Influence of trap densities in ITO thin film on the optical, electrical, and surface plasmon resonance properties

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Abstract. Indium–tin–oxide (ITO) is a material having metallic behavior in the infra-red spectral range. Its electrical and optical properties are also easily tuned, making it a suitable alternative plasmonic material in the infra-red region. In this work, electrical and optical simulation modeling was performed to study the effect of trap densities in different carrier scattering mechanisms on the mobility in ITO. This study correlates the micro-structural and opto-electronic parameters to the surface plasmon resonance (SPR) behavior in the ITO thin films. The results indicate that low defect density with high carrier concentration can provide better SPR performance in ITO.

1. Introduction

One of the interesting examples of light-matter interactions that has practical implications is surface plasmon resonance, which is the collective oscillation of free electrons present on the surface of a conducting material when they couple with incident light of a specific wavelength and angle at resonance conditions [1]. Plasmonics finds applications in many fields like medical theranostics, biosensors, chemical sensing, etc. [2, 3]. However, most of the work done in plasmonics has focused on the visible spectrum [4]. Broadening the range of sensing to the near-infrared (NIR) region of the spectrum can enable widespread applications [5]. The wavelength range at which optical resonance takes place depends on the material composition. Plasmonic waveguides in the NIR region can be used for several optoelectronic devices, MOSFET development as well as on-chip data transfer [4]. In addition, electromagnetic waves in the NIR range are best suited for biomedical imaging of deeper tissues [6].

Typically, noble metals have been used for plasmonic applications, which are not successfully applied in the NIR range due to significant optical losses at these wavelengths, creating a lacuna for alternative materials [7]. The free carrier concentration influences the surface plasmon resonance behavior in the material. While free carrier concentration in metals cannot be modified, metal oxides offer the advantages of significant tunability of properties by altering the fabrication conditions including doping. This tunability of electrical properties combined with other advantages like the optical transmission in the visible range, chemical stability, non-toxicity, and CMOS compatibility makes transparent conducting oxides (TCO) a good choice as a plasmonic material. Among different metal oxides, doped zinc oxide (Al-doped-ZnO, Ga-doped-ZnO), doped tin oxide (F or B doped SnO₂), and doped indium oxide (Sn doped In₂O₃) are known for their application as TCOs [8, 9]. The quality of a TCO is determined by the optical gap and the available free carriers in it for conduction.
purposes. Indium oxide has the highest electron affinity, making it easily doped by external dopant atoms leading to the high availability of free conduction electrons [10]. This results in the widening of the bandgap due to the Burstein-Moss effect [8, 9].

Indium tin oxide (ITO) is one of the most successful derivatives of indium oxides in terms of its superior performance in devices. ITO is an n-type degenerate wide bandgap semiconductor with high electrical conductivity, high optical transparency towards visible light, and reflection spectra in the IR region [11, 12]. While extrinsic doping using tin and intrinsic doping with oxygen play crucial roles in the free carrier concentration of the material, it is also true that oxygen vacancies create trap states that hinder mobility [13]. Thus, to obtain suitable ITO material for SPR sensors, the knowledge of the impact of defects and trap states is required, which can suggest the optimum fabrication conditions.

In this report, the results of some theoretical simulation studies exploring the effects of defects on optical and electrical properties of ITO materials and their subsequent effect on the surface plasmon resonance properties of ITO materials are presented. The input parameters of optical and electrical properties of the ITO material required for the simulation of SPR properties were deduced from realistic optical and electrical models by considering different carrier scattering mechanisms. Key material properties like crystallinity, preferred orientation of the crystallites and their sizes, defect density, morphology, shape of the density of the states of carriers, doping, and fabrication temperature, etc., were considered in this modeling studies as these are factors known to have a dominant effect on carrier mobility scattering [8, 9, 14, 15].

2. Theoretical background

The simulation study of the SPR behavior of the ITO thin films employs Kretschmann configuration, a prism coupling method, schematically shown in figure 1. In this optical coupling configuration, surface plasmons can be excited on the conducting ITO films in a resonant way by allowing a TM polarized light to interact at the interface of ITO and dielectric (BK-7 glass) prism surface under the total internal reflection condition [16].

