Conference Paper

Dielectric Properties of SnO₂ Thin Film Using SPR Technique for Gas Sensing Applications

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Focus has been made on the determination of dielectric constant of thin dielectric layer (SnO₂ thin film) using surface plasmon resonance (SPR) technique and exploiting it for the detection of NH₃ gas. SnO₂ thin film has been deposited by rf-sputtering technique on gold coated glass prism (BK-7) and its SPR response was measured in the Kretschmann configuration of attenuated total reflection using a p-polarised light beam at 633 nm wavelength. The SPR response of bilayer film was fitted with Fresnel's equations in order to calculate the dielectric constant of SnO₂ thin film. The air/SnO₂/Au/prism system has been utilized for detecting varying concentration (500 ppm to 2000 ppm) of NH₃ gas at room temperature using SPR technique. SPR curve shows significant shift in resonance angle from 44.8° to 56.7° on exposure of fixed concentration of NH₃ gas (500 ppm to 2000 ppm) with very fast response and recovery speeds.

1. Introduction

Surface Plasmon Resonance (SPR) is a powerful and sensitive technique to study the dielectric and optical properties of metal-dielectric interface, thus it can be exploited for the detection of harmful and toxic gases [1]. There are two configurations for exciting surface plasmon (SP) wave at the metal-dielectric interface: one is Otto configuration [2] and the other is Kretschmann [3] configuration. Kretschmann configuration is the most commonly used, where a light wave is totally reflected at the interface between the prism coupler and the thin metal layer (deposited on the prism surface) and excites a SP wave at the outer boundary of the metal by evanescently tunnelling through the thin metal layer [3]. The changes in the plasmon dispersion relations due to variation in refractive index of the sensing film will cause changes in the SPR reflectance curve [4]. The changes in the SPR curve are used to systematically calibrate the physical factors and hence the system can be exploited as a sensor.

Transparent conducting (metal) oxide thin films have been the subject of research interest over a number of decades specially for gas detection. SnO₂ based systems, in particular, have been the focus of many of these investigations worldwide because it is a naturally nonstoichiometric prototypical transparent semiconducting oxide having rutile structure [5]. It has a high band gap of ~4 eV and when suitably doped, can be used both as a p-type and n-type semiconductor [6]. Although a lot of work has been carried out on SnO₂ based semiconductor gas sensors based conductometric detection technique. However, integration of SPR technique is yet to be carried out with detection of toxic gases at room temperature.

In this work, SnO₂ thin film was deposited by the rf sputtering technique on Au coated BK7 glass prism, and its SPR response in the Kretschmann geometry was measured. The SPR response of SnO₂/Au bi-layer film was fitted with Fresnel's equations by using a MATLAB program. The air/SnO₂/Au/prism system is further exploited for the detection of NH₃ gas at varying concentration from 500 ppm to 2000 ppm.

2. Experimental Details

In the present work, efforts have been made towards studying the dielectric properties of tin oxide thin film especially at optical frequency ($\lambda = 633$ nm), the surface plasmon modes have been excited at the SnO_2 /gold interface in Kretschmann configuration using a right angled BK7 glass prism ($n_p = 1.517$) with the help of a laboratory assembled system. The optimised 40 nm thin film of gold was deposited on the hypotenuse face of glass prism (BK-7) by thermal evaporation technique where gold (Au) wire (99.999% pure) was evaporated. The thickness and deposition rate of the Au thin film were precisely controlled in situ using a quartz crystal, thickness monitor and deposition was carried out at a rate of 5 Å/s. Then the gold plated prisms were annealed at 300°C in air for 1 hour to get the stabilised SPR mode. SnO_2 thin film was deposited on gold plated glass prisms by rf-diode sputtering technique using a 4" diameter metal Sn target (99.999% pure). 110 nm thin SnO_2 film was deposited at a sputtering pressure of 10 mTorr for 1 hr in gas ambient of 60% Ar and 40% O_2 in the sputtering chamber.

Crystallographic studies of SnO_2 thin film have been carried out using a Bruker D 8 X Ray diffractometer. The X-ray diffraction is carried out for SnO_2 thin film after a post deposition annealing treatment at 300°C in air for 3 hours. The band gap of SnO_2 thin film has been estimated from the UV-visible spectra, within the wavelength range of 190–1100 nm using a computer interfaced Perkin Elmer (lambda 35) UV-visible dual beam spectrophotometer.

For gas sensing applications, a special sample cell was indigenously designed having an opening window for attaching the prism such that the sensing thin film (SnO_2) is in contact with the environment inside the cell. Initially, the vacuum was created inside the gas cell using a mechanical pump which ensures the removal of other foreign molecules that could otherwise interfere with the sensing film. NH_3 gas of a particular concentration was inserted into the sample cell using a microsyringe. The SPR reflectance curve was recorded while target gas was inserted inside the gas cell for the entire range of incident angle using an optical power meter and a rotation stage (Make: Optiregion).

3. Results and Discussions

The XRD pattern of the SnO_2 thin film is shown in Figure 1. Reflection peaks at $2\theta = 26.5^\circ$, 33.9° , and 51.8° corresponding to planes (110), (101), and (211) planes of SnO_2 , respectively are in good agreement to the reported values for rutile structure [7], confirming the formation of polycrystalline SnO_2 thin film.

