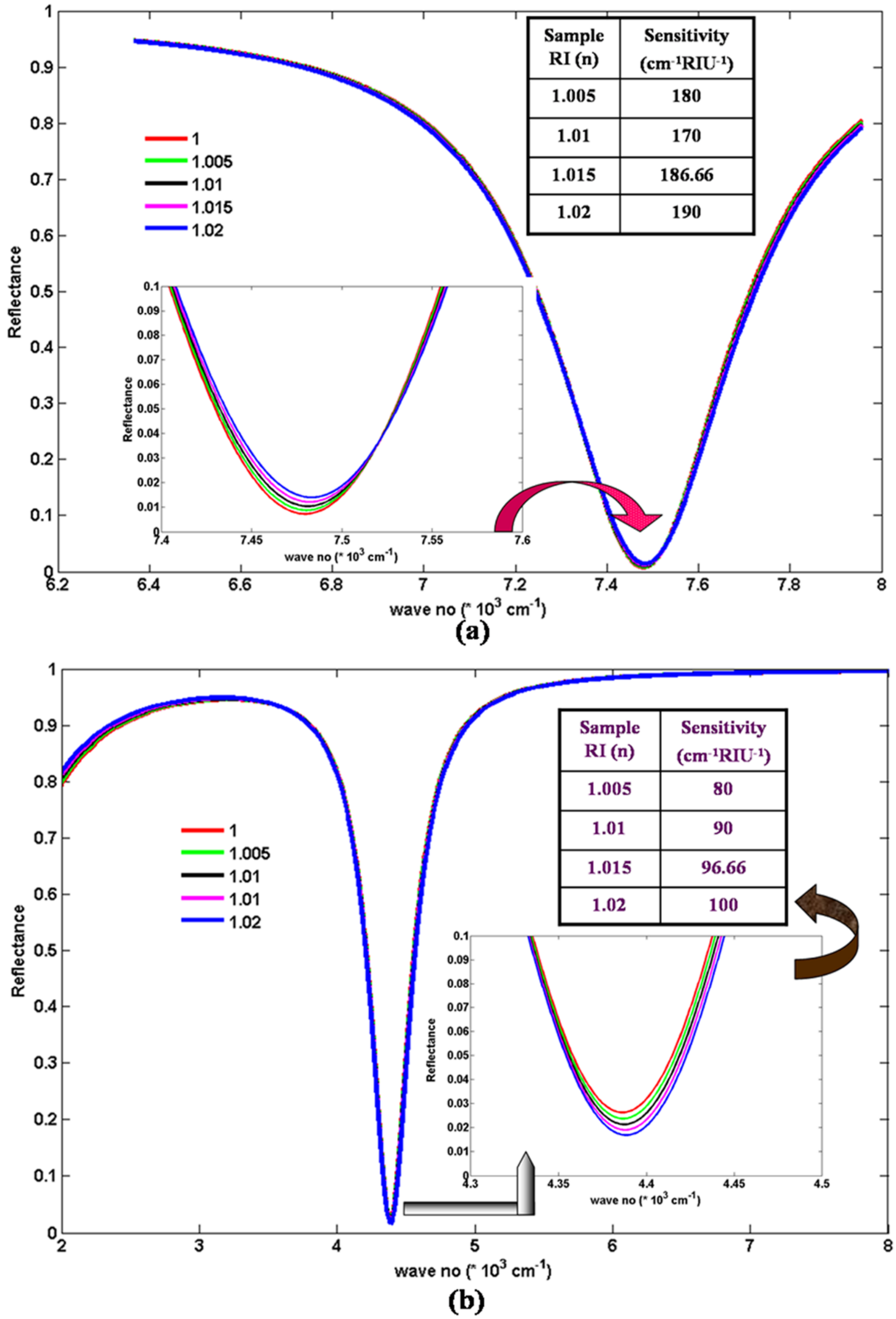

Fig. 8 Sensing of gaseous samples using as deposited ZnO:Ga films. The inset is the magnified view of the dip of resonances in reflection. Refractive index sensitivities obtained by considering air as reference.

One of the prospective approaches to further improving the sensing technique involves both detection accuracy and sensitivity.

6 Conclusions

In this article, we investigate the variation of reflectance with the wave number of the incident radiation and 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 dopped as deposited Zinc oxide it is noticed that surface Plasmon resonance when excited with the incident radiation at 45^0 happened at 7480 cm^{-1} shifted to 7427 cm^{-1}. 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. Again, dependence of the surface Plasmon resonance on different thickness of zinc oxide material are depicted in Fig-2. In case of FWHM, for as deposited it is noticed that for thickness below 100 nm, it decreases linearly

Ga dopped ZnO supports surface plasmon excitations for thin film thickness (below 200nm). As-deposited film supports SPP resonance at higher frequency also.

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