The principle of the configuration mentioned here is based on modulating the wavelength of the reflected light for a fixed angle of incident light. At a resonant wavelength, the intensity of the reflected light reaches its minimum value. This can happen when the momentum phase of evanescent waves matches with that of the surface plasmons, i.e., the wave vector of the incident light in the plane of the surface \( k_s \) should match with the wave vector of the surface plasmon wave in metal \( k_{sp} \):

![Figure 1](image-url)
where $k_s$ is the SPR propagation constant, $k_x$ is the incident wave vector, $n_p$ is the refractive index of the prism, and $\varepsilon_m$ and $\varepsilon_d$ represent complex dielectric permittivity of metal and dielectric (w.r.t wavelength), respectively.

If the incident wavelength of light and the permittivity of the metal layer are known, then for a fixed angle the surface plasmon wave can be simulated, which in turn gives an idea about the spectral response of the reflectivity [16]. For obtaining SPR in the NIR range, ITO thin film instead of a metallic layer is used in the Kretschmann configuration. To obtain the required parameters for equation (1) to study SPR behavior in ITO thin films, the Drude model can be used to describe its optical properties [4]. It gives the dielectric constant, $\varepsilon(\omega)$ as:

$$\varepsilon_{\text{ITO}}(\omega) = \varepsilon_{\text{real}} - i\varepsilon_{\text{imaginary}} = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma^2}$$

(2)

$$\varepsilon_{\text{real}} = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma^2}$$

(3)

$$\varepsilon_{\text{imag}} = \frac{\omega_p^2 \gamma}{\omega^2 + \omega_p^2}$$

(4)

where $\varepsilon_{\text{real}}$ and $\varepsilon_{\text{imag}}$ are the individual real and imaginary components of dielectric permittivity. The principal contributors to the Drude model, plasma frequency ($\omega_p$) and damping constant ($\gamma$) are given by:

$$\omega_p = \sqrt{\frac{nq^2}{m^*\varepsilon_0}}$$

(5)

$$\gamma = \frac{q}{m^*\mu}$$

(6)

where $m^*$ is the effective mass, $\varepsilon_\infty$ is the high-frequency dielectric constant, $n$ is free electron concentration, $q$ is the charge of the electron, $\varepsilon_0$ is vacuum permittivity. Thus, these parameters in the Drude model become the major factors influencing the optical properties of ITO.

Meticulous control over the above-mentioned parameters is essential to mold the ITO material for good electrical and optical properties. However, information on the carrier transport mechanisms and the electronic structure of the ITO is necessary to obtain accurate values of the electrical parameters. Another prominent factor, the electron mobility in metal oxide materials are influenced by three major carrier scattering mechanisms: ionized impurity scattering – mainly due to the dopant ions after giving the free electrons to the conduction band; neutral scattering – due to the inactivated dopant atoms and/or vacancy-dopant clusters; and grain boundary scattering – at the crystal or grain boundaries where defects get segregated. However, their contribution to limiting mobility varies with carrier concentration. While considering the Drude model and the above-mentioned scattering mechanisms, the effective mass of the charge carriers in ITO becomes an important factor. ITO being a degenerate n-type material, with an increase in doping, the shape of its conduction band changes to non-parabolic as opposed to the traditional conduction band of semiconductors [8, 9]. Due to this non-parabolicity of the conduction band, the effective mass becomes a function of carrier concentration which is given by the following equation [9, 13].
\[ m^* = m_0^* \left[ 1 + 2\beta \frac{\hbar^2}{m_0^*} (3\pi^2 n)^{\frac{1}{3}} \right]^2 \]  

Where, \( \beta \) is a constant and its value is reported to be from 0.14 to 1.2. In this work, the value of \( \beta \) is taken as 0.14. In addition to the modified effective mass, which is carrier concentration-dependent, a high-frequency dielectric constant, \( \varepsilon_{\infty} \), also a function of carrier concentration has considered [17].