The optical transmission spectra of the SnO_2 thin film, deposited on quartz substrate, are shown in Figure 2. SnO_2 thin film shows the good optical transparency of about more than 80% in the visible region. A sharp absorption edge at ~ 310 nm is obtained for the SnO_2 thin film. Optical band gap of the SnO_2 thin films was calculated from the intercept on energy axis obtained by extrapolating the linear portion of the Tauc plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) as shown in the inset of Figure 2. Estimated value of bandgap for annealed

FIGURE 1: XRD spectra of SnO_2 thin film.

FIGURE 2: Transmission spectra of SnO_2 thin film.

SnO_2 thin films is found to be 3.58 eV which is close to the values reported by other workers for SnO_2 thin films [8].

Figure 3 shows the SPR reflectance curves obtained for the prepared air/Au/prism and air/ SnO_2 /Au/prism systems. A well-defined and sharp SPR reflectance curve is obtained for the air/Au/prism system (Figure 3). The reflectance was found to decrease rapidly with increase in incident angle, attained a dip (reflectance minima) at a resonance angle (θ_{SPR}) of 43.8° (Figure 3), and thereafter started increasing sharply with further increase in the incident angle. When SnO_2 thin film is deposited on Au coated prism (Au/prism), the SPR curve shifts to higher resonance angle (Figure 3). The observed shift in SPR curve is related to the change in dielectric media from air for the air/Au/prism structure to SnO_2 film for air/ SnO_2 /Au/prism structure. It may be noted from Figure 3 that the minimum value of reflectance at resonance angle (θ_{SPR}) increases significantly from 0.26 to 0.32 on depositing a SnO_2 thin film on Au/prism system.

FIGURE 3: Variation of SPR response with incident angle for air/Au/prism and air/SnO₂/Au/prism systems.

This is attributed to the fact that the backscattered field which is in antiphase with that of the incoming light interferes destructively with the incoming light and hence, maximum light is not able to couple with the SPR mode and the value of reflectance increases on depositing SnO₂ thin film [4, 9]. In order to obtain the complex dielectric constant, the experimentally obtained SPR reflectance curves were fitted with the theoretical SPR curves simulated using Fresnel's equations for one layer system (air/Au/prism) [10]. The best fitted SPR curve (solid curve) for Au/prism system is also shown in Figure 3. The estimated value of dielectric constant of Au film was about $-11.9 + 0.7i$, which is close to the corresponding value reported in literature [3]. The known values of dielectric constant of prism, $\epsilon_0 = (1.517)^2$ and the dielectric constant of air $\epsilon_3 = 1.0$ along with estimated value of dielectric constant of SnO₂ thin films using Fresnel's equations for two layer system (air/SnO₂/Au/prism) [10]. Furthermore, to find out the value of complex refractive index ($n_i + ik_i$) of SnO₂ thin film, the estimated value of complex dielectric constant ($\epsilon_i = \epsilon'_i + i\epsilon''_i$) was utilized [3]. The value of complex dielectric constant estimated at $\lambda = 633$ nm for SnO₂ thin film was about $2.07 + 0.001i$. The room temperature value of complex refractive index ($n_i + ik_i$) for SnO₂ thin film was estimated to be $1.439 + 0.032i$ which is in agreement with the reported results [11].

Since surface plasmon resonance (SPR) is very sensitive to any change occurring at the surface of the metal oxide (dielectric) layer, presence of extremely thin gas sensing coatings on the surface of the noble metal layer (Au) can be used to detect gas molecules based on the change in Plasmon resonance conditions. As reported in literature, SnO₂ is most utilized metal oxide thin film for gas sensing purposes though there are few issues that need the urgent need

FIGURE 4: SPR reflectance curves for air/SnO₂/Au/prism system for varying concentrations of NH₃ gas.

of research community. Hence, gas sensing applications of SnO₂ thin film have been explored to detect NH₃ gas using surface plasmon resonance technique. Figure 4 shows the SPR reflectance curves obtained for the air/SnO₂/Au/prism system at $\lambda = 633$ nm, when the system is exposed to different concentration of NH₃ gas. The SPR dip angle and minimum reflectance increases with increase in the concentrations of NH₃ gas as shown in Figure 4 which is due to increase in the refractive index of SnO₂ thin film in the presence of reducing gas (NH₃). The change in the refractive index of the sensing film introduces the change in the surface plasmon dispersion relations and hence changes the SPR reflectance curve [12]. This may be attributed to the fact that when NH₃ gas interacts with the surface of SnO₂ thin film. It releases free electrons to SnO₂ surface which causes change in SPR conditions leading to shift in SPR reflectance curve.

4. Conclusions

SnO₂ thin film was deposited by the rf-diode sputtering technique on Au coated BK7 glass prisms and its SPR response was measured in the Kretschmann geometry of attenuated total reflection using a p-polarized He-Ne laser beam at 633 nm wavelength. The SPR response of Au/SnO₂ bi-layer film was also simulated with Fresnel's equations in order to compare with experimental data and also to find the complex dielectric constant and refractive index of SnO₂ thin film. The complex dielectric constant and refractive index of SnO₂ thin film were determined to be $2.07 + 0.001i$ and $1.439 + 0.032i$ which are close to the reported values. The SnO₂ thin film is further used for NH₃ gas sensing at room temperature and the initial results demonstrated that NH₃ gas sensing of SnO₂/Au bi-layer films using SPR is feasible.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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