Since structural parameters like crystal size, free carrier concentration, interstitial traps, neutral dopants, dopant ions, and oxygen vacancies are the main causes of scattering, these parameters have incorporated into this model to obtain the accurate values of mobility [18]. Trap density gives a measure of the number of traps in a semiconductor where the carriers may remain “trapped”, unable to participate in carrier transport; in effect, lowering the mobility of the electron charge carriers. It can be varied by adjusting the deposition conditions [8, 9]. If the electron traps are fully occupied, the barrier potential at the grain boundary depends on the grain size as well as on the carrier concentration. If not, it depends on defect density carrier concentration [9]. This study concentrates on the trap density variation by keeping crystal size constant. After calculating the mobility limited by each of these scattering phenomena, according to Matthiessen’s rule, the effective mobility of the electron carriers is calculated by

\[ \frac{1}{\mu_{\text{total}}} = \frac{1}{\mu_{\text{ionization}}} + \frac{1}{\mu_{\text{grain boundary}}} + \frac{1}{\mu_{\text{neutral}}} \]  

3. Results and discussion

Among the numerous techniques available for the preparation of ITO thin films, the rf-magnetron sputtering method is the most versatile method that allows scalable and low-cost fabrication. However, achieving the high quality of ITO films that is required for plasmonic applications can be hindered by the defects associated with rf-sputtering. The free carrier concentration of ITO film is determined by the activated Sn dopants, oxygen vacancies, and microstructural configuration [11]. Post-deposition treatment, like thermal annealing techniques, is reported to activate the Sn dopants, reduce the defects, and restructure the material microstructure [19, 20]. The defects or traps in the ITO can originate from crystal dislocations, interstitial atoms, vacancies, etc. The effect of defects on devices like TFTs and solar cells has been explored extensively [8, 9]. However, studies addressing the influence of defects on surface plasmon resonance properties have not been reported so far.

It can be noticed from the equation (3) and (4) that the parameters of electrical and optical properties of ITO are intricately related to each other. Therefore, it is important to obtain the parameters of electrical and optical properties for different defect densities before proceeding with studies on SPR. It is assumed that the microstructural properties as crystal size of 100 nm, which implies a high temperature deposited material. The range of free carrier concentration is taken to be in the range of \( 10^{19} \text{cm}^{-3} \) to \( 10^{21} \text{cm}^{-3} \), which might have a contribution from both Sn and oxygen vacancies. The variation of defects in the material is considered according to the reported results of variation in \( O_2 \) dilution in the Ar sputtering environment for different metal oxide materials. A value of defect density of \( 7 \times 10^{13} \text{ cm}^{-2} \) that arises from a no-oxygen environment and a value of \( 2 \times 10^{12} \text{ cm}^{-2} \) that arises from a very oxygen-rich environment are considered here [8, 9, 18]. Defect density also contains the contribution of neutral atoms and metal-oxide complexes. Charge of impurity, \( Z \) is taken as one, a constant. In this study, only neutral atoms have considered, which is \( \sim 0.5 \% \) of donor atoms. This value was considered because it is assumed that the material has been grown at a moderately high temperature. For the SPR simulation carried out in Kretschmann configuration (figure 1), the thickness of the ITO layer at the BK-7 glass prism surface was considered to be 140 nm and the angle of the incident light beam was fixed at 55°.

The simulated effective mobilities corresponding to different carrier concentration values of ITO films for two different trap densities, \( 2 \times 10^{12} \text{ cm}^{-2} \) and \( 7 \times 10^{13} \text{ cm}^{-2} \), are displayed in the left-Y-axis of
the panels (a) and (b) of figure 2. The variation in mobility w.r.t. carrier concentration in both the panels can be seen as having three distinct parts: a first segment where at lower carrier concentration values, mobility shows a steep rise even with slight variations in carrier concentration values; a second segment at the middle range of carrier concentration values where the mobility after reaching its maxima, varies slightly with the increase in carrier concentration; and a third segment where the mobility undergoes a gradual fall with the increase in carrier concentration values. The effect of defects can be easily seen in the first segment where the onset of the rise in the mobility shifts to the right-hand side (i.e., at higher carrier concentration values) with the increase in defect. The maximum value of the mobility seen in the second segment are obtained for the $N_t = 2 \times 10^{12}$ cm$^{-2}$ is 160 cm$^2$/Vs at $n = 7 \times 10^{18}$ cm$^{-3}$, whereas for the $N_t = 7 \times 10^{13}$ cm$^{-2}$ is 30.6 cm$^2$/Vs at $n = 8 \times 10^{20}$ cm$^{-3}$.

The percentage of contribution or the losses due to the carrier scattering governed by different mechanisms, corresponding to the mobility values at different carrier concentration values are displayed in the right-Y-axis of the panels (a) and (b) of figure 2. From the figure, it is evident that the contribution of each scattering in limiting the mobility depends on the carrier concentration. The steep rise in the mobility values as seen in segment-1 can be correlated to the fact that the grain-boundary scattering effect starts to reduce with the increase in carrier concentration values. Soon afterward, at higher carrier concentration values, due to increased doping, the ionized impurity scattering assumes dominance. The role of scattering due to the neutral atoms is relatively low here because these defects were not considered to be high in this study, to see the effect of defects that arise due to the oxygen vacancy.

The carrier concentration values of interest for studying the plasmonic effect ranges between $10^{20}$ cm$^{-3}$ to $10^{21}$ cm$^{-3}$. Therefore, to study the optical properties of the ITO with these electrical parameter values, the mobilities values for the carrier concentrations between $7 \times 10^{20}$ cm$^{-3}$ to $2 \times 10^{21}$ cm$^{-3}$ were selected. The simulation results of the optical properties of ITO using the Drude model (equation (3) and (4)) are shown in figure 3. The real and imaginary parts of the dielectric constant are displayed in panels (a) and (b) of figure 3, respectively. In both the panels, the solid lines represent the simulated
The results of the dielectric permittivities corresponding to the $N_t$ value of $2 \times 10^{12}$ cm$^{-2}$, while the dashed lines correspond to the $N_t$ value of $7 \times 10^{13}$ cm$^{-2}$. Similar behavior of spectral dependences of $\varepsilon_{\text{real}}$ and $\varepsilon_{\text{imag}}$ for both the values of defect densities can be observed from Figures 3 (a) and (b). The $\varepsilon_{\text{real}}$ values decrease non-linearly with the increase in wavelength of the light for all the selected carrier concentration values. However, the fall in $\varepsilon_{\text{real}}$ values is more for higher carrier concentration values and at longer wavelengths. It is noteworthy that the decrease in $\varepsilon_{\text{real}}$ values extends far enough so that the value becomes negative, which is typically seen in metals. The corresponding wavelength value where the $\varepsilon_{\text{real}}$ value changes from positive to negative is a crucial parameter, which is discussed later.

The $\varepsilon_{\text{imag}}$ values, on the other hand, keep rising with the increase in wavelength values. For a particular wavelength, the corresponding $\varepsilon_{\text{imag}}$ values of higher carrier concentrations are more compared to that of the lower concentration values. The difference between such two values for every wavelength is less at lower wavelengths and increases towards the longer wavelengths. The values of $\varepsilon_{\text{imag}}$ are higher for higher defect density.

Figure 4 shows the effect of surface plasmon resonance on the reflectance of the light from the ITO/glass interface at different wavelengths, which is generated through optical simulation. The simulation model incorporates the values of dielectric constants for corresponding mobility and carrier concentration values for both values of defect densities, and the other crucial parameters, like effective mass (carrier concentration-dependent), and eps infinity (carrier dependent). The solid lines represent the spectral dependence of reflectance curves simulated for the defect density of $N_t = 2 \times 10^{12}$ cm$^{-2}$, while the dashed lines correspond to those calculated for $N_t = 7 \times 10^{13}$ cm$^{-2}$.

The wavelength at which the reflectance becomes minimum is known as SPR wavelength, $\lambda_{\text{SPR}}$. The $\lambda_{\text{SPR}}$ values corresponding to different carrier concentrations seem to shift towards the longer wavelengths for the lower carrier concentration values. There is no effect of defect densities on the $\lambda_{\text{SPR}}$ values of the corresponding SPR curves. However, there is a visible effect of the defect densities on the shape of the SPR reflectance curves, for both the defect densities. The higher defect density
tends to stretch out the SPR reflectance curves, i.e., increases the F.W.H.M (full width at half maxima) of the SPR curves. The value of reflectance at resonance wavelength ($\lambda_{\text{SPR}}$) is lower for higher defect densities.

The results of this study reveal the effects of traps and their densities on the electrical and optical properties of ITO thin films. The difference between the values of mobility corresponding to lower and higher trap densities decreases with increasing carrier concentration. Thus, the difference between the mobility values corresponding to the two defect densities is $\sim 10$ cm$^2$/Vs for the carrier concentration value of $2 \times 10^{12}$ cm$^{-3}$, whereas the difference between the mobility values increases to $\sim 27$ cm$^2$/Vs for a lower carrier concentration value of $7 \times 10^{13}$ cm$^{-3}$. This correlates well with the observation of higher values of $\varepsilon_{\text{img}}$ obtained for higher defect densities for all the carrier concentration values considered for the studies on optical properties. The difference between the $\varepsilon_{\text{img}}$ values corresponding to these two defect densities widens for lower carrier concentrations, which are more clearly visible at longer wavelengths. For all the carrier concentration values, the $\varepsilon_{\text{img}}$ is found to be less than 1 for wavelength around 1550 nm in this study, which is ideal for telecommunications applications.

The shape of reflectance curves determines the SPR sensitivity of the material. In the analysis of SPR resonance response, the width and depth of the reflectance curve are significant. Narrow curves and minimum reflectance are needed for good quality SPR sensors that can distinguish the slightest variation in the refractive index of a medium or ITO surface. Greater depth indicates better coupling efficiency of surface plasmon polaritons (SPP), and the width of the curve will be narrower if the damping due to the inherent material defects is low [13]. In this study, the presence of defects in the material leads to increased damping, which in turn increases the values of the imaginary part of the

![Figure 4](image_url)

**Figure 4.** Simulated SPR reflectance vs wavelength plot for a set of carrier concentration values (same as used in Fig. 3) obtained for ITO thin films when p-polarized light incident on ITO/glass interface at a fixed angle of 55°. The wavelength modulations of SPR are carried out for the selected carrier concentration for two trap densities of $2 \times 10^{12}$ cm$^{-2}$ and $7 \times 10^{13}$ cm$^{-2}$, shown by solid and dashed lines, respectively.
dielectric constant resulting in the broadening of the shape of the SPR signals. The best curve of lowest reflectance and adequately narrow width is seen for 2×10^{21} \text{cm}^{-3} around the range of telecommunication wavelength.

The incorporation of the consolidated electrical and optical parameters in this SPR simulation model brings out the realistic SPR behavior of ITO materials having different defect values. This study demonstrates a broad tunability of wavelength range from 1300 nm to 1900 nm for observing surface plasmon resonance in ITO material. This optimization is achievable by changing the free carrier concentration levels, which in turn is related to the doping conditions.

4. Summary and conclusion

For obtaining desirable optical parameters of ITO thin films, accurate values of the electrical parameters are needed, which in turn necessitates the knowledge of the underlying transport mechanisms and electronic structure. The influence of microstructure on carrier mobility is again a basic relationship that is crucial to practical applications of ITO thin films as plasmonic sensors. In this study, the impact of trap density resulting from oxygen vacancies on the NIR plasmonic behavior of ITO is numerically studied. Changes caused by two extreme values of trap densities, 2×10^{12} \text{cm}^{-2} and 7×10^{13} \text{cm}^{-2} are particularly focused, assuming a typical crystal size of 100 nm and unit charge of impurity. Results of this study show that films with higher trap densities show reduced carrier mobility, which manifests as increased damping, which increases the imaginary component of the dielectric permittivity of the material. In the context of surface plasmon resonance behavior of ITO, the higher trap densities translate into broadening of the SPR reflectance signals. An oxygen-rich environment during the fabrication of ITO reduces defects but in excess can reduce free carriers. The Sn doping in ITO increases free carrier concentration, but in excess can increase the neutral defects. Results of this study indicate that for better sensitivity in near-infrared SPR sensors, a balance must be maintained between the oxygen and dopant concentration to achieve the desired quality of ITO material.

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